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Volume 13

Radical Reaction Rates in Liquids

Subvolume a

Carbon-Centered Radicals I

A.L.J. Beckwith · D. Griller · J. P. Lorand

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A. L. J. Beckwith · D. Griller · J. P. Lorand

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Vorwort

Die rasche Entwicklung physikalisch-chemischer Meßmethoden, insbesondere solcher auf spektroskopischer Grundlage, hat in den letzten Jahrzehnten das Studium kurzlebiger Zwischenstufen bei chemischen Reaktionen, ihrer Strukturen, sowie ihrer Reaktionen und deren Kinetik sehr begünstigt. Ein äußerst aktiver Zweig ist die Erforschung freier Radikale und ihrer Reaktionen in vielen thermischen, photo- und strahlenchemischen Prozessen von sowohl fundamentaler wie technologischer Bedeutung. Der gewaltige Umfang des heute vorliegenden Datenmaterials ruft nach umfassenden und kritischen Zusammenfassungen, einem Ziel des Landolt-Börnstein. Magnetische Eigenschaften freier Radikale sind in den Bänden II/1 und II/9a–d der neuen Serie bereits tabelliert. Der Band II/13 stellt nun Geschwindigkeitskonstanten und andere kinetische Parameter von Reaktionen freier Radikale in flüssigen Medien vor. Hauptinhalte sind polyatomare organische Radikale unter Einschluß von Biradikalen. Ausgelassen wurden einige freie Radikale in wäßrigen Medien, für die Zusammenstellungen von Geschwindigkeitskonstanten kürzlich in der National Standard Reference Data Reihe des National Bureau of Standards, Washington, D.C., erschienen sind.

Die unerwartet große Datenzahl, verstreut in Tausenden von Publikationen, legte die Verteilung der Aufgaben auf eine ganze Reihe von Autoren nahe, welche ihrem Tätigkeitsbereich entsprechende Kapitel übernahmen. Sie erzwang auch die Aufteilung des Bandes II/13 in fünf Teilbände, von denen Teil II/13c bereits erschienen ist. Der hier vorgelegte Teilband II/13a behandelt Reaktionen von kohlenstoffzentrierten Radikalen, im besonderen Radikal-Radikal-Reaktionen, Additionen an Moleküle, Fragmentierungen und Umlagerungen.

Der Umfang des Gesamtbandes spiegelt den raschen Fortschritt in der Untersuchung der Reaktionskinetik freier Radikale wider, welcher unzweifelhaft auf das Bedürfnis nach gesichertem Zahlenmaterial für die weitere Forschung und die Entwicklung der Technologie gegründet ist. Die noch anwachsende Publikationsrate zeigt, daß das Gebiet noch nicht als einigermaßen abgerundet angesehen werden kann. Dies wird auch dadurch belegt, daß für einige wichtige Reaktionen kinetische Daten bisher fehlen. Es ist dementsprechend geplant, Band II/13 später zu supplementieren, und wir hoffen, daß die hier vorgestellte Zusammenstellung auch die zukünftige Entwicklung des Gebiets befruchtet.

Wir danken allen Autoren des Werks für ihre kompetente, oft mühevolle und zeitraubende Arbeit und die erfreuliche Kooperation. Dank gebührt weiter der Landolt-Börnstein-Redaktion und hier vor allem Frau H. Weise, für die unermüdlich aufmerksame Bearbeitung der Manuskripte und Fahnen. Ferner danken wir dem Springer-Verlag für die sorgfältige Fertigstellung des Bandes, der, wie alle Landolt-Börnstein-Bände, ohne externe finanzielle Unterstützung publiziert wird.

Zürich, im Oktober 1983

Der Herausgeber

Preface

The recent enormous advances in physico-chemical technology, such as molecular spectroscopy, have promoted numerous studies of reactive chemical intermediates, the elucidations of their structures, their formation and decay mechanisms and their reaction rates. Free radicals, in particular, key intermediates in many thermal, photo and radiation chemical processes both of fundamental and technological importance have become the subject of active research. The amount of available quantitative data suggests comprehensive and authorative critical compilations as attempted by the Landolt-Börnstein series. Magnetic properties of about 8 500 free radical species were collected in volumes II/1 and II/9a–d of the New Series. This volume II/13 presents rate constants and other kinetic data of free radical reactions in liquids. Emphasis is on polyatomic organic free radicals, and biradicals are included. Deliberately omitted were selected species in aqueous solutions for which compilations of rate data have been published in the National Standard Reference Data Series of the National Bureau of Standards, Washington D.C., USA.

The huge amount of available data, widely scattered in several thousand individual publications, required the cooperation of experts who took the charge to prepare individual chapters. It also necessitated the subdivision of the volume into five parts to be published successively of which part II/13c has already appeared. The present subvolume II/13a covers data on reactions of carbon-centered radicals, especially radical-radical reactions, addition of radicals to molecules and radical fragmentations and rearrangements.

The unexpected size of the total volume reflects the rapid progress in free radical reaction kinetics which is undoubtedly stimulated by the requirement of accurate data for future research and technical development. The still continuously increasing number of publications shows that the field has not reached saturation and is corroborated by the lack of data for many important reactions as also evident from this volume. Consequently, we plan future supplementations, and do hope that the present critical evaluations will help to stimulate further work.

We thank all the authors for their enormous and time-consuming efforts and for the most enjoyable cooperation. Thanks are also due to the Landolt-Börnstein office, especially to Frau H. Weise for the untiring careful checking of the manuscripts and galleys, and Springer Verlag for their customary care in the preparation of the volumes, which, as all Landolt-Börnstein volumes, is published without exterior financial support.

Zürich, October 1983 **The Editor**

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D. Griller, Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada

2 Carbon-centered radicals: Radical-molecule addition reactions

J. P. Lorand, Central Michigan University, Department of Chemistry, Mount Pleasant, Michigan 48858, U.S.A.

3 Carbon-centered radicals: Fragmentation and rearrangement reactions

A. L. J. Beckwith, Research School of Chemistry, The Australian National University, Canberra, Australia

General introduction

A Definitions and coverage

In the following tables rate constants for reactions of free radicals in liquids are collected. The free radical species covered are paramagnetic molecules deriving their paramagnetism from a single unpaired valence electron. They are neutral molecular fragments or ions with positive or negative charges. Emphasis is on polyatomic organic free radicals. Excluded are some small species like the hydrated electron, the hydrogen and other atoms and a variety of polyatomic inorganic radicals. For reaction rates of these in aqueous solutions recent other compilations are available [73Anb, 75Anb, 75Ros, 77Ros, 79Ros, 83Ros]. A table on organic biradicals is included, however, since their reactions are similar to those of monoradicals.

The volume is divided grossly into sections dealing with individual types of free radicals such as carbon-centered radicals, nitrogen-centered radicals, nitroxyl radicals, oxygen-centered radicals and radicals centered on other heteroatoms. These sections deal mainly with irreversible reactions. In addition, there are sections on reversible electron and proton transfer processes and their equilibria and a chapter on biradicals. An index of radicals formulae will facilitate data retrieval.

The reactions covered involve bimolecular processes between like and unlike radicals and between radicals and molecules via atom, group or electron transfer, or addition and unimolecular processes like fragmentations or rearrangements. Within the chapters dealing with special radical types a subdivision according to the types of reaction is applied. In such subdivisions the entries are organized according to the molecular formula of the radical involved, and formulas are in the order of increasing number of C, H atoms and then all other elements (except D, listed with H) in alphabetical order.

The main subject of the volume is the compilation of absolute rate constants for established reactions. In part they were deduced from published relative rate data if the absolute rate constants of the reference reactions were known. Relative rate constants or qualitative data as reaction half-lifes are included occasionally, in particular for important classes of radicals or radical reactions for which absolute data are not yet available. Thus, the tables do not represent a comprehensive compilation of all reactions known to date, yet of all those with sufficiently characterized reaction kinetics.

For details on subdivision into subvolumes, chapters and ordering within chapters, see *Table of contents* and the introductory sections of individual chapters. The literature is generally covered up to 1981, in parts up to 1983.

B Arrangement and contents of tables

As indicated by the general table headings there is one separate entry for each specific reaction or each set of competing reactions. Besides specifying the reaction the entry contains information on the technique of radical generation, the method of rate determination, and experimental conditions such as solvent and temperature. It lists the rate constants, the equilibrium constants and other rate data, such as activation parameters of the reaction, and gives the pertinent reference plus additional references. Further relevant information is given in footnotes. The following explanations apply to the individual parts of the entries.

Reaction: The reaction or the competing reactions are written in stoichiometric form starting with the reacting radical. For reactions between different radicals the radical appearing first in the adopted ordering of substances (see above) is written first and specifies the location of that entry. A cross reference to this reaction is entered at that later position of the tables which corresponds to the order of the second radical. The same principle is obeyed in the ordering of the substrates in competing radical molecule reactions. Where deviations from this scheme occur the reader is referred to the introduction of the individual chapters. Where necessary structural formulae of radicals, reactants and products are written out in full detail. Repeatedly occuring structures are abbreviated by capital bold letters and an entry R = group may specify a substituent within the general structure. Self-evident structures of products are also abbreviated occasionally as OO- or NN-dimers or otherwise. Product structures are not given if they could not be identified from the original literature.

Radical generation: The technique of radical production is outlined in short using abbreviations given in the *List of symbols and abbreviations.*

Method: The methods in use for the determination of reaction rate data are manifold, and a variety of abbreviations had to be introduced (see also *List of symbols and abbreviations*). Whereas earlier literature mostly applied the rather indirect techniques of measurements of product ratios (PR), the consumption of inhibitors (inh. cons.), rates of oxygen absorption (ROA) or consumption of other reactants (RRC) the progress of time resolved spectroscopy is evident more recently, and the most accurate rate data for irreversible processes are now obtained from kinetic absorption spectroscopy (KAS), kinetic electron spin resonance spectroscopy (KESR) or conductometry (cond.) in conjugation with pulsed radical generation. For reversible processes steady-state techniques of absorption spectroscopy (SAS) or electron spin resonance (SESR) or line-shape analyses in magnetic resonance (ESRLA, NMRLA) are common. For details of the methods, the reader is referred to the original literature.

Solvent: Where possible the solvent is given by its molecular formula or name. Special conditions such as pH or solvent composition are indicated.

Temperature T [K]: The temperature of the sample during the rate measurement is given in K. RT stands for an unspecified room temperature. Where activation parameters of rate constants were measured the column temperature indicates the temperature range of measurement.

Rate data: Rate constants of uni- and bimolecular processes are given in their usual dimensions s^{-1} and $M^{-1}s^{-1}$, equilibrium costants in their corresponding appropriate dimensions. The same applies to ratios of rate constants. All rate constants k are defined for product appearance. Consequently, $2k$ governs the rate of radical disappearance in bimolecular self-reactions of radicals. Since the rate of radical disapperance is often measured in these cases, the value of $2k$ is displayed. If available the Arrhenius activation parameters, i.e. the parameters of the equation $k = A\cdot\exp(-E_a/RT)$ are also listed with A given in logarithmic form and E_a in kJ/mol. The column rate data may also give enthalpies (ΔH^{+}), entropies (ΔS^{+}), and volumes (ΔV^{+}) of activation in SI-units. For acid-base equilibrium pK-values are listed. Errors are given in parentheses in units of the last digit displayed for the data.

Reference/additional references: The first entry specifies the reference from which the data were extracted with the first two numbers for the year of appearance (72 = 1972), the following three letters for the family name of the first author and the last number ordering the publications in the year of publication. Additional references contain earlier less reliable work on the same subject, theoretical treatments of rate data or other relevant information.

The following list of symbols and abbreviations is common for all chapters. Additional symbols and abbreviations may appear as necessary in individual chapters. For these and additional information on contents and coverage, on arrangements and ordering and on special data display the reader is referred to the introductory sections of the individual chapters.

C Important monographs, series, compilations

61Jen Jennings, K.R., Cundall, R.B. (eds.): Progress in Reaction Kinetics. Oxford: Pergamon **1961ff.**
63Gol Gold, V., Bethell, D. (eds.): Advances in Physical Organic Chemistry. New York: Acad. Press **1963ff.**
63Taf Taft, R.W. (ed.): Progress in Physical Organic Chemistry. New York: Wiley **1963ff.**
65Kni Knipe, A.C., Watts, W.E. (eds.): Organic Reaction Mechanism. New York: Wiley **1965ff.**
66Pry Pryor, W.A.: Free Radicals. New York: McGraw-Hill **1966.**
68For Forester, A.R., Hay, J.M., Thomson, R.H.: Organic Chemistry of Free Radicals. New York: Acad. Press **1968.**
70Huy Huyser, E.S.: Free Radical Chain Reactions. New York: Interscience **1970.**
70Roz Rozantsev, E.G.: Free Nitroxyl Radicals. New York: Plenum **1970.**
73Anb Anbar, M., Bambenek, M., Ross, A.B.: Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution. 1. Hydrated Electron. Washington: NSRDS-NBS 43 **1973.**
73Buc Buchachenko, A.L., Wasserman, A.L.: Stable Radicals. Weinheim: Verlag Chemie **1973.**
73Koc Kochi, J.K. (ed.): Free Radicals, Vols. I, II. New York: Wiley **1973.**
73Nor Norman, R.O.C., Ayscough, P.B. (eds.): Electron Spin Resonance. Spec. Per. Rept. London, Chemical Society **1973ff.**
74Den Denisov, E.T.: Liquid-Phase Reaction Rate Constants. New York: Plenum **1974.**
74Non Nonhebel, D.C., Walton, J.C.: Free-Radical Chemistry. Cambridge: University Press **1974.**
74Swa Szwarc, M.: Ions and Ion Pairs in Organic Reactions. New York: Wiley **1974.**
75Anb Anbar, M., Ross, A.B., Ross, F.: Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution. II. Hydrogen Atom. Washington: NSRDS-NBS 51 **1975.**
75Ros Ross, A.B.: Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution. Hydrated Electron, Supplemental Data. Washington: NSRDS-NBS 43 – Supplement **1975.**

76Pry Pryor, W.A. (ed.): Free Radicals in Biology. New York: Acad. Press **1976**ff.

77Ros Ross, F., Ross, A.B.: Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution. III. Hydroxyl Radical and Perhydroxyl Radical and Their Radical Ions. Washington: NSRDS-NBS 59 **1977**.

78Jon Jones, M., Jr., Moss, R.A. (eds.): Reactive Intermediates. New York: Wiley **1978**ff.

79Non Nonhebel, D.C., Tedder, J.M., Walton, J.C.: Radicals, Cambridge: Univ. Press **1979**.

79Ros Ross, A.B., Neta, P.: Rate Constants for Reactions of Inorganic Radicals in Aqueous Solution. Washington: NSRDS-NBS 65 **1979**.

83Ros Ross, A.B., Neta, P.: Rate Constants of Aliphatic Carbon Centered Radicals in Aqueous Solution. Washington: NSRDS-NBS, submitted.

D List of symbols and abbreviations

Symbols

$D(R-X)$	bond dissociation energy
E^0, $E^{0\prime}$	standard reduction potentials
G	radiation chemical yield
H_0	Hammett acidity function
k [s^{-1}, $M^{-1}s^{-1}$]	rate constant
K	equilibrium constant
$2k_t$	rate constant of self-termination
ΔG^*	free enthalpy of activation
ΔH^*	enthalpy of activation
ΔS^*	entropy of activation
ΔV^*	volume of activation
$\Delta^0 H$ [$kJ\,mol^{-1}$]	enthalpy of dissociation
$\Delta^0 S$ [$J\,K^{-1}\,mol^{-1}$]	entropy of dissociation
η [cP]	viscosity
ε_λ	decadic extinction coefficient at wavelength λ
$\varrho(\sigma)$, $\varrho(\sigma^+)$, $\varrho(\sigma^-)$	Hammett's rho based on σ, σ^+ or σ^- scales
$\tau_{1/2}$ [s, min, h, day]	half-life
V/V	volume by volume mixture
1 : 1 m	equimolar mixture

Abbreviations

a) General

absorpt.	absorption
Ac	acyl
add.	addition
Ar	aryl
conc.	concentrated, concentration
cons.	consumption
decomp.	decomposition
e	electron
f	foreward
i	iso
mixt.	mixture
n	normal
phot.	photolysis
pulse rad.	pulse radiolysis
r	reverse
rad.	radiolysis
reduct.	reduction
RT	room temperature
s, sec.	secondary
soln.	solution
spect.	spectroscopy
t, tert.	tertiary
temp.	temperature
temp. dep.	temperature dependence
therm.	thermolysis

b) Methods

chemil.	chemiluminescence
ch. r.	chain reaction
CIDNP	chemically induced dynamic nuclear polarization
Cond.	conductometry
Co-ox.	cooxidation

ESRLA	electron spin resonance lineshape analysis
glc	gas liquid chromatography
inh. cons.	inhibitor consumption
KAS	kinetic absorption spectroscopy
KESR	kinetic electron spin resonance
NMRLA	nuclear magnetic resonance lineshape analysis
PR	product ratio
ROA	rate of oxygen consumption
RRC	rate of reactant consumption
RS	rotating sector
SAS	steady-state absorption spectroscopy
SESR	steady-state electron spin resonance
spin trap.	spin trapping
therm. coup.	thermocouple method

c) Substances

ACHN	α,α′-azo-bis-cyclohexanecarbonitrile
AIBN	α,α′-azo-bis-isobutyronitrile
BMP	2,6-di-*t*-butyl-4-methylphenol
BPO	benzoyl peroxide
DBPO	dibenzoyl peroxide
DCP	di-α-cumyl peroxide
DPA	9,10-diphenylanthracene
DPM	diphenylmethanol
DPPH	α,α-diphenyl-β-picryl hydrazyl
DPPH-H	α,α-diphenyl-β-picryl hydrazine
DTBH	di-*t*-butyl hyponitrite
DTBK	di-*t*-butyl ketone
DTBP	di-*t*-butyl peroxide
DTBPO	di-*t*-butyl peroxalate
EDTA	ethylene diamine tetraacetic acid
EN	ethylene diamine
FAD	flavin adenine dinucleotide
FMN	flavin mononucleotide
LTA	lead tetraacetate
MTBP	methyl-*t*-butyl peroxide
NBS	N-bromosuccinimide
NTA	nitrilo triacetate
PC	dicyclohexylperoxydicarbonate
PNAP	4-nitroacetophenone
PNBPA	pentaamine(4-nitrobenzoato) cobalt(III)$^{2+}$
THF	tetrahydrofuran
THP	tetrahydropyran
H_2O	water
CH_3OH	methanol
C_2H_4	ethylene
C_2H_5OH	ethanol
C_2H_6	ethane
$c\text{-}C_3H_6$	cyclopropane
C_3H_7	propyl
C_3H_7OH	propanol
C_3H_8	propane
$i\text{-}C_4H_{10}$	isobutane
$c\text{-}C_5H_{10}$	cyclopentane
$n\text{-}C_5H_{12}$	*n*-pentane
C_6H_6	benzene
$c\text{-}C_6H_{12}$	cyclohexane
$n\text{-}C_6H_{14}$	*n*-hexane
$n\text{-}C_7H_{16}$	*n*-heptane
$c\text{-}C_8H_{16}$	cyclooctane
$i\text{-}C_8H_{18}$	isooctane
$n\text{-}C_8H_{18}$	*n*-octane

1 Carbon-centered radicals: Radical-radical reactions

1.0 Introduction

1.0.1 General remarks

This chapter covers rate constants for reactions between carbon-centered radicals. The literature has been reviewed up to August 1982. However, readers are cautioned that the tables may not be completely comprehensive. Abstracting information on such reactions is particularly difficult because they are rarely the main subject of research papers and consequently cannot easily be found by the use of "key-word" searches. This is particularly true of studies in pulse radiolysis.

The rate constants reported in the tables refer to the disappearance of radicals. The normal convention requires that rate constants, *k*, define the rate of appearance of a product molecule. Since two radicals are required to form a molecule of a specific product the value reported for the disappearance of a radical will be twice that for product formation, i.e. $2k$. These conventions have not been strictly observed in the literature and wherever possible, manuscripts have been reviewed so as to establish the meaning intended by authors. Where necessary the data have been adjusted to give the $2k$ value.

Error limits specified by authors are reported in the tables. They are not generally based on statistical analysis and hence cannot be accurately defined in terms of σ values. However, readers should be aware of the technical problems of measuring radical concentrations and of the difficulties of maintaining homogeneous radical distributions over the sample volumes being monitored in experiments. These factors are undoubtedly the major source of error in the rate constants reported in this chapter and are not easily quantified. They explain the wide variation in measurements made by different authors on essentially identical systems.

In pulse radiolysis studies, readers should be aware that radicals other than that of interest may be present in the system depending upon the method of generation and that this is a further source of error. Moreover, the standard procedure for estimating the yield of radicals produced on a given pulse has recently been shown to be in error by approximately 10%; see [80Sch1].

As a result of the experimental difficulties described above, values of $2k/\varepsilon$ have been reported in the tables wherever possible. Since they are concentration independent, these values form the most reliable basis of comparison between different experiments.

1.0.2 Arrangement of the tables

Within each table the entries are organized by molecular formula of the radical. Formulas are in order of increasing C, H, and then all other elements (except D) in alphabetical order. Deutero substrates always follow the corresponding H-compound. For polymer radicals ordering is by the molecular formula of the corresponding monomer.

In many instances rate constants for self-reactions of persistent radicals have not been accurately measured. When such information was unavailable the lifetime of a given radical was reported in the tables.

Large numbers of triarylmethyl radicals have been reported on the literature. In general, these radicals are persistent. However, the tables cover only those radicals on which some quantitative measurement such as monomer-dimer equilibrium constant has been made. For a more extensive compilation readers should see Group II, Vol. 9, Part b, Sect. 4.8 of this series.

A number of relative rate constants are reported in Sect. 1.3. However, no effort has been made to search for literature values of $2k/\varepsilon$ where the authors have not at least attempted to define one of these values. In addition, values of combination-disproportionation ratios are not reported. For radicals which are not persistent such ratios are not thought to be related to the values of $2k$ but are thought to reflect the behaviour of radical pairs trapped in a solvent cage, see [78Sch2, 80Bro1, 82Tan1].

1.0.3 General references

For reviews of this subject readers should refer to [75Kor1] and [78Swa1]. Combination-disproportionation ratios have been reviewed in [73Gib1].

1.1 Self-reactions

1.1.1 Primary alkyl radicals

Reaction Radical generation Method	Solvent	T [K]	Rate data	Ref./ add. ref.
$2\dot{C}H_3 \longrightarrow$ products				
React. of methyl iodide with tri-*n*-butyltin hydride				68Car1
RS	c-C_6H_{12}	RT	$2k = 8.9\cdot10^9\ M^{-1}\,s^{-1}$	
React. of methyl iodide with tri-*n*-butylgermanium hydride				69Car1
RS	c-C_6H_{12}	298	$2k = 1.4\cdot10^9\ M^{-1}\,s^{-1}$ 1) $1.2\cdot10^9$ 2)	
Pulse rad. of a soln. containing 10^{-2} M CH_4 and 0.2 M N_2O				72Ste1
KAS	H_2O, pH 5.5	RT	$2k = 2.48(40)\cdot10^9\ M^{-1}\,s^{-1}$ $\lambda = 220$ nm; $\varepsilon = 850\ M^{-1}\,cm^{-1}$	
Phot. of acetyl peroxide				72Wat1
KESR	DTBP	255	$2k = 11.0(10)\cdot10^9\ M^{-1}\,s^{-1}$	
$2\dot{C}H_3 \longrightarrow CH_3CH_3$				
Pulse rad. of aq. $4\cdot10^{-2}$ M CH_4 and $2.5\cdot10^{-3}$ M N_2O				75Hic1/
KAS	H_2O	298	$2k = 3.4\cdot10^9\ M^{-1}\,s^{-1}$ $\lambda = 210$ nm; $\varepsilon = 1460\ M^{-1}\,cm^{-1}$	72Ste1
		3)	$E_a = 16.4(17)\ kJ\,mol^{-1}$	
		298	$2k = 3.2\cdot10^9\ M^{-1}\,s^{-1}$ $\lambda = 213$ nm; $\varepsilon = 1600\ M^{-1}\,cm^{-1}$	
		298	$2k = 3.2\cdot10^9\ M^{-1}\,s^{-1}$ $\lambda = 215$ nm; $\varepsilon = 1535\ M^{-1}\,cm^{-1}$	
		298	$2k = 3.2\cdot10^9\ M^{-1}\,s^{-1}$ $\lambda = 220$ nm; $\varepsilon = 975\ M^{-1}\,cm^{-1}$	
		298	$2k = 3.3\cdot10^9\ M^{-1}\,s^{-1}$ 4) $\lambda = 215$ nm; $\varepsilon = 1535\ M^{-1}\,cm^{-1}$	
$2\dot{C}H_2OH \longrightarrow$ products 5)				
Pulse rad. of aq. methanol				69Sim1
KAS	H_2O, pH = 6	RT	$2k = 2.4\cdot10^9\ M^{-1}\,s^{-1}$	
	pH = 12		$0.9\cdot10^9$	
Phot. of hydrogen peroxide in methanol				76Hel1
KESR	CH_3OH	296	$2k = 2.9\cdot10^9\ M^{-1}\,s^{-1}$	
		273	$1.9\cdot10^9$	
		251	$1.2\cdot10^9$	
		234	$0.7\cdot10^9$	
		213	$0.35\cdot10^9$	
		202	$0.2\cdot10^9$	

(continued)

---

1) Galvanoxyl used as inhibitor.

2) 2,2,6,6-tetramethyl-4-pyridone nitroxide used as inhibitor.

3) Temp. range not given.

4) Solution contained 10^{-2} M CH_4 and $2\cdot10^{-3}$ M CH_3Cl. It was concluded that the methyl radical diffuses more slowly than methane in water.

5) Tentative assignment.

Reaction Radical generation Method	Solvent	T [K]	Rate data	Ref./ add. ref.
$2\dot{C}H_2OH \longrightarrow$ products 5) (continued)				
H abstraction from CH_3OH by photochem. generated $(CH_3)_3CO\cdot$				76Paul
KESR	CH_3OH	288	$2k = 4.9\cdot10^9\ M^{-1}\,s^{-1}$	
		265	$3.6\cdot10^9$	
		248	$2.5\cdot10^9$	
		225	$1.4\cdot10^9$	
		216	$1.1\cdot10^9$	
		208	$0.85\cdot10^9$	
			$\log[A/M^{-1}\,s^{-1}] = 11.70$	
			$E_a = 10.96\ kJ\,mol^{-1}$	
KESR	CH_3OH	243	$2k = 1.6\cdot10^9\ M^{-1}\,s^{-1}$	79Paul
			$\log[A/M^{-1}\,s^{-1}] = 11.72$	
			$E_a = 11.1\ kJ\,mol^{-1}$	
$2\dot{C}H_2NH_2 \longrightarrow$ products				
React. of $\cdot OH$ with methylamine				71Sim3
KAS	H_2O, pH = 12.3	RT	$2k = 4.0\cdot10^9\ M^{-1}\,s^{-1}$	
			$\lambda < 230\ nm$; $\varepsilon > 1800\ M^{-1}\,cm^{-1}$	
$2\dot{C}H_2\overset{+}{N}H_3 \longrightarrow$ products				
React. of $\cdot OH$ with methylamine				71Sim3
KAS	H_2O, pH = 3.8	RT	$2k = 1.8\cdot10^9\ M^{-1}\,s^{-1}$	
			$\lambda < 230\ nm$; $\varepsilon > 1350\ M^{-1}\,cm^{-1}$	
$2\dot{C}H_2CN \longrightarrow NCCH_2CH_2CN$				
Phot. of DTBP in presence of diethylcyanomethylphosphite				83Kor1
KESR	chlorobenzene	223	$2k = 3.24(15)\cdot10^8\ M^{-1}\,s^{-1}$ 5a)	
		236	$5.79(20)\cdot10^8$	
		248	$9.57(95)\cdot10^8$	
		256	$7.92(73)\cdot10^8$	
		268	$8.95(298)\cdot10^8$	
		283	$11.73(334)\cdot10^8$	
			$\log[A/M^{-1}\,s^{-1}] = 11.2(4)$	
			$E_a = 11.3(21)\ kJ\,mol^{-1}$	
$2\dot{C}H_2COO^- \longrightarrow$ products				
Pulse rad. of acetic acid				69Net1
KAS	H_2O, pH = 10	RT	$2k = 1.0\cdot10^9\ M^{-1}\,s^{-1}$	
			$\lambda = 350\ nm$; $\varepsilon = 800\ M^{-1}\,cm^{-1}$	
Pulse rad. of sodium acetate soln. containing $N_2O\cdot$				76Abr1/
KAS	H_2O, pH = 6.5	RT	$2k = 5.5(10)\cdot10^9\ M^{-1}\,s^{-1}$ 6))	69Net1
$2\dot{C}H_2CHO \longrightarrow$ products				
Pulse rad. of an N_2O satd. soln. containing 0.1 M ethylene glycol				73Ban1
KAS	H_2O, pH = 10	RT	$2k = 9\cdot10^8\ M^{-1}\,s^{-1}$	
			$\lambda = 300\ nm$; $\varepsilon = 260\ M^{-1}\,cm^{-1}$	
Pulse rad. of N_2O satd. soln. containing 10^{-3} M acetylene				78And1
KAS	H_2O, pH = 9.8	RT	$2k = 9.0\cdot10^8\ M^{-1}\,s^{-1}$	
			$\lambda = 300\ nm$; $\varepsilon = 260\ M^{-1}\,cm^{-1}$	

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5) Tentative assignment.

5a) Comparison with diffusion theory. The data were also corrected for contribution from first-order termination.

6) Calc. using $\varepsilon = 780\ M^{-1}\,cm^{-1}$ at $\lambda = 366\ nm$ [69Net1].

Reaction Radical generation Method	Solvent	T [K]	Rate data	Ref./ add. ref.
$2\dot{C}H_2COOH \longrightarrow$ products				
Pulse rad. of acetic acid				69Net1
KAS	H_2O, pH = 3	RT	$2k = 1.8 \cdot 10^9\ M^{-1}\,s^{-1}$	
			$\lambda = 320$ nm; $\varepsilon = 650\ M^{-1}\,cm^{-1}$	
$2\dot{C}H_2CONH_2 \longrightarrow$ products				
React. of glycine amide with e^-(aq)				71Sim2
KAS	H_2O, pH = 5.3	RT	$2k = 3.3 \cdot 10^9\ M^{-1}\,s^{-1}$	
$2CH_3\dot{C}H_2 \longrightarrow$ products				
Rad. of ethane				63Fes2
SESR	C_2H_6	98	$2k = 6 \cdot 10^8\ M^{-1}\,s^{-1}$ 7)	
			$E_a = 3.28$ kJ mol^{-1}	
Rad. of liquid ethane				64Fes1
KESR	C_2H_6	196	$2k = 1.7(4) \cdot 10^8\ M^{-1}\,s^{-1}$	
			$\log[A/M^{-1}\,s^{-1}] = 10.11$	
			$E_a = 3.47$ kJ mo!$^{-1}$	
Pulse rad. of an aquerous solution of 10^{-2} M ethane and 0.25 M N_2O				72Ste1
KAS	H_2O, pH = 5.5	RT	$2k = 1.9(4) \cdot 10^9\ M^{-1}\,s^{-1}$ 8)	
Pulse rad. of aqueous $5 \cdot 10^{-2}$ M C_2H_6 and $2.5 \cdot 10^{-3}$ M N_2O				75Hic1/
KAS	H_2O	298	$2k = 2.6 \cdot 10^9\ M^{-1}\,s^{-1}$	72Ste1
			$\lambda = 210$ nm; $\varepsilon = 790\ M^{-1}\,cm^{-1}$	
		298	$2k = 2.2 \cdot 10^9\ M^{-1}\,s^{-1}$	
			$\lambda = 215$ nm; $\varepsilon = 750\ M^{-1}\,cm^{-1}$	
		298	$2k = 2.4 \cdot 10^9\ M^{-1}\,s^{-1}$	
			$\lambda = 220$ nm; $\varepsilon = 700\ M^{-1}\,cm^{-1}$	
		298	$2k = 2.6 \cdot 10^9\ M^{-1}\,s^{-1}$	
			$\lambda = 230$ nm; $\varepsilon = 545\ M^{-1}\,cm^{-1}$	
		298	$2k = 2.0 \cdot 10^9\ M^{-1}\,s^{-1}$	
			$\lambda = 250$ nm; $\varepsilon = 375\ M^{-1}\,cm^{-1}$	
		298	$2k = 2.2 \cdot 10^9\ M^{-1}\,s^{-1}$	
			$\lambda = 220$ nm; $\varepsilon = 700\ M^{-1}\,cm^{-1}$ 9)	
		298	$2k = 2.4 \cdot 10^9\ M^{-1}\,s^{-1}$	
			$\lambda = 220$ nm; $\varepsilon = 700\ M^{-1}\,cm^{-1}$ 10)	
		11)	$E_a = 16.4(13)$ kJ mol^{-1}	
$2\dot{C}H_2COOCH_3 \longrightarrow$ products				
React. of e^-(aq) with glycine methylester				71Sim2
KAS	H_2O, pH = 5.2	RT	$2k = 4.3 \cdot 10^8\ M^{-1}\,s^{-1}$	
$2\,n\text{-}\dot{C}_3H_7 \longrightarrow$ products				
React. of parent thiol with triethyl phosphite				69Bur2
RS	C_6H_6	RT	$2k = 4.2(10) \cdot 10^8\ M^{-1}\,s^{-1}$	
	$c\text{-}C_6H_{12}$	RT	$3.4(8) \cdot 10^9$	

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7) Comparison with diffusion theory.

8) For $\lambda = 210$ nm, $\varepsilon = 520\ M^{-1}\,cm^{-1}$ and $\lambda = 250$ nm, $\varepsilon = 330\ M^{-1}\,cm^{-1}$.

9) Solution containing $5 \cdot 10^{-2}$ M C_2H_6 and $3 \cdot 10^{-3}$ M C_2H_5Cl.

10) Solution containing $5 \cdot 10^{-2}$ M C_2H_6 and $2 \cdot 10^{-3}$ $HClO_4$. It was concluded that the ethyl radical diffuses more slowly than ethane in water.

11) Temp. range not given.