

# Chemical Kinetic Data Base for Combustion Chemistry. Part 3. Propane

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This publication contains evaluated and estimated data on the kinetics of reactions involving propane, isopropyl radical, n-propyl radical, and various small inorganic and organic species which are of importance for proper understanding of propane pyrolysis and combustion. It is meant to be used in conjunction with the kinetic data given in earlier publications which are of direct pertinence to the understanding of methane pyrolysis and combustion, but which also contain a large volume of data that are applicable to the propane system. The temperature range covered is 300–2500 K and the density range  $1 \times 10^{16}$  to  $1 \times 10^{21}$  molecules  $\text{cm}^{-3}$ .

Key words: propane; isopropyl radical; n-propyl radical; gas kinetics; data base; combustion; rate expressions.

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## 1. Introduction

### 1.1. Scope

This is the third of a series of papers,<sup>1,2</sup> containing evaluated kinetic data on the gas phase reactions of organic fuels. The earlier evaluations covered the methane and methanol systems. Reactions of two-carbon hydrocarbons were included in the methane data base. We now expand our coverage to include the reactions involved in the early stages of propane combustion and pyrolysis. The new species that are considered here are propane, n-propyl radical, and isopropyl radical. As in our earlier work we cover all the reactions of these species with the 27 other compounds that have been considered previously as well as the self-reactions. Recommendations on the rate expressions for 71 reactions (129 reactions including multiple product paths) are presented. The  $\text{C}_3$  hydrocarbons considered in this study represent our first expansion into larger and more general hydrocarbon fuels. A number of new elements are introduced into the data base. These include the presence of the secondary C—H bond and the corresponding secondary radical. For the primary radical (n-propyl), there is now the possibility of beta C—C bond cleavage. These data represent building blocks for future work dealing with the oxidative and pyrolytic deg-

radation of increasingly more complex and realistic fuels. Of course, propane is an important fuel in its own right and the cracking of propane is an important source of ethylene. There has been considerable past work on the modeling of such systems.<sup>3</sup> It is the aim of this work to make available to such efforts the best kinetic data inputs. At the same time it is hoped that such information will serve as a ready reference to investigators of more limited aspects of the general problem. In subsequent reports we will extend this data base to cover isobutane, *t*-butyl radical, and isobutyl radical. This will be followed by reactions involving  $\text{C}_3$  and  $\text{C}_4$  unsaturated and ultimately aromatics.

Our approach is to be as inclusive as possible. Having decided on the important species to be considered, we constructed a reaction grid and examined all the possible reactions of these species. In the absence of data a best possible estimate is given. Where data on a particular reaction are not given, it is our judgment that the rate constant is sufficiently small that the reaction can be safely ignored under combustion conditions. The reaction grid containing all the reactions that have been considered can be found in Fig. 1. In all cases we give recommended rate expressions over the temperature range of 300–2500 K and the density range of  $1 \times 10^{16}$ – $1 \times 10^{21}$  molecules  $\text{cm}^{-3}$ .

### 1.2. Organization

The data are presented in the same fashion as in the earlier evaluations on methane and methanol combustion.<sup>1,2</sup>

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Fig. 1. Reaction grid. X: Reactions covered in Refs. 1 and 2. +: Reactions evaluated in current study.

It is expected that the data presented here will be used in conjunction with those in the previous publications. In the following, we provide information necessary for the use of these data.

The data are presented in four sections. The first contains a summary of the recommended rate expressions, the estimated error limits, and the page where a discussion can be found. The second section contains additional information on the individual reactions. It includes a summary of past work and the justification for the recommendations. The third and fourth sections contain relevant thermodynamic and transport property data, respectively.

### 1.3. Guide to Summary Table

The summary table contains all the recommended rate expressions, the uncertainty limits, and the page where a more detailed discussion can be found. In the case of unimolecular processes or the reverse, we give results in terms of the high-pressure limit and the departure from this limit in the form of the ratio  $k/k_\infty$  for 1 atm  $N_2$ .

### 1.4. Guide to Chemical Kinetic Data Tables

This section contains information on past work, our analysis of this literature, recommendations with regard to

rate expressions and uncertainty limits. We retain the numbering system that we use for the methane and methanol combustion system, and to the 27 species that are labeled from 2–26 for the methane system and 38–39 for the methanol system, we now add 40–42 for propane, n-propyl, and isopropyl, respectively. Since pairs of these numbers form a particular reaction, we now consider reactions of these three compounds with all lower numbered species and with themselves. These sequence numbers are at the top left-hand corner of all the data tables. This is followed by a statement of the elementary reaction and, if applicable, the appropriate equilibrium constant.

In the next row is a synopsis of previous work. It begins with a listing of the author(s) and the year of publication. In the case of a review, a note is made to this effect and in many cases this is used as a starting point for our evaluations. This is followed by a summary of the reaction conditions, the derived rate expressions, and the uncertainty limits. The latter are either given by the author or estimated by the reviewer on the basis of similar experiments. Most of the reactions are bimolecular and the units are  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . For unimolecular and termolecular reactions the units are  $\text{s}^{-1}$  and  $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ , respectively. As an aid to the user in those cases where there are considerable experimental data we also include a plot in the Arrhenius form of the data and our recommendations.

The next section contains our recommendations and a brief discussion of our rationale. We have discussed our approach in detail in our earlier paper.<sup>1</sup> Here, we simply note that we have used BEBO<sup>4</sup> transition states to fit hydrogen abstraction data over the 300–2500 K temperature range of interest. This leads in general to a  $T^2$ – $T^4$  temperature dependence for the preexponential factor. Unimolecular reactions and related processes are pressure and species (weak colliders) dependent as well as temperature dependent. We have applied standard RRKM<sup>5</sup> calculations to model the pressure and weak collider dependence. Unfortunately, the results could not be expressed in closed form. We have presented the results in the form of a rate expression for the high-pressure limit and two tables from which rate constants under specified reaction conditions can be obtained by interpolation. The first table is the result of RRKM calculations on the basis of the strong collision assumption, with the collision partner being the reactant itself, and leads to values of  $k/k_\infty$  as a function of temperature and pressure. These are correction factors to the limiting values. The second table gives the collision efficiency,  $\beta(e)$  (on a per collision basis), as a function of step size down (energy removed per collision). The tabulated results are based on the relation of Troe.<sup>6</sup> At the present time there is controversy regarding the magnitude and temperature dependence of this quantity. We have cast it in this form so that users can utilize their own step sizes. The values in the two tables refer to the reactant itself as the collider. In order to convert these values to those for an arbitrary collider we follow the approach of Troe<sup>6</sup> and derive a correction factor,  $\beta(c)$ , which is based on the ratio of the collisional properties of reactant and collider. Multiplying this factor with the collision efficiency derived earlier leads to a total collision efficiency,  $\beta(t) = \beta(e)\beta(c)$ .  $\beta(t)$  is then used to scale the reaction pressure in our table and thus obtain an effective pressure for determining the rate constant ratios.

To illustrate the procedure we carry out fall-off calculations for propane decomposition for the case of a dilute propane in argon mixture at 1500 K. We begin by determining  $\beta(c)$ . It involves the calculation of a number of ratios. In the following, the numerator refers to the properties of the propane–argon mixture, while the denominator refers to pure propane itself. We have carried out these calculations to far more places than is justified by the accuracy of the data being treated. This should prevent any ambiguities and permit the reader to carry out similar calculations necessary for deriving unimolecular rate constants from the data tables. The calculated ratios are the following:

(a) Ratio of reduced masses ( $R$ ); for propane and argon this number is  $20.96(\text{propane-argon})/22.047(\text{propane-propane}) = 0.951$ .

(b) Ratio of collision diameters ( $C$ ); for a propane–argon mixture, this ratio is  $[5.118(\text{propane}) + 3.542(\text{argon})]/[5.118(\text{propane}) \times 2] = 0.846$ .

(c) Ratio of collision integrals ( $W$ ); we use the approximation  $W = 1/\{0.697 + 0.5185 \times \log[kT/\epsilon(\text{gas}_1\text{-gas}_2)]\}$  and  $\epsilon/k = (\text{argon-propane}) = \{[\epsilon(\text{argon-argon})]/[\epsilon(\text{propane-propane})/k]\}^{0.5}$  where  $\epsilon/k$  is the Lennard–Jones well depth.

Since  $\epsilon/k$  is 237.1 K for propane and 93.3 K for argon, the ratio of the collision integrals is  $0.821/0.899 = 0.913$ . The correction factor is then

$$\beta(c) = C^2 W / R^{0.5} = 0.67.$$

For the propane–argon mixture with a  $600 \text{ cm}^{-1}$  step size down collision efficiency on a per collision basis at 1500 K is,  $\beta(e) = 0.04$  (see 40,1). The total collision efficiency is then

$$\beta(t) = \beta(c)\beta(e) = 0.04 \times 0.67 = 0.027.$$

At 20 atm or  $10^{20}$  molecules/ $\text{cm}^3$  this is equivalent to a density of  $2.7 \times 10^{18}$  molecules  $\text{cm}^{-3}$  for propane as a strong collider. From Table A of 40,1 we then find  $k/k_\infty = 0.72$ .

For chemical activation processes the rate expressions can be obtained in an analogous manner. In addition to the possible pressure dependence of the total rate, the ratio of decomposition to stabilization is also of importance. Thus, in these cases we include a table giving this ratio as a function of temperature and pressure on the assumption of strong collisions. Note that the procedure for correction for weak collision effects in the chemical activation systems is an untested approximation. Fortunately, for the systems considered here, pressure effects turned out to be relatively unimportant.

In the course of carrying out the earlier evaluation,<sup>1</sup> we found that the data for unimolecular fall-off can generally be fitted, in the context of weak collisions, by step sizes of 50–100  $\text{cm}^{-1}$  near room temperature and 500–800  $\text{cm}^{-1}$  under high-temperature combustion conditions ( $> 900 \text{ K}$ ). This was also borne out in the present study for propane decomposition with argon as the weak collider. For strong colliders the situation is less clear, but the earlier existing data<sup>1</sup> suggest step sizes down in the 1000–2000  $\text{cm}^{-1}$  range. As an additional aid to the user and to eliminate for some case the need to interpolate in the tables, we also include recommendations for  $k/k_\infty$  values at 0.1, 1.0, and 10 atm for  $\text{N}_2$  and the reactant itself (model for strong collider) in the higher-temperature region.

Finally, for each reaction we give the references used in the evaluation, the evaluator, and the date. Hopefully, all the literature on this reaction previous to this date has been accessed. The author will be grateful to readers who will bring to his attention publications that have been inadvertently omitted.

### 1.5. Guide to Thermodynamic and Transport Tables

This section contains thermodynamic and transport properties of propane and isopropyl radicals and n-propyl radicals. For the thermodynamic properties, the temperature range covered is from 300–1500 K. The properties tabulated include heat capacity, entropy, enthalpy of formation, and Gibbs free energy of formation. In addition, we give a polynomial fit of the logarithm of the equilibrium constant of formation. The sources for these data can be found in a footnote. It should be noted that for the n-propyl and isopropyl radicals in our data base we use higher values than those used in the past. We have given a detailed justification for these numbers in an earlier paper.<sup>8</sup> For the present we note

that if the more familiar lower values<sup>9</sup> were used in the present evaluation, it would have been necessary to reject one or the other set of existing data on alkyl radical decomposition or alkyl radical addition to olefins. Our examination of the large volume of experimental results on these reactions shows no reason to reject any of the results. Indeed, they show a remarkable degree of internal consistency. Thus, in order to satisfy thermodynamics, the higher values of the heat of formation were chosen.

The transport properties are of use for evaluation of fall-off behavior. We therefore include the collision cross section and the Lennard-Jones well depth.

### 1.6. Acknowledgments

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### 1.7. References to the Introduction

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## 2. Index of Reactions and Summary of Recommended Rate Expressions

No.	Reaction	Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Uncertainty factor	Page
40,1	$\text{C}_3\text{H}_8 + \text{C}_2\text{H}_5 + \text{CH}_3$	$k_a = 7.9 \times 10^{22} T^{-1.8} \exp(-44637/T) \text{ s}^{-1}$ $\log k/k_a = -0.32 + 1.14 \times 10^{-3} T - 8.35 \times 10^{-7} T^2$ $-2.16 \times 10^{-11} T^3$ (1 atm $\text{N}_2$ , > 800K)	1.5	896 896
40,3	$\text{C}_3\text{H}_8 + \text{O}_2 \rightarrow \text{n-C}_3\text{H}_7 + \text{HO}_2$ (a) $\rightarrow \text{i-C}_3\text{H}_7 + \text{HO}_2$ (b)	$k_a = 6.6 \times 10^{-11} \exp(-25633/T)$ $k_b = 6.6 \times 10^{-11} \exp(-23950/T)$	10 10	899 899
40,4	$\text{C}_3\text{H}_8 + \text{H} \rightarrow \text{n-C}_3\text{H}_7 + \text{H}_2$ (a) $\rightarrow \text{i-C}_3\text{H}_7 + \text{H}_2$ (b)	$k_a = 2.2 \times 10^{-18} T^{2.54} \exp(-3400/T)$ $k_b = 2.16 \times 10^{-18} T^{2.4} \exp(-2250/T)$	1.3 at 400-900K, 3 at 2500K	900 900
40,5	$\text{C}_3\text{H}_8 + \text{O} \rightarrow \text{n-C}_3\text{H}_7 + \text{OH}$ (a) $\rightarrow \text{i-C}_3\text{H}_7 + \text{OH}$ (b)	$k_a = 3.2 \times 10^{-19} T^{2.68} \exp(-1870/T)$ $k_b = 7.9 \times 10^{-20} T^{2.71} \exp(-1060/T)$	2	901 901
40,6	$\text{C}_3\text{H}_8 + \text{OH} \rightarrow \text{n-C}_3\text{H}_7 + \text{H}_2\text{O}$ (a) $\rightarrow \text{i-C}_3\text{H}_7 + \text{H}_2\text{O}$ (b)	$k_{a+b} = 2.34 \times 10^{-21} T^{2.8} \exp(156/T)$ $k_a/k_b = 0.98 T^{-0.1} \exp(-448/T)$	1.3	903 903
40,7	$\text{C}_3\text{H}_8 + \text{HO}_2 \rightarrow \text{n-C}_3\text{H}_7 + \text{H}_2\text{O}_2$ (a) $\rightarrow \text{i-C}_3\text{H}_7 + \text{H}_2\text{O}_2$ (b)	$k_a = 7.9 \times 10^{-20} T^{2.55} \exp(-8300/T)$ $k_b = 1.6 \times 10^{-20} T^{2.6} \exp(-7000/T)$	2 at 753K, 10 at 300K and 2500K	903 903
40,15	$\text{C}_3\text{H}_8 + \text{HCO} \rightarrow \text{n-C}_3\text{H}_7 + \text{H}_2\text{CO}$ (a) $\rightarrow \text{i-C}_3\text{H}_7 + \text{H}_2\text{CO}$ (b)	$k_a = 3.4 \times 10^{-19} T^{2.5} \exp(-9275/T)$ $k_b = 1.8 \times 10^{-17} T^{1.9} \exp(-8558/T)$	3 3	904 904
40,16	$\text{C}_3\text{H}_8 + \text{CH}_3 \rightarrow \text{n-C}_3\text{H}_7 + \text{CH}_4$ (a) $\rightarrow \text{i-C}_3\text{H}_7 + \text{CH}_4$ (b)	$k_a = 1.5 \times 10^{-24} T^{3.65} \exp(-3600/T)$ $k_b = 2.5 \times 10^{-24} T^{3.46} \exp(-2758/T)$	1.5 1.5	904 904
40,17	$\text{C}_3\text{H}_8 + \text{C}_2\text{H}_5 \rightarrow \text{n-C}_3\text{H}_7 + \text{C}_2\text{H}_6$ (a) $\rightarrow \text{i-C}_3\text{H}_7 + \text{C}_2\text{H}_6$ (b)	$k_a = 1.5 \times 10^{-24} T^{3.65} \exp(-4600/T)$ $k_b = 2.5 \times 10^{-24} T^{3.46} \exp(-3758/T)$	2.5 2.5	906 906
40,19	$\text{C}_3\text{H}_8 + \text{C}_2\text{H}_3 \rightarrow \text{n-C}_3\text{H}_7 + \text{C}_2\text{H}_4$ (a) $\rightarrow \text{i-C}_3\text{H}_7 + \text{C}_2\text{H}_4$ (b)	$k_a = 1 \times 10^{-21} T^{3.3} \exp(-5285/T)$ $k_b = 1.7 \times 10^{-21} T^{3.1} \exp(-4443/T)$	10 10	906 906
40,21	$\text{C}_3\text{H}_8 + \text{C}_2\text{H} \rightarrow \text{C}_2\text{H}_2 + \text{n-C}_3\text{H}_7$ (a) $\rightarrow \text{C}_2\text{H}_2 + \text{i-C}_3\text{H}_7$ (b)	$k_a = 6 \times 10^{-12}$ $k_b = 2 \times 10^{-12}$	3 3	906 906
40,22	$\text{C}_3\text{H}_8 + \text{CH}_3\text{CO} \rightarrow \text{n-C}_3\text{H}_7 + \text{CH}_3\text{CHO}$ (a) $\rightarrow \text{i-C}_3\text{H}_7 + \text{CH}_3\text{CHO}$ (b)	$k_a = 1.7 \times 10^{-19} T^{2.6} \exp(-8886/T)$ $k_b = 8.8 \times 10^{-18} T^2 \exp(-8173/T)$	3 3	907 907
40,23	$\text{C}_3\text{H}_8 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{OOH} + \text{n-C}_3\text{H}_7$ (a) $\rightarrow \text{CH}_3\text{OOH} + \text{i-C}_3\text{H}_7$ (b)	$k_a = 1 \times 10^{-11} \exp(-9750/T)$ $k_b = 3.3 \times 10^{-12} \exp(-8581/T)$	2 at 500- 800K, 10 at 2500K	907 907
40,24	$\text{C}_3\text{H}_8 + \text{CH}_3\text{O} \rightarrow \text{n-C}_3\text{H}_7 + \text{CH}_3\text{OH}$ (a) $\rightarrow \text{i-C}_3\text{H}_7 + \text{CH}_3\text{OH}$ (b)	$k_a = 7.2 \times 10^{-13} \exp(-3250/T)$ $k_b = 2.4 \times 10^{-13} \exp(-2300/T)$	5 5	908 908

## Index of Reactions and Summary of Recommended Rate Expressions -- Continued

No.	Reaction	Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Uncertainty factor	Page
40,25	$\text{C}_3\text{H}_8 + {}^1\text{CH}_2 \rightarrow 2\text{C}_2\text{H}_5$ (a)	$k_a = 1.6 \times 10^{-10}$	3	908
	$\rightarrow i\text{-C}_3\text{H}_7 + \text{CH}_3$ (b)	$\log(k_a/k_{a+c}) = -7.85 + 1.33 \times 10^{-2}T$ $-7.51 \times 10^{-6}T^2 + 1.41 \times 10^{-9}T^3$		908
	$\rightarrow n\text{-C}_4\text{H}_{10}$ (c)	$k_b = 7.1 \times 10^{-11}$	3	908
	$\rightarrow i\text{-C}_4\text{H}_{10}$ (d)	$\log(k_b/k_{b+d}) = -7.85 + 1.33 \times 10^{-2}T$ $-7.51 \times 10^{-6}T^2 + 1.41 \times 10^{-9}T^3$		908
40,26	$\text{C}_3\text{H}_8 + {}^3\text{CH}_2 \rightarrow n\text{-C}_3\text{H}_7 + \text{CH}_3$ (a)	$k_a = 1.5 \times 10^{-24} T^{3.65} \exp(-3600/T)$	10	910
	$\rightarrow i\text{-C}_3\text{H}_7 + \text{CH}_3$ (b)	$k_b = 2.5 \times 10^{-24} T^{3.46} \exp(-3758/T)$	10	910
40,39	$\text{C}_3\text{H}_8 + \text{CH}_2\text{OH} \rightarrow n\text{-C}_3\text{H}_7 + \text{CH}_3\text{OH}$ (a)	$k_a = 3.3 \times 10^{-22} T^{2.95} \exp(-7033/T)$	5	910
	$\rightarrow i\text{-C}_3\text{H}_7 + \text{CH}_3\text{OH}$ (b)	$k_b = 1 \times 10^{-22} T^{2.95} \exp(-6033/T)$	5	910
41,1	$n\text{-C}_3\text{H}_7 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3$ (a)	$k_a = 1.2 \times 10^{13} \exp(-15249/T) \text{ s}^{-1}$	1.5	911
	$\rightarrow \text{C}_3\text{H}_6 + \text{H}$ (b)	$\log(k_a/k_{a+b}) = -0.47 + 1.91 \times 10^{-3}T$ $-1.70 \times 10^{-6}T^2$ (1 atm $\text{N}_2$ , >800K)	2	911
		$k_{a+b}/k_{b+c} = 1.1 \exp(2500/T)$	1.3	911
41,2	$n\text{-C}_3\text{H}_7 + \text{H}_2 \rightarrow \text{C}_3\text{H}_8 + \text{H}$	$3 \times 10^{-21} T^{2.84} \exp(-4600/T)$	1.5	913
41,3	$n\text{-C}_3\text{H}_7 + \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2$ (a)	$k_a = 1.5 \times 10^{-13}$ (500-900K)	3	914
	$\rightarrow n\text{-C}_3\text{H}_7\text{O}$ (b)	$k_b = 2.7 \times 10^{-5} / T^{2.7}$ (300-550K)	1.3	914
41,4	$n\text{-C}_3\text{H}_7 + \text{H} \rightarrow \text{C}_3\text{H}_6 + \text{H}_2$ (a)	$k_a = 3 \times 10^{-12}$	2	915
	$\rightarrow \text{C}_3\text{H}_8$ (b)	$k_{b+c} = 6 \times 10^{-11}$	1.5	915
	$\rightarrow \text{C}_2\text{H}_5 + \text{CH}_3$ (c)	$\log(k_c/k_{b+c}) = -3.092 + 3.5 \times 10^{-3}T$ $-9.51 \times 10^{-7}T^2$	2	915
41,5	$n\text{-C}_3\text{H}_7 + \text{O} \rightarrow \text{HCHO} + \text{C}_2\text{H}_5$ (a)	$k_{a+b} = 1.6 \times 10^{-10}$	2	917
	$\rightarrow \text{C}_2\text{H}_5\text{CHO} + \text{H}$ (b)	$k_b/k_a = 6$	1.3	917
41,6	$n\text{-C}_3\text{H}_7 + \text{OH} \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2$ (a)	$k_a = 4 \times 10^{-11}$	3	917
	$\rightarrow n\text{-C}_3\text{H}_7\text{OH}$ (b)	$k_b = 4 \times 10^{-11}$	3	917
41,7	$n\text{-C}_3\text{H}_7 + \text{HO}_2 \rightarrow \text{C}_2\text{H}_5 + \text{OH} + \text{CH}_2\text{O}$	$4 \times 10^{-11}$	2	918
41,8	$n\text{-C}_3\text{H}_7 + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{C}_3\text{H}_8$	$3.1 \times 10^{-20} T^{2.11} \exp(-1294/T)$	5	918
41,10	$n\text{-C}_3\text{H}_7 + \text{CH}_4 \rightarrow \text{C}_3\text{H}_8 + \text{CH}_3$	$4 \times 10^{-26} T^{4.02} \exp(-5473/T)$	2	918
41,11	$n\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_6 \rightarrow \text{C}_3\text{H}_8 + \text{C}_2\text{H}_5$	$4.2 \times 10^{-25} T^{3.82} \exp(-4550/T)$	3	919
41,12	$n\text{-C}_3\text{H}_7 + \text{HCHO} \rightarrow \text{C}_3\text{H}_8 + \text{CHO}$	$5 \times 10^{-21} T^{2.9} \exp(-2950/T)$	4	919

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## Index of Reactions and Summary of Recommended Rate Expressions -- Continued

No.	Reaction	Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Uncertainty factor	Page
41,15	$n\text{-C}_3\text{H}_7 + \text{HCO} \rightarrow \text{C}_3\text{H}_8 + \text{CO}$ (a)	$k_a = 1 \times 10^{-10}$	4	919
	$\rightarrow \text{C}_3\text{H}_7\text{CHO}$ (b)	$k_b = 2 \times 10^{-11}$	2	919
41,16	$n\text{-C}_3\text{H}_7 + \text{CH}_3 \rightarrow n\text{-C}_4\text{H}_{10}$ (a)	$k_a = 3.2 \times 10^{-10} T^{-0.32}$	1.4	920
	$\rightarrow \text{CH}_4 + \text{C}_3\text{H}_6$ (b)	$k_b = 1.9 \times 10^{-11} T^{-0.32}$	1.7	920
41,17	$n\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_5 \rightarrow n\text{-C}_5\text{H}_{12}$ (a)	$k_a = 3.3 \times 10^{-11}$	1.3	921
	$\rightarrow \text{C}_3\text{H}_6 + \text{C}_2\text{H}_6$ (b)	$k_b = 2.4 \times 10^{-12}$	1.4	921
	$\rightarrow \text{C}_3\text{H}_8 + \text{C}_2\text{H}_4$ (c)	$k_c = 1.9 \times 10^{-12}$	1.4	921
41,18	$n\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_4 \rightarrow i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_4$	$8 \times 10^{-14} \exp(-3500/T) \times \exp(-1000/T) / (1 + \exp(-1000/T))$	3	921
41,19	$n\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_4 + \text{C}_3\text{H}_6$ (a)	$2 \times 10^{-12}$	3	922
	$\rightarrow \text{C}_3\text{H}_8 + \text{C}_2\text{H}_2$ (b)	$2 \times 10^{-12}$	3	922
	$\rightarrow \text{C}_5\text{H}_{10}$ (c)	$1.6 \times 10^{-11}$	2.5	922
41,20	$n\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_5 + \text{C}_2\text{H}_4$ (a)	$1.2 \times 10^{-12} \exp(-4531/T)$	3	923
	$\rightarrow n\text{-C}_3\text{H}_7\text{CH}=\text{CH}$ (b)			923
41,21	$n\text{-C}_3\text{H}_7 + \text{C}_2\text{H} \rightarrow \text{C}_2\text{H}_2 + \text{C}_3\text{H}_6$ (a)	$1 \times 10^{-11}$	3	924
	$\rightarrow \text{C}_3\text{H}_3 + \text{C}_2\text{H}_5$ (b)	$2 \times 10^{-11}$	2	924
41,22	$n\text{-C}_3\text{H}_7 + \text{CH}_3\text{CO} \rightarrow \text{CH}_3\text{COC}_3\text{H}_7$	$3.6 \times 10^{-11}$	1.5	924
41,23	$n\text{-C}_3\text{H}_7 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{CH}_2\text{O} + \text{C}_2\text{H}_5$	$6 \times 10^{-11}$	1.5	924
41,24	$n\text{-C}_3\text{H}_7 + \text{CH}_3\text{O} \rightarrow \text{C}_3\text{H}_8 + \text{H}_2\text{CO}$ (a)	$k_a = 4 \times 10^{-11}$	3	924
	$\rightarrow n\text{-C}_3\text{H}_7\text{OCH}_3$ (b)	$k_b = 1.6 \times 10^{-11}$	3	924
41,25	$n\text{-C}_3\text{H}_7 + {}^1\text{CH}_2 \rightarrow \text{C}_2\text{H}_5 + \text{C}_2\text{H}_4$ (a)	$k_a + k_b = 6 \times 10^{-11}$	3	925
	$\rightarrow \text{C}_3\text{H}_6 + \text{CH}_3$ (b)	$k_a/k_b \geq 2.5$	3	925
41,26	$n\text{-C}_3\text{H}_7 + {}^3\text{CH}_2 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5$ (a)	$k_a = 3 \times 10^{-11}$	3	925
	$\rightarrow \text{C}_3\text{H}_6 + \text{CH}_3$ (b)	$k_b = 3 \times 10^{-12}$	3	925
41,38	$n\text{-C}_3\text{H}_7 + \text{CH}_3\text{OH} \rightarrow \text{C}_3\text{H}_8 + \text{CH}_2\text{OH}$ (a)	$k_a = 5.3 \times 10^{-23} T^{3.17} \exp(-4610/T)$	3	925
	$\rightarrow \text{CH}_3\text{O} + \text{C}_3\text{H}_8$ (b)	$k_b = 2.4 \times 10^{-23} T^{3.1} \exp(-4500/T)$	3	925
41,39	$n\text{-C}_3\text{H}_7 + \text{CH}_2\text{OH} \rightarrow n\text{-C}_4\text{H}_9\text{OH}$ (a)	$k_a = 1.6 \times 10^{-11}$	2	926
	$\rightarrow \text{C}_3\text{H}_8 + \text{H}_2\text{CO}$ (b)	$k_b = 1.6 \times 10^{-12}$	3	926
	$\rightarrow \text{C}_3\text{H}_6 + \text{CH}_3\text{OH}$ (c)	$k_c = 0.8 \times 10^{-12}$	3	926
41,40	$n\text{-C}_3\text{H}_7 + \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_8 + i\text{-C}_3\text{H}_7$	$1.4 \times 10^{-27} T^4 \exp(-2378/T)$	1.5 at 400K	926

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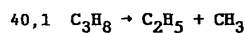
No.	Reaction	Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Uncertainty factor	Page
41,41	$\text{CH}_3\text{CH}_2\text{CH}_2 + \text{CH}_3\text{CH}_2\text{CH}_2 \rightarrow$ $\text{C}_3\text{H}_6 + \text{C}_3\text{H}_8$ (a)	$k_a = 2.8 \times 10^{-12}$	1.5	927
	$\rightarrow n\text{-C}_6\text{H}_{14}$ (b)	$k_b = 1.7 \times 10^{-11}$	1.5	927
42,1	$i\text{-C}_3\text{H}_7 \rightarrow \text{C}_3\text{H}_6 + \text{H}$	$k_w = 1.6 \times 10^{13} \exp(-17991/T) \text{ s}^{-1}$	2	928
		$\log(k_a/k_{aw}) = -1.119 + 3.73 \times 10^{-3} T$ $-3.33 \times 10^{-6} T^2 + 4.68 \times 10^{-10} T^3$	2	928
	(1 atm $\text{N}_2$ , >700K)			928
		$k_{aw}/k_{bw} = 1.1 \exp(2500/T)$	1.3	928
42,2	$i\text{-C}_3\text{H}_7 + \text{H}_2 \rightarrow \text{C}_3\text{H}_8 + \text{H}$	$5.8 \times 10^{-22} T^{3.28} \exp(-4363/T)$	3	930
42,3	$i\text{-C}_3\text{H}_7 + \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2$ (a)	$2.1 \times 10^{-13}$ (>700K)	3	931
	$\rightarrow \text{C}_3\text{H}_7\text{O}_2$ (b)			
42,4	$i\text{-C}_3\text{H}_7 + \text{H} \rightarrow \text{C}_3\text{H}_6 + \text{H}_2$ (a)	$k_a = 6 \times 10^{-12}$	2	932
	$\rightarrow \text{C}_3\text{H}_8$ (b)	$k_{b+c} = 4 \times 10^{-11}$	2	932
	$\rightarrow \text{CH}_3 + \text{C}_2\text{H}_5$ (c)	$\log(k_b/k_{b+c}) = -0.626 + 1.02 \times 10^{-2} T$ $-5.44 \times 10^{-6} T^2 + 9.46 \times 10^{-10} T^3$ (1 atm $\text{N}_2$ )		932
42,5	$i\text{-C}_3\text{H}_7 + \text{O} \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}$ (a)	$k_{a+b} = 1.6 \times 10^{-10}$	2	933
	$\rightarrow \text{CH}_3\text{CHO} + \text{CH}_3$ (b)	$k_a/k_b = 1$	1.5	933
42,6	$i\text{-C}_3\text{H}_7 + \text{OH} \rightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O}$	$4 \times 10^{-11}$	3	934
42,7	$i\text{-C}_3\text{H}_7 + \text{HO}_2 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3 + \text{OH}$	$4 \times 10^{-11}$	2	934
42,8	$i\text{-C}_3\text{H}_7 + \text{H}_2\text{O}_2 \rightarrow \text{C}_3\text{H}_8 + \text{HO}_2$	$4.8 \times 10^{-22} T^{2.83} \exp(-2037/T)$	3	935
			10 at 2500K	
42,10	$i\text{-C}_3\text{H}_7 + \text{CH}_4 \rightarrow \text{C}_3\text{H}_8 + \text{CH}_3$	$1.2 \times 10^{-27} T^{4.4} \exp(-5434/T)$	3	935
42,11	$i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_6 \rightarrow \text{C}_3\text{H}_8 + \text{C}_2\text{H}_5$	$1.4 \times 10^{-26} T^{4.2} \exp(-4386/T)$	2	935
42,12	$i\text{-C}_3\text{H}_7 + \text{HCHO} \rightarrow \text{C}_3\text{H}_8 + \text{CHO}$	$1.8 \times 10^{-13} \exp(-3500/T)$	2.5	936
42,15	$i\text{-C}_3\text{H}_7 + \text{HCO} \rightarrow \text{C}_3\text{H}_8 + \text{CO}$ (a)	$k_a = 2 \times 10^{-10}$	3	936
	$\rightarrow \text{C}_3\text{H}_7\text{CHO}$ (b)	$k_b = 3 \times 10^{-11}$	3	936
42,16	$i\text{-C}_3\text{H}_7 + \text{CH}_3 \rightarrow i\text{-C}_4\text{H}_{10}$ (a)	$k_a = 4.7 \times 10^{-11} (300/T)^{0.68}$	1.5	937
	$\rightarrow \text{CH}_4 + \text{C}_3\text{H}_6$ (b)	$k_b/k_a = 0.16$	1.1	937
42,17	$i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_5 \rightarrow \text{C}_5\text{H}_{12}$ (a)	$k_a = 2.6 \times 10^{-11} (300/T)^{0.35}$	1.8	937
	$\rightarrow \text{C}_3\text{H}_8 + \text{C}_2\text{H}_4$ (b)	$k_b/k_a = 0.16$	1.1	937
	$\rightarrow \text{C}_3\text{H}_6 + \text{C}_2\text{H}_6$ (c)	$k_c/k_a = 0.20$	1.1	937



## Index of Reactions and Summary of Recommended Rate Expressions -- Continued

No.	Reaction	Rate Constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Uncertainty factor	Page
42,18	$i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_6 + \text{C}_2\text{H}_5$	$4.4 \times 10^{-14} \exp(-3324/T)$	2	938
42,19	$i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_3$			
	$\rightarrow \text{C}_2\text{H}_4 + \text{C}_3\text{H}_6$ (a)	$k_a/k_{c+d}=0.18$	1.5	939
	$\rightarrow \text{C}_2\text{H}_2 + \text{C}_3\text{H}_8$ (b)	$k_b/k_{c+d}=0.18$	1.5	939
	$\rightarrow \text{C}_5\text{H}_{10}$ (c)	$k_{c+d}=2.6 \times 10^{-11} (300/T)^{0.7}$	2	939
	$\rightarrow \text{C}_4\text{H}_7 + \text{CH}_3$ (d)	$\log(k_d/k_{c+d}) = -7.49 + 9.91 \times 10^{-3} T - 3.98 \times 10^{-6} T^2 + 4.36 \times 10^{-10} T^3$	2	939
42,20	$i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_2 \rightarrow \text{CH}_3 + 1,3\text{-C}_4\text{H}_6$	$4.6 \times 10^{-14} \exp(-3273/T)$	2	941
42,21	$i\text{-C}_3\text{H}_7 + \text{C}_2\text{H} \rightarrow \text{C}_2\text{H}_2 + \text{C}_3\text{H}_6$ (a)	$k_a=6 \times 10^{-12}$	2	941
	$\rightarrow \text{C}_5\text{H}_8$ (b)	$k_{b+c}=2.6 \times 10^{-11}$	2	941
	$\rightarrow \text{C}_4\text{H}_5 + \text{CH}_3$ (c)	$\log(k_c/k_{b+c})(1, N_2) = -4.01 + 6.80 \times 10^{-3} T - 3.73 \times 10^{-6} T^2 + 4.36 \times 10^{-10} T^3$	2	941
42,22	$i\text{-C}_3\text{H}_7 + \text{CH}_3\text{CO} \rightarrow i\text{-C}_3\text{H}_7\text{COCH}_3$	$1.5 \times 10^{-11} (300/T)^{0.35}$	2	943
42,23	$i\text{-C}_3\text{H}_7 + \text{CH}_3\text{O}_2 \rightarrow$ $\text{CH}_3\text{O} + \text{CH}_3 + \text{CH}_3\text{CHO}$	$4 \times 10^{-11}$	3	943
42,24	$i\text{-C}_3\text{H}_7 + \text{CH}_3\text{O} \rightarrow \text{C}_3\text{H}_8 + \text{CH}_2\text{O}$ (a)	$k_a=2 \times 10^{-11}$	5	943
	$\rightarrow i\text{-C}_3\text{H}_7\text{OCH}_3$ (b)	$k_b=1 \times 10^{-11}$	5	943
42,25	$i\text{-C}_3\text{H}_7 + {}^1\text{CH}_2 \rightarrow \text{C}_4\text{H}_8 + \text{H}$ (a)	$k_{a+b}=2 \times 10^{-11}$	1.5	944
	$\rightarrow \text{C}_3\text{H}_6 + \text{CH}_3$ (b)	$k_a/k_b=0.16$		944
42,26	$i\text{-C}_3\text{H}_7 + {}^3\text{CH}_2 \rightarrow \text{C}_3\text{H}_6 + \text{CH}_3$	$5 \times 10^{-11}$	2	944
42,38	$i\text{-C}_3\text{H}_7 + \text{CH}_3\text{OH} \rightarrow \text{C}_3\text{H}_8 + \text{CH}_2\text{OH}$ (a)	$k_a=5.3 \times 10^{-23} T^{3.7} \exp(-5300/T)$	3	944
	$\rightarrow \text{C}_3\text{H}_8 + \text{CH}_3\text{O}$ (b)	$k_b=2.4 \times 10^{-23} T^{3.1} \exp(-5200/T)$	5	944
42,39	$i\text{-C}_3\text{H}_7 + \text{CH}_2\text{OH} \rightarrow i\text{-C}_3\text{H}_7\text{CH}_2\text{OH}$ (a)	$k_a=2.4 \times 10^{-11}$	2	945
	$\rightarrow \text{C}_3\text{H}_8 + \text{CH}_2\text{O}$ (b)	$k_b=3.9 \times 10^{-12}$	5	945
	$\rightarrow \text{C}_3\text{H}_6 + \text{CH}_3\text{OH}$ (c)	$k_c=4.8 \times 10^{-12}$	5	945
42,40	$i\text{-C}_3\text{H}_7 + \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_8 + n\text{-C}_3\text{H}_7$	$1.4 \times 10^{-26} T^{4.2} \exp(-4386/T)$	2	945
42,41	$i\text{-C}_3\text{H}_7 + n\text{-C}_3\text{H}_7 \rightarrow$ $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$ (a)	$k_a=2.9 \times 10^{-11} (300/T)^{0.35}$	2	945
	$\rightarrow \text{C}_3\text{H}_6 + \text{C}_3\text{H}_8$ (b)	$k_b/k_a=0.4$		945
42,42	$i\text{-C}_3\text{H}_7 + i\text{-C}_3\text{H}_7 \rightarrow \text{C}_6\text{H}_{14}$ (a)	$k_a=1 \times 10^{-11} (300/T)^{0.7}$	1.5 at 300K,	946
	$\rightarrow \text{C}_3\text{H}_6 + \text{C}_3\text{H}_8$ (b)	$k_b/k_a=0.65$	2 at 946K	946

## 3. Chemical Kinetic Data Tables



Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $cm^{-3}$		
$\log K_p = 9.0359 - 19035.75/T - 116576/T^2 + 1.48086 \times 10^7/T^3$				
Al-Alami, Kiefer (1983)	1400-1800	$(1.0-4.0) \times 10^{18}$ Kr	$7.74 \times 10^{11} \exp(-28030/T) s^{-1}$	2.5
	1800-2300	$(0.5-1.1) \times 10^{18}$ Kr (Shock tube)	$4.45 \times 10^{-7} \exp(-28300/T) s^{-1}$	
Kanan, et al (1983)	773-793	$2.5 \times 10^{18}$ $C_3H_8$ (Static reactor)	$5.0 \times 10^{16} \exp(-42000/T) s^{-1}$	2
Simmie, et al (1982)	1300-1700	$10^{19}$ ; 5% $C_3H_8$ in Ar (Shock tube)	$3.6 \times 10^{14} \exp(-37600/T) s^{-1}$	4
Hautman, et al (1981)	1110-1235	$6.0 \times 10^{18}$ 0.1-1% $C_3H_8$ in $N_2$ (Atm flow reactor)	$4.0 \times 10^{16} \exp(-42800/T) s^{-1}$	1.5
Juste, et al (1981)	873-1053	$2.0 \times 10^{18}$ $N_2$ , ~10% $C_3H_8$ (Stirred reactor)	$4.48 \times 10^{16} \exp(-42650/T) s^{-1}$	1.5
Chiang, Skinner (1981)	1200-1450	$1.5 \times 10^{19}$ Ar, 5-100 ppm $C_3H_8$ (Shock tube)	$6.7 \times 10^{16} \exp(-45400/T) s^{-1}$	2
Tsang (1981) (calc.)	1100		$k_{\infty} = 5.0 \times 10^{16} \exp(-42600/T) s^{-1}$	1.5
Kolke, Gardiner (1980)	1300-1700	~ $10^{19}$ argon,	$2.5 \times 10^{16} \exp(-41400/T) s^{-1}$	4
		4.3% propane.		
Bradley (1979)	1210-1680	~ $5 \times 10^{18}$ argon,	$k(1250) = 12.5 s^{-1}$	4
		1% propane.	$k(1350) = 37.6 s^{-1}$	
			$k(1450) = 82.6 s^{-1}$	
			$k(1550) = 153 s^{-1}$	
Lifshitz, Frenklach (1976)	1050-1250	~ $1.0 \times 10^{19}$ Ar, 0.4-1.6% $C_3H_8$ (Shock tube)	$1.3 \times 10^{16} \exp(-41800/T) s^{-1}$	4
Allara, Edelson (1975)	817	$1.0 \times 10^{18}$ propane. (Modeling of static expts)	$4.0 \times 10^{16} \exp(-42550/T) s^{-1}$	1.5
Tsang (1969) (calc.)	1100		$k_{\infty} = 1.5 \times 10^{16} \exp(-41300/T) s^{-1}$	2
Recommended value			$k_{\infty} = 7.9 \times 10^{22} T^{-1.8} \exp(-44637/T) s^{-1}$	1.5
Recommended value	>800	1 atm, $N_2$	$\log k/k_{\infty} = -0.32 + 1.14 \times 10^{-3} T$ $-8.35 \times 10^{-7} T^2 - 2.16 \times 10^{-11} T^3$	

## Comments and Recommendations

There seems to be very little question regarding the high pressure rate expression in the temperature range 300-1200 K. Combining the equilibrium constant with the rate expression for the reverse combination process (see 17,16) leads to  $k(C_3H_8 \rightarrow C_2H_5 + CH_3) = 7.9 \times 10^{22} (1/T)^{1.79} \exp(-44637/T) s^{-1}$ , with an uncertainty of  $\pm 50\%$ . However, the rate constants of Kanan et al. are about 2.5 times larger. Fall-off behavior on a strong collision basis can be found in Table A. Table B gives the collision efficiencies as a function of step size down and temperatu-

re. The results of El-Alami and Kiefer are consistent with a step size down of approximately  $700 \text{ cm}^{-1}$  (in Kr). All the other studies are at pressures too close to the high pressure limit to permit accurate derivation of collision efficiencies. The work of Chiang and Skinner suggests a step size down of  $100 \text{ cm}^{-1}$  and on that basis would be far into the fall-off region. However, the activation energy is not compatible with this possibility. Many of the higher temperature studies involve complex processes. Rate constants are derived from modeling and it is difficult to make an uncertainty estimate.

Table A.  $\log(k/k_0)$  for propane decomposition as a function of temperature and pressure assuming strong collisions

log[M]	T/K									
	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.06	-0.20	-0.41	-0.67	-1.0	-1.33	-1.67	-2.0	-2.32	-2.63
16.5	-0.03	-0.11	-0.26	-0.47	-0.75	-1.03	-1.34	-1.64	-1.93	-2.20
17.0	-0.01	-0.05	-0.15	-0.31	-0.53	-0.77	-1.03	-1.30	-1.56	-1.81
17.5		-0.02	-0.08	-0.19	-0.35	-0.54	-0.76	-0.99	-1.21	-1.44
18.0		-0.01	-0.04	-0.10	-0.21	-0.36	-0.53	-0.71	-0.91	-1.10
18.5			-0.02	-0.05	-0.12	-0.21	-0.34	-0.48	-0.64	-0.79
19.0			-0.01	-0.02	-0.06	-0.11	-0.20	-0.30	-0.42	-0.53
19.5					-0.02	-0.06	-0.10	-0.17	-0.25	-0.33
20.0					-0.01	-0.02	-0.05	-0.08	-0.13	-0.17
20.5						-0.01	-0.02	-0.035	-0.06	-0.08
21.0							-0.01	-0.01	-0.02	-0.03

Table B. Collision efficiency  $\beta(e)$  for propane decomposition as a function of temperature and downward step size

T/K	Step-size ( $\text{cm}^{-1}$ )				
	150	300	600	1200	2400
300	0.14	0.3	0.5	0.69	0.82
500	0.065	0.6	0.33	0.54	0.71
700	0.033	0.095	0.22	0.41	0.61
900	0.018	0.057	0.15	0.31	0.51
1100	0.01	0.035	0.09	0.23	0.42
1300	0.006	0.021	0.065	0.16	0.33
1500	0.0036	0.013	0.04	0.11	0.25
1700	0.0021	0.0078	0.026	0.078	0.19
1900	0.0012	0.0046	0.016	0.05	0.13
2100	0.0007	0.0026	0.0094	0.031	0.09
2300	0.00037	0.0012	0.0053	0.018	0.057
2500	0.00019	0.0008	0.0020	0.01	0.034

We recommend the following expressions for fall-off behavior at 0.1, 1 and 10 atm over the temperature range 900-2500 K for  $N_2$  and  $C_3H_8$  using step sizes of  $450\text{ cm}^{-1}$  and  $1000\text{ cm}^{-1}$  respectively:

$$\log k(N_2, 0.1)/k_\infty = -0.49 + 1.99 \times 10^{-3}T - 1.87 \times 10^{-6}T^2 + 2.12 \times 10^{-10}T^3$$

$$\log k(N_2, 1.0)/k_\infty = -0.32 + 1.14 \times 10^{-3}T - 8.35 \times 10^{-7}T^2 - 2.16 \times 10^{-11}T^3$$

$$\log k(N_2, 10)/k_\infty = -0.10 + 2.23 \times 10^{-3}T + 8.9 \times 10^{-8}T^2 - 2.05 \times 10^{-10}T^3$$

and

$$\log k(C_3H_8, 0.1)/k_\infty = -0.36 + 1.35 \times 10^{-3}T - 1.13 \times 10^{-6}T^2 + 5.06 \times 10^{-11}T^3$$

$$\log k(C_3H_8, 1.0)/k_\infty = -0.21 + 6.9 \times 10^{-4}T - 3.9 \times 10^{-7}T^2 - 8.89 \times 10^{-11}T^3$$

$$\log k(C_3H_8, 10)/k_\infty = -0.03 - 2.38 \times 10^{-4}T + 4.77 \times 10^{-4}T^2 - 2.56 \times 10^{-10}T^3$$

Our estimated uncertainty is a factor of 3.

Figure 2 contains Arrhenius plots of the experimental values of rate constants for propane decomposition from 750-1250 K (B) and 1250-2300 K (A) and the recommended values with argon as the third body. "Inf" refers to the infinite high pressure rate constants. The numbers are the logarithms of the particle density followed by the chemical symbol of the bath gas. The default third body is Ar.

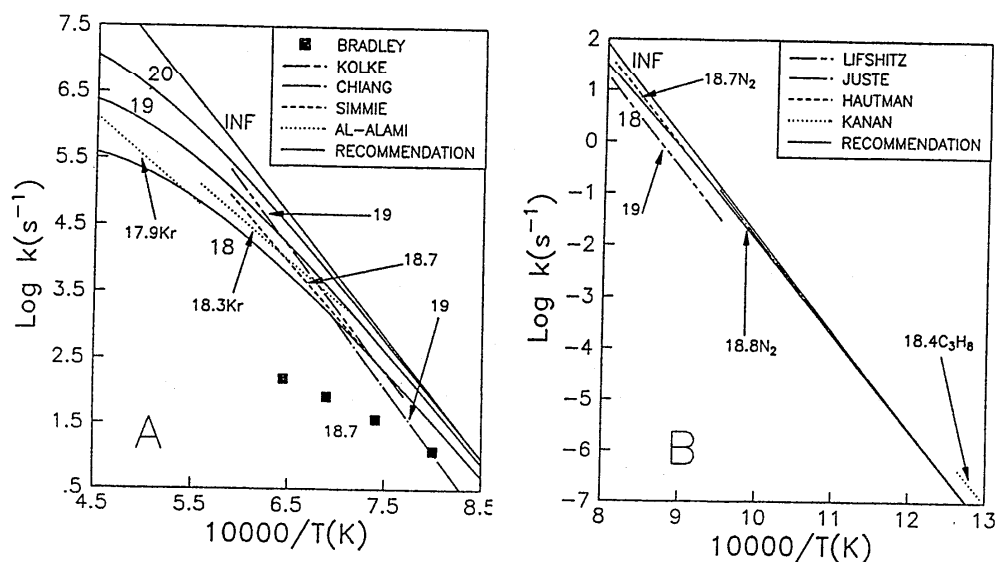


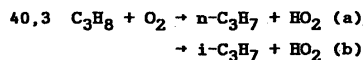
Fig. 2. Summary of experimental and recommended rate constants for the Rn.  $C_3H_8 + C_2H_5 + CH_3$

(W. Tsang, May 1985)

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Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Walker (review) (1974)	670-815		$k_a = 6.6 \times 10^{-11} \exp(-25633/T)$ $k_b = 6.6 \times 10^{-11} \exp(-23950/T)$	
Recommended value			$k_a = 6.6 \times 10^{-11} \exp(-25633/T)$	10
Recommended value			$k_b = 6.6 \times 10^{-11} \exp(-23950/T)$	10

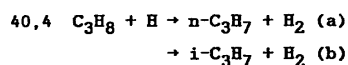
#### Comments and Recommendations

There are no data. The numbers given above are estimates and will be uncertain by an order of magnitude.

(W. Tsang, May 1985)

#### References

- Walker, R. W., "Rate Constants for Gas Phase Hydrocarbon Oxidation," in *React. Kinet.* (P. G. Ashmore, ed) Chem. Soc. Vol. I, 161 (1974)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Marshall, et al (1984)	370-534	$\sim 1.2 \times 10^{17}$ He. Flow dis-	$k_{a+b} = 1.07 \times 10^{-10} \exp(-3466/T)$	1.3
	298-370	charge. MS detection.	$k_{a+b} = 1.07 \times 10^{-11} \exp(-2626/T)$	2
Baldwin, Walker (1979) review	300-753		$k_a = 2.2 \times 10^{-10} \exp(-4715/T)$	1.5 at 700-800K
Lede, Villermaux (1977), (1978)	295	3.0 to $30.0 \times 10^{18}$ . (Tubular and stirred flow reactors). H detected by $\text{H}+\text{HgO}+\text{Hg}+\text{OH}$ .	$2.5 \times 10^{-16}$	1.5
Recommended value			$k_a = 2.2 \times 10^{-18} T^{2.54} \exp(-3400/T)$	1.3 at
Recommended value			$k_b = 2.16 \times 10^{-18} T^{2.4} \exp(-2250/T)$	400-900K, 3 at 2500K

#### Comments and Recommendations

The reported data are in substantial agreement in the 500-800 K range. We have used a BEBO transition state to fit the results. This leads to the expressions:  $k_a = 2.2 \times 10^{-18} T^{2.54} \exp(-3400/T)$  and  $k_b = 2.16 \times 10^{-18} T^{2.4} \exp(-2250/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , with an uncertainty of a factor of 1.3 in the 400-900 K range, increasing to 3 at 2500 K. The rate expression for  $k_a$  is in substantial agreement with our recommended expression for  $\text{C}_2\text{H}_6 + \text{H}$  (11,3). The results of Ledé and Villermaux may be indicative of a much smaller Arrhenius plot curvature than that estimated here.

Figure 3 contains Arrhenius plots of the experimental and our recommended values of  $k_a+k_b$  (a and b index abstractions of primary and secondary H, respectively).

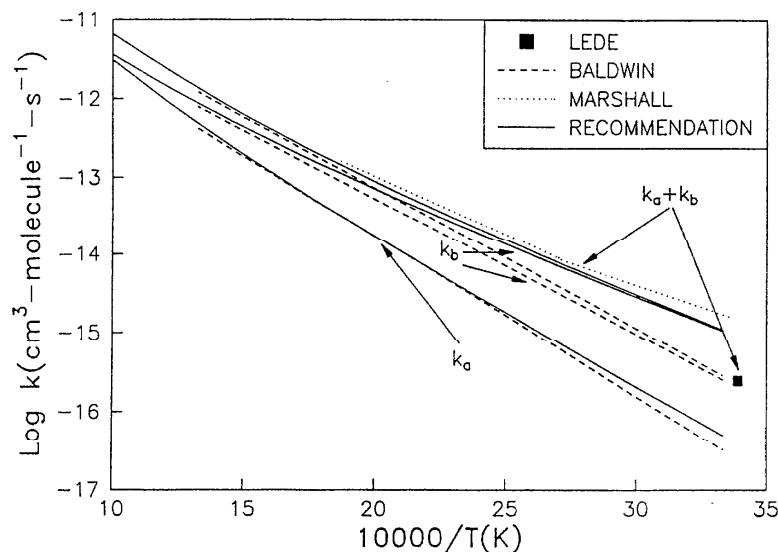
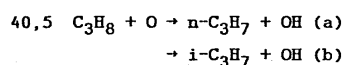


Fig. 3. Summary of experimental and recommended rate data for the Rns.  
 $\text{H} + \text{C}_3\text{H}_8 \rightarrow n\text{-C}_3\text{H}_7 + \text{H}_2$  ( $k_a$ ) and  $\text{H} + \text{C}_3\text{H}_8 \rightarrow i\text{-C}_3\text{H}_7 + \text{H}_2$  ( $k_b$ )

(W. Tsang, May 1985)

## References

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- Marshall, R. M., Furnell, H., and Sheppard, A., "Reaction of Hydrogen Atoms with Propane in the Temperature Range 298-534 K," J. Chem. Soc. Faraday Trans. 1 80, 2999 (1984)



Reference	Temp./K	Conditions [M]/molecule cm <sup>-3</sup>	Reaction rate constant, k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Uncertainty factor
Cohen, Westberg (1986) review	300-2000		$k_a = 6.2 \times 10^{-18} T^{2.4} \exp(-2770/T)$ $k_b = 9.1 \times 10^{-19} T^{2.5} \exp(-1580/T)$	2 2
Michael, et al. (1983)	411-1018	(Flash photolysis-resonance fluorescence, discharge flow)	$k_{a+b} = 1.66 \times 10^{-10} \exp(-3167/T)$	1.3
Jewell, et al (1981)	306	5.0x10 <sup>16</sup> N <sub>2</sub> (Discharge flow, O from N + NO)	$k_{a+b} = 7.8 \times 10^{-15}$	1.4
Harker, Burton (1975)	329±5	0.3-1.2x10 <sup>19</sup> He or N <sub>2</sub> N <sub>2</sub> O, C <sub>3</sub> H <sub>8</sub> (Modulation spectroscopy of OH)	$k_{a+b} = 6.5 \times 10^{-14}$	1.2
Herron, Huie (1973) review	300		$k_{a+b} = 1.48 \times 10^{-14}$	2
Recommended value			$k_a = 3.2 \times 10^{-19} T^{2.68} \exp(-1870/T)$	2
Recommended value			$k_b = 7.9 \times 10^{-20} T^{2.71} \exp(-1060/T)$	2

## Comments and Recommendations

There are surprisingly few measurements on these reactions and the existing data show considerable scatter. We have fitted the results of a BEBO calculation using Herron and Huie's recommendations as a fixed point by adjusting the activation energy. This leads to

$$k_a = 3.2 \times 10^{-19} T^{2.68} \exp(-1870/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_b = 7.9 \times 10^{-20} T^{2.71} \exp(-1060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

These values are in excellent agreement with the extensive study of Michael et al. and the review of Cohen and Westberg. We estimate the uncertainties as a factor of 2. These rate expressions reproduce satisfactorily the general trends summarized by Herron and Huie for primary and secondary H abstraction by O-atoms.

Figure 4 contains Arrhenius plots of the experimental values of rate constants for the reactions of oxygen atoms with propane and our recommended values. The subscripts a and b represent abstraction of the primary and secondary hydrogens, respectively.

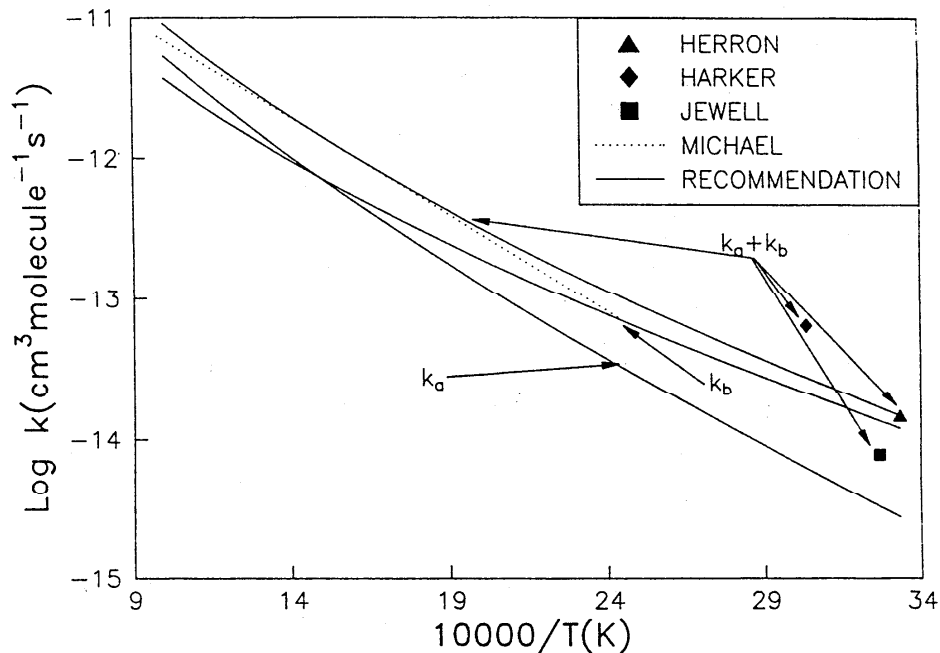
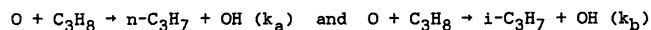


Fig. 4. Summary of experimental and recommended rate data for the Rns.

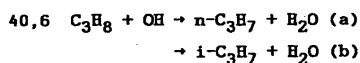


(W. Tsang, May 1986)

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Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Cohen (1982) review	300-1220		$k_a+k_b=2.34 \times 10^{-21} T^{2.8} \exp(156/T)$	1.3
			$k_a/k_b = 0.98 T^{-0.1} \exp(-448/T)$	1.5
Recommended value			$k_{a+b}=2.34 \times 10^{-21} T^{2.8} \exp(156/T)$	1.3
Recommended value			$k_a/k_b=0.98 T^{-0.1} \exp(-448/T)$	1.5

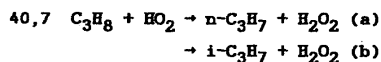
**Comments and Recommendations**

Extensive studies on this reaction have been reviewed by Cohen and his recommended expression should be used. Note that more recently he has recommended modifying his expression by multiplying with a factor of  $1.26^{300/T}$  (J. F. Bott, and N. Cohen, "A Shock Tube Study of the Reaction of Hydroxyl Radical with Propane," Aerospace Report No. ATR-84(8519)-1, Aerospace Corp., El Segundo, CA 90245, May 1984). Our BEBO calculations yield  $T^{2.6}$  for the temperature dependence of the pre-exponential factor. The  $k_a$  to  $k_b$  ratio is inferred from room temperature determinations on related compounds and a measurement at 673 K. Additional data would be useful.

(W. Tsang, May 1985)

**References**

Cohen, N., "The Use of Transition-State Theory to Extrapolate Rate Coefficients for Reaction of OH with Alkenes," *Int. J. Chem. Kinet.* **14**, 1329 (1982)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Walker, R. W. (1977) review	300-800		$k_a = 4.9 \times 10^{-13} \exp(-7521/T)$	2
			$k_b = 1.6 \times 10^{-13} \exp(-6330/T)$	2
Recommended value			$k_a = 7.9 \times 10^{-20} T^{2.55} \exp(-8300/T)$	2 at 753K,
Recommended value			$k_b = 1.6 \times 10^{-20} T^{2.6} \exp(-7000/T)$	10 at 300K and 2500K

**Comments and Recommendations**

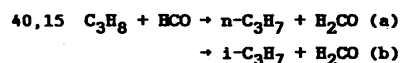
The rate expressions given by Walker are probably most reliable at 753 K. Extrapolation may lead to serious errors. Our BEBO calculations lead to a temperature dependence of  $\sim T^{2.5}$  for both reactions. Using 753 K as a fixed point, we find  $k_a = 7.9 \times 10^{-20} T^{2.5} \exp(-8300/T)$  and  $k_b = 1.55 \times 10^{-20} T^{2.6} \exp(-7000/T)$   $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  with an uncertainty of a factor of 2 at 753 K and factor of 10 at the extremities of 300 K and 2500 K. The rate expression for  $k_a$  is supported by the subsequent results of Baldwin et al. on  $\text{HO}_2$  attack on tetramethylbutane

(R.R. Baldwin, Mohamed W. H. Hisham, A. Keen and R. W. Walker, J. Chem. Soc. Faraday Trans. 1 78, 1165 (1982).

(W. Tsang, May 1985)

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Reference	Conditions		Reaction rate constant, $\text{k}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
	$\log K_p(\text{a}) = 0.56145 - 2607.89/T - 3975/T^2 - 3.5277 \times 10^6/T^3$			
	$\log K_p(\text{b}) = 0.16955 - 1846.63/T - 120369/T^2 + 8.5243 \times 10^6/T^3$			
Recommended value			$k_a = 3.4 \times 10^{-19} T^{2.5} \exp(-9275/T)$	3
Recommended value			$k_b = 1.8 \times 10^{-17} T^{1.9} \exp(-8558/T)$	3

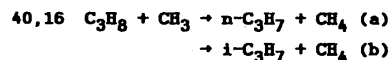
#### Comments and Recommendations

There are no data. From the data for the reverse reaction (41,12) and the equilibrium constant, we find for (a) the following expression:

$k_a = 3.4 \times 10^{-19} T^{2.5} \exp(-9275/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , with an uncertainty of a factor of 3. Using a similar rate constant for isopropyl radical attack on  $\text{H}_2\text{CO}$  we find

$k_b = 1.78 \times 10^{-17} T^{1.9} \exp(-8558/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , also with an uncertainty of a factor of 3. Note that the rate constants for alkyl radical attack on aldehydic hydrogens seem to be equal at  $182^\circ\text{C}$  (J.A. Kerr and A.F. Trotman-Dickenson, "The Reactions of Alkyl Radicals," Prog. React. Kinet. 1, 105 (1961)).

(W. Tsang, May 1985)



Reference	Conditions		Reaction rate constant, $\text{k}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Kerr, Parsonage (1976) review	550-750		$k_a = 7.9 \times 10^{-13} \exp(-5790/T)$ $k_b = 3.3 \times 10^{-13} \exp(-4834/T)$	1.3 1.3
Camilleri, et al.	676-813	$\sim 2 \times 10^{17}$ propane, 0.7-1.2% azomethane.	$k_{a+b} = 3.3 \times 10^{-12} \exp(-5692/T)$ (for $T < 743 \text{ K}$ ) $k_{a+b} = 8.32 \times 10^{-9} \exp(-11600/T)$ (for $T > 743 \text{ K}$ )	2 2
Recommended value			$k_a = 1.5 \times 10^{-24} T^{3.65} \exp(-3600/T)$	1.5
Recommended value			$k_b = 2.5 \times 10^{-24} T^{3.46} \exp(-2758/T)$	1.5

## Comments and Recommendations

The recommendations of Kerr and Parsonage are undoubtedly valid in their temperature range. The higher temperature results of Camilleri are distorted due to their neglect of the fall-off behavior of the reference reaction  $2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ . We have used the curvature from BEBO calculations to arrive at the rate expressions

$$k_a = 1.5 \times 10^{-24} T^{3.65} \exp(-3600/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \quad \text{and}$$

$$k_b = 2.5 \times 10^{-24} T^{3.46} \exp(-2758/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

with an uncertainty of a factor of 1.5.

Figure 5 contains Arrhenius plots of the experimental values of rate constants for the reactions of methyl radicals with propane and our recommended values. The subscripts a and b represent abstraction of the primary and secondary hydrogens, respectively.

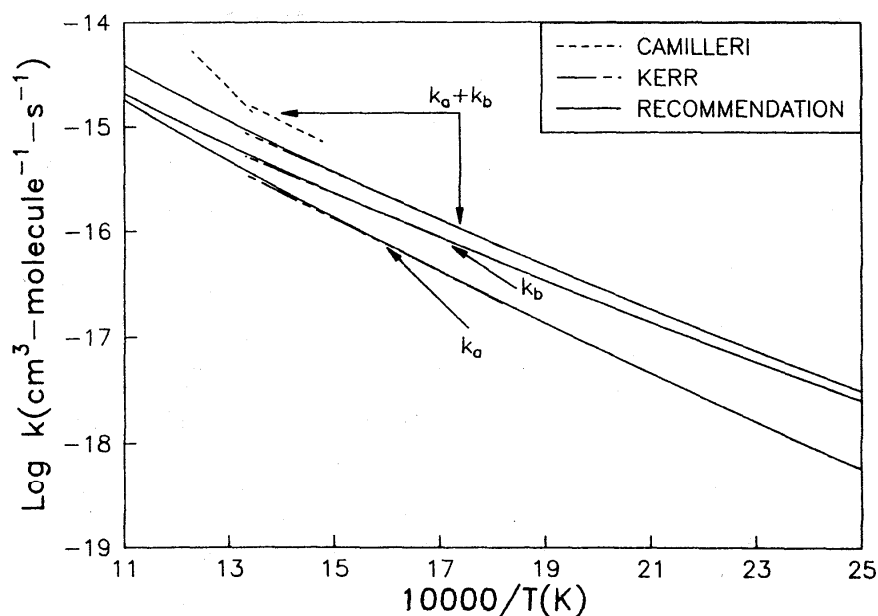
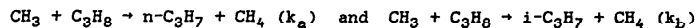


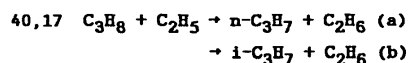
Fig. 5. Summary of experimental and recommended rate data for the Rns.



(W. Tsang, May 1985)

## References

- Camilleri, P., Marshall, R. M., and Furnell, H., "Arrhenius Parameters for the Unimolecular Decompositions of Azomethane and n-Propyl and Isopropyl Radicals and for Methyl Radical Attack on Propane," *J. Chem. Soc. Faraday Trans. 1* 71, 1491 (1975)



Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $cm^{-3}$		
Recommended value			$k_a = 1.5 \times 10^{-24} T^{3.65} \exp(-4600/T)$	2.5
Recommended value			$k_b = 2.5 \times 10^{-24} T^{3.46} \exp(-3758/T)$	2.5

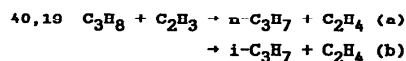
#### Comments and Recommendations

There are no data. From the general trends in going from methyl to ethyl abstraction reactions we suggest an increase of 8.5 kJ in activation energy. This leads to (in  $cm^3molecule^{-1}s^{-1}$ ):

$$k_a = 1.5 \times 10^{-24} T^{3.65} \exp(-4600/T) \text{ and } k_b = 2.5 \times 10^{-24} T^{3.46} \exp(-3758/T)$$

with an uncertainty of a factor of 2.5. These expressions are compatible with experimental results for  $C_2D_5$  attack on n-butane and neopentane (Boddy and Steacie, Can. J. Chem. 38, 1756 (1960)).

(W. Tsang, May 1985)

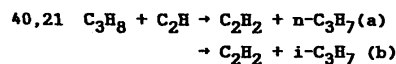


Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $cm^{-3}$		
Recommended value			$k_a = 1 \times 10^{-21} T^{3.3} \exp(-5285/T)$	10
Recommended value			$k_b = 1.7 \times 10^{-21} T^{3.1} \exp(-4443/T)$	10

#### Comments and Recommendations

There are no data. We assume for reaction (a) the same rate expression as for  $C_2H_3 + C_2H_6 \rightarrow C_2H_4 + C_2H_5$  (19,11). Thus,  $k_a = 1.0 \times 10^{-21} T^{3.3} \exp(-5285/T) cm^3molecule^{-1}s^{-1}$ . Since this is an estimated value we assign an uncertainty of a factor of 10. For Rn. (b), we assume the ratio for secondary to primary H abstraction by  $CH_3$  from propane (40,19) and obtain  $k_b = 1.7 \times 10^{-21} T^{3.1} \exp(-4443/T) cm^3molecule^{-1}s^{-1}$ . The uncertainty is also a factor of 10.

(W. Tsang, May 1985)

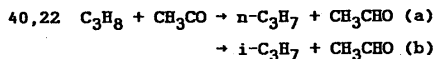


Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $cm^{-3}$		
Recommended value			$k_a = 6 \times 10^{-12}$	3
Recommended value			$k_b = 2 \times 10^{-12}$	3

Comments and Recommendations

There are no data for these reactions. We take the rate constant for (a) to be the same as that for C<sub>2</sub>H<sub>6</sub> and recommend  $k_a = 6.0 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  with an uncertainty of a factor of 2. For  $k_b$ , in view of the highly exothermic nature of this reaction, we assume the abstraction reaction to depend only on the availability of H-atoms and this leads to  $k_b = 2.0 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , with an uncertainty of a factor of 3.

(W. Tsang, May 1985)



Reference	Conditions		Reaction rate constant, k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Uncertainty factor
	Temp./K	[M]/molecule cm <sup>-3</sup>		
log K <sub>p</sub> (a) = 0.5445 - 2431.69/T - 33368/T <sup>2</sup> + 2.9117x10 <sup>6</sup> /T <sup>3</sup>				
log K <sub>p</sub> (b) = 0.1526 - 1670.43/T - 149762/T <sup>2</sup> + 1.49637x10 <sup>6</sup> /T <sup>3</sup>				
Recommended value			$k_a = 1.7 \times 10^{-19} T^{2.6} \exp(-8886/T)$	3
Recommended value			$k_b = 8.8 \times 10^{-18} T^2 \exp(-8173/T)$	3

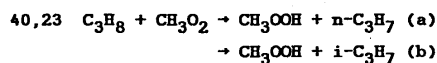
Comments and Recommendations

There are no data. From the equilibrium constant and the estimated reverse rate constant (J.A. Kerr and A.F. Trotman-Dickenson, "The Reactions of Alkyl Radicals," Prog. React. Kinet. 1, 105 (1961)) we obtain (in cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>):

$$k_a = 1.7 \times 10^{-19} T^{2.6} \exp(-8886/T) \quad \text{and} \quad k_b = 8.8 \times 10^{-18} T^2 \exp(-8173/T)$$

The uncertainty is a factor of 3.

(W. Tsang, May 1985)

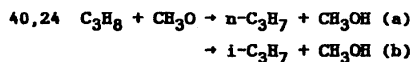


Reference	Conditions		Reaction rate constant, k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Uncertainty factor
	Temp./K	[M]/molecule cm <sup>-3</sup>		
Walker (1984) review			$k_a = 1 \times 10^{-11} \exp(-9750/T)$ $k_b = 3.3 \times 10^{-12} \exp(-8581/T)$	
Recommended value			$k_a = 1 \times 10^{-11} \exp(-9750/T)$	2 at 500-
Recommended value			$k_a = 1 \times 10^{-11} \exp(-9750/T)$	2 at 500-800K,
Recommended value			$k_b = 3.3 \times 10^{-12} \exp(-8581/T)$	10 at 2500K

Comments and Recommendations

There are no data. We recommend use of rate expressions derived from Walker's review with an uncertainty of a factor of 2 from 500-800 K, increasing to a factor of 10 at 2500 K.

(W. Tsang, May 1985)



Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $cm^{-3}$		
Berces, Trotman- Dickenson (1961)	523		$k_a/k_b \cong 0.5$	
Shaw, Trotman- Dickenson (1960)	473-673	$1-2 \times 10^{17}$ propane with dimethyl- peroxide or methyl nitrate	$k_{a+b} = 6.6 \times 10^{-13} \exp(-2620/T)$	2
Recommended value			$k_a = 7.2 \times 10^{-13} \exp(-3250/T)$	5
Recommended value			$k_b = 2.4 \times 10^{-13} \exp(-2300/T)$	5

#### Comments and Recommendations

We recommend the use of the experimentally determined rate constants. If we assume that on a per hydrogen atom basis the A-factors are equal, then there is a factor of 3 difference in reaction degeneracy between attack on primary and secondary H-atoms. In order to obtain the factor of 0.5 difference at 523 K, this then leads to (in  $cm^3molecule^{-1}s^{-1}$ ):

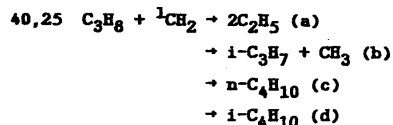
$$k_a = 7.2 \times 10^{-13} \exp(-3250/T) \quad \text{and} \quad k_b = 2.4 \times 10^{-13} \exp(-2300/T)$$

The uncertainty is a factor of 5.

(W. Tsang, May 1985)

#### References

- Berces, T., and Trotman-Dickenson, A. F., "The Reactions of Methoxyl Radical with Cyclopropane and Isobutene," J. Chem. Soc., 348 (1961)
- Shaw, R., and Trotman-Dickenson, A. F., "The Reaction of Methoxyl Radicals with Allenes," J. Chem. Soc., 3210 (1960)



Reference	Conditions		Reaction rate constant, $k/cm^3molecule^{-1}s^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $cm^{-3}$		
Halberstadt, Crump (1982)	300	$3.0-2.5 \times 10^{19}$ (Ketene photolysis in propane)	$k_{a+b}/k({}^1CH_2+CH_4) = 3.3$ $k_b/k_a = 0.43$	1.5 1.5
Recommended value			$k_a = 1.6 \times 10^{-10}$	3
Recommended value			$\log k_a/k_{a+c} = -7.85 + 1.33 \times 10^{-2}T$ $-7.51 \times 10^{-6}T^2 + 1.41 \times 10^{-9}T^3$	
Recommended value			$k_b = 7.1 \times 10^{-11}$	3
Recommended value			$\log k_b/k_{b+d} = -7.85 + 1.33 \times 10^{-2}T$ $-7.51 \times 10^{-6}T^2 + 1.41 \times 10^{-9}T^3$	

## Comments and Recommendations

There are no direct measurements of rate constants for these reactions. Using the results of Halberstadt and Crump and our recommended value for  $k(^1\text{CH}_2 + \text{CH}_4)$  (25,10) leads to:  $k_a = 1.6 \times 10^{-10}$  and  $k_b = 7.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Under combustion conditions there is a tendency for those chemically activated molecules to fragment. Our RRKM calculations, on a strong collision basis, for n-butane decomposition can be found in Table A (the subscript s refers to the stabilization of the adduct). Results for isobutane are quite similar. Collision efficiency, as a function of step size down and temperature, can be found in Table B.

Table A. log of fractional decomposition ( $\log k_a/k_{a+s}$ ) of normal butane following  $^1\text{CH}_2$  insertion into propane on a strong collision basis as a function of temperature and pressure

log[M]	T/K												
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500	
16.0	-1.06	-0.58	-0.26	-0.11	-0.05	-0.02	-0.01						
17.0	-2.01	-1.39	-0.72	-0.43	-0.22	-0.10	-0.05	-0.02	-0.01				
18.0	-3.01	-2.36	-1.62	-1.05	-0.64	-0.37	-0.21	-0.11	-0.06	-0.032	-0.01	-0.01	
19.0	-4.01	-3.36	-2.60	-1.94	-1.37	-0.93	-0.63	-0.39	-0.25	-0.16	-0.10	-0.07	
20.0	-5.01	-4.36	-3.59	-2.91	-2.29	-1.77	-1.40	-0.99	-0.73	-0.54	-0.39	-0.29	
21.0	-6.01	-5.36	-4.59	-3.91	-3.28	-2.75	-2.35	-1.86	-1.53	-1.26	-1.04	-0.88	

Table B. Collision efficiency  $\beta(e)$  for propane decomposition as a function of temperature and downward step size

T/K	Step-size ( $\text{cm}^{-1}$ )				
	150	300	600	1200	2400
300	0.14	0.30	0.50	0.69	0.82
500	$6.2 \times 10^{-2}$	0.16	0.33	0.53	0.71
700	$2.8 \times 10^{-2}$	$8.3 \times 10^{-2}$	0.20	0.38	0.59
900	$1.6 \times 10^{-2}$	$5.0 \times 10^{-2}$	0.13	0.29	0.49
1100	$8.9 \times 10^{-3}$	$3.0 \times 10^{-2}$	$8.6 \times 10^{-2}$	0.21	0.39
1300	$5.0 \times 10^{-3}$	$1.8 \times 10^{-2}$	$5.5 \times 10^{-2}$	0.14	0.30
1500	$2.8 \times 10^{-3}$	$1.0 \times 10^{-2}$	$3.4 \times 10^{-2}$	$9.6 \times 10^{-2}$	0.22
1700	$1.5 \times 10^{-3}$	$5.7 \times 10^{-3}$	$2.0 \times 10^{-2}$	$6.1 \times 10^{-2}$	0.16
1900	$8.0 \times 10^{-4}$	$3.1 \times 10^{-3}$	$1.1 \times 10^{-2}$	$3.6 \times 10^{-2}$	0.10
2100	$4.0 \times 10^{-4}$	$1.5 \times 10^{-3}$	$5.7 \times 10^{-3}$	$2.0 \times 10^{-2}$	$6.0 \times 10^{-2}$
2300	$1.9 \times 10^{-4}$	$7.2 \times 10^{-4}$	$2.7 \times 10^{-3}$	$9.9 \times 10^{-3}$	$3.2 \times 10^{-2}$
2500	$7.9 \times 10^{-5}$	$3.1 \times 10^{-4}$	$1.2 \times 10^{-3}$	$4.5 \times 10^{-3}$	$1.6 \times 10^{-2}$

At 0.1, 1.0 and 10 atm of  $\text{N}_2$  and over the temperature range 700-2500 K we recommend:

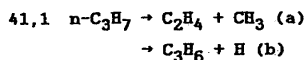
$$\log k(\text{fractional decomp, } \text{N}_2, 0.1) = -4.87 + 9.09 \times 10^{-3} T - 5.56 \times 10^{-6} T^2 + 1.11 \times 10^{-9} T^3$$

$$\log k(\text{fractional decomp, } \text{N}_2, 1.0) = -7.85 + 1.33 \times 10^{-2} T - 7.51 \times 10^{-6} T^2 + 1.41 \times 10^{-9} T^3$$

$$\log k(\text{fractional decomp, } \text{N}_2, 10) = -9.02 + 1.27 \times 10^{-2} T - 5.91 \times 10^{-6} T^2 + 9.05 \times 10^{-10} T^3$$







Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Kerr, Trotman-Dickenson (1959)	543-694	$\sim 3.0 \times 10^{17}$ n-butylaldehyde.	$k_a = 1.6 \times 10^{11} \exp(-12690/T) \text{s}^{-1}$	2
Calvert, Sleppy (1958)	471-549	$\sim 2 \times 10^{18}$ n-butylaldehyde.	$k_a = 4 \times 10^{15} \exp(-17573/T) \text{s}^{-1}$	2
Kerr, Calvert (1961)	488-563	$\sim 2.5 \times 10^{17}$ azopropane; also experiments with up to $8 \times 10^{18}$ $\text{CO}_2$ .	$k_a = 7.2 \times 10^{14} \exp(-17372/T) \text{s}^{-1}$	1.5
Back, Takamuku (1964)	573-673	$\sim 4.0 \times 10^{18}$ propane.	$k_a = 2 \times 10^{11} \exp(-12638/T) \text{s}^{-1}$	3
Lin, Laidler (1966)	533-573	$\sim 0.5\text{-}2.0 \times 10^{18}$ propane.	$k_a = 2.3 \times 10^{13} \exp(-15810/T) \text{s}^{-1}$	1.3
Papic, Laidler (1971)	523-625	$\sim 0.5\text{-}7.0 \times 10^{18}$ propane.	$k_a = 1.5 \times 10^{14} \exp(-16415/T) \text{s}^{-1}$	1.3
Camilleri, et al. (1975)	678-813	$\sim 2.0 \times 10^{17}$ propane.	$k_a = 6.3 \times 10^{12} \exp(-16367/T) \text{s}^{-1}$	2
Recommended value			$k_a = 1.2 \times 10^{13} \exp(-15249/T) \text{s}^{-1}$	1.5
Recommended value	>800	1 atm, $\text{N}_2$	$\log(k_a/k_{a0}) = -0.47 + 1.91 \times 10^{-3}T - 1.70 \times 10^{-6}T^2$	2
Recommended value			$k_{a0}/k_{b0} = 1.1 \exp(2500/T)$	1.3

#### Comments and Recommendations

All quantitative results deal with reaction (a). This is the main reaction. Experimental results are in the form of  $k_a/k^{0.50}(2n\text{-C}_3\text{H}_7 \rightarrow \text{C}_6\text{H}_{14})$ . We have used  $k(2n\text{-C}_3\text{H}_7 \rightarrow \text{C}_6\text{H}_{14}) = 1.7 \times 10^{11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ . Although the rate parameters are widely scattered, the actual rates are in fairly good agreement especially after correction for small pressure effects. They yield the rate expression:

$$k_a = 1.2 \times 10^{13} \exp(-15249/T) \text{s}^{-1} \text{ with an uncertainty of } \pm 50\%.$$

The hydrogen ejection channel (b) is small compared to (a). We recommend, as a maximum,  $k_a/k_b = 1.07 \exp(2500/T)$ . This is based on our calculated value for the processes  $k(s\text{-C}_4\text{H}_9 \rightarrow \text{C}_3\text{H}_6 + \text{CH}_3)$  and  $k(s\text{-C}_4\text{H}_9 \rightarrow 2\text{-C}_4\text{H}_8 + \text{H})$ . Experimentally, at 1100 K, the branching ratio ( $k_a/k_b$ ) for n-propyl decomposition has been found to be  $>10$ . (Tsang, W., Int. J. Chem. Kinet. 10, 667 (1978)). Note that as one goes further into the fall-off region, the lower energy channel ( $\text{CH}_3$  ejection) is expected to become more important. Fall-off behavior on the basis of strong collisions can be found in Table A and the collision efficiencies in Table B.

Fall-off characteristics at 0.1, 1, and 10 atm in  $\text{N}_2$  and  $\text{C}_3\text{H}_8$ , based on a step size down of  $500 \text{ cm}^{-1}$  and  $1000 \text{ cm}^{-1}$  respectively, applicable over the temperature range 600-1500 K, are as follows:

$$\log k(\text{N}_2, 0.1)/k_\infty = -0.37 + 1.81 \times 10^{-3}T - 2.077 \times 10^{-6}T^2$$

$$\log k(\text{N}_2, 1.0)/k_\infty = -0.47 + 1.906 \times 10^{-3}T - 1.695 \times 10^{-6}T^2$$

$$\log k(\text{N}_2, 10)/k_\infty = -0.337 + 1.248 \times 10^{-3}T - 9.891 \times 10^{-7}T^2$$

$$\log k(\text{C}_3\text{H}_8, 0.1)/k_\infty = -0.41 + 1.78 \times 10^{-3}T - 1.747 \times 10^{-6}T^2$$

$$\log k(\text{C}_3\text{H}_8, 1.0)/k_\infty = -0.374 + 1.43 \times 10^{-3}T - 1.18036 \times 10^{-6}T^2$$

$$\log k(\text{C}_3\text{H}_8, 10)/k_\infty = -0.193 + 6.97 \times 10^{-4}T - 5.26 \times 10^{-7}T^2$$

We estimate the uncertainties for these expressions to be a factor of 2.

Figure 6 contains Arrhenius plots of the experimental values of rate constants for n-propyl radical decomposition and the recommended high pressure rate constants. The numbers associated with the experimental lines are estimated factors to be added to the respective experimental measurements (in log units) to take into account fall off effects. The default value is zero and implies that the experiments are near the high pressure limit. These have been derived on the basis of RRKM calculations.

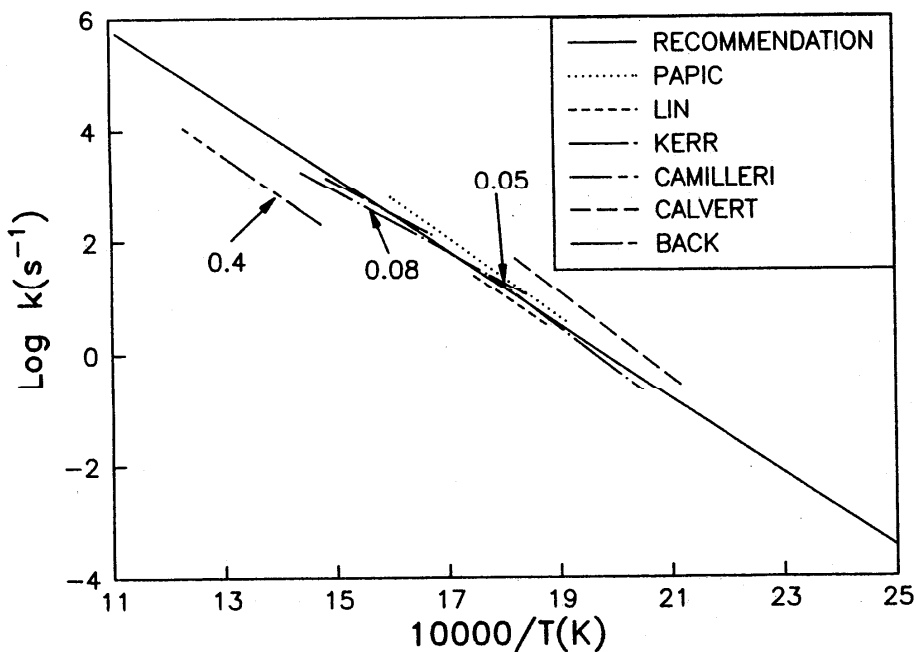


Fig. 6. Summary of experimental and recommended rate constants for the Rn.  $n\text{-C}_3\text{H}_7 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3$

Table A.  $\log(k/k_\infty)$  for n-propyl decomposition as a function of temperature and pressure for strong colliders

log(M)	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.039	-0.15	-0.37	-0.65	-0.96	-1.29	-1.61	-1.90	-2.17	-2.41	-2.62	-2.79
16.5	-0.014	-0.072	-0.21	-0.42	-0.66	-0.94	-1.21	-1.47	-1.72	-1.94	-2.14	-2.31
17.0	-0.005	-0.03	-0.10	-0.24	-0.41	-0.64	-0.86	-1.08	-1.29	-1.50	-1.68	-1.84
17.5		-0.01	-0.044	-0.12	-0.23	-0.39	-0.56	-0.74	-0.92	-1.09	-1.24	-1.38
18.0			-0.016	-0.05	-0.11	-0.21	-0.33	-0.46	-0.59	-0.726	-0.85	-0.957
18.5				-0.02	-0.05	-0.10	-0.17	-0.25	-0.34	-0.43	-0.53	-0.61
19.0					-0.02	-0.04	-0.07	-0.12	-0.17	-0.22	-0.28	-0.34
19.5						-0.015	-0.03	-0.05	-0.07	-0.10	-0.13	-0.15
20.0							-0.01	-0.016	-0.026	-0.037	-0.05	-0.06
20.5									-0.01	-0.01	-0.02	-0.02
21.0												-0.01

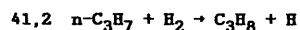
Table B. Collision efficiency  $\beta_e$  as a function of downward step size and temperature

T/K	Step-size ( $\text{cm}^{-1}$ )				
	150	300	600	1200	2400
300	0.13	0.28	0.47	0.67	0.81
500	0.049	0.13	0.28	0.48	0.67
700	0.02	0.06	0.16	0.32	0.53
900	0.0085	0.028	0.083	0.20	0.38
1100	0.0034	0.012	0.04	0.11	0.25
1300	0.0013	0.005	0.017	0.053	0.14
1500	0.0005	0.002	0.0064	0.022	0.066

(W. Tsang, May 1985)

## References

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Reference	Conditions		Reaction rate constant, $\text{k}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Baldwin, et al. (1973)	723	$10^{18}$ (Static oxidation of butyraldehyde, with and without $\text{H}_2$ )	$1.5 \times 10^{-16}$	5
Recommended value			$3 \times 10^{-21} T^{2.84} \exp(-4600/T)$	1.5

## Comments and Recommendations

The only measurement is that of Baldwin and coworkers. It is, however, dependent on three other rate constants: n-propyl attack on n-butyraldehyde, n-propyl

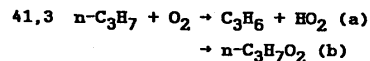
recombination and n-propyl attack on  $O_2$ . From the thermodynamics and the rate constant for the reverse reaction we obtain a result that is a factor of 3.5 times larger. There have, however, been changes in the rates of the reference reactions used by Baldwin. We have chosen to use their experimental value for  $k(n-C_3H_7 + O_2)/k(n-C_3H_7 + H_2)$  and their latest recommendation for  $k(n-C_3H_7 + O_2)$  at 723 K of  $1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (a 20% correction has been made to place the results at this temperature). This leads to:

$k(n-C_3H_7 + H_2) = 2.9 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Averaging this with our calculated value  $5.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , we obtain  $4.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The recommended rate expression is that which we derived from the thermodynamics and the reverse reaction except that we have made a small adjustment of the activation energy, i.e.  $k(n-C_3H_7 + H_2) = 3 \times 10^{-21} T^{2.84} \exp(-4600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , so as to match our average value at 723 K. It is in excellent agreement with our recommendations for  $k(C_2H_5 + H_2)$ . The uncertainty is a factor of 2.5.

(W. Tsang, Oct. 1986)

#### References

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Reference	Conditions		Reaction rate constant, $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Slagle, et al (1984)	635	1.2-12x10 <sup>16</sup> He or N <sub>2</sub>	2.4x10 <sup>-13</sup>	1.5
	550		1.1x10 <sup>-13</sup>	
Baldwin, et al (1980) review	753		1.2x10 <sup>-13</sup>	
Walker (1975) review	723		3.0x10 <sup>-14</sup>	2
	753		3.6x10 <sup>-14</sup>	2
Recommended value	500-900		$k_a = 1.5 \times 10^{-13}$	3
Recommended value	300-550		$k_b = 2.7 \times 10^{-5} / T^{2.7}$	1.3

#### Comments and Recommendations

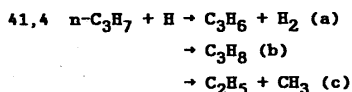
The recent work of Slagle et al. demonstrated that while the absolute rate constant for  $n-C_3H_7$  disappearance decreased with temperature, the fractional conversion to  $C_3H_6$  increased. They suggested that the controlling mechanism involved the formation of an excited n-propylperoxy complex. The details of the mechanism have not yet been worked out. It is surprising that there is no observable pressure effect on propene formation. We recommend use of  $k_a = 1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in the 500-900 K temperature range with an uncertainty of a factor of 3. At lower temperatures, the addition reaction predominates and, on the basis of the results of Slagle et al., leads to the following rate expression

$k_p = 2.7 \times 10^{-5} / T^{2.7} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range of 300-500 K. The uncertainty is a factor of 1.3. At higher temperatures this reaction is reversed and there are increasingly important contributions from the disproportionation reaction. At temperatures above 1000 K the instability of the n-propyl radical is such that these reactions become unimportant.

(W. Tsang, Oct. 1986)

#### References

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- Walker, R. W., "A Critical Survey of Rate Constants for Reactions in Gas Phase Hydrocarbon Oxidation" in React. Kinet., Vol. I [P.G. Ashmore, ed] Chem. Soc. London, W1VOBN p. 169 (1975)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$k_a = 3 \times 10^{-12}$	2
Recommended value			$k_{b+c} = 6 \times 10^{-11}$	1.5
Recommended value			$\log(k_c/k_{b+c}) = -3.092 + 3.5 \times 10^{-3}T - 9.51 \times 10^{-7}T^2$	2

#### Comments and Recommendations

There are no data for these reactions. For reaction (a) we recommend the rate constant for H disproportionation with ethyl i.e.  $k_a = 3.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with an uncertainty of a factor of 2. Reaction (c) involves the decomposition of excited  $\text{C}_3\text{H}_8$ . The total rate  $k_p + k_c$  should be very close to that for  $\text{H} + \text{C}_2\text{H}_5$  (17,4), i.e.  $k_{p+c} = 6.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , with an uncertainty factor of 1.5 and no pressure dependence.

The ratio  $k_c/k_{p+c}$  is given in Table A assuming strong collisions. Collision efficiencies as a function of temperature and step size down, can be found in Table B. At 0.1, 1.0 and 10 atm of  $\text{N}_2$  and  $\text{C}_3\text{H}_8$ , using a step size down of 500  $\text{cm}^{-1}$  and 1000  $\text{cm}^{-1}$  respectively, the fractional quantity decomposed is given as follows:

$$\log k_c/k_{p+c}(\text{C}_3\text{H}_8, 0.1) = -1.99 + 2.28 \times 10^{-3}T - 6.29 \times 10^{-7}T^2$$

$$\log k_c/k_{p+c}(\text{C}_3\text{H}_8, 1.0) = -4.0 + 4.364 \times 10^{-3}T - 1.162 \times 10^{-6}T^2$$

$$\log k_c/k_{p+c}(\text{C}_3\text{H}_8, 10) = -6.056 + 6.082 \times 10^{-3}T - 1.519 \times 10^{-6}T^2$$

and

$$\log k_c/k_{b+c}(N_2, 0.1) = -1.312 + 1.533 \times 10^{-3}T - 4.29 \times 10^{-4}T^2$$

$$\log k_c/k_{b+c}(N_2, 1.0) = -3.092 + 3.5 \times 10^{-3}T - 9.514 \times 10^{-7}T^2$$

$$\log k_c/k_{b+c}(N_2, 10) = -5.29 + 5.62 \times 10^{-3}T - 1.465 \times 10^{-6}T^2$$

The uncertainty is a factor of 2.

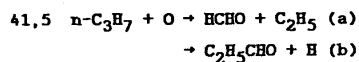
Table A.  $\log(k_c/k_{b+c})$  for the reactions  $H + n-C_3H_7 \rightarrow C_3H_8 \rightarrow C_2H_5 + CH_3$  on a strong collision basis

log[M]	T/K											
	300	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.46	-0.25	-0.11	-0.05	-0.02	-0.01						
16.5	-0.82	-0.48	-0.24	-0.11	-0.05	-0.02	-0.01					
17.0	-1.26	-0.82	-0.45	-0.23	-0.12	-0.06	-0.03	-0.01	-0.01			
17.5	-1.74	-1.23	-0.75	-0.42	-0.24	-0.13	-0.07	-0.04	-0.02	-0.01		
18.0	-2.24	-1.70	-1.13	-0.71	-0.43	-0.25	-0.15	-0.08	-0.05	-0.03	-0.02	-0.01
18.5	-2.73	-2.18	-1.56	-1.06	-0.70	-0.45	-0.28	-0.17	-0.11	-0.07	-0.04	-0.03
19.0	-3.23	-2.67	-2.04	-1.48	-1.03	-0.72	-0.49	-0.32	-0.21	-0.15	-0.09	-0.07
19.5	-3.73	-3.17	-2.53	-1.95	-1.47	-1.10	-0.79	-0.56	-0.40	-0.25	-0.20	-0.14
20.0	-4.23	-3.67	-3.03	-2.43	-1.93	-1.50	-1.15	-0.81	-0.65	-0.50	-0.38	-0.30
20.5	-4.73	-4.17	-3.53	-2.93	-2.42	-1.96	-1.58	-1.25	-1.0	-0.81	-0.65	-0.53
21.0	-5.23	-4.67	-4.03	-3.43	-2.91	-2.45	-2.05	-1.72	-1.42	-1.20	-1.01	-0.87

Table B. Collision efficiency  $\beta_e$  as a function of step size down and temperature

T/K	Step-size ( $\text{cm}^{-1}$ )				
	150	300	600	1200	2400
300	0.14	0.3	0.5	0.69	0.82
500	0.065	0.16	0.33	0.54	0.71
700	0.033	0.095	0.22	0.41	0.61
900	0.018	0.057	0.15	0.31	0.51
1100	0.01	0.035	0.09	0.23	0.42
1300	0.006	0.021	0.065	0.16	0.33
1500	0.0036	0.013	0.04	0.11	0.25
1700	0.0021	0.0078	0.026	0.078	0.19
1900	0.0012	0.0046	0.016	0.05	0.13
2100	0.0007	0.0026	0.0044	0.031	0.09
2300	0.00037	0.0012	0.0053	0.018	0.057
2500	0.00019	0.00075	0.0020	0.01	0.034

(W. Tsang, May 1985)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Hoyerman, Sievert (1979)	300	$0.3\text{-}30 \times 10^{16}$	$k_b/k_a = 6$	1.4
Recommended value			$k_{a+b} = 1.6 \times 10^{-10}$	2
Recommended value			$k_b/k_a = 6$	1.3

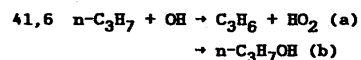
**Comments and Recommendations**

The product distribution indicates a 1,2 hydrogen migration. The overall rate should be close to collisional or  $1.6 \times 10^{-10} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  with an uncertainty of a factor of 2.

(W. Tsang, May 1985)

**References**

Hoyerman, K., and Sievert, R., "The Reactions of Alkyl Radicals with Oxygen Atom: Identification of Primary Products at Low Pressure," Symp. Int. Combust. Proc. 17, 517 (1979)

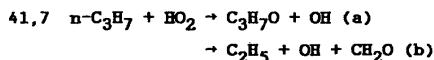


Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$k_a = 4 \times 10^{-11}$	3
Recommended value			$k_b = 4 \times 10^{-11}$	3

**Comments and Recommendations**

There are no data for these reactions. Step (a) is a disproportionation process and we recommend a rate constant similar to that for the OH reaction with  $\text{C}_2\text{H}_5$  i.e.  $k_a = 4.0 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ . Step (b) is a combination process and we suggest using  $k_b = 4.0 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ . There is the possibility that the hot  $n\text{-C}_3\text{H}_7\text{OH}$  molecule will decompose to  $\text{C}_3\text{H}_6 + \text{H}_2\text{O}$  or to  $\text{C}_2\text{H}_5 + \text{CH}_2\text{OH}$ . Due to the uncertainty in the high pressure rate parameters for the former, we are unable to give definitive recommendations. For C-C bond breaking, our results for propane decomposition suggest that, except at the highest temperatures, stabilization is the main process. The uncertainty is a factor of 3.

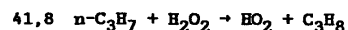
(W. Tsang, May 1985)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$4 \times 10^{-11}$	2

**Comments and Recommendations**

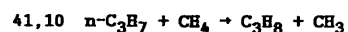
There are no data. In view of the weak O-O bond it can be assumed that the reaction will involve combination followed by disruption of the hot molecule. The recommended rate is  $\sim 4.0 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ , with an uncertainty factor of 2. (W. Tsang, May 1985)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
$\log K_p = -1.5965 + 3291.1/T - 76962.6/T^2 + 9.11 \times 10^6/T^3$				
Recommended value			$3.1 \times 10^{-20} T^{2.11} \exp(-1294/T)$	5

**Comments and Recommendations**

There are no data. We have used our rate expression for the reverse reaction [40,7] and the equilibrium constant to determine  $k = 3.1 \times 10^{-20} T^{2.21} \exp(-1294/T) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ . The uncertainty is a factor of 5. (W. Tsang, May 1985)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
$\log K_p = -0.2935 - 967.5/T - 7410/T^2 + 6.676 \times 10^6/T^3$				
Recommended value			$4 \times 10^{-26} T^{4.02} \exp(-5473/T)$	2

**Comments and Recommendations**

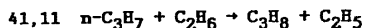
There are no data. We have derived a rate based on the rate expression for the reverse reaction [40,16] and the equilibrium constant. This leads to

$$k(n\text{-C}_3\text{H}_7 + \text{CH}_4 \rightarrow \text{CH}_3 + \text{C}_3\text{H}_8) = 4 \times 10^{-26} T^{4.02} \exp(-5473/T) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

The uncertainty is a factor of 2.

(W. Tsang, May 1985)

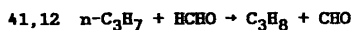




Reference	Conditions		Reaction rate constant, $\text{k}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
$\log K_p = 0.0227 + 54.47/T - 12475/T^2 + 4.57 \times 10^6/T^3$				
Recommended value			$4.2 \times 10^{-25} T^{3.82} \exp(-4550/T)$	3

**Comments and Recommendations**

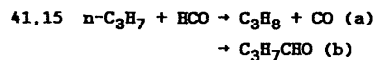
There are no data. We suggest the use of the rate expression  $4.2 \times 10^{-25} T^{3.82} \exp(-4550/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ . This is derived from our rate expression for the reverse reaction [40,17] and the equilibrium constant. The uncertainty is a factor of 3.  
(W. Tsang, May 1985)



Reference	Conditions		Reaction rate constant, $\text{k}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$5 \times 10^{-21} T^{2.9} \exp(-2950/T)$	4

**Comments and Recommendations**

There are no data for. We recommend the expression  $k = 5 \times 10^{-21} T^{2.9} \exp(-2950/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ . This is essentially the rate expression for  $\text{CH}_3 + \text{H}_2\text{CO}$  except that we have lowered the pre-exponential factor to bring the rate constants in the lower temperature range more in line with that for  $n\text{-C}_3\text{H}_7 + n\text{-C}_3\text{H}_7\text{CHO}$  (J.A. Kerr, and A.F. Trotman-Dickenson, "The Reactions of Alkyl Radicals," Prog. React. Kinet. 1, 105 (1961)). We estimate the uncertainty at a factor of 4.  
(W. Tsang, May 1985)

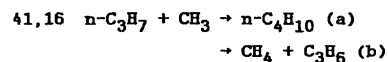


Reference	Conditions		Reaction rate constant, $\text{k}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$k_a = 1 \times 10^{-10}$	4
Recommended value			$k_b = 2 \times 10^{-11}$	2

**Comments and Recommendations**

There are no data. We believe that disproportionation will be favored and sug-

gest a rate of  $1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and an uncertainty factor of 4. The combination rate is estimated to be  $2.0 \times 10^{-11}$  with an uncertainty factor of 2. (W. Tsang, May 1985)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Terry, Futrell (1967)	300	$10^{17}$ - $10^{18}$ (Photolysis of azo compounds)	$k_b/k_a = 0.065$	1.1
Grotewold, Kerr (1963)	391-417	$1.0 \times 10^{18}$ acetone, $2.0 \times 10^{17}$ azo n-propane	$k_b/k_a = 0.041$	1.25
Thynne (1962)	346-465	$1.6 \times 10^{18}$ acetone, $0.3$ - $2.0 \times 10^{18}$ n-propyl formate.	$k_b/k_a = 0.082$	1.3
Ausloos, Murad (1958)	300	$10^{18}$ 2-pentanone- 1,1,1,3,3-d <sub>5</sub> . (Photolysis)	$k_b/k_a = 0.05$	1.2
Recommended value			$k_a = 3.2 \times 10^{-10} T^{-0.32}$	1.4
Recommended value			$k_b = 1.9 \times 10^{-11} T^{-0.32}$	1.7

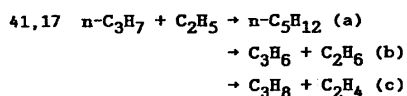
#### Comments and Recommendations

There are no direct measurements on (a). From the geometric mean rule and Rns. (16,16) and (41,41) we suggest  $k_a = 3.2 \times 10^{-10} T^{-0.32} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with an uncertainty of a factor of 1.4. At temperatures in excess of 1000 K fall-off effects will make some contributions. The instability of n-propyl radical will render this reaction unimportant at the higher temperatures. With  $k_b/k_a = 0.06$  we find  $k_b = 0.19 \times 10^{-10} T^{-0.32} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with an uncertainty of a factor of 1.7.

(W. Tsang, May 1985)

#### References

- Ausloos, P., and Murad, E., "The Photolyses of 2-Pentanone and 2-Pentanone-1,1,1,3,3-d<sub>5</sub>," J. Am. Chem. Soc. 80, 5929 (1958)
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- Terry, J. O., and Futrell, J. H., "Disproportionation and Combination Reactions of Simple Alkyl Radicals: Methyl, Ethyl, n-Propyl, and Isopropyl," Can. J. Chem. 45, 2327 (1967)
- Thynne, J. C. J., "Reactions of Alkyl Radicals, Part 2. Methyl Radical Photo-sensitized Decomposition of n-Propyl and iso-Propyl Formates," Trans. Faraday Soc. 58, 1392 (1962)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Terry, Futrell (1969)	300	$10^{17}\text{-}10^{18}$	$k_b/k_a = 0.065$	1.2
		(Photolysis of azo compounds)	$k_c/k_a = 0.054$	1.2
Grotewold, Kerr (1963)	391-417	$\sim 2.0 \times 10^{18}$ diethyl ketone.	$k_b/k_a = 0.081$	1.2
		$\sim 2.5 \times 10^{17}$ azo-n-propane. (Photolysis)	$k_c/k_a = 0.058$	1.2
Recommended value			$k_a = 3.3 \times 10^{-11}$	1.3
Recommended value			$k_b = 2.4 \times 10^{-12}$	1.4
Recommended value			$k_c = 1.9 \times 10^{-12}$	1.4

**Comments and Recommendations**

There are no measurements on (a). However since the combination rates for ethyl and n-propyl are known [see (17,17) and (41,41)], the geometric mean rule gives  $k_a = 3.3 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ , with an uncertainty of a factor of 1.3.

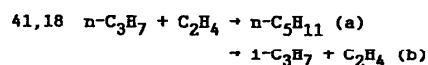
With  $k_b/k_a = 0.073$ ,  $k_b = 2.4 \times 10^{-12} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$

and with  $k_c/k_a = 0.056$ ,  $k_c = 1.85 \times 10^{-12} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ , with an uncertainty of a factor of 1.5.

(W. Tsang, May 1985)

**References**

- Grotewold, J., and Kerr, J. A., "The Interactions of the Lower Alkyl Radicals, Part I. Methyl, Ethyl and n-Propyl Radicals," J. Chem. Soc., Chem. Commun. 4337 (1963)
- Terry, J. O., and Futrell, J. H., "Disproportionation and Combination Reactions of Simple Alkyl Radicals: Methyl, Ethyl n-Propyl and Isopropyl," Can. J. Chem. 45, 2327 (1969)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Kerr, Trotman-Dickenson (1959)	450-490	$\sim 3.0 \times 10^{17}$ n-butyraldehyde, ethylene.	$4.2 \times 10^{-14} \exp(-3273/T)$	1.2
Watkins, Lawson (1971)	330-373	$(1.4\text{-}700) \times 10^{16}$ ethylene, azopropane.	$1.5 \times 10^{-13} \exp(-3726/T)$	1.2
Recommended value			$8 \times 10^{-14} \exp(-3500/T) \times$ $\exp(-1000/T)/(1+\exp(-1000/T))$	3

**Comments and Recommendations**

The experimental results for addition are in very good agreement. However, under most combustion conditions, step (a) will be reversed. Alternatively, the n-pentyl radical can isomerize to form the 2-pentyl radical. The latter can decompose to form i-C<sub>3</sub>H<sub>7</sub> and C<sub>2</sub>H<sub>4</sub>. Since n-pentyl radicals are not yet in our data base we suggest for this reaction the use of the following composite rate constant

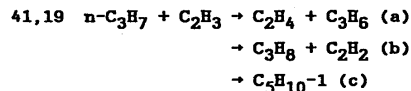
$$k_b = 8.0 \times 10^{-14} \exp(-3500/T) \times (\exp(-1000/T) / (1 + \exp(-1000/T))) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

with an uncertainty factor of 3. The first term represents an average of the published rate expressions while the second term is a reflection of the different bond energies. Note that we have changed the published values of the rate parameters to reflect the  $k(n\text{-C}_3\text{H}_7 + n\text{-C}_3\text{H}_7)$  used here (41,41). The uncertainty is a factor of 3.

(W. Tsang, May 1985)

**References**

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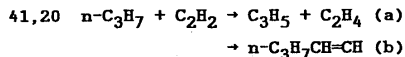


Reference	Conditions		Reaction rate constant, k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Uncertainty factor
	Temp./K	[M]/molecule cm <sup>-3</sup>		
Recommended value			2x10 <sup>-12</sup>	3
Recommended value			2x10 <sup>-12</sup>	3
Recommended value			1.6x10 <sup>-11</sup>	2.5

**Comments and Recommendations**

There are no data for these reactions. Steps (a) and (b) are disproportionation processes. Based on the comparable reaction of ethyl and n-propyl, we assign for  $k_a$  and  $k_b$   $2.0 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  with an uncertainty of a factor of 3. Hot 1-pentene is formed upon the combination of vinyl and n-propyl. At lower temperatures (up to 1000 K), combination,  $k_c$ , is the predominant process. We assign this process a rate constant of  $1.6 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  with an uncertainty of a factor of 2.5. At high temperatures two fragmentation processes are possible, 1) molecular elimination to form C<sub>3</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>, and 2) allylic-C-C bond cleavage. However, due to the thermal instability of vinyl and n-propyl, these reaction channels cannot be very important under combustion conditions.

(W. Tsang, May 1985)



Reference	Conditions		Reaction rate constant, $\text{k}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Watkins, Olsen (1972)	319-405	$(2.0\text{-}13.0)\times 10^{18} \text{C}_2\text{H}_2$	$1.2\times 10^{-12}\exp(-4531/T)$	1.2
Recommended value			$1.2\times 10^{-12}\exp(-4531/T)$	3

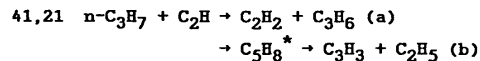
#### Comments and Recommendations

The results of Watkins and Olsen are very much in line with the data for other alkyl radical additions to acetylene. Of particular interest is the observation of isomerization of the 1-pentenyl-1 radical to 4-pentenyl-1 radical. Thus at combustion temperatures one expects their rate expression for  $k_b$  to hold for the process  $k_a$  ( $n\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_5 + \text{C}_2\text{H}_4$ ). Watkins and Olsen also observe some contribution (~10%) from the cyclization of the 4-pentenyl-1 radical to form cyclopentyl. We estimate the uncertainty over all applicable temperature ranges of a factor of 3.

(W. Tsang, May 1985)

#### References

Watkins, K. W., and Olsen, D. K., "Cyclization and Decomposition of 4-Penten-1-yl Radicals in the Gas Phase," J. Phys. Chem. 76, 1089 (1972)

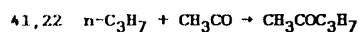


Reference	Conditions		Reaction rate constant, $\text{k}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$1\times 10^{-11}$	3
Recommended value			$2\times 10^{-11}$	2

#### Comments and Recommendations

There are no data for these reactions. Reaction (a) is a disproportionation reaction and is more exothermic than the comparable reaction  $\text{CH}_3 + n\text{-C}_3\text{H}_7$  (41,16). We suggest using a value a factor of 3 larger, i.e.  $k=1.0\times 10^{-11}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  with an uncertainty of a factor of 3. Reaction (b) involves formation of hot 1-pentyne followed by decomposition. The hot 1-pentyne has about 170 kJ excess energy. Under combustion conditions, the combination reaction with a rate constant of  $2.0\times 10^{-11}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  and an uncertainty of a factor of 2 will be followed by fragmentation to propargyl and ethyl. Hot 1-pentyne can also decompose molecularly to allene and ethylene. This represents an even lower energy decomposition pathway. However, the lower A-factor makes it noncompetitive as a result of the high energy of the adduct. Between 300-700 K, and at pressures of 1 atm and higher, RRKM calculations indicate that substantial portion of the hot 1-pentyne can be stabilized.

(W. Tsang, May 1985)

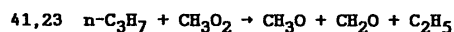


Reference	Conditions		Reaction rate constant, $\text{k}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$3.6 \times 10^{-11}$	1.5

**Comments and Recommendations**

There are no data for this reaction. We recommend the use of a rate constant equal to that derived from the geometric mean rule and the rates of self combination for acetyl (22,22) and n-propyl (41,41)  $\sim 3.6 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  with an uncertainty of 50%. This is a maximum rate since at the highest temperatures, fall-off effects will be of some consequence. However, in view of the instability of these radicals, their concentration levels should be miniscule at temperatures above 1300 K.

(W. Tsang, May 1985)

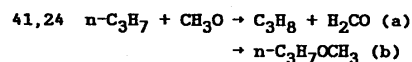


Reference	Conditions		Reaction rate constant, $\text{k}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$6 \times 10^{-11}$	1.5

**Comments and Recommendations**

There are no data. We suggest the use of a rate that is close to collisional or  $\sim 6.0 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  with an uncertainty of  $\pm 50\%$ . The mechanism involves formation of the peroxide followed by decomposition to various fragments.

(W. Tsang, May 1985)

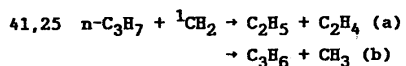


Reference	Conditions		Reaction rate constant, $\text{k}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$k_a = 4 \times 10^{-11}$	3
Recommended value			$k_b = 1.6 \times 10^{-11}$	3

**Comments and Recommendations**

There are no data. In view of the propensity of oxygenated radicals to disproportionate, we recommend a rate constant of  $4.0 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  for (a). For combination (b), we recommend a rate constant of  $1.6 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ . The uncertainties are a factor of 3.

(W. Tsang, May 1985)

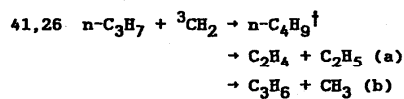


Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$k_a+k_b=6\times 10^{-11}$	2
Recommended value			$k_a/k_b \geq 2.5$	2

**Comments and Recommendations**

There are no data. Since singlet methylene is known to insert indiscriminantly into C-H bonds at collisional rates and the hot radicals are unstable, we suggest  $k_{a+b} = 6.0 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  with  $k_a/k_b \geq 2.5$ . The uncertainty in the former is a factor of 2.

(W. Tsang, May 1985)

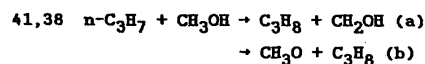


Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$3 \times 10^{-11}$	3
Recommended value			$3 \times 10^{-12}$	5

**Comments and Recommendations**

There are no data. The main process will be addition followed by the hot radical decomposition. The rate constant should be about  $3.0 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , with an uncertainty of a factor of 3. The disproportionation process should not exceed 10% of the combination or  $< 0.3 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , with an uncertainty of a factor of 5.

(W. Tsang, May 1985)

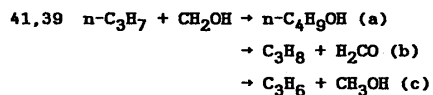


Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
			$\log K_p(a) = 968.4/T + 13462/T^2 + 3.164 \times 10^6/T^3$	
			$\log K_p(b) = -1.56 - 848.85/T + 62578/T^2 - 7.273 \times 10^6/T^3$	
Recommended value			$k_a = 5.3 \times 10^{-23} T^{3.17} \exp(-4610/T)$	3
Recommended value			$k_b = 2.4 \times 10^{-23} T^{3.1} \exp(-4500/T)$	3

**Comments and Recommendations**

There are no data for these reactions. We suggest the use of the estimated rate expression for ethyl attack on methanol (38,17)  $k_a = 5.3 \times 10^{-23} T^{3.17} \exp(-4610/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_b = 2.4 \times 10^{-23} T^{3.1} \exp(-4500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . These expressions are in good agreement with that which can be derived from the equilibrium constant and the rate constants for the reverse reactions (40,39) and (40,24). The uncertainty is a factor of 3.

(W. Tsang, May 1985)

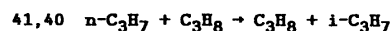


Reference	Conditions		Reaction rate constant, $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$k_a = 1.6 \times 10^{-11}$	2
Recommended value			$k_b = 1.6 \times 10^{-12}$	3
Recommended value			$k_c = 0.8 \times 10^{-12}$	3

**Comments and Recommendations**

There are no data. The rate constant for combination should be very close to that for n-propyl radicals or  $1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with an uncertainty of a factor of 2. We estimate  $k_c/k_a = 0.051$  and  $k_b/k_a = 0.1$  with an uncertainty of a factor of 3.

(W. Tsang, April 1985)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Berkley, et al. (1969)	333-505	$25.0 \times 10^{18}$ propane. (Photolysis of azo-n-propane)	$2.0 \times 10^{-15} \exp(-3978/T)$	1.5
Recommended value			$1.4 \times 10^{-27} T^4 \exp(-2378/T)$	1.5 at 400K 5 at 2000K

**Comments and Recommendations**

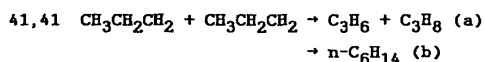
Assuming a  $T^4$  dependence of the pre-experimental factor, we recommend the rate expression  $1.43 \times 10^{-27} T^4 \exp(-2378/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with an uncertainty of a factor of 1.5 at 400 K and increasing to a factor of 5 at 2500 K.

(W. Tsang, May 1985)



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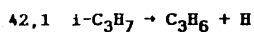
Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Adachi, Basco, (1981)	300	$1.2-2.4 \times 10^{19}$ $\text{N}_2$ ,	$k_a = 3.1 \times 10^{-12}$	1.2
		$1.0-30.0 \times 10^{17}$ n-pentane,	$k_b = 1.67 \times 10^{-11}$	1.2
		$1.3-3.2 \times 10^{17}$ azopropane.		
Terry, Futrell (1969)	300	$10^{17}-10^{18}$ azo compds. (Photolysis)	$k_a/k_b = 0.154$	1.2
Kerr, Calvert (1961)	488-563	$2.5 \times 10^{17}$ azopropane.	$k_a/k_b = 0.16$	1.2
Recommended value			$k_a = 2.8 \times 10^{-12}$	1.5
Recommended value			$k_b = 1.7 \times 10^{-11}$	1.5

## Comments and Recommendations

Rate constants for these reactions have been measured only at room temperature. We believe that these values are applicable at all temperatures. We recommend  $k_a = 2.8 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  and  $k_b = 1.67 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ . At the higher temperatures some effects due to fall-off will lower this rate. The uncertainty is 20% at room temperatures, increasing to 50% at 1000 K. (W. Tsang, May 1985)

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- Terry, J. O., and Futrell, J. H., "Disproportionation and Combination Reactions of Simple Alkyl Radicals: Methyl, Ethyl, n-Propyl and Isopropyl," Can. J. Chem. 45, 2327 (1969)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Tsang (1985) review	300-800		$k_\infty = 2.2 \times 10^{13} \exp(-18726/T) \text{s}^{-1}$	2
Camilleri, et al (1975)	678-813	$7\text{-}20 \times 10^{17}$ (Azomethane-sensitized decomposition of propane)	$6.1 \times 10^{13} \exp(-20405/T) \text{s}^{-1}$	2
Papic, Laidler (1971)	523-623	$6\text{-}800 \times 10^{16}$ (Hg-sensitized decomposition of propane)	$6.5 \times 10^{13} \exp(-19330/T) \text{s}^{-1}$	1.5
Back, Takamuku (1961)	573-673	$4.5 \times 10^{18}$ (Hg-sensitized decomposition of propane)	$1.7 \times 10^{13} \exp(-18490/T) \text{s}^{-1}$	2
Kerr, Trotman-Dickenson	673-773	$4 \times 10^{17}$ (Photolysis of isobutyraldehyde)	$0.98 \times 10^{13} \exp(-17450/T) \text{s}^{-1}$	2
Heller, Gordon (1958)	673-773	$2 \times 10^{17}$ (Photolysis of diisopropyl- $\text{d}_2$ ketone)	$1.6 \times 10^{12} \exp(-17440/T) \text{s}^{-1}$	3
Recommended value			$k_\infty = 1.6 \times 10^{13} \exp(-17991/T) \text{s}^{-1}$	2
Recommended value	>700	1 atm, $\text{N}_2$	$\log(k_a/k_{a\infty}) = -1.119 + 3.73 \times 10^{-3}T - 3.33 \times 10^{-6}T^2 + 4.68 \times 10^{-10}T^3$	
Recommended value			$k_{a\infty}/k_{p\infty} = 1.1 \exp(2500/T)$	1.3

**Comments and Recommendations**

The recommended rate expression,  $k_\infty = 1.6 \times 10^{13} \exp(-17991/T) \text{s}^{-1}$ , is in substantial agreement with all the direct measurements on the decomposition of the isopropyl radical. It is also consistent with the rate constants for the reverse addition process and the thermodynamics. We recommend its use over all temperatures. RRKM calculations which lead to the determination of departure from unimolecular behavior are summarized in Table A [for strong colliders]. Collision efficiencies, as a function of temperature and step size down, can be found in Table B.

For  $\text{N}_2$  as a collision partner and assuming a step size down of  $500 \text{ cm}^{-1}$  we find at 0.1, 1 and 10 atm, and at temperatures in excess of 700 K

$$\log k(\text{N}_2, 0.1)/k_\infty = -0.691 + 3.00 \times 10^{-3}T - 3.55 \times 10^{-6}T^2 + 5.83 \times 10^{-10}T^3$$

$$\log k(\text{N}_2, 1)/k_\infty = -1.119 + 3.73 \times 10^{-3}T - 3.33 \times 10^{-6}T^2 + 4.68 \times 10^{-10}T^3$$

$$\log k(\text{N}_2, 10)/k_\infty = -1.00 + 2.89 \times 10^{-3}T - 2.08 \times 10^{-6}T^2 + 1.57 \times 10^{-10}T^3$$

For a larger polyatomic molecule as the collision partner ( $\text{C}_3\text{H}_8$ ), assuming a step size down of  $1000 \text{ cm}^{-1}$ , at 0.1, 1 and 10 atm and at temperatures in excess of 700K, we find:

$$\log k(\text{C}_3\text{H}_8, 0.1)/k_\infty = -0.864 + 3.18 \times 10^{-3}T - 3.21 \times 10^{-6}T^2 + 4.7 \times 10^{-10}T^3$$

$$\log k(\text{C}_3\text{H}_8, 1)/k_\infty = -1.00 + 3.07 \times 10^{-3}T - 2.44 \times 10^{-6}T^2 + 2.52 \times 10^{-10}T^3$$

$$\log k(\text{C}_3\text{H}_8, 10)/k_\infty = -0.61 + 1.58 \times 10^{-3}T - 8.33 \times 10^{-7}T^2 - 1.14 \times 10^{-10}T^3$$

The uncertainties are a factor of 2.

Figure 7 contains Arrhenius plots of the experimental values of rate constants for i-propyl radical decomposition and the recommended high pressure rate constants. The numbers associated with the experimental lines are estimated factors to be added to the respective experimental measurements (in log units) to take into account fall off effects. These have been derived on the basis of RRKM calculations.

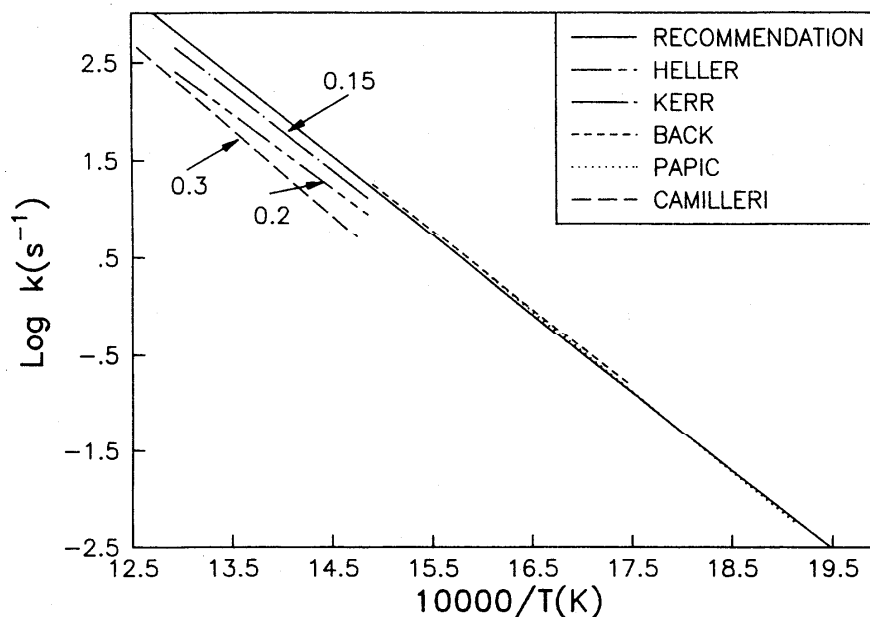


Fig. 7. Summary of experimental and recommended rate constants for the Rn.  $i\text{-C}_3\text{H}_7 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3$

Table A.  $\log(k/k_0)$  for the decomposition of isopropyl radical (strong collider)

log[M]	T/K										
	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.19	-0.44	-0.77	-1.14	-1.51	-1.88	-2.22	-2.55	-2.84	-3.11	-3.35
16.5	-0.10	-0.27	-0.53	-0.84	-1.16	-1.49	-1.80	-2.10	-2.38	-2.64	-2.87
17.0	-0.04	-0.15	-0.34	-0.58	-0.85	-1.13	-1.41	-1.68	-1.94	-2.18	-2.40
17.5	-0.02	-0.08	-0.20	-0.37	-0.58	-0.81	-1.05	-1.29	-1.52	-1.74	-1.94
18.0		-0.03	-0.10	-0.22	-0.37	-0.55	-0.74	-0.94	-1.13	-1.32	-1.50
18.5		-0.01	-0.05	-0.11	-0.21	-0.33	-0.48	-0.63	-0.79	-0.95	-1.10
19.0			-0.02	-0.05	-0.10	-0.18	-0.28	-0.39	-0.51	-0.63	-0.75
19.5				-0.02	-0.05	-0.09	-0.14	-0.21	-0.29	-0.38	-0.47
20.0					-0.02	-0.04	-0.06	-0.10	-0.14	-0.20	-0.25
20.5						-0.01	-0.02	-0.04	-0.06	-0.09	-0.12
21.0								-0.01	-0.02	-0.03	-0.05

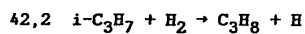
Table B.  $\beta(e)$  for isopropyl decomposition as a function of temperature and downward step size

T/K	Step-size (cm <sup>-1</sup> )				
	150	300	600	1200	2400
500	5.14x10 <sup>-2</sup>	1.37x10 <sup>-1</sup>	2.91x10 <sup>-1</sup>	4.92x10 <sup>-1</sup>	6.08x10 <sup>-1</sup>
700	2.31x10 <sup>-2</sup>	6.97x10 <sup>-2</sup>	1.75x10 <sup>-1</sup>	3.42x10 <sup>-1</sup>	5.50x10 <sup>-1</sup>
900	1.08x10 <sup>-2</sup>	3.53x10 <sup>-2</sup>	1.00x10 <sup>-1</sup>	2.31x10 <sup>-1</sup>	4.21x10 <sup>-1</sup>
1100	4.97x10 <sup>-3</sup>	1.73x10 <sup>-2</sup>	5.42x10 <sup>-2</sup>	1.43x10 <sup>-1</sup>	3.01x10 <sup>-1</sup>
1300	2.23x10 <sup>-3</sup>	8.12x10 <sup>-3</sup>	2.73x10 <sup>-2</sup>	8.05x10 <sup>-2</sup>	1.95x10 <sup>-1</sup>
1500	9.44x10 <sup>-4</sup>	3.56x10 <sup>-3</sup>	1.27x10 <sup>-2</sup>	4.09x10 <sup>-2</sup>	1.13x10 <sup>-1</sup>
1700	3.74x10 <sup>-4</sup>	1.44x10 <sup>-3</sup>	5.34x10 <sup>-3</sup>	1.86x10 <sup>-2</sup>	5.75x10 <sup>-2</sup>
1900	1.37x10 <sup>-4</sup>	5.35x10 <sup>-4</sup>	2.04x10 <sup>-3</sup>	7.49x10 <sup>-3</sup>	2.54x10 <sup>-2</sup>
2100	4.64x10 <sup>-5</sup>	1.83x10 <sup>-4</sup>	7.13x10 <sup>-4</sup>	2.70x10 <sup>-3</sup>	9.77x10 <sup>-3</sup>
2300	1.46x10 <sup>-5</sup>	5.80x10 <sup>-5</sup>	2.29x10 <sup>-4</sup>	8.87x10 <sup>-4</sup>	3.35x10 <sup>-3</sup>
2500	4.34x10 <sup>-5</sup>	1.73x10 <sup>-5</sup>	6.86x10 <sup>-5</sup>	2.70x10 <sup>-4</sup>	1.05x10 <sup>-3</sup>

(W. Tsang, May 1985)

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- Tsang, W., "The Stability of Alkyl Radicals," J. Am. Chem. Soc. 107, 2872 (1985)



Reference	Conditions		Reaction rate constant, k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Uncertainty factor
	Temp./K	[M]/molecule cm <sup>-3</sup>		
Baldwin et al. (1976)	713	0.3-5x10 <sup>18</sup> N <sub>2</sub> and H <sub>2</sub> , traces of i-C <sub>3</sub> H <sub>7</sub> CHO, O <sub>2</sub> . (Boric acid coated reactor with gas chromatographic detection of products)	1x10 <sup>-16</sup>	3
Recommended value			5.8x10 <sup>-23</sup> T <sup>3.28</sup> exp(-4363/T)	3

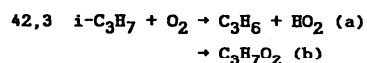
**Comments and Recommendations**

The measurement of Baldwin et al is dependent on the rate constant for the reaction  $2i\text{-C}_3\text{H}_7 \rightarrow \text{C}_6\text{H}_{14}$  (42,42). We have changed their number slightly in order to make it consistent with our value for isopropyl combination (42,42). From our rate expression for the reverse process (40,4), we derive the rate expression:  $k(i\text{-C}_3\text{H}_7 + \text{H}_2 \rightarrow \text{C}_3\text{H}_8 + \text{H}) = 5.8 \times 10^{-23} T^{3.28} \exp(-4363/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This leads to a rate constant of  $3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 713 K. We therefore recommend this rate expression with an uncertainty of a factor of 3.

(W. Tsang, April 1986)

**References**

Baldwin, R. R., Cleugh, J., and Walker, R. W., "Reaction of Isopropyl Radicals with: Oxygen, Hydrogen and Deuterium," J. Chem. Soc. Faraday Trans. I 72, 175 (1976)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Baldwin, et al (1975)	713	5-13x10 <sup>16</sup> $i\text{-C}_3\text{H}_7\text{CHO}$ , 1.4-76x10 <sup>16</sup> $\text{O}_2$ , 0-5x10 <sup>18</sup> $\text{N}_2$ . (Boric acid coated static vessel with gas chromatographic detection)	$2.1 \times 10^{-13}$	1.4
Recommended value	>700		$2.1 \times 10^{-13}$	3

**Comments and Recommendations**

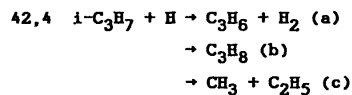
The results of Baldwin et al represent the only report on the rate constant for this process. More recent work by Gutman and coworkers [on ethyl +  $\text{O}_2$ ] have led to the conclusion that reactions (a) and (b) may be coupled through a common intermediate. There are, however, considerable uncertainties on the quantitative details (see Baldwin, Dean, and Walker). For the present, we recommend the use of the rate constant given by Baldwin et al. over all temperature ranges with an uncertainty of a factor of 3. This is the predominant reaction at temperatures in excess of 700 K. Near room temperature (b) is the predominant process. Reaction (a) and the reverse of (b) become increasingly important as the temperature increases. The uncertainties are a factor of 3.

(W. Tsang, April 1986)

**References**

Baldwin, R. R., Cleugh, C. J., and Walker, R. W., "Reactions of iso-Propyl Radicals with Oxygen Hydrogen and Deuterium," J. Chem. Soc., Faraday Trans. 1, 72, 175 (1976)

- Baldwin, R., Dean, C. E., and Walker, R. W., "Reactive Rate Study of the Addition of HO<sub>2</sub> Radicals to C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub>," J. Chem. Soc., Faraday Trans. 2, **82**, 1445 (1986)
- Slagle, I. R., Feng, Q., and Gutman, D., "Kinetics of the Reaction of Ethyl Radicals with Molecular Oxygen from 294 to 1002 K," J. Phys. Chem. **88**, 3648 (1984)



Reference	Conditions		Reaction rate constant, k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Uncertainty factor
	Temp./K	[M]/molecule cm <sup>-3</sup>		
Recommended value			$k_a = 6 \times 10^{-12}$	2
Recommended value			$k_{b+c} = 4 \times 10^{-11}$	2
Recommended value		1 atm, N <sub>2</sub>	$\log(k_b/k_{b+c}) = -0.626 + 1.02 \times 10^{-2}T$ $-5.44 \times 10^{-6}T^2 + 9.46 \times 10^{-10}T^3$	

#### Comments and Recommendations

There are no data. The following represent our estimates. Rn. (a) is a disproportionation and we assign to it a rate constant twice that for  $\text{H} + \text{C}_2\text{H}_5 \rightarrow \text{H}_2 + \text{C}_2\text{H}_4$  (17,4), i.e.  $k_a = 6 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  with an uncertainty of a factor of 2. Rns. (b) and (c) are the consequence of addition of H to isopropyl. Following the  $\text{H} + \text{C}_2\text{H}_5$  (17,4) Rn., we assign  $k_{b+c} = 4 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ . RRKM calculations show that, due to the presence of the exothermic decomposition channel, the overall rate constant is not dependent on pressure.

On a strong collision basis, the dependence of the ratio of decomposition to addition (decomposition + stabilization) as a function of temperature and pressure is given in Table A. Table B gives the collision efficiencies as a function of step size down and temperature. With N<sub>2</sub> as the collider and assuming a step size down of 500 cm<sup>-1</sup>, ratios of decomposition to (decomposition + stabilization) are given by the following expressions:

$$\begin{aligned} \log k_c/k_{b+c}(\text{N}_2, 0.1) &= -4.12 + 7.37 \times 10^{-3}T - 4.22 \times 10^{-6}T^2 + 7.76 \times 10^{-10}T^3 \\ \log k_c/k_{b+c}(\text{N}_2, 1) &= -6.26 + 1.02 \times 10^{-2}T - 5.44 \times 10^{-6}T^2 + 9.46 \times 10^{-10}T^3 \\ \log k_c/k_{b+c}(\text{N}_2, 10) &= -7.66 + 1.07 \times 10^{-2}T - 4.99 \times 10^{-6}T^2 + 7.71 \times 10^{-10}T^3 \end{aligned}$$

With propane as the collider, a 1000 cm<sup>-1</sup> step size down leads to:

$$\begin{aligned} \log k_c/k_{b+c}(\text{C}_3\text{H}_8, 0.1) &= -4.86 + 8.30 \times 10^{-3}T - 4.59 \times 10^{-6}T^2 + 8.23 \times 10^{-10}T^3 \\ \log k_c/k_{b+c}(\text{C}_3\text{H}_8, 1) &= -6.67 + 1.01 \times 10^{-2}T - 5.02 \times 10^{-6}T^2 + 8.27 \times 10^{-10}T^3 \\ \log k_c/k_{b+c}(\text{C}_3\text{H}_8, 10) &= -7.65 + 9.43 \times 10^{-3}T - 3.65 \times 10^{-6}T^2 + 5.19 \times 10^{-10}T^3 \end{aligned}$$

The uncertainties in  $k_{b+c}$  are a factor of 2, while the  $k(\text{dec})/k(\text{dec+stab})$  ratios have an additional uncertainty of a factor of 2.

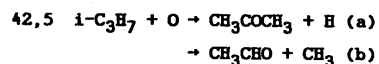
Table A.  $\log(k_c/k_{b+c})$  as a function of T and P assuming strong collisions

log[M]	T/K										
	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.39	-0.18	-0.07	-0.03	-0.01	-0.01					
16.5	-0.68	-0.34	-0.16	-0.07	-0.03	-0.02	-0.01				
17.0	-1.06	-0.59	-0.31	-0.16	-0.08	-0.04	-0.02	-0.01			
17.5	-1.50	-0.92	-0.53	-0.29	-0.16	-0.09	-0.05	-0.02	-0.01	-0.01	
18.0	-1.97	-1.32	-0.83	-0.50	-0.30	-0.17	-0.10	-0.06	-0.03	-0.02	-0.01
18.5	-2.46	-1.77	-1.20	-0.79	-0.50	-0.31	-0.19	-0.12	-0.07	-0.05	-0.03
19.0	-2.96	-2.25	-1.63	-1.14	-0.78	-0.53	-0.35	-0.23	-0.15	-0.10	-0.07
19.5	-3.46	-2.74	-2.10	-1.56	-1.14	-0.82	-0.58	-0.41	-0.29	-0.21	-0.15
20.0	-3.96	-3.24	-2.59	-2.03	-1.56	-1.19	-0.89	-0.67	-0.51	-0.38	-0.29
20.5	-4.46	-3.73	-3.08	-2.51	-2.02	-1.62	-1.28	-1.02	-0.81	-0.64	-0.51
21.0	-4.96	-4.23	-3.58	-3.01	-2.51	-2.08	-1.73	-1.43	-1.19	-0.99	-0.84

 Table B.  $\beta(e)$  for excited propane decomposition as a function of temperature and downward step-size

T/K	Step-size ( $\text{cm}^{-1}$ )				
	150	300	600	1200	2400
300	0.14	0.3	0.5	0.69	0.82
500	0.065	0.6	0.33	0.54	0.71
700	0.033	0.095	0.22	0.41	0.61
900	0.018	0.057	0.15	0.31	0.51
1100	0.01	0.035	0.09	0.23	0.42
1300	0.006	0.021	0.065	0.16	0.33
1500	0.0036	0.013	0.04	0.11	0.25
1700	0.0021	0.0078	0.026	0.078	0.19
1900	0.0012	0.0046	0.016	0.05	0.13
2100	0.0007	0.0026	0.0094	0.031	0.09
2300	0.00037	0.0012	0.0053	0.018	0.057
2500	0.00019	0.0005	0.0020	0.01	0.034

(W. Tsang, October 1984)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Hoyermann, Sievert (1979)	300	$0.3\text{-}3.2 \times 10^{16}$ He	$k_a/k_b = 1$	1.5
Recommended value			$k_{a+b} = 1.6 \times 10^{-10}$	2
Recommended value			$k_a/k_b = 1$	1.5

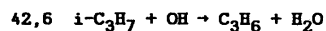
**Comments and Recommendations**

The product distribution of Hoyermann and Sievert suggests 1,2 hydrogen shift. The overall rate should be close to collisional or to  $1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with an uncertainty of a factor of 2.

(W. Tsang, April 1986)

**References**

Hoyermann, K., and Sievert, R., "The Reactions of Alkyl Radicals with Oxygen Atoms: Identification of Primary Products at Low Pressure," Symp. Combust. 17, (Combustion Institute, Pittsburgh, 1977) 517



Reference	Conditions		Reaction rate constant, $\text{k/cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$4 \times 10^{-11}$	3

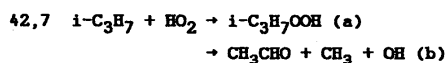
**Comments and Recommendations**

There are no data for this reaction. However, both abstraction and addition followed by decomposition of the hot adduct, will lead to the same product under combustion conditions. We suggest the use of a rate constant of

$$k(i\text{-C}_3\text{H}_7 + \text{OH} \rightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O}) = 4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty factor of 3. At low temperatures and high pressure stabilization of the hot adduct to form isopropanol may also be important.

(W. Tsang, April 1986)



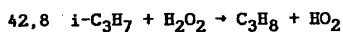
Reference	Conditions		Reaction rate constant, $\text{k/cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$4 \times 10^{-11}$	2

**Comments and Recommendations**

There are no rate data for this system. Combination (a) and the resulting break-up of the unstable hydroperoxide and isopropoxy radical (b) must be the most important process. For most high temperature processes (b) must be the preferred reaction channel. We estimate a rate constant of  $4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with an uncertainty of a factor of 2.

(W. Tsang, April 1986)





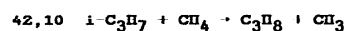
Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
$\log K_p = -1.1938 + 2508.04/T - 52263.4/T^2 - 5.082 \times 10^6/T^3$				
Recommended value			$4.8 \times 10^{-22} T^{2.83} \exp(-2037/T)$	3 10 at 2500K

**Comments and Recommendations**

There are no measurements for this process. On the basis of detail balance and the rate of the reverse process (40,7) we find

$k(i\text{-C}_3\text{H}_7 + \text{H}_2\text{O}_2 \rightarrow \text{C}_3\text{H}_8 + \text{HO}_2) = 4.8 \times 10^{-22} T^{2.83} \exp(-2037/T) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$   
with an uncertainty of a factor of 3 at 723 K and increasing to an order of magnitude at 300 and 2500 K.

(W. Tsang, April 1986)



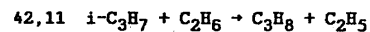
Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
$\log K_p = 0.1092 - 1750.6/T + 1.218 \times 10^5/T^2 - 7.427 \times 10^6/T^3$				
Recommended value			$1.2 \times 10^{-27} T^{4.4} \exp(-5434/T)$	2

**Comments and Recommendations**

There are no rate data for this reaction. From the equilibrium constant we obtain

$k(i\text{-C}_3\text{H}_7 + \text{CH}_4 \rightarrow \text{C}_3\text{H}_8 + \text{CH}_3) = 1.2 \times 10^{-27} T^{4.4} \exp(-5434/T) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$   
with an uncertainty of a factor of 2.

(W. Tsang, April 1986)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
$\log K_p = 0.4254 - 728.59/T + 116751/T^2 - 9.6223 \times 10^6/T^3$				
Szirovicza, Marta (1976)	496-548	$4 \times 10^{18}$ ethane with azoisopropane.	$2 \times 10^{-13} \exp(-6500/T)$	1.3
Recommended value			$1.4 \times 10^{-26} T^{4.2} \exp(-4386/T)$	2

**Comments and Recommendations**

The measurements of Szirovicza and Marta are for the ratio  $k(i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_6)/k^{1/2}(2i\text{-C}_3\text{H}_7 \rightarrow \text{C}_6\text{H}_{14})$ . Using our value for  $k(2i\text{-C}_3\text{H}_7 \rightarrow \text{C}_6\text{H}_{14})$  (42,42) we obtain the expression given above. The rate constants at the reaction temperatures are consistent with the rate expression derived from the estimated rate expression for the reverse process (40,17) and the thermodynamics. We therefore recommend:  $k(i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_6) = 1.4 \times 10^{-26} T^{4.2} \exp(-4386/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ . We estimate an uncertainty of a factor of 2 over all temperatures.

(W. Tsang, April 1986)

**References**

- Szirovicza, L., and Marta, F., "Some Reactions of the Isopropyl Radical," Int. J. Chem. Kinet. 8, 897 (1976)

**42,12  $i\text{-C}_3\text{H}_7 + \text{HCHO} \rightarrow \text{C}_3\text{H}_8 + \text{CHO}$** 

Reference	Conditions		Reaction rate constant, $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$1.8 \times 10^{-13} \exp(-3500/T)$	2.5

**Comments and Recommendations**

There are no measurements on the rate constant for this reaction. We recommend:

$$k(i\text{-C}_3\text{H}_7 + \text{HCHO} \rightarrow \text{C}_3\text{H}_8 + \text{CHO}) = 1.8 \times 10^{-13} \exp(-3500/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

This is twice the rate expression for the reaction  $i\text{-C}_3\text{H}_7 + \text{isobutyraldehyde}$  (J.A. Kerr and A.F. Trotman-Dickenson, Trans. Faraday Soc. 55, 921 (1959)). We have corrected the published numbers in order to take into account the value of isopropyl combination that is used here. The uncertainty is a factor 2.5.

(W. Tsang, April 1986)

**42,15  $i\text{-C}_3\text{H}_7 + \text{HCO} \rightarrow \text{C}_3\text{H}_8 + \text{CO}$  (a)  
 $\rightarrow \text{C}_3\text{H}_7\text{CHO}$  (b)**

Reference	Conditions		Reaction rate constant, $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$k_a = 3 \times 10^{-10}$	3
Recommended value			$k_b = 3 \times 10^{-11}$	3

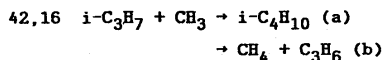
**Comments and Recommendations**

There are no rate data for this reaction. We recommend numbers similar to that for  $k(\text{C}_2\text{H}_5 + \text{HCO})$  (17,15) i.e.

$$k_a = 2 \times 10^{-10} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \quad \text{and} \quad k_b = 3 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

The uncertainty is a factor of 3.

(W. Tsang, April 1986)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Gibian, Corley (1973) review			$k_b/k_a = 0.16$	1.1
Arthur, Anastasi	308	Modulation spectroscopy.	$k_{a+b} = 3.1 \times 10^{-11}$	1.3
Recommended value			$k_a = 4.7 \times 10^{-11} (300/T)^{0.68}$	1.5
Recommended value			$k_b/k_a = 0.16$	1.1

**Comments and Recommendations**

Except for the measurement of Arthur and Anastasi, there have not been any studies on the rate constants for this process. Their study is in substantial agreement with that derived from the rate constant for methyl (16,16) and isopropyl combination (42,42) and the geometrical mean rule. We recommend the expression:

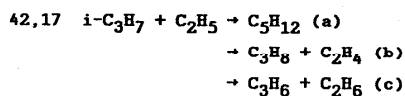
$$k_{a0} = 4.7 \times 10^{-11} (300/T)^{0.68} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

This is applicable under all pressures up to 700 K. Above this temperature fall-off effects begin to exert an influence. However, in view of the instability of the isopropyl radical, it is not likely that this process is of major importance at the higher temperatures. The uncertainty is a factor 1.5. For the disproportionation rate the recommendation of Gibian and Corley should be used.

(W. Tsang, April 1986)

**References**

- Arthur, N. L., and Anastasi, C., "Rate Constants for the Reactions of  $\text{CH}_3$  Radicals with  $\text{C}_2\text{H}_5$ ,  $i\text{-C}_3\text{H}_7$  and  $t\text{-C}_4\text{H}_9$  Radicals," *Bull. Soc. Chim. Belg.* **92**, 647 (1983)
- Gibian, M. J., and Corley, R. C., "Organic Radical-Radical Reactions. Disproportionation vs Combination," *Chem. Rev.* **73**, 445 (1973)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Gibian, Corley (1973) review			$k_b/k_a = 0.16$ $k_c/k_a = 0.20$	
Recommended value			$k_a = 2.6 \times 10^{-11} (300/T)^{0.35}$	1.8
Recommended value			$k_b/k_a = 0.16$	1.1
Recommended value			$k_c/k_a = 0.20$	1.1

**Comments and Recommendations**

There are no measurements on the rate constant for the combination process. From the geometric mean rule we obtain

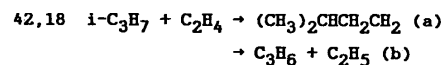
$$k_a = 2.6 \times 10^{-11} (300/T)^{0.35} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

The estimated uncertainty is a factor of 50% at room temperature and increasing to a factor of 2 at 1000 K. The disproportionation combination ratio has an uncertainty of 10%.

(W. Tsang, April 1986)

**References**

Gibian, M. J., and Corley, R. C., "Organic Radical Radical Reactions Disproportionation vs Combination," Chem. Rev. 73, 441 (1973)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Kerr, Parsonage (1972) review	350-460		$k_a = 6.6 \times 10^{-14} \exp(-3324/T)$	1.5
Recommended value			$4.4 \times 10^{-14} \exp(-3324/T)$	2

**Comments and Recommendations**

The rate expression given by Kerr and Parsonage [corrected here to take into account  $k_r(i\text{-C}_3\text{H}_7)$ (42,42)] is for the addition process. Under combustion conditions this is readily reversed. On the other hand there is also the possibility of 1-4 hydrogen transfer followed by decomposition to propylene and an ethyl radical. Using the reaction path degeneracy as the sole criterion, we recommend

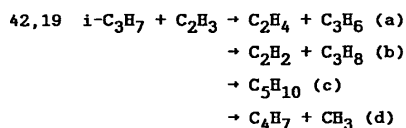
$$k_b = 4.4 \times 10^{-14} \exp(-3324/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

or two-thirds the measured addition process. The uncertainty is a factor of 2.

(W. Tsang, April 1986)

**References**

Kerr, J. A., and Parsonage, M. J., "Evaluated Kinetic Data on Gas Phase Addition Reactions", Butterworths, London (1972)



Reference	Conditions		Reaction rate constant, $\text{k}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$k_a/k_{c+d}=0.18$	1.5
Recommended value			$k_b/k_{c+d}=0.18$	1.5
Recommended value			$k_{c+d}=2.6 \times 10^{-11}(300/T)^{0.7}$	2
Recommended value		1 atm, $\text{N}_2$	$\log(k_d/k_{c+d})=-7.49+9.91 \times 10^{-3}T$ $-3.98 \times 10^{-6}T^2+4.36 \times 10^{-10}T^3$	2

#### Comments and Recommendations

There are no data for these reactions. We suggest for reactions (a) and (b) the use of the comparable values for  $i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_5$ . (42,17). This leads to  $k_b/k_{c+d} \approx k_a/k_{c+d} \approx 0.18$  with an uncertainty of 50%. The combination process is assumed to follow that for ethyl and isopropyl or  $k_{c+d} = 2.6 \times 10^{-11}(300/T)^{0.7} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$  with an uncertainty of a factor of 2. Due to the presence of the exothermic reaction channel there are no fall off effects. Branching ratios on a strong collision basis can be found in Table A. Table B gives the estimated collision efficiencies on a per collision basis.

For  $\text{N}_2$  and 3-methylbutene-1 as weak colliders and assuming respective step sizes down of  $500 \text{ cm}^{-1}$  and  $1000 \text{ cm}^{-1}$ , we obtain the following expressions for  $k_d/k_{c+d}$ :

$$\begin{aligned} \log k_d/k_{c+d}(\text{N}_2, 0.1) &= -7.01 + 0.0123T - 7.24 \times 10^{-6}T^2 + 1.404 \times 10^{-9}T^3 \\ \log k_d/k_{c+d}(\text{N}_2, 1) &= -7.49 + 9.91 \times 10^{-3}T - 3.98 \times 10^{-6}T^2 + 4.36 \times 10^{-10}T^3 \\ \log k_d/k_{c+d}(\text{N}_2, 10) &= -7.87 + 7.63 \times 10^{-3}T - 1.62 \times 10^{-6}T^2 - 1.12 \times 10^{-10}T^3 \end{aligned}$$

and

$$\begin{aligned} \log k_d/k_{c+d}(\text{C}_5\text{H}_{10}, 0.1) &= -7.11 + 0.0145T - 9.926 \times 10^{-6}T^2 + 2.27 \times 10^{-9}T^3 \\ \log k_d/k_{c+d}(\text{C}_5\text{H}_{10}, 1) &= -7.56 + 1.16 \times 10^{-2}T - 5.63 \times 10^{-6}T^2 + 8.27 \times 10^{-10}T^3 \\ \log k_d/k_{c+d}(\text{C}_5\text{H}_{10}, 10) &= -7.87 + 8.88 \times 10^{-3}T - 2.497 \times 10^{-6}T^2 - 2.83 \times 10^{-12}T^3 \end{aligned}$$

These expressions are valid in  $\text{N}_2$  and polyatomic media at temperatures in excess of 800 K with an uncertainty of a factor of 2. Note, that above 1500 K decomposition is the only pathway.

(W. Tsang, May 1985)

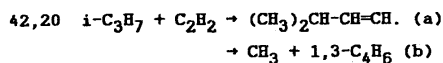
Table A.  $\log(k_d)/(k_{c+d})$  for the combination of vinyl and isopropyl as a function of temperature and pressure assuming strong collisions

log[M]	T/K										
	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.80	-0.37	-0.17	-0.07	-0.03	-0.01					
16.5	-1.21	-0.65	-0.32	-0.15	-0.06	-0.03	-0.01				
17.0	-1.66	-1.00	-0.56	-0.29	-0.14	-0.06	-0.03	-0.01	-0.01		
17.5	-2.15	-1.43	-0.88	-0.50	-0.27	-0.14	-0.07	-0.04	-0.02	-0.01	-0.01
18.0	-2.64	-1.89	-1.27	-0.79	-0.47	-0.27	-0.15	-0.08	-0.05	-0.03	-0.02
18.5	-3.14	-2.38	-1.72	-1.16	-0.75	-0.47	-0.29	-0.18	-0.11	-0.07	-0.04
19.0	-3.64	-2.87	-2.19	-1.59	-1.11	-0.76	-0.51	-0.34	-0.22	-0.15	-0.10
19.5	-4.14	-3.37	-2.68	-2.06	-1.54	-1.12	-0.81	-0.58	-0.41	-0.30	-0.22
20.0	-4.64	-3.87	-3.18	-2.55	-2.00	-1.56	-1.20	-0.91	-0.70	-0.54	-0.42
20.5	-5.14	-4.37	-3.68	-3.04	-2.40	-2.03	-1.64	-1.33	-1.07	-0.80	-0.73
21.0	-5.64	-4.87	-4.18	-3.54	-2.99	-2.51	-2.12	-1.79	-1.51	-1.30	-1.13

Table B. Collision efficiency  $\beta_0$  as a function of downward step size and temperature for the decomposition of activated 4-methylbutene-1

T/K	Step-size (cm <sup>-1</sup> )				
	150	300	600	1200	2400
500	5.65x10 <sup>-2</sup>	1.48x10 <sup>-1</sup>	3.08x10 <sup>-1</sup>	5.10x10 <sup>-1</sup>	6.94x10 <sup>-1</sup>
700	2.77x10 <sup>-2</sup>	8.14x10 <sup>-2</sup>	1.97x10 <sup>-1</sup>	3.78x10 <sup>-1</sup>	5.80x10 <sup>-1</sup>
900	1.43x10 <sup>-2</sup>	4.55x10 <sup>-2</sup>	1.24x10 <sup>-1</sup>	2.71x10 <sup>-1</sup>	4.69x10 <sup>-1</sup>
1100	7.47x10 <sup>-3</sup>	2.53x10 <sup>-2</sup>	7.53x10 <sup>-2</sup>	1.86x10 <sup>-1</sup>	3.63x10 <sup>-1</sup>
1300	3.86x10 <sup>-3</sup>	1.37x10 <sup>-2</sup>	4.39x10 <sup>-2</sup>	1.20x10 <sup>-1</sup>	2.65x10 <sup>-1</sup>
1500	1.93x10 <sup>-3</sup>	7.09x10 <sup>-3</sup>	2.41x10 <sup>-2</sup>	7.23x10 <sup>-2</sup>	1.80x10 <sup>-1</sup>
1700	9.12x10 <sup>-4</sup>	3.44x10 <sup>-3</sup>	1.23x10 <sup>-2</sup>	3.98x10 <sup>-2</sup>	1.11x10 <sup>-1</sup>
1900	3.96x10 <sup>-4</sup>	1.52x10 <sup>-3</sup>	5.64x10 <sup>-3</sup>	1.95x10 <sup>-2</sup>	6.01x10 <sup>-2</sup>
2100	1.54x10 <sup>-4</sup>	6.02x10 <sup>-4</sup>	2.30x10 <sup>-3</sup>	8.36x10 <sup>-3</sup>	2.81x10 <sup>-2</sup>
2300	5.29x10 <sup>-5</sup>	2.09x10 <sup>-4</sup>	8.11x10 <sup>-4</sup>	3.07x10 <sup>-3</sup>	1.10x10 <sup>-2</sup>
2500	1.58x10 <sup>-5</sup>	6.26x10 <sup>-5</sup>	2.46x10 <sup>-4</sup>	9.55x10 <sup>-4</sup>	3.59x10 <sup>-3</sup>

(W. Tsang, October 1984)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Kerr, Parsonage (1972) review			$4.6 \times 10^{-14} \exp(-3323/T)$	1.5
Recommended value			$4.6 \times 10^{-14} \exp(-3273/T)$	2

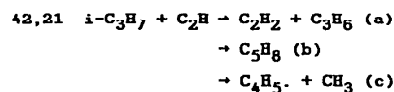
**Comments and Recommendations**

On the basis of the observation of Watkins and Olsen (J. Phys. Chem. 76, 1089, 1972) the addition will be followed by 1,4 hydrogen migration. Under combustion conditions step (b) is the predominant reaction channel. We recommend the use of the rate expression given by Kerr and Parsonage. Note that we have changed the rate expression slightly to reflect our choice for the rate constant for combination of isopropyl radicals. The uncertainty is a factor of 2.

(W. Tsang, April 1986)

**References**

Kerr, J. A., and Parsonage, M. J., "Evaluated Kinetic Data on Gas Phase Addition Reactions," (Butterworths, London, 1972)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$k_a = 6 \times 10^{-12}$	2
Recommended value			$k_{b+c} = 2.6 \times 10^{-11}$	2
Recommended value		1 atm, $\text{N}_2$	$\log(k_c/k_{b+c}) = -4.01 + 6.80 \times 10^{-3}T - 3.73 \times 10^{-6}T^2 + 6.65 \times 10^{-10}T^3$	2

**Comments and Recommendations**

There are no data for these reactions. We estimate the rate constant for reaction (a) to be  $k_a = 6 \times 10^{-12} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ , with an uncertainty of a factor of 3, or typical of disproportionation processes.  $k_{b+c}$  is estimated to be  $2.6 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  or similar to the combination of isopropyl and ethyl. The uncertainties are factors of 2. The existence of an exothermic decomposition channel prevents any pressure dependence. Table A gives the ratio of  $k_c/k_{b+c}$  as a function of temperature and pressure on a strong collision basis. Table B contains data on the collision efficiency as a function of step size down and temperature on a per collision basis. Expressions for  $k_c/k_{b+c}$  for  $\text{N}_2$  and  $\text{C}_5\text{H}_8$  as weak colliders at 0.1, 1 and 10 atms, with step size down of  $500 \text{cm}^{-1}$  and  $1000 \text{cm}^{-1}$  respectively, are as follows:

$$\log k_c/k_{b+c}(N_2, 0.1) = -1.815 + 3.37 \times 10^{-3}T - 1.985 \times 10^{-6}T^2 + 3.73 \times 10^{-10}T^3$$

$$\log k_c/k_{b+c}(N_2, 1) = -4.01 + 6.80 \times 10^{-3}T - 3.73 \times 10^{-6}T^2 + 6.65 \times 10^{-10}T^3$$

$$\log k_c/k_{b+c}(N_2, 10) = -5.61 + 7.91 \times 10^{-3}T - 3.689 \times 10^{-6}T^2 + 5.68 \times 10^{-10}T^3$$

and

$$\log k_c/k_{b+c}(C_5H_8, 0.1) = -3.60 + 7.94 \times 10^{-3}T - 5.92 \times 10^{-6}T^2 + 1.49 \times 10^{-9}T^3$$

$$\log k_c/k_{b+c}(C_5H_8, 1) = -4.63 + 7.18 \times 10^{-3}T - 3.65 \times 10^{-6}T^2 + 5.97 \times 10^{-10}T^3$$

$$\log k_c/k_{b+c}(C_5H_8, 10) = -5.06 + 4.9 \times 10^{-3}T - 9.31 \times 10^{-7}T^2 - 1.37 \times 10^{-10}T^3$$

These expressions should be applicable at temperatures in excess of 800 K. The uncertainty limits are a factor of 2.

Table A.  $\log(k_c)/(k_{b+c})$  for the decomposition of activated 4-methylbutyne-1 as a function of temperature and pressure assuming strong collisions

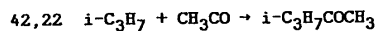
log[M]	T/K										
	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
16.0	-0.06	-0.03	-0.01	-0.01							
16.5	-0.15	-0.07	-0.04	-0.02	-0.01						
17.0	-0.35	-0.19	-0.10	-0.05	-0.03	-0.01	-0.01				
17.5	-0.67	-0.40	-0.24	-0.14	-0.08	-0.04	-0.02	-0.01	-0.01		
18.0	-1.08	-0.73	-0.48	-0.30	-0.18	-0.11	-0.06	-0.04	-0.02	-0.01	-0.01
18.5	-1.54	-1.14	-0.82	-0.55	-0.36	-0.23	-0.15	-0.10	-0.06	-0.04	-0.03
19.0	-2.03	-1.61	-1.24	-0.91	-0.65	-0.45	-0.31	-0.22	-0.15	-0.11	-0.08
19.5	-2.53	-2.09	-1.70	-1.34	-1.02	-0.77	-0.57	-0.42	-0.32	-0.24	-0.18
20.0	-3.03	-2.59	-2.19	-1.81	-1.46	-1.17	-0.93	-0.73	-0.58	-0.46	-0.37
20.5	-3.53	-3.09	-2.69	-2.30	-1.94	-1.62	-1.36	-1.13	-0.95	-0.80	-0.67
21.0	-4.03	-3.59	-3.18	-2.79	-2.43	-2.11	-1.83	-1.59	-1.39	-1.22	-1.07

Table B. Collision efficiency  $\beta_e$  as a function of downward step size and temperature for the decomposition of activated 4-methylbutyne-1

T/K	Step-size (cm <sup>-1</sup> )				
	150	300	600	1200	2400
500	$6.16 \times 10^{-2}$	$1.58 \times 10^{-1}$	$3.24 \times 10^{-1}$	$5.26 \times 10^{-1}$	$7.07 \times 10^{-1}$
700	$3.21 \times 10^{-2}$	$9.24 \times 10^{-2}$	$2.17 \times 10^{-1}$	$4.05 \times 10^{-1}$	$6.05 \times 10^{-1}$
900	$1.79 \times 10^{-2}$	$5.58 \times 10^{-2}$	$1.46 \times 10^{-1}$	$3.06 \times 10^{-1}$	$5.07 \times 10^{-1}$
1100	$1.04 \times 10^{-2}$	$3.42 \times 10^{-2}$	$9.74 \times 10^{-2}$	$2.26 \times 10^{-1}$	$4.16 \times 10^{-1}$
1300	$6.11 \times 10^{-3}$	$2.10 \times 10^{-2}$	$6.41 \times 10^{-2}$	$1.63 \times 10^{-1}$	$3.31 \times 10^{-1}$
1500	$3.61 \times 10^{-3}$	$1.28 \times 10^{-2}$	$4.14 \times 10^{-2}$	$1.14 \times 10^{-1}$	$2.56 \times 10^{-1}$
1700	$2.11 \times 10^{-3}$	$7.71 \times 10^{-3}$	$2.61 \times 10^{-2}$	$7.73 \times 10^{-2}$	$1.89 \times 10^{-1}$
1900	$1.21 \times 10^{-3}$	$4.50 \times 10^{-3}$	$1.58 \times 10^{-2}$	$4.99 \times 10^{-2}$	$1.33 \times 10^{-1}$
2100	$6.67 \times 10^{-4}$	$2.54 \times 10^{-3}$	$9.20 \times 10^{-3}$	$3.06 \times 10^{-2}$	$8.87 \times 10^{-2}$
2300	$3.54 \times 10^{-4}$	$1.36 \times 10^{-3}$	$5.07 \times 10^{-3}$	$1.77 \times 10^{-2}$	$5.51 \times 10^{-2}$
2500	$1.78 \times 10^{-4}$	$6.92 \times 10^{-4}$	$2.63 \times 10^{-3}$	$9.51 \times 10^{-3}$	$3.16 \times 10^{-2}$

(W. Tsang, May 1985)

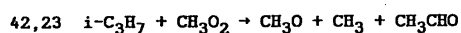




Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$1.5 \times 10^{-11} \exp(300/T)^{0.35}$	2

**Comments and Recommendations**

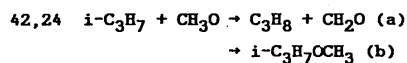
There are no data. Measurements for the self combination of the two radicals exist [(42,42) and (22,22)], and through the geometrical mean rule lead to  $1.4 \times 10^{-11} (300/T)^{0.25} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ , with an uncertainty of a factor of 2.  
(W. Tsang, May 1985)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$4 \times 10^{-11}$	3

**Comments and Recommendations**

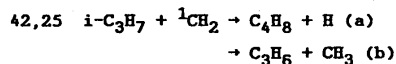
There are no data. However the mechanism under combustion conditions is clear-cut. The recommended rate constant is  $\sim 4 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ , with an uncertainty of a factor of 3.  
(W. Tsang, May 1985)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$k_a = 2 \times 10^{-11}$	5
Recommended value			$k_b = 1 \times 10^{-11}$	5

**Comments and Recommendations**

There are no data. On the basis of the rate constants for  $\text{CH}_3 + \text{CH}_3\text{O}$  (24,16), we recommend  $k_a = 2 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  and  $k_b = 1 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ . We estimate the uncertainty as a factor of 5.  
(W. Tsang, May 1985)

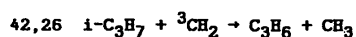


Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$k_{a+b}=2 \times 10^{-11}$	1.5
Recommended value			$k_a/k_b=0.16$	

**Comments and Recommendations**

Although rate constants for these reactions do not exist, Langford and Ashfold (see 25,10, 25,11) have established that  ${}^1\text{CH}_2$  inserts at a collisional rate. This is consistent with the nonselectivity of these reactions. Thus we assign an overall insertion rate constant of  $2 \times 10^{-10} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$  and  $k_a/k_b = 0.16$ . The uncertainties are a factor of 1.5.

(W. Tsang, May 1985)

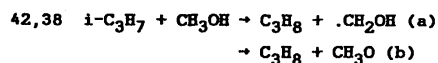


Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$5 \times 10^{-11}$	2

**Comments and Recommendations**

There are no data. We believe the main process to be combination leading to chemically activated isobutyl radicals which will readily decompose. The estimated rate constant is  $5 \times 10^{-11}$  with an uncertainty factor of 2.

(W. Tsang, May 1985)



Recommended value			$k_a = 5.3 \times 10^{-23} T^{3.7} \exp(-5300/T)$	3
Recommended value			$k_b = 2.4 \times 10^{-23} T^{3.1} \exp(-5200/T)$	5

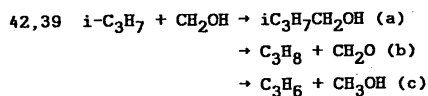
**Comments and Recommendations**

There are no data. From our rate expression for ethyl attack on  $\text{H-CH}_2\text{OH}$  (38,17), and increasing the activation energy by 6 kJ to reflect the greater reaction endothermicity, we recommend:

$$k_a = 5.28 \times 10^{-23} T^{3.7} \exp(-5300/T) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an uncertainty of a factor of 3. Similarly, from ethyl attack on the methoxy hydrogen in methanol (38,17), we estimate  $k_b = 2.4 \times 10^{-23} T^{3.1} \exp(-5200/T) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ . The uncertainty is a factor of 5.

(W. Tsang, May 1985)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$k_a = 2.4 \times 10^{-11}$	2
Recommended value			$k_b = 3.9 \times 10^{-12}$	5
Recommended value			$k_c = 4.8 \times 10^{-12}$	5

**Comments and Recommendations**

There are no data. We suggest using the information for the isopropyl + ethyl reaction [42,17]. This leads to:

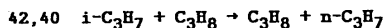
$$k_a = 2.4 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1},$$

$$k_b = 3.9 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1},$$

$$k_c = 4.8 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}.$$

Uncertainties are factors of 2, 5 and 5, respectively.

(W. Tsang, May 1985)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Recommended value			$1.4 \times 10^{-26} T^{4.2} \exp(-4386/T)$	2

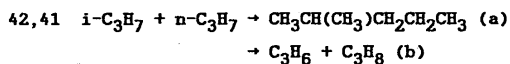
**Comments and Recommendations**

Although there are no data, there can be little doubt that the rate expression will be the same as that for  $i\text{-C}_3\text{H}_7 + \text{C}_2\text{H}_6$ . We therefore recommend:

$$k(i\text{-C}_3\text{H}_7 + \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_8 + n\text{-C}_3\text{H}_7) = 1.4 \times 10^{-26} T^{4.2} \exp(-4368/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

with an uncertainty of a factor of 2.

(W. Tsang, May 1985)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Gibian, Corley (1973)			$k_b/k_a = 0.4$	
Recommended value			$\log k_a = 2.9 \times 10^{-11} (300/T)^{0.35}$	2
Recommended value			$k_b/k_a = 0.4$	

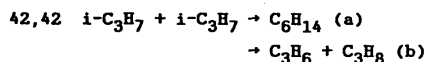
## Comments and Recommendations

There are no direct measurements for combination. From the rate constants for self combination (42,42) and (39,39) and the geometric mean rule, we obtain

$$k_a = 2.9 \times 10^{-11} (300/T)^{0.35} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}. \text{ This then leads to}$$

$$k_b = 1.04 \times 10^{-11} (300/T)^{0.35} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}. \text{ The uncertainty is 50\%}.$$

(W. Tsang, May 1986)



Reference	Conditions		Reaction rate constant, $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	Uncertainty factor
	Temp./K	[M]/molecule $\text{cm}^{-3}$		
Adachi, Basco (1981)	300	1.2-2.4x10 <sup>19</sup> N <sub>2</sub> or Ar with 1-2% azoisopropane and 0-10% n-C <sub>5</sub> H <sub>12</sub> . (Flash photolysis)	$k_a = (1.3 \pm 0.3) \times 10^{-11}$ $k_b/k_a = 0.65$	1.3 1.3
Arrowsmith, Kirsch (1979)	301-422	2x10 <sup>19</sup> N <sub>2</sub> , ~ 1% azoisopropane. (Modulation spectr.)	$k_a = 1.4 \times 10^{-11} \exp(-161/T)$ $k_b = 5 \times 10^{-12} \exp(25/T)$	1.3
Parkes, Quinn (1976)	300	2.4x10 <sup>19</sup> N <sub>2</sub> , 0.6-2% azoisopropane. (Modulation spectr.)	$k_a = (8.3 \pm 2) \times 10^{-12}$ $k_b/k_a = 0.65$	1.3
Golden, et al. (1974)	683-808	(Very low pressure pyrolysis)	$k_a = (5 \pm 2.5) \times 10^{-12}$ $k_b/k_a = 0.75-1.5$	2
Gibian, Corley (1973) review			$k_b/k_a = 0.66 \pm 0.02$	
Recommended value			$k_a = 1 \times 10^{-11} (300/T)^{0.7}$	1.5 at 300K,
Recommended value			$k_b/k_a = 0.65$	2 at 1000K

## Comments and Recommendations

The room temperature data vary by 50%. Additional high temperature information is needed. We recommend using the expression

$k_a = 1 \times 10^{-11} (300/T)^{0.7} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , with an uncertainty of 40% at room temperature and increasing to a factor of 2 at 1000 K.

$k_b/k_a$  is 0.65 with an uncertainty of 10%.

Figure 8 contains the experimental data on isopropyl combination and our recommendations.

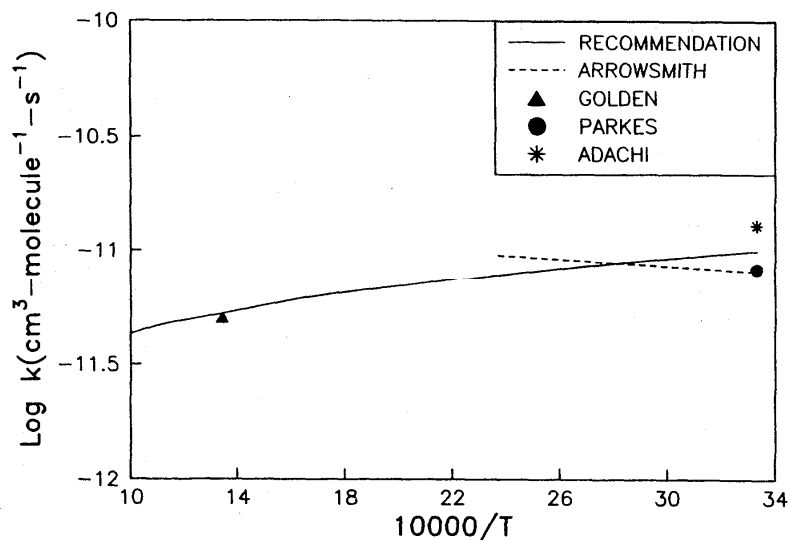


Fig. 8. Summary of experimental and recommended rate constants for the Rn.  $2i\text{-C}_3\text{H}_7 \rightarrow \text{C}_6\text{H}_{14}$

(W. Tsang, May 1985)

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## 4. Thermodynamic Data Tables

Thermodynamic properties of C<sub>3</sub>H<sub>8</sub> (Species No. 40)

T/K	J mol <sup>-1</sup> K <sup>-1</sup>		kJ mol <sup>-1</sup>	
	C <sub>p</sub>	S	ΔH <sub>f</sub>	ΔG <sub>f</sub>
300	73.89	270.37	-103.96	-23.18
500	113.14	317.52	-115.57	34.43
700	143.09	360.54	-123.39	95.94
900	165.73	399.45	-127.95	159.20
1100	183.05	434.55	-130.08	223.17
1300	196.19	466.31	-130.50	287.36
1500	206.10	494.93	-129.96	351.79

$$\log K_p = -17.1105 + 7582.31/T - 477858/T^2 + 3.18821 \times 10^7/T^3$$

September 1985

Rossini, F. D., Pitzer, K. S., Arnett, R. L., Braun, R. M. and Pimentel, G. C., 'Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds,' (Carnegie Press, Carnegie Institute of Technology, Pittsburg Pa., 1953)

Thermodynamic properties of n-C<sub>3</sub>H<sub>7</sub> (Species No. 41)

T/K	J mol <sup>-1</sup> K <sup>-1</sup>		kJ mol <sup>-1</sup>	
	C <sub>p</sub>	S	ΔH <sub>f</sub>	ΔG <sub>f</sub>
300	71.53	289.41	100.63	156.29
500	106.16	334.05	90.49	196.24
700	132.06	374.22	84.34	239.75
900	151.49	409.91	79.93	284.77
1100	166.38	441.83	77.76	330.18
1300	177.59	470.44	76.89	376.20
1500	186.12	496.41	76.97	422.57

$$\log K_p = -12.259 - 3425.19/T - 393860/T^2 + 2.27714 \times 10^7/T^3$$

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Frequencies (degeneracy): 3100 (2), 2960 (5), 1440 (5), 1390 (1), 1100 (1), 990 (4), 980 (1), 960 (1), 530 (1), 330 (1); 1 hindered rotor with barrier, 15 kJ and  $I=4.2 \times 10^{-40}$  gm-cm<sup>2</sup> with symmetry 3 and 1 free rotor with  $I=2.7 \times 10^{-40}$  gm-cm<sup>2</sup> and symmetry 2. Moment of Inertia,  $2.54 \times 10^{-115}$  gm-cm<sup>2</sup>, symmetry 1, ground state degeneracy 2.

Pacansky, J., Horne, D. E., Gardini, G. P. and Bargon, J., J. Phys. Chem. **81**, 23, (1977)

Purnell, J. H. and Quinn, C. P., J. Chem. Soc., 4049 (1964)

Tsang, W., J. Am. Chem. Soc. **107**, 2782 (1985)

Thermodynamic properties of s-C<sub>3</sub>H<sub>7</sub> (Species No. 42)

T/K	J mol <sup>-1</sup> K <sup>-1</sup>		kJ mol <sup>-1</sup>	
	C <sub>p</sub>	S	ΔH <sub>f</sub>	ΔG <sub>f</sub>
300	66.61	289.80	93.30	148.84
500	99.94	331.68	82.49	189.02
700	127.16	369.84	74.74	233.11
900	147.86	404.41	69.70	279.06
1100	163.65	435.68	66.89	325.90
1300	175.65	464.04	65.58	373.08
1500	184.77	489.84	65.15	420.46

$$\log K_p = -12.6509 - 2663.93/T - 510254/T^2 + 3.48234 \times 10^7/T^3$$

September 1985

Frequencies (degeneracy): 3100 (1), 2960 (6), 1440 (6),  
 1300 (1), 1200 (1), 990 (4), 950 (1), 397 (1), 367 (1);  
 2 free rotors,  $I = 4.2 \times 10^{-40}$  gm-cm<sup>2</sup> with symmetry 3.  
 Moment of Inertia,  $2.67 \times 10^{-115}$  gm-cm<sup>2</sup>, symmetry 2;  
 ground state degeneracy 2.

Purnell J. H. and Quinn, C. P., J. Chem. Soc., 4049 (1964)  
 Pacansky, J. and Coufal, H., J. Chem. Phys. 12, 3298 (1980)  
 Tsang, W., J. Am. Chem. Soc. 107, 2872 (1985)