Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement VI

IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry

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This paper updates and extends part of the previous data base of critical evaluations of the kinetics and photochemistry of gas-phase chemical reactions of neutral species involved in atmospheric chemistry [J. Phys. Chem. Ref. Data **9**, 295 (1980); **11**, 327 (1982); **13**, 1259 (1984); **18**, 881 (1989); **21**, 1125 (1992); **26**, 521 (1997)]. The present evaluation is limited to the following families of atmospherically important reactions: O_x, HO_x, NO_x, and SO_x. The work has been carried out by the authors under the auspices of the IUPAC Subcommittee on Gas Phase Kinetic Data Evaluation for Atmospheric Chemistry. Data sheets have been prepared for 151 thermal and photochemical reactions, containing summaries of the available experimental data with notes giving details of the experimental procedures. For each thermal reaction, a preferred value of the rate coefficient at 298 K is given together with a temperature dependence where possible. The selection of the preferred value is discussed and estimates of the accuracies of the rate coefficients and temperature coefficients have been made for each reaction. For each photochemical reaction the data sheets list the preferred values of the photoabsorption cross-sections and the quantum yields of the photochemical reactions together with comments on how they were selected. The data sheets are intended to provide the basic physical chemical data needed as input for calculations which model atmospheric chemistry. A table summarizing the preferred rate data is provided, together with an appendix listing the available data on enthalpies of formation of the reactant and product species. *© 1997 American Institute of Physics and American Chemical Society.* [S0047-2689(97)00106-2]

Key words: air pollution; atmospheric chemistry; chemical kinetics; data evaluation; gas phase; photoabsorption cross-section, photochemistry; quantum yield; rate coefficient.

Contents

1. Preface

This paper is Supplement VI to the original set of critically evaluated kinetic and photochemical rate parameters for atmospheric chemistry, published by the CODATA Task Group on Gas Phase Chemical Kinetics in 1980[1] and subsequently updated by Supplement I in 1982[2] and Supplement II in 1984.[3] The original evaluation and Supplements I and II were primarily intended to furnish a kinetic data base for modeling middle atmosphere chemistry (10–55 km altitude).

In 1985 the International Union of Pure and Applied Chemistry (IUPAC) set up a group to continue and enlarge upon the work initiated by CODATA. The Subcommittee on Gas Phase Kinetic Data Evaluation for Atmospheric Chemistry is chaired by J. A. Kerr and is part of the Commission on Chemical Kinetics (I.4) of the IUPAC Physical Chemistry Division.

This subcommittee produced Supplement III in 1989,[4] Supplement IV in 1992,[5] and Supplement V in 1997,[6] in which the original data base was extended and updated to include more reactions involved in tropospheric chemistry. Since it was not possible to cope with all of the very large number of chemical reactions involved in tropospheric chemistry, it was originally decided to limit the coverage to those organic reactions for which kinetic or photochemical data exist for species containing up to three carbon atoms.

With the publication of Supplement V in 1997,[6] the data base had become so extensive that the Subcomittee decided that future supplements would be limited to dealing in turn with parts of the set of over 700 gas-phase and heterogeneous reactions. To this end the present Supplement VI is an update and extension of the following families of gas-phase reactions: O_x, HO_x, NO_x, and SO_x. Future supplements will deal with (i) organic reactions, (ii) halogen reactions, and (iii) heterogeneous reactions. Since the present and future supplements will be much smaller than Supplement V, it is intended that they will be published on a shorter time scale than those between Supplements I through V.

Following the pattern of Supplement V,[6] here we provide a data sheet for each of the reactions of the families considered. Supplement VI, however, contains the amendment o listing the data used in the selection of the Preferred Value for each reaction. This means that in Supplement VI some o the earlier data, omitted during the evolvement of Supplements I–V, have been re-entered on the data sheets. Thi change is intended to aid the reader in appreciating how th Preferred Values were selected.

For each reaction, the data sheet includes a list of the dat upon which the preferred rate coefficient is based togethe with a statement of the assigned uncertainty limits, a comment giving the basis for the recommendation, and a list o the relevant references. To the extent that this informatio suffices, the reader can use the present publication withou need to refer to the previous publications in the series. However, it should be emphasized that in preparing the updated data sheets, we have not listed all of the previous data contained in the original evaluation[1] and Supplements I–V.[2-6] Consequently for many reactions, to obtain the complete data-set and background to the preferred rate parameters, it is essential that the present supplement be read in conjunction with its predecessors.[1-6]

The following reactions, relevant to the present supplement for which data sheets were prepared in previous evaluations, have now been omitted because they appear to be unimportant in atmospheric chemistry:

$O + O_2 \rightarrow O_3^*$
$O_3^* + M \rightarrow O_3 + M$
$O + O_3^* \rightarrow \text{products}$
$O_2(^1\Sigma_g^+)^* + O_2 \rightarrow O_2(^1\Sigma_g^+) + O_2$
$H + O_3 \rightarrow HO + O_2$
$H + O_3 \rightarrow HO^* + O_2$
$O + H_2 \rightarrow HO + H$
$HO + H_2(\nu=1) \rightarrow H_2O + H$
$HO^* + M \rightarrow HO + M$
$HO^* + O_3 \rightarrow \text{products}$
$O + N_2O_5 \rightarrow \text{products}$
$N + HO \rightarrow NO + H$
$N + O_2 \rightarrow NO + O$
$N + O_2(^1\Delta_g) \rightarrow NO + O$
$N + O_3 \rightarrow NO + O_2$
$N + NO \rightarrow N_2 + O$

$N + NO_2 \rightarrow N_2O + O$
$NH_2 + HO \rightarrow$ products
$NH_2 + HO_2 \rightarrow$ products
$NO + h\nu \rightarrow$ products
$O(^1D) + CN \rightarrow$ products
$CN + O_2 \rightarrow$ products
$O + H_2S \rightarrow HO + HS$
$CH_3O_2 + SO_2 \rightarrow$ products

These reactions are no longer included in the present Summary of Reactions, and in referring to them in previous evaluations[1–6] it should be noted that the data sheets may no longer be up-to-date for any particular reaction.

The cutoff point for literature searching for this supplement was September 1996. As in our previous evaluations, we also include data which were available to us in preprint form at that point.

2. Summary of Reactions and Preferred Rate Data

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta \log k_{298}$ ^{a}	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
	O_x Reactions						
1342	$O + O_2 + M \rightarrow O_3 + M$	6.0×10^{-34} [O_2]	(k_0)	±0.05	$6.0\times10^{-34}(T/300)^{-2.8}$ [O_2]	100–300	$\Delta n = \pm 0.5$
		5.6×10^{-34} [N_2]	(k_0)	±0.05	$5.6\times10^{-34}(T/300)^{-2.8}$ [N_2]	100–300	$\Delta n = \pm 0.5$
1343	$O + O_3 \rightarrow 2O_2$	8.0×10^{-15}		±0.08	$8.0\times10^{-12}\exp(-2060/T)$	200–400	±200
1344	$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	4.0×10^{-11}		±0.05	$3.2\times10^{-11}\exp(67/T)$	200–350	±100
1345	$O(^1D) + O_3 \rightarrow O_2 + 2O(^3P)$	1.2×10^{-10}		±0.1			
	$\rightarrow 2O_2(^3\Sigma_g^-)$	1.2×10^{-10}		±0.1	2.4×10^{-10}	100–400	$\Delta \log k = \pm 0.05$
1346	$O_2^{\ddagger} + O_3 \rightarrow O + 2O_2$	See data sheet					
1346	$O_2(^3\Sigma_g^-, v') + M \rightarrow O_2(^3\Sigma_g^-, v'') + M$	See data sheet					
1347	$O_2(^1\Delta_g) + M \rightarrow O_2(^3\Sigma_g^-) + M$	1.6×10^{-18}	(M = O_2)	±0.2	$3.0\times10^{-18}\exp(-200/T)$	100–450	±200
		$\approx 1.4\times10^{-19}$	(M = N_2)				
		5×10^{-18}	(M = H_2O)	±0.3			
		$\leqslant 2\times10^{-20}$	(M = CO_2)				
1348	$O_2(^1\Delta_g) + O_3 \rightarrow 2O_2 + O$	3.8×10^{-15}		±0.10	$5.2\times10^{-11}\exp(-2840/T)$	280–360	±500
1349	$O_2(^1\Sigma_g^+) + M \rightarrow O_2(^3\Sigma_g^-) + M$ $\rightarrow O_2(^1\Delta_g) + M$	4.1×10^{-17}	(M = O_2)	±0.3			
		2.1×10^{-15}	(M = N_2)	±0.10	2.1×10^{-15}	200–350	±200
		8.0×10^{-14}	(M = $O(^3P)$)	±0.3			
		4.6×10^{-12}	(M = H_2O)	±0.3			
		4.1×10^{-13}	(M = CO_2)	±0.10	4.1×10^{-13}	245–360	±200
1350	$O_2(^1\Sigma_g^+) + O_3 \rightarrow 2O_2 + O$						
	$\rightarrow O_2(^1\Delta_g) + O_3$	2.2×10^{-11}		±0.06	2.2×10^{-11}	295–360	±300
	$\rightarrow O_2(^3\Sigma_g^-) + O_3$						
1351	$O_2 + h\nu \rightarrow$ products	See data sheet					
1353	$O_3 + h\nu \rightarrow$ products	See data sheet					
	HO_x Reactions						
1358	$H + HO_2 \rightarrow H_2 + O_2$	5.6×10^{-12}		±0.5	5.6×10^{-12}	245–300	$\Delta \log k = \pm 0.5$
	$\rightarrow 2HO$	7.2×10^{-11}		±0.1	7.2×10^{-11}	245–300	$\Delta \log k = \pm 0.1$
	$\rightarrow H_2O + O$	2.4×10^{-12}		±0.5	2.4×10^{-12}	245–300	$\Delta \log k = \pm 0.5$
1359	$H + O_2 + M \rightarrow HO_2 + M$	5.4×10^{-32} [N_2]	(k_0)	±0.1	$5.4\times10^{-32}(T/300)^{-1.8}$ [N_2]	200–600	$\Delta n = \pm 0.6$
		7.5×10^{-11}	(k_∞)	±0.3	7.5×10^{-11}	200–400	$\Delta n = \pm 0.6$
		$F_c = 0.55$		$\Delta F_c = \pm 0.15$	$F_c = \exp(-T/498)$	200–400	
1360	$O + HO \rightarrow O_2 + H$	3.3×10^{-11}		±0.1	$2.3\times10^{-11}\exp(110/T)$	220–500	±100
1360	$O + HO_2 \rightarrow HO + O_2$	5.8×10^{-11}		±0.08	$2.7\times10^{-11}\exp(224/T)$	220–400	±100
1361	$O + H_2O_2 \rightarrow HO + HO_2$	1.7×10^{-15}		±0.3	$1.4\times10^{-12}\exp(-2000/T)$	280–390	±1000
1362	$O(^1D) + H_2 \rightarrow HO + H$	1.1×10^{-10}		±0.1	1.1×10^{-10}	200–350	±100
1363	$O(^1D) + H_2O \rightarrow 2HO$	2.2×10^{-10}		±0.1	2.2×10^{-10}	200–350	±100
1364	$HO + H_2 \rightarrow H_2O + H$	6.7×10^{-15}		±0.1	$7.7\times10^{-12}\exp(-2100/T)$	200–450	±200
1365	$HO + HO \rightarrow H_2O + O$	1.9×10^{-12}		±0.15	$7.9\times10^{-14}(T/298)^{2.6}\exp(945/T)$	200–500	±250

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta \log k_{298}$^{a}	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
1366	$HO + HO + M \rightarrow H_2O_2 + M$	6.9×10^{-31} [N$_2$]	(k_0)	±0.1	$6.9\times10^{-31}(T/300)^{-0.8}$ [N$_2$]	200–400	$\Delta n = \pm0.5$
		2.6×10^{-11}	(k_∞)	±0.2	2.6×10^{-11}	200–400	$\Delta \log k_\infty = \pm0.2$
		$F_c=0.5$		$\Delta F_c = \pm0.05$	$F_c=0.5$	200–400	
1367	$HO + HO_2 \rightarrow H_2O + O_2$	1.1×10^{-10}		±0.1	4.8×10^{-11} exp(250/T)	250–400	±200
1368	$HO + H_2O_2 \rightarrow H_2O + HO_2$	1.7×10^{-12}		±0.1	2.9×10^{-12} exp($-160/T$)	240–460	±100
1369	$HO + O_3 \rightarrow HO_2 + O_2$	6.7×10^{-14}		±0.15	1.9×10^{-12} exp($-1000/T$)	220–450	±300
1370	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	1.6×10^{-12}		±0.15	2.2×10^{-13} exp(600/T)	230–420	±200
1370	$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$	5.2×10^{-32} [N$_2$]		±0.15	1.9×10^{-33} exp(980/T) [N$_2$]	230–420	±300
		4.5×10^{-32} [O$_2$]		±0.15			
		See data sheet for effect of H$_2$O					
1371	$HO_2 + O_3 \rightarrow HO + 2O_2$	2.0×10^{-15}		±0.2	1.4×10^{-14} exp($-600/T$)	250–350	$^{+500}_{-100}$
1372	$H_2O + h\nu \rightarrow HO + H$	See data sheet					
1373	$H_2O_2 + h\nu \rightarrow 2HO$	See data sheet					
	NO_x Reactions						
1375	$O + NO + M \rightarrow NO_2 + M$	1.0×10^{-31} [N$_2$]	(k_0)	$\pm$ 0.1	$1.0\times10^{-31}(T/300)^{-1.6}$ [N$_2$]	200–300	$\Delta n = \pm0.3$
		3.0×10^{-11}	(k_∞)	±0.3	$3.0\times10^{-11}(T/300)^{0.3}$	200–1500	$\Delta n = \pm0.3$
		$F_c=0.85$			F_c=exp($-T$/1850)	200–300	
1376	$O + NO_2 \rightarrow O_2 + NO$	9.7×10^{-12}		±0.06	6.5×10^{-12} exp(120/T)	220–360	±120
1377	$O + NO_2 + M \rightarrow NO_3 + M$	9.0×10^{-32} [N$_2$]	(k_0)	±0.10	$9.0\times10^{-32}(T/300)^{-2.0}$ [N$_2$]	200–400	$\Delta n = \pm1$
		2.2×10^{-11}	(k_∞)	±0.2	2.2×10^{-11}	200–400	$\Delta n = \pm0.5$
		$F_c=0.8$			F_c=exp($-T$/1300)	200–400	
1378	$O + NO_3 \rightarrow O_2 + NO_2$	1.7×10^{-11}		±0.3			
1378	$O(^1D) + N_2 + M \rightarrow N_2O + M$	9×10^{-37} [N$_2$]	(k_0)	±0.5			
1379	$O(^1D) + N_2 \rightarrow O(^3P) + N_2$	2.6×10^{-11}		±0.1	1.8×10^{-11} exp(107/T)	100–350	±100
1380	$O(^1D) + N_2O \rightarrow N_2 + O_2$	4.4×10^{-11}		±0.1	4.4×10^{-11}	200–350	±100
	$\rightarrow 2NO$	7.2×10^{-11}		±0.1	7.2×10^{-11}	200–350	±100
1381	$HO + NH_3 \rightarrow H_2O + NH_2$	1.6×10^{-13}		±0.1	3.5×10^{-12} exp($-925/T$)	230–450	±200
1382	$HO + HONO \rightarrow H_2O + NO_2$	6.5×10^{-12}		±0.15	2.7×10^{-12} exp(260/T)	290–380	±260
1383	$HO + HONO_2 \rightarrow H_2O + NO_3$	1.5×10^{-13}	(1 bar)	±0.1	See data sheet		
1385	$HO + HO_2NO_2 \rightarrow$ products	5.0×10^{-12}		±0.2	1.5×10^{-12} exp(360/T)	240–340	$^{+300}_{-600}$
1386	$HO + NO + M \rightarrow HONO + M$	7.4×10^{-31} [N$_2$]	(k_0)	±0.10	$7.4\times10^{-31}(T/300)^{-2.4}$ [N$_2$]	200–400	$\Delta n = \pm0.5$
		3.3×10^{-11}	(k_∞)	±0.2	3.3×10^{-11}	200–400	$\Delta \log k = \pm0.2$
		$F_c=0.81$			F_c=exp($-T$/1420)	250–400	
1387	$HO + NO_2 + M \rightarrow HONO_2 + M$	2.6×10^{-30} [N$_2$]	(k_0)	±0.1	$2.6\times10^{-30}(T/300)^{-2.9}$ [N$_2$]	200–400	$\Delta n = \pm0.3$
		7.5×10^{-11}	(k_∞)	±0.10	$7.5\times10^{-11}(T/300)^{-0.6}$	200–400	$\Delta n = \pm0.5$
		$F_c=0.41$			F_c=exp($-T$/340)	250–400	

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$ ^{a}	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
1389	$HO + NO_3 \rightarrow HO_2 + NO_2$	2.0×10^{-11}		±0.3			
1390	$HO_2 + NO \rightarrow NO_2 + HO$	8.3×10^{-12}		±0.1	$3.4\times10^{-12}\exp(270/T)$	200–400	±100
1391	$HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$	1.8×10^{-31} $[N_2]$	(k_0)	±0.10	$1.8\times10^{-31}(T/300)^{-3.2}$ $[N_2]$	220–360	$\Delta n=\pm1$
		4.7×10^{-12}	(k_∞)	±0.2	4.7×10^{-12}	220–360	$\Delta n=\pm1$
		$F_c=0.6$			$F_c=0.6$		
1393	$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$	1.3×10^{-20} $[N_2]$	(k_0/s^{-1})	±0.3	$4.1\times10^{-5}\exp(-10650/T)$ $[N_2]$	260–300	±500
		0.30	(k_∞/s^{-1})	±0.5	$5.7\times10^{15}\exp(-11170/T)$	260–300	±500
		$F_c=0.5$			$F_c=0.5$	260–300	
1394	$HO_2 + NO_3 \rightarrow O_2 + HNO_3$ $\rightarrow HO + NO_2 + O_2$	4.0×10^{-12}		±0.2			
1395	$NH_2 + O_2 \rightarrow$ products	$<6\times10^{-21}$					
1396	$NH_2 + O_3 \rightarrow$ products	1.7×10^{-13}		±0.5	$4.9\times10^{-12}\exp(-1000/T)$	250–380	±500
1397	$NH_2 + NO \rightarrow$ products	1.6×10^{-11}		±0.2	$1.6\times10^{-11}(T/298)^{-1.5}$	210–500	$\Delta n=\pm0.5$
1399	$NH_2 + NO_2 \rightarrow$ products	2.0×10^{-11}		±0.2	$2.0\times10^{-11}(T/298)^{-2.0}$	250–500	$\Delta n=\pm0.7$
1400	$2NO + O_2 \rightarrow 2NO_2$	2.0×10^{-38} (cm^6 molecule^{-2} s^{-1})		±0.1	$3.3\times10^{-39}\exp(530/T)$	270–600	±400
1401	$NO + O_3 \rightarrow NO_2 + O_2$	1.8×10^{-14}		±0.08	$1.8\times10^{-12}\exp(-1370/T)$	195–304	±200
1402	$NO + NO_2 + M \rightarrow N_2O_3 + M$	3.1×10^{-34} $[N_2]$	(k_0)	±0.3	$3.1\times10^{-34}(T/300)^{-7.7}$ $[N_2]$	200–300	$\Delta n=\pm1$
		7.9×10^{-12}	(k_∞)	±0.3	$7.9\times10^{-12}(T/300)^{1.4}$	200–300	$\Delta n=\pm0.5$
		$F_c=0.6$					
1403	$N_2O_3 + M \rightarrow NO + NO_2 + M$	1.6×10^{-14} $[N_2]$	(k_0/s^{-1})	±0.4	$1.9\times10^{-7}(T/300)^{-8.7}\exp(-4880/T)$ $[N_2]$	225–300	±200 $\Delta n=\pm1$
		3.6×10^{8}	(k_∞/s^{-1})	±0.3	$4.7\times10^{15}(T/300)^{0.4}\exp(-4880/T)$	225–300	±100 $\Delta n=\pm1$
		$F_c=0.6$					
1404	$NO + NO_3 \rightarrow 2NO_2$	2.6×10^{-11}		±0.1	$1.8\times10^{-11}\exp(110/T)$	200–420	±100
1405	$NO_2 + O_3 \rightarrow NO_3 + O_2$	3.5×10^{-17}		±0.06	$1.4\times10^{-13}\exp(-2470/T)$	230–360	±150
1406	$NO_2 + NO_2 + M \rightarrow N_2O_4 + M$	1.4×10^{-33} $[N_2]$	(k_0)	±0.3	$1.4\times10^{-33}(T/300)^{-3.8}$ $[N_2]$	300–500	$\Delta n=\pm1$
		1.0×10^{-12}	(k_∞)	±0.3	1.0×10^{-12}	250–300	$\Delta\log k=\pm0.3$
		$F_c=0.40$					
1407	$N_2O_4 + M \rightarrow NO_2 + NO_2 + M$	6.1×10^{-15} $[N_2]$	(k_0/s^{-1})	±0.3	$1.3\times10^{-5}(T/300)^{-3.8}\exp(-6400/T)$ $[N_2]$	300–500	±500
		4.4×10^{6}	(k_∞/s^{-1})	±0.4	$1.15\times10^{16}\exp(-6460/T)$	250–300	±500
		$F_c=0.40$					
1409	$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$	2.8×10^{-30} $[N_2]$	(k_0)	±0.10	$2.8\times10^{-30}(T/300)^{-3.5}$ $[N_2]$	200–400	$\Delta n=\pm0.5$
		2.0×10^{-12}	(k_∞)	±0.2	$2.0\times10^{-12}(T/300)^{0.2}$	200–500	$\Delta n=\pm0.6$
		$F_c=0.45$			$F_c=\{2.5\exp(-1950/T)+0.9\exp(-T/430)\}$	200–500	
1411	$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$	9.5×10^{-20} $[N_2]$	(k_0/s^{-1})	±0.2	$1.0\times10^{-3}(T/300)^{-3.5}\exp(-11000/T)$ $[N_2]$	200–400	$\Delta n=\pm0.5$
		6.9×10^{-2}	(k_∞/s^{-1})	±0.3	$9.7\times10^{14}(T/300)^{0.1}\exp(-11080/T)$	200–300	$\Delta n=\pm0.2$
		$F_c=0.45$			$F_c=\{2.5\exp(-1950/T)+0.9\exp(-T/430)\}$	200–300	
1412	$N_2O_5 + H_2O \rightarrow 2HNO_3$	$<2\times10^{-21}$					
1413	$HONO + h\nu \rightarrow$ products	See data sheet					
1414	$HONO_2 + h\nu \rightarrow$ products	See data sheet					

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$ ^{a}	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
1416	$HO_2NO_2 + h\nu \to$ products	See data sheet					
1418	$NO_2 + h\nu \to$ products	See data sheet					
1421	$NO_3 + h\nu \to$ products	See data sheet					
1424	$N_2O + h\nu \to$ products	See data sheet					
1426	$N_2O_5 + h\nu \to$ products	See data sheet					
	SO_x Reactions						
1428	$O + CS \to CO + S$	2.1×10^{-11}		±0.1	$2.7\times10^{-10}\exp(-760/T)$	150–300	±250
1429	$O + CH_3SCH_3 \to CH_3SO + CH_3$	5.0×10^{-11}		±0.1	$1.3\times10^{-11}\exp(409/T)$	270–560	±100
1430	$O + CS_2 \to$ products	3.6×10^{-12}		±0.2	$3.2\times10^{-11}\exp(-650/T)$	210–500	±100
1431	$O + CH_3SSCH_3 \to CH_3SO + CH_3S$	1.5×10^{-10}		±0.3	$6.5\times10^{-11}\exp(250/T)$	290–570	±100
1432	$O + OCS \to SO + CO$	1.2×10^{-14}		±0.2	$1.6\times10^{-11}\exp(-2150/T)$	230–500	±150
1433	$O + SO_2 + M \to SO_3 + M$	$1.4\times10^{-33}[N_2]$	(k_0)	±0.3	$4.0\times10^{-32}\exp(-1000/T)$ $[N_2]$	200–400	±200
1434	$S + O_2 \to SO + O$	2.1×10^{-12}		±0.2	2.1×10^{-12}	250–430	±200
1434	$S + O_3 \to SO + O_2$	1.2×10^{-11}		±0.3			
1435	$Cl + H_2S \to HCl + HS$	7.4×10^{-11}		±0.1	$3.7\times10^{-11}\exp(208/T)$	200–430	±100
1436	$Cl + OCS \to SCl + CO$	$<1.0\times10^{-16}$					
1436	$Cl + CS_2 \xrightarrow{O_2}$ products	$\approx4\times10^{-15}$	(1 bar air)				
1437	$Cl + CH_3SH \to$ products	2.0×10^{-10}		±0.1	$1.2\times10^{-10}\exp(150/T)$	190–430	±100
1438	$Cl + CH_3SCH_3 \to$ products	3.3×10^{-10}	(1 bar N_2)	±0.15			
1439	$HO + H_2S \to H_2O + HS$	4.7×10^{-12}		±0.08	$6.1\times10^{-12}\exp(-80/T)$	220–520	±80
1440	$HO + SO_2 + M \to HOSO_2 + M$	$4.0\times10^{-31}[N_2]$	(k_0)	±0.3	$4.0\times10^{-31}(T/300)^{-3.3}$ $[N_2]$	300–400	$\Delta n=\pm1$
		2×10^{-12}	(k_∞)	±0.3	2×10^{-12}	200–300	$\Delta\log k=\pm0.3$
		$F_c=0.45$					
1442	$HOSO_2 + O_2 \to HO_2 + SO_3$	4.3×10^{-13}		±0.10	$1.3\times10^{-12}\exp(-330/T)$	290–430	±200
1443	$HO + OCS \to$ products	2.0×10^{-15}		±0.3	$1.1\times10^{-13}\exp(-1200/T)$	250–490	±500
1444	$HO + CS_2 + M \to HOCS_2 + M$	$8\times10^{-31}[N_2]$	(k_0)	±0.5	$8\times10^{-31}[N_2]$	250–320	$\Delta\log k=\pm0.5$
		8×10^{-12}	(k_∞)	±0.5	8×10^{-12}	250–300	$\Delta\log k=\pm0.5$
		$F_c=0.8$					
1446	$HO + CS_2 \to HS + OCS$	$<2\times10^{-15}$					
1446	$HOCS_2 + M \to HO + CS_2 + M$	$4.8\times10^{-14}[N_2]$	(k_0/s^{-1})	±0.5	$1.6\times10^{-6}\exp(-5160/T)$ $[N_2]$	250–300	±500
		4.8×10^{5}	(k_∞/s^{-1})	±0.5	$1.6\times10^{13}\exp(-5160/T)$	250–300	±500
		$F_c=0.8$					
1448	$HOCS_2 + O_2 \to$ products	2.8×10^{-14}		±0.15	2.8×10^{-14}	240–350	$\Delta\log k=\pm0.15$
1450	$HO + CH_3SH \to$ products	3.3×10^{-11}		±0.10	$9.9\times10^{-12}\exp(356/T)$	240–430	±100
1451	$HO + CH_3SCH_3 \to H_2O + CH_2SCH_3$	4.8×10^{-12}		±0.10	$1.13\times10^{-11}\exp(-253/T)$	240–400	±150
	$\to CH_3S(OH)CH_3$	1.7×10^{-12}	(1 bar air)	±0.3	See data sheet		
1453	$HO + CH_3SSCH_3 \to$ products	2.3×10^{-10}		±0.10	$7.0\times10^{-11}\exp(350/T)$	250–370	±200
1454	$HO_2 + H_2S \to$ products	$<3\times10^{-15}$					
1454	$HO_2 + SO_2 \to$ products	$<1\times10^{-18}$					
1455	$HO_2 + CH_3SH \to$ products	$<4\times10^{-15}$					
1455	$HO_2 + CH_3SCH_3 \to$ products	$<5\times10^{-15}$					
1456	$NO_3 + H_2S \to$ products	$<1\times10^{-15}$					
1457	$NO_3 + CS_2 \to$ products	$<1\times10^{-15}$					

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}		$\Delta\log k_{298}$ ^{a}	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
1457	$NO_3 + OCS \rightarrow$ products	$<1\times10^{-16}$					
1458	$NO_3 + SO_2 \rightarrow$ products	$<1\times10^{-19}$					
1459	$NO_3 + CH_3SH \rightarrow$ products	9.2×10^{-13}		±0.15	9.2×10^{-13}	250–370	±400
1460	$NO_3 + CH_3SCH_3 \rightarrow CH_3SCH_2 + HNO_3$	1.1×10^{-12}		±0.15	$1.9\times10^{-13}\exp(520/T)$	250–380	±200
1461	$NO_3 + CH_3SSCH_3 \rightarrow$ products	7×10^{-13}		±0.3	7×10^{-13}	300–380	±500
1462	$HS + O_2 \rightarrow$ products	$<4\times10^{-19}$					
1462	$HS + O_3 \rightarrow HSO + O_2$	3.7×10^{-12}		±0.2	$9.5\times10^{-12}\exp(-280/T)$	290–440	±250
1463	$HS + NO + M \rightarrow HSNO + M$	$2.4\times10^{-31}[N_2]$	(k_0)	±0.3	$2.4\times10^{-31}(T/300)^{-2.5}[N_2]$	250–300	$\Delta n=\pm1$
		2.7×10^{-11}	(k_∞)	±0.5	2.7×10^{-11}	250–300	$\Delta\log k=\pm0.5$
		$F_c=0.6$					
1464	$HS + NO_2 \rightarrow HSO + NO$	5.8×10^{-11}		±0.3	$2.6\times10^{-11}\exp(240/T)$	220–420	±200
1465	$HSO + O_2 \rightarrow$ products	$\leqslant2.0\times10^{-17}$					
1466	$HSO + O_3 \rightarrow$ products	1.1×10^{-13}		±0.2			
1467	$HSO + NO \rightarrow$ products	$<1.0\times10^{-15}$					
1467	$HSO + NO_2 \rightarrow$ products	9.6×10^{-12}		±0.3			
1468	$HSO_2 + O_2 \rightarrow$ products	3.0×10^{-13}		±0.8			
1468	$SO + O_2 \rightarrow SO_2 + O$	7.6×10^{-17}		±0.15	$1.6\times10^{-13}\exp(-2280/T)$	230–420	±500
1469	$SO + O_3 \rightarrow SO_2 + O_2$	8.9×10^{-14}		±0.1	$4.5\times10^{-12}\exp(-1170/T)$	230–420	±150
1470	$SO + NO_2 \rightarrow SO_2 + NO$	1.4×10^{-11}		±0.1	1.4×10^{-11}	210–360	±100
1471	$SO_3 + H_2O \rightarrow$ products	No recommendation; see data sheet					
1472	$SO_3 + NH_3 \rightarrow$ products	5.8×10^{-11}		±0.2			
1472	$CS + O_2 \rightarrow$ products	2.9×10^{-19}		±0.6			
1473	$CS + O_3 \rightarrow OCS + O_2$	3.0×10^{-16}		±0.5			
1474	$CS + NO_2 \rightarrow OCS + NO$	7.6×10^{-17}		±0.5			
1474	$CH_2SH + O_2 \rightarrow$ products	6.6×10^{-12}		±0.3			
1475	$CH_2SH + O_3 \rightarrow$ products	3.5×10^{-11}		±0.3			
1476	$CH_2SH + NO \rightarrow$ products	1.5×10^{-11}		±0.3			
1476	$CH_2SH + NO_2 \rightarrow$ products	4.4×10^{-11}		±0.5			
1477	$CH_3S + O_2 + M \rightarrow CH_3SOO + M$	See data sheet					
1478	$CH_3SOO + M \rightarrow CH_3S + O_2 + M$	See data sheet					
1479	$CH_3S + O_3 \rightarrow$ products	5.4×10^{-12}		±0.2	$2.0\times10^{-12}\exp(290/T)$	290–360	±200
1480	$CH_3S + NO + M \rightarrow CH_3SNO + M$	$3.2\times10^{-29}[N_2]$	(k_0)	±0.3	$3.2\times10^{-29}(T/300)^{-4}[N_2]$	250–450	$\Delta n=\pm2$
		4×10^{-11}	(k_∞)	±0.5	4×10^{-11}	250–450	$\Delta\log k=\pm0.5$
		$F_c=0.60$			$F_c=\exp(-T/580)$		
1481	$CH_3S + NO_2 \rightarrow CH_3SO + NO$	5.8×10^{-11}		±0.15	$2.0\times10^{-11}\exp(320/T)$	240–350	±300
1482	$CH_3SO + O_3 \rightarrow$ products	6.0×10^{-13}		±0.3			
1483	$CH_3SO + NO_2 \rightarrow$ products	1.2×10^{-11}		±0.5			
1483	$CH_3SOO + O_3 \rightarrow$ products	$<8\times10^{-13}$	(227 K)				
1484	$CH_3SOO + NO \rightarrow$ products				1.1×10^{-11}	227–256	$\Delta\log k=\pm0.3$
1484	$CH_3SOO + NO_2 \rightarrow$ products				2.2×10^{-11}	227–246	$\Delta\log k=\pm0.3$
1485	$CH_3SCH_2 + O_2 \rightarrow CH_3SCH_2O_2$	5.7×10^{-12}	(1 bar)	±0.4			
1485	$CH_3SCH_2O_2 + NO \rightarrow CH_3SCH_2O + NO_2$	1.9×10^{-11}		±0.4			
1486	$CH_3SCH_2O_2 + NO_2 + M \rightarrow CH_3SCH_2O_2NO_2 + M$	9×10^{-12}	(1 bar)	±0.5			
1486	$CH_3SCH_2O_2 + CH_3SCH_2O_2 \rightarrow$ products	$\leqslant8\times10^{-12}$					
1487	$CH_3SS + O_3 \rightarrow$ products	4.6×10^{-13}		±0.3			

TABLE 2. (a) Gas Phase Reactions - Summary of Reactions and Preferred Rate Data - Continued

Page Number	Reaction	k_{298} cm^3 molecule^{-1} s^{-1}	$\Delta \log k_{298}$ ^{a}	Temp. dependence of k/cm^3 molecule^{-1} s^{-1}	Temp. range/K	$\Delta(E/R)$/K^a
1488	$CH_3SS + NO_2 \rightarrow$ products	1.8×10^{-11}	±0.3			
1488	$CH_3SSO + NO_2 \rightarrow$ products	4.5×10^{-12}	±0.3			
1489	$O_3 + CH_3SCH_3 \rightarrow$ products	$<1\times10^{-18}$				
1489	$ClO + CH_3SCH_3 \rightarrow$ products	9×10^{-15}	±0.5			
1490	$BrO + CH_3SCH_3 \rightarrow$ products	2.6×10^{-13}	±0.2	1.5×10^{-14} exp(845/T)	240–320	±300
1491	$IO + CH_3SCH_3 \rightarrow$ products	1.2×10^{-14}	±0.5			
1492	$OCS + h\nu \rightarrow$ products	See data sheet				
1493	$CS_2 + h\nu \rightarrow$ products	See data sheet				
1494	$CH_3SSCH_3 + h\nu \rightarrow$ products	See data sheet				
1495	$CH_3SNO + h\nu \rightarrow$ products	See data sheet				

[a] The cited uncertainty is an expanded uncertainty corresponding approximately to a 95% confidence limit.

3. Guide to the Data Sheets

3.1. Gas-Phase Reactions

The data sheets are principally of two types: (i) those for individual thermal reactions and (ii) those for the individual photochemical reactions.

3.1.1. Thermal Reactions

The data sheets begin with a statement of the reactions including all pathways which are considered feasible. This is followed by the corresponding enthalpy changes at 298 K, calculated from the enthalpies of formation summarized in Appendix 1.

The available kinetic data on the reactions are summarized under three headings: (i) Absolute Rate Coefficients, (ii) Relative Rate Coefficients, and (iii) Reviews and Evaluations. Under headings (i) and (ii), we include new data which have been published since the last IUPAC evaluation[6] as well as the data used in deriving the preferred values. Under heading (iii) are listed the preferred rate data from the most recently published NASA evaluation[7] available at the date of submission of this evaluation and our own IUPAC evaluations, together with data from any new review or evaluation source. Under all three of the headings above, the data are presented as absolute rate coefficients. If the temperature coefficient has been measured, the results are given in a temperature-dependent form over a stated temperature range. For bimolecular reactions, the temperature dependence is usually expressed in the normal Arrhenius form, $k=A\ \exp(-B/T)$, where $B=E/R$. For a few bimolecular reactions, we have listed temperature dependences in the alternative form, $k=A'T^{-n}$ or $CT^{n}\ \exp(-D/T)$, where the original authors have found this to give a better fit to their data. For pressure-dependent combination and dissociation reactions, the non-Arrhenius temperature dependence is used. This is discussed more fully in a subsequent section of the Introduction.

Single temperature data are presented as such and wherever possible the rate coefficient at, or close to, 298 K is quoted directly as measured by the original authors. This means that the listed rate coefficient at 298 K may differ slightly from that calculated from the Arrhenius parameters determined by the same authors. Rate coefficients at 298 K marked with an asterisk indicate that the value was calculated by extrapolation of a measured temperature range which did not include 298 K. The tables of data are supplemented by a series of comments summarizing the experimental details. The following list of abbreviations, relating to experimental techniques, is used in the Techniques and Comments sections:

A - absorption
AS - absorption spectroscopy
CIMS - chemical ionization mass spectroscopy/spectrometric
CL - chemiluminescence
DF - discharge flow
EPR - electron paramagnetic resonance
F - flow system
FP - flash photolysis
FTIR - Fourier transform infrared
FTS - Fourier transform spectroscopy
GC - gas chromatography/gas chromatographic
HPLC - high performance liquid chromatography
IR - infrared
LIF - laser induced fluorescence
LMR - laser magnetic resonance
LP - laser photolysis
MM - molecular modulation
MS - mass spectrometry/mass spectrometric
P - steady state photolysis
PLP - pulsed laser photolysis
PR - pulsed radiolysis
RA - resonance absorption
RF - resonance fluorescence
RR - relative rate
S - static system
TDLS - tunable diode laser spectroscopy
UV - ultraviolet
UVA - ultraviolet absorption
VUVA - vacuum ultraviolet absorption

For measurements of relative rate coefficients, wherever possible the comments contain the actual measured ratio of rate coefficients together with the rate coefficient of the reference reaction used to calculate the absolute rate coefficient listed in the data table. The absolute value of the rate coefficient given in the table may be different from that reported by the original author owing to a different choice of rate coefficient of the reference reaction. Whenever possible the reference rate data are those preferred in the present evaluation.

The preferred rate coefficients are presented (i) at a temperature of 298 K and (ii) in temperature-dependent form over a stated temperature range.

This is followed by a statement of the uncertainty limits in $\log k$ at 298 K and the uncertainty limits either in (E/R) or in n, for the mean temperature in the range. Some comments on the assignment of uncertainties are given later in this introduction.

The "Comments on Preferred Values" describe how the selection was made and give any other relevant information. The extent of the comments depends upon the present state of our knowledge of the particular reaction in question. The data sheets are concluded with a list of the relevant references.

3.1.2. Conventions Concerning Rate Coefficients

All of the reactions in the table are elementary processes. Thus the rate expression is derived from a statement of the reaction, e.g.,

$$A + A \rightarrow B + C$$

$$\frac{-1/2\,d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A]^2.$$

Note that the stoichiometric coefficient for A, i.e., 2, appears in the denominator before the rate of change of [A] (which is equal to $2k[\mathrm{A}]^2$) and as a power on the right-hand side.

3.1.3. Treatment of Combination and Dissociation Reactions

The rates of combination and the reverse dissociation reactions

$$\mathrm{A} + \mathrm{B} + \mathrm{M} \rightleftarrows \mathrm{AB} + \mathrm{M}$$

depend on the temperature T, and the nature and concentration of the third body [M]. The rate coefficients of these reactions have to be expressed in a form which is more complicated than those for simple bimolecular reactions. The combination reactions are described by a pseudo second-order rate law

$$\frac{d[\mathrm{AB}]}{dt} = k[\mathrm{A}][\mathrm{B}]$$

in which the second-order rate coefficient depends on [M]. The low-pressure third-order limit is characterized by k_0,

$$k_0 = \lim_{[\mathrm{M}]\to 0} k([\mathrm{M}])$$

which is proportional to [M]. The high-pressure second-order limit is characterized by k_∞,

$$k_\infty = \lim_{[\mathrm{M}]\to\infty} k([\mathrm{M}])$$

which is independent of [M]. For a combination reaction in the low-pressure range, the summary table gives a second-order rate coefficient expressed as the product of a third-order rate coefficient and the third body concentration, which is expressed in molecule cm^{-3}. The transition between the third-order and the second-order range is represented by a reduced falloff expression of k_0/k_∞ as a function of

$$k_0/k_\infty = [\mathrm{M}]/[\mathrm{M}]_c,$$

where the "center of the falloff curve" $[\mathrm{M}]_c$ indicates the third-body concentration for which the extrapolated k_0 would be equal to k_∞. The dependence of k on [M] in general is complicated and has to be analyzed by unimolecular rate theory. For moderately complex molecules at not too high temperatures, however, a simple approximate relationship holds,

$$k = \left\{ \frac{k_0 k_\infty}{k_0 + k_\infty} \right\} F = k_0 \left\{ \frac{1}{1 + k_0/k_\infty} \right\} F = k_\infty \left\{ \frac{k_0/k_\infty}{1 + k_0/k_\infty} \right\} F,$$

where the first factors on the right-hand side represent the Lindemann–Hinshelwood expression, and the additional broadening factor F, at not too high temperature, is approximately given by[8-10]

$$\log F \cong \frac{\log F_c}{1 - [\log(k_0/k_\infty)]^2}.$$

With increasing temperature, a better representation is obtained[8-10] by replacing $[\log(k_0/k_\infty)]^2$ by $[\log(k_0/k_\infty)/N]^2$ with $N = \{0.75 - 1.27 \log F_c\}$. In this way the three quantities k_0, k_∞, and F_c characterize the falloff curve for the present application.

Alternatively, the three quantities k_∞, $[\mathrm{M}]_c$, and F_c (or k_0, $[\mathrm{M}]_c$, and F_c) can be used. The temperature dependence of F_c, which is sometimes significant, can be estimated by the procedure of Troe.[8-10] The results can usually be represented approximately by an equation

$$F_c = (1 - a)\exp(-T/T^{***}) + a\exp(-T/T^{*}) + \exp(-T^{**}/T).$$

Whereas the two first terms are of importance for atmospheric conditions, the last term in most cases becomes relevant only at much higher temperatures. In Ref. 2, for simplicity $a = 1$ and $T^{**} = 4T^{*}$ were adopted. Often $F_c = \exp(-T/T^{*})$ is sufficient for low temperature conditions. With molecules of increasing complexity, additional broadening of the falloff curves may have to be taken into account.[8-10] For simplicity these effects are neglected in the present evaluation. An even simpler policy was chosen in Ref. 7 where a temperature independent standard value of $F_c = 0.6$ was adopted. This choice, however, often oversimplifies the representation.

If a given falloff curve is fitted, changes in F_c require changes in the limiting k_0 and k_∞ values. For the purpose of this evaluation, this is irrelevant, if the preferred k_0 and k_∞ are used consistently together with the preferred F_c values. If the selected value of F_c is too large, the values of k_0 and k_∞, obtained by fitting the falloff expression to the experimental data, are underestimated. Theoretical predictions of F_c have been derived from rigid Rice, Ramsberger, Kassell, and Marcus (RRKM)-type models including weak collision effects.[8-10]

The dependence of k_0 and k_∞ on the temperature T is represented in the form,

$$k \propto T^{-n}$$

except for cases with an established energy barrier in the potential. We have used this form of temperature dependence because it often gives a better fit to the data over a wider range of temperature than does the Arrhenius expression. The dependence of k_0 on the nature of the third-body M generally is represented by the relative efficiencies of M_1 and M_2,

$$k_0(\mathrm{M}_1)/[\mathrm{M}_1]:k_0(\mathrm{M}_2)/[\mathrm{M}_2].$$

The few thermal dissociation reactions of interest in the present application are treated by analogy with combination reactions, and are assigned pseudo-first-order rate coefficients $k([\mathrm{M}])$. The limiting low- and high-pressure rate coefficients expressed in units of s^{-1} are denoted in the tables by the symbols (k_0/s^{-1}) and $(k_\infty/\mathrm{s}^{-1})$. Obviously, F_c should be the same in combination and dissociation reactions.

3.1.4. Photochemical Reactions

The data sheets begin with a list of feasible primary photochemical transitions for wavelengths usually down to 170 nm, along with the corresponding enthalpy changes at 0 K where possible or alternatively at 298 K, calculated from the data in Appendix 1. Calculated threshold wavelengths corresponding to these enthalpy changes are also listed, bearing in mind that the values calculated from the enthalpy changes at 298 K are not true "threshold values."

This is followed by tables summarizing the available experimental data concerning (i) absorption cross-sections and (ii) quantum yields. These data are supplemented by a series of comments.

The next table lists the preferred absorption cross-section data and the preferred quantum yields at appropriate wavelength intervals. For absorption cross-sections the intervals are usually 1, 5 or 10 nm. Any temperature dependence of the absorption cross-sections is also given where possible. The aim in presenting these preferred data is to provide a basis for calculating atmospheric photolysis rates. For absorption continua the temperature dependence is often represented by Sulzer–Wieland type expressions.[11]

The comments again describe how the preferred data were selected and include other relevant points. The photochemical data sheets are also concluded with a list of references.

3.1.5. Conventions Concerning Absorption Cross-Sections

These are presented in the data sheets as "absorption cross-sections per molecule, base e." They are defined according to the equations

$$I/I_0=\exp(-\sigma[N]l),$$

$$\sigma=\{1/([N]l)\}\ln(I_0/I),$$

where I_0 and I are the incident and transmitted light intensities, σ is the absorption cross-section per molecule (expressed in this paper in units of cm^2), [N] is the number concentration of absorber (expressed in molecule cm^{-3}), and l is the path length (expressed in cm). Other definitions and units are frequently quoted. The closely related quantities "absorption coefficient" and "extinction coefficient" are often used, but care must be taken to avoid confusion in their definition; it is always necessary to know the units of concentration and of path length and the type of logarithm (base e or base 10) corresponding to the definition. To convert an absorption cross-section to the equivalent Naperian (base e) absorption coefficient of a gas at a pressure of one standard atmosphere and temperature of 273 K (expressed in cm^{-1}), multiply the value of σ in cm^2 by 2.69×10^{19}.

3.1.6. Assignment of Uncertainties

Under the heading "reliability," estimates have been made of the absolute accuracies of the preferred values of k at 298 K and of the preferred values of E/R over the quoted temperature range. The accuracy of the preferred rate coefficient at 298 K is quoted as the term $\Delta\log k$, where $\Delta\log k=D$ and D is defined by the equation, $\log_{10} k=C\pm D$. This is equivalent to the statement that k is uncertain to a factor of F, where $D=\log_{10} F$. The accuracy of the preferred value of E/R is quoted as the term $\Delta(E/R)$, where $\Delta(E/R)=G$ and G is defined by the equation $E/R=H\pm G$. D and G are expanded uncertainties corresponding approximately to a 95% confidence limit.

For second-order rate coefficients listed in this evaluation, an estimate of the uncertainty at any given temperature within the recommended temperature range may be obtained from the equation:

$$\Delta\log k(T)=\Delta\log k(298\ \mathrm{K})+0.4343\left|\frac{\Delta E}{R}\left(\frac{1}{T}-\frac{1}{298}\right)\right|.$$

The assignment of these absolute uncertainties in k and E/R is a subjective assessment of the evaluators. They are not determined by a rigorous, statistical anlysis of the data base, which is generally too limited to permit such an analysis. Rather, the uncertainties are based on a knowledge of the techniques, the difficulties of the experimental measurements, the potential for systematic errors, and the number of studies conducted and their agreement (or not). Experience shows that for rate measurements of atomic and free radical reactions in the gas phase, the precision of the measurement, i.e., the reproducibility, is usually good. Thus, for single studies of a particular reaction involving one technique, standard deviations, or even 90% confidence limits, of ±10% or less are frequently reported in the literature. Unfortunately, when evaluators come to compare data for the same reaction studied by more than one group of investigators and involving different techniques, the rate coefficients often differ by a factor of 2 or even more. This can only mean that one or more of the studies has involved large systematic errors which are difficult to detect. This is hardly surprising since, unlike molecular reactions, it is not always possible to study atomic and free radical reactions in isolation, and consequently mechanistic and other difficulties frequently arise.

The arbitrary assignment of errors made here is based mainly on our state of knowledge of a particular reaction which is dependent upon factors such as the number of independent investigations carried out and the number of different techniques used. On the whole, our assessment of error limits tends towards the cautious side. Thus, in the case where a rate coefficient has been measured by a single investigation using one particular technique and is unconfirmed by independent work, we suggest that minimum uncertainty limits of a factor of 2 are appropriate.

In contrast to the usual situation for the rate coefficients of thermal reactions, where intercomparison of results of a number of independent studies permits a realistic assessment of reliability, for many photochemical processes there is a scarcity of apparently reliable data. Thus, we do not feel justified at present in assigning uncertainty limits to the parameters reported for the photochemical reactions.

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4. Gas-Phase Reactions—Data Sheets

4.1 Oxygen Species

$O + O_2 + M \rightarrow O_3 + M$

$\Delta H° = -106.5$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$6.75\times10^{-35}\exp[(635\pm18)/T]$ [O_2]	262–319	Arnold and Comes, 1979[1]	FP-RA
$(5.69\pm0.40)\times10^{-34}$ [O_2]	298		
$1.82\times10^{-35}\exp[(995\pm37)/T]$ [N_2]	262–309		
$(5.13\pm0.60)\times10^{-34}$ [N_2]	298		
$(6.9\pm1.0)\times10^{-34}\,(T/300)^{-(1.25\pm0.2)}$ [O_2]	219–368	Klais, Anderson, and Kurylo, 1980[2]	FP-RF
$(6.2\pm0.9)\times10^{-34}\,(T/300)^{-(2.0\pm0.5)}$ [N_2]	219–368		
$(5.69\pm0.34)\times10^{-34}\,(T/300)^{-(2.37\pm0.37)}$ [O_2]	227–353	Lin and Leu, 1982[3]	FP-RF
$(5.70\pm0.19)\times10^{-34}\,(T/300)^{-(2.62\pm0.18)}$ [N_2]	218–366		
$5.5\times10^{-34}\,(T/300)^{-2.6}$ [N_2]	100–400	Hippler, Rahn, and Troe, 1990[4]	PLP-UVA (a)
$5.2\times10^{-35}\,(T/1000)^{-1.3}$ [N_2]	700–900		
Reviews and Evaluations			
$6.0\times10^{-34}\,(T/300)^{-2.3}$ (air)	200–300	NASA, 1997[5]	(b)
$5.6\times10^{-34}\,(T/300)^{-2.8}$ [N_2]	100–300	IUPAC, 1997[6]	(c)
$6.0\times10^{-34}\,(T/300)^{-2.8}$ [O_2]	100–300		

Comments

(a) The O_3 product was monitored by UV absorption at 265 nm. Data for $T > 400$ K are based on dissociation experiments. The reaction is suggested to follow the energy transfer mechanism at high temperatures. At low temperatures a radical-complex mechanism apparently dominates with contributions from metastable excited electronic states of O_3.

(b) Based on an average of rate coefficients from Refs. 2 and 3 in agreement with rate coefficients from Ref. 4.

(c) Based on the results from Ref. 4.

Preferred Values

$k_0 = 5.6\times10^{-34}\,(T/300)^{-2.8}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 100–300 K.

$k_0 = 6.0\times10^{-34}\,(T/300)^{-2.8}$ [O_2] cm^3 molecule^{-1} s^{-1} over the temperature range 100–300 K.

Reliability

$\Delta \log k_0 = \pm0.05$ at 298 K.

$\Delta n = \pm0.5$.

Comments on Preferred Values

The results from Ref. 4 obtained over extended temperature and pressure ranges confirm the large negative values of n and also confirm the absolute values of k_0 at 298 K from earlier work. The experiments from Ref. 4 under low-temperature and high-pressure conditions indicate anomalous falloff behavior different from the formalism described for the energy transfer mechanism in the Introduction. These effects are not relevant for atmospheric conditions such that they are not included in this evaluation. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[6]

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$O + O_3 \rightarrow 2O_2$

$\Delta H^\circ = -391.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.1\times10^{-11}\exp(-2155/T)$	269–409	McCrumb and Kaufman, 1972[1]	(a)
$2.0\times10^{-11}\exp(-2280/T)$	220–353	Davis, Wong, and Lephardt, 1973[2]	PLP-RF
8.3×10^{-15}	298	West, Weston, and Flynn, 1978[3]	PLP-RF
$2.12\times10^{-11}\exp(-2337/T)$	262–335	Arnold and Comes, 1979[4]	FP-RA
$5.6\times10^{-12}\exp(-1959/T)$	220–377	Wine *et al.*, 1983[5]	PLP-RF
8.26×10^{-15}	297		
Reviews and Evaluations			
$8.0\times10^{-12}\exp(-2060/T)$	220–410	NASA, 1997[6]	(b)
$8.0\times10^{-12}\exp(-2060/T)$	220–400	IUPAC, 1997[7]	(c)

Comments

(a) Flow system used, with $O(^3P)$ atoms being produced by the pyrolysis of O_3.

(b) Obtained by Wine *et al.*[5] from an unweighted linear least-squares fit of the data of Wine *et al.*,[5] McCrumb and Kaufman,[1] Davis *et al.*,[2] West *et al.*[3] and Arnold and Comes.[4]

(c) See Comments on Preferred Values.

Preferred Values

$k = 8.0\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 8.0\times10^{-12}\exp(-2060/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta\log k = \pm0.08$ at 298 K.

$\Delta(E/R) = \pm200$ K.

Comments on Preferred Values

The study of Wine *et al.*[5] yields values of k in close agreement with those from other studies, over the whole temperature range covered. Our preferred values are based on the least squares expression obtained by Wine *et al.*[5] from a fit of their data plus those of McCrumb and Kaufman,[1] Davis *et al.*,[2] West *et al.*,[3] and Arnold and Comes,[4] and are identical to those in our previous evaluation, IUPAC, 1997.[7] Computed rate constants[8] using variational transition state theory are in satisfactory agreement with the experimental results.

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$$\begin{aligned} O(^1D) + O_2 &\rightarrow O(^3P) + O_2(^1\Sigma_g^+) \quad (1)\\ &\rightarrow O(^3P) + O_2(^1\Delta_g) \quad (2)\\ &\rightarrow O(^3P) + O_2(^3\Sigma_g^-) \quad (3)\end{aligned}$$

$\Delta H°(1) = -32.8 \text{kJ}\cdot\text{mol}^{-1}$
$\Delta H°(2) = -95.4 \text{ kJ}\cdot\text{mol}^{-1}$
$\Delta H°(3) = -189.7 \text{ kJ}\cdot\text{mol}^{-1}$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	*Technique/Comments*
Absolute Rate Coefficients			
2.9×10^{-11} exp[$(67\pm11)/T$]	104–354	Streit *et al.*, 1976[1]	(a)
3.6×10^{-11}	298		
$(4.2\pm0.2)\times10^{-11}$	295	Amimoto *et al.*, 1979[2]	PLP-RA (b)
$(4.0\pm0.6)\times10^{-11}$	298	Brock and Watson, 1979[3]	PLP-RF (b)
Branching Ratios			
$k_1/k = 0.77\pm0.2$	300	Lee and Slanger, 1978[4]	(c)
$k_2/k \leqslant 0.05$	300	Gauthier and Snelling, 1971[5]	(d)
Reviews and Evaluations			
3.2×10^{-11} exp$(70/T)$	200–300	NASA, 1997[6]	(e)
3.2×10^{-11} exp$(67/T)$	200–350	IUPAC, 1997[7]	(f)

Comments

(a) $O(^1D)$ atoms were produced by flash photolysis of O_3 and detected by $O(^1D) \rightarrow O(^3P)$ emission at 630 nm.
(b) $O(^3P)$ atom product detected by resonance absorption[2] or resonance fluorescence.[3]
(c) $O(^1D)$ atoms detected by $O(^1D) \rightarrow O(^3P)$ emission at 630 nm. $O_2(^1\Sigma_g^+)$ was monitored from the $O_2(^1\Sigma_g^+) \rightarrow O_2(^3\Sigma_g^-)$ (1–1) and (0–0) band emission. $O_2(^1\Sigma_g^+)$ is only formed in the $\nu=0$ and 1 levels, with $k(1)/k(0) - 0.7$.
(d) $O(^1D)$ atom production by the photolysis of O_3.
(e) Based on the results of Streit *et al.*,[1] Amimoto *et al.*,[2] Brock and Watson,[3] and Lee and Slanger.[4]
(f) See Comments on Preferred Values.

Preferred Values

$k = 4.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.2\times10^{-11}$ exp$(67/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–350 K.
$k_1/k = 0.8$ at 298 K.
$k_2/k \leqslant 0.05$ at 298 K.

Reliability

$\Delta \log k = \pm0.05$ at 298 K.
$\Delta(E/R) = \pm100$ K.
$\Delta \log (k_1/k) = \pm0.1$ at 298 K.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1982.[8] The earlier controversy between measurements using $O(^1D)$ emission at 630 nm and absorption at 115 nm has been resolved, since $O(^3P)$ atom detection by absorption at 130 nm and fluorescence support the $O(^1D)$ emission results. Apparently the γ value in the Lambert–Beer law used for the $O(^1D)$ absorption results was too small. The preferred 298 K rate coefficient is the average of the results from Streit *et al.*,[1] Amimoto *et al.*,[2] and Brock and Watson.[3] The temperature dependence is that measured by Streit *et al.*[1] The branching ratios of Lee and Slanger[3] and Gauthier and Snelling[4] are recommended. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[7]

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$$\begin{aligned} O(^1D) + O_3 &\rightarrow O_2 + 2O(^3P) && (1)\\ &\rightarrow O(^3P) + O_3 && (2)\\ &\rightarrow 2O_2(^1\Delta_g) && (3)\\ &\rightarrow O_2(^1\Sigma_g^+) + O_2(^3\Sigma_g^-) && (4)\\ &\rightarrow 2O_2(^3\Sigma_g^-) && (5) \end{aligned}$$

$\Delta H^\circ = -83.2$ kJ·mol^{-1}
$\Delta H^\circ = -189.7$ kJ·mol^{-1}
$\Delta H^\circ = -393.0$ kJ·mol^{-1}
$\Delta H^\circ = -424.7$ kJ·mol^{-1}
$\Delta H^\circ = -581.6$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4 + k_5$)

k/cm^3 molecule^{-1} s^{-1}	Temp/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.4 \pm 0.5) \times 10^{-10}$	103–393	Streit *et al.*, 1976[1]	(a)
$(2.5 \pm 0.5) \times 10^{-10}$	300	Amimoto *et al.*, 1978;[2] 1980[3]	PLP-RA (b)
$(2.28 \pm 0.23) \times 10^{-10}$	298	Wine and Ravishankara, 1981[4]	PLP-RF (b)
$(2.5 \pm 0.2) \times 10^{-10}$	298	Greenblatt and Wiesenfeld, 1983[5]	PLP-RF (b)
Branching Ratios			
$k_1/(k_3+k_4+k_5) = 1$	~298	Davenport *et al.*, 1972[6]	FP-RF (b)
$k_1/k = 0.53$	298	Cobos, Castellano, and Schumacher, 1983[7]	(c)
$k_5/k = 0.47$			
Reviews and Evaluations			
2.4×10^{-10}	200–300	NASA, 1997[8]	(d)
$k_1/k = k_5/k = 0.5$	298		
2.4×10^{-10}	100–400	IUPAC, 1997[9]	(e)
$k_1/k = k_5/k = 0.5$	298		

Comments

(a) $O(^1D)$ atoms produced by flash photolysis of O_3 in a flow system and detected by emission at 630 nm.

(b) The product $O(^3P)$ atoms were detected by resonance absorption[2,3] or resonance fluorescence.[4,5]

(c) Steady-state photolysis of pure O_3 and O_3-inert gas mixtures. Ozone removal was monitored manometrically at high pressures and spectrophotometrically at lower pressures. The quantum yield of O_3 removal was interpreted in terms of a complex reaction scheme.

(d) Based on the data of Streit *et al.*,[1] Amimoto *et al.*,[2,3] Wine and Ravishankara,[4] and Davenport *et al.*[6]

(e) See Comments on Preferred Values.

Preferred Values

$k = 2.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 100–400 K.

$k_1/k = k_5/k = 0.5$ at 298 K.

Reliability

$\Delta \log k = \pm 0.05$ over the temperature range 100–400 K.

$\Delta k_1/k = \Delta k_5/k = \pm 0.1$ at 298 K.

Comments on Preferred Values

The recommendation for the rate coefficient is based on the data of Streit *et al.*,[1] Amimoto *et al.*,[2,3] Wine and Ravishankara,[4] and Greenblatt and Wiesenfeld.[5] The branching ratios are based on these studies plus the work of Davenport *et al.*[6] and Cobos *et al.*[7] The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[9]

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C. Cobos, E. Castellano, and H. J. Schumacher, J. Photochem. **21**, 291 (1983).

[8] NASA Evaluation No. 12, 1997 (see references in Introduction).

[9] IUPAC, Supplement V, 1997 (see references in Introduction).

$O_2^* + O_3 \rightarrow O + 2O_2$

Comments

These Comments are reproduced from our previous evaluation, IUPAC, 1997.[1] Arnold and Comes[2,3] have studied this reaction of vibrationally excited oxygen molecules in the ground electronic state with ozone and they report a rate coefficient of 2.8×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K. The vibrationally excited oxygen molecules were produced in the reaction of O(^{1}D) atoms with O_3 following the UV photolysis of ozone. This is the only reported study of this rate coefficient, and we make no recommendation. For further discussion the reader is referred to the review by Steinfeld *et al.*[4]

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$O_2(^3\Sigma_g^-,v) + M \rightarrow O_2(^3\Sigma_g^-,v') + M$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	M	v	Temp./K	Reference	Comments
Absolute Rate Coefficients					
$(4.7 \pm 0.3) \times 10^{-15}$	O_2	19	295	Price *et al.*, 1993[1]	(a)
$(3.2 \pm 0.3) \times 10^{-15}$		20			
$(5.8 \pm 1.2) \times 10^{-15}$		21			
$(5.4 \pm 0.8) \times 10^{-14}$		22			
$(1.2 \pm 0.4) \times 10^{-14}$		23			
$(0.84 \pm 0.04) \times 10^{-14}$		24			
$(1.8 \pm 0.05) \times 10^{-11}$		25			
$(4.7 \pm 0.2) \times 10^{-14}$		26			
$(2.3 \pm 0.1) \times 10^{-14}$	O_2	19	460		
$(3.1 \pm 0.08) \times 10^{-14}$		20			
$(2.2 \pm 0.9) \times 10^{-14}$		21			
$(3.7 \pm 0.3) \times 10^{-14}$		22			
$(4.1 \pm 0.6) \times 10^{-14}$		23			
$(6.9 \pm 0.5) \times 10^{-14}$		24			
$(11.7 \pm 0.2) \times 10^{-14}$		25			
$(16.4 \pm 2) \times 10^{-14}$		26			
$>8.3 \times 10^{-14}$		27			
$>1.2 \times 10^{-11}$		28			
6.5×10^{-14}	O_2	8	300	Park and Slanger, 1994[2]	(b)
$>1.3 \times 10^{-13}$	He	22			
$(1.53 \pm 0.25) \times 10^{-11}$	O_3	22			
2×10^{-13}	CO_2	14			
9×10^{-14}		22			

Comments

(a) Vibrationally highly excited electronic ground state O_2 molecules were generated by stimulated emission pumping, and detected by LIF.

(b) Vibrationally highly excited electronic ground state O_2 molecules were formed by ozone photodissociation at 248 nm (Hartley band). The excited molecules were detected by LIF. Rate coefficients were evaluated using a cascade model, in which relaxation through single-quantum V-V and V-T steps was assumed.

Preferred Values

See table.

Reliability

$\Delta \log k = \pm 0.5$.

Comments on Preferred Values

The results given from Ref. 1, and more results presented in graphical form from Ref. 2, appear consistent with each other.

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$O_2(^1\Delta_g) + M \rightarrow O_2(^3\Sigma_g^-) + M$

$\Delta H = -94.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}		Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients				
$(1.51\pm0.05)\times10^{-18}$	O_2	298	Borrell, Borrell, and Pedley, 1977[1]	DF-CL (a)
$(1.47\pm0.05)\times10^{-18}$	O_2	298	Leiss *et al.*, 1978[2]	(b)
$(1.65\pm0.07)\times10^{-18}$	O_2	298	Raja, Arora, and Chatha, 1986[3]	DF-CL (a)
$3.15\times10^{-18}\exp(-205/T)$	O_2	100–450	Billington and Borrell, 1986[4]	DF-CL (a)
1.57×10^{-18}		298		
1.4×10^{-19}	N_2	300	Collins, Husain, and Donovan, 1973[5]	FP-VUVA (c)
5.6×10^{-18}	H_2O	298	Findlay and Snelling, 1971[6]	(d)
$<1.5\times10^{-20}$	CO_2	298		
$(4\pm1)\times10^{-18}$	H_2O	298	Becker, Groth, and Schurath, 1971[7]	(e)
Reviews and Evaluations				
$3.6\times10^{-18}\exp(-220/T)$	O_2	100–450	NASA, 1997[8]	(f)
$<10^{-20}$	N_2	298		
4.8×10^{-18}	H_2O	298		
$<2\times10^{-20}$	CO_2	298		
$3.0\times10^{-18}\exp(-200/T)$	O_2	100–450	IUPAC, 1997[9]	(g)
$\leq1.4\times10^{-19}$	N_2	298		
5.0×10^{-18}	H_2O	298		
$\leq2\times10^{-20}$	CO_2	298		

Comments

(a) Discharge flow system. $O_2(^1\Delta)$ was monitored by dimol emission at 634 nm or from $O_2(^1\Sigma)$ emission at 762 nm.

(b) Large static reactor. $O_2(^1\Delta)$ was monitored by emission at 1.27 μm.

(c) $O_2(^1\Delta)$ was detected by time-resolved absorption at 144 nm.

(d) Flow system, with photolysis of C_6H_6–O_2 mixtures at 253.7 nm to produce $O_2(^1\Delta)$. $O_2(^1\Delta)$ was measured by 1.27 μm emission.

(e) As (b) but using dimol emission.

(f) The rate coefficients are based on the studies of: O_2, Steer *et al.*,[10] Findlay and Snelling,[6] Borrell *et al.*,[1] Leiss *et al.*,[2] Tachibana and Phelps,[11] Billington and Borrell,[4] Raja *et al.*,[3] and Wildt *et al.*;[12] N_2, Findlay *et al.*[13] and Becker *et al.*;[7] H_2O, Becker *et al.*[7] and Findlay and Snelling;[6] and CO_2, Findlay and Snelling[6] and Leiss *et al.*[2]

(g) See Comments on Preferred Values.

Preferred Values

$k = 1.6\times10^{-18}$ cm^3 molecule^{-1} s^{-1} for $M=O_2$ at 298 K.

$k = 3.0\times10^{-18}\exp(-200/T)$ cm^3 molecule^{-1} s^{-1} for $M=O_2$ over the temperature range 100–450 K.

$k \leq 1.4\times10^{-19}$ cm^3 molecule^{-1} s^{-1} for $M = N_2$ at 298 K.

$k = 5\times10^{-18}$ cm^3 molecule^{-1} s^{-1} for $M = H_2O$ at 298 K.

$k \leq 2\times10^{-20}$ cm^3 molecule^{-1} s^{-1} for $M = CO_2$ at 298 K.

Reliability

$\Delta\log k = \pm0.2$ for $M=O_2$ at 298 K.

$\Delta(E/R) = \pm200$ K for $M=O_2$.

$\Delta\log k = \pm0.3$ for $M=H_2O$ at 298 K.

Comments on Preferred Values

The preferred value for $k(M=O_2)$ is based on the data of Borrell *et al.*,[1] Leiss *et al.*,[2] Raja *et al.*,[3] and Billington and Borrell,[4] which also gives the temperature dependence adopted. For other quenching gases the recommendation for $k(M=N_2)$ is based on the data of Collins *et al.*,[5] for $k(M=H_2O)$ on the data of Findlay and Snelling[6] and Becker *et al.*,[7] and for $k(M=CO_2)$ on the data of Leiss *et al.*[2] and Findlay and Snelling.[6] The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[9]

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$O_2(^1\Delta_g) + O_3 \rightarrow 2O_2 + O$

$\Delta H° = 12.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$4.5\times10^{-11}\exp(-2830/T)$	283–321	Findlay and Snelling, 1971[1]	F-CL (a)
3.4×10^{-15}	298		
$6.0\times10^{-11}\exp(-2850/T)$	296–360	Becker, Groth, and Schurath, 1972[2]	S-CL (b)
4.2×10^{-15}	298		
Reviews and Evaluations			
$5.2\times10^{-11}\exp(-2840/T)$	280–360	NASA, 1997[3]	(c)
$5.2\times10^{-11}\exp(-2840/T)$	280–360	IUPAC, 1994[4]	(d)

Comments

(a) $O_2(^1\Delta_g)$ produced by photolysis of O_3 at 253.7 nm.
(b) $O_2(^1\Delta_g)$ produced by a microwave discharge of O_2 and flowed into the large static reaction vessel.
(c) Based on the data of Clark *et al.*,[5] Findlay and Snelling,[1] Becker *et al.*,[2] and Collins *et al.*[6]
(d) See Comments on Preferred Values.

Preferred Values

$k = 3.8\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.2\times10^{-11}\exp(-2840/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 280–360 K.

Reliability

$\Delta\log k = \pm0.10$ at 298 K.

$\Delta(E/R) = \pm500$ K.

Comments on Preferred Values

The preferred values are mean values from the studies listed.[1,2] While the data of Clark *et al.*[5] are in good agreement with these studies[1,2] for the room temperature value, their temperature coefficient[5] is substantially lower. In view of the consistency of the results from Findlay and Snelling[1] and Becker *et al.*,[2] which were obtained by two completely different techniques, we favor their temperature coefficient over that from Ref. 5. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[4]

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$O_2(^1\Sigma_g^+) + M \rightarrow O_2(^3\Sigma_g^-) + M$ (1)

$\rightarrow O_2(^1\Delta_g) + M$ (2)

$\Delta H^\circ(1) = -156.9$ kJ·mol^{-1}
$\Delta H^\circ(2) = -62.6$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}		Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients				
$(4.6 \pm 1) \times 10^{-17}$	O_2	294	Thomas and Thrush, 1975[1]	DF-CL
4.6×10^{-12}	H_2O	294		
$(4.0 \pm 0.4) \times 10^{-17}$	O_2	298	Martin, Cohen, and Schatz, 1976[2]	FP-CL
$(2.2 \pm 0.1) \times 10^{-15}$	N_2	298		
$(3.8 \pm 0.3) \times 10^{-17}$	O_2	300	Lawton *et al.*, 1977[3]	FP-CL
$(2.5 \pm 0.2) \times 10^{-17}$	O_2	298	Chatha *et al.*, 1979[4]	DF-CL
$(1.7 \pm 0.1) \times 10^{-15}$	N_2	298		
$1.7 \times 10^{-15} \exp(48/T)$	N_2	203–349	Kohse-Hoinghaus and Stuhl, 1980[5]	PLP (a)
$(8.0 \pm 2.0) \times 10^{-14}$	$O(^3P)$	300	Slanger and Black, 1979[6]	FP (a)
4.4×10^{-13}	CO_2	298	Filseth, Zia, and Welge, 1970[7]	FP (a)
$(3.0 \pm 0.5) \times 10^{-13}$	CO_2	298	Noxon, 1970[8]	FP (a)
$(4.1 \pm 0.3) \times 10^{-13}$	CO_2	298	Davidson, Kear, and Abrahamson, 1972[9]	FP (a)
$(4.53 \pm 0.29) \times 10^{-13}$	CO_2	298	Avilés, Muller, and Houston, 1980[10]	PLP (a)
$(5.0 \pm 0.3) \times 10^{-13}$	CO_2	298	Muller and Houston, 1981[11]	PLP (a)
$(3.4 \pm 0.4) \times 10^{-13}$	CO_2	293	Borrell, Borrell, and Grant, 1983[12]	DF-CL
$(1.7 \pm 0.1) \times 10^{-15}$	N_2	298	Choo and Leu, 1985[13]	DF (a)(b)
$(4.6 \pm 0.5) \times 10^{-13}$	CO_2	245–262		
5.6×10^{-17}	O_2	302	Knickelbein *et al.*, 1987[14]	PLP (a)
$(2.2 \pm 0.2) \times 10^{-15}$	N_2	298	Wildt *et al.*, 1988[15]	PLP-CL (c)
$(2.4 \pm 0.4) \times 10^{-13}$	CO_2	298		
$< 1.0 \times 10^{-16}$	O_2	298	Shi and Barker, 1990[16]	PLP-CL (d)
$(2.32 \pm 0.14) \times 10^{-15}$	N_2	298		
$(4.0 \pm 0.1) \times 10^{-13}$	CO_2	298		
Reviews and Evaluations				
3.9×10^{-17}	O_2	298	NASA, 1997[17]	(e)
2.1×10^{-15}	N_2	200–300		(f)
8×10^{-14}	$O(^3P)$	298		(g)
5.4×10^{-12}	H_2O	298		(h)
4.2×10^{-13}	CO_2	200–300		(i)
4.0×10^{-17}	O_2	298	IUPAC, 1997[18]	(j)
2.0×10^{-15}	N_2	200–350		
8.0×10^{-14}	$O(^3P)$	298		
4.0×10^{-12}	H_2O	298		
4.1×10^{-13}	CO_2	245–360		

Comments

(a) Time-resolved emission from $O_2(^1\Sigma)$ measured near 762 nm.

(b) Negligible temperature dependence observed for quenching by CO_2 over the range 245–362 K, with $E/R < \pm 200$ K.

(c) Direct laser excitation of $O_2(^1\Sigma)$ from O_2 by photolysis at 600–800 nm.

(d) $O_2(^1\Sigma)$ formed by the reaction $O(^1D) + O_2 \rightarrow O(^3P) + O_2(^1\Sigma)$.

(e) Based on the data of Martin *et al.*,[2] Lawton *et al.*,[3] and Lawton and Phelps.[19]

(f) Based on the data of Izod and Wayne,[20] Stuhl and Welge,[21] Filseth *et al.*,[7] Martin *et al.*,[2] Kohse-Höinghaus and Stuhl,[5] Choo and Leu,[13] Wildt *et al.*,[15] and Shi and Barker.[16]

(g) Based on the data of Slanger and Black.[6]

(h) Based on the data of Stuhl and Niki,[22] Filseth *et al.*,[7] Wildt *et al.*,[15] and Shi and Barker.[16]

(i) Based on the data of Filseth *et al.*,[7] Davidson *et al.*,[9] Avilés *et al.*,[10] Muller and Houston,[11] Choo and Leu,[13] Wildt *et al.*,[15] and Shi and Barker.[16]

(j) See Comments on Preferred Values.

Preferred Values

$k = 4.1 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} for $M = O_2$ at 298 K.

$k=2.1\times10^{-15}$ cm^3 molecule^{-1} s^{-1} for M=N_2 over the temperature range 200–350 K.
$k=8.0\times10^{-14}$ cm^3 molecule^{-1} s^{-1} for M=O(^{3}P) at 298 K.
$k=4.6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} for M=H_2O at 298 K.
$k=4.1\times10^{-13}$ cm^3 molecule^{-1} s^{-1} for M=CO_2 over the temperature range 245–360 K.

Reliability

$\Delta\log k=\pm0.3$ for M=O_2, O(^{3}P) and H_2O at 298 K.
$\Delta\log k=\pm0.10$ for M=N_2, CO_2 at 298 K.
$\Delta(E/R)=\pm200$ K for M=N_2, CO_2.

Comments on Preferred Values

The preferred value for k(M=O_2) is based on the data of Thomas and Thrush,[1] Martin *et al.*,[2] Lawton *et al.*,[3] Chatha *et al.*,[4] and Knickelbein *et al.*[14] For M=N_2 the value is based on the data of Kohse-Höinghaus and Stuhl,[5] Martin *et al.*,[2] Chatha *et al.*,[4] Choo and Leu,[13] Wildt *et al.*,[15] and Shi and Barker.[16] The value of Slanger and Black[6] is adopted for M=O(^{3}P) and the value of Thomas and Thrush[1] for M = H_2O. For k(M = CO_2) the results of Choo and Leu,[13] Filseth *et al.*,[7] Noxon,[8] Davidson *et al.*,[9] Avilés *et al.*,[10] Muller and Houston,[11] Borrell *et al.*,[12] Wildt *et al.*,[15] and Shi and Barker[16] are used.

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$O_2(^1\Sigma_g^+) + O_3 \rightarrow 2O_2 + O$ (1)

$\rightarrow O_2(^1\Delta_g) + O_3$ (2)

$\rightarrow O_2(^3\Sigma_g^-) + O_3$ (3)

$\Delta H^\circ(1) = -50.4$ kJ·mol^{-1}
$\Delta H^\circ(2) = -62.6$ kJ·mol^{-1}
$\Delta H^\circ(3) = -156.9$ kJ·mol^{-1}

Rate coefficient data ($k=k_1+k_2+k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.5\pm0.5)\times10^{-11}$	295	Gilpin, Schiff, and Welge, 1971[1]	FP-CL (a)
$(2.3\pm0.5)\times10^{-11}$	295	Snelling, 1974[2]	FP (a)
$(2.2\pm0.2)\times10^{-11}$	300	Slanger and Black, 1979[3]	(a) (b)
$(1.8\pm0.2)\times10^{-11}$	295	Amimoto and Wiesenfeld, 1980[4]	FP-RA
$(2.2\pm0.3)\times10^{-11}$	295–361	Choo and Leu, 1985[5]	DF-CL (c)
$(1.96\pm0.09)\times10^{-11}$	300	Shi and Barker, 1990[6]	PLP-CL (d)
$(2.06\pm0.22)\times10^{-11}$	300	Turnipseed *et al.*, 1991[7]	PLP-RF (e)
Reviews and Evaluations			
2.2×10^{-11}	200–350	NASA, 1997[8]	(f)
2.2×10^{-11}	295–360	IUPAC, 1997[9]	(g)
$k_1=1.5\times10^{-11}$	298		

Comments

(a) $O_2(^1\Sigma_g^+)$ detected in emission.
(b) Flow system with $O_2(^1\Sigma_g^+)$ being produced by the modulated photolysis of O_2 at 147.0 nm to produce $O(^1D)$ atoms, followed by $O(^1D) + O_2 \rightarrow O(^3P) + O_2(^1\Sigma_g^+)$.
(c) Negligible temperature dependence was observed, with $E/R < \pm 300$ K.
(d) $O_2(^1\Sigma_g^+)$ generated by the reaction $O(^1D) + O_2 \rightarrow O + O_2(^1\Sigma_g^+)$, with $O(^1D)$ atoms being produced from 308 nm pulsed laser photolysis of O_3.
(e) Rate coefficient for global reaction of $O_2(^1\Sigma_g^+)$ with O_3 was derived by modeling the temporal behavior of $O(^3P)$ and $O(^1D)$ atoms.
(f) Based on the data of Gilpin *et al.*,[1] Slanger and Black,[3] Choo and Leu,[5] and Shi and Barker.[6]
(g) See Comments on Preferred Values.

Preferred Values

$k = 2.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 295–360 K.

$k_1 = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta \log k_1 = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred value at 298 K is based on all of the studies cited in the table,[1–7] which show very good agreement at room temperature. The temperature independence reported in the study of Choo and Leu[5] is adopted in the evaluation. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[9] Channel (1) accounts for 70±20% of the total reaction.[3,4]

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$O_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$O_2 + h\nu \rightarrow O(^3P) + O(^3P)$	494	242
$\rightarrow O(^3P) + O(^1D)$	683	175
$\rightarrow O(^1D) + O(^1D)$	873	137
$\rightarrow O(^3P) + O(^1S)$	898	132

Absorption cross-section data

Wavelength range/nm	Reference	Comment
230–280	Oshima, Okamoto, and Koda, 1995[1]	(a)
240–270	Yoshino *et al.*, 1995[2]	(b)
205–240	Yoshino *et al.*, 1988[3]	(c)

Comments

(a) The effect of pressurized foreign gases on the photoabsorption of O_2 in the Herzberg bands and Herzberg continuum (230–280 nm) was studied. The values of the cross-sections in O_2 and O_2–N_2 mixtures under various pressures were in good agreement with the previous literature.
(b) High resolution FT spectrometry (0.06 cm^{-1}) was used to measure photoabsorption cross-sections of O_2 in the Herzberg I bands (240–270 nm). Precise band oscillator strengths of the (4,0)–(11,0) bands were obtained, which were significantly higher than previous experimental values.
(c) Analysis and combination of data of Cheung *et al.*[4] and Jenouvrier *et al.*[5]

Preferred Values

Absorption cross-section of O_2 in the 205–240 nm region of the Herzberg continuum

λ/nm	10^{24} σ/cm²	λ/nm	10^{24} σ/cm²
205	7.35	223	3.89
207	7.05	225	3.45
209	6.68	227	2.98
211	6.24	229	2.63
213	5.89	231	2.25
215	5.59	233	1.94
217	5.13	235	1.63
219	4.64	237	1.34
221	4.26	239	1.10
		240	1.01

Comments on Preferred Values

The recommended absorption cross-section values for the Herzberg continuum are taken from the study of Yoshino *et al.*,[3] where values are tabulated for every nm from 205 to 240 nm. These values were derived from an analysis and combination of the data of Cheung *et al.*[4] and Jenouvrier *et al.*[5] These data are in agreement with the results of Johnston *et al.*,[6] and are consistent with the lower absorption cross-section values inferred from balloon-borne measurements of solar irradiance attenuation in the stratosphere by Frederick and Mentall,[7] Herman and Mentall,[8] and Anderson and Hall.[9] Herzberg continuum cross-section values under the Schumann-Runge (S-R) bands (<200 nm) have recently been determined more accurately by Yoshino *et al.*[10] and are significantly smaller than any previous values. The new data from Oshima *et al.*[1] and Yoshino *et al.*[2] relate to the Herzberg bound system in the region beyond the photodissociation threshold for O_2, and do not affect the preferred cross-sections for the photolysis of atmospheric O_2.

In the Schumann-Runge wavelength region (175–200 nm), a detailed analysis of the penetration of solar radiation requires absorption cross-section measurements with very high spectral resolution. Absorption cross-section values for the (0, 0)–(12, 0) S-R bands measured by the Harvard–Smithsonian group[10–19] are the first set of values which are independent of instrumental resolution. Band oscillator strengths for these bands have been determined by direct numerical integration of these absolute cross-section values. Minschwaner *et al.*[20,21] have fitted O_2 cross-sections for the frequency range 49 000–57 000 cm^{-1} (175–204 nm) with temperature-dependent polynomial expressions for the temperature range 130–500 K using the latest laboratory spectroscopic data. This model provides an efficient and accurate means of determining S-R band absorption cross-sections at 0.5 cm^{-1} resolution. These high resolution calculated values differ from the WMO[22] recommendations by up to 10–20% at some wavelengths. Mean-band parameterizations of O_2 absorption in the S-R bands for calculating UV transmission and photolysis rates have been presented by Murtagh[23] and by Nicolet and Kennes.[24]

The effect on ozone formation in the 214 nm photolysis of oxygen due to O_2–O_2 collision pairs at high O_2 pressure and the effect of high N_2 pressure has been studied by Horowitz *et al.*[25] Greenblatt *et al.*[26] studied the absorption spectrum of O_2 and O_2–O_2 collision pairs over the wavelength range 330–1140 nm for O_2 pressures from 1 to 55 bar at 298 K. Band centers, bandwidths, and absorption cross-sections were reported for the absorption features in this wavelength region.[26]

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$O_3 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$O_3 + h\nu \rightarrow O(^3P) + O_2(^3\Sigma_g^-)$	(1)	101	1180
$\rightarrow O(^3P) + O_2(^1\Delta_g)$	(2)	196	611
$\rightarrow O(^3P) + O_2(^1\Sigma_g^+)$	(3)	258	463
$\rightarrow O(^1D) + O_2(^3\Sigma_g^-)$	(4)	291	411
$\rightarrow O(^1D) + O_2(^1\Delta_g)$	(5)	386	310
$\rightarrow O(^1D) + O_2(^1\Sigma_g^+)$	(6)	448	267
$\rightarrow 3O(^3P)$	(7)	595	201

Absorption cross-section data

Wavelength range/nm	Reference	Comment
245–350	Bass and Paur, 1985[1]	(a)
185–350	Molina and Molina, 1986[2]	(b)
253.7	Mauersberger *et al.*, 1986[3,4]	(c)
175–360	WMO, 1986[5]	(d)
410–760	Burkholder and Talukdar, 1994[6]	(e)
195–345	Malicet *et al.*, 1995[7]	(f)

Quantum yield data

Measurement	λ/nm	Reference	Comment
$\phi\,[O(^3P)]$	275	Fairchild *et al.*, 1978[8]	(g)
$\phi\,[O(^3P)]$	266	Sparks *et al.*, 1980[9]	(h)
$\phi\,[O(^1D)]$	297.5–325	Brock and Watson, 1980[10]	(i)
$\phi\,[O(^1D)]$	266	Brock and Watson, 1980[11]	(j)
$\phi\,[O(^1D)]$	248	Amimoto *et al.*, 1980[12]	(k)
$\phi\,[O(^1D)]$	248	Wine and Ravishankara, 1983[13]	(l)
$\phi\,[O(^1D)]$	275–325	Trolier and Wiesenfeld, 1988[14]	(m)
$\phi\,[O(^1D)]$	222,193	Turnipseed *et al.*, 1991[15]	(n)
$\phi\,[O(^1D)]$	221–243.4	Cooper *et al.*, 1993[16]	(o)
$\phi\,[O_2(^1\Delta_g)]$	300–322	Ball and Hancock, 1995[17]	(p)
$\phi\,[O_2(^1\Delta_g)]$	287–331	Ball *et al.*, 1995[18]	(q)
$\phi\,[O_2(^1\Delta_g)]$	300–322	Ball, Hancock, and Winterbottom, 1995[19]	(r)
$\phi\,[O(^1D)]$	300–355	Armerding, Comes, and Schulke, 1995[20]	(s)
$\phi\,[O(^1D),O(^3P),O_2]$	193	Stranges *et al.*, 1995[21]	(t)
$\phi\,[O(^1D),O(^3P)]$	308–326	Takahashi, Matsumi, and Kawasaki, 1996[22]	(u)
$\phi\,[O(^1D)]$	301–336	Silvente *et al.*, 1996[23]	(v)

Comments

(a) Measured at 226–298 K with a spectral resolution of 0.07 nm.

(b) Measured at 200–300 K with a spectral resolution of 0.025 nm. Relative values were normalized to a value of 1147×10^{-20} cm^2 at the 253.65 nm mercury line.

(c) Measured at 297 K and, in a later study,[4] over the temperature range 195–351 K at the 253.65 nm mercury line.

(d) Critical review of all published data. Recommended values were given for standard spectral intervals from 175–360 nm for 203 and 273 K.

(e) Measured with a diode array spectrometer. The cross-sections were independent of temperature.

(f) Absolute cross-sections for O_3 absorption in the range 195–345 nm were measured at high resolution ($\Delta\lambda = 0.01-0.02$ nm) using a conventional absorption cell - monochromator combination, with ozone being measured manometrically. The temperature dependence of absorption in the Hartley and Huggins bands was also measured over the range 218–295 K. A small increase in σ with decreasing temperature (1.0% over the whole temperature range) was observed at $\lambda = 253.6$ nm, near the maximum in the Hartley band, in agreement with earlier data;[4] at 298 K, σ(253.65 nm)=$(113.05\pm1.1)\times10^{-19}$ cm^2 molecule^{-1}. In the Huggins bands (300–345 nm) there was a larger temperature dependence (up to 50%), which increased progressively to longer wavelengths. In contrast to the Hartley band there was a decrease in σ with decreasing temperature.

(g) Photofragment spectroscopy of O_3. The co-product is $O_2(^3\Sigma^-)$ with a value of $\phi(1)=0.1$.

(h) High resolution photofragment spectroscopy, giving $\phi(1)=0.1$.

(i) Laser photolysis of O_3–N_2O mixtures. The NO product of the $O(^1D)$ atom reaction with N_2O was measured by chemiluminescence from NO_2.

(j) Pulsed laser photolysis. $O(^3P)$ atoms were monitored by RF. $\phi(1)=0.12\pm0.02$ at 266 nm.

(k) Pulsed laser photolysis. $O(^3P)$ atoms were monitored by RA. $\phi(1)=0.15\pm0.02$ at 248 nm.

(l) Pulsed laser photolysis. $O(^3P)$ atoms were monitored by RA. $\phi[O(^3P)]=0.093\pm0.028$ and $\phi[O(^1D)]=0.907\pm0.028$ at 248 nm.

(m) Pulsed laser photolysis of O_3–N_2O mixtures. $O(^1D)$ atom quenching by CO_2 was monitored by infrared chemiluminescence from CO_2.

(n) Pulsed laser photolysis. $O(^3P)$ atoms were monitored by RF. $\phi[O(^3P)]=0.12\pm0.02$ and $\phi[O(^1D)]=0.87$ at 222 nm.

(o) Pulsed laser photolysis. $O(^1D)$ atoms were detected by weak 630 nm fluorescence emission from $O(^1D) \rightarrow O(^3P)$. Relative measurements of $\phi[O(^1D)]$ were normalized to $\phi[O(^1D)]=0.87$ at 222 nm using the data of Turnipseed *et al.*.[15]

(p) Relative quantum yields of $O_2(^1\Delta)$ from pulsed laser photolysis of O_3 in the range $300<\lambda<322$ nm were measured by {2+1} resonance enhanced multiphoton ionization (REMPI) at 227 K. For $\lambda>309$ nm, $\phi[O_2(^1\Delta)]$ at 227 K falls more rapidly than observed at 298 K,[24] confirming that the internal energy of O_3 contributes to formation of $O_2(^1\Delta)$, just beyond the 310 nm threshold for spin allowed production of the two singlet products of channel (5). At $\lambda>320$ nm, $\phi[O_2(^1\Delta)]$ was approximately equal at the two temperatures, and substantially larger than recent measurements of $\phi(O^1D)$, suggesting a spin-forbidden channel for $O_2(^1\Delta)$ production [e.g., channel (2)], with $\phi(2)=0.1$ at 320 nm.

(q) Kinetic energies of the $O_2(^1\Delta)$ fragment of O_3 photolysis in the range 287.57 and 331.52 nm were measured by time-of-flight mass spectrometry. Between 308 and 318 nm, dissociation is dominated by the spin-allowed dissociation channel (5). At longer wavelengths, photofragments with higher kinetic energies are produced, consistent with the occurrence of the spin forbidden process, channel (2).

(r) The data for the temperature dependence of $\phi[O_2(^1\Delta)]$ reported in earlier publications[17,18,24] were compared with earlier data for $\phi[O(^1D)]$. At 300–309 nm there is no temperature dependence of the yield of either photoproduct. In the falloff region, at 307–319 nm there is good agreement between the measured yields of $O_2(^1\Delta)$ and recent modeling calculations by Michelson *et al.*,[25] which take into account dissociation of internally excited ozone molecules for the formation of $O(^1D)$ atoms.

(s) $\phi[O(^1D)]$ in the wavelength range 300–330 nm and at 355 nm were determined by observation of the LIF of OH radicals produced by the reaction of photofragment $O(^1D)$ with H_2O. $\phi[O(^1D)]$ was determined to be unity at 302.5 nm, decreasing to 0.6 at 310 nm with a characteristic "saddle" point at 315 nm and with a long wavelength tail extending to a threshold between 331 and 333 nm. No $O(^1D)$ was detected at 355 nm.

(t) Photodissociation of O_3 at 193 nm studied using high resolution photofragment translation spectroscopy. Time-of-flight spectra for O_2 and O were determined. O_2 production in $^1\Delta_g$, $^1\Sigma_g^+$ and highly excited triplet states was observed. Evidence was seen for a small contribution from channel (7).

(u) The photofragment yield spectra of $O(^1D)$ and $O(^3P)$ atoms produced in the photodissociation of O_3 in the Huggins band system over the range 308–326 nm were determined using vacuum ultraviolet LIF. The $O(^3P)$ atom yield exhibited vibrational structure as in the absorption spectrum in the Huggins band, while $O(^1D)$ showed a smooth dependence on wavelength. The quantum yield of $O(^1D)$, calculated using the absorption spectrum of Molina and Molina,[2] showed a distinct "tail" for the region beyond the threshold for channel (5) at 310 nm, as has been reported in some previous studies,[10,14] and for the co-product from the spin allowed channel (5), $O_2(^1\Delta)$, reported by Ball and coworkers.[17–19,24] The "tail" in $\phi[O(^1D)]$ in the wavelength range 310–321 nm is attributed to hot band excitation of the repulsive limb of the excited state ($^1B_2$ or $^2A_1$) correlating to the singlet products. The non-zero formation of $O(^1D)$ at $\lambda>321$ nm was tentatively attributed to the spin forbidden process producing $O(^1D)+O_2(^3\Sigma_g^-)$.

(v) Relative quantum yields for $O(^1D)$ measured indirectly via LIF detection of vibrationally excited OH radicals produced in the $O(^1D)+H_2$ reaction. Use of blue-shifted LIF gave high detection sensitivity and eliminated probe laser interference. A significant $O(^1D)$ quantum yield at $\lambda>320$ nm was confirmed. A measurable quantum yield of ~0.05 was observed out to 336 nm, which was assigned to the spin-forbidden channel (4).

Preferred Values

Ozone absorption cross-sections averaged over spectral intervals

Int #	λ/nm	10^{20} σ/cm^2 273 K	Int #	λ/nm	10^{20} σ/cm^2 273 K	10^{20} σ/cm^2 203 K
1	175.4–177.0	81.1	31	238.1–241.0	797	797
2	178.6	79.9	32	243.9	900	900
3	180.2	78.6	33	246.9	1000	1000
4	181.8	76.3	34	250.1	1080	1085
5	183.5	72.9	35	253.2	1130	1140
6	185.2	68.8	36	256.4	1150	1160
7	186.9	62.2	37	259.7	1120	1130
8	188.7	57.6	38	263.2	1060	1060
9	190.5	52.6	39	266.7	965	959
10	192.3	47.6	40	270.3	834	831
11	194.2	42.8	41	274.0	692	689
12	196.1	38.3	42	277.8	542	535
13	198.0	34.7	43	281.7	402	391
14	200.0	32.3	44	285.7	277	267
15	202.0	31.4	45	289.9	179	173
16	204.1	32.6	46	294.1	109	104
17	206.2	36.4	47	298.5	62.4	58.5
18	208.3	43.4	48	303.0	34.3	31.6
19	210.5	54.2	49	307.7	18.5	16.6
20	212.8	69.9	50	312.5	9.80	8.67
21	215.0	92	51	317.5	5.01	4.33
22	217.4	119	52	322.5	2.49	2.09
23	219.8	155	53	327.5	1.20	0.937
24	222.2	199	54	332.5	0.617	0.471
25	224.7	256	55	337.5	0.274	0.198
26	227.3	323	56	342.5	0.117	0.077
27	229.9	400	57	347.5	0.059	0.017
28	232.6	483	58	352.5	0.027	-
29	235.3	579	59	357.5	0.011	-
30	238.1	686	60	362.5	0.005	-

$\sigma=(1143\pm 15)\times 10^{-20}$ cm^2 molecule^{-1} at 253.7 nm at 298 K.
$\sigma=(1154\pm 15)\times 10^{-20}$ cm^2 molecule^{-1} at 253.7 nm at 220 K.

Ozone absorption cross-sections in the visible spectral region

λ/nm	10^{23} σ/cm^2	λ/nm	10^{23} σ/cm^2
410	1.2	560	394
420	2.2	580	459
440	11.2	600	511
460	32.8	620	400
480	68.4	640	296
500	122	660	209
520	182	680	136
540	291	700	91

σ is independent of temperature in the wavelength region 410–700 nm.

Quantum yields for $O(^1D)$ production from O_3 photolysis at 298 K

Wavelength/nm	$\phi[O(^1D)]$	Wavelength/nm	$\phi[O(^1D)]$
300	0.950	314	0.238
301	0.965	315	0.235
302	0.975	316	0.221
303	0.985	317	0.209
304	0.990	318	0.194
305	0.980	319	0.178
306	0.950	320	0.148
307	0.877	321	0.121
308	0.773	322	0.097
309	0.667	323	0.092
310	0.600	324	0.080
311	0.388	325	0.070
312	0.303	330	0.050
313	0.262	335	0.050

$271<\lambda<300$: $\phi\,[O(^1D)]=\{1.98-(301/\lambda)\}$ where λ is the wavelength in nm.
$222<\lambda<271$: $\phi\,[O(^1D)]=0.87$.
$222<\lambda<271$: $\phi\,[O(^3P)]=0.13$.

Comments on Preferred Values

Absorption cross-sections. The recommended absorption cross-section values at 273 K for the wavelength range 175–362 nm are averaged values for the standard spectral intervals used in atmospheric modeling calculations. These values have been adopted from earlier evaluations (NASA 1994;[26] IUPAC, 1997[27]) which accepted the values tabulated in the WMO review,[5] except for the region 185–225 nm where the values were taken from the study of Molina and Molina.[2] Recommended values at 203 K in the Huggins bands are also taken from the WMO review[5] and are based on the data of Bass and Paur.[1]

The new work of Malicet *et al.*[7] provides detailed data on the absolute absorption cross-sections of ozone and their temperature dependence (218–295 K) over the wavelength range 195–345 nm. The measurements are at sufficient resolution to resolve the vibrational structure in the Huggins bands. The data are generally in excellent agreement with earlier measurements, although there are small differences in detail in specific regions of the spectrum. At wavelengths below 240 nm the cross-sections are identical with those of Molina and Molina,[2] confirming the basis of the recommended values in this range. In the range 240–335 nm the new data are between 1.5% and 3.0% lower than Molina and Molina[2] but about 1.5% higher than Yoshino *et al.*,[28] and are very close to the data of Bass and Paur[1] up to 310 nm. In the Huggins bands (λ>310 nm), shifts of +0.05 nm in the vibrational structure are apparent in the Bass and Paur[1] data, which may be due to error in the wavelength calibration. This gives rise to small but significant differences in the individual cross-sections and their temperature dependence. Nevertheless the small differences do not influence the averaged cross-sections sufficiently to warrant revision of the recommended values for calculation of the atmospheric photoabsorption rates of ozone in the Huggins bands. For cross-

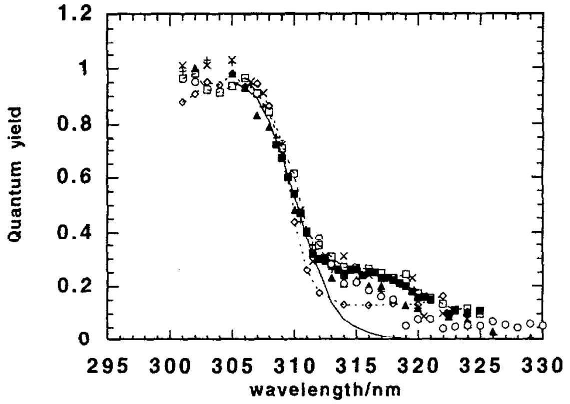

FIG. 1. Recent measurements of the quantum yields for production of $\mathrm{O}(^1\mathrm{D})$ and $\mathrm{O_2}(^1\Delta)$ from photolysis of ozone. $\phi[\mathrm{O}(^1\mathrm{D})]$: (+)=Brock and Watson (Ref. 10); (×)=Trolier and Wieseneld (Ref. 14); (▲)=Armerding *et al.* (Ref. 20); (■)=Takahashi *et al.* (Ref. 22); (○)=Silvente *et al.* (Ref. 23); $\phi[\mathrm{O_2}(^1\Delta)]$; (□)=Ball *et al.* (Refs. 19 and 24); (△)=Ball and Hancock (Ref. 17) (298 K); (◇) Ball and Hancock (Ref. 17) (222 K). (—) shows our previous recommendation (IUPAC, 1997) (Ref. 27) which is the same as in the NASA 1994 evaluation (Ref. 26).

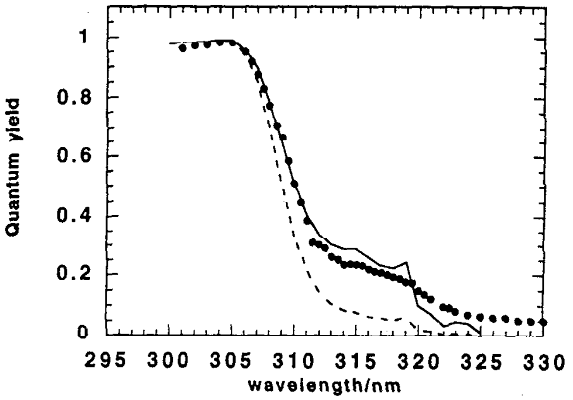

FIG. 2. Quantum yields for production of $\mathrm{O}(^1\mathrm{D})$ and $\mathrm{O_2}(^1\Delta)$ from photolysis of ozone. (●)=ϕ[O(1D)], preferred values from this evaluation at 298 K; (○)=$\phi[\mathrm{O_2}(^1\Delta)]$ at 227 K, Ball and Hancock (Ref. 17). (—) calculated curve for $\phi[\mathrm{O}(^1\mathrm{D})]$ from Michelson *et al.* (Ref. 25) at 298 K; (---) calculated curve for $\phi[\mathrm{O}(^1\mathrm{D})]$ from Michelson *et al.* (Ref. 25) at 227 K.

sections at high resolution, the data of Malicet *et al.*,[7] which is available in digital form from the authors, is recommended.

Malicet *et al.*[7] observed a weak temperature dependence near the maximum in the Hartley band, leading to an increase of approximately 1% in σ between 295 and 218 K, in agreement with earlier work of Molina and Molina[2] and Barnes and Mauersberger.[4] The values recommended for the cross-section at 253.7 nm have been obtained by averaging the data of Daumont *et al.*,[29] Malicet *et al.*,[7] Hearn,[30] Molina and Molina,[2] and Mauersberger and coworkers[3,4] The new recommendation is slightly lower than previously given on the basis of the latter three studies.

Ozone cross sections in the Chappuis bands (450–750 nm), which are independent of temperature, are taken from Burkholder and Talukdar.[6]

Quantum Yields. Recent data for the quantum yield for $\mathrm{O}(^1\mathrm{D})$ atom production and its co-product in the spin-allowed dissociation channel (5) give clear evidence for substantially enhanced dissociation into electronically excited products beyond the threshold at 310 nm. This warrants a complete revision in the recommended quantum yields for $\mathrm{O}(^1\mathrm{D})$ production, compared to previous NASA[26] and IUPAC[27] evaluations, which neglected the "tail" in $\phi[\mathrm{O}(^1\mathrm{D})]$ observed in some studies at wavelengths beyond 312 nm.

The recent data for $\mathrm{O}(^1\mathrm{D})$ atom and $\mathrm{O_2}(^1\Delta_g)$ quantum yields at room temperature as a function of wavelength are given in Figures 1 and 2, together with earlier data from Brock and Watson[10] and Trolier and Wiesenfeld.[14] Several points relevent to the evaluation can be noted. Firstly, $\phi[\mathrm{O}(^1\mathrm{D})]$ at 305 nm as measured by Brock and Watson,[10] Trolier and Wiesenfeld,[14] and Armerding *et al.*[20] is close to unity, i.e., higher than the value of 0.95 which was previously recommended for the range 280–305 nm. In the "tail" region ($\lambda > 310$ nm) there is a distinct shoulder between 314 and 318 nm where $\phi[\mathrm{O}(^1\mathrm{D})]$ and $\phi[\mathrm{O_2}(^1\Delta_g)]$ are approximately invariant with wavelength. At $\lambda > 318$ nm both quantum yields decline; $\phi[\mathrm{O_2}(^1\Delta_g)]$ remains in excess of 0.1 out to 325 nm, while $\phi[\mathrm{O}(^1\mathrm{D})]$ declines to between 0.05 and 0.1 at 325 nm and the provisional data of Silvente *et al.*,[23] using a sensitive indirect technique, indicate $\phi[\mathrm{O}(^1\mathrm{D})]$ of ~ 0.05 out to 336 nm.

The recommended values for $\phi[\mathrm{O}(^1\mathrm{D})]$ covering the range 300–335 nm at 298 K, are obtained by taking a smooth curve through the mean of the experimental values reported by Brock and Watson,[10] Trolier and Wiesenfeld,[14] Armerding *et al.*,[20] Takahashi *et al.*,[22] and Silvente *et al.*[23] (for $\lambda > 325$ nm only).

There are several studies (Brock and Watson,[11] Amimoto *et al.*,[12] Wine and Ravishankara,[13] Turnipseed *et al.*[15] and Cooper *et al.*[16]) which show that in the wavelength range 222–275 nm $\phi[\mathrm{O}(^1\mathrm{D})]$ is between 0.85 and 0.90 without significant variation. Fairchild *et al.*[8] and Sparks *et al.*[9] report significant $\mathrm{O}(^3\mathrm{P})$ production in the Hartley Band at 275 and 266 nm. Brock and Watson,[10] Trolier and Wiesenfeld[14] and Armerding *et al.*[20] observed a decline in $\phi[\mathrm{O}(^1\mathrm{D})]$ below 305 nm. The preferred values for ϕ $[\mathrm{O}(^1\mathrm{D})]$ at wavelengths below 300 nm follow the recommendation of Michelson *et al.*[25] on the basis of these data, i.e., for $271 < \lambda < 300$ the expression is a linear fit to the data of Trolier and Wiesenfeld:[14] $\phi[\mathrm{O}(^1\mathrm{D})] = \{1.98 - (301/\lambda)\}$ where λ is the wavelength in nm; for $222 < \lambda < 271$ nm, $\phi[\mathrm{O}(^1\mathrm{D})] = 0.87$. These are in much better overall agreement with experiment than the previous NASA[26] and IUPAC[27] recommendations.

There are currently no direct measurements of $\phi[\mathrm{O}(^1\mathrm{D})]$ at lower temperatures. Recent data on the temperature dependence of $\phi[\mathrm{O_2}(^1\Delta_g)]$ show a more rapid fall off at wavelengths >310 nm at 227 K compared to room temperature (see Figure 1). However, at both temperatures $\phi[O_2(^1\Delta_g)]$ declines to a limiting value of ~0.13 which, together with the evidence from the time-of-flight experiments of Ball *et al.*[18] strongly points to a contribution from the spin-forbidden channel (2). This precludes making a recommendation for the temperature dependence of $\phi[O(^1D)]$ on the basis of the $\phi[O_2(^1\Delta_g)]$ measurements. Earlier indirect measurements of Lin and DeMore[31] (275–320 nm) at 233 K and Kuis *et al.*[32] (313 nm) in the range 221–293 K show that $\phi[O(^1D)]$ falls off more rapidly at wavelengths >310 nm at low temperature. These temperature effects have recently been considered in a model in which vibrationally and rotationally excited ozone molecules contribute to excited product formation in channel (5).[25] This model[25] gives a reasonable description in the region between 310 and 320 nm of the recommended 298 K data as well as the low temperature data for $\phi[O_2(^1\Delta_g)]$ at $\lambda<315$ nm, as shown in Figure 2. The model does not include any contribution from the spin-forbidden channels, which are likely to show much less temperature dependence. Very recent data reported by Takahashi *et al.*,[33] who have observed Doppler profiles of the nascent $O(^1D)$ atom photofragments at 227 K, confirm that the $O(^1D)$ atoms formed by photolysis at wavelengths corresponding to the peaks in the O_3 absorption spectrum in the range 317–327 nm arise from the hitherto unobserved spin-forbidden predissociation $O(^1D)+O_2(^3\Sigma_g)$ products. Earlier recommendations for the temperature dependence were based on the work of Moortgat and Kudszus,[34] but these are not considered reliable in the light of the recent work. However, in the absence of experimental data no preferred values are given for $\phi[O(^1D)]$ at low temperatures. For atmospheric modeling, the parameterization for $\phi[O(^1D)]$ given by Michelson *et al.*[25] is recommended, with an additional term of 0.05 for $\lambda>320$ nm to account for the spin-forbidden component. At wavelengths below 305 nm, experiments show that $\phi[O(^1D)]$ is invariant with temperature.

In view of the indications that both spin-allowed and forbidden dissociation channels occur in parallel, it is not possible to assign the yields of $O(^1D)$ or $O(^3P)$ atoms to specific reactions over much of the range. In the Hartley band, time-of-flight measurements indicate that the spin-allowed channels (1) and (5) account for the observed products. In the Huggins bands, additional minor contributions from (2) and (4) are evidently occurring. In the Chappuis bands, dissociation to ground state products is generally assumed.

Two field studies in which chemical actinometer measurements of $\phi(O^1D)$ have been compared with values calculated from simultaneously measured actinic flux spectra have been reported recently by Muller *et al.*,[35] and Shetter *et al.*[36] Both support the existence of the long wavelength tail in $\phi(O^1D)$ in atmospheric photolysis rates.

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4.2. Hydrogen Species

$$\begin{aligned} H + HO_2 &\rightarrow H_2 + O_2 \quad (1)\\ &\rightarrow 2HO \quad (2)\\ &\rightarrow H_2O + O \quad (3) \end{aligned}$$

$\Delta H°(1) = -232.6$ kJ·mol^{-1}
$\Delta H°(2) = -154.0$ kJ·mol^{-1}
$\Delta H°(3) = -225.2$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(7.4 \pm 1.2) \times 10^{11}$	245–300	Sridharan, Qiu, and Kaufman, 1982[1]	DF-RF
$(8.7 \pm 1.5) \times 10^{11}$	245–300	Keyser, 1986[2]	DF-RF
Branching Ratios			
$k_1/k = 0.08 \pm 0.04$	245–300	Keyser, 1986[2]	
$k_2/k = 0.90 \pm 0.04$			
$k_3/k = 0.02 \pm 0.04$			
Reviews and Evaluations			
8.1×10^{-11}	245–300	NASA, 1997[3]	(a)
8.0×10^{-11}	245–300	IUPAC, 1997[4]	(b)

Comments

(a) Based on the data of Sridharan *et al.*[1] and Keyser.[2]
(b) See Comments on Preferred Values.

Preferred Values

$k = 8.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 245–300 K.

$k_1 = 5.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 245–300 K.

$k_2 = 7.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 245–300 K.

$k_3 = 2.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 245–300 K.

Reliability

$\Delta \log k = \pm 0.1$ over the temperature range 245–300 K.
$\Delta(E/R) = \pm 200$ K.
$\Delta \log k_1 = \pm 0.5$ over the temperature range 245–300 K.
$\Delta \log k_2 = \pm 0.1$ over the temperature range 245–300 K.
$\Delta \log k_3 = \pm 0.5$ over the temperature range 245–300 K.

Comments on Preferred Values

The study of Keyser[2] is the most detailed to date. Several species were monitored and the possible effects of side reactions were carefully analyzed. Values obtained for the overall rate coefficient and the branching ratios agree with the values obtained by Sridharan *et al.*[1] who used a similar technique. The recommended values for k and the branching ratios are the means of the values from these two studies.[1,2] In both cases,[1,2] k_1/k was not measured directly but obtained by difference. A direct measurement of this branching ratio is desirable.

The yield of $O_2(^1\Sigma_g^+)$ has been measured by Hislop and Wayne,[5] Keyser *et al.*,[6] and Michelangeli *et al.*[7] who report values of $(2.8 \pm 1.3) \times 10^{-1}$, $< 8 \times 10^{-3}$, and $< 2.1 \times 10^{-2}$, respectively.

Keyser[2] observed no effect of temperature on the rate coefficient k over the small range studied. This suggests that the value of $k_2 = 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 349 K obtained by Pagsberg *et al.*[8] is too low or there is a substantial negative temperature coefficient. We provisionally recommend $E/R = 0$ but only over the temperature range 245–300 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[4]

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$H + O_2 + M \rightarrow HO_2 + M$

$\Delta H^\circ = -203.4$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$5.33\times10^{-32}\ (T/298)^{-1.77}\ [N_2]$	226–298	Kurylo, 1972[1]	FP-RF
$(5.46\pm0.7)\times10^{-32}\ (T/298)^{-1.50}\ [N_2]$	220–298	Wong and Davis, 1974[2]	FP-RF
$6.5\times10^{-32}\ [N_2]$	298	Cobos, Hippler, and Troe, 1985[3]	PLP-UVA (a)
$6.2\times10^{-32}\ (T/300)^{-1.66}\ [N_2]$	298–639	Hsu *et al.*, 1989[4]	DF-RF
$2.9\times10^{-33}\ \exp[(825\pm130)/T]\ [N_2]$	298–580	Carleton, Kessler, and Marinelli, 1993[5]	PLP-LIF/RA
$4.6\times10^{-32}\ [N_2]$	298		
$3.9\times10^{-32}\ \exp[(600\pm1050)/T]\ [H_2O]$	575–750		
Reviews and Evaluations			
$5.7\times10^{-32}\ (T/300)^{-1.6}$ [air]	220–600	NASA, 1997[6]	(b)
$5.4\times10^{-32}\ (T/300)^{-1.8}\ [N_2]$	200–600	IUPAC, 1997[7]	(c)

Comments

(a) Measurements of the falloff curve between 1 and 200 bar, with determination of k_0, k_∞, and F_c.

(b) Based on the data of Kurylo,[1] Wong and Davis,[2] and Hsu *et al.*[4]

(c) See Comments on Preferred Values.

Preferred Values

$k_0 = 5.4\times10^{-32}\ (T/300)^{-1.8}\ [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–600 K.

Reliability

$\Delta \log k_0 = \pm0.1$ at 298 K.

$\Delta n = \pm0.6$.

Comments on Preferred Values

The preferred values are an average of the results from Refs. 1–5. There is a single study of the full falloff curve[3] which leads to $k_\infty = 7.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and a broadening factor of $F_c = 0.55\pm0.15$ at 298 K. Theoretical modeling gives $F_c = 0.66$ at 298 K and suggests a practically temperature-independent value of k_∞ over the temperature range 200–400 K.

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$O + HO \rightarrow O_2 + H$

$\Delta H° = -70.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.01×10^{-11} exp[(112±29)/T]	221–499	Lewis and Watson, 1980[1]	DF-RF
6.65×10^{-10} $T^{(-0.50\pm0.12)}$	250–500	Howard and Smith, 1981[2]	DF/FP-RF
Reviews and Evaluations			
2.2×10^{-11} exp(120/T)	220–500	NASA, 1997[3]	(a)
2.3×10^{-11} exp(110/T)	220–500	IUPAC, 1997[4]	(b)

Comments

(a) Based on the data of Westenberg and deHaas,[5] Lewis and Watson,[1] and Howard and Smith.[2]

(b) See Comments on Preferred Values.

Preferred Values

$k = 3.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.3\times10^{-11}$ exp(110/T) cm^3 molecule^{-1} s^{-1} over the temperature range 220–500 K.

Reliability

$\Delta\log k = \pm0.1$ at 298 K.

$\Delta(E/R) = \pm100$ K.

Comments on Preferred Values

The recommended temperature dependence is based on a least-squares fit of the data of Lewis and Watson[1] and Howard and Smith,[2] which are in close agreement. Other studies at ambient temperatures[6–8] are also in excellent agreement with these results. The reaction has been the subject of a number of theoretical studies; see Troe[9] and Miller.[10] The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[4]

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$O + HO_2 \rightarrow HO + O_2$

$\Delta H° = -224.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
3.1×10^{-11} exp[(200±28)/T]	229–372	Keyser, 1982[1]	DF-RF
$(6.1\pm0.4)\times10^{-11}$	299		
$(5.4\pm0.9)\times10^{-11}$	296	Sridharan, Qiu, and Kaufman, 1982[2]	DF-RF
$(6.2\pm1.1)\times10^{-11}$	298	Ravishankara, Wine, and Nicovich, 1983[3]	PLP-RF
$(5.2\pm0.8)\times10^{-11}$	300	Brune, Schwab, and Anderson, 1983[4]	DF-RF
2.91×10^{-11} exp[(228±75)/T]	266–391	Nicovich and Wine, 1987[5]	PLP-RF
$(6.30\pm0.91)\times10^{-11}$	298		
Reviews and Evaluations			
3.0×10^{-11} exp(200/T)	220–400	NASA, 1997[6]	(a)
2.7×10^{-11} exp(224/T)	200–400	IUPAC, 1997[7]	(b)

Comments

(a) Based on the data of Keyser,[1] Sridharan *et al.*,[2] Ravishankara *et al.*,[3] Brune *et al.*[4] and Nicovich and Wine.[5]
(b) See Comments on Preferred Values.

Preferred Values

$k = 5.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.7 \times 10^{-11} \exp(224/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–400 K.

Reliability
$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The recommended rate coefficient at 298 K is the mean of those obtained in the studies of Keyser,[1] Sridharan *et al.*,[2] Ravishankara *et al.*,[3] Brune *et al.*,[4] and Nicovich and Wine,[5] all of which are in excellent agreement. The temperature coefficient is the mean of the values obtained by Keyser[1] and Nicovich and Wine,[5] with the pre-exponential factor being based on this value of E/R and the recommended value of k at 298 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[7]

In the two most recent studies of the reaction mechanism, Keyser *et al.*[8] have shown that the yield of $O_2(^1\Sigma_g^+)$ from the reaction is $<1 \times 10^{-2}$ per HO_2 radical removed and Sridharan *et al.*[9] have shown, in an ^{18}O labeling experiment, that the reaction proceeds via formation of an $HO_2-^{18}O$ intermediate which dissociates to HO and ^{18}OO by rupture of an O–O bond rather than via a four center intermediate yielding $H^{18}O$ + OO.

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$O + H_2O_2 \rightarrow HO + HO_2$

$\Delta H° = -59.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.75 \times 10^{-12} \exp[-(2125 \pm 261)/T]$	283–368	Davis, Wong, and Schiff, 1974[1]	FP-RF
2.1×10^{-15}	298		
$1.13 \times 10^{-12} \exp[-(2000 \pm 160)/T]$	298–386	Wine *et al.*, 1983[2]	FP-RF
$(1.45 \pm 0.29) \times 10^{-15}$	298		
Reviews and Evaluations			
$1.4 \times 10^{-12} \exp(-2000/T)$	280–390	NASA, 1997[3]	(a)
$1.4 \times 10^{-12} \exp(-2000/T)$	250–390	IUPAC, 1997[4]	(b)

Comments

(a) Based on the data of Davis *et al.*[1] and Wine *et al.*[2]
(b) See Comments on Preferred Values.

Preferred Values

$k = 1.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.4 \times 10^{-12} \exp(-2000/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 280–390 K.

Reliability
$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 1000$ K.

Comments on Preferred Values

The preferred values are based on the results of Davis *et al.*[1] and Wine *et al.*[2] and are identical to those in our previous evaluation, IUPAC, 1997.[4] These two studies are in agreement with regard to the temperature coefficient of the rate coefficient, but the absolute values of k differ by a factor of 2 throughout the range. In both cases the pre-exponential factor obtained is low compared with other atom–molecule reactions. To obtain the preferred values the temperature coefficient is accepted and the pre-exponential factor adjusted to obtain agreement with the recommended value of k at 298 K, which is the mean of the values found in the two studies.

Roscoe[5] has discussed earlier work on this reaction, which was invalidated by secondary reactions affecting the measurements.

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$O(^1D) + H_2 \rightarrow HO + H$ (1)

$\rightarrow O(^3P) + H_2$ (2)

$\Delta H°(1) = -181.6$ kJ·mol^{-1}
$\Delta H°(2) = -189.7$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(9.9 \pm 3) \times 10^{-11}$	204–352	Davidson *et al.*, 1976;[1] 1977[2]	(a)
$(1.18 \pm 0.12) \times 10^{-10}$	297	Wine and Ravishankara, 1981[3]	PLP-RF (b)
$(1.0 \pm 0.1) \times 10^{-10}$	298	Force and Wiesenfeld, 1981[4]	(c)
$(1.2 \pm 0.1) \times 10^{-10}$	298	Talukdar and Ravishankara, 1996[5]	PLP-RF (d)
Reviews and Evaluations			
1.1×10^{-10}	200–350	NASA, 1997[6]	(e)
1.1×10^{-10}	200–350	IUPAC, 1997[7]	(f)

Comments

(a) Pulsed laser photolysis of O_3 at 266 nm, with $O(^1D)$ atoms being monitored by time-resolved emission at 630 nm.

(b) $O(^3P)$ atoms were monitored by time-resolved resonance fluorescence.

(c) Pulsed laser photolysis of O_3 at 248 nm. H and $O(^3P)$ atoms were monitored by time-resolved absorption spectroscopy.

(d) $O(^3P)$ and H atom products were monitored by resonance fluorescence.

(e) Based on the data of Davidson *et al.*,[1,2] Wine and Ravishankara,[3,8] Force and Wiesenfeld,[4] and Talukdar and Ravishankara.[5]

(f) See Comments on Preferred Values.

Preferred Values

$k = 1.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–350 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The recommended value is the mean of the values of Davidson *et al.*,[1,2] Wine and Ravishankara,[3] Force and Wiesenfeld,[4] and Talukdar and Ravishankara,[5] all of which are in excellent agreement. Channel (1) appears to be the dominant pathway (>95%)[8] for the reaction. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[7]

Absolute rate constants and isotopic branching ratios have recently been reported[9] for the reaction of $O(^1D)$ with HD. The k values were insigificantly different from the recommendation for H_2, with a branching ratio OH/OD = 1.35 ± 0.20.[9]

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$$O(^1D) + H_2O \rightarrow 2HO \quad (1)$$
$$\rightarrow H_2 + O_2 \quad (2)$$
$$\rightarrow O(^3P) + H_2O \quad (3)$$

$\Delta H^\circ(1) = -118.5\ kJ \cdot mol^{-1}$
$\Delta H^\circ(2) = -197.1\ kJ \cdot mol^{-1}$
$\Delta H^\circ(3) = -189.7\ kJ \cdot mol^{-1}$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.3 \pm 0.4) \times 10^{-10}$	253–353	Streit *et al.*, 1976[1]	PLP (a)
$(1.95 \pm 0.3) \times 10^{-10}$	295	Amimoto *et al.*, 1979[2]	PLP-RA (b)
$(2.6 \pm 0.5) \times 10^{-10}$	300	Lee and Slanger, 1979[3]	PLP (c)
$k_1 = (2.02 \pm 0.41) \times 10^{-10}$	298	Gericke and Comes, 1981[4]	PLP-RA
$(1.95 \pm 0.2) \times 10^{-10}$	298	Wine and Ravishankara, 1981[5]	PLP-RF (d)
Branching Ratios			
$k_2/k = 0.01(^{+0.005}_{-0.01})$	298	Zellner, Wagner, and Himme, 1980[6]	FP-RA (e)
$k_3/k = 0.049 \pm 0.032$	298 ± 2	Wine and Ravishankara, 1982[7]	PLP-RF (d)
$k_2/k = 0.006(^{+0.007}_{-0.006})$	298	Glinski and Birks, 1985[8]	(f)
Reviews and Evaluations			
2.2×10^{-10}	200–350	NASA, 1997[9]	(g)
2.2×10^{-10}	200–350	IUPAC, 1997[10]	(h)

Comments

(a) $O(^1D)$ atoms were monitored by time-resolved emission from the $O(^1D) \rightarrow O(^3P)$ transition at 630 nm.
(b) $O(^3P)$ atoms were measured by resonance absorption.
(c) $O(^1D)$ atoms were measured by emission at 630 nm and, indirectly by $O_2(^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-)$ emission at 720 nm.
(d) $O(^3P)$ atom formation was monitored by RF.
(e) The H_2 yield was measured by GC, together with the OH radical concentration by resonance absorption.
(f) Photolysis of O_3–H_2O mixtures at 253.7 nm. The H_2 yield was measured by GC.
(g) Based on the data of Streit *et al.*,[1] Amimoto *et al.*,[2] Lee and Slanger,[3] Gericke and Comes,[4] and Wine and Ravishankara.[5,7]
(h) See Comments on Preferred Values.

Preferred Values

$k = 2.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–350 K.
$k_1 = 2.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 < 2.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_3 < 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.
$\Delta \log k_1 = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred value for k is a mean of the values of Streit *et al.*,[1] Amimoto *et al.*,[2] Lee and Slanger,[3] Gericke and Comes,[4] and Wine and Ravishankara,[5] all of which are in good agreement. Our recommendations for k_2/k and k_3/k are based on the data of Zellner *et al.*[6] and Glinski and Birks[8] (k_2/k), and Zellner *et al.*[6] and Wine and Ravishankara[7] (k_3/k). The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[10]

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$HO + H_2 \rightarrow H_2O + H$

$\Delta H^\circ = -63.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
7.0×10^{-15}	300	Greiner, 1969[1]	FP-RA
$(7.1\pm1.1)\times10^{-15}$	298	Stuhl and Niki, 1972[2]	FP-RF
7.6×10^{-15}	298	Westenberg and deHaas, 1973[3]	DF-EPR
$1.8\times10^{-11}\exp(-2330/T)$	210–460	Smith and Zellner, 1974[4]	FP-RA
7.1×10^{-15}			
$(5.79\pm0.26)\times10^{-15}$	300	Overend, Paraskevopoulos, and Cvetanovic, 1975[5]	FP-RA
$5.9\times10^{-12}\exp[-(2008\pm151)/T]$	298–425	Atkinson, Hansen, and Pitts, 1975[6]	FP-RF
$(6.97\pm0.70)\times10^{-15}$	298		
$4.12\times10^{-19}\,T^{2.44}\exp(-1281/T)$	298–992	Tully and Ravishankara, 1980[7]	FP-RF
$(6.08\pm0.37)\times10^{-15}$	298		
6.1×10^{-15}	298	Zellner and Steinert, 1981[8]	DF-RF
$4.9\times10^{-12}\exp[-(1990\pm340)/T]$	250–400	Ravishankara *et al.*, 1981[9]	FP-RF
$(5.64\pm0.60)\times10^{-15}$	295		
$7.2\times10^{-20}\,T^{2.69}\exp(-1150/T)$	230–420	Talukdar *et al.*, 1996[10]	FP/PLP-LIF (a)
$(6.65\pm0.36)\times10^{-15}$	298		
Reviews and Evaluations			
$5.5\times10^{-12}\exp(-2000/T)$	200–450	NASA, 1997[11]	(b)
$7.7\times10^{-12}\exp(-2100/T)$	200–450	IUPAC, 1997[12]	(b)

Comments

(a) Both flash lamp and pulsed laser photolysis were used. The OH radical reactions with HD and D_2 were also studied.

(b) Based on the data from Refs. 1–9.

Preferred Values

$k=6.7\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=7.7\times10^{-12}\exp(-2100/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–450 K.

Reliability

$\Delta\log k=\pm0.1$ at 298 K.

$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

There are several studies in good agreement concerning both the temperature dependence and absolute values of the rate coefficient. The preferred value of k at 298 K is the mean of the results of Greiner,[1] Stuhl and Niki,[2] Westenberg and deHaas,[3] Smith and Zellner,[4] Overend *et al.*,[5] Atkinson *et al.*,[6] Tully and Ravishankara,[7] Zellner and Steinert,[8] and Ravishankara *et al.*[9] The preferred value of E/R is the mean of the values of Smith and Zellner,[4] Atkinson *et al.*,[6] and Ravishankara *et al.*[9] The pre-exponential factor in the rate expression is calculated to fit the preferred value of k at 298 K and that of E/R. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[12] The recent results of Talukdar *et al.*[10] are in excellent agreement with this recommendation. There have been several recent quantum mechanical calculations of the rate coefficient for this reaction, and these are in reasonable agreement with experiment.[13,14]

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$HO + HO \rightarrow H_2O + O$

$\Delta H^\circ = -71.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.3\pm0.3)\times10^{-12}$	350	Westenberg and de Haas, 1973[1]	DF-EPR
$(2.1\pm0.5)\times10^{-12}$	298	McKenzie, Mulcahy, and Steven, 1973[2]	DF-EPR
$(1.4\pm0.2)\times10^{-12}$	300	Clyne and Down, 1974[3]	DF-RF/RA
$(2.1\pm0.1)\times10^{-12}$	300	Trainor and von Rosenberg, 1974[4]	FP-RA
$(1.7\pm0.2)\times10^{-12}$	298	Farquharson and Smith, 1980[5]	DF-RF
$3.2\times10^{-12}\exp(-242/T)$	250–580	Wagner and Zellner, 1981[6]	FP-RA
$(1.43\pm0.3)\times10^{-12}$	298		
Reviews and Evaluations			
$4.2\times10^{-12}\exp(-240/T)$	200–500	NASA, 1997[7]	(a)
1.9×10^{-12}	298	IUPAC, 1997[8]	(b)
$7.9\times10^{-14}(T/298)^{2.6}\exp(945/T)$	200–500		

Comments

(a) Based on an average of the data from Refs. 1–6, with the temperature dependence from Ref. 6.
(b) See Comments on Preferred Values.

Preferred Values

$k = 1.9\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 7.9\times10^{-14}\ (T/298)^{2.6}\exp(945/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–500 K.

Reliability

$\Delta\log k = \pm0.15$ at 298 K.
$\Delta(E/R) = \pm250$ K.

Comments on Preferred Values

There are a number of measurements of k at temperatures close to 298 K.[1-6,9-12] falling in the range $(1.4–2.3)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. We take the mean of the more recent studies[1-6] for our preferred value at 298 K. This value is confirmed by recent measurements[13] of the pressure dependence of the $HO + HO + M$ reaction system which allow the reactions $HO + HO \rightarrow H_2O + O$ and $HO + HO \rightarrow H_2O_2$ to be separated. The temperature coefficient is taken from an *ab initio* modeling study[14] which well accommodates the experimental high temperature results. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[8]

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$HO + HO + M \rightarrow H_2O_2 + M$

$\Delta H° = -214.9$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.5 \pm 0.3) \times 10^{-31}$ [N$_2$]	300	Trainor and von Rosenberg, 1974[1]	FP-RA
6.9×10^{-31} $(T/300)^{-0.8}$ [N$_2$]	253–353	Zellner *et al.*, 1988[2]	FP-RA
3.7×10^{-31} [He]	298	Forster *et al.*, 1995[3]	PLP-LIF (a)
Reviews and Evaluations			
6.2×10^{-31} $(T/300)^{-1.0}$ [air]	200–350	NASA, 1997[4]	(b)
6.9×10^{-31} $(T/300)^{-0.8}$ [N$_2$]	200–400	IUPAC, 1997[5]	(c)

Comments

(a) Measurements were carried out with saturated LIF at total gas densities in the range 3.9×10^{19} to 3.4×10^{21} molecule cm^{-3}, covering the major part of the falloff curve. The apparent discrepancy between the results of Refs. 1 and 2 disappears when the contribution of the reaction $HO + HO \rightarrow H_2O + O$ is separated by means of the falloff plot.

(b) Based on the data of Zellner *et al.*[2] and Forster *et al.*[3]

(c) See Comments on Preferred Values.

Preferred Values

$k_0 = 6.9 \times 10^{-31}$ $(T/300)^{-0.8}$ [N$_2$] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The analysis of the complete falloff curve by Forster *et al.*[3] shows that the measurements from Refs. 1–3 are all consistent. It is essential that falloff effects are taken into account, as noted in the comments on k_∞. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[5]

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.5×10^{-11}	253–353	Zellner *et al.*, 1988[2]	FP-RA
2.2×10^{-11}	298	Forster *et al.*, 1995[3]	PLP-LIF (a)
$(2.6 \pm 0.8) \times 10^{-11}$	200–400	Fulle *et al.*, 1996[6]	PLP-LIF (b)
Reviews and Evaluations			
2.6×10^{-11}	200–350	NASA, 1997[4]	(c)
2.6×10^{-11}	200–300	IUPAC, 1997[5]	(d)

Comments

(a) See comment (a) for k_0.

(b) See comment (a) for k_0. Measurements were carried out over the temperature range 200–700 K, indicating a negative temperature coefficient of k_∞, depending on uncertainties concerning the contribution from the reaction $HO + HO \rightarrow H_2O + O$.

(c) Based on the data of Zellner *et al.*[2] and Forster *et al.*[3]

(d) See Comments on Preferred Values.

Preferred Values

$k_\infty = 2.6\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability

$\Delta\log k_\infty = \pm0.2$ over the temperature range 200–300 K.

Comments on Preferred Values

The measurements from Refs. 3 and 6 now provide complete falloff curves of the reaction which are consistent with the preferred values of k_0 and k_∞ and a value of $F_c = 0.5\pm0.05$ over the temperature range 200–400 K. Earlier constructions of the falloff curve from Refs. 7 and 8 are superseded by the results of Refs. 3 and 6. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[5]

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$HO + HO_2 \rightarrow H_2O + O_2$

$\Delta H^\circ = -295.7$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.8\times10^{-11}\exp[(250\pm50)/T]$	254–383	Keyser, 1988[1]	DF-RF
$(1.1\pm0.3)\times10^{-10}$	299		
3.3×10^{-11}	1100	Hippler, Neunaber, and Troe, 1995[2]	(a)
1.8×10^{-11}	1250		
7.5×10^{-11}	1600		
Reviews and Evaluations			
$4.8\times10^{-11}\exp(250/T)$	250–400	NASA, 1997[3]	(b)
$4.8\times10^{-11}\exp(250/T)$	250–400	IUPAC, 1997[4]	(c)

Comments

(a) Thermal decomposition of H_2O_2 in a shock tube. HO radicals were monitored by resonance absorption.
(b) Based on the data of Keyser.[1]
(c) See Comments on Preferred Values.

Preferred Values

$k = 1.1\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.8\times10^{-11}\exp(250/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–400 K.

Reliability

$\Delta\log k = \pm0.1$ at 298 K.
$\Delta(E/R) = \pm200$ K.

Comments on Preferred Values

There has been some controversy over the effects of pressure on the rate coefficient for this reaction. Early discharge-flow measurements at low pressures of 1.3–13 mbar (1–10 Torr) consistently gave values of k approximately a factor of 2 lower than those obtained by other techniques at pressures close to atmospheric. The discharge-flow study of Keyser[1] appears to have resolved the problem. These results[1] suggest that the presence of small quantities of H and O atoms present in previous discharge-flow studies led to erroneously low values of k, and that there is no evidence for any variation in k with pressure. These findings[1] are accepted and we take the expression of Keyser[1] for k as our recommendation. There are a number of other studies in excellent agreement with the value recommended for k at 298 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[4]

In another discharge-flow study, Keyser *et al.*,[5] by monitoring the $O_2(b\ ^1\Sigma_g^+) - X(^3\Sigma_g^-)$ transition at 762 nm, have shown that the yield of $O_2(b\ ^1\Sigma_g^+)$ from the reaction is small ($<1\times10^{-3}$). The anomalous temperature dependence observed in the recent high temperature study[2] suggests a mechanism involving intermediate complex formation.

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$HO + H_2O_2 \rightarrow H_2O + HO_2$

$\Delta H^\circ = -130.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.96\times10^{-12}\exp[-(164\pm52)/T]$	250–459	Sridharan, Reimann, and Kaufman, 1980[1]	DF-LIF
$(1.69\pm0.26)\times10^{-12}$	298		
$2.51\times10^{-12}\exp[-(126\pm76)/T]$	245–423	Keyser, 1980[2]	DF-RF
$(1.64\pm0.32)\times10^{-12}$	298		
$3.7\times10^{-12}\exp[-(260\pm50)/T]$	273–410	Wine, Semmes, and Ravishankara, 1981[3]	PLP-RF
$(1.59\pm0.08)\times10^{-12}$	297		
$(1.67\pm0.33)\times10^{-12}$	296	Temps and Wagner, 1982[4]	DF-LMR
$(1.81\pm0.24)\times10^{-12}$	298	Marinelli and Johnston, 1982[5]	PLP-RF
$2.93\times10^{-12}\exp[-(158\pm52)/T]$	250–370	Kurylo *et al.*, 1982[6]	FP-RF
$(1.79\pm0.14)\times10^{-12}$	296		
$2.76\times10^{-12}\exp[-(110\pm60)/T]$	273–410	Vaghjiani, Ravishankara, and Cohen, 1989[7]	PLP-LIF
$(1.86\pm0.18)\times10^{-12}$	298		
Reviews and Evaluations			
$2.9\times10^{-12}\exp(-160/T)$	240–460	NASA, 1997[8]	(a)
$2.9\times10^{-12}\exp(-160/T)$	240–460	IUPAC, 1997[9]	(b)

Comments

(a) Based on the data of Sridharan *et al.*,[1] Keyser,[2] Wine *et al.*,[3] Kurylo *et al.*,[6] and Vaghjiani *et al.*[7]

(b) See Comments on Preferred Values.

Preferred Values

$k = 1.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.9\times10^{-12}\exp(-160/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–460 K.

Reliability

$\Delta\log k = \pm0.1$ at 298 K.

$\Delta(E/R) = \pm100$ K.

Comments on Preferred Values

There are a number of studies in excellent agreement on the value of the rate coefficient k.[1-7] The recommended expression is a fit to the data in Refs. 1–7, and is identical to our previous evaluation, IUPAC, 1997.[9] The recent high temperature study of Hippler *et al.*[10] shows that above 800 K there is a strong increase in k with temperature, the data being best represented by the biexponential expression $k = \{3.3\times10^{-12}\exp(-215/T) + 2.8\times10^{-6}\exp(-14800/T)\}$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–1700 K.

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$HO + O_3 \rightarrow HO_2 + O_2$

$\Delta H^\circ = -167.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.3\times10^{-12}\exp(-956/T)$	220–450	Anderson and Kaufman, 1973[1]	DF-RF
5.3×10^{-14}	298		
$(6.5\pm1.0)\times10^{-14}$	298	Kurylo, 1973[2]	FP-RF
$1.82\times10^{-12}\exp[-(930\pm50)/T]$	238–357	Ravishankara, Wine, and Langford, 1979[3]	PLP-RF
$(7.96\pm0.39)\times10^{-14}$	298		
$(6.5\pm1.0)\times10^{-14}$	300	Zahniser and Howard, 1980[4]	DF-LMR (a)
$1.52\times10^{-12}\exp[-(890\pm60)/T]$	240–295	Smith *et al.*, 1984[5]	FR-RF (b)
$(7.46\pm0.16)\times10^{-14}$	295		
Relative Rate Coefficients			
$(7.0\times0.8)\times10^{-14}$	300	Zahniser and Howard, 1980[4]	DF-LMR (c)
Reviews and Evaluations			
$1.6\times10^{-12}\exp(-940/T)$	220–450	NASA, 1997[6]	(d)
$1.9\times10^{-12}\exp(-1000/T)$	220–450	IUPAC, 1997[7]	(e)

Comments

(a) Discharge flow system used. HO radicals were generated from the $H + NO_2$ reaction and monitored by LMR.

(b) Flash photolysis of O_3–H_2O mixtures in 1 atm He. HO radicals were monitored by resonance fluorescence.

(c) Discharge flow system used. HO radicals were generated from the $H + NO_2$ and $H + O_3$ reactions, and HO_2 radicals were generated from the reaction $H + O_2 + M$. HO_2 and HO radicals were monitored by LMR. A rate coefficient ratio of $k/k(HO_2 + O_3) = 35\pm4$ (average of three systems studied) was obtained and placed on an absolute basis by use of $k(HO_2 + O_3) = 2.0\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 300 K (this evaluation).

(d) Based on the work of Anderson and Kaufman,[1] Kurylo,[2] Ravishankara *et al.*,[3] Zahniser and Howard,[4] and Smith *et al.*[5]

(e) See Comments on Preferred Values.

Preferred Values

$k = 6.7\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.9\times10^{-12}\exp(-1000/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–450 K.

Reliability

$\Delta\log k = \pm0.15$ at 298 K.

$\Delta(E/R) = \pm300$ K.

Comments on Preferred Values

There is good agreement among the various studies[1-5] for the rate coefficient k. The recommended value for E/R is the mean of the values of Anderson and Kaufman,[1] Ravishankara *et al.*[3] and Smith *et al.*[5] The recommended 298 K rate coefficient is the mean of the values from these studies[1,3,5] plus those of Kurylo[2] and Zahniser and Howard.[4] The pre-exponential factor is derived from the recommended values of E/R and the 298 K rate coefficient. The preferred values are identical to those in our previous evaluation, IUPAC, 1977.[7]

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$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad (1)$$

$$HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M \quad (2)$$

$\Delta H°(1) = \Delta H°(2) = -165.5$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
3.8×10^{-14} exp[(1250±200)/T]	273–339	Cox and Burrows, 1979[1]	MM (a)
$(2.35\pm0.2)\times10^{-12}$	298		
2.4×10^{-13} exp[(560±200)/T]	298–359	Thrush and Tyndall, 1982[2]	FP-TDLS (b)
$(1.6\pm0.1)\times10^{-12}$	298		
2.5×10^{-12} (1 bar N_2)	296	Simonaitis and Heicklen, 1982[3]	FP-UVA
$k_1=(1.4\pm0.2)\times10^{-12}$	296		
$k_1=2.2\times10^{-13}$ exp(620/T)	230–420	Kircher and Sander, 1984[4]	FP-UVA (c)
$k_1=(1.7\pm0.22)\times10^{-12}$	298		
$k_2=1.9\times10^{-33}$ exp(980/T) [N_2]	230–420	Kircher and Sander, 1984[4]	FP-UVA (c)
$k_2=(5.4\pm3.1)\times10^{-32}$ [N_2]	298		
$k_1=1.88\times10^{-12}$	298	Kurylo, Ouellette, and Laufer, 1986[5]	FP-UVA (d)
$k_2=4.53\times10^{-32}$ [O_2]	298		
$k_2=5.95\times10^{-32}$ [N_2]	298		
$k_1=2.0\times10^{-13}$ exp[(595±120)/T]	253–390	Takacs and Howard, 1986[6]	DF-LMR
$k_1=(1.54\pm0.07)\times10^{-12}$	294		
$(3.3\pm0.9)\times10^{-12}$	298	Lightfoot, Veyret, and Lesclaux, 1988[7]	FP-UVA
$(1.5\pm0.5)\times10^{-12}$	418		
$(8.8\pm1.2)\times10^{-13}$	577		
$(8.2\pm2.0)\times10^{-13}$	623		
$(8.1\pm1.5)\times10^{-13}$	677		
$(7.6\pm1.4)\times10^{-13}$	723		
$(9.1\pm2.5)\times10^{-13}$	777		
Reviews and Evaluations			
$k_1=2.2\times10^{-13}$ exp(600/T)	230–420	Wallington *et al.*, 1992[8]	(e)
$k_2=1.9\times10^{-33}$ exp(980/T)	230–420		
$k_1=2.3\times10^{-13}$ exp(600/T)	230–420	NASA, 1997[9]	(f)
$k_2=1.7\times10^{-33}$ exp(1000/T) [M]	230–420		
$k_1=2.2\times10^{-13}$ exp(600/T)	230–420	IUPAC, 1997[10]	(g)
$k_2=1.9\times10^{-33}$ exp(980/T) [N_2]	230–420		

Comments

(a) HO_2 radicals were monitored by molecular modulation spectrometry. The data cited refer to a total pressure of 1 bar and absence of H_2O.

(b) HO_2 radicals were monitored by diode laser spectroscopy. Pressure =9–27 mbar (7–20 Torr) of O_2.

(c) Pressure range was 0.133–0.933 bar (100–700 Torr) of Ar and N_2. Enhancement of k by added water was observed, in a linear fashion independent of the pressure of other gases, according to the equation $k_{obs}=k\times(1-1.4\times10^{-21}\exp(2200/T)\,[H_2O])$.

(d) Total pressure range was 0.033–1.01 bar (25–760 Torr).

(e) Recommendation was based on a wide range of published data, including those cited here.

(f) Expression for k_1 was based on the results of Cox and Burrows,[1] Thrush and Tyndall,[2,11] Kircher and Sander,[4] Sander,[12] Kurylo *et al.*,[5] and Takacs and Howard.[6] The recommendation for k_2 was based on the work of Sander *et al.*,[13] Simonaitis and Heicklen,[3] Kircher and Sander,[4] and Kurylo *et al.*[5]

(g) See Comments on Preferred Values.

Preferred Values

$k_1=1.6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2=5.2\times10^{-32}$ [N_2] cm^3 molecule^{-1} s^{-1} at 298 K.

$k_2=4.5\times10^{-32}$ [O_2] cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1=2.2\times10^{-13}$ exp(600/T) cm^3 molecule^{-1} s^{-1} over the temperature range 230–420 K.

$k_2=1.9\times10^{-33}$ exp(980/T) [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 230–420 K.

In the presence of H_2O the expressions for k_1 and k_2 should be multiplied by the factor $\{1-1.4\times10^{-21}\,[H_2O]\times\exp(2200/T)\}$, where $[H_2O]$ is in molecule cm^{-3} units.

Reliability

$\Delta \log k_1 = \Delta \log k_2 = 0.15$ at 298 K.
$\Delta(E_1/R) = \pm 200$ K.
$\Delta(E_2/R) = \pm 300$ K.

Comments on Preferred Values

The preferred values given here are identical with the values derived by Kircher and Sander[1] and also recommended in the review by Wallington *et al.*[8] which we adopted in our previous evaluation, IUPAC, 1997.[10]

At temperatures close to 298 K, the reaction proceeds by two channels, one bimolecular and the other termolecular. The preferred values for k_1 are based on the work of Cox and Burrows,[1] Thrush and Tyndall,[2] Kircher and Sander,[4] Kurylo *et al.*,[5] Takacs and Howard,[6] and Lightfoot *et al.*[7] The work of Kurylo *et al.*[5] and of Lightfoot *et al.*[7] has confirmed quantitatively the effects of pressure previously observed by Simonaitis and Heicklen[3] and Kircher and Sander.[4] The recommendations for k_2 are based on the work of Kircher and Sander[4] and Kurylo *et al.*,[5] with the temperature coefficient of k_2 being taken from Kircher and Sander[4] and Lightfoot *et al.*[7] At higher temperatures, $T > 600$ K, Hippler *et al.*[14] and Lightfoot *et al.*[7] observe a sharp change in the temperature coefficient with upward curvature of the Arrhenius plot.

The marked effect of water on this reaction was established in the work of Lii *et al.*[15] and Kircher and Sander.[4] The recommended multiplying factor for k_1 and k_2 in the presence of water is based on these two studies.[4,15]

Mozurkewich and Benson[16] have considered the $HO_2 + HO_2$ reaction theoretically and conclude that the negative temperature dependence, the pressure dependence, and the observed isotope effects can most reasonably be explained in terms of a cyclic hydrogen bonded, H_2OHO_2, intermediate to alternative structures suggested by others.

Sahetchian *et al.*[17] reported the formation of H_2 (~10% at 500 K) in the reaction system but this is contrary to earlier evidence of Baldwin *et al.*[18] and the more recent and careful study of Stephens *et al.*,[19] who find less than 0.01 fractional contribution from the channel leading to $H_2 + 2O_2$. Keyser *et al.*[20] have measured a yield of $O_2(b\ ^1\Sigma_g^+)$ of $<3\times10^{-2}$ per HO_2 consumed.

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$HO_2 + O_3 \rightarrow HO + 2O_2$

$\Delta H^\circ = -118$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.4×10^{-14} exp[$-(580\pm100)/T$]	245–365	Zahniser and Howard, 1980[1]	DF LMR
2.0×10^{-15}	298		
1.8×10^{-14} exp[$-(680\pm148)/T$]	253–400	Wang, Suto, and Lee, 1988[2]	DF (a)
$(1.3\pm0.3)\times10^{-15}$	233–253		
$(1.9\pm0.3)\times10^{-15}$	298		
Reviews and Evaluations			
1.1×10^{-14} exp$(-500/T)$	240–400	NASA, 1997[3]	(b)
1.4×10^{-14} exp$(-600/T)$	250–350	IUPAC, 1997[4]	(c)

Comments

(a) HO_2 radicals were monitored by photodissociation at 147 nm and HO radicals were detected by HO(A-X) fluorescence at 310 nm.
(b) Based on the work of Zahniser and Howard,[1] Manzanares *et al.*,[5] Sinha *et al.*,[6] and Wang *et al.*[2]
(c) See Comments on Preferred Values.

Preferred Values

$k = 2.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.4 \times 10^{-14} \exp(-600/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–350 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = {}^{+500\ \mathrm{K}}_{-100\ \mathrm{K}}$

Comments on Preferred Values

A number of studies[1,2,5,6] are in close agreement on the value of k at 298 K, but there is some divergence concerning the temperature coefficient of k. The studies of Sinha *et al.*[6] and Wang *et al.*[2] both agree that k exhibits non-Arrhenius behavior, apparently approaching a constant value of approximately 1×10^{-15} cm^3 molecule^{-1} s^{-1} at $T < 250$ K. There are experimental difficulties in working at these temperatures and this finding[2,6] is not incorporated in our recommendation without further confirmation. At higher temperature the results from these two studies[2,6] also diverge, giving values of k differing by nearly a factor of 2 at 400 K. We therefore limit the temperature range of our recommendation to $T < 350$ K until this discrepancy is resolved.

The preferred values for the range 250–350 K are based on the results of Zahniser and Howard[1] and Wang *et al.*[2] For modeling at temperatures in the range 200–250 K a value of $k = 1.2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} should be used. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[4]

Isotopic exchange studies[7] of the reaction between $H^{18}O_2$ and O_3 show that at room temperatures the reaction proceeds almost exclusively by H atom transfer rather than by transfer of an oxygen atom. Moreover there is little change in this finding with temperature over the range 226–355 K,[7] indicating that any curvature on the Arrhenius plot cannot be due to competition between these two reaction paths.

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$H_2O + h\nu \rightarrow$ products

Primary photochemical transitions

Reactions		$\Delta H°$/kJ·mol^{-1}	$\lambda_{\mathrm{threshold}}$/nm
$H_2O + h\nu \rightarrow H_2 + O(^3P)$	(1)	491.0	243
$\rightarrow H + HO$	(2)	499.1	239
$\rightarrow H_2 + O(^1D)$	(3)	680.7	176

Absorption cross-section data

Wavelength range/nm	Reference	Comments
176–185	Watanabe and Zelikoff, 1953[1]	(a)
185–198	Thompson, Harteck, and Reeves, 1963[2]	(b)
175–185	Laufer and McNesby, 1965[3]	(c)
175–182	Schurgers and Welge, 1968[4]	(d)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1 \leq 0.003$	174	Chou, Lo, and Rowland, 1974[5]	(e)

Comments

(a) Static system. H_2O was determined by pressure measurement over the range 0.08–8 Torr. Resolution was approximately 0.1 nm. Only graphical presentation of data.

(b) Static system double beam spectrophotometer used with a 10 cm pathlength. H_2O pressure was 27 mbar (20 Torr). No details of pressure measurement or resolution were given. Only graphical presentation of data.

(c) Static system. H_2O was determined by pressure measurement. 0.5 m grating monochromator, with a 0.66 nm bandwidth. Only graphical presentation of data.

(d) Flowing system. H_2O was determined using a membrane manometer. 0.5 m grating monochromator, with 0.25 nm bandwidth. Only graphical presentation of data.

(e) Photolysis involved HTO. It was shown that the decomposition path is almost entirely via the reactions HTO + $h\nu \rightarrow$ H + OT and HTO + $h\nu \rightarrow$ T + HO, with $\leq$0.003 of the molecules decomposing via the reaction HTO + $h\nu \rightarrow$ HT + O.

Preferred Values

λ/nm	$10^{20}\ \sigma/\mathrm{cm}^2$	ϕ_2
175.5	263	1.0
177.5	185	1.0
180.0	78	1.0
182.5	23	1.0
185.0	5.5	1.0
186.0	3.1	1.0
187.5	1.6	1.0
189.3	0.70	1.0

Comments on Preferred Values

Water vapor has a continuous spectrum between 175 and 190 nm, and the cross-section decreases rapidly towards longer wavelengths. The cross-section data from four studies[1–4] are in reasonable agreement. None of these studies report numerical data. The preferred values of the absorption cross-section are taken from the review of Hudson,[6] and were obtained by drawing a smooth curve through the data of Watanabe and Zelikoff,[1] Thompson *et al.*,[2] and Schurgers and Welge.[4]

On the basis of the nature of the spectrum and the results of Chou *et al.*[5] on the photolysis of HTO, it is assumed that over the wavelength region 175–190 nm reaction (2) is the only primary process and that $\phi_2 = 1.0$.[7]

These recommendations are identical to those in our previous evaluation, IUPAC, 1997.[8]

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$H_2O_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reactions		$\Delta H^\circ/\mathrm{kJ \cdot mol^{-1}}$	$\lambda_{\mathrm{threshold}}/\mathrm{nm}$
$H_2O_2 + h\nu \rightarrow HO + HO$	(1)	215	557
$\rightarrow H_2O + O(^1D)$	(2)	333	359
$\rightarrow H + HO_2$	(3)	369	324
$\rightarrow HO + HO(^2\Sigma)$	(4)	606	197

Quantum yield data

$(\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4)$

Measurement	Wavelength Range/nm	Reference	Comments
$\phi_3 = 0.12$	193	Gerlach–Meyer *et al.*, 1987[1]	(a)
$\phi_1 = 1.04 \pm 0.18$	248	Vaghjiani and Ravishankara, 1990[2]	(b)
$\phi_2 < 0.002$	248		
$\phi_3 < 0.0002$	248		
$\phi_1 = 1.01 \pm 0.17$	222	Vaghjiani *et al.*, 1992[3]	(c)
$\phi_2 < 0.002$	222		
$\phi_3 = 0.024 \pm 0.012$	222		
$\phi_3 = 0.16 \pm 0.04$	193		
$\phi_1 = 0.79 \pm 0.12$	248	Schiffman, Nelson, and Nesbitt, 1993[4]	(d)

Comments

(a) Pulsed laser photolysis of H_2O_2 with H atom detection by laser-induced fluorescence.

(b) Pulsed photolysis of flowing mixtures of H_2O_2–H_2O–N_2 (or He) and of O_3–H_2O–N_2 (or He) at 298 K. H_2O_2 and O_3 were determined by UV absorption at 213.9 nm or 228.8 nm. Quantum yield of HO radical formation from H_2O_2–H_2O mixture was measured relative to that from O_3–H_2O mixture. These relative yields were placed on an absolute basis using the known quantum yield of HO radical production from the photolysis of O_3–H_2O mixtures at 248 nm, taken as $\phi(HO) = 1.73 \pm 0.09$.[2,5] O and H atom yields were determined by resonance fluorescence.

(c) Pulsed laser photolysis of H_2O_2–N_2 or SF_6 mixtures at 222 nm and 248 nm. [HO] monitored by LIF. The quantum yield of HO radical production at 248 nm was assumed to be 2.0 and the value at 222 nm was determined from this and the relative HO yields at the two wavelengths. H atom concentrations were monitored by resonance fluorescence. The quantum yield was determined by reference to CH_3SH photolysis at 193 nm. $O(^3P)$ atom formation was investigated using resonance fluorescence but only a very small signal was detected, possibly due to secondary chemistry.

(d) Pulsed laser photolysis of H_2O_2 mixtures. Energy, and hence number of photons, of laser pulse absorbed determined by calorimetry. HO radical concentrations were monitored by infrared absorption using a color center dye laser (2.35–3.40 μm) and interferometer for wavelength measurement. Absolute HO radical concentrations were obtained using integrated absorption cross-sections measured in the same laboratory.[6]

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\ \sigma$/cm^2	ϕ_1	λ/nm	$10^{20}\ \sigma$/cm^2	ϕ_1
190	67.2		275	2.6	1.0
195	56.3		280	2.0	1.0
200	47.5		285	1.5	1.0
205	40.8		290	1.2	1.0
210	35.7		295	0.90	1.0
215	30.7		300	0.68	1.0
220	25.8	1.0	305	0.51	1.0
225	21.7	1.0	310	0.39	1.0
230	18.2	1.0	315	0.29	1.0
235	15.0	1.0	320	0.22	1.0
240	12.4	1.0	325	0.16	1.0
245	10.2	1.0	330	0.13	1.0
250	8.3	1.0	335	0.10	1.0
255	6.7	1.0	340	0.07	1.0
260	5.3	1.0	345	0.05	1.0
265	4.2	1.0	350	0.04	1.0
270	3.3	1.0			

Quantum Yields

$\phi_1 = 1.0$ for $\lambda > 230$ nm; $\phi_1 = 0.85$, $\phi_3 = 0.15$ at 193 nm.

Comments on Preferred Values

There have been no new measurements of the absorption cross-sections and our recommendations are unchanged from those in our previous evaluation, IUPAC, 1997.[7] The preferred values are the mean of those determined by Lin *et al.*,[8] Molina and Molina,[9] Nicovich and Wine,[10] and Vaghjiani and Ravishankara.[11] These agree with the earlier values of Holt *et al.*[12] The absorption cross-sections have also been measured at other temperatures by Troe[13] (220–290 nm at 600 K and 1100 K) and by Nicovich and Wine[10] (260–250 nm, 200–400 K). Both Nicovich and Wine[10] and Troe[13] have expressed their results in an analytical form.

It has long been assumed that channel (1) is the only significant primary photochemical channel at $\lambda > 200$ nm. There are measurements by Vaghjiani and Ravishankara[2] and Vaghjiani *et al.*[3] at 248 nm and 222 nm which support this. However, measurements at 193 nm by Vaghjiani *et al.*[3] show a decline in the HO radical quantum yield (1.51 relative to an assumed value of 2 at 248 nm) with a growth in the H atom quantum yield, a feature previously observed by Gerlach-Meyer *et al.*[1] The results of Schiffman *et al.*[4] also agree well with this relative change in HO radical production in going from 248 nm to 193 nm. However, Schiffman *et al.*[4] obtain much lower absolute values for the quantum yield of HO radical production than obtained by Vaghjiani and Ravishankara.[2]

The evidence therefore indicates that there is a decline in the relative importance of channel (1) in going from 248 nm to 193 nm but the point of onset of this decline and its form are uncertain. Furthermore, the reason for the difference in the absolute values of the quantum yield between the studies of Schiffman *et al.*[4] and Vaghjiani and Ravishankara[2] is unclear; further work is urgently required to clarify this. Recent measurements[14] of the translational energy of the H atom photofragments from 193 nm photolysis of H_2O_2 originate from the same upper state ($\tilde{A}^1A$) which is responsible for OH production at longer wavelengths.

We continue to recommend the use of a quantum yield of 2 for HO radical production ($\phi_1 = 1.0$) at $\lambda > 230$ nm.

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4.3. Nitrogen Species

$O + NO + M \rightarrow NO_2 + M$

$\Delta H° = -306.2$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.55\times10^{-32}\exp[(584\pm35)/T]$ $[N_2]$ $(1.18\pm0.15)\times10^{-31}(T/300)^{-1.82}$ $[N_2]$	217–250	Whytock, Michael, and Payne, 1976[1]	FP-RF (a)
8.8×10^{-32} $(T/300)^{-1.44}$ $[N_2]$	200–370	Schieferstein, Kohse-Höinghaus, and Stuhl, 1983[2]	FP-CL (a)
Reviews and Evaluations			
$9.0\times10^{-32}(T/300)^{-1.5}$ [air]	200–370	NASA, 1997[3]	(b)
$1.0\times10^{-31}(T/300)^{-1.6}$ $[N_2]$	200–300	IUPAC, 1997[4]	(c)

Comments

(a) NO_2 formation detected by NO_2 chemiluminescence.

(b) Based on measurements from Ref. 2 and their reanalysis of the data from Ref. 1.

(c) See Comments on Preferred Values.

Preferred Values

$k_0 = 1.0\times10^{-31}$ $(T/300)^{-1.6}$ $[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta\log k_0 = \pm0.1$ at 298 K.

$\Delta n = \pm0.3$.

Comments on Preferred Values

The preferred values are based on data from Refs. 1, 2, and 5–7, and are identical to those in our previous evaluation, IUPAC, 1997.[4] The full falloff curve has been determined in the relative rate measurements from Ref. 8, leading to $k_\infty = 3\times10^{-11}$ $(T/300)^{0.3}$ cm^3 molecule^{-1} s^{-1} and $F_c = \exp(-T/1850)$ ($F_c = 0.85$ at 300 K) over the temperature range 200–1500 K.

References

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[3] NASA Evaluation No. 12, 1997 (see references in Introduction).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

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$O + NO_2 \rightarrow O_2 + NO$

$\Delta H° = -192.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9.12 \pm 0.44) \times 10^{-12}$	230–339	Davis, Herron, and Huie, 1973[1]	FP-RF
9.3×10^{-12}	296	Slanger, Wood, and Black, 1973[2]	DF-CL (a)
1.05×10^{-11}	240		
$1.85 \times 10^{-10} T^{-0.53}$	298–1055	Bemand, Clyne, and Watson, 1974[3]	DF (b)
$(9.5 \pm 1.1) \times 10^{-12}$	298		
$(1.00 \pm 0.10) \times 10^{-11}$	298	Ongstad and Birks, 1984[4]	DF-CL (a)
$6.58 \times 10^{-12} \exp[(142 \pm 23)/T]$	224–354	Ongstad and Birks, 1986[5]	DF-CL (a)
$(1.03 \pm 0.09) \times 10^{-11}$	298		
$5.21 \times 10^{-12} \exp[(202 \pm 27)/T]$	233–357	Geers-Müller and Stuhl, 1987[6]	PLP-CL (c)
$(1.02 \pm 0.02) \times 10^{-11}$	301		
Reviews and Evaluations			
$6.5 \times 10^{-12} \exp(120/T)$	220–360	NASA, 1997[7]	(d)
$6.5 \times 10^{-12} \exp(120/T)$	230–350	IUPAC, 1997[8]	(e)

Comments

(a) O(^{3}P) atoms were monitored by O + NO chemiluminescence.

(b) Two independent detection techniques were used to follow the reaction. O(^{3}P) atoms were monitored by resonance fluorescence and [NO_2] monitored by mass spectrometry. The results from the two methods were in good agreement. The high temperature results showed appreciable scatter.

(c) O(^{3}P) atoms were generated by photolysis of NO. O(^{3}P) monitored by O + NO chemiluminescence. Values for k(O + N_2O_4) and k(O + N_2O_5) were also estimated from the results.

(d) Based on the data of Davis *et al.*,[1] Slanger *et al.*,[2] Bemand *et al.*,[3] Ongstad and Birks,[5] and Geers-Müller and Stuhl.[6]

(e) See Comments on Preferred Values.

Preferred Values

$k = 9.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.5 \times 10^{-12} \exp(120/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–360 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.

$\Delta(E/R) = \pm 120$ K.

Comments on Preferred Values

The preferred value at 298 K is the average of the values reported by Davis *et al.*,[1] Slanger *et al.*,[2] Bemand *et al.*,[3] Ongstad and Birks,[4,5] and Geers-Müller and Stuhl.[6] The recommended temperature dependence results from a least-squares fit to the data of Davis *et al.*,[1] Ongstad and Birks,[5] and Geers-Müller and Stuhl.[6] The pre-exponential factor is adjusted to fit the preferred value at 298 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[8]

References

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[7] NASA Evaluation No. 12, 1997 (see references in Introduction).

[8] IUPAC, Supplement V, 1997 (see references in Introduction).

$O + NO_2 + M \rightarrow NO_3 + M$

$\Delta H^\circ = -208.7$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(9.2\pm 1)\times 10^{-32}$ [N_2]	297	Harker and Johnston, 1973[1]	RR (a)
$(8.0\pm 1)\times 10^{-32}$ [N_2]	295	Hippler, Schippert, and Troe, 1975[2]	RR (b)
Reviews and Evaluations			
$9.0\times 10^{-32}(T/300)^{-2.0}$ [air]	200–300	NASA, 1997[3]	(c)
$9.0\times 10^{-32}(T/300)^{-2.0}$ [N_2]	200–400	IUPAC, 1997[4]	(d)

Comments

(a) $O(^3P)$ atoms were generated by the photolysis of NO_2 in the presence of 1 bar of N_2. NO_2 and N_2O_5 concentrations were monitored by IR absorption. The measured value of $k/k(O + NO_2)$ was evaluated with $k(O + NO_2) = 9.3\times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The rate coefficient has been reevaluated by increasing the measured rate coefficient by 10% to account for a 10% falloff below k_0, as measured by Gaedtke *et al.*[5]

(b) $O(^3P)$ atoms were generated by the photolysis of NO_2 at various N_2 pressures. NO_2 was monitored by UV absorption. The measured value of $k/k(O + NO_2)$ was evaluated with $k(O + NO_2) = 9.3\times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, taking N_2O_5 reactions and falloff effects into account.

(c) Based on the recommended values of Ref. 6.

(d) See Comments on Preferred Values.

Preferred Values

$k_0 = 9.0\times 10^{-32}\ (T/300)^{-2.0}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.10$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred value at 298 K is from the relative rate measurements of Harker and Johnston[1] and Hippler *et al.*[2] The temperature coefficient is obtained from a simulation by unimolecular rate theory. Absolute rate measurements are required. The reaction is in the falloff regime at pressures near 1 bar. The pressure dependence of the rate coefficient can be expressed using the falloff expressions given in the Introduction and employing the extrapolated high pressure rate constant $k_\infty = 2.2\times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (estimated to be temperature-independent over the range 200–400 K) from the relative rate measurements of Ref. 2. Broadening factors of $F_c(300\ K) = 0.8$ with an estimated temperature dependence of $F_c = \exp(-T/1300)$ (from simulation by unimolecular rate theory) have to be taken into account. The choice of F_c influences the values of the extrapolated rate coefficients k_0 and k_∞. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[4]

References

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[3] NASA Evaluation No. 12, 1997 (see references in Introduction).

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[5] H. Gaedtke, K. Glänzer, H. Hippler, K. Luther, and J. Troe, *14th International Symposium on Combustion* (The Combustion Institute, Pittsburgh, 1973), p. 295.

[6] CODATA, 1980 (see references in Introduction).

$O + NO_3 \rightarrow O_2 + NO_2$

$\Delta H° = -289.7$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.7 \pm 0.6) \times 10^{-11}$	297	Canosa-Mas, Carpenter, and Wayne, 1989[1]	DF-RF/A (a)
Reviews and Evaluations			
1.0×10^{-11}	290–330	NASA, 1997[2]	(b)
1.7×10^{-11}	298	IUPAC, 1997[3]	(c)

Comments

(a) $[O(^3P)]$ monitored by RF, $[NO_3]$ by absorption at 662 nm using $\sigma = 1.9 \times 10^{-17}$ cm^2 molecule^{-1}. Excess of $[NO_3]$ over [O] was not sufficient to give purely first-order kinetics. Analysis of the data took account of this and of the possibility of other interfering reactions.

(b) Based on the study of Graham and Johnston.[4]

(c) See Comments on Preferred Values.

Preferred Values

$k = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is that reported by Canosa-Mas *et al.*,[1] which is the only direct measurement of the rate coefficient. The earlier relative value of Graham and Johnston[4] is consistent with the preferred value, taking into account the experimental uncertainties. The temperature dependence is probably near zero, by analogy with the reaction of $O(^3P)$ atoms with NO_2. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[3]

References

[1] C. E. Canosa-Mas, P. J. Carpenter, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2 **85**, 697 (1989).
[2] NASA Evaluation No. 12, 1997 (see references in Introduction).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).
[4] R. A. Graham and H. S. Johnston, J. Phys. Chem. **82**, 254 (1978).

$O(^1D) + N_2 + M \rightarrow N_2O + M$

$\Delta H° = -356.9$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.8×10^{-36} $[N_2]$	300	Gaedtke *et al.*, 1973[1]	(a)
6.5×10^{-37} $[N_2]$	296	Kajimoto and Cvetanovic, 1976[2]	(b)
$(8.8 \pm 3.3) \times 10^{-37}$ $[N_2]$	298	Maric and Burrows, 1992[3]	(c)
Reviews and Evaluations			
$3.5 \times 10^{-37} (T/300)^{-0.6}$ [air]	200–300	NASA, 1997[4]	(d)

Comments

(a) Steady-state photolysis of O_3–O_2 mixtures at 260 nm in the presence of 1–200 bar of N_2. The rate of N_2O formation was measured relative to O_3 consumption and analyzed in terms of the ratio $k/k[O(^1D) + O_3 - 2O_2]$.

(b) See comment (a), measurements between 25 and 115 bar.

(c) Steady-state photolysis of synthetic air at 185 and 254 nm.

(d) Based on the results of Ref. 2 and a theoretical analysis of the temperature dependence. The cited value is in disagreement with the data from Ref. 2.

Preferred Values

$k_0 = 9\times10^{-37}$ $[N_2]$ cm^3 molecule^{-1} s^{-1} at 298 K.
$\Delta\log k_0 = \pm0.5$ at 298 K.

Comments on Preferred Values

The slow rate of the reaction, in competition with the fast electronic quenching reaction $O(^1D) + N_2 \rightarrow O(^3P) + N_2$, makes the measurement of the N_2O yield a difficult task. The differences between the three studies[1-3] reflect this experimental problem. We prefer the measurement of Maric and Burrows[3] which is consistent with Ref. 2. A theoretical analysis should be made in relation to the thermal decomposition of $N_2O \rightarrow N_2 + O(^3P)$ in the low- and high-pressure ranges.

References

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[3] D. Maric and J. P. Burrows, J. Photochem. Photobiol. A **66**, 291 (1992).
[4] NASA Evaluation No. 12, 1997 (see references in Introduction).

$O(^1D) + N_2 \rightarrow O(^3P) + N_2$

$\Delta H° = -189.7$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$2.0\times10^{-11}\exp[(107\pm8)/T]$	104–354	Streit *et al.*, 1976[1]	PLP (a)
$(2.8\pm0.6)\times10^{-11}$	300		
$(2.4\pm0.1)\times10^{-11}$	295	Amimoto *et al.*, 1979[2]	PLP-RA (b)
$(2.77\pm0.40)\times10^{-11}$	298	Brock and Watson, 1980[3]	PLP-RF (b)
$(2.52\pm0.25)\times10^{-11}$	297	Wine and Ravishankara, 1981[4]	PLP-RF (b)
Relative Rate Coefficients			
$(2.6\pm0.3)\times10^{-11}$	296	Shi and Barker, 1990[5]	(c)
Reviews and Evaluations			
$1.8\times10^{-11}\exp(110/T)$	100–350	NASA, 1997[6]	(d)
$1.8\times10^{-11}\exp(107/T)$	200–350	IUPAC, 1997[7]	(e)

Comments

(a) $O(^1D)$ atoms were monitored by time-resolved detection of $O(^1D) \rightarrow O(^3P)$ emission.

(b) $O(^3P)$ atom product monitored.

(c) The kinetics of deactivation of $O_2(^1\Sigma_g^+)$ were studied by time-resolved emission from $O_2(^1\Sigma_g^+)$ produced by the reaction of $O(^1D)$ atoms with O_2 following pulsed laser photolysis of O_3. The effect of N_2 (and other quenchers) on the initial fluorescence intensity gave the rate coefficient for $O(^1D)$ deactivation relative to that for O_2. The rate coefficient for the reaction of $O(^1D)$ with O_2 (this evaluation) is used to obtain k.

(d) Based on the data of Streit *et al.*,[1] Amimoto *et al.*,[2] Brock and Watson,[3] Wine and Ravishankara,[4] and Shi and Barker.[5]

(e) See Comments on Preferred Values.

Preferred Values

$k = 2.6\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.8\times10^{-11}\exp(107/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 100–350 K.

Reliability

$\Delta\log k = \pm0.1$ at 298 K.
$\Delta(E/R) = \pm100$ K.

Comments on Preferred Values

The preferred value at 298 K is the average of the results of Streit *et al.*,[1] Amimoto *et al.*,[2] Brock and Watson,[3] Wine and Ravishankara,[4] and Shi and Barker.[5] The temperature dependence of Streit *et al.*[1] is accepted and the pre-exponential factor is adjusted to fit the value of k at 298 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[7]

References

[1] G. E. Streit, C. J. Howard, A. L. Schmeltekopf, J. A. Davidson, and H. I. Schiff, J. Chem. Phys. **65**, 4761 (1976).

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[7] IUPAC, Supplement V, 1997 (see references in Introduction).

$$\begin{aligned} O(^1D) + N_2O &\rightarrow N_2 + O_2 && (1)\\ &\rightarrow 2NO && (2)\\ &\rightarrow O(^3P) + N_2O && (3) \end{aligned}$$

$\Delta H°(1) = -521.0\ kJ\cdot mol^{-1}$
$\Delta H°(2) = -340.4\ kJ\cdot mol^{-1}$
$\Delta H°(3) = -189.7\ kJ\cdot mol^{-1}$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.1 \pm 0.2) \times 10^{-10}$	204–359	Davidson *et al.*, 1977[1]	PLP (a)
$(1.20 \pm 0.1) \times 10^{-10}$	295	Amimoto *et al.*, 1979[2]	PLP-RA (b)
$(1.17 \pm 0.12) \times 10^{-10}$	298	Wine and Ravishankara, 1981[3]	PLP-RF (b)
Branching Ratios			
$k_2/k = 0.62 \pm 0.02$	298	Marx, Bahe, and Schurath, 1979[4]	P-GC/CL
$k_2/k = 0.62 \pm 0.09$	177–296	Lam *et al.*, 1981[5]	P-CL
$k_2/k = 0.61 \pm 0.08$	296	Cantrell, Shetter, and Calvert, 1994[6]	(c)
Reviews and Evaluations			
$k_1 = 4.9 \times 10^{-11}$	200–350	NASA, 1997[7]	(d)
$k_2 = 6.7 \times 10^{-11}$	200–350		
$k_1 = 4.4 \times 10^{-11}$	200–350	IUPAC, 1997[8]	(e)
$k_2 = 7.2 \times 10^{-11}$	200–350		
$k_3 < 1 \times 10^{-12}$	200–350		

Comments

(a) O(^{1}D) atoms were monitored by time-resolved detection of O(^{1}D) → O(^{3}P) emission.
(b) O(^{3}P) atom product monitored.
(c) Static photolysis of N_2O–O_3 mixtures at $\lambda > 240$ nm with product analysis by FTIR spectroscopy. The amount of NO formed in reaction (2) was determined from the yield of HNO_3 formed by total oxidation and hydration of NO_x products, corrected for losses to the wall. The value of k_2/k obtained from the experimental data was 0.57 ± 0.08; the value given in the table was obtained by averaging the experimental value with selected literature data.
(d) Based on the measurements of Davidson *et al.*,[1,9] Amimoto *et al.*,[2] Wine and Ravishankara,[3] Volltrauer *et al.*,[10] Marx *et al.*[4] and Lam *et al.*[5]
(e) See Comments on Preferred Values.

Preferred Values

$k_1 = 4.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–350 K.
$k_2 = 7.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–350 K.
$k_3 < 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–350 K.

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \pm 0.1$ at 298 K.
$\Delta(E_1/R) = (E_2/R) = \pm 100$ K.

Comments on Preferred Values

The data and recommendation for the branching ratio at room temperature of $k_2/k = 0.61 \pm 0.08$ given by Cantrell *et al.*[6] are in complete accord with the earlier results of Marx *et al.*[4] and Lam *et al.*[5] The overall rate coefficient values at room temperature are the average of the results of Davidson *et al.*,[1] Amimoto *et al.*,[2] and Wine and Ravishankara,[3] all of which are in close agreement. The temperature independence reported by Davidson *et al.*[1] is accepted. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[8]

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[2] S. T. Amimoto, A. P. Force, R. G. Gulotty, Jr., and J. R. Weisenfeld, J. Chem. Phys. **71**, 3640 (1979).

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[7] NASA Evaluation No. 12, 1997 (see references in Introduction).

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$HO + NH_3 \rightarrow H_2O + NH_2$

$\Delta H^\circ = -66.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.5 \pm 0.4) \times 10^{-13}$	298	Stuhl, 1973[1]	FP-RF
$2.3 \times 10^{-12} \exp(-800/T)$	228–472	Smith and Zellner, 1975[2]	FP-RA
1.57×10^{-13}	298		
$2.93 \times 10^{-12} \exp[-(860 \pm 150)/T]$	298–427	Perry, Atkinson, and Pitts, 1979[3]	FP-RF
$(1.64 \pm 0.16) \times 10^{-13}$	298		
$5.41 \times 10^{-12} \exp[-(1070 \pm 70)/T]$	294–1075	Silver and Kolb, 1980[4]	DF-RF
$(1.44 \pm 0.29) \times 10^{-13}$	294		
$4.55 \times 10^{-12} \exp[-(973 \pm 78)/T]$	297–364	Stephens, 1984[5]	DF-RF
$(1.73 \pm 0.11) \times 10^{-13}$	297		
$3.29 \times 10^{-12} \exp[-(922 \pm 100)/T]$	273–433	Diau, Tso, and Lee, 1990[6]	PLP-FP (a)
$(1.47 \pm 0.07) \times 10^{-13}$	297		
Reviews and Evaluations			
$1.7 \times 10^{-12} \exp(-710/T)$	220–300	NASA, 1997[7]	(b)
$3.5 \times 10^{-12} \exp(-925/T)$	230–450	IUPAC, 1997[8]	(c)

Comments

(a) Pulsed laser photolysis and conventional flash photolysis of H_2O and H_2O_2 used as source of HO radicals. The total pressure was varied over the range 0.091–0.672 bar (68–504 Torr).

(b) Based on the results of Stuhl,[1] Smith and Zellner,[2] Perry *et al.*,[3] Silver and Kolb,[4] Stephens,[5] and Diau *et al.*[6] Only data below 300 K were used for the temperature dependence of k.

(c) See Comments on Preferred Values.

Preferred Values

$k = 1.6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.5 \times 10^{-12} \exp(-925/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–450 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred values are obtained from a least squares fit to the data of Stuhl,[1] Smith and Zellner,[2] Perry *et al.*,[3] Stephens,[5] Diau *et al.*,[6] and the data of Silver and Kolb[4] below 450 K. The relative rate measurement of k/k(HO + HONO) by Cox *et al.*[9] at 298 K is in good agreement with the preferred values when the value of k(HO + HONO) from this review is used. Results from other low temperature studies[10–12] are well outside the error limits obtained from the six direct studies cited[1–6] and are not used in this evaluation.

There are numerous high temperature studies which, together with the studies cited here, indicate a distinct curvature on the Arrhenius plot,[13] but the simple Arrhenius expression given here as the preferred expression for k is sufficiently precise over the temperature range cited. The curvature of the Arrhenius plot is also responsible for the differences between the preferred expressions in the NASA[7] and IUPAC[8] evaluations since different temperature ranges are considered. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[8]

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$HO + HONO \rightarrow H_2O + NO_2$

$\Delta H° = -168.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.80\times10^{-11}\exp[-(390\pm80)/T]$	278–342	Jenkin and Cox, 1987[1]	MM-RA
$(4.5\pm1.5)\times10^{-12}$	297		
$2.8\times10^{-12}\exp[(260\pm140)/T]$	298–373	Burkholder *et al.*, 1992[2]	PLP-LIF (a)
$(7.05\pm0.26)\times10^{-12}$	298		
Relative Rate Coefficients			
$(6.3\pm0.3)\times10^{-12}$	296	Cox, Derwent, and Holt, 1976[3]	(b)
Reviews and Evaluations			
$1.8\times10^{-11}\exp(-390/T)$	270–350	NASA, 1997[4]	(c)
$2.7\times10^{-12}\exp(260/T)$	250–400	IUPAC, 1997[5]	(d)

Comments

(a) HO radicals were monitored by LIF with HONO in excess. [HONO] and [NO_2] were also monitored using *in situ* diode-array spectroscopy.

(b) Photolysis of HONO in the presence of added H_2, CH_4, CO_2, CO, and NO at a total pressure of 1 bar. A value of $k/k(HO+H_2)=945\pm48$ was obtained. The value of k given here is calculated using $k(HO + H_2) = 6.7\times10^{-15}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(c) Based on the study of Jenkin and Cox.[1]

(d) See Comments on Preferred Values.

Preferred Values

$k = 6.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.7\times10^{-12}\exp(260/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–380 K.

Reliability

$\Delta\log k = \pm0.15$ at 298 K.

$\Delta(E/R) = \pm260$ K.

Comments on Preferred Values

There are significant differences between the two direct studies of Jenkin and Cox[1] and Burkholder *et al.*,[2] particularly with respect to the temperature dependence of k. The work of Burkholder *et al.*[2] has substantially better precision than that of Jenkin and Cox[1] and also receives support from the relative rate study of Cox *et al.*[3] Furthermore, the small negative temperature dependence of k found by Burkholder *et al.*[2] is consistent with that observed for the analogous reaction of HO radicals with $HONO_2$.

The preferred value of k at 298 K is a weighted average of the values of Jenkin and Cox,[1] Burkholder *et al.*,[2] and Cox *et al.*[3] The temperature dependence of k is that given by Burkholder *et al.*[2] with the pre-exponential factor chosen to fit the preferred value of k at 298 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[5]

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$$HO + HONO_2 \rightarrow H_2O + NO_3 \quad (1)$$

$$\rightarrow [H_2NO_4] \rightarrow H_2O + NO_3 \quad (2)$$

$\Delta H^\circ = -72.4\ \mathrm{kJ \cdot mol^{-1}}$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} cm^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.9 \pm 1.3) \times 10^{-14}$	270–470	Margitan, Kaufman, and Anderson, 1975[1]	DF-RF (a)
$1.52 \times 10^{-14} \exp[(649 \pm 69)/T]$	224–366	Wine *et al.*, 1981[2]	FP-RF
$(1.25 \pm 0.05) \times 10^{-13}$	298		
$(1.25 \pm 0.13) \times 10^{-13}$	298	Ravishankara, Eisele, and Wine, 1982[3]	PLP-RA (b)
$5.7 \times 10^{-15} \exp[(896 \pm 145)/T]$	228–298	Margitan and Watson, 1982[4]	FP-RF (c)
$(1.19 \pm 0.12) \times 10^{-13}$	298		
$1.05 \times 10^{-14} \exp[(759 \pm 100)/T]$	225–296	Kurylo, Cornett, and Murphy, 1982[5]	FP-RF (d)
$(1.38 \pm 0.20) \times 10^{-13}$	296		
$7.3 \times 10^{-15} \exp[(867 \pm 85)/T]$	251–403	Jourdain, Poulet, and Le Bras, 1982[6]	DF-EPR (e)
$(1.25 \pm 0.07) \times 10^{-13}$	296		
$1.52 \times 10^{-14} \exp[(644 \pm 79)/T]$	218–363	Marinelli and Johnston, 1982[7]	FP-RF (f)
$(1.31 \pm 0.24) \times 10^{-13}$	298		
$8.3 \times 10^{-15} \exp[(850 \pm 40)/T]$	240–370	Smith *et al.*, 1984[8]	FP-RF (g)
$(1.36 \pm 0.04) \times 10^{-13}$	295		
$5.4 \times 10^{-15} \exp(843/T)$	253–295	Devolder *et al.*, 1984[9]	DF-RF (h)
$(9.3 \pm 1.0) \times 10^{-14}$	295		
$2.0 \times 10^{-14} \exp[(430 \pm 60)/T]$	237–404	Connell and Howard, 1985[10]	DF-LMR
$(8.4 \pm 1.2) \times 10^{-14}$	301		
$(1.26 \pm 0.11) \times 10^{-13}$	298	Jolly, Paraskevopoulos, and Singleton, 1985[11]	PLP-RA (i)
$(1.28 \pm 0.10) \times 10^{-13}$	297	Stachnik, Molina, and Molina, 1986[12]	PLP-RA (j)
Reviews and Evaluations			
See Comment	200–300	NASA, 1997[13]	(k)
See Comment	220–300	IUPAC, 1997[14]	(k)

Comments

(a) The value given is the mean of the rate coefficients measured at 295, 420, and 465 K. A slightly higher value obtained at 272 K was considered by the authors to be less reliable.

(b) The value of k tabulated is at 67 mbar (50 Torr) Ar; k was also measured at 80 mbar (60 Torr) SF_6 and at 251 K. The reaction stoichiometry was measured by monitoring NO_3 radical production using optical absorption at 662 nm and using the initial [HO] value. The figures given for the stoichiometry have since been revised as a result of a remeasurement of the absorption coefficient of NO_3.[15] The new values are 0.85 at 298 K and 0.88 at 251 K for $[NO_3]_{produced}/[HO]_{consumed}$.

(c) k was found to depend on both temperature and pressure. k was reported to increase by 10% from 27 to 133 mbar (20–100 Torr) He at 298 K and by 40% over the same range at 238 K. The Arrhenius expression tabulated is a least squares fit to the data for 53 mbar (40 Torr) He over the temperature range 228–298 K. Significant nonlinear Arrhenius behavior was observed above 298 K at each value of the total pressure. k was also determined at 27 mbar (20 Torr) He and 133 mbar (100 Torr) He. For the linear portion of the Arrhenius plots (at or below 298 K) the following values of E/R are derived: −735 K (27 mbar He) and −1000 K (133 mbar He). The authors made linear extrapolations to zero pressure and reported an E/R value of −700 K for data at or below 298 K.

(d) k was studied over the temperature range 225–443 K and over the pressure range 40–67 mbar (30–50 Torr) of Ar and of SF_6. k was observed to exhibit significant nonlinear Arrhenius behavior above 296 K, with no dependence on total pressure.

(e) Pressure ~1.3 mbar (1 Torr). k was reported to exhibit linear Arrhenius behavior over the entire temperature range but a greater temperature dependence ($E/R = -1119$ K) is derived using only data at or below 298 K. The NO_3 radicals produced were measured by adding excess NO and monitoring its removal by EPR. The stoichiometry so obtained was $[NO_3]_{produced}/[HO]_{consumed} = 1.03 \pm 0.05$.

(f) Pressure of 13–67 mbar (10–50 Torr) Ar. k was reported to exhibit linear Arrhenius behavior over the entire temperature range, but a greater temperature dependence ($E/R = -697$ K) is derived using only data at and below 298 K.

(g) The pressure was varied from 0.067 to 1.01 bar (50–760 Torr) He, with no observed effect on the value of k. Linear Arrhenius behavior was observed.

(h) The rate coefficient was measured up to 373 K. The increase in the rate coefficient was observed to level off above room temperature. The Arrhenius expression tabulated applies to results below room temperature.

(i) The value given is for pressures of 1.3–21 mbar (1–16 Torr) HNO_3. Experiments were also carried out in the presence of 0.667 bar (500 Torr) N_2 and 0.800 bar (600 Torr) SF_6. After corrections for the contribution of the reaction HO + NO_2 + M were made, no significant effect of total pressure on k was observed.

(j) Measurements were made at 0.013, 0.080, and 0.973 bar (10, 60, and 730 Torr) He, N_2, and SF_6. NO_2 was determined to be less than 0.1%. The data were fitted to the fall-off function given in Lamb *et al.*[15] The extrapolated zero-pressure rate constant corresponds to $E/R = -710$ K.

(k) Based on the data in Refs. 1–12. See Comments on Preferred Values.

Preferred Values

$k = 1.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar.

See Comments on Preferred Values for the expression to be used under other conditions of temperature and pressure.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

Similar error limits apply to values of k at other temperatures and pressures over the range 200–300 K.

Comments on Preferred Values

The data have been carefully assessed by the NASA Panel.[13] and their recommendations and analysis are adopted in this evaluation. There is now general agreement on the following major features of the data for k: (a) a clear negative temperature dependence below room temperature with a much weaker temperature dependence above room temperature which appears to level off near 500 K; (b) a small but measurable pressure dependence at room temperature which increases at low temperatures. The pressure dependence has been determined by Margitan and Watson[4] over the range 27–133 mbar (20–100 Torr) at temperatures of 225–298 K and by Stachnik *et al.*[12] for the range 0.013–0.973 bar (10–730 Torr) at 297 K and 248 K. The two studies are in excellent agreement and show that the high pressure limit is about 50% greater than the low pressure limit at 298 K and approximately a factor of 2 greater than the low pressure value at 240 K.

Lamb *et al.*[16] have proposed a mechanism involving formation of a bound, relatively long-lived, intermediate complex (channel 2) as well as the direct reaction (channel 1). This mechanism gives a rate coefficient which combines a low pressure limiting rate constant, k_1, and a Lindemann–Hinshelwood expression for the pressure dependence. This mechanism has been used by the NASA Panel[13] to fit the available data and their expression[13] is adopted. The overall rate constant can be expressed as:

$$k = k_1(T) + k_2(\mathrm{M},T)$$

where, $k_2(\mathrm{M},T) = k_3\,[\mathrm{M}]/(1 + k_3\,[\mathrm{M}]/k_4)$.

The expressions for the elementary rate constants are:

$k_1 = 7.2 \times 10^{-15} \exp(785/T)$ cm^3 molecule^{-1} s^{-1}

$k_3 = 1.9 \times 10^{-33} \exp(725/T)$ cm^6 molecule^{-2} s^{-1}

$k_4 = 4.1 \times 10^{-16} \exp(1440/T)$ cm^3 molecule^{-1} s^{-1}.

All expressions are valid over the temperature range 200–300 K.

This expression has been used to calculate the preferred value at 298 K and a pressure of 1 bar. A more detailed discussion of the reaction is given in the NASA, 1997 evaluation.[13] The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[14]

There is no evidence for products other than NO_3 and H_2O. Studies of the reaction stoichiometry have given values of 0.85[3,15] and 1.03.[6] Bossard *et al.*[17] and Singleton *et al.*[18] have reported a pressure and temperature dependence, respectively, of the rate coefficient of the related reaction DO + DNO_3.

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$HO + HO_2NO_2 \rightarrow H_2O + O_2 + NO_2$ (1)
$\rightarrow H_2O_2 + NO_3$ (2)

$\Delta H^\circ(1) = -191$ kJ·mol^{-1}
$\Delta H^\circ(2) = -45$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.0 \pm 1.6) \times 10^{-12}$	246–324	*Trevor, Black, and Barker*, 1982[1]	FP-RF (a)
$5.9 \times 10^{-13} \exp[(650 \pm 30)/T]$	240–340	Smith *et al.*, 1984[2]	FP-RF (b)
$(5.24 \pm 0.19) \times 10^{-12}$	295		
Relative Rate Coefficients			
$(5.5 \pm 1.4) \times 10^{-12}$	268–295	Barnes *et al.*, 1986[3]	(c)
Reviews and Evaluations			
$1.3 \times 10^{-12} \exp(380/T)$	240–340	NASA, 1997[4]	(d)
$1.5 \times 10^{-12} \exp(360/T)$	240–340	IUPAC, 1997[5]	(e)

Comments

(a) The rate coefficient was independent of the total pressure over the range 4–20 mbar (3–15 Torr) He.

(b) The total pressure was 1.01 bar (760 Torr) of He.

(c) Relative rate study in a 420 L vessel. FTIR was used to monitor the concentration of HO_2NO_2, and the concentrations of the reference hydrocarbons (C_3H_6, n-C_4H_{10}) were monitored by GC. The effect of pressure was studied over the range 1.3–400 mbar (1–300 Torr) of He or N_2. The rate coefficient was observed to be pressure and temperature independent over the ranges studied. A rate coefficient of $k(HO + n\text{-}C_4H_{10}) = 2.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} was used and values of $k(HO + C_3H_6)$, which is pressure dependent, were taken from Klein *et al.*[6] Results from this study supersede earlier results obtained using similar but less sensitive techniques.[7]

(d) Based on the data of Trevor *et al.*,[1] Smith *et al.*,[2] and Barnes *et al.*[3,7]

(e) See Comments on Preferred Values.

Preferred Values

$k = 5.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.5 \times 10^{-12} \exp(360/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–340 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = {}^{+300}_{-600}$ K.

Comments on Preferred Values

The preferred values are based upon a least-squares fit to the data of Trevor *et al.*,[1] Smith *et al.*,[2] and Barnes *et al.*[3] Trevor *et al.*[1] studied the reaction from 246 to 324 K at low pressures [4–20 mbar (3–15 Torr He)] and recommended a temperature-independent rate coefficient but also reported an Arrhenius expression with $E/R = (193 \pm 194)$ K. In contrast, Smith *et al.*[1] reported a negative temperature dependence of k with $E/R = -(650 \pm 30)$ K over the range 240–340 K at 1.01 bar (760 Torr) of He. It is possible that this difference is due to the reaction mechanism being complex, leading to different temperature dependences at low and high pressure. At 220 K, the values of k derived from these studies differ by a factor of 3 but the recommended error limits on E/R encompass the results from both studies.

The most recent study by Barnes *et al.*[3] is the only one over an extended pressure range [6.7–400 mbar (5–300 Torr) He at 278 K]. They reported the rate coefficient to be pressure independent over this range, and the same value of k was found at 295 K (low pressure) and at 268 K [133 mbar (100 Torr) He]. They also reported no change with synthetic air as the buffer gas. A TST calculation by Lamb *et al.*[8] suggests that the pressure dependence of this rate coefficient will be much less than that for the corresponding reaction of HO with HNO_3. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[5]

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$HO + NO + M \rightarrow HONO + M$

$\Delta H° = -209.0$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.1 \pm 0.1) \times 10^{-30}$ [N$_2$]	293	Burrows, Wallington, and Wayne, 1983[1]	DF-RF
$(7.0 \pm 2.0) \times 10^{-31}$ $(T/300)^{-(2.6 \pm 0.3)}$ [N$_2$]	90–220	Atkinson and Smith, 1994[2]	DF-LIF (a)
8.9×10^{-31} $(T/298)^{-2.1}$ [N$_2$]	80–301	Sharkey *et al.*, 1994[3]	PLP-LIF (b)
Reviews and Evaluations			
7.0×10^{-31} $(T/300)^{-2.6}$ [air]	200–300	NASA, 1997[4]	(c)
7.4×10^{-31} $(T/300)^{-2.4}$ [N$_2$]	200–400	IUPAC, 1997[5]	(d)

Comments

(a) HO radicals were generated by a cold cathode discharge and detected by LIF. The experiments were carried out in a supersonic expansion at total pressures corresponding to 10^{16}–10^{18} molecule cm^{-3}.

(b) Experiments were carried out in a cryogenically cooled cell and in a supersonic expansion. At 52 K, rate coefficients have been determined at total gas densities from 5.1×10^{16} to 8.2×10^{17} molecule cm^{-3}.

(c) The recommended value is a weighted average of the data from Refs. 1, 2, and 6–15.

(d) See Comments on Preferred Values.

Preferred Values

$k_0 = 7.4 \times 10^{-31}$ $(T/300)^{-2.4}$ [N$_2$] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.10$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred values are derived following the analysis of earlier data and measurements of the falloff curve with M=He from Ref. 16 and other bath gases from Ref. 17.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
3.0×10^{-11}	298	Zabarnick, 1993[17]	PLP-LIF (a)
3.3×10^{-11}	298	Forster *et al.*, 1995[16]	PLP-LIF (b)
Reviews and Evaluations			
3.6×10^{-11} $(T/300)^{-0.1}$	200–300	NASA, 1997[4]	(c)
4.5×10^{-11}	200–400	IUPAC, 1997[5]	(d)

Comments

(a) Falloff extrapolations with M=Ar and SF$_6$ at pressures below 1 bar.

(b) Measurements in He up to 200 bar using saturated LIF for detection.

(c) Based on the data of Anastasi and Smith,[15] Sharkey *et al.*,[3] Forster *et al.*,[16] and Donahue *et al.*[18]

(d) Based on the preliminary results of Ref. 16.

Preferred Values

$k_\infty = 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ over the temperature range 200–400 K.

Comments on Preferred Values

The preferred values are taken from the determination of the complete falloff curve from Ref. 16 and unpublished extensions of this work to the range 250–400 K, which gave $n=-0.3\pm0.3$. The falloff curve corresponds to $F_c=\exp(-T/1420\ \mathrm{K})$ and F_c (300 K)=0.81.

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$HO + NO_2 + M \rightarrow HONO_2 + M$

$\Delta H^\circ = -207.6\ \mathrm{kJ \cdot mol^{-1}}$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$2.3\times10^{-30}\ (T/295)^{-2.5}\ [N_2]$	240–450	Anderson, Margitan, and Kaufman, 1974[1]	DF-RF (a)
$2.9\times10^{-30}\ [N_2]$	296	Howard and Evenson, 1974[2]	DF-LMR (b)
$2.6\times10^{-30}\ (T/296)^{-2.6}\ [N_2]$	220–550	Anastasi and Smith, 1976[3]	FP-RA (c)
$(2.6\pm0.4)\times10^{-30}\ (T/300)^{-2.8}\ [N_2]$	247–352	Wine, Kreutter, and Ravishankara, 1979[4]	FP-RF (d)
$(2.7\pm0.2)\times10^{-30}\ [N_2]$	295	Burrows, Wallington, and Wayne, 1983[5]	DF-RF (e)
Reviews and Evaluations			
$2.5\times10^{-30}\ (T/300)^{-4.4}$ [air]	220–400	NASA, 1997[6]	(f)
$2.6\times10^{-30}\ (T/300)^{-2.9}\ [N_2]$	200–400	IUPAC, 1997[7]	(g)

Comments

(a) The pressure range was 1.3–13 mbar (1–10 Torr).

(b) The pressure range was 0.5–6.7 mbar (0.4–5 Torr).

(c) Bath gas concentrations of $(3.2-160)\times10^{19}$ molecule cm^{-3} were used.

(d) Bath gas concentrations $(5.4-230)\times10^{17}$ molecule cm^{-3} were used. The experiments covered an essential part of the falloff curve, approaching the low pressure limit.

(e) The pressure range was 1.3–6.7 mbar (1–5 Torr).

(f) Based on the data from Refs. 1–5 and 8–10.

(g) Based on the data from Refs. 1–5 and the analysis of the complete falloff curve from Ref. 11.

Preferred Values

$k_0=2.6\times10^{-30}\ (T/300)^{-2.9}\ [N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

$\Delta n = \pm 0.3$.

Comments on Preferred Values

The preferred values are based on the data from Refs. 1–5, consistent with the falloff analysis from Ref. 11. The falloff curve is constructed with the values of k_∞ and F_c given below.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
3.5×10^{-11}	297	Wine, Kreutter, and Ravishankara, 1979[4]	FP-RF (a)
$\geq 3.0\times10^{-11}$	295	Robertshaw and Smith, 1982[9]	PLP-LIF (b)
7.5×10^{-11}	298	Forster *et al.*, 1995[11]	PLP-LIF (c)
Reviews and Evaluations			
$1.6\times10^{-11}\ (T/300)^{-1.7}$	200–300	NASA, 1997[6]	(d)
$6.7\times10^{-11}\ (T/300)^{-0.6}$	200–400	IUPAC, 1997[7]	(e)

Comments

(a) See comment (d) for k_0. Extrapolation of the falloff curve with F_c=0.70 leads to $k_\infty \geq 3.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1}.

(b) At Ar pressure up to 4 atm and CF_4 pressure up to 8.6 atm.

(c) Measurements in He were carried out over the range 7.6×10^{18}–3.6×10^{21} molecule cm^{-3}.

(d) Based on the data of Refs. 1–5 and 8–10.

(e) Based on a theoretical simulation of the falloff curve from Ref. 11.

Preferred Values

$k_\infty = 7.5\times10^{-11}\ (T/300)^{-0.6}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta\log k_\infty = \pm 0.10$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred values are based on the measured complete falloff curve for 300 K from Forster *et al.*[11] and the related simulation by unimolecular rate theory. The values are consistent with unpublished extensions over the range 270–400 K of the experimental falloff curve from Ref. 11. The falloff curves are constructed with broadening factors $F_c=\exp(-T/340\ \mathrm{K})$ over the range 250–400 K and F_c=0.41 at 300 K.

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$HO + NO_3 \rightarrow HO_2 + NO_2$

$\Delta H° = -65.2$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.6\pm0.6)\times10^{-11}$	298	Mellouki, Le Bras, and Poulet, 1988[1]	DF-EPR (a)
$(2.0\pm0.6)\times10^{-11}$	298	Boodaghians *et al.*, 1988[2]	DF-RF (b)
$(1.22\pm0.35)\times10^{-11}$	298	Becker, Rahman, and Schindler, 1992[3]	DF-RF/MS (c)
$(2.1\pm1.0)\times10^{-11}$	297	Mellouki *et al.*, 1993[4]	DF-LMR (d)
Reviews and Evaluations			
2.2×10^{-11}	298	NASA, 1997[5]	(e)
2.0×10^{-11}	298	IUPAC, 1997[6]	(f)

Comments

(a) Both [HO] and [HO_2] (after conversion to HO) were monitored in the presence of excess NO_3 radicals. [NO_3] was measured by titration with NO or 2,3-dimethyl-2-butene. A complex kinetics analysis accounting for secondary chemistry was required to extract values of k.

(b) Measured rate coefficient k was corrected for the effects of secondary reactions which accelerate the removal of HO radicals.

(c) [HO] was monitored by RF, and [NO_3] and [HO_2] were monitored by MS. Identical values of k were obtained from HO produced by the $H + NO_2$ reaction *in situ*, or by injection of HO radicals produced from the $H + NO_2$ or $F + H_2O$ reactions. A complex analysis accounting for the secondary chemistry was required to extract values of k.

(d) [HO], [HO_2], and [NO_2] were monitored by LMR in an excess of NO_3 radicals.

(e) Based on the data of Mellouki *et al.*,[1] Boodaghians *et al.*,[2] Becker *et al.*,[3] and Mellouki *et al.*[4]

(f) See Comments on Preferred Values.

Preferred Values

$k = 2.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm0.3$.

Comments on Preferred Values

The value of k obtained by Becker *et al.*[3] is substantially lower than the values reported in the other three studies[1,2,4] which are in good agreement, although the error limits quoted are large. In all of the studies it proved necessary to make extensive corrections for secondary reactions. The preferred value of k is a simple average of all of the reported values and is identical to that reported in our previous evaluation, IUPAC, 1997.[6]

No measurements have been made of the temperature dependence of k but a small negative value is expected by analogy with similar reactions.

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$HO_2 + NO \rightarrow NO_2 + HO$

$\Delta H° = -32.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.1 \pm 1.5) \times 10^{-12}$	296	Howard and Evenson, 1977[1]	DF-LMR (a)
$3.3 \times 10^{-12} \exp[(254 \pm 50)/T]$	230–400	Howard, 1979[2]	DF-LMR
8.01×10^{-12}	299		
$5.7 \times 10^{-12} \exp[(130 \pm 270)/T]$	270–425	Leu, 1979[3]	DF-RF (b)
$(9.8 \pm 1.6) \times 10^{-12}$	298		
$(1.1 \pm 0.3) \times 10^{-11}$	297	Glaschick-Schimpf *et al.*, 1979[4]	DF (c)
$(7.6 \pm 1.7) \times 10^{-12}$	293	Hack *et al.*, 1980[5]	DF-LMR/EPR (d)
$3.57 \times 10^{-12} \exp[(226 \pm 41)/T]$	423–1271	Howard, 1980[6]	DF-LMR (e)
7.6×10^{-12}	298*		
$(8.5 \pm 1.3) \times 10^{-12}$	297	Jemi-Alade and Thrush, 1990[7]	DF-LMR (f)
$3.0 \times 10^{-12} \exp[(290 \pm 30)/T]$	206–295	Seeley *et al.*, 1996[8]	DF-MS (g)
$(8.0 \pm 0.5) \times 10^{-12}$	294		
Relative Rate Coefficients			
$(7.3 \pm 0.7) \times 10^{-12}$	298	Thrush and Wilkinson, 1981[9]	DF-LMR (h)
Reviews and Evaluations			
$3.5 \times 10^{-12} \exp(250/T)$	200–430	NASA, 1997[10]	(i)
$3.7 \times 10^{-12} \exp(240/T)$	230–500	IUPAC, 1997[11]	(j)

Comments

(a) $[HO_2]$ monitored. An upper limit of 4.5×10^{-30} cm^6 molecule^{-2} s^{-1} was established for the rate coefficient of the potential pressure-dependent third-order channel.

(b) $[HO]$ monitored.

(c) $[HO_2]$ monitored in excess NO by emission at 1.43 μm after energy transfer from $O_2(^1\Delta)$ produced by a microwave discharge in NO.

(d) $[HO_2]$ monitored by both LMR and EPR. The rate coefficient was observed to be pressure independent over the range 2.1–16.7 mbar (1.6–12.5 Torr).

(e) Same technique used as in similar studies[1,2] from the same laboratory. The author combined data with those from the earlier studies at lower temperatures[1,2] to derive the expression $k = 3.51 \times 10^{-12} \exp[(240 \pm 30)/T]$ cm^3 molecule^{-1} s^{-1} for the temperature range 232–1271 K. The rate coefficient for the reverse reaction was also measured over the range 452–1115 K and from the two studies a value of $\Delta H_f^0(HO_2) = (10.5 \pm 2.5)$ kJ mol^{-1} at 298 K was derived. The value of k at 298 K tabulated is obtained by extrapolation of the high temperature expression.

(f) $[HO_2]$ monitored by LMR. HO radicals scavenged by reaction with C_2F_3Cl. k was observed to be independent of pressure over the range 1.1–17 mbar (0.8–13 Torr).

(g) Turbulent flow technique. High pressure chemical ionization mass spectrometry was used for the detection of HO_2, HO, and NO_2. The value of k was observed to be independent of pressure [93–253 mbar (70–190 Torr) N_2] at 294 K.

(h) $[HO]$ and $[HO_2]$ were monitored by LMR. Steady-state $[HO]$ and $[HO_2]$ were measured in a system where their relative concentrations are described by $[HO]/[HO_2] = k/k(HO + H_2O_2)$. The value of k was calculated using a rate coefficient of $k(HO + H_2O_2) = 1.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(i) Based on the data from Refs. 1–5 and 7–9.

(j) Based on the data from Refs. 1–3 and 5–7.

Preferred Values

$k = 8.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.4 \times 10^{-12} \exp(270/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred value of k at 298 K is the mean of the determinations of Howard and Evenson,[1] Howard,[2] Leu,[3] Hack *et al.*,[5] Jemi-Alade and Thrush,[7] and Seeley *et al.*[8] The temperature dependence is the mean of the values of Howard[2] and of Seely *et al.*,[8] which are preferred to the less precise value of Leu.[3] The pre-exponential factor is adjusted to fit the preferred value of k at 298 K.

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$HO_2 + NO_2 + M \rightarrow HO_2\dot{N}O_2 + M$

$\Delta H^\circ = -105$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.09\pm0.52)\times10^{-31}$ [N_2]	300	Howard, 1977[1]	DF-LMR (a)
$(2.5\pm0.5)\times10^{-31}$ [N_2]	283	Cox and Patrick, 1979[2]	(b)
$(2.3\pm0.6)\times10^{-31}(T/300)^{-4.6}$ [N_2]	229–362	Sander and Peterson, 1984[3]	(c)
1.5×10^{-31} [N_2]	298	Kurylo and Ouellette, 1986[4]	(d)
1.8×10^{-31} $(T/300)^{-3.2\pm0.4}$ [N_2]	228–358	Kurylo and Ouellette, 1987[5]	(d)
Reviews and Evaluations			
1.8×10^{-31} $(T/300)^{-3.2}$ [air]	220–360	NASA, 1997[6]	(e)
1.8×10^{-31} $(T/300)^{-3.2}$ [N_2]	200–300	IUPAC, 1997[7]	(f)

Comments

(a) Discharge flow system study with laser magnetic resonance detection of HO_2. The pressure range was 0.7–4 mbar (0.5–3 Torr). The linear plot of k_0 as a function of [M] with a nonzero intercept was interpreted as contribution from the reaction $HO_2 + NO_2 \rightarrow HONO + O_2$.

(b) Molecular modulation UV spectrometry. HO_2 radicals were generated by Cl_2 photolysis in the presence of H_2 and O_2. O_2–N_2 mixtures used in the pressure range 53–800 mbar (40–600 Torr).

(c) Flash photolysis-UV absorption study in the pressure range 67–930 mbar (50–700 Torr). A strong enhancement of reaction in the presence of water vapor was observed, suggested to be due to formation of HO_2–H_2O complexes.

(d) Flash photolysis of Cl_2–CH_3OH–NO_2 mixtures in the presence of O_2 or N_2, with HO_2 detection at 225 nm. The falloff curve measured over the pressure range 33–800 mbar (25–600 Torr). The rate coefficient was evaluated using $F_c = 0.6$ and $k_\infty = 4.7\times10^{-12}$ $(T/300)^{-1.4\pm1.0}$ cm^3 molecule^{-1} s^{-1}.

(e) Based on the data of Sander and Peterson[3] and Kurylo and Ouellette.[5]

(f) See Comments on Preferred Values.

Preferred Values

$k_0 = 1.8\times10^{-31}$ $(T/300)^{-3.2}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 220–360 K.

Reliability

$\Delta \log k_0 = \pm 0.10$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The studies of Howard,[1] Cox and Patrick,[2] Sander and Peterson,[3] and Kurylo and Ouellette[4,5] are in reasonable agreement. The preferred values are based on the study of Kurylo and Ouellette,[5] with the rate coefficient k_0 being evaluated with the value for k_∞ given below and $F_c = 0.6$, and are identical to those in our recent evaluation, IUPAC, 1997.[7] Modification of F_c will lead to minor changes in k_0 and k_∞.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$>1.7\times10^{-12}$	283	Graham, Winer, and Pitts, 1977[8]	(a)
$>(1.5\pm0.5)\times10^{-12}$	283	Cox and Patrick, 1979[2]	(b)
$(4.2\pm1.0)\times10^{-12}\,(T/300)^{0.2\pm1.0}$	229–362	Sander and Peterson, 1984[3]	(c)
5.5×10^{-12}	298	Kurylo and Ouellette, 1986[4]	(d)
$4.7\times10^{-12}\,(T/300)^{-1.4\pm1.0}$	228–358	Kurylo and Ouellette, 1987[5]	(d)
Reviews and Evaluations			
$4.7\times10^{-12}\,(T/300)^{-1.4}$	220–360	NASA, 1997[6]	(e)
4.7×10^{-12}	200–300	IUPAC, 1997[7]	(f)

Comments

(a) From thermal decomposition of HO_2NO_2 in a static reactor with FTIR spectroscopic analysis of HO_2NO_2. Measurements at 1 bar of N_2 converted to recombination rate coefficients with the equilibrium constants given in Ref. 9.

(b) See comment (b) for k_0. Determination of k_∞ by extrapolation of a curved Lindemann–Hinshelwood plot gave an internally consistent falloff plot. The measured value was $k=9.2\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 800 mbar (600 Torr) of a 1:1 mixture of N_2 and O_2.

(c) See comment (c) for k_0.

(d) See comment (d) for k_0.

(e) Based on the data of Sander and Peterson[3] and Kurylo and Ouellette.[5]

(f) See Comments on Preferred Values.

Preferred Values

$k_\infty=4.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 220–360 K.

Reliability

$\Delta\log k_\infty=\pm0.2$ at 298 K.
$\Delta n=\pm1$.

Comments on Preferred Values

The preferred values are based on the measurements and the falloff analysis of Kurylo and Ouellette,[5] and are identical to those in our recent evaluation, IUPAC, 1997.[7] The k_0 and k_∞ values are based on $F_c=0.6$. Modification of the standard value of F_c will lead to minor changes in k_0 and k_∞.

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$HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$

$\Delta H° = 105$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.5×10^{-20} [N$_2$]	298	Cox and Patrick, 1979[1]	(a)
$5.2\times10^{-6}\exp[-(10014\pm250)/T]$ [N$_2$]	261–295	Graham, Winer, and Pitts, 1978[2]	(b)
1.3×10^{-20} [N$_2$]	298		
$4.1\times10^{-5}\exp[-(10645\pm260)/T]$ [N$_2$]	261–307	Zabel, 1995[3]	(c)
1.2×10^{-20} [N$_2$]	298		
Reviews and Evaluations			
1.3×10^{-20} [N$_2$]	298	IUPAC, 1997[4]	(d)
$5\times10^{-6}\exp(-10000/T)$ [N$_2$]	260–300		

Comments

(a) Derived from measurements of the reverse reaction. Conversion of the data to the dissociation reaction of HO_2NO_2 using the equilibrium constant $K_c = 1.68 \times 10^{28}\exp(-11977/T)$ cm^3 molecule^{-1} from Ref. 5 and comparison with earlier dissociation data.

(b) FTIR study in a 5800 L chamber. Measurements were made at 1.3–9.3 mbar (1–7 Torr) of N$_2$. At higher pressures ($\geq$9.3 mbar), deviations from low pressure behavior were observed.

(c) FTIR study in a 420 L chamber. The pressure range was 14–1027 mbar (10–772 Torr). The falloff curve was evaluated with $F_c = 0.5$.

(d) Based on data of Refs. 1–3.

Preferred Values

$k_0 = 1.3\times10^{-20}$ [N$_2$] s^{-1} at 298 K.

$k_0 = 4.1\times10^{-5}\exp(-10650/T)$ [N$_2$] s^{-1} over the temperature range 260–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values are from the study of Zabel,[3] and are in close agreement with those from Graham *et al.*[2] The data from Ref. 3 provide the most consistent picture of all RO_2NO_2 dissociation reactions. Falloff curves are constructed with $F_c = 0.5$.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
>0.018	278	Graham, Winer, and Pitts, 1978[2]	(a)
$5.7\times10^{15}\exp(-11170/T)$	261–307	Zabel, 1995[3]	(b)
0.30	298		
Reviews and Evaluations			
0.34	298	IUPAC, 1997[4]	(c)
$2.6\times10^{15}\exp(-10900/T)$	260–300		

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Comments *Reliability*

$NH_2 + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.2\times10^{-12}\exp[-(1250\pm250)/T]$	298–380	Kurasawa and Lesclaux, 1980[1]	FP-LIF
$(6.3\pm1.0)\times10^{-14}$	298		
$(1.2\pm0.3)\times10^{-13}$	298	Bulatov *et al.*, 1980[2]	FP (a,b)
$2.01\times10^{-12}\exp[-(710\pm50)/T]$	250–358	Hack, Horie, and Wagner, 1981[3]	DF-LIF (b)
$(1.84\pm0.16)\times10^{-13}$	295		
$1.57\times10^{-11}\exp[-(1151\pm123)/T]$	272–348	Patrick and Golden, 1984[4]	PLP-RA
$(3.25\pm0.27)\times10^{-13}$	298		
$(1.5\pm0.3)\times10^{-13}$	298	Cheskis *et al.*, 1985[5]	PLP-LIF (c)
Reviews and Evaluations			
$4.3\times10^{-12}\exp(-930/T)$	250–360	NASA, 1997[6]	(d)
$4.9\times10^{-12}\exp(-1000/T)$	250–380	IUPAC, 1997[7]	(e)

Comments

(a) $[NH_2]$ monitored by intracavity laser absorption spectroscopy.

(b) Deviation from first-order kinetics observed at high O_3 pressures, and interpreted as due to formation of NH_2O which regenerates NH_2 by reaction with O_3.

(c) The rate coefficients of reaction of vibrationally excited NH_2 with O_3 were also measured and found to be a factor of 10 greater than that of NH_2 in its ground vibrational state.

(d) Based on the data of Bulatov *et al.*,[2] Hack *et al.*,[3] Patrick and Golden,[4] and Cheskis *et al.*[5]

(e) See Comments on Preferred Values.

Preferred Values

$k=1.7\times10^{-13}$ cm^{-3} molecule^{-1} s^{-1} at 298 K.

$k=4.9\times10^{-12}\exp(-1000/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–380 K.

Reliability

$\Delta\log k=\pm0.5$ at 298 K.

$\Delta(E/R)=\pm500$ K.

Comments on Preferred Values

The reported rate coefficients at 298 K vary by a factor of 5. There is no convincing argument for rejecting any of the studies and, therefore, the preferred rate coefficient at 298 K is taken as the average of the results of Kurasawa and Lesclaux,[1] Bulatov *et al.*,[2] Hack *et al.*,[3] Patrick and Golden,[4] and Cheskis *et al.*[5] The temperature dependence of k is obtained by averaging the values of Kurasawa and Lesclaux,[1] Hack *et al.*,[3] and Patrick and Golden.[4] Although the products of the reaction have not been characterized, the most likely process is transfer of an oxygen atom to form $NH_2O + O_2$. It has been suggested[2,3] that NH_2 may be regenerated by reaction with O_3, but the study of Patrick and Golden[4] indicates that this reaction must be slow. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[7]

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$NH_2 + NO \rightarrow N_2 + H_2O$ (1)
$\rightarrow N_2H + HO$ (2)
$\rightarrow N_2 + H + HO$ (3)

$\Delta H^\circ(1) = -500.8$ kJ·mol^{-1}

$\Delta H^\circ(3) = -16.5$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.7×10^{-11}	300	Gordon, Mulac, and Nangia, 1971[1]	(a)
$(8.3\pm1.7)\times10^{-12}$	298	Gehring *et al.*, 1973[2]	DF-MS (b)
$2.1\times10^{-8}\ T^{-1.25}$	300–500	Lesclaux *et al.*, 1975[3]	FP (c)
$(1.8\pm0.3)\times10^{-11}$	300		
$(2.1\pm0.2)\times10^{-11}$	298	Hancock *et al.*, 1975[4]	FP-LIF
$(1.7\pm0.4)\times10^{-11}$	298	Sarkisov, Cheskis, and Sviridenkov, 1978[5]	FP (d)
$4.5\times10^{-7}\ T^{-1.85}$	210–500	Hack *et al.*, 1979[6]	DF-LIF
9.7×10^{-12}	298		
$2.77\times10^{-7}\ T^{-1.67}$	216–480	Stief *et al.*, 1982[7]	FP-LIF (e)
$(2.10\pm0.31)\times10^{-11}$	298		
$4.4\times10^{-5}\ T^{-2.3}\exp(-684/T)$	294–1215	Silver and Kolb, 1982[8]	DF-LIF (f)
$(9.59\pm2.4)\times10^{-12}$	298		
$(1.7\pm0.5)\times10^{-11}$	295	Andresen *et al.*, 1982[9]	PLP (g)
$(1.81\pm0.12)\times10^{-11}$	297	Whyte and Phillips, 1983[10]	PLP-LIF
1.7×10^{-11}	298	Dreier and Wolfrum, 1985[11]	PLP (h)
$(1.3\pm0.4)\times10^{-11}$	298		
$1.31\times10^{-8}\ T^{-(1.17\pm0.25)}$	294–1027	Atakan *et al.*, 1989[12]	PLP-LIF (i)
$(1.67\pm0.25)\times10^{-11}$	298		
$2.0\times10^{-11}\ (T/298)^{-2.2}$	295–620	Bulatov *et al.*, 1989[13]	FP (d)
$5.43\ T^{-4.02}\exp(-1034/T)$	293–612	Wolf, Yang, and Durant, 1994[14]	PLP-LIF
$(1.9\pm0.1)\times10^{-11}$	295		
$2.2\times10^{-12}\exp[(525\pm80)/T]$	297–673	Diau *et al.*, 1994[15]	PLP (j)
$(1.45\pm0.08)\times10^{-11}$	297		
Branching Ratios			
$(k_2+k_3)/k=0.1\pm0.025$	300	Atakan *et al.*, 1989[12]	PLP-LIF (i)
$k_1/k=0.85$	295	Stephens *et al.*, 1993[16]	PLP-AS (k)
$(k_2+k_3)/k=0.10$	295		
$k_1/k=0.89\pm0.04$	302	Park and Lin, 1996[17]	PLP-MS (l)
$(k_2+k_3)/k=0.11\pm0.02$	302		
Reviews and Evaluations			
$4.0\times10^{-12}\exp(450/T)$	210–500	NASA, 1997[18]	(m)
$1.6\times10^{-11}\ (T/298)^{-1.5}$	210–500	IUPAC, 1997[19]	(n)
$(k_2+k_3)/k=0.1$	298		

Comments

(a) Pulsed radiolysis of NH_3–NO mixtures at 670 mbar (500 Torr) total pressure. [NH_2] was monitored by absorption spectroscopy.

(b) NO_2 was added to excess H atoms followed by addition of excess NH_3. Analysis by time-of-flight mass spectrometry. Vibrationally excited H_2O product was observed. Addition product NH_2NO also observed, to the extent of 5% of the N_2 formed.

(c) [NH_2] was monitored by absorption spectroscopy. No pressure dependence of k was observed over the range 2.7–930 mbar (2–700 Torr) of N_2.

(d) [NH_2] was monitored by intracavity laser absorption.

(e) [NH_2] was monitored by LIF. Production of HO looked for by resonance fluorescence and found under static conditions, but not under flowing conditions. An upper limit to $(k_2+k_3)/k$ of <0.22 was obtained.

(f) [NH_2] was monitored by LIF. HO production detected by RF or by LIF. A rate coefficient ratio of $(k_2+k_3)/k = (0.4\pm0.1)$ was obtained, but the data were later reanalyzed by the authors to give a value of 0.12. H-atom production looked for using RF; an upper limit of 0.05 for channels leading to H atoms found.

(g) Rate coefficient determined by monitoring production of vibrationally excited H_2O by observation of infrared and visible emissions. RA and LIF were used to monitor [HO]. $k_2/k \geqslant 0.65$ obtained, with H-atom production being $\leqslant 0.05$.

(h) [NH_2] and [N_2] monitored by coherent anti-Stokes Raman spectroscopy (CARS). Independent value of rate coefficient obtained by monitoring the IR fluorescence of vibrationally excited H_2O.

(i) [HO] monitored by LIF. HO yield also measured using HO production from H_2O_2 photolysis to calibrate for [HO].

(j) NH_2 monitored by cavity ring-down absorption at 537.6 nm.

(k) Pulsed laser photolysis of NH_3–NO mixtures. [H_2O], [HO], [NH_3], and [NH_2] monitored by infrared absorption spectroscopy.

(l) Pulsed laser photolysis of NH_3/NO/CO mixtures. Time resolved MS measurement of NH_3, H_2O, and CO_2 produced by scavenging of HO by CO.

(m) Based on the data of Lesclaux *et al.*,[3] Hancock *et al.*,[4] Sarkisov *et al.*,[5] Stief *et al.*,[7] Andresen *et al.*,[9] Whyte and Phillips,[10] Dreier and Wolfrum,[11] Atakan *et al.*,[12] Wolf *et al.*,[14] Diau *et al.*,[15] and Imamura and Washida.[20]

(n) Based on the data of Refs. 1–13.

Preferred Values

$k = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.6 \times 10^{-11} (T/298)^{-1.5}$ cm^3 molecule^{-1} s^{-1} over the temperature range 210–500 K.

$k_1/k = 0.9$ at 298 K.

$(k_2 + k_3)/k = 0.1$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta n = \pm 0.5$.

$\Delta k_1/k_2 = \pm 0.1$ at 298 K.

$\Delta(k_2 + k_3)/k = \pm 0.03$ at 298 K.

Comments on Preferred Values

The rate coefficients obtained in the pulsed photolysis studies are significantly higher than those obtained using the discharge flow technique. The reason for this discrepancy is not known. The preferred value at 298 K is therefore taken as the average of the values reported in Refs. 2–15. The temperature dependence is based on the data below 500 K in the six temperature dependence studies of Lesclaux *et al.*,[3] Hack *et al.*,[6] Stief *et al.*,[7] Silver and Kolb,[8] Atakan *et al.*,[12] and Bulatov *et al.*[13]

The preferred value of the branching ratio is based on the direct measurements of Atakan *et al.*,[12] Stephens *et al.*,[16] and Park and Lin.[17] The less direct measurement of Bulatov *et al.*[13] is in good agreement. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[19]

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$NH_2 + NO_2 \rightarrow N_2O + H_2O$ (1)
$\rightarrow N_2 + H_2O_2$ (2)
$\rightarrow H_2NO + NO$ (3)

$\Delta H^\circ(1) = -361.7$ kJ·mol^{-1}
$\Delta H^\circ(2) = -335.2$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference*	Technique/Comments
Absolute Rate Coefficients			
$3.2\times10^{-4}\ T^{-3.0}$	250–500	Hack *et al.*, 1979[1]	DF-LIF/MS (a)
1.0×10^{-11}	295		
$3.8\times10^{-8}\ T^{-1.30}$	298–505	Kurasawa and Lesclaux, 1979[2]	FP-LIF
$(2.3\pm0.2)\times10^{-11}$	298		
$(2.11\pm0.18)\times10^{-11}$	297	Whyte and Phillips, 1983[3]	PLP-LIF
$(2.26\pm0.08)\times10^{-11}$	298	Xiang, Torres, and Guillory, 1985[4]	PLP-LIF (b)
$(2.1\pm0.4)\times10^{-11}\ (T/298)^{-1.7}$	295–620	Bulatov *et al.*, 1989[5]	FP (c)
Branching Ratios			
$k_1/k = 0.14\pm0.02$	298	Quandt and Hershberger, 1996[6]	PLP-TDLS (d)
Reviews and Evaluations			
$2.1\times10^{-12}\ \exp(650/T)$	250–510	NASA, 1997[7]	(e)
$2.0\times10^{-11}\ (T/298)^{-2.0}$	250–500	IUPAC, 1997[8]	(f)

Comments

(a) $[NH_2]$ was monitored by LIF for the rate coefficient determination. A separate flow system was used for a study of products by mass spectrometry. Product analysis suggested that 95% of the reaction proceeds by channel (1).

(b) NH_2 formed by multiphoton dissociation of NH_3. The variation of the rate coefficient with the degree of excitation of NH_2 was also studied.

(c) $[NH_2]$ was monitored by intracavity absorption. k was found to be independent of pressure over the range 13–870 mbar (10–650 Torr).

(d) Pulsed laser photolysis of NH_3–NO_2 mixtures. Time resolved infrared laser spectroscopy was used to detect N_2O, H_2O, and NO. Large amounts of NO were produced by unidentified secondary chemistry.

(e) Based on the data of Hack *et al.*,[1] Kurasawa and Lesclaux,[2] Whyte and Phillips,[3] and Xiang *et al.*[4]

(f) See Comments on Preferred Values.

Preferred Values

$k = 2.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.0\times10^{-11}\ (T/298)^{-2.0}$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–500 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta n = \pm 0.7$.

Comments on Preferred Values

The value of k obtained by Hack *et al.*[1] at 298 K using a discharge-flow technique is significantly lower than the values obtained in the four other studies,[2-5] all of which used flash photolysis and which are in excellent agreement. A similar discrepancy between discharge flow and flash photolysis results is observed for the reaction of NH_2 with NO.

The preferred value at 298 K is the average of the values reported in Refs. 1–5. The temperature dependence is the average of the values of Hack *et al.*,[1] Kurasawa and Lesclaux,[2] and Bulatov *et al.*[5] The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[8]

Ab initio calculations[9] suggest that channels (1) and (3) are the most likely. Hack *et al.*[1] investigated product formation and concluded that 95% of the reaction proceeds by channel (1). There is also some support for the predominence of channel (1) from the flow reaction and kinetic modeling study of Glarborg *et al.*[10] However, a direct measurement[6] gives $k_1/k = 0.14\pm0.02$. At this stage no recommendations are made concerning the branching ratios.

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$2NO + O_2 \rightarrow 2NO_2$

$\Delta H^\circ = -114.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^6 molecule^{-2} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.0\pm0.1)\times10^{-38}$	298	Stedman and Niki, 1973[1]	(a)
$1.8\times10^{-47}\ T^{2.7}\exp(1600/T)$	226–758	Olbregts, 1985[2]	(b)
2.1×10^{-38}	298		
Reviews and Evaluations			
$3.3\times10^{-39}\exp(530/T)$	273–660	Baulch *et al.*, 1973[3]	(c)
$3.3\times10^{-39}\exp(530/T)$	273–600	IUPAC, 1997[4]	(d)

Comments

(a) Static system. Photolysis of 1–100 ppm mixing ratios of NO_2 in air using chemiluminescence detectors to monitor NO, NO_2, and O_3.

(b) Static 1 L reactor. Total pressure was measured with a differential micromanometer, and $[NO_2]$ measured in absorption at 436 nm. Pressures of NO and O_2 ranged up to 35 mbar (26 Torr). Non-Arrhenius behavior was observed with k first decreasing with increasing temperature, reaching a minimum value at 600 K, and then increasing with increasing temperature.

(c) Based on an evaluation of a substantial quantity of consistent data reported up to 1972.

(d) Accepts the evaluation of Baulch *et al.*[3]

Preferred Values

$k = 2.0\times10^{-38}$ cm^6 molecule^{-2} s^{-1} at 298 K.

$k = 3.3\times10^{-39}\exp(530/T)$ cm^6 molecule^{-2} s^{-1} over the temperature range 270–600 K.

Reliability

$\Delta\log k = \pm0.1$ at 298 K.

$\Delta(E/R) = \pm400$ K.

Comments on Preferred Values

The preferred values are those recommended in the evaluation by Baulch *et al.*[3] The results of studies performed since that evaluation, which are given in the table, are in excellent agreement with the preferred values.

Olbregts[2] observed non-Arrhenius behavior over the entire temperature range studied and expressed k by a modified Arrhenius expression and also as the sum of two Arrhenius expressions. However, from 250 K to about 600 K the total rate coefficient of Olbregts[2] is in good agreement with the value calculated from the expression recommended here and is adequate for atmospheric modeling purposes. Olbregts[2] interpreted his results in terms of a multi-step mechanism involving NO_3 or the dimer $(NO)_2$. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[4]

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$NO + O_3 \rightarrow NO_2 + O_2$

$\Delta H^\circ = -199.8$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$2.34\times10^{-12}\exp[-(1450\pm50)T]$	203–361	Birks *et al.*, 1976[1]	(a)
$(1.73\pm0.09)\times10^{-14}$	297		
$4.3\times10^{-12}\exp[-(1598\pm50)/T]$	283–443	Lippmann, Jesser, and Schurath, 1980[2]	(b)
$(2.14\pm0.11)\times10^{-14}$	304		
$3.16\times10^{-12}\exp[-(1556\pm40)/T]$	212–422	Ray and Watson, 1981[3]	DF-MS
$(1.80\pm0.04)\times10^{-14}$	299		
$2.6\times10^{-12}\exp[-(1435\pm64)/T]$	195–369	Michael, Allen, and Brobst, 1981[4]	(c)
$(2.0\pm0.2)\times10^{-14}$	298		
$8.9\times10^{-19}\,T^{2.2}\exp(-765/T)$	204–353	Borders and Birks, 1982[5]	(d)
$(1.72\pm0.04)\times10^{-14}$	298		
Reviews and Evaluations			
$2.0\times10^{-12}\exp(-1400/T)$	200–300	NASA, 1997[6]	(e)
$1.8\times10^{-12}\exp(-1370/T)$	195–304	IUPAC, 1997[7]	(f)

Comments

(a) Fast flow system, with $[O_3]$ in excess and with NO being monitored by mass spectrometry.

(b) First order decay of $[O_3]$ in the presence of excess NO monitored by chemiluminescent detection under stopped-flow conditions in a 220 m^3 stainless steel spherical vessel at pressures below 0.13 mbar (0.1 Torr).

(c) Three independent low pressure fast-flow studies. The extent of reaction was monitored by NO_2 chemiluminescence under conditions of excess NO or excess O_3. In other experiments the decay of NO in excess O_3 was monitored by RF. The results from all studies were in good agreement. An Arrhenius plot of the data showed significant curvature with E/R varying from 1258 K (195–260 K) to 1656 K (260–369 K).

(d) Dual flow tube technique with NO_2 chemiluminescence used to monitor the reaction progress. The authors claim that this technique gives accurate values of E/R over temperature intervals as small as 10 K. Nonlinear Arrhenius behavior was observed with E/R increasing from a value of 1200 K at the lowest temperature studied to 1470 K at the highest temperature.

(e) Based on the data in Refs. 1–5.

(f) See Comments on Preferred Values.

Preferred Values

$k = 1.8\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.8\times10^{-12}\exp(-1370/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 195–304 K.

Reliability

$\Delta \log k = \pm0.08$ at 298 K.

$\Delta(E/R) = \pm200$ K.

Comments on Preferred Values

The preferred Arrhenius expression is based on a least-squares analysis of the data over the range 195–304 K reported by Birks *et al.*,[1] Lippman *et al.*,[2] Ray and Watson,[3] Michael *et al.*,[4] and Borders and Birks.[5] The data at closely spaced temperatures reported by Lippmann *et al.*[2] and by Borders and Birks[5] were grouped to give equal weight to the five studies. The temperature range was limited because of the nonlinear Arrhenius behavior observed by Clyne *et al.*,[8] Clough and Thrush,[9] Birks *et al.*,[1] Michael *et al.*,[4] and by Borders and Birks.[5] Earlier room temperature results of Stedman and Niki[10] and Bemand *et al.*[11] are in good agreement with the preferred value at 298 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[7]

Clyne *et al.*,[8] Birks *et al.*,[1] Schurath *et al.*,[12] and Michael *et al.*[4] have reported individual Arrhenius expressions for each of two primary reaction channels, one to produce NO_2 in its ground electronic state and the other leading to electronically excited NO_2.

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$NO + NO_2 + M \rightarrow N_2O_3 + M$

$\Delta H^\circ = -40.5$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.7 \pm 0.6) \times 10^{-33}$ [Ar]	207 ± 2	Smith and Yarwood, 1987[1]	FP (a)
$(9.1 \pm 0.7) \times 10^{-33}$ [N_2]	208 ± 2		
$(2.8 \pm 2.8) \times 10^{-15}\ T^{-(7.7 \pm 0.8)}$ [Ar]	227–260	Markwalder, Gozel, and van den Bergh, 1993[2]	(b)
4.1×10^{-33} [Ar]	207		
Reviews and Evaluations			
$3.1 \times 10^{-34}\ (T/300)^{-7.7}$ [N_2]	208–300	IUPAC, 1997[3]	(c)

Comments

(a) Partial photodissociation of N_2O_3 in equilibrium NO_2–N_2O_4–NO–N_2O_3–M mixtures with M=He, Ar, Ne, N_2, and CF_4 (see also Ref. 4). The relaxation to equilibrium was monitored by observing the absorption of N_2O_3 at the ν_1 band at 1829.59 cm^{-1}. The total pressure was 253–667 mbar (190–500 Torr). Falloff curves were extrapolated using $F_c = 0.60$ for Ar and N_2.

(b) CO laser-induced temperature jump measurements with NO_2–N_2O_4–N_2O_3–NO–SiF_4–Ar equilibrium mixtures. The subsequent relaxation toward equilibrium was monitored by UV absorption of N_2O_3 at 253 nm.

(c) See Comments on Preferred Values.

Preferred Values

$k_0 = 3.1 \times 10^{-34}\ (T/300)^{-7.7}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the data from Markwalder *et al.*[2] after conversion by the ratio $k_0(N_2)/k_0(Ar) = 1.36$ of Smith and Yarwood,[1] and are identical to those in our previous evaluation, IUPAC, 1997.[3]

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.4 \pm 1) \times 10^{-12}$	208	Smith and Yarwood, 1987[1]	FP (a)
$(2.7 \pm 0.9) \times 10^{-15}\ T^{(1.4 \pm 0.2)}$	227–260	Markwalder, Gozel, and van den Bergh, 1993[2]	(b)
4.7×10^{-12}	208		
Reviews and Evaluations			
$7.9 \times 10^{-12}\ (T/300)^{1.4}$	208–300	IUPAC, 1997[3]	(c)

Comments

(a) See comment (a) for k_0.
(b) See comment (b) for k_0.
(c) See Comments on Preferred Values.

Preferred Values

$k_\infty = 7.9\times10^{-12}\ (T/300)^{1.4}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred values are those from Ref. 2, where the largest ranges of the falloff curve were investigated, and are identical to those in our previous evaluation, IUPAC, 1997.[3] At 208 K, the values of k_∞ from Refs. 1 and 2 are in reasonable agreement.

References

[1] I. W. M. Smith and G. Yarwood, Faraday Discuss Chem. Soc. **84**, 205 (1987).
[2] B. Markwalder, P. Gozel, and H. van den Bergh, J. Phys. Chem. **97**, 5260 (1993).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).
[4] I. W. M. Smith and G. Yarwood, Chem. Phys. Lett. **130**, 24 (1986).

$N_2O_3 + M \rightarrow NO + NO_2 + M$

$\Delta H^\circ = 40.5$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$5.0\times10^{14}\ T^{-(8.7\pm0.9)} \exp(-4880/T)$ [Ar]	225–260	Markwalder, Gozel, and van den Bergh, 1993[1]	(a)
Reviews and Evaluations			
$1.9\times10^{-7}\ (T/300)^{-8.7} \exp(-4880/T)\ [N_2]$	225–300	IUPAC, 1997[2]	(b)

Comments

(a) CO_2 laser-induced temperature jump measurements with NO_2-N_2O_4-N_2O_3-NO-SiF_4-Ar equilibrium mixtures. The subsequent relaxation toward equilibrium was monitored by UV absorption of N_2O_3 at 253 nm. Dissociation rate coefficients were derived from the measured recombination rate coefficients and the equilibrium constant from Chao *et al.*[3] of $K_c = 1.8\times10^{-29}\ T^{-1} \exp(-4880/T)$ molecule cm^{-3}. Falloff curves with M=Ar were obtained over the pressure range 0.5–200 bar and extrapolated to k_0 and k_∞ with F_c=0.6. $k_0(N_2)/k_0$ (Ar)=1.36 was taken from Smith and Yarwood[4] (see reaction NO + NO_2 + M → N_2O_3 + M).
(b) See Comments on Preferred Values.

Preferred Values

$k_0 = 1.6\times10^{-14}\ [N_2]$ s^{-1} at 298 K.
$k_0 = 1.9\times10^{-7}\ (T/300)^{-8.7} \exp(-4880/T)\ [N_2]$ s^{-1} over the temperature range 225–300 K.

Reliability

$\Delta \log k_0 = \pm 0.4$ at 298 K.
$\Delta n = \pm 1$.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred values are based on the data of Ref. 1, which are consistent with a theoretical analysis of the results (leading to collision efficiencies β_c(Ar)=0.3). The preferred values correspond to an analysis of the falloff curve with F_c=0.6 and the value of k_∞ given below, and are identical to those in our previous evaluation, IUPAC, 1997.[2]

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$4.8\times10^{14}\ T^{(0.4\pm0.1)}\exp(-4880/T)$	225–260	Markwalder, Gozel, and van den Bergh, 1993[1]	(a)
Reviews and Evaluations			
$4.7\times10^{15}\ (T/300)^{0.4}\exp(-4880/T)$	225–300	IUPAC, 1997[2]	(b)

Comments

(a) See comment (a) for k_0.

(b) See Comments on Preferred Values.

Preferred Values

$k_\infty = 3.6\times10^{8}\ \mathrm{s}^{-1}$ at 298 K.

$k_\infty = 4.7\times10^{15}\ (T/300)^{0.4}\exp(-4880/T)\ \mathrm{s}^{-1}$ over the temperature range 225–300 K.

Reliability

$\Delta\log k_\infty = \pm0.3$ at 298 K.

$\Delta n = \pm1$.

$\Delta(E/R) = \pm100$ K.

Comments on Preferred Values

The preferred values are based on the values of Ref. 1 converted to dissociation data with the equilibrium constant of Ref. 3.

References

[1] B. Markwalder, P. Gozel, and H. van den Bergh, J. Phys. Chem. **97**, 5260 (1993).

[2] IUPAC, Supplement V, 1997 (see references in Introduction).

[3] J. Chao, R. C. Wilhoit, and B. J. Zwolinski, Thermochim. Acta **10**, 359 (1974).

[4] I. W. M. Smith and G. Yarwood, Faraday Discuss. Chem. Soc. **84**, 205 (1987).

$NO + NO_3 \rightarrow 2NO_2$

$\Delta H^\circ = -97.6\ \mathrm{kJ\cdot mol^{-1}}$

Rate coefficient data

$k/\mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.55\times10^{-11}\exp(195/T)$	209–299	Hammer, Dlugokencky, and Howard, 1986[1]	DF-LIF (a)
$(2.95\pm0.16)\times10^{-11}$	299–414		
$1.59\times10^{-11}\exp(122/T)$	224–328	Sander and Kircher, 1986[2]	FP-A (b)
$(2.41\pm0.48)\times10^{-11}$	298		
$1.68\times10^{-11}\exp(103/T)$	223–400	Tyndall *et al.*, 1991[3]	DF-LIF (c)
$(2.34\times0.24)\times10^{-11}$	298		
Reviews and Evaluations			
$1.5\times10^{-11}\exp(170/T)$	200–420	NASA, 1997[4]	(d)
$1.8\times10^{-11}\exp(110/T)$	220–400	IUPAC, 1997[5]	(e)

Comments

(a) Arrhenius behavior was observed for k over the temperature range 209–299 K, with a constant value of the rate coefficient above room temperature.

(b) $[NO_3]$ was monitored by optical absorption. Total pressure was varied from 67 to 930 mbar (50–700 Torr) of He and N_2.

(c) $[NO_3]$ was monitored by LIF in excess NO. In these experiments NO_3 was produced by the reaction of F with HNO_3 and of NO_2 with O_3. In other experiments, the decay of [NO] in excess NO_3 was monitored by chemiluminescence. The value at 298 K is the mean of values from all three systems.

(d) Based on the data in Refs. 1–3.

(e) See Comments on Preferred Values.

Preferred Values

$k = 2.6\times10^{-11}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$ at 298 K.

$k = 1.8 \times 10^{-11} \exp(110/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 200–420 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred value of k at 298 K is the mean of the values reported by Hammer *et al.*,[1] Sander and Kircher,[2] and Tyndall *et al.*,[3] all of which are in good agreement. The preferred temperature dependence is the average of the values of Sander and Kircher[2] and Tyndall *et al.*,[3] with the pre-exponential factor in the Arrhenius expression being adjusted to fit the value of k at 298 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[5]

References

[1] P. D. Hammer, E. J. Dlugokencky, and C. J. Howard, J. Phys. Chem. **90**, 2491 (1986).
[2] S. P. Sander and C. C. Kircher, Chem. Phys. Lett. **126**, 149 (1986).
[3] G. S. Tyndall, J. J. Orlando, C. A. Cantrell, R. E. Shetter, and J. G. Calvert, J. Phys. Chem. **95**, 4381 (1991).
[4] NASA Evaluation No. 12, 1997 (see references in Introduction).
[5] IUPAC, Supplement V, 1997 (see references in Introduction).

$NO_2 + O_3 \rightarrow NO_3 + O_2$

$\Delta H° = -102.2$ $kJ \cdot mol^{-1}$

Rate coefficient data

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.2 \pm 0.5) \times 10^{-17}$	298	Ghormley, Ellsworth, and Hochanadel, 1973[1]	FP (a)
$9.76 \times 10^{-14} \exp[-(2427 \pm 140)/T]$	260–343	Davis *et al.*, 1974[2]	(b)
$(3.42 \pm 0.27) \times 10^{-17}$	303		
$1.34 \times 10^{-13} \exp[-(2466 \pm 30)/T]$	231–298	Graham and Johnston, 1974[3]	(c)
$(3.49 \pm 0.23) \times 10^{-17}$	298		
$1.57 \times 10^{-13} \exp[-(2509 \pm 76)/T]$	259–362	Huie and Herron, 1974[4]	(d)
$(3.78 \pm 0.07) \times 10^{-17}$	297		
$(3.45 \pm 0.12) \times 10^{-17}$	296	Cox and Coker, 1983[5]	(e)
Reviews and Evaluations			
$1.2 \times 10^{-13} \exp(-2450/T)$	230–360	NASA, 1997[6]	(f)
$1.2 \times 10^{-13} \exp(-2450/T)$	230–360	IUPAC, 1997[7]	(g)

Comments

(a) Flash photolysis system. $[O_3]$ and $[NO_2]$ were monitored by optical absorption.

(b) Stopped flow system with detection of O_3 by time-of-flight mass spectrometry. The pre-exponential factor given in the abstract is incorrect; the correct value is tabulated here (D. D. Davis, private communication).

(c) Longpath static cell. $[O_3]$ and $[NO_2]$ monitored in separate experiments by UV absorption spectrometry. Stoichiometric ratio $(\Delta NO_2/\Delta O_3)$ was measured to be 1.89 ± 0.08.

(d) Stopped-flow system. $[O_3]$ monitored by molecular-beam sampling mass spectrometry.

(e) Static system. Experiments performed with both NO_2 and with O_3 in excess. Time-resolved absorption spectroscopy was used to monitor N_2O_5 with a diode laser infrared source, and NO_2 and O_3 were monitored at 350 and 255 nm, respectively, using conventional UV techniques. Total pressure, 13 mbar (10 Torr) N_2. N_2O_5 was shown to be the only stable nitrogen-containing product. Overall stoichiometry $(\Delta NO_2/\Delta O_3)$ was determined to have the value 1.85 ± 0.09. Minor role for unsymmetrical NO_3 species suggested to account for a stoichiometric factor of less than 2.

(f) Based on the data of Davis *et al.*,[2] Graham and Johnston,[3] Huie and Herron,[4] and Cox and Coker.[5]

(g) Based on the data of Davis *et al.*,[2] Graham and Johnston,[3] and Huie and Herron.[4]

Preferred Values

$k = 3.5 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k = 1.4 \times 10^{-13} \exp(-2470/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 230–360 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

The preferred value at 298 K is taken as the mean of the five values tabulated,[1-5] corrected where necessary for the difference between the temperature of the measurement and 298 K. The temperature coefficient is taken as the mean of the values obtained by Davis *et al.*,[2] Graham and Johnston,[3] and Huie and Herron,[4] which are in excellent agreement. Verhees and Adema[8] obtained a significantly higher temperature coefficient for k and a higher pre-exponential factor, but wall reactions were shown to be important in their work. There are also a number of other measurements of k at, or close to 298 K, which have not been used in deriving the preferred values because of their substantial deviation from the majority of the other studies.

References

[1] J. A. Ghormley, R. L. Ellsworth, and C. J. Hochanadel, J. Phys. Chem. **77**, 1341 (1973); Erratum **78**, 2698 (1974).
[2] D. D. Davis, J. Prusazcyk, M. Dwyer, and P. Kim, J. Phys. Chem. **78**, 1775 (1974).
[3] R. A. Graham and H. S. Johnston, J. Chem. Phys. **60**, 4628 (1974).
[4] R. E. Huie and J. T. Herron, Chem. Phys. Lett. **27**, 411 (1974).
[5] R. A. Cox and G. B. Coker, J. Atmos. Chem. **1**, 53 (1983).
[6] NASA Evaluation No. 12, 1997 (see references in Introduction).
[7] IUPAC, Supplement V, 1997 (see references in Introduction).
[8] P. W. C. Verhees and E. H. Adema, J. Atmos. Chem. **2**, 387 (1985).

$NO_2 + NO_2 + M \rightarrow N_2O_4 + M$

$\Delta H^\circ = -57.3$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.4 \pm 0.2) \times 10^{-33}$ [N$_2$]	298	Borrell, Cobos, and Luther, 1988[1]	PLP (a)
$(1.0 \pm 0.1) \times 10^{-33}$ [N$_2$]	224	Brunning, Frost, and Smith, 1988[2]	FP (b)
$(2.1 \pm 0.2) \times 10^{-12}\ T^{(-9.0 \pm 0.9)}$ [He]	255–273	Markwalder, Gozel, and van den Bergh, 1992[3]	(c)
Reviews and Evaluations			
$4.7 \times 10^{-35} \exp(860/T)$ [N$_2$]	250–350	Baulch, Drysdale, and Horne, 1973[4]	(d)
$1.4 \times 10^{-33} (T/300)^{-3.8}$ [N$_2$]	300–500	IUPAC, 1997[5]	(e)

Comments

(a) Relaxation of NO_2–N_2O_4–N_2 equilibrium mixtures after low intensity pulsed laser photolysis of N_2O_4 at 248 nm. The relaxation to equilibrium was obtained by measuring the change in N_2O_4 absorption at 220 nm. Falloff curves (1–207 bar) were extrapolated with $F_c=0.40$ and N=1.26.

(b) Perturbation of equilibrium mixture of N_2O_4 and NO_2 by photolysis of a fraction of the N_2O_4. The relaxation rate was monitored by IR absorption of N_2O_4 at 1565.5 cm^{-1}.

(c) Temperature jumps induced by IR absorption of SiF_4 in equilibrium mixtures of NO_2–N_2O_4–He–SiF_4. The relaxation to equilibrium was followed by measuring NO_2 and N_2O_4 concentrations by absorption spectroscopy at 420 and 250 nm, respectively. Falloff curves (0.3–200 bar) were extrapolated with $F_c=0.52$ and N=1.10 (see also earlier data from Ref. 6).

(d) Based on data for the reverse reactions previous to 1970 and the equilibrium constant.

(e) See Comments on Preferred Values.

Preferred Values

$k_0 = 1.4 \times 10^{-33} (T/300)^{-3.8}$ [N$_2$] cm^3 molecule^{-1} s^{-1} over the temperature range 300–500 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are from the most extensive study of Borrell *et al.*,[1] where a complete falloff curve was measured. Earlier less extensive measurements are in reasonable agreement with this curve, which uses $F_c=0.40$. The temperature dependence given is from the theoretical modeling of Ref. 1, rather than from the limited experimental information of Ref. 3. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[5]

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.3\pm1.0)\times10^{-13}$	298	Borrell, Cobos, and Luther, 1988[1]	PLP (a)
$(3.7\pm0.3)\times10^{-18}\ T^{(2.3\pm0.2)}$	255–273	Markwalder, Gozel, and van den Bergh, 1992[3]	(b)
Reviews and Evaluations			
1.0×10^{-12}	250–300	IUPAC, 1997[5]	(c)

Comments

(a) See comment (a) for k_0.
(b) See comment (c) for k_0.
(c) See Comment on Preferred Values.

Preferred Values

$k_\infty = 1.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–300 K.

Reliability

$\Delta\log k_\infty = \pm0.3$ over the temperature range 250–300 K.

Comments on Preferred Values

The preferred rate coefficient is the mean of the values of Borrell *et al.*[1] and Markwalder *et al.*,[3] and are identical to those in our previous evaluation, IUPAC, 1997.[5] The temperature dependence of k_0 and k_∞ derived from the measurements of Ref. 3 appears to be the result of fitting of incomplete falloff curves.

References

[1] P. Borrell, C. J. Cobos, and K. Luther, J. Phys. Chem. **92**, 4377 (1988).
[2] J. Brunning, M. J. Frost, and I. W. M. Smith, Int. J. Chem. Kinet. **20**, 957 (1988).
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[5] IUPAC, Supplement V, 1997 (see references in Introduction).
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$N_2O_4 + M \rightarrow NO_2 + NO_2 + M$

$\Delta H^\circ = 57.3$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.29\times10^{-5}\ (T/300)^{-3.8}\exp(-6460/T)\ [N_2]$	300–500	Borrell, Cobos, and Luther, 1988[1]	PLP (a)
$1.6\times10^{19}\ T^{-(10.0\pm1.0)}\exp[-(6790\pm700)/T]\ [He]$	255–273	Markwalder, Gozel, and van den Bergh, 1992[2]	(b)
Reviews and Evaluations			
$4.2\times10^{-7}\exp(-5550/T)\ [N_2]$	250–350	Baulch, Drysdale, and Horne, 1973[3]	(c)
$1.3\times10^{-5}\ (T/300)^{-3.8}\exp(-6400/T)\ [N_2]$	300–500	IUPAC, 1997[4]	(d)
$6.1\times10^{-15}\ [N_2]$	298		

Comments

(a) Relaxation of NO_2–N_2O_4–N_2 equilibrium mixtures after pulsed laser photolysis of N_2O_4 at 248 nm. The relaxation to equilibrium was followed by observing N_2O_4 in absorption at 220 nm. Falloff curves (1–207 bar) were extrapolated with $F_c=0.40$ and N=1.26. The equilibrium constant from Ref. 5 was employed.

(b) Temperature jumps induced by IR absorption of SiF_4 in equilibrium mixtures of NO_2–N_2O_4–He–SiF_4. The relaxation to equilibrium was followed by absorption spectroscopy of NO_2 and N_2O_4 at 420 and 250 nm.

respectively. Falloff curves (0.3–200 bar) were extrapolated with F_c=0.52 and N=1.10. Equilibrium constants from Ref. 6 were employed.

(c) Based on the shock-wave studies of Refs. 7 and 8.

(d) See Comments on Preferred Values.

Preferred Values

k_0=6.1×10^{-15} [N_2] s^{-1} at 298 K.

k_0=1.3×10^{-5} $(T/300)^{-3.8}$ exp(−6400/T) [N_2] s^{-1} over the temperature range 300–500 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values are from the measurements of Borrell *et al.*[1] in combination with the equilibrium constants from Ref. 5, and are identical to those in our previous evaluation, IUPAC, 1997.[4] These data are based on the most complete falloff curve at 300 K, using F_c=0.40. The temperature dependence is from a theoretical analysis, in good agreement with the evaluation of Ref. 3.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$7.7\times10^{15}\,(T/300)^{1.1}\exp(-6460/T)$	300–600	Borrell, Cobos, and Luther, 1988[1]	PLP (a)
$2.8\times10^{13}\,T^{(1.3\pm0.2)}\exp[-(6790\pm700)/T]$	255–273	Markwalder, Gozel, and van den Bergh, 1992[2]	(b)
Reviews and Evaluations			
4.4×10^{6}	298	IUPAC, 1997[4]	(c)
$1.15\times10^{16}\exp(-6460/T)$	250–300		

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0.

(c) See Comments on Preferred Values.

Preferred Values

k_∞ =4.4×10^{6} s^{-1} at 298 K.

k_∞ =1.15×10^{16} exp(−6460/T) s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.4$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred rate coefficient at room temperature is the average of the values of Borrell *et al.*[1] and Markwalder *et al.*,[2] and is identical to that in our previous evaluation, IUPAC, 1997.[4] The recommended temperature coefficient corresponds to a temperature-independent value of k_∞ for the reverse recombination. Measurements from Refs. 9 and 10 in the intermediate falloff range at 298 K are consistent with the preferred values of k_0, k_∞ and F_c=0.4 at 300 K.

References

[1] P. Borrell, C. J. Cobos, and K. Luther, J. Phys. Chem. **92**, 4377 (1988).

[2] B. Markwalder, P. Gozel, and H. van den Bergh, J. Chem. Phys. **97**, 5472 (1992).

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$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$

$\Delta H° = -95.6$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$9.6\times 10^{-33}\exp(1550/T)\,[N_2]$	262–295	Connell and Johnston, 1979[1]	(a)
$1.7\times 10^{-30}\,[N_2]$	298		
$1.35\times 10^{-32}\exp(1270/T)\,[N_2]$	285–384	Viggiano *et al.*, 1981[2]	(b)
$9.6\times 10^{-31}\,[N_2]$	298		
$(4.5\pm 1.1)\times 10^{-30}\,(T/300)^{-(3.4\pm 1.3)}\,[N_2]$	236–358	Kircher, Margitan, and Sander, 1984[3]	FP-A (c)
$2.12\times 10^{-30}\,[N_2]$	298	Smith, Ravishankara, and Wine, 1985[4]	DF-A (d)
$2.8\times 10^{-30}\,(T/300)^{-3.5}\,[N_2]$	236–358	Orlando *et al.*, 1991[5]	DF-LIF (e)
Reviews and Evaluations			
$2.2\times 10^{-30}\,(T/300)^{-3.9}$ [air]	200–300	NASA, 1997[6]	(f)
$2.7\times 10^{-30}\,(T/300)^{-3.4}\,[N_2]$	200–400	IUPAC, 1997[7]	(g)

Comments

(a) From study of N_2O_5 decomposition. Static reaction vessel with multi-reflection White-cell optical arrangement for the time-resolved detection of N_2O_5 by IR absorption at 8.028 μm. Converted to recombination rate coefficients with the equilibrium constant $K_c = 8.4\times 10^{26}\exp(-11180/T)$ molecule cm^{-3} from Ref. 8.

(b) From study of N_2O_5 decomposition. Flow system reactors of various size. N_2O_5 was detected by ion–molecule reactions in a flowing afterglow system. Measurements were carried out at $[N_2] = 2.5\times 10^{17}-2.7\times 10^{19}$ molecule cm^{-3}. Converted to recombination rate coefficients with the equilibrium constant $K_c = 8.4\times 10^{26}\exp(-11180/T)$ molecule cm^{-3} from Ref. 8.

(c) Visible absorption of NO_3 monitored under pseudo-first-order conditions. Falloff curve measured over the pressure range 27–930 mbar (20–700 Torr) and extrapolated using reduced falloff curve representation with $F_c = 0.34$ at 298 K.

(d) Visible absorption of NO_3 monitored. Pressure range 1.3–10.7 mbar (1–8 Torr) in He. and 0.7–8 mbar (0.5–6 Torr) in N_2. Reduced falloff curves extrapolated with $F_c = 0.47$ for N_2 at 298 K.

(e) Detection of NO_3. Experiments were conducted over the pressure range 0.7–10.7 mbar (0.5–8 Torr) and the data evaluated using $F_c = \{2.5\exp(-1950/T) + 0.9\exp(-T/430)\}$ (F_c(298 K)$=0.45$).

(f) Based on data from Refs. 3, 4, 9, and 10, and $F_c = 0.6$.

(g) Based on rate coefficients from Ref. 11 and those discussed in Ref. 12, with $F_c = 0.34$ at 298 K.

Preferred Values

$k_0 = 2.8\times 10^{-30}\,(T/300)^{-3.5}\,[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.10$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred values are based on the data of Orlando *et al.*[5] and the falloff extrapolation using $F_c(298) = 0.45$. Different choices of F_c lead to different values of the extrapolated k_0 and k_∞, although the various representations all agree well with the experimental data.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.1\times10^{-10}\exp(-1360/T)$	262–295	Connell and Johnston, 1979[1]	(a)
2.2×10^{-12}	298		
$1.5\times10^{-10}\exp(-1610/T)$	285–384	Viggiano *et al.*, 1981[2]	(b)
6.8×10^{-13}	298		
$(2.2\pm0.5)\times10^{-12}$	293	Croce de Cobos, Hippler, and Troe, 1984[11]	(c)
$(1.65\pm0.15)\times10^{-12}\ (T/300)^{-(0.4\pm0.5)}$	236–358	Kircher, Margitan, and Sander, 1984[3]	FP-A (d)
1.85×10^{-12}	298	Smith, Ravishankara, and Wine, 1985[4]	DF-A (e)
$1.7\times10^{-12}\ (T/300)^{-0.2}$	236–358	Orlando *et al.*, 1991[5]	DF-LIF (f)
Reviews and Evaluations			
$1.5\times10^{-12}\ (T/300)^{-0.7}$	200–300	NASA, 1997[6]	(g)
$2.0\times10^{-12}\ (T/300)^{0.2}$	200–500	IUPAC, 1997[7]	(h)

Comments

(a) See comment (a) for k_0.
(b) See comment (b) for k_0. Data obtained from extrapolation of data in a relatively narrow pressure range near to the center of the falloff curve.
(c) Laser flash photolysis of N_2O in the presence of NO_2. NO_3 radicals were monitored by visible absorption under pseudo-first order conditions. The falloff curve was measured over the pressure range 1–200 bar in N_2, and extrapolated with $F_c=0.34$.
(d) See comment (c) for k_0.
(e) See comment (d) for k_0.
(f) See comment (e) for k_0.
(g) See comment (f) for k_0.
(h) See Comments on Preferred Values.

Preferred Values

$k_\infty=2.0\times10^{-12}\ (T/300)^{0.2}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–500 K.

Reliability

$\Delta\log k_\infty=\pm0.2$ at 298 K.
$\Delta n=\pm0.6$.

Comments on Preferred Values

The preferred values are based on the average of the extrapolated k_∞ data of the studies used in IUPAC, 1992,[12] and the data of Orlando *et al.*,[5] using a theoretical estimate of the temperature coefficient from Ref. 11.

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$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$

$\Delta H^\circ = 95.6\ \text{kJ}\cdot\text{mol}^{-1}$

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.04\times10^{-3}\ (T/300)^{-3.5}\exp(-11000/T)\ [N_2]$	253–384	Cantrell *et al.*, 1993[1]	(a)
Reviews and Evaluations			
$8.2\times10^{-4}\ (T/300)^{-3.9}\exp(-11000/T)\ [\text{air}]$	200–300	NASA, 1997[2]	(b)
$9.5\times10^{-20}\ [N_2]$	298	IUPAC, 1997[3]	(c)
$1.0\times10^{-3}\ (T/300)^{-3.5}\exp(-11000/T)\ [N_2]$	200–400		

Comments

(a) Thermal decomposition of N_2O_5 in the presence of NO in N_2. FTIR analysis of N_2O_5 in a stainless steel cell equipped with multiple path optics. Falloff curves over the gas density 4.3×10^{14}–1.1×10^{20} molecule cm^{-3} were analyzed using $F_c=[2.5\ \exp(-1950/T)+0.9\ \exp(-T/430)]$ $[F_c(298\ \text{K})=0.45]$. In the analysis, data from Refs. 4 and 5 were also taken into account.

(b) Rate coefficients were evaluated from the recommended rate coefficients for the reverse reaction and the equilibrium constant.

(c) See Comments on Preferred Values.

Preferred Values

$k_0 = 9.5\times10^{-20}\ [N_2]\ \text{s}^{-1}$ at 298 K.

$k_0=1.0\times10^{-3}\ (T/300)^{-3.5}\ \exp(-11000/T)\ [N_2]\ \text{s}^{-1}$ over the temperature range 200–400 K.

Reliability

$\Delta\log k_0 = \pm0.2$ at 298 K.

$\Delta n = \pm0.5$.

Comments on Preferred Values

The preferred values are based on the study of Cantrell *et al.*[2] and are identical to those in our previous evaluation, IUPAC, 1997.[3] The recombination and dissociation rate coefficients are internally consistent. At room temperature, the equilibrium constant $K_c=2.3\times10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}$ compares well with other recently reported values.[6,7]

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$6.22\times10^{14}\ (T/300)^{-0.2}\exp(-11000/T)$	253–384	Cantrell *et al.*, 1993[1]	(a)
Reviews and Evaluations			
$5.5\times10^{14}\ (T/300)^{-0.7}\exp(-11000/T)$	200–300	NASA, 1997[2]	(b)
6.9×10^{-2}	298	IUPAC, 1997[3]	(c)
$9.7\times10^{14}\ (T/300)^{0.1}\exp(-11080/T)$	200–300		

Comments

(a) See comment (a) for k_0.

(b) See comment (b) for k_0.

(c) See Comments on Preferred Values.

Preferred Values

$k_\infty=6.9\times10^{-2}\ \text{s}^{-1}$ at 298 K.

$k_\infty=9.7\times10^{14}\ (T/300)^{0.1}\ \exp(-11080/T)\ \text{s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.

$\Delta n = \pm 0.2$.

Comments on Preferred Values

The preferred values are based on the evaluation of Malko and Troe,[8] and are identical to those in our previous evaluation, IUPAC, 1997.[3] The preferred values agree well with the recent determination of Cantrell *et al.*[1] For the equilibrium constant, see Comments on Preferred Values for k_0.

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$N_2O_5 + H_2O \rightarrow 2HNO_3$

$\Delta H^\circ = -39.6\ \text{kJ}\cdot\text{mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<1.3\times10^{-21}$	298	Tuazon *et al.*, 1981[1]	(a)
$<1.5\times10^{-21}$	298	Atkinson *et al.*, 1986[2]	(b)
$<1.1\times10^{-21}$	298	Hjorth *et al.*, 1987[3]	(c)
$<2.8\times10^{-21}$	296	Hatakeyama and Leu, 1989[4]	(d)
Reviews and Evaluations			
$<2\times10^{-21}$	298	NASA, 1997[5]	(e)
$<2\times10^{-21}$	298	IUPAC, 1997[6]	(f)

Comments

(a) N_2O_5 decay rate was monitored by FTIR absorption spectroscopy in two large volume (3800 and 5800 L) Teflon or Teflon-coated environmental chambers.

(b) Same technique as in (a) but 2500 L Teflon chamber used. Authors suggested that the observed removal of N_2O_5 was due only to heterogeneous processes.

(c) N_2O_5 decay monitored by FTIR absorption spectroscopy using a 1500 L FEP-Teflon chamber.

(d) N_2O_5 decay monitored in a 320 L Pyrex chamber by FTIR absorption spectroscopy.

(e) Based on the studies of Tuazon *et al.*,[1] Atkinson *et al.*,[2] and Hjorth *et al.*[3]

(f) See Comments on Preferred Values.

Preferred Values

$k < 2\times10^{-21}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This upper limit is based on the data of Tuazon *et al.*,[1] Atkinson *et al.*,[2] Hjorth *et al.*,[3] and Hatakeyama and Leu.[4] It is possible that the removal of N_2O_5 observed in these studies proceeds entirely by heterogeneous processes and that the lower value of Sverdrup *et al.*[7] ($<3\times10^{-22}$ cm^3 molecule^{-1} s^{-1}) may be closer to the value of the rate coefficient for the homogeneous gas phase reaction. However, the measurement of Sverdrup *et al.*[7] was less direct and we prefer the more conservative recommendation given here. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[6]

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HONO + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
HONO + $h\nu \rightarrow$ HO+NO	(1)	209	572
$\rightarrow$ H + NO_2	(2)	331	361
$\rightarrow$ HNO + O(^{3}P)	(3)	428	280

Absorption cross-section data

Wavelength range/nm	Reference	Comments
185–270	Kenner, Rohrer, and Stuhl, 1986[1]	(a)
310–393	Vasudev, 1990[2]	(b)
300–400	Bongartz *et al.*, 1991;[3] 1994[4]	(c)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
ϕ(OH*)	193	Kenner, Rohrer, and Stuhl, 1986[1]	(d)
ϕ(H)	355	Burkholder *et al.*, 1992[5]	(e)

Comments

(a) Relative absorption spectrum measured in the range 185–270 nm with absolute determinations at 193 and 215 nm; $\sigma = 1.6 \times 10^{-18}$ cm^2 molecule^{-1} at 193 nm. Two different methods used to prepare HONO gave similar results. The σ values agreed with the results of Cox and Derwent[6] in the wavelength region 220–270, but the peak at 215 nm seen in the earlier study,[6] which could have been due to NO absorption, was not observed.

(b) Relative absorption cross-sections determined by tunable laser photolysis with LIF detection of the HO product. Absolute values were based on $\sigma = 4.97 \times 10^{-19}$ cm^2 molecule^{-1} at 354 nm as reported by Stockwell and Calvert.[7] Measurements actually provide the product of the HONO cross-section and the quantum yield, ϕ_1.

(c) Absolute absorption cross-sections determined using conventional absorption spectroscopy, and with low, nonequilibrium concentrations of HONO determined by a combination of gas-phase and wet chemical analysis. Spectral resolution was 0.1 nm; cross-sections averaged over 0.5 nm given in a table. In their later work,[4] improved conditions were used, specifically higher HONO mole fractions, greater stability of HONO in the absorption chamber, and determination of NO_2 by interference-free optical absorption at 440 nm.

(d) Laser photolysis of nitrous acid at 193 nm. HO* measured by emission spectroscopy. A low quantum yield of about 10^{-5} was determined.

(e) Relative yield of H atoms inferred from secondary HO radical production observed in the laser photolysis of HONO at 355 nm. HO radicals were produced via the reaction H + $NO_2 \rightarrow$ HO + NO, involving impurity of NO_2. The data obtained were consistent with $\phi_2 = 0.1$ at 355 nm.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	127	260	8.0	330	9.3
195	172	265	5.2	335	6.5
200	197	270	3.4	340	16.8
205	220	275	2.5	345	9.6
210	214	280	-	350	11.5
215	179	285	-	355	23.6
220	146	290	-	360	8.0
225	120	295	-	365	16.1
230	86	300	0.0	370	20.5
235	60	305	0.7	375	4.9
240	42	310	1.6	380	9.2
245	30	315	2.5	385	14.5
250	18.5	320	4.4	390	2.4
255	12.4	325	5.0	395	0.6

Quantum Yields

$\phi_1+\phi_2+\phi_3=1.0$ throughout this wavelength range.
$\phi_1=1.0$ at $\lambda>366$ nm, decreasing to 0.4 at $\lambda=310$ nm.
$\phi_2=0.0$ at $\lambda>366$ nm, increasing to 0.6 at $\lambda=310$ nm.

Comments on Preferred Values

The preferred values for the cross-sections in the 300–395 nm range are obtained from the data of Bongartz *et al.*[3,4] In their later work,[4] cross-sections were measured under better controlled conditions than in their earlier study[3] and it was shown that their earlier data were consistently too high by, on average, 14.5%. The preferred values have been obtained, therefore, by averaging the data from Ref. 3 over 5 nm intervals centered on the wavelengths specified in the table and reducing these values by 14.5% as directed in Ref. 4.

The laser photolysis experiments of Burkholder *et al.*[5] in the first absorption band at 355 nm show strong indirect evidence for the production of H atoms in HONO photolysis at wavelengths below the threshold for reaction (2), as originally proposed by Cox.[8] Further evidence for an increasing contribution from reaction (2) with decreasing wavelength in the first absorption band comes from a comparison of the relative absorption spectra determined by conventional light absorption methods and by laser photofragment spectroscopy of the HO radical product from channel (1). When the spectra are normalized to peaks at $\lambda>370$ nm, the cross-section values of Vasudev[2] at $\lambda<350$ nm obtained from the HO radical yield are consistently smaller than those measured in absorption by Bongartz *et al.*[3,4] The difference increases approximately linearly to approximately 60% at 310 nm. This difference could be attributed to a decrease in ϕ(HO) from unity at 366 nm to 0.4 at 310 nm. The balance could be attributed to H atom production, ϕ_2, with $\phi_1+\phi_2=1.0$ in the first absorption band.

In the second absorption band, cross-sections over the range 185–275 nm are based on the data of Kenner *et al.*,[1] which also show that reaction (1) is the main photodissociation channel in this region. However, in view of the clear indication of H atom production in the first absorption band a contribution from reaction (2) at shorter wavelengths seems likely.

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$HONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$HONO_2 + h\nu \rightarrow HO + NO_2$	(1)	200	598
$\rightarrow HONO + O(^3P)$	(2)	298	401
$\rightarrow H + NO_3$	(3)	418	286
$\rightarrow HONO + O(^1D)$	(4)	488	245
$\rightarrow HO + NO + O(^3P)$	(5)	499	239

Absorption cross-section data

Wavelength range/nm	References	Comments
195–350	Burkholder *et al.*, 1993[1]	(a)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi_1=1.0$	200–315	Johnston, Chang, and Whitten, 1974[2]	(b)
$\phi_1=0.89\pm0.08$	222	Jolly *et al.*, 1986[3]	(c)
ϕ [HO], ϕ [O(^{3}P)], ϕ [O(^{1}D)], ϕ [H(^{2}S)]	248, 222, 193	Turnipseed *et al.*, 1992[4]	(d)
ϕ(1), ϕ(4), ϕ(5)	193	Felder, Yang, and Huber, 1993[5]	(e)

Comments

(a) The temperature dependence of HNO_3 absorption cross-sections were measured using a diode array spectrometer with a resolution of <0.4 nm between 240 and 360 K. Absorption cross-sections were determined using both absolute pressure measurements at 298 K and a dual cell arrangement to measure absorption at various temperatures relative to 298 K. A review of all previous experimental values was given together with an assessment of temperature-dependence effects on the stratospheric photolysis rates of HNO_3.

(b) Photolysis of HNO_3 in the presence of excess CO and excess O_2 to prevent complications due to secondary reactions. Results were interpreted by a complex reaction scheme.

(c) Pulsed laser photolysis with a KrCl excimer laser. HO radicals detected by time-resolved resonance absorption at 308.3 nm. The error estimate quoted does not include the uncertainty of +17%, −8% resulting from an analysis of potential systematic errors.

(d) Quantum yields for HO radicals, O[(^{3}P) + (^{1}D)] atoms, O(^{1}D) atoms, and H atoms were measured in pulsed laser photolysis systems at 248, 222, and 193 nm, using LIF detection for HO(X $^2\Pi$) radicals and atomic resonance fluorescence for O(^{3}P) and H(^{2}S) atoms. ϕ [HO] was measured relative to the yield of HO radicals from H_2O_2 photolysis (ϕ [HO]$=2.00\pm0.05$ at 248 nm[6] and ϕ[HO]$=1.51\pm0.18$ at 193 nm[7]). ϕ[O{(^{3}P) + (^{1}D)}] was measured relative to the O atom yield from ozone photolysis at 248 nm ($\phi=1$) and 193 nm ($\phi=1.20\pm0.15$).[5,8] ϕ [H(^{2}S)] was measured relative to the H atom yield from the photolysis of O_3–H_2 mixtures where the H atoms are produced in the O(^{1}D) + H_2 reaction. Measurements gave: ϕ[HO]$=0.95\pm0.09$ at 248 nm, 0.90 ± 0.11 at 222 nm, and 0.33 ±0.06 at 193 nm. ϕ [O{(^{3}P) + (^{1}D)}] was observed to be 0.031 ± 0.010, 0.20 ± 0.03, 0.81 ± 0.13 at 248, 222, and 193 nm, respectively, with exclusively O(^{3}P) production at 248 nm. ϕ [O(^{1}D)] was 0.074 ±0.03 at 222 nm and 0.28 ± 0.13 at 193 nm. H atom yields were very low; only at 193 nm were any H atoms detected with ϕ[H(^{2}S)]$\leqslant0.012$.

(e) Photofragment translation spectroscopy investigation of $HONO_2$ photolysis at 193 nm. The primary processes and their relative yields were deduced from photofragment time-of-flight signals at masses 16 (O^-), 17 (OH^+), 30 (NO^+), and 46 (NO_2^+). Relative yields for reactions (1) and (4) of 0.6 ± 0.1 and 0.4 ± 0.1, respectively, were obtained. Hot NO_2 photofragments were produced in reaction (1) in the ratio 2:1, relative to stable NO_2, leading to production of O(^{3}P) atoms via reaction channel (5).

Preferred Values

Absorption cross-sections at 298 K[a]

λ/nm	10^{20} σ/cm^2	10^3 B/K^{-1}	λ/nm	10^{20} σ/cm^2	10^3 B/K^{-1}
190	1360	0	270	1.62	1.45
195	1016	0	275	1.38	1.60
200	588	1.66	280	1.12	1.78
205	280	1.75	285	0.858	1.99
210	104	1.97	290	0.615	2.27
215	36.5	2.17	295	0.412	2.61
220	14.9	2.15	300	0.263	3.10
225	8.81	1.90	305	0.150	3.64
230	5.75	1.80	310	0.081	4.23
235	3.75	1.93	315	0.041	5.20
240	2.58	1.97	320	0.020	6.45
245	2.11	1.68	325	0.0095	7.35
250	1.97	1.34	330	0.0043	9.75
255	1.95	1.16	335	0.0022	10.1
260	1.91	1.14	340	0.0010	11.8
265	1.80	1.20	345	0.0006	11.2
			350	0.0004	9.30

[a] Temperature dependence given by the expression: $\log_e \sigma=\log_e \sigma(298)+B(T-298)$ with T in K.

Quantum yields

	λ/nm		
	⩾248	222	193
$\phi(1)+\phi(5)$	>0.97	0.90 ± 0.10	0.60 ± 0.20
$\phi(2)$	0.03 ± 0.03		
$\phi(3)$	<0.01	<0.01	0.01
$\phi(4)$		0.10 ± 0.10	0.39 ± 0.20
$\phi(5)$		0.13 ± 0.03	0.40 ± 0.20

Comments on Preferred Values

The results of Burkholder *et al.*[1] for the cross-section provide a high quality and comprehensive data set over the range of temperatures and wavelengths of significance for the atmospheric photolysis of HNO_3. Over the wavelength range 205–310 nm there is good agreement with the earlier studies of Rattigan *et al.*,[9] Biaume,[10] Molina and Molina,[11] and Johnston and Graham.[12] At $\lambda < 205$ nm, the data from different studies show small but unexplained discrepancies. At $\lambda > 310$ nm, the room temperature results[1] are increasingly higher than all previously reported data except those of Rattigan *et al.*,[9] which are in good agreement. The preferred values are those given by Burkholder *et al.*[1] and are identical to those in our previous evaluation, IUPAC, 1997.[13]

The temperature dependence reported by Burkholder *et al.*[1] is weaker than that reported previously by Rattigan *et al.*[9] However, if the data at the lowest temperature (239 K) from Ref. 9 are omitted the agreement is good, and Burkholder *et al.*[1] give values for the temperature coefficient, B, based on the two data sets[9] (excluding the 239 K data from Ref. 9), and these are adopted here.

The new data for the quantum yield confirm that, although reaction (1) is the dominant channel at $\lambda \geqslant 260$ nm with $\phi(1)$ close to unity, other channels become important at shorter wavelengths as suggested by the earlier work of Kenner *et al.*[14] The results of Turnipseed *et al.*[4] and Schiffman *et al.*[15] are in excellent agreement at 248 nm when the relative measurements of Turnipseed *et al.*[4] are normalized to the same value of the quantum yield for HO radical production from H_2O_2. The agreement is less good at 193 nm, where the direct measurements of Schiffman *et al.*[15] give an HO radical yield higher by about 50%. The value of $\phi(H_2O_2)$ obtained by Schiffman *et al.*[15] is about 25% lower at both 248 and 193 nm than the values obtained by Vaghjiani *et al.*[7,8] (2.0 at 248 nm and 1.5 at 193 nm) which are recommended in the present evaluation.

The preferred values of the quantum yields $\phi(1)+\phi(5)$ [HO production] are based on the indirect studies of Johnston *et al.*[2] and the direct observations of Jolly *et al.*[3] at 222 nm, Turnipseed *et al.*[4] and Felder *et al.*[5] The data of Schiffman *et al.*[15] are not used in view of the inconsistency of their absolute $\phi(\mathrm{HO})$ values for H_2O_2 dissociation. At 193 nm, O-atom production becomes a major channel but HO and O production is not mutually exclusive since reaction (5) can occur at $\lambda \leqslant 239$ nm, either through excited NO_2^* or HONO*. Felder *et al.*[5] show that $\phi(5)=0.4$ at 193 nm. Ground state HONO is the likely co-product of $O(^1D)$ atoms and hence the data of Turnipseed *et al.*[4] imply $\phi(4)=0.28$ at 193 nm and 0.074 at 222 nm, which is consistent within the experimental uncertainty with the results of Felder *et al.*[5] In the absence of direct measurements of HONO at longer wavelengths, $\phi(2)$ cannot be determined; this channel is probably responsible for the small amount of O-atom production at $\lambda \geqslant 239$ nm, as measured, for example, by Margitan and Watson[16] with $\phi[O(^3P)]=0.03$ at 266 nm. The data of Turnipseed *et al.*[4] show that H-atom production, and hence $\phi(3)$, is significant only at 193 nm with $\phi(3)=0.011 \pm 0.008$. The values of the quantum yields are identical to those in our previous evaluation, IUPAC, 1997.[13]

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$HO_2NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°/\mathrm{kJ \cdot mol^{-1}}$	$\lambda_{\mathrm{threshold}}/\mathrm{nm}$
$HO_2NO_2 + h\nu \rightarrow HO_2 + NO_2$ (1)	105	1141
$\rightarrow HO + NO_3$ (2)	170	704

Absorption cross-section data

Wavelength range/nm	Reference	Comments
190–330	Molina and Molina, 1981[1]	(a)
210–330	Singer *et al.*, 1989[2]	(b)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
ϕ_2	248	Mac Leod, Smith, and Golden, 1988[3]	(c)

Comments

(a) Measured at 298 K and 1 atm total pressure. HO_2NO_2 was prepared in flowing N_2 stream in the presence of H_2O, H_2O_2, HNO_3, and HO_2. The composition of the mixture was established by FTIR spectroscopy, by the absorption spectrum in the visible and by chemical titration after absorption in aqueous solutions. Two methods were used to prepare HO_2NO_2. The first mixed 70% nitric acid with 90% H_2O_2, while in the second method solid nitroniumtetrafluoroborate (NO_2BF_4) was added to a solution of 90% H_2O_2.

(b) Cross-sections were measured at 298, 273, and 253 K. Pernitric acid was produced *in situ* by photolysis of Cl_2–H_2–NO_2–air mixtures with averaged absorption measurements at small extents of reaction. Relative spectrum over the range 210–230 nm determined in flowing mixtures of pernitric acid vapor obtained from the reaction of BF_4NO_2 and H_2O_2, after correction for impurity of NO_2, H_2O_2, and HNO_3, which was determined by IR spectroscopy. Resolution=1 nm.

(c) Laser photolysis of pernitric acid at 248 nm. HO radicals were measured by LIF and the yield determined relative to the yield from H_2O_2, assuming the rotational distribution of HO from photolysis of HO_2NO_2 and H_2O_2 was the same under the conditions of the experiment. A value of $\phi_2=0.34\pm0.16$ was obtained after correction for impurity in the pernitric acid sample. Fluorescence from NO_2^* was also observed after photolysis which was assigned to production via channel (1). The upper limit for NO_2^* production was 30%. It was concluded that under atmospheric conditions $\phi_1\approx0.65$ and $\phi_2\approx0.35$.

Preferred Values

Absorption cross-sections at 296 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190	1010	260	28.4
195	816	265	22.9
200	563	270	18.0
205	367	275	13.3
210	239	280	9.3
215	161	285	6.2
220	118	290	3.9
225	93.2	295	2.4
230	78.8	300	1.4
235	68.0	305	0.85
240	57.9	310	0.53
245	49.7	315	0.39
250	41.1	320	0.24
255	34.9	325	0.15
		330	0.09

Quantum Yields

$\phi_1=0.61$ at 248 nm.
$\phi_2=0.39$ at 248 nm.

Comments on Preferred Values

The preferred absorption cross-section values are based on the data of Molina and Molina[1] and Singer *et al.*,[2] which are in excellent agreement at wavelengths in the range 210–300nm. Between 300 and 320 nm the cross-sections of Singer *et al.*[2] are approximately a factor of 2 lower. A simple mean of the two data sets is taken over the whole range.

For the quantum yield we recommend values based on the measurements of Mac Leod *et al.*[3] at 248 nm with a small upward revision of ϕ_2 to take into account the present recommendation for the absorption cross-section for H_2O_2. The uncertainties on the quantum yields are large and it should be noted that they are based on data at a single wavelength. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[4]

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$NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$NO_2 + h\nu \rightarrow NO + O(^3P)$ (1)	300	398
$\rightarrow NO + O(^1D)$ (2)	490	244

Absorption cross-section data

Wavelength range/nm	Reference	Comments
200–700	Schneider *et al.*, 1987[1]	(a)
264–649	Davidson *et al.*, 1988[2]	(b)
310–570	Harwood and Jones, 1994[3]	(c)
300–500	Mérienne, Jenouvrier, and Coquart, 1995[4]	(d)
400–500	Coquart, Jenouvrier, and Mérienne, 1995[5]	(e)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
ϕ_1	295–445	Jones and Bayes, 1973[6]	(f)
ϕ_1	375–420	Harker, Ho, and Ratto, 1977[7]	(g)
ϕ_1	390–420	Davenport, 1978[8]	(h)
ϕ_1	334–404	Gardner, Sperry, and Calvert, 1987[9]	(i)
ϕ_1	388–411	Roehl *et al.*, 1994[10]	(j)

Comments

(a) Measured at 298 K with spectral resolution of 0.04 nm. Averaged values over 1 nm intervals are tabulated. Also averaged values over 5 nm intervals are tabulated and compared with corresponding values derived from previous studies. Generally good agreement with results of Bass *et al.*[11] except for higher values near the absorption minimum at 260 nm and at wavelengths less than 220 nm.

(b) Cross-sections measured over a wide range of temperature (233–397 K) and with low NO_2 concentrations $(3.4-73)\times 10^{13}$ molecule cm^{-3}, so that absorption due to N_2O_4 was minimized. Low resolution (1.5 nm) spectra were recorded using a diode array, and high resolution spectra (0.3–2.5 cm^{-1}) by FTIR.

(c) Cross-sections measured over the temperature range of 213–298 K and with NO_2 concentrations of $(1.5-20.0)\times 10^{15}$ molecule cm^{-3} using a diode array spectrometer. Absorption due to N_2O_4 was corrected for using data for the cross-sections for N_2O_4 and K_p for dimerization of NO_2 determined simultaneously in the same experiments. The spectral resolution was 0.54 nm FWHM. Averaged cross-sections over 5 nm intervals were given as well as high-resolution data.

(d) Cross-sections measured at 293±0.3 K with NO_2 concentrations of $(3-9)\times 10^{14}$ molecule cm^{-3}. Conventional spectrometer used with multipass cell giving a total path length of 60.7 m. Spectral bandwidth <0.01 nm at $\lambda>400$ nm and <0.15 nm at $\lambda<400$ nm. Cross-sections measured at 0.01 nm intervals with a wavelength accuracy of 0.01 nm. Corrections made for the presence of N_2O_4. Averaged cross-sections over 5 nm intervals given for the range 305–425 nm. Complete data-set available on request.

(e) Same technique as in (d). Data were obtained at 220 and 240 K. Data given at 1 nm intervals over the range 400–500 nm. Features in spectrum sharpen with decrease in temperature but no change found in cross-sections.

(f) Relative quantum yields for NO production measured and normalized to literature values at 313 and 366 nm.

(g) Quantum yield for NO_2 photodissociation by pulsed dye laser measured at 1 nm intervals. Values given here are taken from tabulated results provided by the authors.

(h) Quantum yield for NO production measured relative to NO production from NOCl photolysis at six wavelengths for $T=300$ and 223 K.

(i) Primary quantum yield ϕ_1 derived from measurement of (1) quantum yield of NO_2 reactant loss (optical absorption); (2) quantum yield of NO product formation (mass spectrometry); and (3) quantum yield of O_2 product formation (mass spectrometry). Light intensity measured by NOCl actinometry. ϕ_1 found to be near unity for wavelengths less than 395 nm. At 404 nm measurements were also made from 273 K to 370 K. Results found to be in qualitative agreement with the simple theory that for $\lambda > 398$ nm the energy deficiency for photodissociation is made up from internal rotational and vibrational energy of the NO_2 molecules. On the basis of later experiments in the same laboratory by Calvert *et al.*,[12] in which the absorption cross section at 404.7 nm was measured from 273 to 370 K, the authors concluded that vibrationally excited NO_2 molecules absorb more strongly than unexcited molecules. They were thereby able to derive a reasonable fit to the variation of primary quantum yield with temperature for photodecomposition in the energy-deficient region at 404.7 nm.

(j) Quantum yield for NO production from NO_2 photodissociation by a dye laser was measured at 248 K and 298 K relative to NO production from NOCl photodissociation. Quantum yields were measured at very high resolution (0.001 nm). These are the first measurements of ϕ_1 at low temperatures throughout the falloff region.

Preferred Values

Absorption cross-sections[a]

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
190		315	21.61	440	46.91
195		320	24.68	445	47.71
200		325	27.94	450	48.58
205	43.06	330	31.04	455	41.62
210	47.20	335	34.41	460	42.41
215	49.54	340	38.43	465	40.26
220	45.61	345	40.31	470	32.97
225	37.88	350	43.92	475	37.64
230	27.39	355	47.54	480	32.70
235	16.69	360	48.64	485	24.69
240	9.31	365	52.32	490	29.85
245	1.74	370	53.49	495	28.20
250	2.48	375	56.02	500	17.22
255	1.95	380	56.75	505	22.48
260	2.24	385	58.05	510	21.61
265	2.73	390	60.56	515	14.95
270	4.11	395	58.36	520	15.00
275	4.90	400	61.94	525	16.58
280	5.92	405	57.21	530	14.18
285	7.39	410	60.38	535	9.88
290	9.00	415	57.25	540	10.10
295	10.91	420	58.16	545	11.83
300	13.07	425	55.26	550	10.17
305	15.89	430	52.43	555	7.34
310	18.71	435	53.60	560	5.62
				565	7.87

[a] Absorption cross-sections in the range 190–565 nm, averaged over 5 nm intervals, are independent of temperature.

Quantum Yields

λ/nm	φ	λ/nm	φ	λ/nm	φ
<310	1.00	370	0.98	406	0.29
315	0.99	375	0.98	408	0.18
320	0.99	380	0.97	410	0.13
325	0.99	385	0.97	412	0.09
330	0.99	390	0.96	414	0.07
335	0.99	392	0.96	416	0.05
340	0.99	394	0.95	418	0.03
345	0.99	396	0.92	420	0.02
350	0.99	398	0.82	422	0.01
355	0.99	400	0.82	424	0.00
360	0.98	402	0.69		
365	0.98	404	0.42		

Comments on Preferred Values

Since our previous evaluation, IUPAC, 1997,[13] there have been new high resolution (0.01 nm) measurements of the NO_2 absorption cross-sections over the range 300–500 nm at 293 K by Mérienne *et al.*[4] and at 220 K and 240 K by Coquart *et al.*[5] There is also work by Frost *et al.*[14] in which relative cross-sections have been measured.

The 5 nm averaged values of the cross-sections obtained by Mérienne *et al.*[4] are slightly higher than the preferred values given in IUPAC, 1997,[13] which were based on the studies of Davidson *et al.*[2] and Harwood and Jones.[3] The present preferred values over the range 320–420 nm were obtained by averaging the results of Davidson *et al.*,[2] Harwood and Jones,[3] and Mérienne *et al.*[4]

For the remainder of the wavelength range covered, the 5 nm averaged cross-sections over the range 425–495 nm are based on the work of Harwood and Jones[3] and of Mérienne *et al.*,[4] while those for the range 495–565 nm are taken from Harwood and Jones.[3] The values for the range 185–320 nm are taken from Table 4 of Schneider *et al.*[1]

Harwood and Jones[3] found no significant temperature dependence of the 0.5 nm averaged cross-sections in the wavelength region 320–535 nm over the temperature range 213–298 K. The study at higher resolution by Coquart *et al.*,[5] at temperatures of 220 K, 240 K, and 293 K, confirms this finding. These results support the suggestion by Davidson *et al.*[2] that the discrepancies observed by Bass *et al.*,[11] Davenport *et al.*,[8] and Hicks *et al.*[15] can be accounted for by incorrect compensation for the effects of N_2O_4. Roscoe and Hind[16] have reached similar conclusions in their critical review of the implications of the $2NO_2 \rightleftharpoons N_2O_4$ equilibrium for earlier determinations of NO_2 absorption cross-sections. The preferred values over the range 185–565 nm can be taken to be temperature independent.

Both Harwood and Jones[3] and Coquart *et al.*[5] find that there is a sharpening of the spectral features as the temperature is decreased. However, there are no shifts in wavelength as reported by Schneider *et al.*[1] and Davidson *et al.*,[2] which may have been due to small calibration errors.

The preferred quantum yields are those recommended by Gardner *et al.*[9] They are based on a best fit to the data of Gardner *et al.*[9] for 334–404 nm, Jones and Bayes[6] for 297–412 nm, Davenport[8] for 400–420 nm, and Harker *et al.*[7] (corrected for cross-sections) for 397–420 nm. The results of Gardner *et al.*[9] support the results of Jones and Bayes[6] showing that the primary quantum yield is nearly unity throughout the entire wavelength region of 290–390 nm, and that the low values reported by Harker *et al.*[7] for the 375–396 nm region must be in error. Possible reasons for these low values are discussed by Gardner *et al.*[9] Roehl *et al.*[10] report values of ϕ_1 for 388–411 nm at 298 K and at 248 K. Their room temperature data for 388–397 nm are slightly lower than the recommended values and their observed falloff above 398 nm occurs at longer wavelengths than recommended here. The quantum yields at 248 K were observed to be lower than those at room temperature (by 10% at 400 nm, increasing to 50% at 411 nm).

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$NO_3 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°/kJ\cdot mol^{-1}$	$\lambda_{threshold}/nm$
$NO_3 + h\nu \rightarrow NO + O_2(^3\Sigma)$	(1)	10.9	11000
$\rightarrow NO + O_2(^1\Delta)$	(2)	105.2	1137
$\rightarrow NO + O_2(^1\Sigma)$	(3)	167.8	712
$\rightarrow NO_2 + O(^3P)$	(4)	203.9	587

Absorption cross-section data

Wavelength range/nm	Reference	Comments
400–700	Sander, 1986[1]	(a)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\phi(NO + O_2)$, $\phi(4)$	570–635	Orlando *et al.*, 1993[2]	(b)

Comments

(a) Two methods were used to produce NO_3. In one, NO_3 radicals were generated from the flash photolysis of Cl_2–$ClONO_2$ mixtures, with NO_3 formation and $ClONO_2$ loss being monitored by UV absorption. Measurements were made at 230, 250, and 298 K. The value of $\sigma(NO_3)$ at 662 nm determined by this method (2.28×10^{-17} cm^2 molecule^{-1}) was preferred by the author. The cross-section was observed to increase by a factor of 1.18 at 230 K. NO_3 was also produced in a discharge flow system by the $F+HNO_3$ reaction. The value of $\sigma(NO_3)$ at 662 nm determined by this method was 1.83×10^{-17} cm^2 molecule^{-1}. Values of σ were tabulated for 1 nm intervals from 400 to 700 nm for 298 and 230 K.

(b) The photodissociation of NO_3 was studied at 298 K using pulsed laser photolysis, with resonance fluorescence detection of $O(^3P)$ atoms and $NO(X\,^2\Pi)$. $\phi[O(^3P)]$ was 1.0 over the range 570–585 nm, decreasing to a value <0.1 at 635 nm. $\phi(NO)$ was <0.1 at 580 nm and about 0.20 ± 0.10 at 590 nm. These data were combined with earlier results of Magnotta and Johnston[3] to provide quantum yields $\phi(NO+O_2)$ and $\phi(4)$ as a function of wavelength (586–639 nm) and to calculate photolysis rates for overhead sun at the earth's surface, with $J(NO_2 + O)=0.19$ s^{-1}; $J(NO + O_2)=0.016$ s^{-1}.

Preferred Values

Absorption cross-sections at 298 K and 230 K

λ/nm	10^{19} σ/cm^2 298 K	10^{19} σ/cm^2 230 K	λ/nm	10^{19} σ/cm^2 298 K	10^{19} σ/cm^2 230 K	λ/nm	10^{19} σ/cm^2 298 K	10^{19} σ/cm^2 230 K
400	0.0	0.4	500	11.3	12.3	600	27.6	29.7
401	0.0	0.5	501	11.1	11.4	601	28.6	30.4
402	0.0	0.5	502	11.1	11.1	602	33.2	35.7
403	0.2	0.5	503	11.1	11.9	603	38.0	43.0
404	0.0	0.3	504	12.6	13.3	604	43.7	51.4
405	0.3	0.7	505	12.8	14.0	605	43.6	53.2
406	0.2	0.6	506	13.4	15.0	606	33.2	39.6
407	0.1	0.5	507	12.8	14.0	607	24.0	26.5
408	0.3	0.5	508	12.7	13.0	608	18.5	19.1
409	0.0	0.8	509	13.5	14.1	609	17.1	17.7
410	0.1	0.5	510	15.1	16.5	610	17.7	18.5
411	0.2	0.8	511	17.3	20.0	611	19.1	20.7
412	0.5	0.4	512	17.7	21.1	612	22.3	25.2
413	0.5	0.7	513	16.0	19.2	613	26.3	32.0
414	0.2	1.2	514	15.8	17.3	614	25.5	30.5
415	0.6	0.8	515	15.8	17.0	615	22.6	25.8
416	0.6	0.8	516	15.6	17.5	616	20.9	22.5
417	0.7	1.1	517	14.9	15.4	617	21.1	22.0
418	0.5	1.1	518	14.4	14.9	618	23.9	24.4
419	0.8	1.1	519	15.4	15.9	619	25.6	27.1
420	0.8	1.4	520	16.8	17.3	620	32.7	35.8
421	0.8	1.3	521	18.3	18.9	621	52.4	62.9
422	0.9	1.3	522	19.3	20.6	622	101.8	121.3
423	1.1	1.3	523	17.7	19.1	623	147.3	174.5
424	0.9	1.4	524	16.4	16.8	624	120.5	138.7
425	0.7	1.7	525	15.8	16.0	625	83.8	100.7
426	1.4	1.6	526	16.3	16.8	626	73.0	88.2
427	1.4	1.3	527	18.1	19.3	627	75.3	96.1
428	1.2	1.6	528	21.0	23.8	628	73.7	94.3
429	1.1	1.4	529	23.9	27.3	629	69.8	90.3
430	1.7	1.7	530	22.3	24.7	630	67.6	89.7
431	1.3	1.8	531	20.9	22.7	631	48.4	61.0
432	1.5	1.8	532	20.2	22.0	632	32.7	39.8
433	1.8	2.0	533	19.5	21.1	633	21.7	25.1
434	1.8	2.2	534	20.4	22.7	634	16.4	17.3
435	1.6	2.4	535	23.0	26.6	635	14.4	14.0
436	1.5	2.3	536	25.7	30.6	636	16.9	16.2
437	1.8	2.0	537	25.8	30.5	637	20.7	20.1
438	2.1	2.2	538	23.4	26.0	638	20.3	18.9
439	2.0	2.8	539	20.4	22.4	639	15.8	14.2
440	1.9	2.4	540	21.0	22.6	640	12.3	11.3
441	1.8	2.5	541	20.4	21.8	641	10.0	9.5
442	2.1	2.3	542	18.8	19.7	642	9.2	8.4
443	1.8	2.3	543	16.8	17.5	643	9.7	8.1
444	1.9	2.4	544	17.0	17.3	644	9.5	8.4
445	2.0	2.9	545	19.6	21.3	645	8.6	8.0
446	2.4	2.9	546	24.2	26.5	646	7.5	6.9
447	2.9	3.3	547	29.1	33.0	647	7.0	6.8
448	2.4	3.6	548	29.8	33.4	648	6.2	6.3
449	2.8	3.3	549	27.1	29.7	649	5.4	5.3
450	2.9	3.3	550	24.8	27.8	650	5.0	5.0
451	3.0	3.7	551	24.3	27.6	651	5.5	5.6
452	3.3	4.0	552	24.7	28.5	652	6.1	6.6
453	3.1	3.7	553	25.3	29.4	653	7.1	7.9
454	3.6	4.0	554	27.8	33.1	654	8.2	9.2
455	3.6	4.1	555	31.1	38.0	655	9.8	11.0
456	3.6	3.6	556	32.6	39.2	656	13.3	14.4
457	4.0	4.2	557	32.9	39.3	657	17.1	18.5
458	3.7	4.7	558	35.1	42.2	658	24.2	25.9
459	4.2	4.5	559	37.2	45.3	659	40.7	42.7
460[a]	4.0	4.6	560[a]	33.2	38.5	660[a]	74.5	79.0

[a] Continued on next page.

Absorption cross-sections at 298 K and 230 K—Continued

λ/nm	$10^{19}\ \sigma/\mathrm{cm}^2$ 298 K	$10^{19}\ \sigma/\mathrm{cm}^2$ 230 K	λ/nm	$10^{19}\ \sigma/\mathrm{cm}^2$ 298 K	$10^{19}\ \sigma/\mathrm{cm}^2$ 230 K	λ/nm	$10^{19}\ \sigma/\mathrm{cm}^2$ 298 K	$10^{19}\ \sigma/\mathrm{cm}^2$ 230 K
461	3.9	4.3	561	29.8	33.8	661	144.8	167.5
462	4.0	4.0	562	29.0	32.7	662	210.0	266.9
463	4.1	4.8	563	28.0	32.1	663	174.4	229.7
464	4.8	5.1	564	27.2	30.8	664	112.9	145.5
465	5.1	5.4	565	27.3	31.0	665	74.1	92.9
466	5.4	5.7	566	28.5	33.0	666	49.6	62.9
467	5.7	6.0	567	28.1	31.4	667	30.4	37.4
468	5.6	5.9	568	28.5	32.0	668	19.0	23.3
469	5.8	6.0	569	28.9	32.6	669	12.5	14.5
470	5.9	5.7	570	27.9	31.1	670	9.5	11.2
471	6.2	6.2	571	27.6	30.9	671	7.9	9.4
472	6.4	6.5	572	27.4	30.5	672	7.6	9.7
473	6.2	6.5	573	27.8	30.9	673	6.4	8.1
474	6.2	6.4	574	28.6	31.9	674	5.2	6.3
475	6.8	7.4	575	30.8	36.0	675	4.8	5.5
476	7.8	8.3	576	32.7	38.7	676	4.9	5.2
477	7.7	8.2	577	33.8	39.5	677	5.9	6.2
478	7.3	7.4	578	33.1	38.5	678	7.5	7.2
479	7.3	7.4	579	32.4	38.3	679	7.8	7.3
480	7.0	7.5	580	33.4	39.9	680	6.9	6.4
481	7.1	7.4	581	35.5	43.9	681	5.3	5.3
482	7.1	7.3	582	32.8	39.5	682	4.0	4.4
483	7.2	7.1	583	29.3	34.6	683	3.0	3.2
484	7.7	7.4	584	28.2	32.8	684	2.6	2.8
485	8.2	8.2	585	28.9	34.0	685	1.8	2.4
486	9.1	9.5	586	33.2	39.7	686	1.6	1.5
487	9.2	9.4	587	41.6	51.8	687	1.2	2.3
488	9.5	9.2	588	50.4	63.8	688	1.2	2.0
489	9.6	10.6	589	61.3	77.3	689	1.2	1.9
490	10.3	11.2	590	59.6	71.8	690	1.0	2.1
491	9.9	10.3	591	54.4	64.6	691	0.7	1.7
492	9.9	10.6	592	51.1	60.2			
493	10.1	10.9	593	45.8	53.2			
494	10.1	10.1	594	41.9	50.2			
495	10.6	11.1	595	42.9	52.8			
496	12.1	12.9	596	46.2	58.1			
497	12.2	14.0	597	43.6	54.0			
498	12.0	13.2	598	36.7	43.7			
499	11.7	12.6	599	31.0	36.5			

Quantum Yields

$\phi(4) = 1.0$ for $\lambda \leq 583$ nm.

Comments on Preferred Values

Since our previous evaluation, IUPAC, 1997,[4] absorption cross-section measurements have been made over the range 440–720 nm by Yokelson *et al.*[5] using a diode array spectrometer working at a resolution of 0.1 nm. These new data,[5] which supersede previous data from the same laboratory,[6] are in good agreement with those of Sander,[1] which are the basis of our preferred absorption cross-sections. They were obtained by normalizing the values of Sander[1] in the range 400–691 nm to the value of 2.1×10^{-17} cm^2 $\mathrm{molecule}^{-1}$ for the peak value at 662 nm. This peak value is adopted from the evaluation of Wayne *et al.*[7]

Yokelson *et al.*[5] also studied the effects of temperature change on the cross-sections. Measurements at 298, 258, 230, and 200 K gave results agreeing closely with those of Sander.[1] A significant increase in cross-section is found as temperature is lowered, in contrast to the findings of Cantrell *et al.*,[8] where temperature change was observed to have little effect. In our previous evaluation the temperature dependence of σ, and the values of σ at 230 K, were adopted from the evaluation of Wayne *et al.*[7] who based their values on a mean of the results of Sanders[1] and Cantrell *et al.*[8] In view of the new study of Yokelson *et al.*[5] supporting strongly the results of Sander,[1] we now accept the data of Sander[1] as the preferred values of σ at 230 K. To obtain the temperature dependence of the 662 nm band we combine our preferred values at 298 and 230 K to give

$\sigma(T) = \{4.59 \times 10^{-17} - (8.37 \times 10^{-20}\ T)\}$ cm^2 $\mathrm{molecule}^{-1}$ at 662 nm.

The measurements of Orlando *et al.*[2] confirm qualitatively the wavelength dependence of $\phi(\mathrm{NO} + \mathrm{O}_2)$ and $\phi(4)$ observed in the earlier room temperature measurements of

Magnotta and Johnston,[3] and provide more accurate values for $\phi(4)$. The earlier problem[3] of total quantum yields in excess of 1.4 was not encountered in the work of Orlando *et al.*,[2] which confirms that NO_3 radical dissociation is exclusively to $NO_2 + O(^3P)$ at wavelengths <585 nm.

A molecular beam study of Davis *et al.*[9] has provided considerable insight into the photodissociation of the NO_3 radical. There is a very sharp threshold for channel (4) at 587 nm for internally cold NO_3. Any dissociation at longer wavelengths via channel (4) must occur from photolysis of internally excited NO_3. At $\lambda \geq 588$ this process competes with photodissociation of NO_3 to form $NO + O_2$ via a three-center transition state from the vibrationally excited ground state. The yield of this process falls off above 600 nm and may only occur from hot band absorption above 605 nm. These facts imply that the branching ratio for bulk, thermally equilibrated NO_3 radicals will depend very strongly on temperature, especially near the threshold for the NO_2-forming channel, where higher temperatures will tend to favor dissociation via the simple bond fission channel (4).

Using the measured energy thresholds from the molecular beam experiments, Johnston *et al.*[10] have modeled product yields from the excited NO_3 resulting from photon absorption. They have calculated values of $\phi(NO)$, $\phi(NO_2)$, and ϕ(fluorescence) as a function of wavelength in the range 401–690 nm at temperatures of 190, 230, and 298 K. The values at 298 K agree well with the experimental findings of Orlando *et al.*,[2] with only some departures for $\phi(NO_2)$ in the 605–620 nm region.

On the basis of their measured quantum yields, Orlando *et al.*[2] have suggested photodissociation rates for an overhead sun at the earth's surface and the wavelength range 400–700 nm, of $J(NO_2 + O) = 0.19\ s^{-1}$ and $J(NO + O_2) = 0.016\ s^{-1}$. These are preferred for atmospheric calculations. The experimental values of Magnotta and Johnston[3] are in agreement, and the calculations of Johnston *et al.*[10] also provide support for these photodissociation rates.

The information from the molecular beam experiments of Davis *et al.*[9] dictates that these values of J only apply for temperatures close to room temperature. Calculated values are available for lower temperatures, but further measurements of the quantum yields for NO_3 radical photolysis in bulk samples at lower temperatures are required before recommendations can be made for atmospheric photolysis rates at stratospheric temperatures.

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$N_2O + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$N_2O + h\nu \rightarrow N_2 + O(^3P)$ (1)	161	742
$\rightarrow N_2 + O(^1D)$ (2)	351	341
$\rightarrow N + NO$ (3)	475	252
$\rightarrow N_2 + O(^1S)$ (4)	565	212

Absorption cross-section data

Wavelength range/nm	Reference	Comments
173–240	Selwyn, Podolske, and Johnston, 1977[1]	(a)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\phi(-N_2O)=2.0$ $\phi(NO)=1.0$ $\phi(O_2)=0.5$	184.9	Greiner, 1967[2]	(b)
$\phi_1\leqslant 0.03$	214	Paraskevopoulos and Cvetanovic, 1969[3]	(c)
$\phi_3\leqslant 0.01$	185–230	Preston and Barr, 1971[4]	(d)

Comments

(a) Measured at five temperatures from 194 to 302 K, with a resolution of 0.7 nm. Values were tabulated at 1 nm intervals. A nine parameter fit expressing σ as a function of λ and T was also given.

(b) N_2O photolyzed at 184.9 nm in static system at temperatures of 299–301 K. Mass spectrometric analysis of N_2O, NO, and O_2. No other products observed but the analysis system was not sensitive to NO_2. Pressure was varied in the range 5.3–285 mbar (4–214 Torr) of N_2O. From results obtained in this and other studies, it was concluded that $\phi(-N_2O)=2.0$, $\phi(NO)=1.0$, and $\phi(O_2)=0.5$ over the range 138–210 nm.

(c) Photolysis of N_2O at 298 K in the presence of neopentane, 1-butene, and added gases. The yield of $O(^3P)$ atoms was determined from yield of addition products with 1-butene.

(d) Photolysis of N_2O containing 1% ^{15}NO at 296 K and λ=185, 214, and 229 nm. The isotopic composition of product N_2 was measured.

Preferred Values

Absorption cross-sections

λ/nm	$10^{20}\ \sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$
175	12.6	210	0.755
180	14.6	215	0.276
185	14.3	220	0.092
190	11.1	225	0.030
195	7.57	230	0.009
200	4.09	235	0.003
205	1.95	240	0.001

Temperature dependence of absorption cross-sections

$$\ln \sigma(\lambda,T)=A_1+A_2\lambda+A_3\lambda^2+A_4\lambda^3+A_5\lambda^4$$
$$+(T-300)\exp(B_1+B_2\lambda+B_3\lambda^2+B_4\lambda^3)$$

where

$A_1=68.21023$ $B_1=123.4014$

$A_2=-4.071805$ $B_2=-2.116255$

$A_3=4.301146\times 10^{-2}$ $B_3=1.111572\times 10^{-2}$

$A_4=-1.777846\times 10^{-4}$ $B_4=-1.881058\times 10^{-5}$

$A_5=2.520672\times 10^{-7}$

for λ=173–240 nm and T=194–302 K.

Quantum Yields

$\phi_2=1.0$ for λ=185–230 nm.

Comments on Preferred Values

The preferred absorption cross-sections and the expression for ln σ (λ, T) are from Selwyn *et al.*[1] These cross-section values have been confirmed both at room temperature and at 208 K by the results of Hubrich and Stuhl[5] and Mérienne *et al.*,[6] who also determined the temperature dependence. Several publications with additional information on this process have appeared since our original evaluation. Selwyn and Johnston[7] studied the ultraviolet absorption spectrum of nitrous oxide and its ^{15}N isotopes over the wavelength range 172–197 nm and the temperature range 150–500 K. Lee and Suto[8] measured the photoabsorption and fluorescence cross-sections in the 106–160 nm region and studied the production and quenching of excited photofragments. Yoshino *et al.*[9] made high-resolution room temperature cross-section measurements in the 170–222 nm range. Recent state-resolved photofragment spectroscopy studies of N_2O photodissociation at 193 nm[10] and 205 nm[11] show that 43% of the energy deposited in the molecule appears as translational energy of the $O(^1D)$ atom fragment.

The preferred value of the quantum yield ($\phi_2=1.0$) is based on the results reported by Greiner,[2] Paraskevopoulos and Cvetanovic,[3] and Preston and Barr.[4] Greenblatt and Ravishankara[12] have measured the quantum yield for production of $NO(^2\Pi)$ and $N(^4S)$ atoms at 193 nm to be $<8\times 10^{-3}$.

The recommendations are identical to those given in our previous evaluation, IUPAC, 1997.[13]

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$N_2O_5 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$N_2O_5 + h\nu \rightarrow NO_3 + NO_2$	(1)	89	1340
$\rightarrow NO_3 + NO + O$	(2)	390	307
$\rightarrow NO_3 + NO_2^* \rightarrow NO_3 + NO_2 + h\nu$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
200–380	Yao, Wilson, and Johnston, 1982[1]	(a)
240–420	Harwood *et al.*, 1993[2]	(b)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi(NO_3)$	249–350	Swanson, Kan, and Johnston, 1984[3]	(c)
$\phi(NO_3)$, ϕ [O(^{3}P)]	290	Barker *et al.*, 1985[4]	(d)
$\phi(NO_3)$, ϕ [O(^{3}P)]	248–289	Ravishankara *et al.*, 1986[5]	(e)

Comments

(a) Measured over the temperature range 223–300 K. For the wavelength range 200–280 nm, no temperature dependence was observed, and values were tabulated at 5 nm intervals. For 285–380 nm a pronounced temperature dependence was observed and the results were presented by an equation expressing σ as a function of λ and T.

(b) Measurements at 233–313 K using a dual-beam diode array spectrometer. Absolute cross-sections were based on pressure measurements and determination of NO_2 and HNO_3 impurities by UV and IR spectroscopic methods. For 260–380 nm, a pronounced temperature dependence was observed and the results were expressed in the form $\log_{10}(\sigma) = A + 1000\ B/T$.

(c) Pulsed laser photolysis, mostly at 249 nm with a few experiments at 350 nm. The NO_3 quantum yield was measured to be 0.89 ± 0.15. At low reactant concentration, the quantum yield approached a value of 1.0 ± 0.1.

(d) Pulsed laser photolysis. The quantum yield for production of O(^{3}P) atoms was determined to be <0.1 in experiments with resonance fluorescence detection of oxygen atoms. Optoacoustic techniques with added NO were used to determine $\phi(NO_3)$ to be 0.8 ± 0.2.

(e) Pulsed laser photolysis. The quantum yield for NO_3 production at 248 nm was determined to be unity in experiments with detection of NO_3 by absorption at 662 nm. The quantum yield for O(^{3}P) production was determined by resonance fluorescence and observed to decrease from 0.72 ± 0.17 at 248 nm to 0.15 ± 0.05 at 289 nm.

Absorption cross-section at 298 K

λ/nm	$10^{20}\ \sigma_{298}/\mathrm{cm}^2$	B/K
200	920	
205	820	
210	560	
215	370	
220	220	
225	144	
230	99	
235	77	
240	62	
245	52	
250	40	
255	32	
260	26.3	−0.091
265	20.5	−0.100
270	16.5	−0.104
275	13.3	−0.112
280	11.4	−0.112
285	8.72	−0.126
290	6.80	−0.135
295	5.15	−0.152
300	3.90	−0.170
305	2.93	−0.194
310	2.19	−0.226
315	1.63	−0.253
320	1.22	−0.294
325	0.90	−0.338
330	0.68	−0.388
335	0.50	−0.409
340	0.38	−0.492
345	0.280	−0.530
350	0.217	−0.583
355	0.167	−0.719
360	0.126	−0.770
365	0.095	−0.801
370	0.074	−0.885
375	0.054	−0.765
380	0.042	−0.992
385	0.033	−0.992
390	0.0234	−0.949
395	0.0174	−0.845
400	0.0135	−0.966
405	0.0103	−1.00
410	0.0080	−1.16

Temperature dependence: $\log_{10}\sigma_T$ (cm^2 molecule^{-1})$=\log_{10}\sigma_{298}+1000\,B(1/T-1/298)$.

Quantum yields

$\phi_1+\phi_2+\phi_3=1.0$ for $\lambda=248\text{–}350$ nm

λ/nm	ϕ_2
248	0.72±0.17
266	0.38±0.10
287	0.21±0.05
289	0.15±0.05

Comments on Preferred Values

The absorption cross-section values reported by Harwood *et al.*[2] show good agreement with the earlier data of Yao *et al.*[1] For wavelengths less than 280 nm, the σ values of Harwood *et al.*[2] are 7% lower than those of Yao *et al.*[1] and within 5% of the earlier values of Graham and Johnston.[6] No significant temperature dependence was observed at $\lambda \leqslant 260$ nm by Harwood *et al.*,[2] but for the region 265–410 nm there is a significant effect of temperature. In general, the temperature dependence from Harwood *et al.*[2] agrees well with that of Yao *et al.*[1] except at the longest wavelengths where the results in the former study show a slightly larger dependence, leading to σ values at 380 nm about 30% lower at 233 K than predicted from the earlier parameterization. The preferred values for the cross-section at room temperature were obtained by averaging the results from Harwood *et al.*[2] and Yao *et al.*,[1] and the temperature dependence parameters are taken from Harwood *et al.*[2]

The preferred quantum yield of unity for NO_3 radical production is based on the results of Swanson *et al.*[3] at 249 and 350 nm, those of Ravishankara *et al.*[5] at 248 nm, and those of Barker *et al.*[4] at 290 nm. The preferred quantum yield values for O atom production are those reported by Ravishankara *et al.*[5] The study of Oh *et al.*[7] indicates that electronically excited NO_2 in the $^2B_1$ state is produced, and photolysis induced fluorescence (PIF) quantum yield values are reported. For calculation of photodissociation rates in the atmosphere, channel (3) is equivalent to channel (1). In summary, it appears that NO_3 radicals are produced with unit quantum yield throughout the region 248–350 nm, and that the quantum yield for oxygen atom production decreases at longer wavelengths and appears to be approaching zero in the neighborhood of the thermodynamic threshold for O atom production at 307 nm.

The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[8]

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4.4. Sulfur Species

O + CS → CO + S

$\Delta H° = -355\ \text{kJ}\cdot\text{mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp/K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.06 \pm 0.14) \times 10^{-11}$	305	Slagle *et al.*, 1975[1]	DF-MS
$(2.24 \pm 0.36) \times 10^{-11}$	300	Bida, Breckenridge, and Kolln, 1976[2]	DF-UVA
$2.6 \times 10^{-10} \exp[-(760 \pm 140)/T]$	156–215	Lilenfeld and Richardson, 1977[3]	DF-EPR/MS
2.0×10^{-11}	298*		
Relative Rate Coefficients			
2.2×10^{-11}	298	Hancock and Smith, 1971[4]	RR (a)
Reviews and Evaluations			
$2.7 \times 10^{-10} \exp(-760/T)$	150–300	NASA, 1997[5]	(b)
$2.7 \times 10^{-10} \exp(-760/T)$	150–300	IUPAC, 1997[6]	(c)

Comments

(a) Discharge flow system. $O(^3P)$ was added to CS_2, and the infrared chemiluminescence from the O + CS reaction monitored. NO_2 was added to compete for O atoms. A rate coefficient ratio of $k/k(O + NO_2) = 2.3$ was obtained, and placed on an absolute basis by use of $k(O + NO_2) = 9.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Based on the data of Slagle *et al.*,[1] Bida *et al.*,[2] Lilenfeld and Richardson,[3] and Hancock and Smith.[4]

(c) See Comments on Preferred Values.

Preferred Values

$k = 2.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.7 \times 10^{-10} \exp(-760/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 150–300 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

Because of its significance in the CO chemical laser, this reaction has been the subject of a number of studies.[1–4] The values of k obtained at 298 K fall within a range of about 20%. The preferred value is the mean of these measurements,[1–4] all of which seem reliable. To obtain the preferred expression for k, the only available value of E/R is accepted[3] and the pre-exponential factor is adjusted to fit the preferred 298 K rate coefficient. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[6]

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$O + CH_3SCH_3 \rightarrow CH_3SO + CH_3$

$\Delta H^\circ = -133$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.42 \times 10^{-11} \exp[(366 \pm 15)/T]$	268–424	Lee, Timmons, and Stief, 1976[1]	FP-RF
$(4.84 \pm 0.52) \times 10^{-11}$	298		
$1.28 \times 10^{-11} \exp[(404 \pm 30)/T]$	272–472	Lee, Tang, and Klemm, 1980[2]	DF-RF
$(4.83 \pm 0.46) \times 10^{-11}$	296		
$1.11 \times 10^{-11} \exp[(460 \pm 41)/T]$	296–557	Nip, Singleton, and Cvetanovic, 1981[3]	(a)
5.11×10^{-11}	297		
Reviews and Evaluations			
$1.3 \times 10^{-11} \exp(410/T)$	270–560	NASA, 1997[4]	(b)
$1.3 \times 10^{-11} \exp(409/T)$	270–560	IUPAC, 1997[5]	(c)

Comments

(a) $O(^3P)$ atoms were generated by the mercury-photosensitized photolysis of N_2O using a sinusoidally modulated mercury lamp, and monitored by NO_2 chemiluminscence using a phase-shift technique.

(b) Based on the results of Lee *et al.*[1,2] and Nip *et al.*[3]

(c) See Comments on Preferred Values.

Preferred Values

$k = 5.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.3 \times 10^{-11} \exp(409/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270–560 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The data of Nip *et al.*[3] are in excellent agreement, over the entire temperature range studied, with both of the studies of Lee *et al.*[1,2] The preferred values of k at 298 K and (E/R) are obtained from a least-squares fit of the data from those three studies[1–3] and are identical to those in our previous evaluation, IUPAC, 1997.[5] The product study of Cvetanovic *et al.*[6] suggests that at high pressures (0.39–1.58 bar) the reaction proceeds almost entirely by addition followed by rapid fragmentation to $CH_3 + CH_3SO$. A broad chemiluminescence spectrum in the range 240–460 nm from this reaction at 1.3 mbar (1 Torr) pressure has been reported by Pavanaja *et al.*[7] They identified the emitting species as electronically excited HO and SO_2, and by numerical integration they showed that production of these excited species is consistent with secondary chemistry following the initial reaction to give the products shown above.

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$$O + CS_2 \rightarrow SO + CS \quad (1)$$

$$\rightarrow CO + S_2 \quad (2)$$

$$\rightarrow OCS + S \quad (3)$$

$\Delta H°(1) = -89$ kJ·mol^{-1}
$\Delta H°(2) = -348$ kJ·mol^{-1}
$\Delta H°(3) = -231$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.0\times10^{-11}\exp[-(300\pm150)/T]$	305–410	Callear and Smith, 1967[1]	FP-UVA
4.2×10^{-12}	305		
$8.3\times10^{-11}\exp(-950/T)$	300–920	Homann, Krome, and Wagner, 1968[2]	DF-MS
3.5×10^{-12}	300		
$(2.08\pm0.08)\times10^{-12}$	227	Westenberg and deHaas, 1968[3]	DF-EPR/MS
$(3.0\pm0.3)\times10^{-12}$	297		
$(7.8\pm0.3)\times10^{-12}$	538		
$(3.7\pm0.3)\times10^{-12}$	298	Callear and Hedges, 1970[4]	FP-UVA
$(4.0\pm0.3)\times10^{-12}$	302	Slagle, Gilbert, and Gutman, 1974[5]	(a)
$2.8\times10^{-11}\exp[-(650\pm35)/T]$	218–293	Wei and Timmons, 1975[6]	DF-EPR
$(3.1\pm0.2)\times10^{-12}$	293		
$(2.9\pm0.2)\times10^{-12}$	249	Graham and Gutman, 1977[7]	DF-MS
$(3.6\pm0.3)\times10^{-12}$	273		
$(4.1\pm0.2)\times10^{-12}$	295		
$(5.1\pm0.6)\times10^{-12}$	335		
$(6.6\pm0.3)\times10^{-12}$	376		
$(8.5\pm0.6)\times10^{-12}$	431		
$(11.2\pm0.8)\times10^{-12}$	500		
Reviews and Evaluations			
$3.2\times10^{-11}\exp(-650/T)$	210–500	NASA, 1997[8]	(b)
$3.2\times10^{-11}\exp(-650/T)$	200–500	IUPAC, 1997[9]	(c)

Comments

(a) Studied by using crossed molecular beams with photoionization mass spectrometric detection of products.
(b) Based on the studies of Callear and Smith,[1] Homann *et al.*,[2] Westenberg and deHaas,[3] Callear and Hedges,[4] Slagle *et al.*,[5] Wei and Timmons,[6] and Graham and Gutman.[7]
(c) See Comments on Preferred Values.

Preferred Values

$k = 3.6\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.2\times10^{-11}\exp(-650/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 210–500 K.
$k_1/k \geq 0.90$ over the temperature range 210–500 K.

Reliability
$\Delta\log k = \pm0.2$ at 298 K.
$\Delta(E/R) = \pm100$ K.

Comments on Preferred Values

There are several determinations of k at 298 K using a variety of techniques, which are in good agreement. The preferred value is an average of the values of Callear and Smith,[1] Homann *et al.*,[2] Westenberg and deHaas,[3] Callear and Hedges,[4] Slagle *et al.*,[5] Wei and Timmons,[6] and Graham and Gutman.[7] The preferred temperature coefficient is that of Wei and Timmons.[6] There is evidence to suggest that the Arrhenius plot is not linear over a wide temperature range but over the range for which our preferred values apply the other studies of the temperature dependence of k[2,7] are in good agreement with the value of Wei and Timmons.[6]

The reported values for the branching ratios show considerable scatter. For k_3/k values of 0.093,[5] 0.006,[10] 0.015,[11] 0.30,[12] and 0.085[13] have been reported and for k_2/k values of 0.05–0.20,[5] 0.006,[10] 0.014,[14] and 0.030.[13] Channel (1) is clearly the major channel but at this stage our only recommendation is that $k_1/k \geq 0.90$. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[9]

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$O + CH_3SSCH_3 \rightarrow CH_3SO + CH_3S$

$\Delta H^\circ = -167$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.12\pm0.22)\times10^{-10}$	270–329	Lee and Tang, 1980[1]	DF-RF
$4.35\times10^{-11}\exp[(251\pm61)/T]$	298–571	Nip, Singleton, and Cvetanovic, 1981[2]	(a)
$(1.0\pm0.3)\times10^{-10}$	298		
Reviews and Evaluations			
$5.5\times10^{-11}\exp(250/T)$	290–570	NASA, 1997[3]	(b)
$5.5\times10^{-11}\exp(250/T)$	290–570	IUPAC, 1997[4]	(b)

Comments

(a) $O(^3P)$ atoms were generated by the mercury-photosensitized photolysis of N_2O using a sinusoidally modulated mercury lamp, and monitored by NO_2 chemiluminescence using a phase-shift technique.

(b) Based on the results of Lee and Tang[1] and Nip *et al.*[2]

Preferred Values

$k = 1.5\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.5\times10^{-11}\exp(250/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–570 K.

Reliability

$\Delta\log k = \pm0.3$ at 298 K.

$\Delta(E/R) = \pm100$ K.

Comments on Preferred Values

The data of Nip *et al.*,[2] obtained using a modulated photolysis technique, are about a factor of 2 lower than the data from the earlier discharge flow-resonance fluorescence study of Lee and Tang,[1] who reported no temperature dependence over the rather limited range 270–329 K. The cause of the discrepancy between the two measurements is not clear. The preferred value at 298 K is an average of the values from the two studies.[1,2] The temperature dependence is that from Nip *et al.*[2] with the A factor adjusted to yield the preferred value at 298 K.

The product study of Cvetanovic *et al.*[5] suggests that at high pressures, 0.39–1.58 bar, the reaction proceeds mainly by addition followed by rapid fragmentation to $CH_3S + CH_3SO$. A broad chemiluminescence spectrum in the range 240–460 nm from this reaction at 1.3 mbar (1 Torr) pressure has been reported by Pavanaja *et al.*[6] They identified the emitting species as electronically excited HO and SO_2, and showed from a computer simulation that production of these excited species is consistent with secondary chemistry following the initial reaction to give the products shown above.

References

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$$\mathrm{O + OCS \rightarrow SO + CO} \quad (1)$$

$$\mathrm{\rightarrow CO_2 + S} \quad (2)$$

$\Delta H°(1) = -213$ kJ·mol^{-1}
$\Delta H°(2) = -224$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9.0 \pm 1.3) \times 10^{-15}$	298	Sullivan and Warneck 1965[1]	DF-MS
$2.0 \times 10^{-10} \exp(-2920/T)$	290–465	Hoyermann, Wagner, and Wolfrum, 1967[2]	DF-EPR
1.2×10^{-14}	300		
$1.08 \times 10^{-10} \exp(-2770/T)$	300–1150	Homann, Krome, and Wagner, 1968[3]	DF-MS
1.1×10^{-14}	300		
$3.2 \times 10^{-11} \exp(-2280/T)$	273–808	Westenberg and deHaas, 1969[4]	DF-EPR/MS
$(1.4 \pm 0.1) \times 10^{-14}$	297		
$(1.19 \pm 0.06) \times 10^{-14}$	297	Breckenridge and Miller, 1972[5]	DF-MS
$1.65 \times 10^{-11} \exp[-(2165 \pm 30)/T]$	263–502	Klemm and Stief, 1974[6]	FP-RF
$(1.2 \pm 0.1) \times 10^{-14}$	298		
$2.0 \times 10^{-11} \exp[-(2140 \pm 40)/T)]$	239–404	Wei and Timmons, 1975[7]	DF-EPR
$(1.35 \pm 0.13) \times 10^{-14}$	295		
$(1.39 \pm 0.14) \times 10^{-14}$	296	Manning, Braun, and Kurylo 1976[8]	FP-RF
$(1.17 \pm 0.12) \times 10^{-14}$	298	Yoshida and Saito, 1978[9]	DF-A (a)
Reviews and Evaluations			
$2.1 \times 10^{-11} \exp(-2200/T)$	230–500	NASA, 1997[10]	(b)
$1.6 \times 10^{-11} \exp(-2150/T)$	220–500	IUPAC, 1997[11]	(c)

Comments

(a) SO radicals were monitored by microwave absorption at 13044 MHz.

(b) Based on the work of Westenberg and deHaas,[4] Breckenridge and Miller,[5] Klemm and Stief,[6] Wei and Timmons,[7] and Manning *et al.*[8]

(c) See Comments on Preferred Values.

Preferred Values

$k = 1.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.6 \times 10^{-11} \exp(-2150/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–500 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

The values obtained for k by a variety of techniques[1-9] are in excellent agreement over a wide range of temperatures and pressures (≤ 340 mbar). The available evidence suggests that at low temperatures the reaction proceeds by channel (1) and that channel (2) may only become significant at temperatures above 600 K.

Because of the possible enhancement of the rate by channel (2) at high temperatures, the recommended value of E/R is the mean of the values obtained in studies by Klemm and Stief [6] and Wei and Timmons[7] which were limited to temperatures below 502 K. The value of k at 298 K is the mean of the values in Refs. 1–9, and the preexponential factor is adjusted to fit this value of k and the recommended value of E/R. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[11]

Approximate measurements of k_2/k_1 are: 10^{-3} at 298 K (Ref. 12) and 10^{-2} at 500 K.[3]

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$O + SO_2 + M \rightarrow SO_3 + M$

$\Delta H^\circ = -348.1$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$3.1\times10^{-32}\exp(-1009/T)$ [Ar]	299–400	Atkinson and Pitts, 1978[1]	FP-CL (a)
1.05×10^{-33} [Ar]	298		
1.37×10^{-33} [N_2]	298		
Reviews and Evaluations			
$1.1\times10^{-31}(T/1000)^{-4}\exp(-2646/T)$ [Ar]	250–2500	Troe, 1978[2]	(b)
$1.3\times10^{-33}(T/300)^{3.6}$ [air]	299–400	NASA, 1997[3]	(c)
$4.0\times10^{-32}\exp(-1000/T)$ [N_2]	200–400	IUPAC, 1997[4]	(d)
$8.3\times10^{-31}(T/1000)^{-3.75}\exp(-2650/T)$ [Ar]	200–2500		

Comments

(a) Flash photolysis technique with detection of $O(^3P)$ atoms by NO_2 chemiluminescence. Relative efficiencies of $k(M=N_2)$: $k(M=Ar)$: $k(M=SO_2)=1.0:0.77:6.9$ were determined.

(b) Theoretical analysis of dissociation and recombination data, fitting a barrier of 22 kJ·mol^{-1} for the spin-forbidden reaction $O(^3P) + SO_2(^1A_1) \rightarrow SO_3(^1A_1)$.

(c) Based on the data of Atkinson and Pitts.[1]

(d) Based on the data from Ref. 1, the high temperature dissociation results from Ref. 5, and a theoretical analysis from Ref. 2. A summary of earlier data was also given.

Preferred Values

$k_0 = 1.4\times10^{-33}$ [N_2] cm^3 molecule^{-1} s^{-1} at 298 K.

$k_0 = 4.0\times10^{-32}\exp(-1000/T)$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200–400 K.

Reliability

$\Delta\log k_0 = \pm0.3$ at 300 K.

$\Delta(E/R) = \pm200$ K over the temperature range 200–400 K.

Comments on Preferred Values

The preferred values are based on the absolute rate coefficient study of Atkinson and Pitts[1] [see also comment (c)], and are identical to those in our previous evaluation, IUPAC, 1997.[4] Because the reaction has an activation barrier, the Arrhenius form is chosen. The falloff transition to the high pressure range is expected at pressures not too far above 1 bar. However, as yet no experimental data are available in this pressure region.

References

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$S + O_2 \rightarrow SO + O$

$\Delta H^\circ = -23.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Commen
Absolute Rate Coefficients			
$(2.0 \pm 0.5) \times 10^{-12}$	298	Fair and Thrush, 1969[1]	DF-CL
$(2.8 \pm 0.3) \times 10^{-12}$	298	Fair, Van Roodselaar, and Strausz, 1971[2]	FP-A
$2.2 \times 10^{-12} \exp[(0 \pm 50)/T]$	252–423	Davis, Klemm, and Pilling, 1972[3]	FP-RF
$(1.7 \pm 0.3) \times 10^{-12}$	298	Donovan and Little, 1972[4]	FP-A
$(1.5 \pm 0.3) \times 10^{-12}$	298	Clyne and Townsend, 1975[5]	DF-RF
$1.7 \times 10^{-12} \exp[(153 \pm 108)/T]$	296–393	Clyne and Whitefield, 1979[6]	DF-RF
$(2.6 \pm 0.3) \times 10^{-12}$	298		
Reviews and Evaluations			
2.3×10^{-12}	250–430	NASA, 1997[7]	(a)
2.1×10^{-12}	230–400	IUPAC, 1997[8]	(b)

Comments

(a) Based primarily on the data of Davis *et al.*[3]
(b) See Comments on Preferred Values.

Preferred Values

$k = 2.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–430 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

All of the available measurements of k^{1-6} are in good agreement. Clyne and Whitefield[6] observed a small decrease in k with increasing temperature, but until more definitive measurements of E/R are made a temperature independent k is recommended with error limits encompassing the existing measured values. The preferred value at 298 K is the mean of values from Refs. 1–6, and is identical to that in our previous evaluation, IUPAC, 1997.[8]

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$S + O_3 \rightarrow SO + O_2$

$\Delta H^\circ = -415$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.2 \pm 0.3) \times 10^{-11}$	298	Clyne and Townsend, 1975[1]	DF-RF
Reviews and Evaluations			
1.2×10^{-11}	298	NASA, 1997[2]	(a)
1.2×10^{-11}	298	IUPAC, 1997[3]	(b)

Comments

(a) Based on the data of Clyne and Townsend.[1]
(b) See Comments on Preferred Values.

Preferred Values

$k = 1.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = +0.3$ at 298 K.

Comments on Preferred Values

The only available experimental determination[1] is accepted as the preferred value. The method was direct, and in the same study a number of other rate coefficients for S atom reactions were measured giving results in good agreement with other techniques. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[3]

References

[1] M. A. A. Clyne and L. W. Townsend, Int. J. Chem. Kinet. **Symp. 1**, 73 (1975).
[2] NASA Evaluation No. 12, 1997 (see references in Introduction).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$Cl + H_2S \rightarrow HCl + HS$

$\Delta H^\circ = -50.0$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(7.3 \pm 0.9) \times 10^{-11}$	298	Nesbitt and Leone, 1980[1]	PLP-CL
$(4.00 \pm 0.08) \times 10^{11}$	296	Clyne and Ono, 1983[2]	DF-RF
$(5.1 \pm 0.7) \times 10^{-11}$	296	Clyne *et al.*, 1984[3]	DF-MS
$(6.29 \pm 0.46) \times 10^{11}$	211–353	Nava, Brobst, and Stief, 1984[4]	FP-RF
$3.69 \times 10^{-11} \exp[(208 \pm 24)/T]$	202–430	Nicovich, Wang, and Wine, 1995[5]	PLP-RF
$(7.4 \pm 1.1) \times 10^{-11}$	298		
Reviews and Evaluations			
$3.7 \times 10^{-11} \exp(210/T)$	200–430	NASA, 1997[6]	(a)
5.7×10^{-11}	210–350	IUPAC, 1997[7]	(b)

Comments

(a) Based on the data of Nicovich *et al.*[5]
(b) Based on the data of Nesbitt and Leone,[1] Clyne and Ono,[2] Clyne *et al.*,[3] and Nava *et al.*[4]

Preferred Values

$k = 7.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.7 \times 10^{-11} \exp(208/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–430 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred value accepts the results of the recent study of Nicovich *et al.*[5] which was an extensive study conducted over a wide range of experimental conditions. In that study the value of k at room temperature was found to be independent of pressure over the range studied [33–800 mbar (25–600 Torr)]. The room temperature value of k reported by Nesbitt and Leone[1] is in excellent agreement with the preferred value, that of Nava *et al.*[4] is 15% lower, and those of Clyne and Ono[2] and Clyne *et al.*[3] are significantly lower. In the study of Nicovich *et al.*,[5] experimental conditions were adjusted to minimize interferences from radical–radical secondary reactions.

References

[1] D. J. Nesbitt and S. R. Leone, J. Chem. Phys. **72**, 722 (1980).
[2] M. A. A. Clyne and Y. Ono, Chem. Phys. Lett. **94**, 597 (1983).
[3] M. A. A. Clyne, A. J. MacRobert, T. P. Murrells, and L. J. Stief, J. Chem. Soc. Faraday Trans. 2 **80**, 877 (1984).
[4] D. F. Nava, W. D. Brobst, and L. J. Stief, J. Phys. Chem. **89**, 4703 (1985).
[5] J. M. Nicovich, S. Wang, and P. H. Wine, Int. J. Chem. Kinet. **27**, 359 (1995).
[6] NASA Evaluation No. 12, 1997 (see references in Introduction).
[7] IUPAC, Supplement V, 1997 (see references in Introduction).

$Cl + OCS \rightarrow SCl + CO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<1.1\times10^{-16}$	298	Eibling and Kaufman, 1983[1]	DF-MS
$<4\times10^{-15}$	298	Clyne *et al.*, 1984[2]	DF-MS
$<1\times10^{-14}$	298	Nava, Brobst, and Stief, 1985[3]	FP-RF
Reviews and Evaluations			
$<1.0\times10^{-16}$	298	NASA, 1997[4]	(a)
$<1.0\times10^{-16}$	298	IUPAC, 1997[5]	(b)

Comments

(a) Accepted the upper limit obtained by Eibling and Kaufman.[1]

(b) See Comments on Preferred Values.

Preferred Values

$k<1.0\times10^{-16}$ at 298 K.

Comments on Preferred Values

The reaction of Cl atoms with OCS is extremely slow and only upper limits to the rate coefficient have been obtained.[1-3] The lowest of these[1] is the preferred value, which is identical to that in our previous evaluation, IUPAC, 1997.[5]

References

[1] R. E. Eibling and M. Kaufman, Atmos. Environ. **17**, 429 (1983).
[2] M. A. A. Clyne, A. J. MacRobert, T. P. Murrells, and L. J. Stief, J. Chem. Soc. Faraday Trans. 2 **80**, 877 (1984).
[3] D. F. Nava, W. D. Brobst, and L. J. Stief, J. Phys. Chem. **89**, 4703 (1985).
[4] NASA Evaluation No. 12, 1997 (see references in Introduction).
[5] IUPAC, Supplement V, 1997 (see references in Introduction).

$Cl + CS_2 \xrightarrow{O_2} products$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<5\times10^{-15}$ (Air, 400 mbar)	293	Nicovich, Shackelford, and Wine, 1990[1]	PLP-RF (a)
Relative Rate Coefficients			
$(8.3\pm1.7)\times10^{-14}$ (Air, 1013 mbar)	293	Martin, Barnes, and Becker, 1987[2]	RR (b)
$<4\times10^{-15}$ (Air, 933 mbar)	298	Wallington *et al.*, 1991[3]	RR (c)
Reviews and Evaluations			
$<4\times10^{-15}$ (Air, 1 bar)	298	NASA, 1997[4]	(d)
$<4\times10^{-15}$ (Air, 1 bar)	298	IUPAC, 1997[5]	(e)

Comments

(a) Pulsed laser photolysis of Cl_2 in CS_2, N_2, O_2 mixtures over the pressure range 40–400 mbar (30–300 Torr) and the temperature range 193–258 K. [Cl] monitored by resonance fluorescence. Experiments in the absence of O_2 revealed reversible adduct formation and the establishment of an equilibrium between Cl, CS_2, and CS_2Cl. The thermodynamic parameters for equilibrium were derived. The upper limit tabulated for the overall removal of CS_2 in the presence of O_2 is for all channels of the $CS_2Cl + O_2$ reaction which do not lead to Cl atom formation.

(b) Steady-state photolysis of Cl_2 in the presence of CS_2, N_2, O_2, and a reference compound (CH_4 or CH_3Cl). [CS_2] and [CH_4] (or [CH_3Cl]) were monitored by quadrupole mass spectrometry. Constant total pressure of 1 bar (760 Torr). [N_2]/[O_2] varied. Values of k(Cl

$+ CH_3Cl) = 4.6 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} and $k(Cl + CH_4) = 9.6 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} were used.[5]

(c) Steady state photolysis of Cl_2 in the presence of CS_2, N_2, O_2, and CHF_2Cl with FTIR monitoring. Value of $k(Cl + CHF_2Cl)/k(Cl + CH_4) < 0.04$ measured in same study and combined with $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} (Ref. 5) and the measured rate coefficient ratio $k(Cl + CS_2)/k(Cl + CHF_2Cl)$ in the presence of O_2 to give the tabulated upper limit to k.

(d) Based on the upper limits to the rate coefficient measured by Nicovich *et al.*.[1] and Wallington *et al.*[3]

(e) See Comments on Preferred Values.

Preferred Values

$k \leq 4 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K in air at 1 bar.

Comments on Preferred Values

The overall reaction of Cl with CS_2 appears to be too slow to be of importance in the atmosphere. Nicovich *et al.*[1] have shown that it proceeds initially by rapid formation of the $ClCS_2$ adduct, as suggested earlier by Martin *et al.*,[2] but the subsequent reaction of the adduct with O_2 appears to be slow.

The recommended upper limit is that of Wallington *et al.*[3] which agrees with the work of Nicovich *et al.*[1] Wallington *et al.*[3] have suggested that the value obtained by Martin *et al.*[2] was erroneously high due to complexities in their system arising from HO radical production from the reference compounds which were chosen. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[5]

References

[1] J. M. Nicovich, C. J. Shackelford, and P. H. Wine, J. Phys. Chem. **94**, 2896 (1990).

[2] D. Martin, I. Barnes, and K. H. Becker, Chem. Phys. Lett. **140**, 195 (1987).

[3] T. J. Wallington, J. M. Andino, A. R. Potts, and P. H. Wine, Chem. Phys. Lett. **176**, 103 (1991).

[4] NASA Evaluation No. 12, 1997 (see references in Introduction).

[5] IUPAC, Supplement V, 1997 (see references in Introduction).

$Cl + CH_3SH \rightarrow HCl + CH_3S$ (1)

$\rightarrow HCl + CH_2SH$ (2)

$\Delta H°(1) = -66.1$ $kJ \cdot mol^{-1}$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.8 \pm 0.4) \times 10^{-10}$	298	Nesbitt and Leone, 1980[1]	PLP-CL
$k_2 = (4.3 \pm 1) \times 10^{-12}$	298	Nesbitt and Leone, 1981[2]	PLP-CL
$(1.1 \pm 0.4) \times 10^{-10}$	298	Mellouki, Jourdain, and Le Bras, 1988[3]	DF-EPR/MS
$1.19 \times 10^{-10} \exp[(151 \pm 38)/T]$	193–430	Nicovich, Wang, and Wine, 1995[4]	PLP-RF
$(2.0 \pm 0.3) \times 10^{-10}$	298		
Reviews and Evaluations			
$1.2 \times 10^{-10} \exp(150/T)$	190–430	NASA, 1997[5]	(a)

Comments

(a) Based on the results of Nicovich *et al.*[4]

Preferred Values

$k = 2.0 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

$k = 1.2 \times 10^{-10} \exp(150/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 190–430 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred value accepts the results of the recent study of Nicovich *et al.*,[4] which was an extensive study conducted over a wide range of experimental conditions. In that study the value of k at room temperature was found to be independent of pressure over the range studied [33–200 mbar (25–150 Torr)]. The room temperature value of k reported by Nesbitt and Leone[1] is in good agreement with the preferred value, but the Mellouki *et al.*[3] reported value is lower by a factor of two. The results of Nesbitt and Leone[2] show that only about 2% of the total reaction occurs by channel (2), via abstraction from the methyl group.

References

[1] D. J. Nesbitt and S. R. Leone, J. Chem. Phys. **72**, 1722 (1980).
[2] D. J. Nesbitt and S. R. Leone, J. Chem. Phys. **75**, 4949 (1981).
[3] A. Mellouki, J. L. Jourdain, and G. Le Bras, Chem. Phys. Lett. **148**, 231 (1988).
[4] J. M. Nicovich, S. Wang, and P. H. Wine, Int. J. Chem. Kinet. **27**, 359 (1995).
[5] NASA Evaluation No. 12, 1997 (see references in Introduction).

$$\mathrm{Cl} + \mathrm{CH_3SCH_3} \rightarrow \mathrm{CH_3SCH_2} + \mathrm{HCl} \quad (1)$$

$$\rightarrow \mathrm{CH_3SClCH_3} \quad (2)$$

$\Delta H°(1) = -39.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.8×10^{-10} (4 mbar N$_2$)	297	Stickel *et al.*, 1992[1]	PLP-RF
$(3.3\pm0.5)\times10^{-10}$ (933 mbar N$_2$)	297		
Relative Rate Coefficients			
$(3.2\pm0.3)\times10^{-10}$ (987 mbar N$_2$)	295	Nielsen *et al.*, 1990[2]	RR (a)
$(3.61\pm0.21)\times10^{-10}$ (1013 mbar N$_2$)	298	Kinnison, Mengon, and Kerr, 1996[3]	RR (b)
Branching Ratios			
$k_1/k > 0.97$ (1.3 mbar He)	298	Butkovskaya, Poulet, and Le Bras, 1995[4]	DF-MS
$k_1/k > 0.98$ (13–40 mbar N$_2$)	298	Zhao, Stickel, and Wine, 1996[5]	PLP TDLS
Reviews and Evaluations			
3.3×10^{-10} (1 bar N$_2$)	298	NASA, 1997[6]	(c)
3.3×10^{-10} (1 bar N$_2$)	298	IUPAC, 1997[7]	(c)

Comments

(a) Photolysis of mixtures of COCl$_2$–CH$_3$SCH$_3$–cyclohexane–N$_2$ in a Teflon chamber. [Cyclohexane] and [CH$_3$SCH$_3$] measured at intervals by GC. A rate coefficient of k(Cl + cyclohexane) = 3.1×10^{-10} cm^3 molecule^{-1} s^{-1} was used.[8]

(b) Photolysis of mixtures of COCl$_2$–CH$_3$SCH$_3$–n-butane–N$_2$ in a Teflon chamber. [n-Butane] and [CH$_3$SCH$_3$] measured by GC. k(Cl + n-butane) = 1.94×10^{-10} cm^3 molecule^{-1} s^{-1} used.[8]

(c) Based on the results of Stickel *et al.*[1]

Preferred Values

$k = 3.3\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar N$_2$.

Reliability

$\Delta\log k = \pm0.15$ at 298 K and 1 bar N$_2$.

Comments on Preferred Values

The study of this reaction by Stickel *et al.*[1] shows the reaction kinetics to have a complex dependency on temperature and pressure. The overall reaction rate is close to collisional and increases with decreasing temperature and with increasing pressure. The HCl yield (measured by TDLS) approaches unity as the pressure tends to zero but decreases to a value of ~0.5 at 270 mbar (203 Torr) N$_2$ and 297 K.[1]

These findings are interpreted in terms of the occurrence of two reaction channels, Cl abstraction and adduct formation. At low pressures the abstraction channel is dominant (Refs. 1, 4, and 5) but with increasing pressure the adduct can be stabilized leading to an increase in the total k as pressure increases and temperature decreases.

Until the reaction is studied in more detail and a complete analysis of the temperature and pressure dependence can be made, our recommendations are limited to high pressures and 298 K. They are based on the results of Stickel *et al.*,[1] Nielsen *et al.*,[2] and Kinnison *et al.*,[3] which are in excellent agreement. There is also a value of 2.0×10^{-10} cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar N$_2$ reported by Barnes *et al.*,[9] but no experimental details are given.

References

[1] R. E. Stickel, J. M. Nicovich, S. Wang, Z. Zhao, and P. H. Wine, J. Phys. Chem. **96**, 9875 (1992).
[2] O. J. Nielsen, H. W. Sidebottom, L. Nelson, O. Rattigan, J. Treacy, and D. J. O'Farrell, Int. J. Chem. Kinet. **22**, 603 (1990).
[3] D. J. Kinnison, W. Mengon, and J. A. Kerr, J. Chem. Soc. Faraday Trans. **92**, 369 (1996).
[4] N. I. Butkovskaya, G. Poulet, and G. Le Bras, J. Phys. Chem. **99**, 4536 (1995).
[5] Z. Zhao, R. E. Stickel, and P. H. Wine, Chem. Phys. Lett. **251**, 59 (1996).

[6] NASA Evaluation No. 12, 1997 (see references in Introduction).
[7] IUPAC, Supplement V, 1997 (see references in Introduction).
[8] R. Atkinson and S. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).
[9] I. Barnes, V. Bastian, K. H. Becker, and D. Martin, *Biogenic Sulfur in the Environment*, E. S. Saltzman and W. J. Cooper, ACS Symposium Series 393 (ACS, Washington, DC, 1989), p. 476.

$HO + H_2S \rightarrow H_2O + HS$

$\Delta H° = -117.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.2\pm0.5)\times10^{-12}$	298–423	Perry, Atkinson, and Pitts, 1976[1]	FP-RF
$6.4\times10^{-12}\exp[-(55\pm58)/T]$	245–366	Wine *et al.*, 1981[2]	FP-RF
$(5.13\pm0.57)\times10^{-12}$	297		
$2.27\times10^{-19}T^{2.5}\exp(725/T)$	228–518	Leu and Smith, 1982[3]	DF-RF
$(3.9\pm0.7)\times10^{-12}$	298		
$(5.01\pm0.55)\times10^{-12}$	228–437	Michael *et al.*, 1982[4]	FP-RF
$7.8\times10^{-12}\exp[-(146\pm105)/T]$	239–425	Lin, 1982[5]	FP-RF
$(4.42\pm0.48)\times10^{-12}$	295		
$(4.3\pm0.6)\times10^{-12}$	300	Wang and Lee, 1985[6]	DF-RF
$3.81\times10^{-19}T^{2.43}\exp(732/T)$	245–450	Lin *et al.*, 1985[7]	DF-RF
$(4.4\pm0.7)\times10^{-12}$	299		
$(4.9\pm0.9)\times10^{-12}$	245	Lafage *et al.*, 1987[8]	DF-RF/LIF
$(3.8\pm0.6)\times10^{-12}$	263		
$1.32\times10^{-11}\exp[-(394\pm190)/T]$	294–450		
$(3.3\pm0.5)\times10^{-12}$	294		
Reviews and Evaluations			
$6.0\times10^{-12}\exp(-75/T)$	220–520	NASA, 1997[9]	(a)
$6.3\times10^{-12}\exp(-80/T)$	200–300	IUPAC, 1997[10]	(b)

Comments

(a) Based on the absolute data of Perry *et al.*,[1] Wine *et al.*,[2] Leu and Smith,[3] Michael *et al.*,[4] Lin,[5] Lin *et al.*,[7] and Lafage *et al.*[8] and the relative rate data of Cox and Sheppard[11] and Barnes *et al.*[12]

(b) Based on the absolute rate data of Westenberg and deHaas,[13] Perry *et al.*,[1] Wine *et al.*,[2] Leu and Smith,[3] Michael *et al.*,[4] and Lin.[5]

Preferred Values

$k = 4.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 6.1\times10^{-12}\exp(-80/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–520 K.

Reliability

$\Delta\log k = \pm0.08$ at 298 K.

$\Delta(E/R) = \pm80$ K.

Comments on Preferred Values

The preferred values are obtained from a unit-weighted least-squares analysis of the absolute rate constants of Perry *et al.*,[1] Wine *et al.*,[2] Leu and Smith,[3] Michael *et al.*,[4] Lin,[5] Wang and Lee,[6] Lin *et al.*,[7] and Lafage *et al.*[8] The studies of Leu and Smith,[3] Lin *et al.*,[7] and Lafage *et al.*[8] show non-Arrhenius behavior of the rate coefficient, with a shallow minimum in the rate coefficient at ~270–300 K. The rate coefficient is independent of pressure[3–5,7] and the nature of the diluent gas.[7] These findings[3–5,7] cast some doubt upon the suggestion that the non-Arrhenius behavior is due to the occurrence of both addition and abstraction channels.

Despite the non-Arrhenius behavior of the rate coefficient k over an extended temperature range, the preferred expression is given in the Arrhenius form which is satisfactory for the temperature range covered by our recommendation.

References

[1] R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Chem. Phys. **64**, 3237 (1976).
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[10] IUPAC, Supplement V, 1997 (see references in Introduction).
[11] R. A. Cox and D. W. Sheppard, Nature (London) **284**, 330 (1980).
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[13] A. A. Westenberg and N. deHaas, J. Chem. Phys. **59**, 665 (1973).

$HO + SO_2 + M \rightarrow HOSO_2 + M$

$\Delta H° = -127$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(7.2\pm2.6)\times10^{-31}$ [N_2]	300	Harris and Wayne, 1975[1]	DF-RF
7.0×10^{-31} $(T/300)^{-2.9}$ [N_2]		Erler, Field, and Zellner, 1975[2]	DF-RF (a)
4.9×10^{-31} [N_2]	300	Davis, 1976[3]	(b)
2.9×10^{-31} [N_2]	300	Atkinson, Perry, and Pitts, 1976[4]	FP-RF (c)
3.6×10^{-31} [N_2]	300	Erler and Zellner, 1978[5]	FP-RA
$(2.54\pm0.33)\times10^{-31}$ [N_2]	298	Leu, 1982[6]	DF-RF (d)
$(7.91\pm0.24)\times10^{-32}$ $(T/298)^{-(2.85\pm0.21)}$ [He]	261–414		
1.6×10^{-31} [N_2]	297	Paraskevopoulos, Singleton, and Irwin, 1983[7]	FP-RA (e)
5.8×10^{-31} $(T/300)^{-2.6}$ [N_2]	260–420	Wine *et al.*, 1984[8]	FP-RF (f)
$(2.4\pm0.7)\times10^{-31}$ [N_2]	298	Lee, Kao, and Lee, 1990[9]	DF-RF
$(1.1\pm0.3)\times10^{-32}$ exp$(640/T)$ [He]	280–413		
Reviews and Evaluations			
$3.0\times10^{-31}(T/300)^{-3.3}$ [air]	260–420	NASA, 1997[10]	(g)
$4.0\times10^{-31}(T/300)^{-3.3}$ [N_2]	300–400	IUPAC, 1997[11]	(h)

Comments

(a) Temperature range not cited.
(b) Measurements cited in Ref. 12 in the pressure range 6.7–670 mbar (5–500 Torr), extrapolated to k_0 and k_∞.
(c) Converted from M=Ar with an assumed relative efficiency N_2:Ar=1.8:1. Pressure range 33–870 mbar (25–650 Torr) extrapolated with Lindemann–Hinshelwood plot to k_0 and k_∞.
(d) Measurements at pressures near 1.3 mbar (1 Torr).
(e) Pressure range 73–1013 mbar (55–760 Torr). Falloff extrapolation using Lindemann–Hinshelwood (i.e., neglecting broadening factors), and hence responsible for low value.
(f) Temperature range 260–420 K, pressure range 17–928 mbar (13–696 Torr), bath gases He, Ar, N_2, and SF_6.
(g) Based on the rate coefficients of Ref. 6.
(h) See Comments on Preferred Values.

Preferred Values

$k_0 = 4.0\times10^{-31}$ $(T/300)^{-3.3}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 300–400 K.

Reliability

$\Delta \log k_0 = \pm0.3$ at 300 K.
$\Delta n = \pm1$.

Comments on Preferred Values

The preferred values are based on an average of the data from Refs. 1–9, correcting for inadequate falloff extrapolations, and are identical to those in our previous evaluation, IUPAC, 1997.[11] Falloff curves are constructed with F_c=0.45 near 300 K and k_∞ such as given below. The difference between k_0 from Refs. 10 and 11 is due to the use of F_c=0.6 in Ref. 10.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.8×10^{-12}	435	Gordon and Mulac, 1975[13]	(a)
9.0×10^{-13}	300	Davis, 1976[3]	(b)
8.3×10^{-13}	300	Atkinson, Perry, and Pitts, 1976[4]	FP-RF (c)
1.2×10^{-12}	297	Paraskevopoulos, Singleton, and Irwin, 1983[7]	FP-RA (d)
$1.26\times10^{-12}(T/300)^{-0.7}$	260–420	Wine *et al.*, 1984[8]	FP-RF (e)
Reviews and Evaluations			
1.5×10^{-12}	260–420	NASA, 1997[10]	(f)
2×10^{-12}	200–300	IUPAC, 1997[11]	(g)

Comments

(a) Pulsed radiolysis in H_2O vapor at 1 bar.

(b) See comment (b) for k_0.

(c) See comment (c) for k_0.

(d) See comment (e) for k_0.

(e) See comment (f) for k_0. The negative temperature coefficient from the falloff extrapolation may indicate that the true k_∞ is still higher.

(f) Based on a fit of the data of Refs. 6–8.

(g) See Comments on Preferred Values.

Preferred Values

$k_\infty = 2\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta\log k_\infty = \pm0.3$ over the temperature range 200–300 K.

Comments on Preferred Values

See Comments on Preferred Values for k_0. Falloff representation with $F_c=0.45$ near 300 K.

References

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$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$

$\Delta H^\circ = 4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4 \pm 2) \times 10^{-13}$	250	Margitan, 1984[1]	FP-RF (a)
$(4 \pm 2) \times 10^{-13}$	298		
$(3.5 \pm 1) \times 10^{-13}$	298	Martin, Jourdain, and Le Bras, 1986[2]	DF-EPR (b)
$(4.37 \pm 0.66) \times 10^{-13}$	298	Gleason, Sinha, and Howard, 1987[3]	DF-CIMS (c)
$1.34 \times 10^{-12} \exp[-(330 \pm 70)/T]$	297–423	Gleason and Howard, 1988[4]	DF-CIMS (c)
$(4.37 \pm 0.66) \times 10^{-13}$	297		
Reviews and Evaluations			
$1.3 \times 10^{-12} \exp(-330/T)$	290–430	NASA, 1997[5]	(d)
$1.3 \times 10^{-12} \exp(-330/T)$	290–430	IUPAC, 1997[6]	(e)

Comments

(a) The reaction was studied at 53 and 133 mbar (40 and 100 Torr) of Ar diluent at 250 and 298 K. HO radicals were removed by the $HO + SO_2 + M \rightarrow HOSO_2 + M$ reaction, but the addition of O_2 and NO regenerated HO radicals by the reactions $HOSO_2 + O_2 \rightarrow HO_2 + SO_3$ and $HO_2 + NO \rightarrow HO + NO_2$. The effects of varying the amounts of O_2 were studied. The same rate coefficient was measured at 250 K and 298 K, but it was suggested[1] that this was due to a lack of precision in the technique rather than indicating that k is temperature independent.

(b) The effects of addition of NO and O_2 on the HO radical decays were studied. A system of 12 reactions was used to model the reaction system to obtain the rate coefficient k.

(c) HO radicals were produced by the $H + NO_2$ reaction, and SO_2 and O_2 were added down-stream. $HOSO_2$ was monitored by sampling into a flowing afterglow containing Cl^- ions. SO_3^- ions, formed by the reaction $Cl^- + HOSO_2 \rightarrow SO_3^- + HCl$, were detected by quadrupole MS. The SO_3 product of the reaction was also detected by $Cl^- + SO_3 + M \rightarrow (ClSO_3)^- + M$ with MS measurement of $(ClSO_3)^-$. The total pressure was varied over the range 2.7–10.7 mbar (2–8 Torr), and no change in k was observed, allowing an upper limit of 3.4×10^{-31} cm^6 molecule^{-2} s^{-1} ($M = N_2$) for the rate coefficient for the reaction $HOSO_2 + O_2 + M \rightarrow HOSO_2O_2 + M$ to be set.

(d) Based on the studies of Gleason *et al.*[3] and Gleason and Howard.[4]

(e) See Comments on Preferred Values.

Preferred Values

$k = 4.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.3 \times 10^{-12} \exp(-330/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–430 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

In the earlier studies,[1,2] HO radical decays due to the reaction $HO + SO_2 + M \rightarrow HOSO_2 + M$ were monitored in the presence of NO and O_2. The reaction sequence $HOSO_2 + O_2 \rightarrow HO_2 + SO_3$ and $HO_2 + NO \rightarrow HO + NO_2$ then regenerates HO radicals. Modeling of the NO decay led to the rate coefficient k. This method of determining k is less direct than the more recent measurements of Gleason and Howard[4] and of Gleason *et al.*,[3] where $HOSO_2$ radicals were monitored by MS. We therefore accept the temperature-dependent expression obtained by Gleason and Howard.[4] The earlier results,[1,2] though less precise, are in good agreement with the preferred values, which are identical to those in our previous evaluation, IUPAC, 1997.[6]

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HO + OCS → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.3\times10^{-12}\exp[-(2300\pm100)/T]$	300–517	Leu and Smith, 1981[1]	DF-RF (a)
$(6\pm4)\times10^{-16}$	300		
$1.13\times10^{-13}\exp[(-1200\pm400)/T]$	255–483	Cheng and Lee, 1986[2]	DF-RF (b)
$(2.0^{+0.4}_{-0.8})\times10^{-15}$	300		
$(1.92\pm0.25)\times10^{-15}$	298	Wahner and Ravishankara, 1987[3]	FP/PLP-LIF (c)
Reviews and Evaluations			
$1.1\times10^{-13}\exp(-1200/T)$	250–490	NASA, 1997[4]	(d)
$1.1\times10^{-13}\exp(-1200/T)$	250–500	IUPAC, 1997[5]	(e)

Comments

(a) The measured HO radical decay rates were corrected for the presence of H_2S in the OCS sample used ($0.01\pm0.003\%$ H_2S for the experiments at 300–421 K and $0.04\pm0.01\%$ H_2S for the experiments at 517 K). At 300 K the measured rate coefficient, uncorrected for the presence of H_2S, was 1.0×10^{-15} cm^3 molecule^{-1} s^{-1}.

(b) The purity of OCS was checked by FTIR spectroscopy, showing that H_2S was present at less than 0.005%. The measured rate coefficient k was independent of pressure [1.2–7.9 mbar (0.9–5.9 Torr)] and the addition of O_2 (up to 18% or 0.36 mbar of O_2).

(c) The rate coefficient k was independent of pressure [120–400 mbar (90–300 Torr)], the nature of buffer gas, and the addition of O_2 (up to 48 mbar).

(d) Based on the results of Cheng and Lee[2] and Wahner and Ravishankara.[3]

(e) See Comments on Preferred Values.

Preferred Values

$k = 2.0\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.1\times10^{-13}\exp(-1200/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–490 K.

Reliability

$\Delta\log k = \pm0.3$ at 298 K.

$\Delta(E/R) = \pm500$ K.

Comments on Preferred Values

The rate coefficients measured by Cheng and Lee[2] and Wahner and Ravishankara[3] are approximately a factor of 3 higher at 298 K than the earlier value of Leu and Smith.[1] This may be due to the corrections applied by Leu and Smith[1] to account for the presence of traces of H_2S in their system since in the absence of any correction to the measured rate coefficient of Leu and Smith[1] there is reasonable agreement between the studies.[1–3] Cheng and Lee[2] took care to keep the H_2S level in their OCS very low and this, together with the confirmatory measurements of Wahner and Ravishankara,[3] leads us to recommend their values. These recommendations are compatible with the earlier upper limits given by Atkinson *et al.*[6] and Ravishankara *et al.*,[7] but not with the higher value obtained by Kurylo,[8] which may have been due to the occurrence of interfering secondary chemistry and/or excited state reactions. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[5]

Kurylo and Laufer[9] have suggested that the reaction proceeds through adduct formation, as found for the reaction of HO with CS_2, followed by decomposition of the adduct to yield mainly HS + CO_2. This is supported by the product study of Leu and Smith[1] at 517 K. However, in contrast to the HO + CS_2 reaction, there is no marked effect of O_2 on the rate coefficient. Furthermore, very little oxygen atom exchange between $H^{18}O$ and OCS is found,[10] which may suggest that any adduct formed is weakly bound and short-lived.

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$HO + CS_2 + M \rightarrow HOCS_2 + M$ (1)

$HO + CS_2 \rightarrow HS + OCS$ (2)

$\Delta H°(1) = -46.0$ kJ·mol^{-1}
$\Delta H°(2) = -156$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_{01} [M]/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1×10^{-12} at 93 mbar [N_2]	247–299	Hynes, Wine, and Nicovich, 1988[1]	PLP-LIF (a)
6×10^{-13} at 40 mbar [N_2]	259–318	Murrells, Lovejoy, and Ravishankara, 1990[2]	PLP-LIF (b)
7.2×10^{-14} at 31 mbar [He]	298	Diau and Lee, 1991[3]	PLP-LIF (c)
3.4×10^{-13} at 43 mbar [Ar]	246		
Reviews and Evaluations			
8.0×10^{-31} [N_2]	270–300	IUPAC, 1997[4]	(d)

Comments

(a) Photolysis of H_2O_2 at 248 nm in mixtures of CS_2 and He, N_2, air, or O_2. Pressure range 87–920 mbar (65–690 Torr).

(b) Photolysis of H_2O_2 at 248 nm or 266 nm in mixtures of CS_2 and He–N_2 or He–SF_6. Pressure range 12–80 mbar (9–60 Torr). The effect of O_2 [0.7–20 mbar (0.5–15 Torr)] on the rate was studied.

(c) Photolysis of H_2O_2 at 248 nm in mixtures of CS_2 and added He or Ar. Pressure range 12–360 mbar (9–270 Torr) of Ar or He. Effect of CS_2 on rate was studied.

(d) See Comments on Preferred Values.

Preferred Values

$k_{01} = 8\times10^{-31}$ [N_2] cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–320 K.

Reliability

$\Delta \log k_{01} = \pm 0.5$.

Comments on Preferred Values

Because of the low thermal stability of $HOCS_2$, experimental studies have to account for the re-dissociation of the adduct. After clarification of the mechanism, rate coefficients now can be specified. The preferred values are based on a combination of the data for $M=N_2$ from Refs. 1 and 2, with a falloff representation. The data and a falloff representation indicate that the low-pressure limit is approached within 10% only at pressures below about 27 mbar (20 Torr). The strong temperature dependence of k_{01} for M=He derived in Ref. 3 ($E/R = -1610$ K) is apparently not consistent with the results from Refs. 1 and 2. It appears that reaction (2) is slow, with a rate coefficient of $k_2 < 2\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K (see next data sheet). The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[4]

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
5.8×10^{-12} at 0.91 bar [N_2]	250–270	Hynes, Wine, and Nicovich, 1988[1]	PLP-LIF (a)
3.1×10^{-12} at 0.88 bar [N_2]	297		
1.9×10^{-12} at 1.01 bar [Ar]	298	Bulatov *et al.*, 1988[5]	PLP-LIF (b)
1.3×10^{-12} at 1.01 bar [air]	295	Becker *et al.*, 1990[6]	PLP-LIF (c)
Reviews and Evaluations			
8×10^{-12}	250–300	IUPAC, 1997[4]	(d)

Comments

(a) See comment (a) for k_0.

(b) Mixtures of O_2–H_2O–CS_2–Ar. The rates of $HOCS_2$ formation and decomposition were measured, with an equilibrium constant of $K_c=2.6\times10^{-17}$ cm^3 molecule^{-1}.

(c) H_2O_2 photolyzed at 248 nm in mixtures of CS_2 and N_2–O_2 or Ar–O_2. The partial pressure of O_2 was in the range 0.32–1013 mbar (0.24–760 Torr), at a total pressure of 1.01 bar (760 Torr).

(d) See Comments on Preferred Values.

Preferred Values

$k_{\infty 1}=8\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–300 K.

Reliability

$\Delta\log k_{\infty 1}=\pm0.5$ over the temperature range 250–300 K.

Comments on Preferred Values

The preferred rate coefficient $k_{\infty 1}$ is based on a falloff representation of the data from Refs. 1 and 2, with high-pressure data mostly from Ref. 1, and is identical to that in our previous evaluation, IUPAC, 1997.[4] The largest weight is given to the measurements near 250 K where decomposition of the adduct and the subsequent kinetics are of comparably minor influence in contrast to the room temperature experiments. A falloff curve with an estimated value of $F_c=0.8$ was employed for extrapolation. Experiments at 1 bar total pressure are apparently still far below the high-pressure limit. An extensive discussion of the complicated mechanism is given in Refs. 7–9 as well as in Refs. 1, 2, and 10. Rate expressions combining adduct formation, dissociation, and subsequent reaction with O_2 have been proposed which are not reproduced here (see also data sheets on $HOCS_2$ + M and $HOCS_2$ + O_2). More experiments separating the individual steps are required.

References

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$HO + CS_2 \rightarrow HS + OCS$

$\Delta H^\circ = -156$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<9.9\times10^{-15}$	251	Wine, Shah, and Ravishankara, 1980[1]	FP-RF
$<1.5\times10^{-15}$	297		
$<1.6\times10^{-15}$	363		
$\leq2\times10^{-15}$	299	Murrells, Lovejoy, and Ravishankara, 1990[2]	PLP-LIF
$<3\times10^{-15}$	330	Lovejoy *et al.*, 1990[3]	DF-LMR (a)
Reviews and Evaluations			
$<1.5\times10^{-15}$	298	NASA, 1997[4]	(b)
$<2\times10^{-15}$	298	IUPAC, 1997[5]	(c)

Comments

(a) Based on the observed HS radical yield of <50% of the HO radicals consumed and a total HO radical loss rate of 6×10^{-15} cm^3 molecule^{-1} s^{-1}.

(b) Based on the data of Wine *et al.*[1]

(c) Based on the data of Murrells *et al.*[2]

Preferred Values

$k<2\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The upper limit to the preferred value is based on the absolute rate coefficient studies of Wine *et al.*[1] and Murrells *et al.*,[2] and is consistent with the study of Lovejoy *et al.*[3] in which HS radical formation and HO radical decays were measured. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[5]

References

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[4] NASA Evaluation No. 12, 1997 (see references in Introduction).

[5] IUPAC, Supplement V, 1997 (see references in Introduction).

$HOCS_2 + M \rightarrow HO + CS_2 + M$

$\Delta H^\circ = 46.0$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0 [M]/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.3×10^4 at 0.100 bar [N_2]	255	Hynes, Wine, and Nicovich, 1988[1]	PLP-LIF (a)
2.6×10^4 at 0.108 bar [N_2]	280		
4.3×10^3 at 0.020 bar [N_2]	277	Murrells, Lovejoy, and Ravishankara, 1990[2]	PLP-LIF (b)
3.0×10^4 at 0.032 bar [N_2]	298		
7.8×10^3 at 0.031 bar [He]	298	Diau and Lee, 1991[3]	PLP-LIF (c)
1.3×10^3 at 0.043 bar [Ar]	246		
Reviews and Evaluations			
4.8×10^{-14} [N_2]	298	IUPAC, 1997[4]	(d)
1.6×10^{-6} exp($-5160/T$) [N_2]	250–300		

Comments

(a) Photolysis at 298 K in mixtures of CS_2 and He, N_2, air, or O_2. Pressure range 87–920 mbar (65–690 Torr). A value of K_c (297 K)$=1.39\times10^{-17}$ cm^3 $molecule^{-1}$ was obtained for the equilibrium HO + CS_2 $\rightleftharpoons$ $HOCS_2$ as well as K_c (247 K) $= 3.5\times10^{-16}$ cm^3 $molecule^{-1}$.

(b) Photolysis of H_2O_2 at 248 nm and 266 nm in He–N_2–CS_2 or He–SF_6–CS_2 mixtures. Pressure range=12–80 mbar (9–60 Torr). The effect of O_2 [0.7–20 mbar (0.5–15 Torr)] on the rate was studied. K_c (299 K)$=1.7\times10^{-17}$ cm^3 $molecule^{-1}$, K_c (274 K)$=7.5\times10^{-17}$ cm^3 $molecule^{-1}$, and K_c (249 K)$=5.1\times10^{-16}$ cm^3 $molecule^{-1}$ were obtained for the equilibrium HO + CS_2 $\rightleftharpoons$ $HOCS_2$.

(c) Photolysis of H_2O_2 at 248 nm in mixtures of CS_2 and He or Ar. Pressure range 12–360 mbar (9–270) Torr of He. The effect of CS_2 on the rate was studied. K_c (298 K)$=0.87\times10^{-17}$ cm^3 $molecule^{-1}$, K_c (273 K)$=4.2\times10^{-17}$ cm^3 $molecule^{-1}$ and K_c (249 K)$=2.6\times10^{-16}$ cm^3 $molecule^{-1}$ were obtained for the equilibrium HO + CS_2 $\rightleftharpoons$ $HOCS_2$.

(d) See Comments on Preferred Values.

Preferred Values

$k_0=4.8\times10^{-14}$ $[N_2]$ s^{-1} at 298 K.

$k_0=1.6\times10^{-6}\exp(-5160/T)$ $[N_2]$ s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta\log k_0=\pm0.5$ at 298 K.

$\Delta(E/R)=\pm500$ K.

Comments on Preferred Values

The preferred values are based on a falloff representation from Refs. 1 and 2 of the data for the reverse process HO + CS_2 + M $\rightarrow$ $HOCS_2$ + M and the determination of the equilibrium constant from the same work. The data from Ref. 3 are not consistent with this evaluation (with differences of about a factor of 2). $HOCS_2$ formation and dissociation are characterized by an equilibrium constant of $K_c=5.16\times10^{-25}\exp(5160/T)$ cm^3 $molecule^{-1}$, such as derived from the data of Ref. 2. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[4]

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
3.1×10^4 at 0.907 bar $[N_2]$	252	Hynes, Wine, and Nicovich, 1988[1]	PLP-LIF (a)
6.5×10^4 at 0.913 bar $[N_2]$	270		
2.2×10^5 at 0.880 bar $[N_2]$	297		
7.4×10^4 at 200 mbar [Ar]	298	Bulatov *et al.*, 1988[5]	PLP-LIF (b)
Reviews and Evaluations			
4.8×10^5	298	IUPAC, 1997[4]	(c)
$1.6\times10^{13}\exp(-5160/T)$	*250–300*		

Comments

(a) See comment (a) for k_0.

(b) Photolysis of O_3 in the presence of H_2O, CS_2, and Ar. Rate of $HOCS_2$ formation and decomposition measured and evaluated with an equilibrium constant of $K_c=2.6\times10^{-17}$ cm^3 $molecule^{-1}$.

(c) See Comments on Preferred Values.

Preferred Values

$k_\infty=4.8\times10^5$ s^{-1} at 298 K.

$k_\infty=1.6\times10^{13}\exp(-5160/T)$ s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta\log k_\infty=\pm0.5$ at 298 K.

$\Delta(E/R)=\pm500$ K.

Comments on Preferred Values

The preferred values are based on the falloff extrapolation of the data for the reverse reaction and the equilibrium constant $K_c=5.16\times10^{-25}\exp(5160/T)$ cm^3 $molecule^{-1}$ from Ref. 2, and are identical to those in our previous evaluation, IUPAC, 1997.[4] Falloff curves are constructed with an estimated value of $F_c=0.8$. The small pre-exponential factor of k_∞ can be explained theoretically as being due to the low bond energy of $HOCS_2$. For discussion of the mechanism see Refs. 1, 2 and 6–9.

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$HOCS_2 + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.4\times10^{-14}\exp[(217\pm301)/T]$	251–348	Hynes, Wine, and Nicovich, 1988[1]	PLP-LIF (a)
$(3.26\pm0.70)\times10^{-14}$	295±1		
$2.6\pm1.0)\times10^{-14}$	249–299	Murrells, Lovejoy, and Ravishankara, 1990[2]	PLP-LIF
$(2.4\pm0.4)\times10^{-14}$	273	Lovejoy, Kroeger, and Ravishankara, 1990[3]	PLP-LIF (b)
$(3.1\pm0.6)\times10^{-14}$	298	Diau and Lee, 1991[4]	PLP-LIF (c)
Reviews and Evaluations			
2.9×10^{-14}	240–350	NASA, 1997[5]	(d)
3.0×10^{-14}	240–300	IUPAC, 1997[6]	(e)

Comments

(a) The effects of He, N_2, air, and O_2 were studied, and the total pressure was varied over the range 87–920 mbar (65–690 Torr). If the rate coefficient k is assumed to be temperature independent, the average of the measured values is $(2.9\pm1.1)\times10^{-14}$ cm^3 molecule^{-1} s^{-1} over the range 251–348 K.

(b) A rate coefficient for the reaction of the $DOCS_2$ radical with O_2 of $(2.3\pm0.4)\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 273 K was also measured,[3] showing no significant deuterium isotope effect and hence no evidence for a direct H-atom abstraction process.

(c) Values of $k(HOCS_2 + NO)=(7.3\pm1.8)\times10^{-13}$ cm^3 molecule^{-1} s^{-1} and $k(HOCS_2 + NO_2)=(4.2\pm1.0)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} were also obtained in this work. The latter is the first measurement of the rate coefficient for the reaction with NO_2. The rate coefficient for the reaction with NO is in good agreement with the value of $k(HOCS_2 + NO)=(1.1\pm0.3)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} measured by Lovejoy *et al.*[7] at 249 K.

(d) Based on the data of Hynes *et al.*,[1] Murrells *et al.*,[2] and Diau and Lee.[4]

(e) Based on the data of Hynes *et al.*[1] and Murrells *et al.*[2]

Preferred Values

$k=2.8\times10^{-14}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 240–350 K.

Reliability

$\Delta\log k=\pm0.15$ over the temperature range 240–350 K.

Comments on Preferred Values

The reaction of $HOCS_2$ with O_2 is an intermediate step in the overall reaction of the HO radical with CS_2 under atmospheric conditions. The $HOCS_2$ is formed by the addition of HO to CS_2; once formed it may undergo dissociation back to HO and CS_2 or react with O_2.

The four studies[1–4] of the kinetics of this reaction, all using the same general experimental technique, are in good agreement. The rate coefficients measured by Hynes *et al.*[1] over the temperature range 249–348 K could equally well be represented by either the Arrhenius expression in the table cited with a small negative temperature dependence or by a temperature-independent rate coefficient. The results of Murrells *et al.*[2] favor the latter. For the preferred values we assume the rate coefficient to be temperature independent over the temperature range studied and take a mean of the values of Hynes *et al.*,[1] Murrells *et al.*,[2] Lovejoy *et al.*,[3] and Diau and Lee.[4]

Lovejoy *et al.*[7] used LP-LIF to measure an HO_2 radical formation yield of 0.95±0.15 (249–300 K) from the reaction of the HO radical with CS_2 in the presence of O_2 (by converting HO_2 radicals to HO radicals by reaction with NO), and used DF-CIMS to measure an SO_2 yield from the HO radical reaction with CS_2 in the presence of O_2 of 0.90±0.20 at 340 K.

The main steps in the atmospheric oxidation of CS_2 initiated by HO are then

$$HO + CS_2 \rightleftharpoons HOCS_2$$

followed by the overall reaction

$$HOCS_2 + 2O_2 \rightarrow HO_2 + SO_2 + OCS.$$

In the atmosphere, reaction of the $HOCS_2$ with O_2 predominates over reaction with NO or NO_2.

The study by Stickel *et al.*[8] has provided some further insight into the mechanism of this complex reaction. Two types of experiments were performed. In one, the reaction was initiated by pulsed laser photolysis and product concentrations monitored in real time by tunable diode laser absorption spectroscopy. In the other, continuous photolysis was used with FTIR product detection. Products observed were OCS, SO_2, CO, and CO_2. Both experiments gave concordant values for the yields of OCS and CO of 0.83±0.08 and 0.16 ±0.03, respectively. The yield of CO_2 was small (<0.01). The overall yield of SO_2 (1.15±0.10) was made up of two components, a ''prompt'' value of 0.84±0.20 resulting from SO_2 produced in a primary channel of the reaction and a longer time component assumed due to production of SO_2 from reaction of O_2 with S or SO produced in another primary channel. The data of Stickel *et al.*[8] thus suggest two primary channels, the major one leading to OCS and SO_2 and a minor channel leading to CO and SO. There are a number of possible reaction channels leading directly to these species or to their precursors which subsequently produce them on a very short time scale.

Lovejoy *et al.*[9] have used DF-CIMS to investigate the products of the reaction of the $H^{18}O$ radical with CS_2 in $^{16}O_2$ at ~340 K, and observed the formation of $^{16}OS^{18}O$ with a yield of 0.90±0.20. $S^{16}O_2$ formation was observed,[9] and this may be consistent with the formation of S atoms or SO radicals.[8]

These studies suggest that the reaction pathway

$$HOCS_2 + O_2 \rightarrow HCO + SO_2 + S$$

followed by reactions of HCO and S to form HO_2 + CO and SO_2 accounts for ~15% of the overall reaction,[8] with the remainder (~85%) proceeding by[9]

$$HOCS_2 + O_2 \rightarrow HO_2 + CS_2O$$

$$CS_2O + O_2 \rightarrow OCS + SO_2$$

or

$$HOCS_2 + O_2 \rightarrow HOSO + OCS$$

$$HOSO + O_2 \rightarrow HO_2 + SO_2$$

or

$$HOCS_2 + O_2 \rightarrow HOCS + SO_2$$

$$HOCS + O_2 \rightarrow HO_2 + OCS.$$

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HO + CH_3SH → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$8.89\times10^{-12}\exp[(398\pm151)/T]$	300–423	Atkinson, Perry, and Pitts, 1977[1]	FP-RF
$(3.39\pm0.34)\times10^{-11}$	300		
$1.15\times10^{-11}\exp[(338\pm100)/T]$	244–366	Wine *et al.*, 1981[2]	FP-RF
$(3.37\pm0.41)\times10^{-11}$	298		
$1.01\times10^{-11}\exp[(347\pm59)/T]$	254–430	Wine, Thompson, and Semmes, 1984[3]	FP-RF
3.24×10^{-11}	298		
3.69×10^{-11}	270	Hynes and Wine, 1987[4]	PLP-LIF (a)
3.17×10^{-11}	300		
Relative Rate Coefficients			
$(9.68\pm0.97)\times10^{-11}$	297±2	Cox and Sheppard, 1980[5]	RR (b)
$(3.72\pm0.37)\times10^{-11}$	300	Barnes *et al.*, 1986[6]	RR (c)
$(3.50\pm0.49)\times10^{-11}$	313		
Reviews and Evaluations			
$9.9\times10^{-12}\exp(360/T)$	240–430	NASA, 1997[7]	(d)
$9.9\times10^{-12}\exp(356/T)$	240–430	IUPAC, 1997[8]	(e)

Comments

(a) The rate coefficients were observed to be independent of total pressure and of the presence or absence of O_2, up to 196 mbar (147 Torr) O_2 (at 270 K) or 933 mbar (700 Torr) O_2 (at 300 K).

(b) HO radicals were generated by the photolysis of HONO–NO–air mixtures at atmospheric pressure. The decay of CH_3SH was measured relative to that of C_2H_4 by GC, and the relative rate coefficient placed on an absolute basis by use of a rate coefficient of $k(HO + C_2H_4)=8.57\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 297 K and atmospheric pressure of air.[9]

(c) HO radicals were generated by the photolysis of H_2O_2 in N_2 at atmospheric pressure. The decay of CH_3SH was measured relative to that for propene by GC, and the relative rate coefficients placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{propene})=4.85\times10^{-12}\exp(504/T)$ cm^3 molecule^{-1} s^{-1} at atmospheric pressure of air.[9]

(d) Derived from the absolute rate coefficient data of Atkinson *et al.*,[1] Wine *et al.*,[2,3] and Hynes and Wine.[4]

(e) See Comments on Preferred Values.

Preferred Values

$k=3.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=9.9\times10^{-12}\exp(356/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–430 K.

Reliability

$\Delta\log k=\pm0.10$ at 298 K.

$\Delta(E/R)=\pm100$ K.

Comments on Preferred Values

The preferred values are based upon a least-squares analysis of the absolute rate coefficients of Atkinson *et al.*,[1] Wine *et al.*,[2,3] and Hynes and Wine,[4] which are in excellent agreement. The recent relative rate study of Barnes *et al.*[6] shows that erroneous rate coefficient data are obtained in the presence of O_2 and NO, thus accounting for the much higher value of Cox and Sheppard.[5] The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[8]

The study of Hynes and Wine[4] shows that there is no observable effect of O_2 on the measured rate coefficient, and the rate coefficients at 298 K for the reactions of the HO radical with CD_3SH (Ref. 4) and CH_3SD (Ref. 3) are within 15% of that for HO + CH_3SH. These data indicate[3,4] that the reaction proceeds via initial addition of HO to form the adduct $CH_3S(OH)H$.[3]

Tyndall and Ravishankara[10] have determined, by monitoring the CH_3S radical by LIF, a CH_3S radical yield from the reaction of the HO radical with CH_3SH of 1.1±0.2. The reaction then proceeds by

$$HO + CH_3SH \rightarrow [CH_3S(OH)H] \rightarrow H_2O + CH_3S.$$

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$HO + CH_3SCH_3 \rightarrow H_2O + CH_2SCH_3$ (1)

$\rightarrow CH_3S(OH)CH_3$ (2)

$\Delta H^\circ(1) = -107.1$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_1 = 1.15 \times 10^{-11} \exp[-(338 \pm 100)/T]$	248–363	Wine *et al.*, 1981[1]	FP-RF
$k_1 = (4.26 \pm 0.56) \times 10^{-12}$	298		
$(6.28 \pm 0.10) \times 10^{-12}$ (1 bar of air)	298	Hynes, Wine, and Semmes, 1986[2]	PLP-LIF (a)
$k_1 = 1.36 \times 10^{-11} \exp[-(332 \pm 96)/T]$	276–397	Hynes, Wine, and Semmes, 1986[2]	FP-RF
$k_1 = 4.46 \times 10^{-12}$	298		
$k_1 = 1.18 \times 10^{-11} \exp[-(236 \pm 150)/T]$	260–393	Hsu, Chen, and Lee, 1987[3]	DF-RF (b)
$k_1 = (5.54 \pm 0.15) \times 10^{-12}$	298		
$k_1 = 1.35 \times 10^{-11} \exp[-(285 \pm 135)/T]$	297–368	Abbatt, Fenter, and Anderson, 1992[4]	DF-LIF (c)
$k_1 = (4.98 \pm 0.46) \times 10^{-12}$	297±2		
$k_1 = (4.95 \pm 0.35) \times 10^{-12}$	298	Barone, Turnipseed, and Ravishankara, 1996[5]	PLP-LIF
Branching Ratios			
$k_1/k = 0.84 \pm 0.15$	298	Stickel, Zhao, and Wine, 1993[6]	(d)
Reviews and Evaluations			
$k_1 = 1.13 \times 10^{-11} \exp(-254/T)$	248–397	Atkinson, 1994[7]	(e)
$k_2 = \dfrac{1.68 \times 10^{-42}[O_2]\exp(7812/T)}{[1 + 5.53 \times 10^{-31}[O_2]\exp(7460/T)]}$	260–360		
$k_1 = 1.2 \times 10^{-11} \exp(-260/T)$	240–400	NASA, 1994[8]	(f)
$k = 4.8 \times 10^{-12} + \{(4.1 \times 10^{-31}[O_2])/(1 + 4.1 \times 10^{-20}[O_2])\}$	298	IUPAC, 1997[9]	(g) (h)
$k_1 = 1.13 \times 10^{-11} \exp(-254/T)$	250–400		(h)
$k_2 = 1.7 \times 10^{-42}[O_2]\exp(7810/T)/\{1 + 5.5 \times 10^{-31}[O_2]\exp(7460/T)\}$	260–360		(g)

Comments

(a) Detection of HO, with the effects of O_2 being investigated over the temperature range 261–321 K. The measured rate coefficient was observed to depend linearly on the O_2 concentration, and the rate coefficient given in the table is that measured at 1 bar (750 Torr) total pressure of air. The rate coefficient measured in the absence of O_2 is ascribed to reaction (1), with the adduct formed in (2) rapidly dissociating back to the reactants. In the presence of O_2 this adduct reacts rapidly with O_2, and hence the measured rate coefficient increases with the O_2 concentration.

(b) Rate coefficient not affected by the addition of up to 1.3 mbar (1 Torr) of O_2.

(c) HO generated from the $H + NO_2$ reaction. The total pressure was varied over the range 14.1–130 mbar (10.6–97.5 Torr) of N_2. The measured rate coefficient was invariant to the total pressure over this range.

(d) For the reaction $DO + CH_3SCH_3$, HDO was monitored by tunable diode laser absorption spectroscopy, and the branching ratio obtained by assuming a unit HDO yield from the DO radical reaction with *n* hexane and cyclohexane. The branching ratio was independent of total pressure of N_2 [13–40 mbar (10–30 Torr)], temperature (298–348 K) and replacement of 13 mbar (10 Torr) total pressure of N_2 by 13 mbar total pressure of O_2. From the temporal profiles of the HDO signals, rate coefficients k_1 for the reaction of the DO radical with CH_3SCH_3 of $(5.4 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 13 mbar (10 Torr) N_2, $(5.8 \pm 1.9) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 40 mbar (30 Torr) N_2, and $(4.4 \pm 1.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 348 K and 13 mbar (10 Torr) N_2 were also obtained, in agreement with the rate coefficients for the HO radical reaction.

(e) The rate coefficient for the abstraction (1) was derived from the data of Wine *et al.*,[1] Hynes *et al.*,[2] Hsu *et al.*,[3] and Abbatt *et al.*[4] The rate coefficient for the addition process (2) is that of Hynes *et al.*[2]

(f) The rate coefficient for the abstraction process (1) was derived from the absolute rate coefficient data of Wine *et al.*,[1] Hynes *et al.*,[2] Hsu *et al.*,[3] Abbatt *et al.*,[4] and Barone *et al.*[5]

(g) See Comments on Preferred Values.

(h) The rate coefficient k_1 was derived from the data of Wine *et al.*,[1] Hynes *et al.*,[2] Hsu *et al.*,[3] and Abbatt *et al.*[4]

Preferred Values

$k = 4.8\times10^{-12} + \{(4.1\times10^{-31}\,[O_2])/(1+4.1\times10^{-20}\,[O_2]\}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 4.8\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k_1 = 1.13\times10^{-11}\exp(-253/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–400 K.

$k_2 = 1.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar air.

$k_2 = 1.7\times10^{-42}\,[O_2]\,\exp(7810/T)/\{1+5.5\times10^{-31}\,[O_2]\times\exp(7460/T)\}$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–360 K.

Reliability

$\Delta\log k_1 = \pm0.10$ at 298 K.

$\Delta(E_1/R) = \pm150$ K.

$\Delta\log k_2 = \pm0.3$ at 1 bar of air.

Comments on Preferred Values

It is now recognized[2,7,8,10] that this reaction proceeds via the two reaction steps (1) and (2). The $CH_3S(OH)CH_3$ adduct radical decomposes sufficiently rapidly such that in the absence of O_2 only the rate coefficient k_1 is measured. In the presence of O_2 the $CH_3S(OH)CH_3$ radical reacts by $CH_3S(OH)CH_3 + O_2 \rightarrow$ products. Hence only in the presence of O_2 is the addition channel (2) observed, with the rate coefficient being dependent on the O_2 concentration (but, to at least a first approximation, not on the concentration of other third bodies such as N_2, Ar, or SF_6).[2]

The relative rate study of Wallington *et al.*[11] showed that previous relative studies carried out in the presence of NO are dubious. The most recent absolute rate coefficients measured in the absence of O_2[1–5,10–13] agree that the earlier absolute rate coefficients of Atkinson *et al.*[14] and Kurylo[15] are erroneously high, and those of Mac Leod *et al.*[16] were in error because of wall reactions.[12] The preferred rate coefficients k_1 for the abstraction channel (1) are based on the studies of Wine *et al.*,[1] Hynes *et al.*,[2] Hsu *et al.*,[3] Abbatt *et al.*,[4] and Barone *et al.*,[5] and the rate coefficient for the HO radical addition channel (2) utilizes the data of Hynes *et al.*[2] While the expression for k_2 is strictly valid only for 0.93 bar of air[2] (where the rate coefficients for HO addition to CH_3SCH_3 and the reverse dissociation step may be in the falloff region), this equation fits the room temperature data obtained at pressures of air from 0.07 to 0.93 bar. The preferred values are almost identical to those in our previous evaluation, IUPAC, 1997.[9]

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HO + $CH_3SSCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$5.9\times10^{-11}\exp[(380\pm160)/T]$	249–367	Wine *et al.*, 1981[1]	FP-RF
$(1.98\pm0.18)\times10^{-10}$	298		
$6.2\times10^{-11}\exp[(410\pm210)/T]$	297–366	Abbatt, Fenter, and Anderson, 1992[2]	DF-LIF
$(2.39\pm0.30)\times10^{-10}$	297		
$(2.4\pm0.9)\times10^{-10}$	298	Dominé and Ravishankara, 1992[3]	(a)
Relative Rate Coefficients			
$(2.40\pm0.86)\times10^{-10}$	297±2	Cox and Sheppard, 1980[4]	RR (b)
Reviews and Evaluations			
$7.0\times10^{-11}\exp(350/T)$	249–367	Atkinson, 1994[5]	(c)
$6.0\times10^{-11}\exp(400/T)$	249–367	NASA, 1997[6]	(d)
$7.0\times10^{-11}\exp(350/T)$	250–370	IUPAC, 1997[7]	(c)

Comments

(a) Discharge-flow system with photoionization-MS detection of CH_3SOH and CH_3S product species. The temporal profiles of these product species yielded the cited rate coefficient. The CH_3S radical formation yield from the HO radical reaction with CH_3SSCH_3 was measured to be 0.28 ± 0.20 using a pulsed laser photolysis system with LIF detection of CH_3S. The photolysis of CH_3SSCH_3 at 266 nm was used to normalize the CH_3S radical signal, with the CH_3S radical formation yield from the photolysis of CH_3SSCH_3 being 1.8 ± 0.2 at 248 nm.[8]

(b) A rate coefficient ratio of $k(\mathrm{HO} + CH_3SSCH_3)/k(\mathrm{HO} + \mathrm{ethene})=28\pm10$ was measured by GC analyses of CH_3SSCH_3 and ethene in irradiated HONO–CH_3SSCH_3–ethene–air mixtures at atmospheric pressure. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\mathrm{HO} + \mathrm{ethene})=8.57\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 297 K and atmospheric pressure of air.[9]

(c) Obtained from a least-squares analysis of the absolute rate coefficients of Wine *et al.*[1] and Abbatt *et al.*[2]

(d) Based on the absolute rate coefficients of Wine *et al.*[1] and Abbatt *et al.*[2] and the room temperature relative rate coefficient of Cox and Sheppard.[4]

Preferred Values

$k=2.3\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=7.0\times10^{-11}\exp(350/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–370 K.

Reliability

$\Delta\log k=\pm0.10$ at 298 K.

$\Delta(E/R)=\pm200$ K.

Comments on Preferred Values

The absolute rate coefficients of Wine *et al.*,[1] Abbatt *et al.*,[2] and Dominé and Ravishankara[3] are in excellent agreement. The preferred values are derived from a least-squares analysis of the absolute rate coefficients of Wine *et al.*[1] and Abbatt *et al.*,[2] and are identical to those in our previous evaluation, IUPAC, 1997.[7] The magnitude of the rate coefficient and the negative temperature dependence indicates that the reaction proceeds by initial HO radical addition to the S atoms:

$$\mathrm{HO} + CH_3SSCH_3 \rightarrow CH_3SS(OH)CH_3.$$

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$HO_2 + H_2S \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5\pm1)\times10^{-12}$	298	Bulatov *et al.*, 1990[1]	FP-A (a)
$<3\times10^{-15}$	298	Mellouki and Ravishankara, 1994[2]	DF-LMR
Reviews and Evaluations			
$<3.0\times10^{-15}$	298	NASA, 1997[3]	(b)

Comments

(a) HO_2 radicals were monitored by intracavity laser absorption in the near IR.

(b) Based on the results of Mellouki and Ravishankara.[2]

Preferred Values

$k<3\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This upper limit is taken from the study of Mellouki and Ravishankara.[2] It is consistent with the upper limits reported for the corresponding reactions of HO_2 with CH_3SH and CH_3SCH_3. This upper limit is three orders of magnitude lower than the value reported by Bulatov *et al.*[1] from a flash photolysis study using intracavity laser absorption in the near infrared to monitor HO_2. The results of the recent, more direct study[2] are preferred.

References

[1] V. P. Bulatov, S. I. Yereshahuk, F. N. Dzegilenko, O. M. Sarkisov, and V. N. Khabarov, Khim Fiz. **9**, 1214 (1990).

[2] A. Mellouki and A. R. Ravishankara, Int. J. Chem. Kinet. **26**, 355 (1994).

[3] NASA Evaluation No. 12, 1997 (see references in Introduction).

$HO_2 + SO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.0\pm0.2)\times10^{-15}$	300	Payne, Stief, and Davis, 1973[1]	RR (a)
$\leq1\times10^{-18}$	300	Graham *et al.*, 1979[2]	RR (b)
$\leq4.3\times10^{-17}$	~298	Burrows *et al.*, 1979[3]	RR (c)
Reviews and Evaluations			
$<1.0\times10^{-18}$	298	NASA, 1997[4]	(d)
$<1\times10^{-18}$	298	IUPAC, 1997[5]	(e)

Comments

(a) Photolysis of $H_2O-CO-{}^{18}O_2-N_2$ mixtures at 184.9 and 253.7 nm, with formation of $C^{16}O_2$ and $C^{16,18}O_2$ being monitored by MS. $k/k^{1/2}(HO_2 + HO_2)$ was determined. The value tabulated here was calculated using the effective value of $k(HO_2 + HO_2)$ in this system of 4.4×10^{-12} cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Thermal decomposition of HO_2NO_2 monitored by IR absorption. Upper limit to k derived from the absence of a detectable effect of added SO_2 on the HO_2NO_2 decay rate.

(c) DF-LMR study. $k/k(HO + H_2O_2)$ was determined. Value tabulated here was calculated using $k(HO + H_2O_2)=1.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) Accepted the upper limit to the rate coefficient of Graham *et al.*[2]

(e) See Comments on Preferred Values.

Preferred Values

$k<1\times10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The measurement of Burrows *et al.*[3] confirms that the reaction is slower than some earlier results[1] had suggested and supports the even lower upper limit set by Graham *et al.*,[2] which we take as the preferred value. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[5]

References

[1] W. A. Payne, L. J. Stief, and D. D. Davis, J. Am. Chem. Soc. **95**, 7614 (1973).

[2] R. A. Graham, A. M. Winer, R. Atkinson, and J. N. Pitts, Jr., J. Phys. Chem. **83**, 1563 (1979).

[3] J. P. Burrows, D. I. Cliff, G. W. Harris, B. A. Thrush, and J. P. T. Wilkinson, Proc. R. Soc. London Ser. A **368**, 463 (1979).

[4] NASA Evaluation No. 12, 1997 (see references in Introduction).

[5] IUPAC, Supplement V, 1997 (see references in Introduction).

$HO_2 + CH_3SH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<4\times10^{-15}$	298	Mellouki and Ravishankara, 1994[1]	DF-LMR
Reviews and Evaluations			
$<4.0\times10^{-15}$	298	NASA, 1997[2]	(a)

Comments

(a) Based on the results of Mellouki and Ravishankara.[1]

Preferred Values

$k<4\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This upper limit is taken from the study of Mellouki and Ravishankara.[1] It is consistent with the upper limits reported for the corresponding reactions of HO_2 with H_2S and CH_3SCH_3. It is also consistent with results noted in the Barnes *et al.*[3] study of the reactions of the HO radical with various sulfur compounds. In that publication[3] the authors stated that previous experiments in that laboratory had shown that the rate coefficients for reactions of HO_2 with thiols were $<1\times10^{-15}$ cm^3 molecule^{-1} s^{-1}.

References

[1] A. Mellouki and A. R. Ravishankara, Int. J. Chem. Kinet. **26**, 355 (1994).

[2] NASA Evaluation No. 12, 1997 (see references in Introduction).

[3] I. Barnes, V. Bastian, K. H. Becker, E. H. Fink, and W. Nelsen, J. Atmos. Chem. **4**, 445 (1986).

$HO_2 + CH_3SCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<5\times10^{-15}$	298	Mellouki and Ravishankara, 1994[1]	DF-LMR
Reviews and Evaluations			
$<5.0\times10^{-15}$	298	NASA, 1997[2]	(a)

Comments

(a) Based on the results of Mellouki and Ravishankara.[1]

Preferred Values

$k<5\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

This upper limit is taken from the study of Mellouki and Ravishankara.[1] It is consistent with the upper limits reported for the corresponding reactions of the HO_2 radical with H_2S and CH_3SH. It is also consistent with unpublished results of Niki, who in a study of the decay of CH_3SCH_3 in the presence of HO_2 in 1 bar air showed the reaction of HO_2 with CH_3SCH_3 to be very slow with $k < 1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (reported in Mellouki and Ravishankara[1] as a private communication from H. Niki).

References

[1] A. Mellouki and A. R. Ravishankara, Int. J. Chem. Kinet. **26**, 355 (1994).
[2] NASA Evaluation No. 12, 1997 (see references in Introduction).

$NO_3 + H_2S \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 3 \times 10^{-14}$	298±2	Wallington *et al.*, 1986[1]	FP-A
$<8 \times 10^{-16}$	298	Dlugokencky and Howard, 1988[2]	F-LIF
Relative Rate Coefficients			
$<3 \times 10^{-14}$	298	Cantrell *et al.*, 1987[3]	RR (a)
Reviews and Evaluations			
$<8.0 \times 10^{-16}$	298	NASA, 1997[4]	(b)
$<1 \times 10^{-15}$	298	IUPAC, 1997[5]	(c)

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5, and the rate coefficient placed on an absolute basis by use of an equilibrium constant for the $NO_3 + NO_2 \rightleftharpoons N_2O_5$ reactions of 3.41×10^{-11} cm^3 molecule^{-1}.[6]

(b) Based upon the upper limit to the rate coefficient determined by Dlugokencky and Howard.[2]

(c) See Comments on Preferred Values.

Preferred Values

$k < 1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred upper limit to the rate coefficient is based upon the absolute rate coefficient study of Dlugokencky and Howard,[2] and is identical to that in our previous evaluation, IUPAC, 1997.[5]

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys Chem. **90**, 5393 (1986).
[2] E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).
[3] C. A. Cantrell, J. A. Davidson, R. E. Shetter, B. A. Anderson, and J. G. Calvert, J. Phys. Chem. **91**, 6017 (1987).
[4] NASA Evaluation No. 12, 1997 (see references in Introduction).
[5] IUPAC, Supplement V, 1997 (see references in Introduction).
[6] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

$NO_3 + CS_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<4\times10^{-16}$	298	Burrows, Tyndall, and Moortgat, 1985[1]	MM-A
Relative Rate Coefficients			
$<1.1\times10^{-15}$	297±2	Mac Leod *et al.*, 1986[2]	RR (a)
Reviews and Evaluations			
$<4.0\times10^{-16}$	298	NASA, 1997[3]	(b)
$<1\times10^{-15}$	298	IUPAC, 1997[4]	(c)

Comments

(a) NO_3 radicals were generated by thermal decomposition of N_2O_5 at atmospheric pressure of air. The decay rates of CS_2 and propene were monitored by FTIR absorption spectroscopy. The upper limit to the rate coefficient was obtained by use of a rate coefficient of $k(NO_3 + \text{propene}) = 9.4\times10^{-15}$ cm^3 molecule^{-1} s^{-1}.[4]

(b) Based on the upper limit to the absolute rate coefficient determined by Burrows *et al.*[1]

(c) See Comments on Preferred Values.

Preferred Values

$k < 1\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based upon the absolute study of Burrows *et al.*,[1] which is consistent with the slightly higher upper limit derived by Mac Leod *et al.*[2] The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[4]

References

[1] J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, J. Phys. Chem. **89**, 4848 (1985).
[2] H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., J. Geophys. Res. **91**, 5338 (1986).
[3] NASA Evaluation No. 12, 1997 (see references in Introduction).
[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$NO_3 + OCS \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$<4.6\times10^{-17}$	297±2	Mac Leod *et al.*, 1986[1]	RR (a)
Reviews and Evaluations			
$<1.0\times10^{-16}$	298	NASA, 1997[2]	(b)
$<1\times10^{-16}$	298	IUPAC, 1997[3]	(c)

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 at atmospheric pressure of air. The decay rates of OCS and propene were monitored by FTIR absorption spectrosopy. The upper limit to the rate coefficient is obtained by use of a rate coefficient of $k(NO_3 + \text{propene}) = 9.4\times10^{-15}$ cm^3 molecule^{-1} s^{-1}.[3]

(b) Based upon the upper limit to the rate coefficient determined by Mac Leod *et al.*[1]

(c) See Comments on Preferred Values.

Preferred Values

$k < 1\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based upon the sole study of Mac Leod *et al.*,[1] with a somewhat higher upper limit than reported. The preferred value is identical to that in our previous evaluation, IUPAC, 1977.[3]

References

[1] H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., J. Geophys. Res. **91**, 5338 (1986).

[2] NASA Evalution No. 12, 1997 (see references in Introduction).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$NO_3 + SO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<4\times10^{-16}$	298	Burrows, Tyndall, and Moortgat, 1985[1]	MM-A
$\leq4\times10^{-16}$	298 ± 2	Wallington *et al.*, 1986[2]	FP-A
$<1\times10^{-17}$	295 ± 2	Canosa-Mas *et al.*, 1988[3]	DF-A
$<1.2\times10^{-17}$	473	Canosa-Mas *et al.*, 1988[4]	DF-A
$<1\times10^{-15}$	298	Dlugokencky and Howard, 1988[5]	F-LIF
Relative Rate Coefficients			
$<7\times10^{-21}$	303	Daubendiek and Calvert, 1975[6]	RR (a)
Reviews and Evaluations			
$<7.0\times10^{-21}$	298	NASA, 1997[7]	(b)
$<1\times10^{-19}$	298	IUPAC, 1997[8]	(c)

Comments

(a) Derived from the lack of observation of SO_3 formation in N_2O_5–SO_2–O_3 mixtures, using IR absorption spectroscopy to measure the concentrations of SO_3.

(b) Based upon the study of Daubendiek and Calvert.[6]

(c) See Comments on Preferred Values.

Preferred Values

$k<1\times10^{-19}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based upon the relative rate study of Daubendiek and Calvert,[6] with a much higher upper limit. This preferred upper limit to the 298 K rate coefficient is consistent with the upper limits measured in the absolute rate coefficient studies of Burrows *et al.*,[1] Wallington *et al.*,[2] Canosa–Mas *et al.*,[3,4] and Dlugokencky and Howard.[5] The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[8]

References

[1] J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, J. Phys. Chem. **89**, 4848 (1985).

[2] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 5393 (1986).

[3] C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2 **84**, 247 (1988).

[4] C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2 **84**, 263 (1988).

[5] E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).

[6] R. L. Daubendiek and J. G. Calvert, Environ. Lett. **8**, 103 (1975).

[7] NASA Evaluation 12, 1997 (see references in Introduction).

[8] IUPAC, Supplement V, 1997 (see references in Introduction).

$NO_3 + CH_3SH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.0\times10^{-13}\exp[(600\pm400)/T]$	280–350	Wallington *et al.*, 1986[1]	FP-A
$(8.1\pm0.6)\times10^{-13}$	298		
$(7.7\pm0.5)\times10^{-13}$	298	Rahman *et al.*, 1988[2]	DF-MS
$1.09\times10^{-12}\exp[(0\pm50)/T]$	254–367	Dlugokencky and Howard, 1988[3]	F-LIF
$(1.09\pm0.13)\times10^{-12}$	298		
Relative Rate Coefficients			
$(1.00\pm0.22)\times10^{-12}$	297 ± 2	Mac Leod *et al.*, 1986[4]	RR (a)
Reviews and Evaluations			
$4.4\times10^{-13}\exp(210/T)$	250–370	NASA, 1997[5]	(b)
9.2×10^{-13}	250–370	IUPAC, 1997[6]	(c)

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in N_2O_5–NO_2–air mixtures at atmospheric pressure. The decay rates of CH_3SH and *trans*-2-butene were monitored by FTIR and GC respectively, and the measured rate coefficient ratio of $k(NO_3+CH_3SH)/k(NO_3+\textit{trans}\text{-2-butene})=2.57\pm0.55$ is placed on an absolute basis by use of a rate coefficient of $k(NO_3+\textit{trans}\text{-2-butene})=3.89\times10^{-13}$ cm^3 molecule^{-1} s^{-1}.[7]

(b) Derived from the absolute rate coefficient data of Wallington *et al.*,[1] Rahman *et al.*[2] and Dlugokencky and Howard.[3]

(c) See Comments on Preferred Values.

Preferred Values

$k=9.2\times10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–370 K.

Reliability

$\Delta\log k=\pm0.15$ at 298 K.

$\Delta(E/R)=\pm400$ K.

Comments on Preferred Values

The preferred value at 298 K is the mean of the four studies carried out to date,[1–4] which are in reasonably good agreement. Although a significant negative temperature dependence is indicated by the absolute rate coefficient study of Wallington *et al.*,[1] this is due to the rate coefficient measured at 350 K, and the rate coefficients at 280 and 298 K are identical.[1] The temperature independence of the rate coefficient determined by Dluogokencky and Howard[3] is accepted. The experimental data indicate that there is no pressure dependence of the rate coefficient, at least over the range ~0.0013–1 bar. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[6]

The magnitude of the rate coefficient and the lack of a temperature dependence of the rate coefficient shows that this reaction proceeds by initial addition, followed by decomposition of the adduct to yield CH_3S radicals (see also the data sheet on the $NO_3 + CH_3SCH_3$ reaction)

$$NO_3 + CH_3SH \rightleftarrows [CH_3S(ONO_2)H]^{\ddagger} \rightarrow CH_3S + HNO_3.$$

This conclusion is consistent with the product studies carried out by Mac Leod *et al.*[4] and Jensen *et al.*[8] Jensen *et al.*[8] identified CH_3SO_3H (methanesulfonic acid), SO_2, HCHO, CH_3ONO_2, CH_3SNO, and HNO_3 as products of the NO_3 radical reaction with CH_3SH at 295±2 K and 0.99±0.01 bar (740±10 Torr) total pressure of purified air.

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 5393 (1986).

[2] M. M. Rahman, E. Becker, Th. Benter, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **92**, 91 (1988).

[3] E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).

[4] H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., J. Geophys. Res. **91**, 5338 (1986).

[5] NASA Evaluation No. 12, 1997 (see references in Introduction).

[6] IUPAC, Supplement V, 1997 (see references in Introduction).

[7] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

[8] N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, J. Atmos. Chem. **14**, 95 (1992).

$NO_3 + CH_3SCH_3 \rightarrow CH_3SCH_2 + HNO_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.0 \pm 0.2) \times 10^{-12}$	278–318	Tyndall *et al.*, 1986[1]	MM-A
$(9.9 \pm 3.5) \times 10^{-13}$	298		
$(7.5 \pm 0.5) \times 10^{-13}$	298±2	Wallington *et al.*, 1986[2]	FP-A
$4.7 \times 10^{-13} \exp[(170 \pm 130)/T]$	280–350	Wallington *et al.*, 1986[3]	FP-A
$(8.1 \pm 1.3) \times 10^{-13}$	298±2		
$1.79 \times 10^{-13} \exp[(530 \pm 40)/T]$	256–376	Dlugokencky and Howard, 1988[4]	F-LIF
$(1.06 \pm 0.13) \times 10^{-12}$	298		
$(1.3 \pm 0.3) \times 10^{-12}$	298±1	Daykin and Wine, 1990[5]	PLP-A
Relative Rate Coefficients			
$(9.92 \pm 0.20) \times 10^{-13}$	296±2	Atkinson *et al.*, 1984[6]	RR (a)
Reviews and Evaluations			
$1.9 \times 10^{-13} \exp(500/T)$	250–380	NASA, 1997[7]	(b)
$1.9 \times 10^{-13} \exp(520/T)$	250–380	IUPAC, 1997[8]	(c)

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in air at 1 atm total pressure. The concentrations of CH_3SCH_3 and *trans*-2-butene were measured by GC, and the measured rate coefficient ratio of $k(NO_3 + CH_3SCH_3)/k(NO_3 + trans\text{-}2\text{-butene}) = 2.55 \pm 0.05$ are placed on an absolute basis by use of a rate coefficient of $k(NO_3 + trans\text{-}2\text{-butene}) = 3.89 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 296 K.[9]

(b) Derived from the absolute rate coefficients of Tyndall *et al.*,[1] Wallington *et al.*,[3] and Dlugokencky and Howard.[4]

(c) See Comments on Preferred Values.

Preferred Values

$k = 1.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.9 \times 10^{-13} \exp(520/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–380 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The absolute[1–5] and relative[6] rate coefficient studies are in reasonable agreement, although the data of Wallington *et al.*[2,3] are ~20% lower than the other data.[1,4–6] The absolute rate coefficients measured by Tyndall *et al.*,[1] Dlugokencky and Howard,[4] and Daykin and Wine[5] and the relative rate coefficient of Atkinson *et al.*[6] have been fitted to an Arrhenius expression to obtain the preferred values. The experimental data show that the rate coefficient is independent of total pressure over the range ~0.0013–1 bar. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[8]

The magnitude of the rate constant and the negative temperature dependence indicates that this reaction proceeds by initial addition of the NO_3 radical to the S atom. The kinetic data of Daykin and Wine[5] and Jensen *et al.*[10] for CH_3SCH_3 and CD_3SCD_3 show that the rate determining step involves H- (or D-) atom abstraction, indicating that the reaction is

$$NO_3 + CH_3SCH_3 \rightleftarrows [CH_3S(ONO_2)CH_3]^{\ddagger}$$
$$\downarrow$$
$$CH_3SCH_2 + HNO_3.$$

This conclusion is consistent with the product studies of Jensen *et al.*[10,11] and Butkovskaya and Le Bras.[12] Butkovskaya and Le Bras[12] used a DF-MS technique to show that the alternative reaction pathway yielding $CH_3SONO_2 + CH_3$ accounts for <2% of the overall reaction at 298 K and 1.3 mbar (1 Torr) total pressure.

References

[1] G. S. Tyndall, J. P. Burrows, W. Schneider, and G. K. Moortgat, Chem. Phys. Lett. **130**, 463 (1986).

[2] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 4640 (1986).

[3] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 5393 (1986).

[4] E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).

[5] E. P. Daykin and P. H. Wine, Int. J. Chem. Kinet. **22**, 1083 (1990).

[6] R. Atkinson, J. N. Pitts, Jr., and S. M. Aschmann, J. Phys. Chem. **88**, 1584 (1984).

[7] NASA Evaluation No. 12, 1997 (see references in Introduction).

[8] IUPAC, Supplement V, 1997 (see references in Introduction).

[9] R. Atkinson, J. Phys. Chem. Ref. Data **20**, 459 (1991).

[10] N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, J. Atmos. Chem. **14**, 95 (1992).

[11] N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, Atmos. Environ. **25A**, 1897 (1991).

[12] N. I. Butkovskaya and G. Le Bras, J. Phys. Chem. **98**, 2582 (1994).

$NO_3 + CH_3SSCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.9\times10^{-13}\exp[(290\pm50)/T]$	280–350	Wallington *et al.*, 1986[1]	FP-A
$(4.9\pm0.8)\times10^{-13}$	298 ± 2		
$7.4\times10^{-13}\exp[(0\pm200)/T]$	334–382	Dlugokencky and Howard, 1988[2]	F-LIF
$(7.4\pm1.5)\times10^{-13}$	298		
Relative Rate Coefficients			
(See comment)	297 ± 2	Mac Leod *et al.*, 1986[3]	RR (a)
Reviews and Evaluations			
$1.3\times10^{-12}\exp(-270/T)$	280–380	NASA, 1997[4]	(b)
7×10^{-13}	300–380	IUPAC, 1997[5]	(c)

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in N_2O_5–NO_2–air mixtures at atmospheric pressure. The relative decay rates of CH_3SSCH_3 and *trans*-2-butene were monitored by FTIR spectroscopy and GC, respectively. However, the more recent study of Atkinson *et al.*[6] has shown that reliable rate coefficient data cannot be obtained from the chemical system used by Mac Leod *et al.*[3]

(b) Derived from the absolute rate coefficients of Wallington *et al.*[1] and Dlugokencky and Howard.[2]

(c) See Comments on Preferred Values.

Preferred Values

$k=7\times10^{-13}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range $\sim$300–380 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

$\Delta(E/R)=\pm500$ K.

Comments on Preferred Values

The two absolute studies[1,2] are in reasonable agreement with respect to the room temperature rate coefficient. While the reported rate coefficient from the relative rate study[3] was an order of magnitude lower than the absolute data, the recent study of Atkinson *et al.*[6] shows that this was due to complexities in the experimental system used. Accordingly, the preferred values are based upon the absolute rate studies, and mainly on the data of Dlugokencky and Howard,[2] with the error limits being sufficient to encompass the data of Wallington *et al.*[1] The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[5]

As for the NO_3 radical reactions with CH_3SH and CH_3SCH_3, the NO_3 radical reaction with CH_3SSCH_3 is expected to proceed by initial addition, followed by decomposition of the addition adduct[3,7]

$$\begin{array}{c} NO_3 + CH_3SSCH_3 \rightleftarrows [CH_3SS(ONO_2)CH_3]^{\ddagger} \\ \downarrow \\ CH_3S + CH_3SO + NO_2. \end{array}$$

References

[1] T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **90**, 5393 (1986).

[2] E. J. Dlugokencky and C. J. Howard, J. Phys. Chem. **92**, 1188 (1988).

[3] H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., J. Geophys. Res. **91**, 5338 (1986).

[4] NASA Evaluation No. 12, 1997 (see references in Introduction).

[5] IUPAC, Supplement V, 1997 (see references in Introduction).

[6] R. Atkinson, S. M. Aschmann, and J. N. Pitts, Jr., J. Geophys. Res. **93**, 7125 (1988).

[7] N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, J. Atmos. Chem. **14**, 95 (1992).

$HS + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<4\times10^{-17}$	298	Black, 1984[1]	PLP-LIF
$\leq1\times10^{-17}$	298	Friedl, Brune, and Anderson, 1985[2]	DF-LIF
$<1\times10^{-14}$	298	Schoenle, Rahman, and Schindler, 1987[3]	DF-MS
$<4\times10^{-19}$	298	Stachnik and Molina, 1987[4]	PLP-UVA
$<1.5\times10^{-17}$	295	Wang, Lovejoy, and Howard, 1987[5]	DF-LMR
Reviews and Evaluations			
$<4.0\times10^{-19}$	298	NASA, 1997[6]	(a)
$<4\times10^{-19}$	298	IUPAC, 1997[7]	(b)

Comments

(a) Accepted the upper limit determined by Stachnik and Molina.[4]

(b) See Comments on Preferred Values.

Preferred Values

$k<4\times10^{-19}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The reaction of HS with O_2 is so slow that attempts to measure the rate coefficient have yielded only upper limits that fall in the range 4×10^{-19}–4×10^{-17} cm^3 molecule^{-1} s^{-1} at 298 K. The preferred value is from the study of Stachnik and Molina,[4] which gives the lowest upper limit and appears reliable. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[7]

References

[1] G. Black, J. Chem. Phys. **80**, 1103 (1984).

[2] R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1985).

[3] G. Schoenle, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **91**, 66 (1987).

[4] R. A. Stachnik and M. J. Molina, J. Phys. Chem. **91**, 4603 (1987).

[5] N. S. Wang, E. R. Lovejoy, and C. J. Howard, J. Phys. Chem. **91**, 5743 (1987)

[6] NASA Evaluation No. 12, 1997 (see references in Introduction).

[7] IUPAC, Supplement V, 1997 (see references in Introduction).

$HS + O_3 \rightarrow HSO + O_2$

$\Delta H^\circ = -290$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.2\pm1.0)\times10^{-12}$	298	Friedl, Brune, and Anderson, 1985[1]	DF-LIF
$(2.9\pm0.6)\times10^{-12}$	298	Schoenle, Rahman, and Schindler, 1987;[2] Schindler and Benter, 1998[3]	DF-MS
1.1×10^{-11} exp$[-(280\pm50)/T]$	296–431	Wang and Howard, 1990[4]	DF LMR
$(4.39\pm0.88)\times10^{-12}$	298		
Reviews and Evaluations			
9.0×10^{-12} exp$(-280/T)$	290–440	NASA, 1997[5]	(a)
9.5×10^{-12} exp$(-280/T)$	290–450	IUPAC, 1997[6]	(b)

Comments

(a) The temperature coefficient was taken from Wang and Howard.[4] The pre-exponential factor was based on the studies of Friedl *et al.*,[1] Schoenle *et al.*[2] (as revised by Schindler and Benter[3]) and Wang and Howard.[4]

(b) See Comments on Preferred Values.

Preferred Values

$k=3.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 9.5 \times 10^{-12} \exp(-280/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–440 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

The values[1,3,4] of k at 298 K agree reasonably well. A mean of the values from the three studies[1,3,4] is taken as the preferred value. There is only one measurement of the temperature coefficient,[4] which is the basis of the recommended expression, with the pre-exponential factor chosen to fit the recommended value of k at 298 K.

Since there is only one determination of the temperature dependence of k, and in view of the complexity of the secondary chemistry in these systems, substantial error limits are assigned. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[6]

References

[1] R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1985).

[2] G. Schoenle, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **91**, 66 (1987).

[3] R. N. Schindler and Th. Benter, Ber. Bunsenges. Phys. Chem. **92**, 558 (1988).

[4] N. S. Wang and C. J. Howard, J. Phys. Chem. **94**, 8787 (1990).

[5] NASA Evaluation No. 12, 1997 (see references in Introduction).

[6] IUPAC, Supplement V, 1997 (see references in Introduction).

HS + NO + M → HSNO + M

$\Delta H^\circ = -139$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.7 \times 10^{-31} (T/300)^{-2.48}$ [N$_2$]	250–445	Black *et al.*, 1984[1]	PLP-LIF (a)
$(1.4 \pm 0.13) \times 10^{-30}$ [Ar]	293	Bulatov, Kozliner, and Sarkisov, 1985[2]	PLP (b)
Reviews and Evaluations			
$2.4 \times 10^{-31} (T/300)^{-3.0}$ [air]	250–300	NASA, 1997[3]	(c)
$2.4 \times 10^{-31} (T/300)^{-2.5}$ [N$_2$]	200–300	IUPAC, 1997[4]	(d)

Comments

(a) Detection of HS at 334.5 nm. The pressure dependence was studied over the range 40–1013 mbar (30–760 Torr). The falloff curve was represented with $F_c = 0.6$ and $k_\infty = 2.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Theoretical modeling with the given ΔH°.

(b) Intracavity laser spectroscopic detection of HSO radicals at 583 nm in photolyzed H$_2$S–NO–NO$_2$–Ar mixtures, with HSO radicals being formed from the reaction HS + NO$_2$. Measurements were carried out at 16 mbar (12 Torr) total pressure.

(c) Based on the data of Black *et al.*[1]

(d) See Comments on Preferred Values.

Preferred Values

$k_0 = 2.4 \times 10^{-31} (T/300)^{-2.5}$ [N$_2$] cm^3 molecule^{-1} s^{-1} over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred temperature-dependent measurements from Ref. 1 give a consistent picture for the association reaction, and the preferred values are identical to those in our previous evaluation, IUPAC, 1997.[4]

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.7\pm0.5)\times10^{-11}$	250–300	Black *et al.*, 1984[1]	PLP-LIF (a)
Reviews and Evaluations			
2.7×10^{-11}	250–300	NASA, 1997[3]	(b)
2.7×10^{-11}	200–300	IUPAC, 1997[4]	(c)

Comments

(a) See comment (a) for k_0.
(b) Based on the data of Black *et al.*[1]
(c) See Comments on Preferred Values.

Preferred Values

$k_\infty = 2.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–300 K.

Reliability

$\Delta\log k_\infty = 0.5$ over the temperature range 250–300 K.

Comments on Preferred Values

The falloff extrapolation with $F_c=0.6$ of Ref. 1 towards k_∞ appears less certain than to k_0. The preferred values are based on the data of Black *et al.*,[1] and are identical to those in our previous evaluation, IUPAC, 1997.[4]

References

[1] G. Black, R. Patrick, L. E. Jusinski, and T. G. Slanger, J. Chem. Phys. **80**, 4065 (1984).
[2] V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khim Fiz. **4**, 1353 (1985).
[3] NASA Evaluation No. 12, 1997 (see references in Introduction).
[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$HS + NO_2 \rightarrow HSO + NO$

$\Delta H° = -90$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.5\pm0.4)\times10^{-11}$	298	Black, 1984[1]	PLP-LIF
$(2.4\pm0.2)\times10^{-11}$	293	Bulatov, Kozliner, and Sarkisov, 1984[2]	PLP-A (a)
$(3.0\pm0.8)\times10^{-11}$	298	Friedl, Brune, and Anderson, 1985[3]	DF-LIF
$(8.6\pm0.9)\times10^{-11}$	298	Schoenle, Rahman, and Schindler, 1987[4]	DF-MS
$(4.8\pm1.0)\times10^{-11}$	298	Stachnik and Molina, 1987[5]	PLP-UVA
$2.9\times10^{-11}\exp(237/T)$	221–415	Wang, Lovejoy, and Howard, 1987[6]	DF-LMR
$(6.7\pm1.0)\times10^{-11}$	298		
Reviews and Evaluations			
$2.9\times10^{-11}\exp(240/T)$	220–420	NASA, 1997[7]	(b)
$2.6\times10^{-11}\exp(240/T)$	220–450	IUPAC, 1997[8]	(c)

Comments

(a) HSO radical product was monitored by intracavity laser absorption at 583 nm.
(b) Accepted the value of Wang *et al.*[6]
(c) See Comments on Preferred Values.

Preferred Values

$k = 5.8\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.6\times10^{-11}\exp(240/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–420 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

There is considerable scatter in the measured values of k^{1-6} with no obvious correlation with the conditions used or the technique. The presence of H atoms in the system is known to lead to complicating secondary chemistry, and some of the differences may be due to this, particularly where HS has been generated by photolysis of H_2S. In more recent studies,[5,6] care has been taken to eliminate or model such effects, but significant differences still persist. The preferred value at 298 K is the mean of the results of Stachnik and Molina[5] and Wang *et al.*[6] The temperature coefficient is that of Wang *et al.*[6] and the pre-exponential factor is adjusted to fit the recommended value of k at 298 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[8]

The absence of any pressure effect on the rate constant at pressures up to 0.96 bar[1,5] indicates that any addition channel is unimportant up to these pressures.

References

[1] G. Black, J. Chem. Phys. **80**, 1103 (1984).
[2] V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khim. Fiz. **3**, 1300 (1984).
[3] R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1985).
[4] G. Schoenle, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **91**, 66 (1987), revised by R. N. Schindler and Th. Benter, *ibid.* **92**, 558 (1988).
[5] R. A. Stachnik and M. J. Molina, J. Phys. Chem. **91**, 4603 (1987).
[6] N. S. Wang, E. R. Lovejoy, and C. J. Howard, J. Phys. Chem. **91**, 5743 (1987).
[7] NASA Evaluation No. 12, 1997 (see references in Introduction).
[8] IUPAC, Supplement V, 1997 (see references in Introduction).

$HSO + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 2.0 \times 10^{-17}$	296	Lovejoy, Wang, and Howard, 1987[1]	DF-LMR
Reviews and Evaluations			
$< 2.0 \times 10^{-17}$	298	NASA, 1997[2]	(a)
$\leq 2.0 \times 10^{-17}$	298	IUPAC, 1997[3]	(b)

Comments

(a) Based on the rate coefficient of Lovejoy *et al.*[1]
(b) See Comments on Preferred Values.

Preferred Values

$k \leq 2.0 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The reaction is slow and only an upper limit to k is available.[1] The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[3]

References

[1] E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).
[2] NASA Evaluation No. 12, 1997 (see references in Introduction).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$$\mathrm{HSO} + \mathrm{O_3} \rightarrow \mathrm{HS} + 2\mathrm{O_2} \quad (1)$$

$$\rightarrow \mathrm{HO} + \mathrm{SO} + \mathrm{O_2} \quad (2)$$

$$\rightarrow \mathrm{HSO_2} + \mathrm{O_2} \quad (3)$$

$\Delta H°(1) = 4$ kJ·mol^{-1}
$\Delta H°(2) = -94$ kJ·mol^{-1}
$\Delta H°(3) = -361$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.1×10^{-13}	297	Wang and Howard, 1990[1]	DF-LMR
$k_1 = 7\times10^{-14}$	297		
$k_3 = 2.1\times10^{-12}\exp[-(1120\pm320)/T]$	273–423	Lee, Lee, and Wang, 1994[2]	DF-LIF/A
$k_3 = (4.7\pm1.0)\times10^{-14}$	298		
Relative Rate Coefficients			
1.1×10^{-13}	298	Friedl, Brune, and Anderson, 1985[3]	RR (a)
Reviews and Evaluations			
1.0×10^{-13}	298	NASA, 1997[4]	(b)
1.1×10^{-13}	298	IUPAC, 1997[5]	(c)
$k_1 = 6\times10^{-14}$	298		
$k_3 = 5\times10^{-14}$	298		

Comments

(a) Discharge flow system. The HS + O_3 reaction was studied with HS radicals being monitored by LIF. Addition of O_3 gave an initial decrease in [HS], which finally attained a steady state indicating regeneration of HS, postulated to be by the HSO + O_3 reaction. A rate coefficient ratio of $k/k(\mathrm{HS} + \mathrm{O_3}) = 0.031$ was obtained and placed on an absolute basis by use of $k(\mathrm{HS} + \mathrm{O_3}) = 3.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(b) Based on the studies of Wang and Howard[1] and Friedl *et al.*[3]

(c) See Comments on Preferred Values.

Preferred Values

$k = 1.1\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 6\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_3 = 5\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm0.2$ at 298 K.
$\Delta\log k_1 = \pm0.3$ at 298 K.
$\Delta\log k_3 = \pm0.3$ at 298 K.

Comments on Preferred Values

In the recent study by Lee *et al.*,[2] the rate coefficient measured is that for HSO removal by all channels other than channel (1) giving HS as a product, which subsequently regenerates HSO by reaction with the O_3 present. However, in our recommendations the rate coefficients measured by Lee *et al.*[2] are assigned to channel (3) on the grounds that Friedl *et al.*[3] could not detect HO production [channel (2)]; some further support for channel (3) comes from the work of Lovejoy *et al.*[6] who found that HSO_2 is readily formed by the HSO + NO_2 reaction.

The value at 298 K of k_3 obtained by Lee *et al.*[2] is compatible within the assigned error limits with the overall rate coefficient and the value of k_1(7×10^{-14} cm^3 molecule^{-1} s^{-1}) determined by Wang and Howard.[1]

Although Lee *et al.*[2] measured a temperature coefficient for k_3, the preferred values are only given at 298 K until further studies are made on the effects of temperature on all of the rate coefficients. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[5]

References

[1] N. S. Wang and C. J. Howard, J. Phys. Chem. **94**, 8787 (1990).
[2] Y.-Y. Lee, Y.-P. Lee, and N. S. Wang, J. Chem. Phys. **100**, 387 (1994).
[3] R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1985).
[4] NASA Evaluation No. 12, 1997 (see references in Introduction).
[5] IUPAC, Supplement V, 1997 (see references in Introduction).
[6] E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).

$HSO + NO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.6 \pm 0.4) \times 10^{-14}$	293	Bulatov, Kozliner, and Sarkisov, 1985[1]	PLP-A (a)
$\leq 1.0 \times 10^{-15}$	298	Lovejoy, Wang, and Howard, 1987[2]	DF-LMR
Reviews and Evaluations			
$< 1.0 \times 10^{-15}$	298	NASA, 1997[3]	(b)
$< 1.0 \times 10^{-15}$	298	IUPAC, 1997[4]	(c)

Comments

(a) HSO radicals monitored by intracavity laser absorption at 583 nm.
(b) Accepted the results of Lovejoy *et al.*[2]
(c) See Comments on Preferred Values.

Preferred Values

$k < 1.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The only two available measurements of k differ by at least a factor of 26. This is unlikely to be due to the higher pressures used in the Bulatov *et al.*[1] study, but may arise from secondary chemistry in their HSO source which employed relatively large H_2S concentrations. Provisionally, the upper limit to the rate coefficient reported by Lovejoy *et al.*[2] is preferred. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[4]

References

[1] V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khim. Fiz. **4**, 1353 (1985).
[2] E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).
[3] NASA Evaluation No. 12, 1997 (see references in Introduction).
[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$HSO + NO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
4×10^{-12}	293	Bulatov, Kozliner, and Sarkisov, 1984[1]	PLP-A (a)
$(9.6 \pm 2.4) \times 10^{-12}$	298	Lovejoy, Wang, and Howard, 1987[2]	DF-LMR
Reviews and Evaluations			
9.6×10^{-12}	298	NASA, 1997[3]	(b)
9.6×10^{-12}	298	IUPAC, 1997[4]	(c)

Comments

(a) HSO radicals monitored by intracavity laser absorption at 583 nm.
(b) Accepted the rate coefficient of Lovejoy *et al.*[2]
(c) See Comments on Preferred Values.

Preferred Values

$k = 9.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The only two measurements of k differ by at least a factor of 2. Lovejoy *et al.*[2] have suggested that the relatively high H_2S concentrations used by Bulatov *et al.*[1] may have led to side reactions regenerating HSO. The value of Lovejoy *et al.*[2] is preferred, but wide error limits are assigned awaiting confirmatory studies. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[4]

HO_2 was observed as a product of the reaction by Lovejoy *et al.*,[2] which they suggest arises from the reaction sequence

$$HSO + NO_2 \rightarrow HSO_2 + NO$$

$$HSO_2 + O_2 \rightarrow HO_2 + SO_2.$$

References

[1] V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khim. Fiz. **3**, 1300 (1984).
[2] E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).
[3] NASA Evaluation No. 12, 1997 (see references in Introduction).
[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$HSO_2 + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
3.0×10^{-13}	296	Lovejoy, Wang, and Howard, 1987[1]	DF-LMR
Reviews and Evaluations			
3.0×10^{-13}	298	NASA, 1997[2]	(a)
3.0×10^{-13}	298	IUPAC, 1997[3]	(b)

Comments

(a) Based on the rate coefficient of Lovejoy *et al.*[1]
(b) See Comments on Preferred Values.

Preferred Values

$k = 3.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.8$ at 298 K.

Comments on Preferred Values

There is only one study of this reaction.[1] The method used to obtain the rate coefficient was indirect, and this leads us to suggest substantial error limits despite the high quality of the experimental work. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[3]

References

[1] E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).
[2] NASA Evaluation No. 12, 1997 (see references in Introduction).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$SO + O_2 \rightarrow SO_2 + O$

$\Delta H° = -52.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.07 \pm 0.16) \times 10^{-16}$	298	Black, Sharpless, and Slanger, 1982[1]	(a)
$2.4 \times 10^{-13} \exp[-(2370^{+200}_{-250})/T]$	230–420	Black, Sharpless, and Slanger, 1982[2]	(a)
8.4×10^{-17}	298		
$1.00 \times 10^{-13} \exp[-(2180 \pm 117)/T]$	262–363	Goede and Schurath, 1983[3]	(b)
6.7×10^{-17}	298		
Reviews and Evaluations			
$2.6 \times 10^{-13} \exp(-2400/T)$	230–420	NASA, 1997[4]	(c)
$1.6 \times 10^{-13} \exp(-2280/T)$	230–420	IUPAC, 1997[5]	(d)

Comments

- (a) Pulsed laser photolysis of SO_2 at 193 nm, with SO radicals being detected by chemiluminescence from the SO + O_3 reaction. Pseudo-first-order decays of SO were monitored in the presence of excess O_2. Total pressure=133–667 mbar (100–500 Torr) of O_2 + He.
- (b) SO produced from the O + OCS reaction in a flow system. Controlled admission of SO radicals to a static volume where the pseudo-first-order decay of SO in excess O_2 was followed by SO + O_3 chemiluminescence. Total pressure=0.0013–0.27 mbar (1–200 mTorr) O_2. Only an Arrhenius expression was given with no individual rate coefficients at the temperatures studied.
- (c) Based on the work of Black *et al.*[1,2]
- (d) See Comments on Preferred Values.

Preferred Values

$k = 7.6 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.6 \times 10^{-13} \exp(-2280/T)$ over the temperature range 230–420 K.

Reliability
$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

This reaction is very slow and measurement of the rate coefficient k is subject to errors due to impurities. For this reason, Black *et al.*[1,2] favor their lower value of k at 298 K obtained in the temperature dependence study.[2] The Goede and Schurath[3] values are systematically about 35% lower than those from Ref. 2, but appear to have less experimental uncertainty at temperatures <300 K. The preferred value for the rate coefficient k at 298 K and for the temperature dependence are from Black *et al.*[2] and Goede and Schurath.[3] The A factor has been adjusted to give the preferred 298 K rate coefficient. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[5]

References

[1] G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **90**, 55 (1982).
[2] G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **93**, 598 (1982).
[3] H.-J. Goede and U. Schurath, Bull. Soc. Chim. Belg. **92**, 661 (1983).
[4] NASA Evaluation No. 12, 1997 (see references in Introduction).
[5] IUPAC, Supplement V, 1997 (see references in Introduction).

$SO + O_3 \rightarrow SO_2 + O_2$

$\Delta H° = -444.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.5 \times 10^{-12} \exp[-(1057 \pm 202)/T]$	223–300	Halstead and Thrush, 1966[1]	DF-CL
7.2×10^{-14}	298		
$(8.7 \pm 1.6) \times 10^{-14}$	296±4	Robertshaw and Smith, 1980[2]	PLP-CL
$(1.06 \pm 0.16) \times 10^{-13}$	298	Black, Sharpless, and and Slanger, 1982[3]	(a)
$4.8 \times 10^{-12} \exp[-(1170^{+80}_{-120})/T]$	230–420	Black, Sharpless, and Slanger, 1982[4]	(a)
9.46×10^{-14}	298		
Reviews and Evaluations			
$3.6 \times 10^{-12} \exp(-1100/T)$	220–420	NASA, 1997[5]	(b)
$4.5 \times 10^{-12} \exp(-1170/T)$	230–420	IUPAC, 1997[6]	(c)

Comments

- (a) Pulsed laser photolysis of SO_2–O_3 mixtures at 193 nm with SO_2 being monitored by CL from the SO + O_3 reaction. Excess O_3 was determined by UV absorption. The total pressure=267 mbar (200 Torr) of He.
- (b) Based on the studies of Halstead and Thrush,[1] Robertshaw and Smith,[2] and Black *et al.*[3,4]
- (c) See Comments on Preferred Values.

Preferred Values

$k = 8.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.5 \times 10^{-12} \exp(-1170/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–420 K.

Reliability
$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

The studies of Halstead and Thrush,[1] Robertshaw and Smith,[2] and Black *et al.*,[3,4] are in general agreement. The preferred 298 K rate coefficient is the mean of these measurements.[1–4] The temperature dependence of Black *et al.*[4] is accepted since this study covered a much larger temperature range than the earlier study of Halstead and Thrush,[1] which nevertheless gave a value of E/R within the experimental error of the later study.[4] The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[6]

References

[1] C. J. Halstead and B. A. Thrush, Proc. R. Soc. London Ser. A **295**, 380 (1966).

[2] J. S. Robertshaw and I. W. M. Smith, Int. J. Chem. Kinet. **12**, 729 (1980).

[3] G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **90**, 55 (1982).

[4] G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **93**, 598 (1982).

[5] NASA Evaluation No. 12, 1997 (see references in Introduction).

[6] IUPAC, Supplement V, 1997 (see references in Introduction).

$SO + NO_2 \rightarrow SO_2 + NO$

$\Delta H° = -244.5$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.37 \pm 0.07) \times 10^{-11}$	210–363	Brunning and Stief, 1986[1]	DF-MS
Reviews and Evaluations			
1.4×10^{-11}	210–360	NASA, 1997[2]	(a)
1.4×10^{-11}	210–360	IUPAC, 1997[3]	(b)

Comments

(a) Based on the studies of Clyne and MacRobert,[4] Black *et al.*,[5] and Brunning and Stief.[1]

(b) See Comments on Preferred Values.

Preferred Values

$k = 1.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 210–360 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The measurements of Brunning and Stief[1] are the only available temperature dependent study of the rate coefficient and indicate no measurable change in the rate coefficient k over the temperature range 210–363 K. This finding is the basis for our present recommendation for the rate coefficient, and the preferred values are identical to those in our previous evaluation, IUPAC, 1997.[3] All four studies[1,4–6] are in good agreement with respect to the 298 K rate coefficient.

References

[1] J. Brunning and L. J. Stief, J. Chem. Phys. **84**, 4371 (1986).

[2] NASA Evaluation No. 12, 1997 (see references in Introduction).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

[4] M. A. A. Clyne and A. J. MacRobert, Int. J. Chem. Kinet. **12**, 79 (1980).

[5] G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **90**, 55 (1982).

[6] M. A. A. Clyne, C. J. Halstead, and B. A. Thrush, Proc. R. Soc. London Ser. A **295**, 355 (1966).

$SO_3 + H_2O \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
9×10^{-13}	300	Castleman *et al.*, 1974[1]	F-MS
$\leq(5.7\pm0.9)\times10^{-15}$	298	Wang *et al.*,1989[2]	(a)
$\leq2.4\times10^{-15}$	~298	Reiner and Arnold, 1994[3]	(b)
$(1.2\pm0.2)\times10^{-15}$	298	Reiner and Arnold, 1994[4]	(b)
Complex mechanism	295	Kolb *et al.*, 1994[5]	(c)
Complex mechanism	250–360	Lovejoy, Hanson, and Huey, 1996[6]	(d)
Reviews and Evaluations			
See comment	298	NASA, 1997[7]	(e)
$<6.0\times10^{-15}$	298	IUPAC, 1997[8]	(f)

Comments

(a) Flow system with He and N_2 as carrier gases and H_2O in large excess over SO_3. SO_3 was monitored by the photodissociation of SO_3 at 147 nm and detection of SO_2 fluorescence at 300–390 nm. A halocarbon wall coating of the flow tube was used.

(b) Fast flow system at pressures of 31–260 mbar of synthetic air, using CIMS to detect SO_3, H_2O, and H_2SO_4. Small corrections for wall reactions were applied.

(c) Atmospheric pressure turbulent flow reactor using N_2 as a carrier gas and CIMS detection. Both the decrease in SO_3 as well as the increase in H_2SO_4 were monitored. The rate law was found to be first-order in $[SO_3]$ and second-order in $[H_2O]$. Rate constants ranging from 2×10^{-10} cm^3 s^{-1} to 1.4×10^{-12} cm^3 s^{-1} were estimated based on H_2O dimers and the $SO_3\cdot H_2O$ adduct, respectively.

(d) Laminar flow reactor with detection by CIMS. The observations were consistent with rapid association of SO_3 with H_2O to form the adduct $H_2O\cdot SO_3$, which then reacts with water to form H_2SO_4.

(e) Accepts the data of Lovejoy *et al.*,[6] which shows that the mechanism is complex and that the first order expression for SO_3 loss is second-order in $[H_2O]$.

(f) Accepted the upper limit of Wang *et al.*[2]

Preferred Values

No recommendation.

Comments on Preferred Values

This reaction was first considered in our earlier evaluation, CODATA, 1980.[9] No recommendation was made as the only available data at that time, those of Castleman *et al.*,[1] were suspect due to the likely interference of wall reactions in their work. The studies of Wang *et al.*,[2] Reiner and Arnold,[3,4] and Kolb *et al.*[5] have now confirmed that suspicion. Wang *et al.*[2] obtained an upper limit to the rate coefficient which is more than two orders of magnitude lower than the value of Castleman *et al.*,[1] by treatment of the flow tube walls to reduce wall effects, and the studies of Reiner *et al.*,[3,4] using the laminar flow tube method, obtain the lowest values for the rate constant.[3,4] The flow studies of Kolb *et al.*[5] and Lovejoy *et al.*[6] arrive at a rate law second-order in H_2O. Accordingly, we make no recommendation for the rate coefficient for the bimolecular reaction of SO_3 with H_2O.

References

[1] A. W. Castleman, Jr., R. E. Davis, H. R. Munkelwitz, I. N. Tang, and W. P. Wood, Int. J. Chem. Kinet. Symp. **1**, 629 (1975).

[2] X. Wang, Y. G. Yin, M. Suto, L. C. Lee, and H. E. O'Neal, J. Chem. Phys. **89**, 4853 (1989).

[3] T. Reiner and F. Arnold, Geophys. Res. Lett. **20**, 2659 (1993).

[4] T. Reiner and F. Arnold, J. Chem. Phys. **101**, 7399 (1994).

[5] C. E. Kolb, J. T. Jayne, D. R. Worsnop, M. J. Molina, R. F. Meads, and A. A. Viggiano, J. Am. Chem. Soc. **116**, 10314 (1994).

[6] E. R. Lovejoy, D. R. Hanson, and L. G. Huey, J. Phys. Chem. **100**, 19911 (1996).

[7] NASA Evaluation No. 12, 1997 (see references in Introduction).

[8] IUPAC, Supplement V, 1997 (see references in Introduction).

[9] CODATA, 1980 (see references in Introduction).

$SO_3 + NH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.9 \pm 1.5) \times 10^{-11}$	298	Shen, Suto, and Lee, 1990[1]	(a)
$(4.7 \pm 1.3) \times 10^{-11}$	295	Lovejoy and Hanson, 1996[2]	(b)
Reviews and Evaluations			
4.7×10^{-11}	298	NASA, 1997[3]	(c)
6.9×10^{-11}	298	IUPAC, 1997[4]	(d)

Comments

(a) Flow system with NH_3 in large excess. $[SO_3]$ monitored by observation of SO_2 fluorescence in the range 280–390 nm from photofragmentation of SO_3 by 147 nm radiation. He carrier gas at 1.3–2.7 mbar (1–2 Torr) total pressure.

(b) Laminar flow reactor study with N_2 as the carrier gas in the pressure range 13–533 mbar (10–400 Torr), using CIMS detection. Both the decrease of SO_3 as well as the formation of $SO_3 \cdot NH_3$ were monitored.

(c) Accepted the data of Lovejoy and Hanson.[2]

(d) Accepted the value of Shen *et al.*[1]

Preferred Values

$k = 5.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The studies of Shen *et al.*[1] and Lovejoy and Hanson[2] are in good agreement. The preferred value is the average of rate constants from these studies.[1,2] The more recent work[2] showed the product of the reaction to be the association complex $NH_3 \cdot SO_3$.

References

[1] G. Shen, M. Suto, and L. C. Lee, J. Geophys. Res. **95**, 13981 (1990).
[2] E. Lovejoy and D. R. Hanson, J. Phys. Chem. **100**, 4459 (1996).
[3] NASA Evaluation No. 12, 1997 (see references in Introduction).
[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$CS + O_2 \rightarrow CO + SO$ (1)

$\rightarrow OCS + O$ (2)

$\Delta H^\circ(1) = -378$ kJ·mol^{-1}
$\Delta H^\circ(2) = -165$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_2 = (4.5 \pm 1.7) \times 10^{-19}$	293	Richardson, 1975[1]	(a)
$k_2 = (5.9 \pm 1.3) \times 10^{-18}$	495		
$(2.9 \pm 0.4) \times 10^{-19}$	298	Black, Jusinski, and Slanger, 1983[2]	(b)
Branching Ratios			
$k_2/k_1 = 1.2$	298	Wood and Heicklen, 1971,[3] 1973/74[4]	(c)
$k_2/k_1 = 1.2$	341–415	Wood and Heicklen, 1971[5]	(d)
Reviews and Evaluations			
2.9×10^{-19}	298	NASA, 1997[6]	(e)
2.9×10^{-19}	298	IUPAC, 1997[7]	(f)

Comments

(a) Discharge flow system used. CS radicals were produced by a discharge through CS_2. CS, SO_2, CO, and OCS were measured by MS. A very slow linear flow rate ($\simeq 100$ cm s^{-1}) was necessary to observe reaction. SO_2, a product formed via channel (1), was at least one order of magnitude lower in concentration than CO and OCS.

(b) CS radicals were produced by pulsed laser photolysis of CS_2 in He bath gas [32 mbar (24 Torr)], and were monitored by LIF at 257.7 nm.

(c) Photolysis of CS_2-O_2 mixtures, with analysis of CO, OCS, SO_2, and S_2O products by GC. Light of wavelength 313 nm was used in Ref. 3, which has insufficient energy to dissociate the CS_2, but CS was postulated to have been formed by reaction of electronically excited CS_2 with O_2. In the later study,[4] $\lambda = 213.9$ nm was used, which can photodissociate CS_2.

(d) Explosion limits of CS_2-O_2 mixtures were determined by GC. The [CO]/[OCS] ratio was relatively unaffected by pressure and temperature changes, and the value of 0.84 found for this ratio is the same as that observed in photochemical studies.[3,4] The explosion limits were modeled on the basis of an assumed mechanism of eight reactions, and a computer fit to the data yielded the value for k_2/k_1.

(e) Accepted the rate coefficient of Black *et al.*[2]

(f) See Comments on Preferred Values.

Preferred Values

$k = 2.9 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.6$ at 298 K.

Comments on Preferred Values

The reaction of CS with O_2 is slow at 298 K and difficult to study. The technique used by Black *et al.*[2] seems the most suitable for avoiding the difficulties associated with the slowness of the reaction, and their rate coefficient at 298 K is preferred.

The relative importance of the two possible reaction channels is in dispute. Evidence from the photochemical and explosion limit studies[3–5] indicate a comparable importance of channels (1) and (2), but in the more direct flow system study[1] k_1 was found to be at least an order of magnitude less than k_2. However, the value of k_2 obtained in the fast flow study[1] appears to be unacceptably high. We make no recommendation for the branching ratio.

The one available measurement of k at higher temperatures,[1] when combined with the 298 K values, leads to an Arrhenius expression with an extremely low pre-exponential factor. Hence no recommendation is made for the temperature dependence. The preferred value is identical to our previous evaluation, IUPAC 1997.[7]

References

[1] R. J. Richardson, J. Phys. Chem. **79**, 1153 (1975).
[2] G. Black, L. E. Jusinski, and T. G. Slanger, Chem. Phys. Lett. **102**, 64 (1983).
[3] W. P. Wood and J. Heicklen, J. Phys. Chem. **75**, 854 (1971).
[4] W. P. Wood and J. Heicklen, J. Photochem. **2**, 173 (1973/74).
[5] W. P. Wood and J. Heicklen, J. Phys. Chem. **75**, 861 (1971).
[6] NASA Evaluation No. 12, 1997 (see references in Introduction).
[7] IUPAC, Supplement V, 1997 (see references in Introduction).

$CS + O_3 \rightarrow OCS + O_2$

$\Delta H^\circ(1) = -557$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.0 \pm 0.4) \times 10^{-16}$	298	Black, Jusinski, and Slanger, 1983[1]	(a)
Reviews and Evaluations			
3.0×10^{-16}	298	NASA, 1997[2]	(b)
3.0×10^{-16}	298	IUPAC, 1997[3]	(c)

Comments

(a) CS radicals were produced by pulsed laser photolysis of CS_2 at 193 nm, with He as the buffer gas at a total pressure of 67–400 mbar (50–300 Torr). CS radicals were monitored by LIF at 257.7 nm.

(b) Accepted the rate coefficient of Black *et al.*[1]

(c) See Comments on Preferred Values.

Preferred Values

$k = 3.0 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The only available measurement of the rate coefficient k is that of Black *et al.*[1] Their value is accepted, with substantial error limits. The preferred value is identical to our previous evaluation, IUPAC, 1997.[3]

References

[1] G. Black, L. E. Jusinski, and T. G. Slanger, Chem. Phys. Lett. **102**, 64 (1983).
[2] NASA Evaluation No. 12, 1997 (see references in Introduction).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$CS + NO_2 \rightarrow OCS + NO$

$\Delta H°(1) = -357$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(7.6 \pm 1.1) \times 10^{-17}$	298	Black, Jusinski, and Slanger, 1983[1]	(a)
Reviews and Evaluations			
7.6×10^{-17}	298	NASA, 1997[2]	(b)
7.6×10^{-17}	298	IUPAC, 1996[3]	(c)

Comments

(a) CS radicals were produced by pulsed laser photolysis of CS_2 at 193 nm and monitored by LIF at 257.7 nm. He [32 mbar (24 Torr) total pressure] was used as the buffer gas.
(b) Accepted the rate coefficient of Black *et al.*[1]
(c) See Comments on Preferred Values.

Preferred Values

$k = 7.6 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The only available measurement of k is that of Black *et al.*[1] Their value is accepted, but with substantial error limits. The preferred value is identical to our previous evaluation, IUPAC, 1997.[3]

References

[1] G. Black, L. E. Jusinski, and T. G. Slanger, Chem. Phys. Lett. **102**, 64 (1983).
[2] NASA Evaluation No. 12, 1997 (see references in Introduction).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_2SH + O_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.5 \pm 1.0) \times 10^{-12}$	298	Anastasi *et al.*, 1992[1]	(a)
$(4.6 \pm 1.9) \times 10^{-12}$	298	Rahman *et al.*, 1992[2]	(b)
Reviews and Evaluations			
6.5×10^{-12}	298	NASA, 1997[3]	(c)
6.6×10^{-12}	298	IUPAC, 1997[4]	(d)

Comments

(a) Pulsed radiolysis of CH_3SH-O_2-SF_6 mixtures at 1 bar total pressure. CH_2SH and CH_3S radicals were generated by reactions of the radiolytically produced F atoms with CH_3SH. [CH_2SH] was monitored by UV absorption over the range 220–380 nm.
(b) Fast flow discharge study. CH_2SH radicals were gen-

erated by reaction of F atoms with CH_3SH, and $[CH_2SH]$ was monitored by mass spectrometry. The source reactions were simulated to check consumption of F atoms. The total pressure was 3 mbar.

(c) Mean of the rate coefficients of Anastasi *et al.*[1] and Rahman *et al.*[2]

(d) See Comments on Preferred Values.

Preferred Values

$k = 6.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The only two measurements of k differ by almost a factor of 2. The values of $k(CH_2SH + NO_2)$ measured in these two studies also differ, although the error limits are large enough to encompass the two results. Until further studies are carried out, a mean of the two values is recommended, with substantial error limits. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[4]

References

[1] C. Anastasi, M. Broomfield, O. J. Nielsen, and P. Pagsberg, J. Phys. Chem. **96**, 696 (1992).

[2] M. M. Rahman, E. Becker, U. Wille, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **96**, 783 (1992).

[3] NASA Evaluation No. 12, 1997 (see references in Introduction).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_2SH + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.5 \pm 1.2) \times 10^{-11}$	298	Rahman *et al.*, 1992[1]	(a)
Reviews and Evaluations			
3.5×10^{-11}	298	NASA, 1997[2]	(b)
3.5×10^{-11}	298	IUPAC, 1997[3]	(c)

Comments

(a) Fast-flow discharge study. CH_2SH radicals were generated by the reaction of F atoms with CH_3SH, and monitored by MS. Source reactions were simulated to check consumption of F atoms. The total pressure was 3 mbar.

(b) Accepted the rate coefficient of Rahman *et al.*[1]

(c) See Comments on Preferred Values.

Preferred Values

$k = 3.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The only available determination[1] of k is accepted, but with substantial error limits until confirmatory studies can be made. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[3]

References

[1] M. M. Rahman, E. Becker, U. Wille, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **96**, 783 (1992).

[2] NASA Evaluation No. 12, 1997 (see references in Introduction).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_2SH + NO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.5\pm0.2)\times10^{-11}$	298	Anastasi *et al.*, 1992[1]	(a)
Reviews and Evaluations			
1.9×10^{-11}	298	NASA, 1997[2]	(b)
1.5×10^{-11}	298	IUPAC, 1997[3]	(c)

Comments

(a) Pulsed radiolysis of $CH_3SH-O_2-SF_6$ mixtures at 1 bar total pressure. CH_2SH and CH_3S radicals were generated by reactions of the radiolytically produced F atoms with CH_3SH, and $[CH_2SH]$ was monitored by UV absorption over the wavelength range 220–380 nm.

(b) Based on the rate coefficient of Anastasi *et al.*[1]

(c) See Comments on Preferred Values.

Preferred Values

$k = 1.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm0.3$ at 298 K.

Comments on Preferred Values

The only available determination[1] of k is accepted, but with substantial error limits until confirmatory studies are made. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[3]

References

[1] C. Anastasi, M. Broomfield, O. J. Nielsen, and P. Pagsberg, J. Phys. Chem. **96**, 696 (1992).

[2] NASA Evaluation No. 12, 1997 (see references in Introduction).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_2SH + NO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.8\pm1.0)\times10^{-11}$	298	Anastasi *et al.*, 1992[1]	(a)
$(6.9\pm4)\times10^{-11}$	298	Rahman *et al.*, 1992[2]	(b)
Reviews and Evaluations			
5.2×10^{-11}	298	NASA, 1997[3]	(c)
4.4×10^{-11}	298	IUPAC, 1997[4]	(d)

Comments

(a) Pulsed radiolysis of $CH_3SH-O_2-SF_6$ mixtures at 1 bar total pressure. CH_2SH and CH_3S radicals were generated by reactions of the radiolytically produced F atoms with CH_3SH, and $[CH_2SH]$ was monitored by UV absorption over the wavelength range 220–380 nm.

(b) Fast flow discharge study. CH_2SH radicals were generated by the reaction of F atoms with CH_3SH and were monitored by MS. Source reactions were simulated to check consumption of F atoms. The total pressure was 3 mbar.

(c) Average of the rate coefficients of Anastasi *et al.*[1] and Rahman *et al.*[2]

(d) See Comments on Preferred Values.

Preferred Values

$k = 4.4\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm0.5$ at 298 K.

Comments on Preferred Values

The only two measurements[1,2] of k differ substantially but because the error limits are large enough to encompass the two results it is difficult to know whether the difference is significant. In the same two studies the values obtained for $k(CH_2SH + O_2)$ differed to the same degree with much smaller error limits.

Until further studies are carried out, we recommend a weighted mean of the two values and substantial error limits. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[4]

References

[1] C. Anastasi, M. Broomfield, O. J. Nielsen, and P. Pagsberg, J. Phys. Chem. **96**, 696 (1992).

[2] M. M. Rahman, E. Becker, U. Wille, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **96**, 783 (1992).

[3] NASA Evaluation No. 12, 1997 (see references in Introduction).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3S + O_2 + M \rightarrow CH_3SOO + M$

$\Delta H° = -48.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<2\times10^{-17}$	298	Balla, Nelson, and McDonald, 1986[1]	PLP-LIF
$<1\times10^{-16}$	298	Black and Jusinski, 1986[2]	PLP-LIF
$<2.5\times10^{-18}$	298	Tyndall and Ravishankara, 1989[3]	PLP-LIF
$(1.81\pm0.28)\times10^{-13}$ (107 mbar He)	216	Turnipseed, Barone, and Ravishankara, 1992[4]	(a)
$(1.55\pm0.23)\times10^{-13}$ (107 mbar He)	222		
$(1.05\pm0.20)\times10^{-13}$ (107 mbar He)	233		
$(9.0\pm1.6)\times10^{-14}$ (107 mbar He)	237		
$(8.62\pm0.84)\times10^{-14}$ (107 mbar He)	242		
$(7.0\pm2.0)\times10^{-14}$ (107 mbar He)	250		
Relative Rate Coefficients			
2×10^{-14}	298	Hatakeyama and Akimoto, 1983[5]	RR (b)
2.9×10^{-17}	298	Grosjean, 1984[6]	RR (c)
$>2.3\times10^{-16}$	296	Balla and Heicklen, 1985[7]	RR (d)
Reviews and Evaluations			
$<3.0\times10^{-18}$	298	NASA, 1997[8]	(e)
Data of Turnipseed *et al.*, 1992[4]	216–250	IUPAC, 1997[9]	(f)

Comments

(a) Pulsed laser photolysis system with LIF detection of CH_3S radicals. The measured rate coefficients were observed to vary with the total pressure and the diluent gas. An upper limit to the rate coefficient for the reaction of the CH_3SOO radical with O_2 of 4×10^{-17} cm^3 molecule^{-1} s^{-1} at 258 K was also derived. The CH_3S–OO bond energy was determined to be 49 kJ mol^{-1} at 298 K from measurements of the equilibrium constant over the temperature range 216–258 K, with $\Delta H_f(CH_3SOO) = 75.7\pm4.2$ kJ mol^{-1} at 298 K.

(b) Photolysis of CH_3SSCH_3–RONO–NO–air mixtures. The products were analyzed by FTIR and GC-MS and the yields of SO_2 and CH_3SNO measured. From an assumed mechanism, the rate coefficient ratio $k(CH_3S + NO)/k = 2\times10^3$ was derived. A rate coefficient of $k(CH_3S + NO) = 4\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation) was used to obtain the rate coefficient given in the table.

(c) Environmental chamber study using the oxidation of organo–sulfur compounds in air by natural sunlight. Major products were SO_2, CH_3SO_3H, and HCHO. Production of SO_2 and sulphur were related to an unidentified compound (assumed to be CH_3SNO_2) formed from $CH_3S + NO_2$. A rate coefficient ratio of $k(CH_3S + NO_2)/k = 2\times10^6$ was derived, and placed on an absolute basis by use of $k(CH_3S + NO_2) = 5.8\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) From the photolysis of $(CH_3S)_2$–O_2–N_2 mixtures at 253.7 nm, with product analysis by GC and MS. The SO_2 yield was measured as a function of $[(CH_3S)_2]$, $[O_2]$ and light intensity. From an assumed mechanism, a value of $k^2/2k(CH_3S + CH_3S) > 6\times10^{-22}$ cm^3 molecule^{-1} s^{-1} was derived. A rate coefficient of $k(CH_3S + CH_3S) = 4.1\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (from Graham *et al.*[10]) was used to obtain the rate coefficient given in the table.

(e) Based on the data of Tyndall and Ravishankara.[3]

(f) See Comments on Preferred Values.

Preferred Values

Data of Turnipseed *et al.*,[4] given in above table.

Reliability

$\Delta \log k = \pm 0.3$ over the temperature range 216–250 K at 107 mbar He.

Comments on Preferred Values

The study of Turnipseed *et al.*[4] was the first to observe addition of O_2 to the CH_3S radical to form CH_3SOO [and not $CH_3S(O)O$, because the reaction was observed to be reversible leading to equilibrium between CH_3S radicals, O_2 and CH_3SOO radicals[4]]. Previous studies[1–3] of the reaction of CH_3S radicals with O_2 at 298 K did not observe the equilibrium addition of O_2 to CH_3S radicals, and the rate coefficients measured correspond to upper limits to the rate coefficients for the reactions

$$CH_3S + O_2 \rightarrow \text{products other than } CH_3SOO$$

and/or

$$CH_3SOO + O_2 \rightarrow \text{products.}$$

The reaction of CH_3S radicals with O_2 to form the CH_3SOO radical, and the reverse reaction, result in ~33% of CH_3S radicals being present as the CH_3SOO adduct at 298 K and ground level,[4] with the $[CH_3SOO]/[CH_3S]$ ratio being strongly temperature dependent.[4]

The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[9]

References

[1] R. J. Balla, H. H. Nelson, and J. R. McDonald, J. Chem. Phys. **109**, 101 (1986).

[2] G. Black and L. E. Jusinski, J. Chem. Soc. Faraday Trans. 2 **82**, 2143 (1986).

[3] G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. **93**, 2426 (1989).

[4] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **96**, 7502 (1992).

[5] S. Hatakeyama and H. Akimoto, J. Phys. Chem. **87**, 2387 (1983).

[6] D. Grosjean, Environ. Sci. Technol. **18**, 460 (1984).

[7] R. J. Balla and J. Heicklen, J. Photochem. **29**, 297 (1985).

[8] NASA Evaluation No. 12, 1997 (see references in Introduction).

[9] IUPAC, Supplement V, 1997 (see references in Introduction).

[10] D. M. Graham, R. L. Mieville, R. H. Pallen, and C. Sivertz, Can. J. Chem. **42**, 2250 (1964).

$CH_3SOO + M \rightarrow CH_3S + O_2 + M$

$\Delta H° = 48.9$ kJ·mol^{-1}

Rate coefficient data

k/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.99 \pm 0.74) \times 10^3$ (107 mbar He)	216	Turnipseed, Barone, and Ravishankara, 1992[1]	(a)
$(3.20 \pm 0.80) \times 10^3$ (107 mbar He)	222		
$(9.1 \pm 2.6) \times 10^3$ (107 mbar He)	233		
$(1.00 \pm 0.12) \times 10^4$ (107 mbar He)	237		
$(1.28 \pm 0.12) \times 10^4$ (107 mbar He)	242		
$(2.4 \pm 0.4) \times 10^4$ (107 mbar He)	250		
$> 3.5 \times 10^4$ (107 mbar He)	258		
Reviews and Evaluations			
Data of Turnipseed *et al.*, 1992[1]	216–250	IUPAC, 1997[2]	(b)

Comments

(a) Pulsed laser photolysis system with LIF detection of CH_3S radicals. The formation and decay rate coefficients of CH_3SOO radicals were derived from the observed time-concentration profiles of CH_3S radicals in the presence of O_2. The measured rate coefficients for the reactions $CH_3S + O_2 \rightleftharpoons CH_3SOO$ were observed to vary with total pressure and with the diluent gas.

(b) See Comments on Preferred Values.

Preferred Values

Data of Turnipseed *et al.*,[1] given in above table.

Reliability

$\Delta \log k = \pm 0.3$ at 107 mbar He over the temperature range 216–250 K.

Comments on Preferred Values

The data presented by Turnipseed *et al.*[1] were the first reported for the dissociation of the CH_3SOO radical (see also the data sheet in this evaluation for the reverse reaction $CH_3S + O_2 + M \rightarrow CH_3SOO + M$). In the atmosphere, ~33% of CH_3S radicals will be present as the CH_3SOO adduct at 298 K and ground level,[1] with the $[CH_3SOO]/[CH_3S]$ ratio being strongly temperature dependent.[1] The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[2]

References

[1] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **96**, 7502 (1992).

[2] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3S + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<8\times10^{-14}$	298	Black and Jusinski, 1986[1]	PLP-LIF
$(4.1\pm2.0)\times10^{-12}$	298	Tyndall and Ravishankara, 1989[2]	PLP-LIF
$(5.7\pm1.4)\times10^{-12}$	300	Dominé, Ravishankara, and Howard, 1992[3]	(a)
$1.98\times10^{-12}\exp[(290\pm40)/T]$	295–359	Turnipseed, Barone, and Ravishankara, 1993[4]	(b)
5.16×10^{-12}	298		
Reviews and Evaluations			
5.4×10^{-12}	298	Tyndall and Ravishankara, 1991[5]	(c)
$2.0\times10^{-12}\exp(290/T)$	290–360	NASA, 1997[6]	(d)
$2.0\times10^{-12}\exp(290/T)$	290–360	IUPAC, 1997[7]	(e)

Comments

(a) Discharge flow study. CH_3S radicals were generated by reaction of Cl with CH_3SH. Photoionization mass spectrometry was used to monitor CH_3S radicals. C_2F_3Cl was added to scavenge OH radicals and hence suppress OH radical-initiated chain reaction which regenerates CH_3S. Some curvature was observed on $[CH_3S]$ logarithmic decay plots in excess O_3. The initial slope was used to calculate k.

(b) Pulsed laser photolysis of $(CH_3)_2S-O_3-O_2-He$ (193 nm) mixtures. $[CH_3S]$ was monitored by LIF. Pressure range 27–267 mbar (20–200 Torr).

(c) Based on the work of Tyndall and Ravishankara[2] and Dominé *et al.*[3] The corrections made in the work of Tyndall and Ravishankara[2] to convert the measured value of $k(5.1\times10^{-12}$ cm^3 molecule^{-1} s$^{-1})$ to the quoted value $(4.1\times10^{-12}$ cm^3 molecule^{-1} s$^{-1})$ are now known to be unjustified.

(d) Derived from the absolute rate coefficients of Tyndall and Ravishankara,[2] Dominé *et al.*,[3] and Turnipseed *et al.*[4]

(e) See Comments on Preferred Values.

Preferred Values

$k = 5.4\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.0\times10^{-12}\exp(290/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–360 K.

Reliability

$\Delta\log k = \pm0.2$ at 298 K.

$\Delta(E/R) = \pm200$ K.

Comments on Preferred Values

It is difficult to study this reaction because in some conditions rapid chain processes involving the reaction products occur to regenerate CH_3S radicals.[2-4] This complication appears to be absent in the most recent study of Turnipseed *et al.*[4] under the conditions used for rate coefficient determinations. Their value of k at 298 K is in good agreement with other studies in which care was taken to allow for this complication.[2,3] The mean of the values from the two most recent studies[3,4] is taken as our recommended value at 298 K.

There is only one study of the temperature dependence of k.[4] Its findings are accepted with substantial error limits and the pre-exponential factor is adjusted to yield the recommended value of k at 298 K. The preferred data are identical to those in our previous evaluation, IUPAC, 1997.[7]

References

[1] G. Black and L. E. Jusinski, J. Chem. Soc. Faraday Trans. 2 **82**, 2143 (1986).

[2] G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. **93**, 4707 (1989).

[3] F. Dominé, A. R. Ravishankara, and C. J. Howard, J. Phys. Chem. **96**, 2171 (1992).

[4] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **97**, 5926 (1993).

[5] G. S. Tyndall and A. R. Ravishankara, Int. J. Chem. Kinet. **23**, 483 (1991).

[6] NASA Evaluation No. 12, 1997 (see references in Introduction).

[7] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3S + NO + M \rightarrow CH_3SNO + M$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.24 \pm 0.36) \times 10^{-29}$ [N_2]	295	Balla, Nelson, and McDonald, 1986[1]	(a)
$(1.43 \pm 0.36) \times 10^{-29}$ [N_2]	351		
$(1.13 \pm 0.20) \times 10^{-29}$ [N_2]	397		
$(5.84 \pm 0.66) \times 10^{-30}$ [N_2]	453		
Reviews and Evaluations			
3.2×10^{-29} $(T/300)^{-4.0}$ [N_2]	290–450	NASA, 1997[2]	(b)
3.2×10^{-29} $(T/298)^{-4}$ [N_2]	250–450	IUPAC, 1997[3]	(c)

Comments

(a) Pulsed laser photolysis of $(CH_3S)_2$–NO–N_2 (or SF_6) mixtures at 266 nm, with CH_3S being monitored by LIF. Lower part of the falloff curves were measured over the pressure range 2–400 mbar (1.5–300 Torr) of N_2. Falloff extrapolations were carried out with fitted values of F_c of 0.6, 0.86, 0.77, and 0.94 at 295, 351, 397, and 453 K, respectively.

(b) Based on the data of Balla *et al.*[1]

(c) See Comments on Preferred Values.

Preferred Values

$k_0 = 3.2 \times 10^{-29}$ $(T/300)^{-4}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 290–450 K.

Reliability

$\Delta \log k_0 = 0.3$ at 298 K.

$\Delta n = \pm 2$.

Comments on Preferred Values

The preferred values are based on the data of Balla *et al.*[1] Although the falloff extrapolations in Ref. 1 were made with a theoretically improbable temperature coefficient of F_c, the low-pressure rate coefficients are much less influenced by this extrapolation than the high-pressure rate coefficients. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[3]

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
1.81×10^{-12} exp(900/T)	295–453	Balla, Nelson, and McDonald, 1986[1]	(a)
Reviews and Evaluations			
$3.9 \times 10^{-11} (T/300)^{-2.7}$	290–450	NASA, 1997[2]	(b)
4×10^{-11}	250–450	IUPAC, 1997[3]	(c)

Comments

(a) See comment (a) for k_0. High-pressure limit was obtained from measurements at 267 and 400 mbar (200 and 300 Torr) of SF_6.

(b) Based on the data of Balla *et al.*[1]

(c) See Comments on Preferred Values.

Preferred Values

$k_\infty = 4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 290–450 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ over the temperature range 250–450 K.

Comments on Preferred Values

The negative temperature coefficient of k_∞ reported in Ref. 1 is most probably due to an increasing underestimate of the falloff corrections with increasing temperature. We recommend the use of the extrapolated k_∞ value at 298 K over large temperature ranges together with $F_c=\exp(-T/580)$. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[3]

Intermediate Falloff Range

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	P/mbar	M	Temp./K	Reference	Comments
Relative Rate Coefficients					
$(1.69\pm0.04)\times10^{-11}$	28	He	227	Turnipseed, Barone, and Ravishankara, 1993[4]	(a)
$(1.30\pm0.09)\times10^{-11}$	25	He	242		
$(1.89\pm0.08)\times10^{-11}$	25	He	242		

Comments

(a) CH_3S radicals were generated by either photolysis of dimethyl sulfide at 193 nm or photolysis of dimethyl disulfide at 248 nm. The decay of CH_3S radical concentrations was followed by LIF. Experiments were performed under slow gas flow conditions.

References

[1] R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **109**, 101 (1986)

[2] NASA Evaluation No. 12, 1997 (see references in Introduction).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

[4] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **97**, 5926 (1993).

$CH_3S + NO_2 \rightarrow CH_3SO + NO$

$\Delta H^\circ = -135$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$8.3\times10^{-11}\exp[(80\pm60)/T]$	295–511	Balla, Nelson, and McDonald, 1986[1]	PLP-LIF
9.8×10^{-11}	295		
$(6.10\pm0.90)\times10^{-11}$	298	Tyndall and Ravishankara, 1989[2]	PLP-LIF
$(5.1\pm0.9)\times10^{-11}$	297	Dominé, Murrells, and Howard, 1990[3]	DF-MS
$2.1\times10^{-11}\exp[(320\pm40)/T]$	242–350	Turnipseed, Barone, and Ravishankara, 1993[4]	(a)
$(6.28\pm0.28)\times10^{-11}$	298		
Reviews and Evaluations			
5.5×10^{-11}	298	Tyndall and Ravishankara, 1991[5]	(b)
$2.1\times10^{-11}\exp(320/T)$	240–350	NASA, 1997[6]	(c)
$2.0\times10^{-11}\exp(320/T)$	240–350	IUPAC, 1997[7]	(d)

Comments

(a) Pulsed laser photolysis at 193 nm or 248 nm of $(CH_3)_2S-NO_2$ or $(CH_3)_2S_2-NO_2$ mixtures in bath gas of He, N_2, or SF_6. $[CH_3S]$ was monitored by LIF. No effect of pressure on k was observed over the range of 27–267 mbar (20–200 Torr) He.

(b) Based on the results of Tyndall and Ravishankara[2] and of Dominé *et al.*[3]

(c) Based on the rate coefficients of Tyndall and Ravishankara[2] and Turnipseed *et al.*[4]

(d) See Comments on Preferred Values.

Preferred Values

$k=5.8\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=2.0\times10^{-11}\exp(320/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–350 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The recommended value at 298 K is the mean of the studies of Tyndall and Ravishankara,[2] Dominé *et al.*,[3] and Turnipseed *et al.*,[4] which are in good agreement. There are two studies[1,4] of the temperature dependence of k, both giving a negative value of E/R but differing significantly in magnitude. Balla *et al.*[1] obtained a very small negative temperature coefficient but obtain values of k nearly twice as large as those found in the other studies. It has been suggested[2] that this could arise from secondary chemistry arising from the higher radical concentrations used in the work of Balla *et al.*[1] The alternative value of Turnipseed *et al.*[4] is preferred but substantial error limits are recommended. The preexponential factor in the expression for k is based on the value of E/R from Turnipseed *et al.*[4] and the recommended value of k at 298 K.

The lack of pressure dependence of k found in the recent[4] and earlier studies[1,2] is consistent with the major pathway for the reaction proceeding directly to NO and CH_3SO rather than by addition to give CH_3SNO_2. Product studies[2,8] are in agreement with this conclusion.

The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[7]

References

[1] R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **109**, 101 (1986).
[2] G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. **93**, 2426 (1989).
[3] F. Dominé, T. P. Murrells, and C. J. Howard, J. Phys. Chem. **94**, 5839 (1990).
[4] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **97**, 5926 (1993).
[5] G. S. Tyndall and A. R. Ravishankara, Int. J. Chem. Kinet. **23**, 483 (1991).
[6] NASA Evaluation No. 12, 1997 (see references in Introduction).
[7] IUPAC, Supplement V, 1997 (see references in Introduction).
[8] I. Barnes, V. Bastian, K. H. Becker, and H. Niki, Chem. Phys. Lett. **140**, 451 (1987).

$CH_3SO + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1×10^{-12}	298	Tyndall and Ravishankara, 1989[1]	PLP-LIF
$(6.0 \pm 3.0) \times 10^{-13}$	300	Dominé, Ravishankara, and Howard, 1992[2]	(a)
Reviews and Evaluations			
6.0×10^{-13}	298	NASA, 1997[3]	(b)
6.0×10^{-13}	298	IUPAC, 1997[4]	(c)

Comments

(a) Discharge flow study. Photoionization mass spectrometry was used to monitor CH_3SO radicals. The reaction of $O(^3P) + C_2H_5SCH_3$ was used as a source of CH_3SO radicals. The rate coefficient obtained was considered preliminary.

(b) Based on the rate coefficient of Dominé *et al.*,[2] which is in agreement with the less direct study of Tyndall and Ravishankara.[1]

(c) See Comments on Preferred Values.

Preferred Values

$k = 6.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The measurement of k by Dominé *et al.*[2] is more direct than the previous study of Tyndall and Ravishankara[1] in which the rate coefficient was derived by a complex analysis of the reaction system. However, there are still a number of uncertainties in the study by Dominé *et al.*,[2] who consider their quoted value of k to be preliminary. This value[2] is accepted but substantial error limits are recommended. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[4]

References

[1] G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. **93**, 4707 (1989).
[2] F. Dominé, A. R. Ravishankara, and C. J. Howard, J. Phys. Chem. **96**, 2171 (1992).
[3] NASA Evaluation No. 12, 1997 (see references in Introduction).
[4] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3SO + NO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3\pm2)\times10^{-11}$	298	Mellouki, Jourdain, and Le Bras, 1988[1]	DF-MS
$(8\pm5)\times10^{-12}$	298	Tyndall and Ravishankara, 1989[2]	PLP-LIF
$(1.2\pm0.25)\times10^{-11}$	298	Dominé, Murrells, and Howard, 1990[3]	DF-MS
Reviews and Evaluations			
1.2×10^{-11}	298	NASA, 1997[4]	(a)
1.2×10^{-11}	298	IUPAC, 1997[5]	(b)

Comments

(a) Based on the rate coefficient of Dominé *et al.*[3]

(b) See Comments on Preferred Values.

Preferred Values

$k = 1.2\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The measured values[1–3] of k at 298 K agree within their error limits, some of which are substantial. The preferred value is that of Dominé *et al.*,[3] which lies between the other two values, both of which have much larger error limits. The rate coefficient for this reaction is difficult to measure because of the lack of a clean primary source of CH_3SO radicals and the complexity of the secondary chemistry. Substantial error limits are therefore suggested. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[5]

References

[1] A. Mellouki, J. L. Jourdain, and G. Le Bras, Chem. Phys. Lett. **148**, 231 (1988).
[2] G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. **93**, 2426 (1989).
[3] F. Dominé, T. P. Murrells, and C. J. Howard, J. Phys. Chem. **94**, 5839 (1990).
[4] NASA Evaluation No. 12, 1997 (see references in Introduction).
[5] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3SOO + O_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<8\times10^{-13}$	227	Turnipseed, Barone, and Ravishankara, 1993[1]	(a)
Reviews and Evaluations			
$<8.0\times10^{-13}$	227	NASA, 1997[2]	(b)
$<8.0\times10^{-13}$	227	IUPAC, 1997[3]	(c)

Comments

(a) Pulsed laser photolysis of $(CH_3)_2S-O_2-O_3$ mixtures at 193 nm in bath gas of He, N_2, or SF_6. $CH_3S + O_2 = CH_3SO_2$ equilibrium established. $[CH_3S]$ was monitored by LIF. $[CH_3S]$ temporal profiles were simulated to obtain k. $k(CH_3S + O_3)$ obtained in the same study was used in the fitting procedure.

(b) Based on the upper limit to the rate coefficient obtained by Turnipseed *et al.*[1]

(c) See Comments on Preferred Values.

Preferred Values

$k < 8\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 227 K.

Comments on Preferred Values

The single study of the rate of this reaction[1] has provided only an upper limit to k at 227 K, which is accepted as the preferred value. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[3]

References

[1] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **97**, 5926 (1993).

[2] NASA Evaluation No. 12, 1997 (see references in Introduction).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3SOO + NO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.10 \pm 0.38) \times 10^{-11}$	227–256	Turnipseed, Barone, and Ravishankara, 1993[1]	(a)
Reviews and Evaluations			
1.1×10^{-11}	227–256	NASA, 1997[2]	(b)
1.1×10^{-11}	227–256	IUPAC, 1997[3]	(c)

Comments

(a) Pulsed laser photolysis of $(CH_3)_2S_2$–O_2–NO mixtures at 248 nm with He or SF_6 as the bath gas. Only a limited pressure range could be studied [21–28 mbar (16–21 Torr) He, 25 mbar (19 Torr) SF_6], but no effect of pressure on k was observed. [CH_3S] was monitored by LIF and the temporal profile simulated to obtain k.

(b) Based on the sole study of Turnipseed *et al.*[1]

(c) See Comments on Preferred Values.

Preferred Values

$k = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 227–256 K.

Reliability

$\Delta \log k = \pm 0.3$ over the range 227–256 K.

Comments on Preferred Values

The value of k obtained in the only study of this reaction[1] is accepted but substantial error limits are assigned until confirmatory studies are made. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[3]

References

[1] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **97**, 5926 (1993).

[2] NASA Evaluation No. 12, 1997 (see references in Introduction).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3SOO + NO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.2 \pm 0.6) \times 10^{-11}$	227–246	Turnipseed, Barone, and Ravishankara, 1993[1]	(a)
Reviews and Evaluations			
2.2×10^{-11}	227–246	IUPAC, 1997[2]	(b)

Comments

(a) Pulsed laser photolysis of $(CH_3)_2S_2$–O_2–NO_2 mixtures at 248 nm in He [107–467 mbar (80–350 Torr)] or SF_6 [87 mbar (65 Torr)]. [CH_3S] was monitored and the temporal profile simulated to obtain k. No variation of k with pressure or temperature was observed.

(b) See Comments on Preferred Values.

Preferred Values

$k = 2.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 227–246 K.

Reliability

$\Delta \log k = \pm 0.3$ over the range 227–246 K.

Comments on Preferred Values

The value of k obtained in the only study[1] of this reaction is accepted but substantial error limits are assigned until confirmatory studies are made. The preferred values are identical to those in our previous evaluation, IUPAC, 1997.[2]

References

[1] A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **97**, 5926 (1993).

[2] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3SCH_2 + O_2 \rightarrow CH_3SCH_2O_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.7 \pm 0.4) \times 10^{-12}$ (1 bar)	298	Wallington, Ellermann, and Nielsen, 1993[1]	(a)
2.3×10^{-13} (1 Torr He)	298	Butkovskaya and Le Bras, 1994[2]	(b)
1.9×10^{-13} (1 Torr He)	298		
Reviews and Evaluations			
5.7×10^{-12} (1 bar)	298	IUPAC, 1997[3]	(c)

Comments

(a) Pulsed radiolysis of SF_6–CH_3SCH_3–O_2 mixtures. CH_3SCH_2 radicals were generated by reaction of F atoms with CH_3SCH_3, and monitored in absorption at 290 nm. The total pressure was approximately 1 bar.

(b) Discharge flow study of the NO_3–CH_3SCH_3–Br_2–O_2 system at 1.3 mbar (1 Torr) He. NO_3 radicals were produced by F + HNO_3 reaction and added to CH_3SCH_3 to give CH_3SCH_2. Subsequent addition of Br_2–O_2 mixtures allowed monitoring of competition between O_2 and Br_2 for CH_3SCH_2. Competition followed by mass spectrometric measurement of [CH_3SCH_2Br] profile. Modeling of profile gives $k = 2.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Similar study of Cl–Cl_2–CH_3SCH_3–O_2 system in which CH_3SCH_2 was produced by Cl + CH_3SCH_3 reaction gave $k = 1.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

(c) See Comments on Preferred Values.

Preferred Values

$k = 5.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar.

Reliability

$\Delta \log k = \pm 0.4$ at 298 K and 1 bar.

Comments on Preferred Values

The preferred value of k is taken from the study of Wallington *et al.*[1] Until confirmatory studies are made we confine our recommendations to 1 bar and assign substantial error limits. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[3]

References

[1] T. J. Wallington, T. Ellermann, and O. J. Nielsen, J. Phys. Chem. **97**, 8442 (1993).

[2] N. I. Butkovskaya and G. Le Bras, J. Phys. Chem. **98**, 2582 (1994).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3SCH_2O_2 + NO \rightarrow CH_3SCH_2O + NO_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.9 \pm 0.6) \times 10^{-11}$	298	Wallington, Ellermann, and Nielsen, 1993[1]	(a)
Reviews and Evaluations			
1.9×10^{-11}	298	NASA, 1997[2]	(b)
1.9×10^{-11}	298	IUPAC, 1997[3]	(c)

Comments

(a) Pulsed radiolysis of CH_3SCH_3–SF_6–O_2–NO mixtures. Generation of $CH_3SCH_2O_2$ radicals occurred by F + $CH_3SCH_3 \rightarrow CH_3SCH_2$ + HF, followed by $CH_3SCH_2 + O_2 \rightarrow CH_3SCH_2O_2$. [$NO_2$] was monitored at 400 nm. Yield of NO_2 compared with yield of F atoms suggested that 80% of the reaction leads to NO_2 production.

(b) Based on the rate coefficient of Wallington *et al.*[1]

(c) See Comments on Preferred Values.

Preferred Values

$k = 1.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.4$ at 298 K.

Comments on Preferred Values

The preferred value of k is taken from the only study of this reaction.[1] Substantial error limits are assigned until confirmatory studies are made. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[3]

References

[1] T. J. Wallington, T. Ellermann, and O. J. Nielsen, J. Phys. Chem. **97**, 8442 (1993).

[2] NASA Evaluation No. 12, 1997 (see references in Introduction).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3SCH_2O_2 + NO_2 + M \rightarrow CH_3SCH_2O_2NO_2 + M$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	P/mbar	M	Temp./K	Reference	Comments
Absolute Rate Coefficients					
$(9.2 \pm 0.9) \times 10^{-12}$	1000	SF_6	296	Nielsen, Sehested, and Wallington, 1995[1]	(a)
$(7.1 \pm 0.9) \times 10^{-12}$	300	SF_6	296		

Comments

(a) Pulsed radiolysis of SF_6–CH_3SCH_3–O_2–NO_2 mixtures with measurement of the rate of decay of NO_2 via its absorption at 400 nm. Insufficient data to obtain k_0 or k_∞, although the reaction was measured near the high-pressure limit.

Preferred Values

$k = 9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 1 bar and 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 1 bar and 298 K.

Comments on Preferred Values

Although the rate coefficients of Nielsen *et al.*[1] seem reasonable for this type of reaction, $RO_2 + NO_2 + M \rightarrow RO_2NO_2 + M$, their study is fairly indirect and we have assigned large error limits.

Reference

[1] O. J. Nielsen, J. Sehested, and T. J. Wallington, Chem. Phys. Lett. **236**, 385 (1995).

$CH_3SCH_2O_2 + CH_3SCH_2O_2 \rightarrow CH_3SCH_2OH + CH_3SCHO + O_2$ (1)

$\rightarrow 2CH_3SCH_2O + O_2$ (2)

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$\leq 7.9 \times 10^{-12}$	298	Wallington, Ellermann, and Nielsen, 1993[1]	(a)
Reviews and Evaluations			
$\leq 8 \times 10^{-12}$	298	IUPAC, 1997[2]	(b)

Comments

(a) k is defined by $-d[CH_3SCH_2O_2]/dt = 2k[CH_3SCH_2O_2]^2$. Pulsed radiolysis study of CH_3SCH_3–O_2–SF_6 mixtures with monitoring of $CH_3SCH_2O_2$ radical concentrations by UV absorption with $\sigma_{250} = (4.3 \pm 0.7) \times 10^{-18}$ cm^2 molecule^{-1}. The observed value of $k_{obs} = (7.9 \pm 1.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} is an upper limit to k because of the possibility of secondary reactions giving rise to an increasing decay rate of $CH_3SCH_2O_2$ radicals (see Comments on Preferred Values).

(b) See Comments on Preferred Values.

Preferred Values

$k \leq 8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

We have recommended an upper limit to the overall rate coefficient at 298 K, as determined by Wallington *et al.*[1] There is no information as yet concerning the products of the self-reactions of the $CH_3SCH_2O_2$ radicals, although it has been suggested that the alkoxy radical CH_3SCH_2O could react as follows: $CH_3SCH_2O \rightarrow CH_3S + HCHO$ and that the CH_3S radical could react with the $CH_3SCH_2O_2$ radical, leading to an enhanced decay rate of these radicals. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[2]

References

[1] T. J. Wallington, T. Ellermann, and O. J. Nielsen, J. Phys. Chem. **97**, 8442 (1993).

[2] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3SS + O_3 \rightarrow$ *products*

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.6 \pm 1.1) \times 10^{-13}$	300	Dominé, Ravishankara, and Howard, 1992[1]	(a)
Reviews and Evaluations			
4.6×10^{-13}	298	NASA, 1997[2]	(b)
4.6×10^{-13}	298	IUPAC, 1997[3]	(c)

Comments

(a) Discharge-flow study. Photoionization mass spectrometry was used to monitor CH_3SS radicals. CH_3S radicals were generated by $Cl + CH_3SH$, and CH_3SS was observed to be formed in the CH_3S source and thought to be due to the $CH_3S + S_2$ reaction on walls. $[CH_3SS]$ was monitored in the presence of excess O_3 to obtain k.

(b) Accepted the value of Dominé *et al.*[1]

(c) See Comments on Preferred Values.

Preferred Values

$k = 4.6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The only available measurement[1] of k is accepted but substantial error limits are assigned until confirmatory studies are made. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[3]

References

[1] F. Dominé, A. R. Ravishankara, and C. J. Howard, J. Phys. Chem. **96**, 2171 (1992).

[2] NASA Evaluation No. 12, 1997 (see references in Introduction).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3SS + NO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.8\pm0.3)\times10^{-11}$	297	Dominé, Murrells, and Howard, 1990[1]	(a)
Reviews and Evaluations			
1.8×10^{-11}	298	NASA, 1997[2]	(b)
1.8×10^{-11}	298	IUPAC, 1997[3]	(c)

Comments

(a) Fast-flow discharge study. CH_3SS radicals were produced as a byproduct of CH_3S radical production. CH_3S radicals were produced by the $Cl + CH_3SH$ reaction. CH_3SS was observed to be formed in the CH_3S source and thought to be due to the $CH_3S + S_2$ reaction on walls. $[CH_3SS]$ was monitored by photoionization mass spectrometry in excess NO_2.

(b) Accepted the value of Dominé *et al.*[1]

(c) See Comments on Preferred Values.

Preferred Values

$k = 1.8\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm0.3$ at 298 K.

Comments on Preferred Values

The study of Dominé *et al.*[1] has provided the only available value for the rate coefficient of this reaction. This value is accepted but with substantial error limits until confirmatory studies are made. The preferred value is identical to that in our previous evaluation, IUPAC, 1997.[3]

References

[1] F. Dominé, T. P. Murrells, and C. J. Howard, J. Phys. Chem. 94, 5839 (1990).

[2] NASA Evaluation No. 12, 1997 (see references in Introduction).

[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$CH_3SSO + NO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(4.5\pm1.2)\times10^{-12}$	297	Dominé, Murrells, and Howard, 1990[1]	(a)
Reviews and Evaluations			
4.5×10^{-12}	298	NASA, 1997[2]	(b)
4.5×10^{-12}	298	IUPAC, 1997[3]	(c)

Comments

(a) Fast-flow discharge system with photoionization mass spectrometric detection of products. CH_3SSO radicals were produced by $CH_3SS + NO_2 \rightarrow CH_3SSO + NO$. Mass 47 peak was monitored in excess NO_2 and the contributions from CH_3S and CH_3SSO (from $CH_3SSO + h\nu \rightarrow CH_3S^+ + e^- + SO$) were separated by modeling using data from other mass peaks.

(b) Accepted the value of Dominé *et al.*[1]

(c) See Comments on Preferred Values.

Preferred Values

$k = 4.5\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm0.3$ at 298 K.

Comments on Preferred Values

The study of Dominé *et al.*[1] has provided the only available value for the rate coefficient of this reaction. This value is accepted but with substantial error limits until confirmatory studies are made. The preferred value is identical to that in our previous evaluation; IUPAC, 1997.[3]

References

[1] F. Dominé, T. P. Murrells, and C. J. Howard, J. Phys. Chem. **94**, 5839 (1990).
[2] NASA Evaluation No. 12, 1997 (see references in Introduction).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$O_3 + CH_3SCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<8.3\times10^{-19}$	296	Martinez and Herron, 1978[1]	(a)
Reviews and Evaluations			
$<1.0\times10^{-18}$	298	NASA, 1997[2]	(b)
$<1\times10^{-18}$	298	IUPAC, 1997[3]	(b)

Comments

(a) Static system with MS detection of O_3.
(b) Based on the study of Martinez and Herron.[1]
(c) See Comments on Preferred Values.

Preferred Values

$k<1\times10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred upper limit to the rate coefficient is based upon the sole study of Martinez and Herron,[1] and is identical to that in our previous evaluation, IUPAC, 1997.[3]

References

[1] R. I. Martinez and J. T. Herron, Int. J. Chem. Kinet. **10**, 433 (1978).
[2] NASA Evaluation No. 12, 1997 (see references in Introduction).
[3] IUPAC, Supplement V, 1997 (see references in Introduction).

$ClO + CH_3SCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.9\pm0.5)\times10^{-14}$	298	Barnes *et al.*, 1989[1]	DF-MS
$(9.5\pm2.0)\times10^{-15}$	298 ± 1	Barnes *et al.*, 1991[2]	DF-MS
Reviews and Evaluations			
9.5×10^{-15}	298	NASA, 1997[3]	(a)
9×10^{-15}	298	IUPAC, 1997[4]	(b)

Comments

(a) Based on the rate coefficient of Barnes *et al.*[2]
(b) See Comments on Preferred Values.

Preferred Values

$k=9\times10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k=\pm0.5$ at 298 K.

Comments on Preferred Values

The two available measurements[1,2] of this rate coefficient are from the same laboratory using basically the same technique. In the earlier study,[1] wall effects were evident and it was recognized that the rate coefficient k obtained was likely to be an upper limit. Better control of wall effects was obtained in the later study,[2] and the rate coefficient obtained was preferred.[2] The reaction is usually assumed to produce $CH_2S(O)CH_3$ + Cl but, although the sulfoxide has been detected,[1] no yields have been measured.

In view of the potential for heterogeneous wall reactions (as evident from the discrepancies between the two studies of Barnes *et al.*[1,2]) the preferred value is based on the rate coefficient reported in the most recent study of Barnes *et al.*,[2] but with substantial error limits, and is identical to that in our previous evaluation, IUPAC, 1997.[4]

References

[1] I. Barnes, K. H. Becker, D. Martin, P. Carlier, G. Mouvier, J. L. Jourdain, G. Laverdet, and G. Le Bras, "*Biogenic Sulfur in the Environment*, edited by E. S. Saltzman and W. J. Cooper, ACS Symposium Series, No. 393 (ACS, Washington, DC, 1989), p. 464.

[2] I. Barnes, V. Bastian, K. H. Becker, and R. D. Overath, Int. J. Chem. Kinet. **23**, 579 (1991).

[3] NASA Evaluation No. 12, 1997 (see references in Introduction).

[4] IUPAC, Supplement V, 1997 (see references in Introduction).

BrO + CH_3SCH_3 →products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.65\pm0.65)\times10^{-13}$	298	Barnes *et al.*, 1989[1]	DF-MS
$(2.7\pm0.5)\times10^{-13}$	298±1	Barnes *et al.*, 1991[2]	DF-MS
$1.5\times10^{-14}\exp[(845\pm175)/T]$	246–320	Bedjanian *et al.*, 1996[3]	DF-MS (a)
$(2.7\pm0.2)\times10^{-13}$	297		
Reviews and Evaluations			
$1.5\times10^{-14}\exp(850/T)$	240–320	NASA, 1997[4]	(b)
$<2.7\times10^{-13}$	298	IUPAC, 1997[5]	(c)

Comments

(a) $CH_3S(O)CH_3$ was observed as a reaction product, with a measured formation yield at 320 K and 1.3 mbar (1 Torr) total pressure of 0.94±0.11.

(b) Based on the rate coefficients of Bedjanian *et al.*[3]

(c) Upper limit to the rate coefficient, based on the study of Barnes *et al.*[2]

Preferred Values

$k=2.6\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=1.5\times10^{-14}\exp(845/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–320 K.

Reliability

$\Delta\log k=\pm0.2$ at 298 K.

$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The three available measurements of the rate coefficient are in good agreement.[1-3] In the first study of this reaction[1] and of the corresponding reaction of ClO with CH_3SCH_3, difficulties were encountered due to wall reactions. In this respect the later studies[2,3] are much improved. The preferred values are taken from the most recent temperature-dependent study of Bedjanian *et al.*[3]

The reaction produces $CH_3S(O)CH_3$ + Br as the dominant, if not only, products under the experimental conditions employed.[3] The reaction is postulated[3] to proceed by:

$$\begin{array}{ll} BrO + CH_3SCH_3 \rightleftharpoons & [CH_3S(OBr)CH_3] \\ & \qquad\downarrow \\ & CH_3S(O)CH_3 + Br. \end{array}$$

References

[1] I. Barnes, K. H. Becker, D. Martin, P. Carlier, G. Mouvier, J. L. Jourdain, G. Laverdet, and G. Le Bras, *Biogenic Sulfur in the Environment*, edited by E. S. Saltzman and W. J. Cooper, ACS Symposium Series, No. 393 (ACS, Washington, DC, 1989), p. 464.

[2] I. Barnes, V. Bastian, K. H. Becker, and R. D. Overath, Int. J. Chem. Kinet. **23**, 579 (1991).

[3] Y. Bedjanian, G. Poulet, and G. Le Bras, Int. J. Chem. Kinet. **28**, 383 (1996).

[4] NASA Evaluation No. 12, 1997 (see references in Introduction).

[5] IUPAC, Supplement V, 1997 (see references in Introduction).

IO + CH_3SCH_3 → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	*Technique/Comments*
Absolute Rate Coefficients			
$(3.0 \pm 1.5 \times 10^{-11}$	296 ± 2	Barnes *et al.*, 1987[1]	(a)
$(1.5 \pm 0.5) \times 10^{-11}$	298	Martin *et al.*, 1987[2]	DF-MS
$\leq 3.5 \times 10^{-14}$	298 ± 2	Daykin and Wine, 1990[3]	PLP-A (b)
$(1.5 \pm 0.2) \times 10^{-14}$	298	Maguin *et al.*, 1991[4]	DF-MS
$(8.8 \pm 2.1) \times 10^{-15}$	298 ± 1	Barnes *et al.*, 1991[5]	DF-MS
Reviews and Evaluations			
1.2×10^{-14}	298	NASA, 1997[6]	(c)
1.2×10^{-14}	298	IUPAC, 1997[7]	(d)

Comments

(a) Photolysis of NO_2–I_2–CH_3SCH_3–N_2 mixtures. Photolytic production of $O(^3P)$ atoms from NO_2 formed IO radicals via the reaction $O(^3P) + I_2 \rightarrow IO + I$. The concentrations of NO, NO_2, CH_3SCH_3, and $CH_3S(O)CH_3$ were followed as a function of time by FTIR absorption spectroscopy. A computer fit of the measured product yields to a 16-step reaction mechanism yielded the cited rate coefficient.

(b) IO radicals were monitored by long-pathlength absorption at 427 nm.

(c) Derived from the rate coefficients of Maguin *et al.*[4] and Barnes *et al.*,[5] which are consistent with the upper limit to the rate coefficient measured by Daykin and Wine.[3]

(d) See Comments on Preferred Values.

Preferred Values

$k = 1.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

In the earlier studies of this reaction by Barnes *et al.*[1] and Martin *et al.*,[2] erroneously high values were obtained which are now believed to have been due to features of the secondary chemistry and heterogeneous processes occurring under the conditions used. The two most recent studies,[4,5] both using the same technique, give much lower values but differ from each other by nearly a factor of 2. Support for these lower values comes from the laser photolysis study by Daykin and Wine,[3] where an upper limit to the rate coefficient was obtained which is some three orders of magnitude lower than those derived in the earlier studies of Barnes *et al.*[1] and Martin *et al.*[2]

$CH_3S(O)CH_3$ has been detected in a number of studies,[1,2,4,5] and a semi-quantitative measurement of the yield by Barnes *et al.*[5] gave a yield of 0.84 ± 0.40. The preferred value is the mean of the rate coefficients of Maguin *et al.*[4] and Barnes *et al.*,[5] and is identical to that in our previous evaluation, IUPAC, 1997.[7] In view of the differences between the rate coefficients obtained from these two studies,[4,5] substantial error limits are assigned.

References

[1] I. Barnes, K. H. Becker, P. Carlier, and G. Mouvier, Int. J. Chem. Kinet. **19**, 489 (1987).

[2] D. Martin, J. L. Jourdain, G. Laverdet, and G. Le Bras, Int. J. Chem. Kinet. **19**, 503 (1987).

[3] E. P. Daykin and P. H. Wine, *J. Geophys. Res.* **95**, *18547 (1990).*

[4] F. Maguin, A. Mellouki, G. Laverdet, G. Poulet, and G. Le Bras, Int. J. Chem. Kinet. **23**, 237 (1991).

[5] I. Barnes, V. Bastian, K. H. Becker, and R. D. Overath, Int. J. Chem. Kinet. **23**, 579 (1991).

[6] NASA Evaluation No. 12, 1997 (see references in Introduction).

[7] IUPAC, Supplement V, 1997 (see references in Introduction).

$OCS + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°/kJ \cdot mol^{-1}$	$\lambda_{threshold}/nm$
$OCS + h\nu \rightarrow CO + S(^3P)$	(1)	308	388
$\rightarrow CO + S(^1D)$	(2)	419	286

Absorption cross-section data

Wavelength range/nm	Reference	Comments
185–300	Molina, Lamb, and Molina, 1981[1]	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength region	Reference	Comments
$\phi_1/\phi_2 = 0.055$	222	Nan, Burak, and Houston, 1993[2]	(b)
$\phi = 1.04 \pm 0.09$	248	Zhao, Stickel, and Wine, 1995[3]	(c)

Comments

(a) At a spectral resolution of 0.2 nm, at temperatures of 295 and 225 K. Data were given in figures and tables showing values averaged over 1 nm and averaged over wavelength intervals generally used in stratospheric photodissociation calculations. A value of $\sigma_{max} = 3.27 \times 10^{-19}$ cm^2 molecule^{-1} was determined at 223 nm.

(b) Pulsed laser photolysis of OCS at 222 nm. Doppler profile of $S(^3P_2)$ was monitored by LIF at 147 nm. CO used to quench $S(^1D)$. $S(^3P_2)$ yield of 0.050 relative to $S(^1D)$ obtained. $S(^3P_1)$ and $S(^3P_0)$ were not monitored but if they were present in statistical amounts then total triplet yield=0.055.

(c) Excimer laser flash photolysis of flowing $OCS-N_2-N_2O$ and $C(O)Cl_2$ N_2 N_2O gas mixtures at 248 nm. Concentration of CO was monitored by TDLS. ϕ was measured relative to the quantum yield for production of CO from photolysis of $C(O)Cl_2$, which is known to be unity. Measurements were carried out at 297 K and pressures of 5–133 mbar (4–100 Torr) $N_2 + N_2O$.

Preferred Values

	10^{21} σ/cm^2		
λ/nm	295 K	225 K	ϕ
300	0.0009		
295	0.0023	0.0013	
290	0.0077	0.0035	
285	0.0218	0.0084	
280	0.0543	0.0206	
275	0.1504	0.0607	
270	0.376	0.156	
265	0.960	0.423	
260	2.52	1.16	1.0
255	6.64	3.46	1.0
250	16.5	9.79	1.0
245	38.2	25.1	1.0
240	81.3	59.3	1.0
235	153.6	123.7	1.0
230	243.8	211.8	1.0
225	310.4	283.0	1.0
220	304.8	287.5	1.0
215	241.6	236.2	1.0
210	150.8	151.6	
205	82.0	82.5	
200	39.3	39.3	
195	20.2	18.9	
190	39.7	26.8	
185	190.3	135.7	

Comments on Preferred Values

There is good agreement among all of the recent cross-section measurements for $\lambda < 280$ nm.[1,4,5] At $\lambda > 280$ nm the data of Molina *et al.*[1] appear to be the most accurate. The higher values in Ref. 4 may be due to the presence of CS_2 or other unidentified trace contaminants or alternatively dimerization of OCS in the pressurized cell employed. The preferred values are 5 nm averages based on the Molina *et al.*[1] data. The results of Locker *et al.*,[5] whose results were presented in graphical form, agree with these values.

The preferred overall quantum yield of 1.0 is based on results reported recently by Zhao *et al.*[3] This value is significantly higher than the preferred value $\phi = 0.8$ given in our previous evaluation,[6] which was the average of the values reported by Rudolph and Inn[4] (0.72) and by Sidhu *et al.*[7] (0.9). Results of all studies indicate that S atoms are produced predominately in the $S(^1D)$ electronically excited state. Sidhu *et al.*[7] reported $\phi_2/\phi \geqslant 0.74$ and Breckenridge and Taube[8] reported $\phi_2/\phi = 0.74 \pm 0.04$. Nan *et al.*[2] reported $\phi_1/\phi_2 = 0.055$, which when combined with the preferred value of $\phi = \phi_1 + \phi_2 = 1.0$ yields $\phi_2/\phi = 0.95$.

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$CS_2 + h\nu \rightarrow$ products

Primary photochemical processes

Reactions		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CS_2 + h\nu \rightarrow CS_2^*$	(1)		>277
$\rightarrow CS + S(^3P)$	(2)	432	281
$\rightarrow CS + S(^1D)$	(3)	543	223

Absorption cross-section data

Wavelength range/nm	Reference	Comments
271–374	Hearn and Joens, 1991[1]	(a)
180–230	Chen and Wu, 1995[2]	(b)

Comments

(a) Spectral resolution 0.06 nm. Deuterium lamp was used as source but results checked using atomic lines (narrow band width) from argon-mercury lamp and by measurements at 260 nm on the well characterized benzene spectrum. Results presented in graphical form in paper but authors provide data points at 0.02 nm intervals on request.

(b) Spectral resolution 0.08 nm. Synchroton radiation was used as a continuum light source. Measurements were made at 203, 295, and 385 K. Significant temperature effects and hot bands were observed. Results were presented in graphical form in paper but authors provide data points at 0.005 nm intervals on request.

Preferred Values

λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\ \sigma$/cm^2
295	10	335	6.0
305	35	345	3.0
315	62	355	0.8
325	37		

Quantum Yields

$\phi_{OCS} = 1.2 \times 10^{-2}$ for 290–360 nm region in 1 bar air.

Comments on Preferred Values

The measurements of Hearn and Joens[1] on the absorption spectrum were carried out using similar conditions of temperature, resolution, pathlength, and gas pressure to those used by Wu and Judge.[3] In both cases the resolution used (0.06 nm) is higher than in the study of Wine *et al.*[4] (0.4 nm). All of these studies confirm the banded nature of the spectrum (280–370 nm). The values of the cross-section obtained by Hearn and Joens[1] are some 10–15% higher than those obtained by Wu and Judge[3] and there are minor differences in the band structures observed. The preferred values given are mean values of unpublished results from the AERE Laboratories, Harwell (quoted as preferred values in IUPAC, 1992[5]) and those of Hearn and Joens.[1]

The recommended quantum yield for OCS production from the photoinitiated oxidation of CS_2 in air is that reported by Jones *et al.*,[6] which is in good agreement with the value estimated by Wine *et al.*[4] from the earlier data of Wood and Heicklen[7] (i.e., ϕ_{OCS}=0.01–0.015). The recommended value might best be considered an upper limit since the observed slow oxidation of the CS_2 could have been due, at least in part, to other mechanisms.

Since there is insufficient energy to dissociate CS_2 at $\lambda > 281$ nm the photochemical reaction yielding OCS and SO_2, studied by Jones *et al.*[6] in the range 290–360 nm and others,[7,8] must arise from reactions involving excited CS_2 molecules; see discussion of this in Goss *et al.*[9]

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$CH_3SSCH_3 + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3SSCH_3 \rightarrow CH_3SS + CH_3$	(1)	238	502
$\rightarrow 2CH_3S$	(2)	274	437

Absorption cross-section data

Wavelength range/nm	Reference	Comments
201–360	Hearn, Turcu, and Joens, 1990[1]	(a)

Quantum yield data

Wavelength range/nm	Reference	Comments
193–248	Barone *et al.*, 1994[2]	(b)

Comments

(a) Cary 2300 double beam UV spectrophotometer used with a resolution of 0.10 nm. Photolysis of $(CH_3)_2S_2$–N_2 mixtures at a constant pressure of 133 mbar (100 Torr). Temperature=300±2 K.

(b) Primary quantum yields for formation of $H(^2S)$ and $CH_3S(^2E)$ from photodissociation at excimer wavelengths 193, 222, and 248 nm were measured, with H atom detection by RF and CH_3S detection by pulsed LIF.

Preferred Values

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
201	1053.0	280	49.8
205	850.0	285	36.0
210	630.0	290	25.15
215	312.0	295	17.06
220	138.7	300	11.27
225	85.6	305	7.24
228 (min)	82.3	310	4.57
230	84.2	315	2.85
235	96.0	320	1.79
240	110.0	325	1.09
245	120.7	330	0.67
250	125.4	335	0.38
251 (max)	125.6	340	0.22
255	123.3	345	0.14
260	113.9	350	0.07
265	99.3	355	0.04
270	82.7	360	<0.01
275	65.4		

Comments on Preferred Values

The preferred values for σ are those of Hearn *et al.*[1] which agree well with the earlier values cited in Calvert and Pitts.[3] Sheraton and Murray's spectrum[4] agrees qualitatively with the other studies, but the reported absorption coefficients are significantly lower.

Barone *et al.*[2] report the primary quantum yield for CH_3S production to be 1.65 ± 0.38 at 248 nm and 1.20 ± 0.14 at 193 nm. These authors report that no H atoms were observed at 248 nm, and that at 193 and 222 nm H atom production was only a minor process and could be due to sample impurities. These results and those of Balla and Heicklen[5] indicate that at wavelengths of importance to atmospheric photochemistry dissociation occurs primarily by S–S bond scission to give $2CH_3S$. The significantly lower value of $\phi(CH_3S)$ at 193 nm implies the existence of an additional channel at these short wavelengths.

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$CH_3SNO + h\nu \rightarrow$ products

Primary photochemical processes

Reaction		ΔH°/kJ·mol^{-1}	λ$_{\text{threshold}}$/nm
$CH_3SNO \rightarrow CH_3S + NO$	(1)		
$\rightarrow CH_3 + SNO$	(2)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
190–430	Niki *et al.*, 1983[1]	(a)

Quantum yield data

No data available

Comments

(a) Cary 14 double beam spectrophotometer used; the spectral resolution was not reported. Measurements of σ were made over the range 190–600 nm, but only the results in the range 190–430 nm were given in graphical form. Values of $\sigma=2.4\times10^{-20}$ and 5.8×10^{-20} cm^2 molecule^{-1} were quoted for 510 and 545 nm, respectively. Values given in the table were taken from the graph. Temperature=298 K.

Preferred Values

Wavelength/nm	10^{19} σ/cm^2	Wavelength	10^{19} σ/cm^2
190	5	310	14.9
195	104	320	18.5
200 (max)	162	330	21.3
205	91	335 (max)	21.6
210 (min)	81	340	21.5
215	98	350	19.6
218 (max)	104	360	16.5
220	96	370	12.7
225	73	380	9.6
230	40	390	6.7
240	16	400	4.5
250	3.5	410	2.9
260	1.7	420	2.0
264 (min)	1.5	430	1.3
270	1.8		
280	2.7	510	0.24
290	5.2	545	0.58
300	9.3		

Comments on Preferred Values

The spectrum of CH_3SNO consists of a weak transition in the 500–600 nm region showing some vibrational fine structure and stronger continuous bands at shorter wavelengths.[2] The CH_3S–NO dissociation energy has been estimated[3] to be approximately 110 kJ mol^{-1} but because more reliable data are not available we do not give wavelength limits for the dissociation channels tabulated.

The only available data for σ values in the gas phase appear to be those of Niki *et al.*[1] who have published their results mainly in the form of graphs covering the range 190–430 nm. Their published spectrum shows no fine structure but appears to consist of overlapping continua with three maxima at approximately 200, 218, and 335 nm. The preferred values of σ in the range 190–430 nm are taken from the graphs of Niki *et al.*[1] and cannot be considered to be very precise. The two values at 510 and 545 nm are numerical values quoted in the same study.[1]

There have been no quantum yield measurements. By analogy with CH_3ONO photolysis the primary products are expected to be CH_3S and NO. This is supported by the work of McCoustra and Pfab[2] who studied the photodissociation of CH_3SNO in a molecular beam and by the study of Niki *et al.*[1] who found CH_3SSCH_3 and NO to be the only major products from CH_3SNO photolysis at 300–400 nm.

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5. Appendix 1

Enthalpy Data

Most of the thermochemical data have been taken from evaluations or reviews. In some cases, we have selected more recent experimental data, which appear to be reliable.

Species	$\Delta_f H^\circ_{298}$/kJ·mol^{-1}	$\Delta_f H^\circ_0$/kJ·mol^{-1}	Reference
H	217.998		24
H_2	0	0	24
O	249.18	246.79	24
$O(^1D)$	438.9	436.6	29
O_2	0	0	24
$O_2(^1\Delta)$	94.3	94.3	29
$O_2(^1\Sigma)$	156.9	156.9	29
O_3	142.7	145.4	63
HO	39.3	39.0	35
HO_2	14.6		35
H_2O	−241.826		24
H_2O_2	−136.32	−130.04	63
N	472.68		24
N_2	0	0	24
NH	352		53
NH_2	168.7		35
NH_3	−45.94		24
NO	90.25	89.75	63
NO_2	33.2	36	63
NO_3	73.7		25
N_2O	82.05	85.50	63
N_2O_4	9.1	18.7	18
N_2O_5	11.3		18,25
HNO	112.9	110.0	28
HNO_2	−79.5	−74	63
HNO_3	−135.06	−125.27	63
HO_2NO_2	−57		51
CH	596.4		35
$CH_2(^3B_1)$	390.4		35
$CH_2(^1A_1)$	428.3		35
CH_3	146.4		35
CH_4	−74.81	−66.82	63
CN	435		18,35
HCN	135		18
HCO	41.8		20
CH_2O	−108.6	−104.7	29
CH_3O	17.2		35
CH_2OH	−17.8		34
CH_3OH	−201.6		23
CO	−110.53		24
NCO	159		18
COOH	−223		35
HCOOH	−378.8	−371.6	23
CH_3O_2	10.4		41
CH_3OOH	−131		18
$HOCH_2O_2$	−162.1		41
CH_3ONO	−65.3		8
CH_3ONO_2	−119.7		8
$CH_3O_2NO_2$	−44		51
CO_2	−393.51		24
C_2H	566.1		35
C_2H_2	228.0		23
C_2H_3	300.0		35
C_2H_4	52.2		23
C_2H_5	120.9		35
C_2H_6	−84.0		23
CH_2CN	243.1		35

Enthalpy Data—Continued

Species	$\Delta_f H^\circ_{298}$/kJ·mol^{-1}	$\Delta_f H^\circ_0$/kJ·mol^{-1}	Reference
CH_3CN	64.3		57
CH_2CO	−47.7		50
CH_3CO	−10.0		35
CH_2CHO	10.5		35
$CH{=}CHOH$	115		56
CH_3CHO	−165.8		23,57
C_2H_5O	−15.5		35
C_2H_4OH	−34		8
CH_3CHOH	−63.6		35
C_2H_5OH	−234.8		23,57
$(CHO)_2$	−211.9		23,57
CH_3CO_2	−207.5		35
CH_3CO_2H	−432.04		23,57
$C_2H_5O_2$	−28.7		41
CH_3OOCH_3	−125.7		23,57
$CH_3C(O)O_2$	−172		41
C_2H_5ONO	−103.8		23,57
$C_2H_5ONO_2$	−154.0		23,57
$C_2H_5O_2NO_2$	−63.2		27
$CH_2{=}CHCH_2$	170.7		35
C_3H_6	20.2		23,57
n-C_3H_7	97.5		35
i-C_3H_7	90.0		35
C_3H_8	−104.5		23,57
CH_3COCH_2	−23.9		35
C_2H_5CHO	−187.4		23,57
CH_3COCH_3	−217.2		23,57
C_3H_6OH	−74		8
n-C_3H_7O	−41.4		35
i-C_3H_7O	−52.3		35
i-C_3H_7OH	−272.5		23,57
CH_3COCHO	−271.1		23,57
$C_3H_5O_2$	87.9		41
i-$C_3H_7O_2$	−68.9		41
n-$C_3H_7ONO_2$	−174.1		23,57
i-$C_3H_7ONO_2$	−190.8		23,57
$CH_3C(O)O_2NO_2$	−258		12
S	277.17		24
HS	143.0		48
H_2S	−20.6		24
HSO	−4		42
SO	5.0	5.0	18
HSO_2	−222		11
SO_2	−296.81		24
$HOSO_2$	−385		43
SO_3	−395.7	−390	63
HSNO	94		10
CH_3S	124.6		48
CH_3SH	−22.9		52
CH_3SCH_2	136.8		32
CH_3SCH_3	−37.24		63
CS	272	268	7
CH_3SO	−67		14
CH_3SOO	75.7	87.9	61
OCS	−142	−142	63
S_2	128.60		24
CH_3SS	68		7
CH_3SSCH_3	−24.3		7
CS_2	117.2	116.6	63
$HOCS_2$	110.5		45
F	79.38		24
HF	−273.30		24
HOF	−98	−95	18

Enthalpy Data—Continued

Species	$\Delta_f H^\circ_{298}$/kJ·mol^{-1}	$\Delta_f H^\circ_0$/kJ·mol^{-1}	Reference
FO	109	108	17
FO_2	25.4	27.2	17
FONO	67		4
FNO_2	−108.8		51
$FONO_2$	10	18	18
CH_2F	−31.8		35
CH_3F	−232.6		37
CH_3CH_2F	−263		40
HCOF		−392.5	64
FCO	−171.5	−172.1	18
F_2	0	0	24
CHF_2	−238.9		35
CH_2F_2	−453		40
CH_3CHF_2	−501		40
CF_2	−194.1		35
COF_2	−634.7	−631.6	63
CHF_3	−697.6		40
CF_3	−467.4		35
CH_2CF_3	−517.1		35
CH_3CF_3	−748.7		36
CH_2FCHF_2	−691		36
CF_3O	−655.6		5
CF_3OH	−923.4		21
CF_3OF	−785		40
CF_3O_2	−614.0		41
CF_3CO_2H	−1031		52
$CF_3O_2NO_2$	−686		27
CF_4	−933	−927	54
Cl	121.30		24
HCl	−92.31		24
HOCl	−78	−75	29,44
ClO	101.6		1
ClOO	97.5		3
OClO	95.6		30,46
sym-ClO_3	232.6		22
ClNO	51.7	53.6	18
$ClNO_2$	12.5	18.0	63
ClONO	56		51
$ClONO_2$	22.9		2
CH_2Cl	121.8		60
CH_2ClO_2	9.2		41
CH_3Cl	−82.0	−74.0	54
CHF_2Cl	−483.7		19
CH_3CHFCl	−313.4		36
CH_3CF_2Cl	−536.2		36
ClCO	−21.8		47
COFCl	−427	−423	18
CFCl	−20		40
CF_2Cl	−279.1		35
CF_2ClO_2	−406.5		41
$CF_2ClO_2NO_2$	−480		38
CF_3Cl	−707.9	−702.9	19
Cl_2	0	0	24
Cl_2O	77.2		58
Cl_2O_2	127.6		46
Cl_2O_3	153		13
CCl_2	239		35
$CHCl_2$	98.3		60
$CHCl_2O_2$	1.6		41
CH_2Cl_2	−95.4	−88.5	54
$CHFCl_2$	−284.9		19
$COCl_2$	−220.1	−218.4	29
$CFCl_2$	−89.1		60
$CFCl_2O_2$	−213.7		41

Enthalpy Data—Continued

Species	$\Delta_f H^\circ_{298}$/kJ·mol^{-1}	$\Delta_f H^\circ_0$/kJ·mol^{-1}	Reference
$CFCl_2O_2NO_2$	−286		38
CF_2Cl_2	−493.3	−489.1	19
CH_2ClCF_2Cl	−543		40
CF_3CHCl_2	−740		40
$CF_2ClCHFCl$	−724		40
CF_2ClCF_2Cl	−925.5		36
CCl_3	71.1	69.9	31
CCl_3O_2	−11.3		41
$CCl_3O_2NO_2$	−83.7		38
$CHCl_3$	−103.3		18
C_2HCl_3	−7.8	−4.3	63
CH_3CCl_3	−144.6		36
$CFCl_3$	−284.9	−281.1	19
$CF_2ClCFCl_2$	−726.8		36
CCl_4	−95.8	−93.6	54
C_2Cl_4	−12.4	−11.9	18
C_2Cl_5	33.5		49
Br	111.87		24
HBr	−36.29		24
HOBr	≥−56.19		55
BrO	125.8	133.3	15
BrNO	82.2	91.5	63
BrONO	103		26
$BrNO_2$	63		39
$BrONO_2$	47		51
CH_2Br	169.0		60
CH_3Br	−38.1		9
CF_3Br	−650		40
CF_2ClBr	−438		40
BrCl	14.6	22.1	18
$Br_2(g)$	30.91		24
Br_2O	107.1		59
$CHBr_2$	188		60
CF_2Br_2	−379		40
CF_2BrCF_2Br	−789.9		36
$CHBr_3$	23.8		9
I	106.76		24
HI	26.50		24
HOI	−90		33
IO	126		6,16
INO	121.3	124.3	62
INO_2	60.2	66.5	62
CH_2I	230.1		35
CH_3I	14.2		23
CF_3I	−589		18
$I_2(g)$	62.42		24

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