

# Selected Specific Rates of Reactions of the Solvated Electron in Alcohols

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Edgar Watson, Jr., and Sathyabhama Roy

Radiation Chemistry Data Center,  
Radiation Laboratory,  
University of Notre Dame,  
Notre Dame, Indiana 46556



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U.S. DEPARTMENT OF COMMERCE, Peter G. Peterson, *Secretary*  
NATIONAL BUREAU OF STANDARDS, Lawrence M. Kushner, *Acting Director*,

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## Foreword

The National Standard Reference Data System provides access to the quantitative data of physical science, critically evaluated and compiled for convenience, and readily accessible through a variety of distribution channels. The System was established in 1963 by action of the President's Office of Science and Technology and the Federal Council for Science and Technology, with responsibility to administer it assigned to the National Bureau of Standards.

The System now comprises a complex of data centers and other activities, carried on in academic institutions and other laboratories both in and out of government. The independent operational status of existing critical data projects is maintained and encouraged. Data centers that are components of the NSRDS produce compilations of critically evaluated data, critical reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data. In addition, the centers and projects establish criteria for evaluation and compilation of data and make recommendations on needed improvements in experimental techniques. They are normally closely associated with active research in the relevant field.

The technical scope of the NSRDS is indicated by the principal categories of data compilation projects now active or being planned: nuclear properties, atomic and molecular properties, solid state properties, thermodynamic and transport properties, chemical kinetics, and colloid and surface properties.

The NSRDS receives advice and planning assistance from the National Research Council of the National Academy of Sciences-National Academy of Engineering. An overall Review Committee considers the program as a whole and makes recommendations on policy, long-term planning, and international collaboration. Advisory Panels, each concerned with a single technical area, meet regularly to examine major portions of the program, assign relative priorities, and identify specific key problems in need of further attention. For selected specific topics, the Advisory Panels sponsor subpanels which make detailed studies of users' needs, the present state of knowledge, and existing data resources as a basis for recommending one or more data compilation activities. This assembly of advisory services contributes greatly to the guidance of NSRDS activities.

The NSRDS-NBS series of publications is intended primarily to include evaluated reference data and critical reviews of long-term interest to the scientific and technical community.

LAWRENCE M. KUSHNER, *Acting Director*

## Preface

This report is one of a series of data publications on radiation chemistry; the aim of the series is to compile, evaluate, and present the numerical results on processes occurring in systems which have been subjected to ionizing radiation. Various kinds of data are important in radiation chemistry. The quantities which were measured first were the observed radiation yields or  $G$  values (molecules formed or destroyed per 100 eV). Various indirect methods based on  $G$  values have been used to determine yields of transient species and relative rates of reactions. The spectral properties (optical, electron spin resonance) of transients have provided a direct method for their identification, and rates of the very fast reactions of transients which occur in irradiated systems have been measured directly by spectroscopic methods. Conductivity and luminescence methods have also provided a means of measuring properties of transients and their kinetics. Some reactions which occur in irradiated systems have also been studied by other methods, such as photochemistry, electric discharge, ultrasonics, chemical initiation, electron impact, etc. The emphasis in these publications is on the data of radiation chemistry, but where other pertinent data exist, they are included.

The data of radiation chemistry are voluminous; thousands of systems have been investigated. As a result there are certain collections, e.g. rate constants of particular types of reactions or certain properties of transients, for which tabulations of the data are considered essential, but for which critical assessment of each value is impossible. On the other hand, certain systems and properties have been studied so extensively that critical examination of these data is desirable and timely. Authors of this series of data publications have been asked to evaluate the extent to which the data can be critically assessed, to describe their criteria for evaluation, and to designate preferred values whenever possible.

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Edgar Watson, Jr., and Sathyabhama Roy

Radiation Chemistry Data Center, Radiation Laboratory,\*  
University of Notre Dame, Notre Dame, Indiana 46556

Solvated electrons are generated in alcohols by radiolysis, photolysis, reaction with sodium, etc. Rates of reactions of  $e_s^-$  with solvent and solute molecules, ions, and transients, in alcohol solutions, have been compiled. Arrhenius parameters are tabulated for some reactions.

Key words: Alcohols; chemical kinetics; data compilation; radiation chemistry; rates; solvated electron.

## Introduction

The nature and chemical properties of solvated electrons in selected solvent media have been the subject of extensive study. One of the important characteristics of this species is its reactivity toward a large number of reagents. The latest rate data compilation for the hydrated electron includes over 700 compounds for which specific rates of reaction have been measured [71-0061].<sup>1</sup> Although several reviews [65-9018; 68-0520; 69-0334; 69-0451; 71-0062] containing rate data for solvated electrons in alcohols have been published, there has been no comprehensive compilation of these data. This compilation of rate constants and Arrhenius parameters has been prepared in order to consolidate the information available in the literature. These data are presented as reported without critical evaluation. Critical assessment of the kinetic parameters of several of the reactions will appear in forthcoming critical reviews [71-0062 and 71-0362].

Rate parameters contained in this compilation include data obtained by pulse radiolysis, flash photolysis, and  $\gamma$ -radiolysis. Competition kinetic studies in alcohols, unlike water, have yielded a large portion of the rate information available. For optimum utilization of the relative rates thus obtained, it is required that the specific rate for one of the competing processes be known. Specific rates obtained from relative rates are listed only when the normalizing rate constants used seemed to be reliable and consistent. Generally, the normalization rate constants are from pulse radiolysis

studies which offer the most reliable kinetic method available to obtain rate data involving the solvated electron. Due to the abundance of relative rates obtained using  $N_2O$  as a competing solute and the lack of consistent measurements of its specific rate (e.g. in methanol  $k(e_s^- + N_2O)$  values obtained from the available data vary over an order of magnitude), the specific rate of reaction of the hydrated electron with  $N_2O$  in water has been used to normalize relative rates involving  $N_2O$ . Hence, specific rates thus obtained are presented only for comparison purposes and should be considered with caution.

An attempt has been made to include all rate data which have been reported for alcohols. Duplication of references has been avoided in cases where it was apparent that two or more publications report the same experimental results.

Temperature when not specified is to be taken as ambient, 15 to 25 °C. Rate constants obtained at other temperatures have the appropriate temperature noted below the constant. No data on glassy or solid alcohols have been included. No corrections have been made for the effect of ionic strength on the reaction rates of  $e_s^-$ , but information pertinent to  $\mu$  has been reported as given in the reference.

Table 4 contains Arrhenius parameters obtained for reactions of  $e_s^-$  in alcohols. Given in this table are:  $\log A$ ,  $E_a$ ,  $\Delta S^\ddagger$ , temperature range, and the reference.

### Arrangement of Tables 1, 2, and 3

*Solute and Reaction.* The first "solute" listed in each table is the solvent (without solute) followed by solvent mixtures (with no solute), and an alphabetical arrangement of the other solutes. The products which have been identified are included

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<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

in the listed reactions. In competition studies the reaction of  $e_s^-$  with the solute of entry appears as reaction (1) and is followed by the competing reaction (2). Solute concentrations were, in most cases  $10^{-3}$  mol  $\text{dm}^{-3}$  or less. Higher concentrations are noted under *Comments*.

$k_1/k_2$ . Relative rate constants listed are unitless (both second order rates in units of  $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ ). Relative constants are listed once [under solute of reaction (1)]. Table 5 gives an index to entries for rate constants with the various solutes (relative and specific) listed in tables 1, 2, and 3.

$k$ . Specific rate constants are listed and are in units of  $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ . In the case of the reaction of  $e_s^-$  with the alcohol, conversion of a second order rate to a first order rate can be made by multiplying the rate constant by the molarity of the alcohol. Half-lives are also given under *Comments*. Specific rates calculated from relative rates are for reaction (1), and the footnote gives the standard specific rate used for normalization. Error limits and ionic strength have been given as reported by authors. Except where otherwise indicated, all solutions are neutral. Most numerical values of  $k$  have been rounded off to one or two significant figures.

*Method*. Abbreviations used under *Method* are:

$\gamma$ -r.	= gamma radiolysis
p.r.	= pulse radiolysis
f. phot.	= flash photolysis
c.k.	= competition kinetics
d.k.	= decay kinetics
calc.	= calculation.

Additional details of the method used are found in the *Comments* column.

*Comments*. Included under *Comments* are additional experimental details not included with the methods:  $t_{1/2}$ , measured quantities, corrections applied, etc. For brevity, the following abbreviations and symbols have been utilized:

$A$	= frequency factor
abs.	= absorption
anal.	= analysis
aq.	= aqueous
av.	= average
conc.	= concentration
const.	= constant
corr.	= correction
d.	= decay
dissochn.	= dissociation
$E_a$	= activation energy
elec. condy.	= electrical conductivity
eq.	= equation
f.o.	= first order
$G$	= radiation yield; (molecules or ions per 100eV absorbed)
$k$	= specific rate
$\mu$	= ionic strength
$P_v$	= vapor pressure
react.	= reaction
S	= alcohol (solvent)
$S_m$	= mixed solvent
$\Delta S^\ddagger$	= entropy of activation
s	= second
scav.	= scavenger
soln.	= solution
spec.	= spectrophotometrically
$t_{1/2}$	= half-life

Units used in tables 1, 2, 3, and 4:

$k, A$	$\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$
$E_a$	$\text{kJ mol}^{-1}$
$\Delta S^\ddagger$	$\text{J mol}^{-1}\text{deg}^{-1}$
$T$	$^\circ\text{C}$
$P_v$	$\text{N m}^{-2}$ .

*References*. The serial number used in Radiation Chemistry Data Center files has been used for reference citation. The first two numbers indicate the year of publication.

TABLE 1. Rate constants of reactions of the solvated electron in methanol

No.	Solute and reaction	$k_1/k_2$	$k(\text{dm}^3\text{mol}^{-1}\text{s}^{-1})$	Method	Comments	Ref.
1.01a	No solute ( $e_s^- + S$ )	.....	$1.48 \times 10^4$	p.r.; d.k.	.....	[64-0080].
1.01b	$e_s^- + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O}^- + \text{H}$ same	.....	$(1.26 \pm 0.04) \times 10^4$	p.r.; d.k.	Methoxide ion conc. $0-10^{-3}$ mol $\text{dm}^{-3}$ ; d.f.o. over 3-4 half-lives; beyond $10^{-3}$ mol $\text{dm}^{-3}$ $\text{CH}_3\text{O}^-$ , $t_{1/2}$ increases to 3.1 $\mu\text{s}$ at 1 mol $\text{dm}^{-3}$ .	[69-0456].
1.01c	same	.....	$0.9 \times 10^4$	p.r.; d.k.	d.f.o. over 3-4 half-lives; little change in $k$ with repeated pulsing ( $\sim 830$ pulses); no $\text{CH}_2\text{OH}$ radical abs. detected.	[69-0146]. [68-0260].
1.01d	same	.....	$1.9 \times 10^4$	p.r.; d.k.	d. curves not of simple order and probably include reaction with counter ion.	[64-0113].

TABLE 1. Rate constants of reactions of the solvated electron in methanol—Continued

No.	Solute and reaction	$k_1/k_2$	$k(\text{dm}^3\text{mol}^{-1}\text{s}^{-1})$	Method	Comments	Ref.
1.01e	same	.....	$1.7 \times 10^4$ (LiCl) $1.9 \times 10^4$ (NaBr) $1.5 \times 10^4$ (NaI) $(8 \rightarrow 5.4) \times 10^3$ (KOH)	p.r.; d.k.	$t_{1/2} = 1.7 \mu\text{s}$ with added LiCl (conc. independent); $t_{1/2} = 1.5 \mu\text{s}$ with added NaBr; $t_{1/2} = 1.9 \mu\text{s}$ with added NaI (conc. independent); conc. of KOH $0.15 \rightarrow 2.65 \text{ mol dm}^{-3}$ .	[70-0246].
1.01f	same	.....	$\sim 3.5 \times 10^3$ ( $T = -78 \pm 2$ )	p.r.; d.k.	d. curves not of simple order and probably include reaction with counter ion.	[66-0082].
1.01g	No solute $e_s^- + e_s^- \rightarrow D_2 + \text{CH}_3\text{O}^-$ ( $S = \text{CH}_3\text{OD}$ )	.....	$(3.3 \pm 2) \times 10^9$	c.k.	Reacted Na with $\text{CH}_3\text{OD}$ and measured $D_2$ , HD, and dissolution rate of Na; $k$ calc. based on diffusion and homogeneous reaction kinetics.	[71-9165]
1.02	$\text{H}_2\text{O}$ (30 mol %) $e_s^- + S_m \rightarrow$	.....	$\sim 1 \times 10^4$	p.r.; d.k.	See 1.01f.	[66-0082].
1.03	$\text{CH}_3\text{CHOHCH}_3$ (50 mol %) $e_s^- + S_m$	.....	$1.9 \times 10^4$ $2.8 \times 10^3$ ( $T = -78$ )	p.r.; d.k.	See 1.01f; after $\sim 20$ pulses $t_{1/2}$ drops from $1.5 \mu\text{s}$ to $0.6 \mu\text{s}$ .	[66-0082].
1.04a	acetone (1) $e_s^- + (\text{CH}_3)_2\text{CO} \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	0.82 <sub>s</sub>	$7.2 \times 10^{9c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ ; $k_1/k_2$ calc. on the basis of two conc. and is an av. value.	[67-0313].
1.04b	same	0.57	$5.0 \times 10^{9c}$	$\gamma$ -r.; c.k.	Two solute system ( $\text{SF}_6$ and $(\text{CH}_3)_2\text{CO}$ ) to determine $\alpha_{\text{acet}}$ ; $k_1/k_2$ obtained from ratio of empirical $\alpha$ values for acetone and $\text{N}_2\text{O}^g$ .	[70-0064].
1.05a	acetophenone (1) $e_s^- + \text{C}_6\text{H}_5\text{COCH}_3 \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	1.8	$1.6 \times 10^{10c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[66-0045].
1.05b	same	1.8 <sub>s</sub>	$1.6 \times 10^{10c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ ; $k_1/k_2$ is an average from two conc.	[67-0313].
1.06a	benzene (1) $e_s^- + \text{C}_6\text{H}_6 \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	$2.3 \times 10^{-3}$	$2.0 \times 10^{7c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[67-0313].
1.06b	same	$2.9 \times 10^{-3}$	$2.5 \times 10^{7c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[66-0045].
1.07a	benzotrile (1) $e_s^- + \text{C}_6\text{H}_5\text{CN} \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	2.05	$1.8 \times 10^{10c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[67-0313].
1.07b	same	2.1	$1.8 \times 10^{10c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[66-0045].
1.08	benzoquinone $e_s^- + \text{C}_6\text{H}_4\text{O}_2 \rightarrow$	.....	$3 \times 10^{10}$	p.r.; d.k.	Corr. made for natural d. of $e_s^-$ .	[70-0198].
1.09a	benzyl chloride $e_s^- + \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \rightarrow$ $\text{C}_6\text{H}_5\text{CH}_2 + \text{Cl}^-$	.....	$(5.0 \pm 1.2) \times 10^9$	p.r.; d.k.	Corr. for d. of $e_s^-$ in pure solvent; benzyl radical identified spec. from 317.1 and 305.5 nm bands.	[64-0113].
1.09b	same	.....	$(5.7 \pm 1.2) \times 10^9$	p.r.; d.k.	Benzyl radical observed spec.; $e_s^-$ conc. varied two-fold.	[63-0059].
1.09c	benzyl chloride (1) $e_s^- + \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	0.725	$6.3 \times 10^{9c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ ; $k_1/k_2$ an average for two conc.	[67-0313].
1.09d	same	$0.36 \pm 0.04$	$3.5 \times 10^{9c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ ; constant $\mu$ maintained using LiCl.	[69-0456].
1.10	carbon tetrachloride (1) $e_s^- + \text{CCl}_4 \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	6.3 4.0	$5.5 \times 10^{10c}$ $3.5 \times 10^{10c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ ; $k_1/k_2$ given for two conc. studied.	[67-0313].

TABLE 1. Rate constants of reactions of the solvated electron in methanol—Continued

No.	Solute and reaction	$k_1/k_2$	$k(\text{dm}^3\text{mol}^{-1}\text{s}^{-1})$	Method	Comments	Ref.
1.11	chloroacetate ion (1) $e_s^- + \text{ClCH}_2\text{COO}^- \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	$\ll 1$	$\ll 8.7 \times 10^{9c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ ; constant $\mu$ maintained using LiCl.	[69-0456].
1.12a	chlorobenzene (1) $e_s^- + \text{C}_6\text{H}_5\text{Cl} \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	$9.5 \times 10^{-2}$	$8.3 \times 10^{8c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[66-0045].
1.12b	same	$9.5 \times 10^{-2}$	$8.3 \times 10^{8c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ ; $k_1/k_2$ is average for two conc.	[67-0313].
1.13	cyanogen iodide (1) $e_s^- + \text{ICN} \rightarrow \text{I} + \text{CN}^-$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	0.53	$4.6 \times 10^{9c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[69-0220].
1.14	duroquinone $e_s^- + \text{C}_{10}\text{H}_{12}\text{O}_2 \rightarrow$ $\text{C}_{10}\text{H}_{12}\text{O}_2^-$	.....	$\sim 10^{10}$	p.r.; d.k.	Corr. for $e_s^-$ d. in pure solvent.	[70-0198].
1.15a	fluorobenzene (1) $e_s^- + \text{C}_6\text{H}_5\text{F} \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	$5.85 \times 10^{-3}$	$5.1 \times 10^{7c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ ; $k_1/k_2$ is average for two conc.	[67-0313].
1.15b	same	$5.9 \times 10^{-3}$	$5.1 \times 10^{7c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[66-0045].
1.16a	$\text{H}_s^+$ $e_s^- + \text{H}_s^+ \rightarrow \text{H}$ ( $\text{H}_2\text{SO}_4$ or HCl)	.....	$(3.7 \pm 1.0) \times 10^{10}$	p.r.; d.k.	Corr. for counter ion contribution ( $\sim 3\%$ ).	[63-0059].
1.16b	same	.....	$(3.9 \pm 0.9) \times 10^{10}$	p.r.; d.k.	Corr. for $e_s^-$ d. in pure solvent.	[64-0113].
1.16c	same	.....	$(6.81 \pm 0.63) \times 10^{10}$	p.r.; d.k.	Measured elec. condy. d.; effect of pH (4-10), $\text{N}_2\text{O}$ , and $\text{H}_2\text{O}$ observed.	[71-0064].
1.16d	$\text{H}_s^+$ (1) $e_s^- + \text{H}_s^+ \rightarrow \text{H}$ ( $\text{H}_2\text{SO}_4$ ) (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	10 ( $\mu=0$ )	$8.7 \times 10^{10c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ ; primary salt effect evident ( $k_1/k_2 = 2.93 \rightarrow 8.00$ ); $k_1/k_2$ at $\mu=0$ obtained from Broensted-Bjerrum plot.	[67-0313].
1.16e	same	3.0	$2.6 \times 10^{10c}$	$\gamma$ -r.; c.k.	Measured $G(\text{H}_2)$ and $G(\text{N}_2)$ .	[66-0094]. [67-0018]. [67-0030].
1.17	iodine (1) $e_s^- + \text{I}_2 \rightarrow$ (2) $e_s^- + \text{S} \rightarrow$	.....	$\leq 10^7$	$\gamma$ -r.; c.k.	Measured $G(\text{H}_2)$ ; $k$ is deduced from inequality conditions applied to scavenging equation.	[70-0064].
1.18a	methyl bromide (1) $e_s^- + \text{CH}_3\text{Br} \rightarrow \text{CH}_3 + \text{Br}^-$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	1.46	$1.3 \times 10^{10c}$	$\gamma$ -r.; c.k.	Measured $G(^{14}\text{CH}_4)$ from $^{14}\text{CH}_3\text{Br}$ ; $\alpha_{\text{CH}_3\text{Br}}$ determined from single solute exp.; $k_1/k_2$ obtained from ratio of empirical $\alpha$ values for $\text{CH}_3\text{Br}$ and $\text{N}_2\text{O}^6$ .	[70-0064].
1.18b	methyl bromide (1) $e_s^- + \text{CH}_3\text{Br} \rightarrow \text{CH}_3 + \text{Br}^-$ (2) $e_s^- + \text{S} \rightarrow$	$1.35 \times 10^6$	$1.2 \times 10^{10a}$	$\gamma$ -r.; c.k.	Measured $G(^{14}\text{CH}_4)$ ; at low conc. of $\text{CH}_3\text{Br}$ empirical $\alpha$ eq. modified to include c. of $e_s^-$ d. as in pure solvent <sup>6</sup> .	[70-0064].
1.19	naphthalene $e_s^- + \text{C}_{10}\text{H}_8 \rightarrow$	.....	$\sim 2 \times 10^9$	p.r.; d.k.	Spectrum shows product is not $\text{C}_{10}\text{H}_8^-$ but probably $\text{C}_{10}\text{H}_9$ radical.	[64-0080].
1.20	nitrate ion (1) $e_s^- + \text{NO}_3^- \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	$\ll 1$	$\ll 8.7 \times 10^{9c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ ; const. $\mu$ maintained.	[69-0456].
1.21	nitrite ion (1) $e_s^- + \text{NO}_2^- \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	$\ll 1$	$\ll 8.7 \times 10^{9c}$	$\gamma$ -r.; c.k.	See 1.20.	[69-0456].
1.22a	nitrobenzene (1) $e_s^- + \text{C}_6\text{H}_5\text{NO}_2 \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	4.1	$3.6 \times 10^{10c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[66-0045].
1.22b	same	4.0	$3.5 \times 10^{10c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[67-0313].



TABLE 1. Rate constants of reactions of the solvated electron in methanol—Continued

No.	Solute and reaction	$k_1/k_2$	$k(\text{dm}^3\text{mol}^{-1}\text{s}^{-1})$	Method	Comments	Ref.
1.23a	nitrous oxide (1) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$ (2) $e_s^- + \text{S} \rightarrow$	$2.7 \times 10^5$ $4.2 \times 10^5$ ( $T = -97$ ) $1.0 \times 10^5$ ( $T = 150$ )	$2.4 \times 10^{9a}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ ; at $T = 150$ , $P_r = 1.32 \times 10^6$ $\text{Nm}^{-2}$ ; see table 4 for Arrhenius parameters.	[68-0610].
1.23b	same	$> 4.55 \times 10^4$	$> 4.1 \times 10^{8a}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[67-0313].
1.23c	nitrous oxide (1) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$ (2) $e_s^- + \text{H}_3^+ \rightarrow \text{H}$	0.126 ( $\mu = 0$ ; $T = 0$ )	$1.95 \times 10^{9a}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ ; $k_1/k_2$ measured as function of $\mu$ . Corr. for counter ion contribution ( $\sim 3\%$ ).	[67-0065]. [63-0059].
1.24a	oxygen $e_s^- + \text{O}_2 \rightarrow \text{O}_2^-$	.....	$(2.1 \pm 0.4) \times 10^{10}$	p.r.; d.k.		
1.24b	same	.....	$(1.9 \pm 0.4) \times 10^{10}$	p.r.; d.k.	Corr. for $e_s^-$ d. in pure solvent.	[64-0113].
1.24c	oxygen (1) $e_s^- + \text{O}_2 \rightarrow \text{O}_2^-$ (2) $e_s^- + \text{H}_3^+ \rightarrow \text{H}$ ( $\text{H}_2\text{SO}_4$ )	$0.36 \pm 0.11$	$1.6 \times 10^{10b}$	$\gamma$ -r.; c.k.	Measured $G(\text{H}_2)$ .	[69-0146]. [68-0260].
1.25	silver ion (1) $e_s^- + \text{Ag}^+ \rightarrow \text{Ag}^0$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	2.4 ( $\mu = 0$ ; $T = 0$ )	$4.7 \times 10^{9e}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ ; $k_1/k_2$ measured as a function of $\mu$ .	[67-0065].
1.26	sulfur hexafluoride (1) $e_s^- + \text{SF}_6 \rightarrow \text{SF}_5 + \text{F}^-$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	3.2	$2.8 \times 10^{10c}$	$\gamma$ -r.; c.k.	Measured $G(^{14}\text{CH}_4)$ from $^{14}\text{CH}_3\text{Br}$ ; two solute system ( $^{14}\text{CH}_3\text{Br} + \text{SF}_6$ ) used to determine $\alpha_{\text{SF}_6}$ ; $k_1/k_2$ from ratio of $\alpha_{\text{SF}_6}$ to $\alpha_{\text{N}_2\text{O}}$ . <sup>g</sup>	[70-0064].
1.27a	toluene (1) $e_s^- + \text{C}_6\text{H}_5\text{CH}_3 \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	$7.2 \times 10^{-4}$	$6.3 \times 10^{6c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[66-0045].
1.27b	same	$5.9 \times 10^{-4}$	$5.1 \times 10^{6c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ ; $k_1/k_2$ from single conc. exp.	[67-0313].
1.28	ubiquinone (Q) <sup>f</sup> $e_s^- + \text{Q} \rightarrow \text{Q}^-$	.....	$1.7 \times 10^{10}$ ( $\pm 20\%$ )	p.r.; d.k.	Corr. for natural d. of $e_s^-$ ; $k$ dependent on conc. of Q; absorption spectrum of radical anion observed.	[70-0198].

<sup>a</sup>  $k(e_s^- + \text{S}) = 9 \times 10^3 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ ; cf. 1.01c.

<sup>b</sup>  $k(e_s^- + \text{H}_3^+) = 4 \times 10^{10} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ ; cf. 1.16a, 1.16b.

<sup>c</sup>  $k(e_s^- + \text{N}_2\text{O}) \sim k(e_{\text{aq}}^- + \text{N}_2\text{O}) = 8.7 \times 10^9 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$  (see Introduction).

<sup>d</sup>  $k(e_s^- + \text{H}_3^+) = 1.54 \times 10^{10} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$  ( $T = 0$ ) obtained by correcting (b) assuming  $E_a = 11 \text{ kJ mol}^{-1}$ .

<sup>e</sup>  $k(e_s^- + \text{N}_2\text{O}) = 1.95 \times 10^9 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$  ( $T = 0$ ); cf. 1.23c.

<sup>f</sup> Ubiquinone is a coenzyme quinone with 6 isoprenoid units in side chain.

<sup>g</sup>  $G$  (product) resulting from the scavenging of  $e_s^-$  by a solute A can be fitted to an empirical equation containing  $\alpha_A$  (or  $\alpha_A, \alpha_B, \dots$  for two or more solutes) as an adjustable parameter. The  $\alpha$ 's are characteristic of the solute and are shown [cf. 70-0064] to be related to the rate constant for scavenging by:

$$\alpha_A = k(e_s^- + A)/\lambda,$$

where  $\lambda$  is a constant for a given medium. Hence, two  $\alpha$ 's measured in the same alcohol have the following relationship:

$$\alpha_A/\alpha_B = k(e_s^- + A)/k(e_s^- + B).$$

TABLE 2. Rate constants of reactions of the solvated electron in ethanol

No.	Solute and reaction	$k_1/k_2$	$k(\text{dm}^3\text{mol}^{-1}\text{s}^{-1})$	Method	Comments	Ref.
2.01a	No solute ( $e_s^- + \text{S}$ ) $e_s^- + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{H}$ $+ \text{C}_2\text{H}_5\text{O}^-$	.....	$6.8 \times 10^3$	p.r.; d.k.	$t_{1/2}$ dose dependent; zero dose $t_{1/2}$ (6 $\mu\text{s}$ ) from computer anal.	[70-0172].
2.01b	same	.....	$(0.8 - 1.0) \times 10^4$	p.r.; d.k.	Sodium ethoxide addition increases $t_{1/2}$ from neutral value, 4 $\mu\text{s}$ , to 5.3 $\mu\text{s}$ .	[70-0172].

TABLE 2. Rate constants of reactions of the solvated electron in ethanol—Continued

No.	Solute and reaction	$k_1/k_2$	$k(\text{dm}^3\text{mol}^{-1}\text{s}^{-1})$	Method	Comments	Ref.
2.01c	same	.....	$1.9 \times 10^3$	f. phot.; d.k.	$e_s^-$ generated from $\text{I}^-$ ; abs. corrected for $\text{I}_2^-$ .	[64-7006].
2.01d	same	.....	$1.35 \times 10^4$	p.r.; d.k.	d. curves not of simple order and probably include reaction with counter ion; $t_{1/2} = 3 \mu\text{s}$ ; $t_{1/2}$ longer in basic soln.	[64-0113]. [63-0059].
2.01e	same	.....	$2.3 \times 10^4$ (LiCl) $2.0 \times 10^4$ (LiBr) $(9 \rightarrow 6) \times 10^3$ (KOH or NaOC <sub>2</sub> H <sub>5</sub> )	p.r.; d.k.	$t_{1/2} = 1.7 \mu\text{s}$ with added LiCl (conc. independent); $t_{1/2} = 2.0 \mu\text{s}$ with added LiBr (> 0.1 mol dm <sup>-3</sup> ); conc. of KOH and NaOC <sub>2</sub> H <sub>5</sub> $(1-6) \times 10^{-1}$ mol dm <sup>-3</sup> .	[70-0246].
2.01f	same	.....	$2.0 \times 10^3$ ( $T = -78 \pm 2$ )	p.r.; d.k.	$t_{1/2} = 20 \mu\text{s}$ ; d. nearly f.o. but shows deviation at early times.	[66-0082].
2.01g	same (1) $e_s^- + \text{S} \rightarrow$ (2) $e_s^- + \text{A} \rightarrow$	.....	$\sim 1.8 \times 10^4$	calc.	G(H <sub>2</sub> ) used c.k. eq.; data from [64-0279] and [65-0501]; A is acetone, acetaldehyde, and Ni <sup>2+</sup> ; $k_1$ estimated using $k(e_s^- + \text{A})$ and is an av. value for three solutes.	[67-0030].
2.01h	No solute $e_s^- + e_s^- \rightarrow \text{D}_2 + \text{C}_2\text{H}_5\text{O}^-$ (S is C <sub>2</sub> H <sub>5</sub> OD)	.....	$(5 \pm 4) \times 10^{9f}$ $(7 \pm 3) \times 10^{9f}$ $(5.3 \pm 2) \times 10^6$ ( $T = -78$ )	c.k.	Reacted Na with C <sub>2</sub> H <sub>5</sub> OD and measured D <sub>2</sub> , HD, and dissolution rate of Na; $k$ calc. based on diffusion and homogeneous reaction kinetics.	[71-9165].
2.02	glycerol (31 & 12 mol %) $e_s^- + \text{S}_m \rightarrow$	.....	$8.2 \times 10^4$ (31 mol %) $5.4 \times 10^4$ (12 mol %)	p.r.; d.k.	$t_{1/2} = 0.50$ and $0.75 \mu\text{s}$ for 31 and 12%, respectively; d. nearly f.o. but shows deviation at early times.	[66-0082].
2.03	H <sub>2</sub> O (10, 20, and 36 mol %) $e_s^- + \text{S}_m \rightarrow$	.....	$1.0 \times 10^5$ (10 mol %) $1.6 \times 10^4$ (20 mol %) $1.8 \times 10^4$ (36 mol %)	p.r.; d.k.	$t_{1/2} = 0.4, 2.5, 2.2 \mu\text{s}$ for 10, 20, and 36 mol %, respectively; see 2.02.	[66-0082].
2.04	NaOH	.....	.....	p.r.; d.k.	Rapid d. on ns time scale; with added NaOH rapid decaying transient reduced; postulated as reaction within spur; $\tau \sim 80$ ns but d. may not be of simple order.	[67-0126].
2.05a	acetaldehyde $e_s^- + \text{CH}_3\text{CHO} \rightarrow$	.....	$(4 \pm 0.5) \times 10^9$	p.r.; d.k.	.....	[70-0172].
2.05b	acetaldehyde (1) $e_s^- + \text{CH}_3\text{CHO} \rightarrow$ (2) $e_s^- + \text{S} \rightarrow$	$1.6 \times 10^5$	$1.1 \times 10^{9a}$	$\gamma$ -r.; c.k.	Measured G(H <sub>2</sub> ).	[64-0279].
2.06a	acetone (1) $e_s^- + (\text{CH}_3)_2\text{CO} \rightarrow$ (2) $e_s^- + \text{S} \rightarrow$	$7.1 \times 10^5$	$4.8 \times 10^{9a}$	$\gamma$ -r.; c.k.	Measured G(H <sub>2</sub> ).	[64-0279].
2.06b	same	$4 \times 10^5$	$2.7 \times 10^{9a}$	$\gamma$ -r.; c.k.	Measured G(H <sub>2</sub> ).	[67-0004].
2.06c	acetone (1) $e_s^- + (\text{CH}_3)_2\text{CO} \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	0.52	$3.1 \times 10^{9c}$	$\gamma$ -r.; c.k.	Measured G( <sup>14</sup> CH <sub>3</sub> ) from two solute system ( <sup>14</sup> CH <sub>3</sub> Br + (CH <sub>3</sub> ) <sub>2</sub> CO) to determine $\alpha_{\text{acet}}$ ; $k_1/k_2$ obtained from the ratio of empirical $\alpha$ values for acetone and N <sub>2</sub> O <sup>d</sup> .	[70-0064].

TABLE 2. Rate constants of reactions of the solvated electron in ethanol—Continued

No.	Solute and reaction	$k_1/k_2$	$k(\text{dm}^3\text{mol}^{-1}\text{s}^{-1})$	Method	Comments	Ref.
2.07	anthracene (1) $e_s^- + \text{C}_{14}\text{H}_{10} \rightarrow$ (2) $e_s^- + \text{S} \rightarrow$	$2.4 \times 10^6$	$1.6 \times 10^{10a}$	$\gamma$ -r.; c.k.	Measured $G(\text{H}_2)$ .	[64-0279].
2.08	benzene (1) $e_s^- + \text{C}_6\text{H}_6 \rightarrow$ (2) $e_s^- + \text{S} \rightarrow$	$8.5 \times 10^2$	$5.8 \times 10^{6a}$	$\gamma$ -r.; c.k.	Measured $G(\text{H}_2)$ : corr. for reaction of $e_s^-$ with impurities.	[69-0651].
2.09a	benzyl chloride $e_s^- + \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \rightarrow$	.....	$5.1 \times 10^9$	p.r.; d.k.	Corr. for $e_s^- d$ in pure S.	[64-0138].
2.09b	same $\text{C}_6\text{H}_5\text{CH}_2 + \text{Cl}^-$	.....	$(5.1 \pm 1.2) \times 10^9$	p.r.; d.k.	Corr. for $e_s^- d$ in pure S; benzyl radical identified spec. from 317.1 and 305.5 nm bands.	[64-0113].
2.09c	same	.....	$(5.3 \pm 1.3) \times 10^9$	p.r.; d.k.	Benzyl radical absorption observed.	[63-0059].
2.10a	biphenyl $e_s^- + \text{C}_{12}\text{H}_{10} \rightarrow \text{C}_{12}\text{H}_{10}^-$	.....	$> 2 \times 10^9$	p.r.; d.k.	Biphenylide ion identified spec. from 405, 610, and 635 nm bands.	[64-0113].
2.10b	biphenyl (1) $e_s^- + \text{C}_{12}\text{H}_{10} \rightarrow \text{C}_{12}\text{H}_{10}^-$ (2) $e_s^- + \text{naphthalene} \rightarrow$	.....	$(4.3 \pm 0.7) \times 10^9$	p.r.; c.k.	O.D. of biphenylide ion measured at midpoint of 0.4 $\mu\text{s}$ pulse in presence of various amounts of $\text{C}_{10}\text{H}_8$ ; see 2.19 for $k(e_s^- + \text{C}_{10}\text{H}_8)$ .	[64-0084].
2.11a	carbon tetrachloride (1) $e_s^- + \text{CCl}_4 \rightarrow$ (2) $e_s^- + \text{S} \rightarrow$	$1.0 \times 10^4$	$6.8 \times 10^{7a}$	$\gamma$ -r.; c.k.	Measured $G(\text{H}_2)$ .	[64-0279].
2.11b	carbon tetrachloride (1) $e_s^- + \text{CCl}_4 \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow$	$< 1.3$	$< 1.1 \times 10^{10c}$	$\gamma$ -r.; c.k.	Dose and base affect $k$ ; upper limit because no corr. for acid formed.	[71-0009].
2.11c	carbon tetrachloride $e_s^- + \text{CCl}_4 \rightarrow$	.....	$1.1 \times 10^{10}$	p.r.; d.k.	Neutral and basic soln.	[71-0009].
2.12a	chloroacetic acid (1) $e_s^- + \text{ClCH}_2\text{COOH} \rightarrow$ (2) $e_s^- + \text{S} \rightarrow$	$1.1 \times 10^3$	$7.5 \times 10^{8a}$	$\gamma$ -r.; c.k.	Measured $G(\text{H}_2)$ .	[64-0279].
2.12b	same	$1.3 \times 10^3$	$8.9 \times 10^{8a}$	$\gamma$ -r.; c.k.	Measured dose effect on $G(\text{H}_2)$ and $G(\text{CH}_3\text{CHO})$ .	[65-0045].
2.12c	same	$1.0 \times 10^3$ $5.0 \times 10^4$ ( $T=0$ ) $7.3 \times 10^3$ ( $T=-20$ ) $4.1 \times 10^3$ ( $T=-72$ )	$6.8 \times 10^{8a}$	$\gamma$ -r.; c.k.	Measured $G(\text{H}_2)$ .	[67-0173].
2.12d	chloroacetic acid (1) $e_s^- + \text{ClCH}_2\text{COOH} \rightarrow$ $\text{Cl}^- + \text{CH}_2\text{COOH}$ (2) $e_s^- + \text{H}_3^+ \rightarrow \text{H}$	$1.0 \pm 0.3_5$	$2 \times 10^{10b}$	$\gamma$ -r.; c.k.	Measured $G(\text{H}_2)$ ; utilized $G(\text{H}_2)$ given in [64-0279] to obtain $k_1/k_2$ .	[65-0501].
2.13a	cyclopentyl bromide (1) $e_s^- + \text{C}_5\text{H}_9\text{Br} \rightarrow \text{Br}^-$ $+ \text{C}_5\text{H}_9$ (2) $e_s^- + \text{H}_3^+ \rightarrow \text{H}$	0.48	$9.6 \times 10^{9b}$	$\gamma$ -r.; c.k.	Conc. of $\text{Cl}^-$ and $\text{C}_5\text{H}_9\text{Br}$ was 0.1 mol $\text{dm}^{-3}$ ; conc. of $\text{H}_3^+$ 0.2 $\rightarrow$ 1 mol $\text{dm}^{-3}$ ; 95% ethanol.	[70-0248].
2.13b	cyclopentyl bromide $e_s^- + \text{C}_5\text{H}_9\text{Br} \rightarrow$	.....	$2.3 \times 10^9$	p.r.; d.k.	.....	[71-0475].
2.14	ethyl acetate (1) $e_s^- + \text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow$ (2) $e_s^- + \text{S} \rightarrow$	$1.1 \times 10^4$	$7.5 \times 10^{7a}$	$\gamma$ -r.; c.k.	Measured $G(\text{H}_2)$ .	[64-0279].
2.15a	$\text{H}_3^+$ $e_s^- + \text{H}_3^+ \rightarrow \text{H}$	.....	$(2.1 \pm 0.4) \times 10^{10}$ (HCl) $(2.2 \pm 0.3) \times 10^{10}$ ( $\text{H}_2\text{SO}_4$ )	p.r.; d.k.	Conc. $\text{H}_3^+$ calc. assuming complete dissoen. of HCl and first dissoen. of $\text{H}_2\text{SO}_4$ .	[63-0059].

TABLE 2. Rate constants of reactions of the solvated electron in ethanol—Continued

No.	Solute and reaction	$k_1/k_2$	$k(\text{dm}^3\text{mol}^{-1}\text{s}^{-1})$	Method	Comments	Ref.
2.15b	same	.....	$(2.0 \pm 0.4) \times 10^{10}$ (HCl and $\text{H}_2\text{SO}_4$ )	p.r.; d.k.	Corr. applied for $e_s^-$ d. in pure solvent; see [63-0059] for $\text{H}^+$ conc.	[64-0113].
2.15c	same	.....	$(4.49 \pm 0.17) \times 10^{10}$	p.r.; d.k.	Measured elec. condy.d.; effect of pH(4-10), $\text{N}_2\text{O}$ , and $\text{H}_2\text{O}$ observed; see table 4 for Arrhenius parameters.	[71-0064].
2.15d	same	.....	$1.1 \times 10^{10}$ (HCl) $1.4 \times 10^{10}$ ( $\text{H}_2\text{SO}_4$ )	p.r.; d.k.	Assumed only single ionization of $\text{H}_2\text{SO}_4$ .	[71-0475].
2.15e	$\text{H}_2^+$ (1) $e_s^- + \text{H}_2^+ \rightarrow \text{H}$ (2) $e_s^- + \text{S} \rightarrow$	$2.0 \times 10^6$	$1.4 \times 10^{10a}$	$\gamma$ -r.; c.k.	Measured $G(\text{H}_2)$ .	[64-0279].
2.15f	$\text{H}_2^+$ (1) $e_s^- + \text{H}_2^+ \rightarrow \text{H}$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	4.1 > 2.9	$3.6 \times 10^{10c}$ > $2.5 \times 10^{10c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ ; $k = 3.6 \times 10^{10}$ based on $k_{\text{diss}}(\text{H}_2\text{SO}_4) = 1.7 \times 10^{-3}$ and $k > 2.5 \times 10^{10}$ is for complete dissocn. of $\text{H}_2\text{SO}_4$ .	[71-0009].
2.16a	methyl bromide (1) $e_s^- + \text{CH}_3\text{Br} \rightarrow \text{CH}_3 + \text{Br}^-$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	1.52	$9.1 \times 10^{9c}$	$\gamma$ -r.; c.k.	Measured $G(^{14}\text{CH}_4)$ from $^{14}\text{CH}_3\text{Br}$ ; $k_1/k_2$ obtained from ratio of empirical $\alpha$ values. <sup>d</sup>	[70-0064].
2.16b	methyl bromide (1) $e_s^- + \text{CH}_3\text{Br} \rightarrow \text{CH}_3 + \text{Br}^-$ (2) $e_s^- + \text{S} \rightarrow$	$1.0 \times 10^6$	$6.8 \times 10^{9a}$	$\gamma$ -r.; c.k.	See 2.16a.	[70-0064].
2.17	methyl chloride (1) $e_s^- + \text{CH}_3\text{Cl} \rightarrow \text{CH}_3 + \text{Cl}^-$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	0.38	$2.3 \times 10^{9c}$	$\gamma$ -r.; c.k.	See 2.06c: two solute system $\text{CH}_3\text{Cl}$ and $^{14}\text{CH}_3\text{Br}$ .	[70-0064].
2.18	naphthacene $e_s^- + \text{C}_{18}\text{H}_{12} \rightarrow$	.....	$(1.02 \pm 0.08) \times 10^{10}$	p.r.; d.k.	.....	[64-0084].
2.19	naphthalene $e_s^- + \text{C}_{10}\text{H}_8 \rightarrow$	.....	$(5.4 \pm 0.5) \times 10^9$	p.r.; d.k.	.....	[64-0084].
2.20	nitrate ion (1) $e_s^- + \text{NO}_3^- \rightarrow \text{NO}_2 + \text{OH}^- + \text{C}_6\text{H}_5\text{O}^-$ (2) $e_s^- + \text{H}_2^+ \rightarrow \text{H}$	$(1.45 \pm 0.45) \times 10^{-1}$	$3 \times 10^{9b}$	$\gamma$ -r.; c.k.	See 2.12d.	[65-0501].
2.21a	nitrous oxide (1) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$ (2) $e_s^- + \text{S} \rightarrow$	$7.1 \times 10^5$ $6.8 \times 10^5$ $5.8 \times 10^5$ ( $T=90$ ) $1.1 \times 10^6$ ( $T=145$ ) $1.0 \times 10^6$ ( $T=145$ ) $5.0 \times 10^5$ ( $T=90$ ) $5.4 \times 10^5$ ( $T=145$ ) $5.4 \times 10^5$ ( $T=-112$ )	$4.8 \times 10^{9a}$	$\gamma$ -r.; c.k.	Data from [68-0047]: at $T=90$ , $P_r = 1.62 \times 10^5 \text{ Nm}^{-2}$ ; at $T=145$ , $P_r = 8.5 \times 10^5 \text{ Nm}^{-2}$ ; see table 4 for Arrhenius parameters.	[69-8025].
2.21b	same	.....	$6.8 \times 10^{9a}$	$\gamma$ -r.; c.k.	Measured $G(\text{H}_2)$ .	[67-0012]. [68-0047].
2.21c	nitrous oxide (1) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$ (2) $e_s^- + \text{CH}_3\text{CHO} \rightarrow$	1.75	$7 \times 10^{9c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[71-0009].
2.22a	oxygen $e_s^- + \text{O}_2 \rightarrow \text{O}_2^-$	.....	$(1.9 \pm 0.3) \times 10^{10}$	p.r.; d.k.	Corr. applied for $e_s^-$ d. in pure S.	[64-0113].
2.22b	same	.....	$(2.0 \pm 0.3) \times 10^{10}$	p.r.; d.k.	.....	[63-0059].
2.23	perfluorocyclohexane $e_s^- + \text{C}_6\text{F}_{12} \rightarrow$	.....	$(2.5 \pm 0.5) \times 10^9$	p.r.; d.k.	.....	[70-0172].
2.24	phenol $e_s^- + \text{C}_6\text{H}_5\text{OH} \rightarrow$	.....	$4.5 \times 10^7$	p.r.; d.k.	.....	[71-0475].

TABLE 2. Rate constants of reactions of the solvated electron in ethanol—Continued

No.	Solute and reaction	$k_1/k_2$	$k(\text{dm}^3\text{mol}^{-1}\text{s}^{-1})$	Method	Comments	Ref.
2.25a	propyl bromide $e_s^- + \text{C}_3\text{H}_7\text{Br} \rightarrow \text{C}_3\text{H}_7 + \text{Br}^-$	.....	$3.0 \times 10^9$	p.r.; d.k.	Neutral and basic soln.	[71-0009].
2.25b	propyl bromide (1) $e_s^- + \text{C}_3\text{H}_7\text{Br} \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	$\leq 0.19$	$\leq 1.7 \times 10^{10c}$	$\gamma$ -r.; c.k.	Dose effect on $k$ ; upper limit for $k$ because no corr. for acid formed.	[71-0009].
2.26	propyl chloride (1) $e_s^- + \text{C}_3\text{H}_7\text{Cl} \rightarrow \text{C}_3\text{H}_7 + \text{Cl}^-$ (2) $e_s^- + \text{H}^+ \rightarrow \text{H}$	$2.4 \times 10^{-2}$	$4.8 \times 10^{10b}$	$\gamma$ -r.; c.k.	Conc. of $\text{Cl}^-$ and $\text{C}_3\text{H}_7\text{Cl}$ was 1 and 0.1 mol $\text{dm}^{-3}$ ; conc. of $\text{H}^+$ 0.05 $\rightarrow$ 1.0 mol $\text{dm}^{-3}$ ; 95% ethanol.	[70-0248].
2.27	sulfur hexafluoride (1) $e_s^- + \text{SF}_6 \rightarrow \text{SF}_5 + \text{F}^-$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	1.5	$1.3 \times 10^{10c}$	$\gamma$ -r.; c.k.	Measured $G(^{14}\text{CH}_4)$ from ( $^{14}\text{CH}_3\text{Br} + \text{SF}_6$ ) soln. to obtain $\alpha_{\text{SF}_6}$ ; see 2.06c.	[70-0064].
2.28	<i>p</i> -terphenyl $e_s^- + \text{C}_{18}\text{H}_{14} \rightarrow \text{C}_{18}\text{H}_{14}^-$	.....	$(7.2 \pm 0.6) \times 10^9$	p.r.; d.k.	$\text{C}_{18}\text{H}_{14}^-$ identified spec. from 435.8 nm band.	[64-0084].
2.29a	tetranitromethane $e_s^- + \text{C}(\text{NO}_2)_4 \rightarrow$	.....	$3.5 \times 10^{10}$	p.r.; d.k.	.....	[71-0009].
2.29b	tetranitromethane (1) $e_s^- + \text{C}(\text{NO}_2)_4 \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	2.7	$2.4 \times 10^{10c}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[71-0009].
2.30	triphenylmethanol $e_s^- + (\text{C}_6\text{H}_5)_3\text{COH} \rightarrow$ $(\text{C}_6\text{H}_5)_3\text{C} + \text{OH}^-$	.....	$(2.0 \pm 0.4) \times 10^8$	p.r.; d.k.	Corr. applied for $e_s^-$ d. in S; triphenylmethyl radical identified spec.	[64-0113].

<sup>a</sup>  $k(e_s^- + \text{S}) = 6.8 \times 10^8 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ ; cf. 2.01a.

<sup>b</sup>  $k(e_s^- + \text{H}^+) = 2 \times 10^{10} \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ ; cf. 2.15.

<sup>c</sup>  $k(e_s^- + \text{N}_2\text{O}) \sim k(e_{\text{aq}}^- + \text{N}_2\text{O}) = 8.7 \times 10^9 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ .

<sup>d</sup> See footnote (g), table 1.

<sup>e</sup>  $k(e_s^- + \text{CH}_3\text{CHO}) = 4 \times 10^9 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ ; cf. 2.05a.

<sup>f</sup>  $k(e_s^- + e_s^-) = (5 \pm 4) \times 10^8 \text{ calc. based on } k(e_s^- + \text{S}) = 5.4 \times 10^8 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ , and  $k(e_s^- + e_s^-) = (7 \pm 3) \times 10^9$  based on  $k(e_s^- + \text{S}) = 6.8 \times 10^8 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ .

TABLE 3. Rate constants of reactions of the solvated electron in 1-propanol (1-PrOH), 2-propanol (2-PrOH), and 1-butanol (1-BuOH)

No.	Solute and reaction	$k_1/k_2$	$k(\text{dm}^3\text{mol}^{-1}\text{s}^{-1})$	Method	Comments	Ref.
3.01a	No solute; S=1-PrOH $e_s^- + \text{C}_3\text{H}_7\text{OH} \rightarrow \text{H} + \text{C}_3\text{H}_7\text{O}^-$	.....	$\sim 2.6 \times 10^4$	p.r.; d.k.	d. not of simple order; probably includes reaction with counter ion; $t_{1/2} \sim 2\mu\text{s}$ .	[64-0113].
3.01b	No solute; S=2-PrOH $e_s^- + \text{CH}_3\text{CHOHCH}_3 \rightarrow \text{H} + (\text{CH}_3)_2\text{CHO}^-$	.....	$\sim 1.1 \times 10^4$	p.r.; d.k.	$t_{1/2} \sim 5\mu\text{s}$ ; see 3.01a.	[64-0113].
3.02a	acetone; S=2-PrOH (1) $e_s^- + (\text{CH}_3)_2\text{CO} \rightarrow$ (2) $e_s^- + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \rightarrow$	$7.7 \times 10^4$	.....	$\gamma$ -r.; c.k.	Measured $G(\text{H}_2)$ .	[67-0004]. [67-0174]. [66-0221].
3.02b	acetone; S=2-PrOH (1) $e_s^- + (\text{CH}_3)_2\text{CO} \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	0.59	$5.1 \times 10^{10a}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ ; single conc. determination.	[66-0027].
3.02c	acetone; S=1-BuOH (1) $e_s^- + (\text{CH}_3)_2\text{CO} \rightarrow$ (2) $e_s^- + \text{CH}_3(\text{CH}_2)_3\text{OH} \rightarrow$	$1.4 \times 10^2$	.....	$\gamma$ -r.; c.k.	Measured $G(\text{H}_2)$ .	[67-0004].
3.03	acetophenone; S=2-PrOH (1) $e_s^- + \text{C}_6\text{H}_5\text{COCH}_3 \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	1.7	$1.5 \times 10^{10a}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[67-0045].
3.04a	benzene; S=2-PrOH (1) $e_s^- + \text{C}_6\text{H}_6 \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	$2.1 \times 10^{-2}$	$1.8 \times 10^{10a}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[66-0045].
3.04b	same	$2.0 \times 10^{-2}$	$1.7 \times 10^{10a}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[66-0027].
3.05	benzotrinitrile; S=2-PrOH (1) $e_s^- + \text{C}_6\text{H}_5\text{CN} \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	1.9	$1.7 \times 10^{10a}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ .	[66-0045].
3.06	benzophenone; S=2-PrOH (1) $e_s^- + (\text{C}_6\text{H}_5)_2\text{CO} \rightarrow$ (2) $e_s^- + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	1.30	$1.1 \times 10^{10a}$	$\gamma$ -r.; c.k.	Measured $G(\text{N}_2)$ ; single conc. determination.	[66-0027].

TABLE 3. Rate constants of reactions of the solvated electron in 1-propanol (1-PrOH), 2-propanol (2-PrOH), and 1-butanol (1-BuOH) - Con.

No.	Solute and reaction	$k_1/k_2$	$k$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	Method	Comments	Ref.
3.07	carbon tetrachloride; S=2-PrOH (1) $e_s^- + CCl_4 \rightarrow$ (2) $e_s^- + N_2O \rightarrow N_2 + O^-$	2.26	$2.0 \times 10^{10a}$	$\gamma$ -r.; c.k.	Measured $G(N_2)$ ; single conc. determination.	[66-0027].
3.08	chlorobenzene; S=2-PrOH (1) $e_s^- + C_6H_5Cl \rightarrow$ (2) $e_s^- + N_2O \rightarrow N_2 + O^-$	0.54	$4.7 \times 10^{10a}$	$\gamma$ -r.; c.k.	Measured $G(N_2)$ .	[66-0045].
3.09	ferric ion; S=1-PrOH (1) $e_s^- + Fe^{+3} \rightarrow Fe^{+2}$ (2) $e_s^- + CH_3CH_2CH_2OH \rightarrow$	$5.6 \times 10^4$	.....	$\gamma$ -r.; c.k.	Measured $G(H_2)$ .	[67-0174].
3.10	fluorobenzene; S=2-PrOH (1) $e_s^- + C_6H_5F \rightarrow$ (2) $e_s^- + N_2O \rightarrow N_2 + O^-$	$5.0 \times 10^{-2}$	$4.4 \times 10^{10a}$	$\gamma$ -r.; c.k.	Measured $G(N_2)$ .	[66-0045].
3.11a	$H_2^+$ ; S=1-PrOH (1) $e_s^- + H_2^+ \rightarrow H(H_2SO_4)$ (2) $e_s^- + N_2O \rightarrow N_2 + O^-$	$5.0$ (pH=2.4) $5.6$ (pH=2.7)	$4.4 \times 10^{10a}$ $4.9 \times 10^{10a}$	$\gamma$ -r.; c.k.	Measured $G(N_2)$ ; $k_1/k_2$ used in calc. of $G(N_2)$ to good fit with exp.; taken from CH <sub>3</sub> OH data [67-0065] and adjusted for $\mu$ .	[69-0387].
3.11b	$H_2^+$ ; S=1-PrOH $e_s^- + H_2^+ \rightarrow H$	.....	$(2.55 \pm 0.19) \times 10^{10}$	p.r.; d.k.	Measured elec. condy. d.; effect of pH(4-10), N <sub>2</sub> O, and H <sub>2</sub> O observed; see table 4 for Arrhenius parameters.	[71-0064].
3.11c	$H_2^+$ ; S=2-PrOH (1) $e_s^- + H_2^+ \rightarrow H(HCl)$ (2) $e_s^- + N_2O \rightarrow N_2 + O^-$	0.5	$4.4 \times 10^{10a}$	$\gamma$ -r.; c.k.	Measured $G(N_2)$ ; $k_1/k_2$ is av. for pH=1.3 → 2.3.	[66-0027].
3.11d	$H_2^+$ ; S=2-PrOH $e_s^- + H_2^+ \rightarrow H$	.....	$(1.67 \pm 0.14) \times 10^{10}$	p.r.; d.k.	Measured elec. condy. d.; effect of pH (4-10), N <sub>2</sub> O, and H <sub>2</sub> O observed. see table 4 for Arrhenius parameters.	[71-0064].
3.12a	nitrobenzene; S=2-PrOH (1) $e_s^- + C_6H_5NO_2 \rightarrow$ (2) $e_s^- + N_2O \rightarrow N_2 + O^-$	2.3	$2.0 \times 10^{10a}$	$\gamma$ -r.; c.k.	Measured $G(N_2)$ .	[66-0045].
3.12b	same	2.3	$2.0 \times 10^{10a}$	$\gamma$ -r.; c.k.	Measured $G(N_2)$ .	[66-0027].
3.13a	nitrous oxide; S=1-PrOH (1) $e_s^- + N_2O \rightarrow N_2 + O^-$ (2) $e_s^- + CH_3CH_2CH_2OH \rightarrow$	$1.5 \times 10^3$ $6.4 \times 10^4$ ( $T=-120$ ) $1.2 \times 10^3$ ( $T=140$ )	.....	$\gamma$ -r.; c.k.	Measured $G(N_2)$ ; at $T=140$ , $P_r=3.3 \times 10^3$ Nm <sup>-2</sup> ; see table 4 for Arrhenius parameters.	[69-0387].
3.13b	nitrous oxide; S=2-PrOH (1) $e_s^- + N_2O \rightarrow N_2 + O^-$ (2) $e_s^- + CH_3CHOHCH_3 \rightarrow$	$5.9 \times 10^3$	.....	$\gamma$ -r.; c.k.	Measured $G(H_2)$ .	[66-0027].
3.13c	same	$\geq 2.2 \times 10^3$ $8.4 \times 10^3$ ( $T=-85$ ) $2.1 \times 10^3$ ( $T=140$ )	.....	$\gamma$ -r.; c.k.	$G(N_2)$ from [68-0042]; at $T=140$ , $P_r=6.6 \times 10^3$ Nm <sup>-2</sup> ; see table 4 for Arrhenius parameters.	[69-8025].
3.14	propionaldehyde; S=1-PrOH (1) $e_s^- + CH_3CH_2CHO \rightarrow$ (2) $e_s^- + CH_3CH_2CH_2OH \rightarrow$	$1 \times 10^5$	.....	$\gamma$ -r.; c.k.	Measured $G(H_2)$ .	[67-0174].
3.15	toluene; S=2-PrOH (1) $e_s^- + C_6H_5CH_3 \rightarrow$ (2) $e_s^- + N_2O \rightarrow N_2 + O^-$	$1.4 \times 10^{-2}$	$1.2 \times 10^{10a}$	$\gamma$ -r.; c.k.	Measured $G(N_2)$ .	[66-0045].

<sup>a</sup>  $k(e_s^- + N_2O) \sim k(e_{aq}^- + N_2O) = 8.7 \times 10^9$  dm<sup>3</sup>mol<sup>-1</sup>s<sup>-1</sup> (see Introduction).

TABLE 4. Arrhenius parameters for reactions of the solvated electron in alcohol solutions

Reaction	Alcohol	log $A$ ( $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ )	$E_a$ ( $\text{kJ mol}^{-1}$ )	$\Delta S^\ddagger$ ( $\text{J mol}^{-1}\text{deg}^{-1}$ )	$T$ ( $^\circ\text{C}$ )	Ref.
$e_s^- + S \rightarrow$	methanol	6.47 <sup>a</sup>	15.5	-88	-97 to 150	[68-0610].
	ethanol	7.16 <sup>a</sup>	19.2	-88	-112 to 145	[69-8025]. [68-0047].
	1-propanol	.....	18.8	-80	-120 to 140	[69-0387].
	2-propanol	.....	26.4	-59	-85 to 140	[69-8025]. [68-0042].
$e_s^- + H_s^+ \rightarrow$	ethanol	11.00	(19.7 $\pm$ 1.3)	-33 <sup>b</sup>	26 to 50	[71-0064].
	1-propanol	10.80	(24.3 $\pm$ 2.1)	-21 <sup>b</sup>	24 to 50	[71-0064].
	2-propanol	10.79	(30.5 $\pm$ 2.1)	-21 <sup>b</sup>	25 to 46	[71-0064].
$e_s^- + e_s^-$	ethanol- $d_1$	.....	(32 $\pm$ 8)	.....	-78 to 25	[71-9165].

<sup>a</sup> Log  $A$  calculated using experimental  $E_a$  and rate constants given in 1.01c and 2.01a.<sup>b</sup>  $\Delta S^\ddagger$  calculated using experimental log  $A$  and the preexponential relationship of the transition-state theory.

TABLE 5. Index of entry numbers (tables 1, 2, and 3) for the reaction of solvated electrons in various alcohol solutions

Solute added	Methanol	Ethanol	1-Propanol	2-Propanol	1-Butanol
None ( $e_s^- + S$ ).....	1.01a, 1.01b, 1.01c, 1.01d, 1.01e, 1.01f, 1.17, 1.18b, 1.23a, 1.23b	2.01a, 2.01b, 2.01c, 2.01d, 2.01e, 2.01f, 2.01g, 2.05b, 2.06a, 2.06b, 2.07, 2.08, 2.11a, 2.12a, 2.12b, 2.12c, 2.14, 2.15e, 2.16b, 2.21a, 2.21b	3.01a, 3.02a, 3.09, 3.13a, 3.14	3.01b, 3.02a, 3.13b, 3.13c	3.02c.
None ( $e_s^- + e_s^-$ ).....	1.01g	2.01h			
acetaldehyde.....		2.05a, 2.05b			
acetone.....	1.04a, 1.04b	2.06a, 2.06b, 2.21b, 2.06c	3.02a	3.02b	3.02c.
acetophenone.....	1.05a, 1.05b			3.03	
anthracene.....		2.07			
benzene.....	1.06a, 1.06b	2.08a, 2.08b		3.04a, 3.04b	
benzotrile.....				3.05	
benzophenone.....				3.06	
benzoquinone.....	1.08				
benzyl chloride.....	1.09a, 1.09b, 1.09c, 1.09d	2.09a, 2.09b, 2.09c			
biphenyl.....		2.10a, 2.10b			
carbon tetrachloride.....	1.10	2.11a, 2.11b, 2.11c		3.07	
chloroacetic acid.....		2.12a, 2.12b, 2.12c, 2.12d			
chloroacetate ion.....	1.11				
chlorobenzene.....	1.12a, 1.12b			3.08	
cyanogen iodide.....	1.13				
cyclopentyl bromide.....		2.13a, 2.13b			
duroquinone.....	1.14				
ethyl acetate.....		2.14			
ferric ion.....			3.09		
$H_s$ .....	1.16a, 1.16b, 1.16c, 1.16d, 1.16e, 1.23c, 1.24c	2.12d, 2.13a, 2.15a, 2.15b, 2.15c, 2.15d, 2.15f, 2.20, 2.24	3.11a, 3.11b	3.11c, 3.11d	
iodine.....	1.17				
methyl bromide.....	1.18a, 1.18b	2.16a, 2.16b			
methyl chloride.....		2.17			
naphthacene.....		2.18		3.03	

TABLE 5. Index of entry numbers (tables 1, 2, and 3) for the reaction of solvated electrons in various alcohol solutions - Continued

Solute added	Methanol	Ethanol	1-Propanol	2-Propanol	1-Butanol
naphthalene.....	1.19	2.10b, 2.19			
nitrate ion.....	1.20	2.20			
nitrite ion.....	1.21				
nitrobenzene.....	1.22a, 1.22b			3.12a, 3.12b	
nitrous oxide.....	1.04a, 1.04b, 1.05a, 1.05b, 1.06a, 1.06b, 1.09c, 1.09d, 1.10, 1.11, 1.12a, 1.12b, 1.13, 1.15a, 1.16d, 1.16e, 1.18a, 1.20, 1.21, 1.22a, 1.22b, 1.23a, 1.23b, 1.23c, 1.25, 1.26, 1.27a, 1.27b	2.06c, 2.11b, 2.15f, 2.16a, 2.17, 2.21a, 2.21b, 2.21c, 2.25b 2.27, 2.29b	3.13a	3.04a, 3.04b, 3.05, 3.06, 3.07, 3.08, 3.10, 3.11a, 3.11c, 3.12a, 3.12b, 3.13b, 3.13c, 3.15	
oxygen.....	1.24a, 1.24b, 1.24c	2.22a, 2.22b			
perfluorocyclohexane.....		2.23			
propionaldehyde.....			3.14		
propyl bromide.....		2.25a, 2.25b			
propyl chloride.....		2.26			
silver ion.....	1.25				
sulfur hexafluoride.....	1.26	2.27			
<i>p</i> -terphenyl.....		2.28			
tetranitromethane.....		2.29a, 2.29b			
toluene.....	1.27a, 1.27b			3.15	
triphenyl methanol.....		2.30			
ubiquinone.....	1.28				

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