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Gesamtherausgabe: K.-H. Hellwege · O. Madelung

Gruppe II: Atom- und Molekularphysik

Band 13

Kinetische Konstanten von
Radikalreaktionen in Flüssigkeiten

Teilband d

Oxyl-, Peroxyl- und verwandte Radikale

J. A. Howard · J. C. Scaiano

Herausgeber: H. Fischer



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Zahlenwerte und Funktionen
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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-Börnsteins. 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, legt 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 die Teile II/13a und II/13c bereits erschienen sind. Der hier vorgelegte Teilband II/13d behandelt Reaktionen von Oxy-, Peroxy- und verwandten Radikalen.

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 weiter 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 Dezember 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 authoritative critical compilations as attempted by the Landolt-Börnstein series. Magnetic properties of about 8500 free radical species were collected in volume 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 parts II/13a and II/13c have already appeared. The present subvolume II/13d covers data on reactions of oxyl-, peroxy- and related radicals.

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, December 1983

The Editor

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Part b

Carbon-Centered Radicals II

Part c

Radicals Centered on N, S, P and other Heteroatoms, Nitroxyls

Part d

Oxyl-, Peroxyl-, and Related Radicals

Part e

Proton and Electron Transfer, Biradicals

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Protonen- und Elektronenaustauschreaktionen, Biradikale

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H. Fischer, Physikalisch-Chemisches Institut der Universität Zürich, Switzerland

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J.A. Howard, J.C. Scaiano, National Research Council Canada,
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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-lives 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 occurring 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 constants 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 disappearance 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^\ddagger), entropies (ΔS^\ddagger), and volumes (ΔV^\ddagger) 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. I. 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 1976ff.
- 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.
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- 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
$E^0, E^{0'}$	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^\ddagger	free enthalpy of activation
ΔH^\ddagger	enthalpy of activation
ΔS^\ddagger	entropy of activation
ΔV^\ddagger	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
$\rho(\sigma), \rho(\sigma^+), \rho(\sigma^-)$	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		reduct.	reduction
absorpt.	absorption	RT	room temperature
Ac	acyl	s, sec.	secondary
add.	addition	soln.	solution
Ar	aryl	spect.	spectroscopy
conc.	concentrated, concentration	t, tert.	tertiary
cons.	consumption	temp.	temperature
decomp.	decomposition	temp. dep.	temperature dependence
e	electron	therm.	thermolysis
f	foreward		
i	iso	b) Methods	
mixt.	mixture	chemil.	chemiluminescence
n	normal	ch. r.	chain reaction
phot.	photolysis	CIDNP	chemically induced dynamic nuclear polarization
pulse rad.	pulse radiolysis		
r	reverse	Cond.	conductometry
rad.	radiolysis	Co-ox.	co-oxidation

General introduction

ESRLA	electron spin resonance lineshape analysis	EDTA	ethylene diamine tetraacetic acid
glc	gas liquid chromatography	EN	ethylene diamine
inh. cons.	inhibitor consumption	FAD	flavin adenine dinucleotide
KAS	kinetic absorption spectroscopy	FMN	flavin mononucleotide
KESR	kinetic electron spin resonance	LTA	lead tetraacetate
NMRLA	nuclear magnetic resonance line-shape analysis	MTBP	methyl- <i>t</i> -butyl peroxide
PR	product ratio	NBS	N-bromosuccinimide
ROA	rate of oxygen consumption	NTA	nitrilo triacetate
RRC	rate of reactant consumption	PC	dicyclohexylperoxydicarbonate
RS	rotating sector	PNAP	4-nitroacetophenone
SAS	steady-state absorption spectroscopy	PNBPA	pentaamine(4-nitrobenzoato)cobalt(III) ²⁺
SESr	steady-state electron spin resonance	THF	tetrahydrofuran
spin trap.	spin trapping	THP	tetrahydropyran
therm. coup.	thermocouple method		

c) Substances

ACHN	α,α' -azo-bis-cyclohexanecarbonitrile	H ₂ O	water
AIBN	α,α' -azo-bis-isobutyronitrile	CH ₃ OH	methanol
BMP	2,6-di- <i>t</i> -butyl-4-methylphenol	C ₂ H ₄	ethylene
BPO	benzoyl peroxide	C ₂ H ₅ OH	ethanol
DBPO	dibenzoyl peroxide	C ₂ H ₆	ethane
DCP	di- α -cumyl peroxide	<i>c</i> -C ₃ H ₆	cyclopropane
DPA	9,10-diphenylanthracene	C ₃ H ₇	propyl
DPM	diphenylmethanol	C ₃ H ₇ OH	propanol
DPPH	α,α -diphenyl- β -picryl hydrazyl	C ₃ H ₈	propane
DPPH-H	α,α -diphenyl- β -picryl hydrazine	<i>i</i> -C ₄ H ₁₀	isobutane
DTBK	di- <i>t</i> -butyl ketone	<i>c</i> -C ₅ H ₁₀	cyclopentane
DTBP	di- <i>t</i> -butyl peroxide	<i>n</i> -C ₅ H ₁₂	<i>n</i> -pentane
DTBPO	di- <i>t</i> -butyl peroxyalate	C ₆ H ₆	benzene
		<i>c</i> -C ₆ H ₁₂	cyclohexane
		<i>n</i> -C ₆ H ₁₄	<i>n</i> -hexane
		<i>n</i> -C ₇ H ₁₆	<i>n</i> -heptane
		<i>c</i> -C ₈ H ₁₆	cyclooctane
		<i>i</i> -C ₈ H ₁₈	isooctane
		<i>n</i> -C ₈ H ₁₈	<i>n</i> -octane

8 Oxy-, peroxy- and related radicals

8.0 General introduction

This chapter covers alkoxy ($\text{R}\dot{\text{O}}$), acyloxy ($\text{RC}(\text{O})\dot{\text{O}}$), phenoxy ($\text{A}\dot{\text{O}}$), HO_2 and peroxy ($\text{R}\dot{\text{O}}_2$) radicals, with one separate Section for each radical, in the order given above. Additional details applicable to each individual species are given at the beginning of each section; only very general aspects are dealt with here.

Our coverage of the literature is reasonably exhaustive until the end of 1980. An effort has been made to include 1981 reports, but some may have been omitted, particularly if they had not appeared in Chemical Abstracts by the end of 1981. Only in rare cases have 1982 reports been included.

The sections on each type of radical have been organized largely on the basis of the molecularity of the reaction involved (radical-radical, unimolecular, radical-molecule, etc.); however, each type of radical presented different problems and the organization had to be adapted accordingly.

Within each table the first entry is organized by molecular formula of the radical, and for each radical by molecular formula of the substrate, if one is involved in the reaction. 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.

An important difference in the treatment of the data for alkoxy (8.1) and peroxy (8.5) radicals should be pointed out. Alkoxy competitive data are reported as such; that is, if a ratio of rate constants was obtained in a study, *only* this ratio is given, regardless of whether the authors estimated or not an absolute rate value from that ratio. In the case of peroxy radicals much of the data was obtained as $k_p/(2k_t)^{1/2}$; from this ratio k_p values are usually obtained. In this case our tables usually reported the k_p value. This difference of criteria reflects by and large the history of studies in each field; the 'best' absolute rates for alkoxy radicals have changed by a factor of 20...50 during the last few years; thus, absolute rates estimated from ratios have lost their significance as measurements improved, while the ratios themselves can in most cases be regarded as very accurate values. More details are given in the Introduction to each section.

8.1 Alkoxy radicals

8.1.0 Introduction

The main subdivision in this chapter reflects the molecularity of the processes studied. The reduced size of sections 8.1.1 and 8.1.2 reflects our very limited knowledge in these areas, with only one absolute measurement in each Part.

Section 8.1.3 deals with radical-molecule reactions; as in other parts to follow, *t*-butoxy radicals are treated separately in consideration of the large volume of information for this particular radical. Only data obtained from time-resolved studies are included in the absolute Section. We note that experiments of this nature usually yield the molecular rate constant with no information on the site reactivity; thus, when a certain reaction path is indicated, it is either the result of other studies, or it can be reasonably inferred from the known radical reactivity of the substrate. When this is not the case the footnotes "assumed site of attack" or "main site of attack" have been included.

Subsection 8.1.3.2 includes competition between radical-molecule reactions. This includes reactions of a given radical with more than one substrate, as well as cases of parallel reaction paths (e.g. abstraction vs. addition, or attack at different sites) involving the same substrate. In the cases of competition between two substrates the ratio of rate constants could in principle be listed under either or both substrates; we have chosen to enter the full reaction scheme under only one substrate, and a cross-reference entry for the second substrate.

Studies employing hypochlorites as alkoxy radical sources may be subject to errors due to the possible involvement of chlorine chains. These errors are only likely to be of significance when both reaction paths involve attack at benzylic hydrogens, and no olefin was present in the experiment. Even in this case the error is unlikely to be more than a factor of two, although it would significantly affect Hammett or similar correlations. Since this problem was fully understood only in 1969, studies before that time are likely to have overlooked the problem. The reader is referred to references [65 Wag 1], [67 Sak 1] and [69 Wal 1] for detailed discussion of this problem.

Section 8.1.4 on the competition of radical-molecule reactions with unimolecular processes refers almost exclusively to competitions between hydrogen abstraction or double bond addition with the β -cleavage of the radical, which is used as a 'clock'. In the case of *t*-butoxy radicals, these studies involve the measurement of *t*-butanol-to-acetone ratios. So in the case of subsection 8.1.3.1, these studies do not provide information on the site of attack, which needs to be derived from infrared or other experiments. The ratios of reactivity reported in this

section are extremely sensitive to the polarity of the media, a fact that must be given careful consideration if this data are used under different conditions to those in which it was obtained. The data on cyclohexane in subsection 8.1.4.2 illustrates particularly well these effects. This reviewer was particularly impressed by the excellent agreement observed among data obtained over more than 30 years in about ten different labs and using different radical sources; if this is a measure of reliability, the data in this subsection (8.1.4.2) can be regarded as extremely reliable.

All rate constants are expressed 'per-molecule', with the only exception of polymer systems where the rates are expressed 'per monomer unit'. The abundant literature where rates are reported 'per-hydrogen' has been converted to a per-molecule basis.

Error limits are usually given as reported by the authors. When the authors report standard deviation (σ), the errors are reported as 2σ (95% confidence limits).

The "Miscellaneous" section (8.1.5) is divided in three parts: subsection 8.1.5.1 on disproportionation-combination ratios is self-explanatory. Subsection 8.1.5.2 on isotope effects includes the results of experiments that yield *only* the isotope effect, as well as ratios derived from data in sections 8.1.3 and 8.1.4; however, special care has been taken to use only data that is fully compatible, avoiding ratios of individual rate constants that had been obtained under different conditions. Subsection 8.1.5.3 on acid-base properties lists only one entry and even this one is a tentative value.

While a number of reviews on alkoxy radicals are available, these have not been used at all in writing this Section. Some of these reviews, including kinetic and/or mechanistic data are: [59 Gra 1, 67 Wal 3, 67 Ing 1, 71 Dav 2, 72 How 1, 73 Koc 1, 74 Dav 2 and 74 Hen 1]. It should be noted that the earliest report on absolute rate constants for *t*-butoxy radicals dates from 1978 [78 Sma 1]; thus, any absolute rates reported in reviews written before this date are likely to be incorrect, usually by more than one order of magnitude.

The thermal decomposition of dicumyl peroxide in rubbers has been the subject of numerous studies; these are beyond the scope of this review, since they have not been carried out in solution. A few references are included here to provide the reader access to some of the excellent kinetic data available in this area: [64 Loa 1, 68 Lal 1].

8.1.1 Radical-radical reactions

8.1.1.1 Self-reactions, partly in competition with radical-molecule reactions

Reaction	Radical generation Method	Solvent	T[K]	Rate data	Ref.
2(CH₃)₃CO\cdot \rightarrow OO-dimer					
Photodecomp. of DTBP	KESR	DTBP	293	$2k_1 = 1.3(5) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$)	81 Won 1
(CH ₃) ₃ COCl, initiated by therm. of AIBN	²⁾	CCl ₄	313	$2k_1 \approx 2.8 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$	67 Wal 2
Phot. of (CH ₃) ₃ COCl	RS	³⁾	297	$2k_1 \approx 2 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ *)	67 Car 2
Phot. of (CH ₃) ₃ COCl	RS ⁵⁾	Freon 113	297	$2k_1 = 1.4(6) \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$	66 Car 1
		CCl ₄	297	$2k_1 = 1.2(7) \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$	
			283... 328	$E_a = 0.0(80) \text{ kJ mol}^{-1}$	
Phot. of DTBP	KESR	DTBP	≈ 295	$2k_1 = 2.6 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ⁶⁾	69 Wei 1

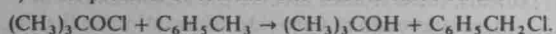
¹⁾ Based on a competition technique, using hydrogen donors as probes (cyclopentane, anisole, methyl *t*-butyl ether or methanol). The value reported is consistent with the hydrogen abstraction rate constants reported in [79 Won 1].

²⁾ Combined analysis of kinetic and cage recombination data taking the fraction of cage recombination as 14%.

³⁾ E.g. CCl₄, Freon 113, benzene, benzonitrile.

⁴⁾ Value probably too low due to complications in the application of rotating sector technique to hypochlorite systems.

⁵⁾ In the presence of toluene. The value is based on $\Delta H = -213.4 \text{ kJ mol}^{-1}$ for the reaction:



⁶⁾ The value is included simply for completeness, since the measurement has been conclusively shown to be wrong. It has been suggested that the value reported corresponds to the ozonide radical (CH₃)₃COO \cdot [69 Sym 1].

Reaction	Radical generation Method	Solvent	T [K]	Rate data	Ref./ add. ref.
$2(\text{CH}_3)_3\text{C}\dot{\text{O}} \xrightarrow{h\nu} \text{OO-dimer}$ $(\text{CH}_3)_3\text{C}\dot{\text{O}} + c\text{-C}_6\text{H}_{12} \xrightarrow{h\nu} (\text{CH}_3)_3\text{COH} + c\text{-C}_6\text{H}_{11}\dot{\text{C}}$	Phot. of $(\text{CH}_3)_3\text{COCl}$ RS	Freon 113 acetic acid CS_2	297	$2k_t/k_a^2 = 0.35 \text{ Ms}$ ≈ 0.51 ≈ 280	67 Car 2
$2(\text{CH}_3)_3\text{C}\dot{\text{O}} \xrightarrow{h\nu} \text{OO-dimer}$ $(\text{CH}_3)_3\text{C}\dot{\text{O}} + \text{C}_6\text{H}_5\text{CH}_3 \xrightarrow{h\nu} (\text{CH}_3)_3\text{COH} + \text{C}_6\text{H}_5\dot{\text{C}}\text{H}_2$	$(\text{CH}_3)_3\text{COCl}$, initiated by therm. of AIBN PR	CCl_4	302.5 312.2 321.6	$2k_t/k_a^2 = 0.88 \text{ Ms}^7)$ $= 0.20^8)$ < 0.80	67 Wal 2
Phot. of $(\text{CH}_3)_3\text{COCl}$ RS	CCl_4 Freon 113 C_6H_6 benzonitrile CS_2	297	$2k_t/k_a^2 = 11.9 \text{ Ms}$ $= 11.1$ $= 4.5$ $= 25$ $= 1100$	67 Car 2	
Decomp. of $(\text{CH}_3)_3\text{COCl}$, initiated photochem. or with AIBN Calorimetry	CCl_4	297 303	$2k_t/k_a^2 = 7.7 \text{ Ms}$ $= 5.7$	67 Car 1	
$2(\text{CH}_3)_3\text{C}\dot{\text{O}} \xrightarrow{h\nu} \text{OO-dimer}$ $(\text{CH}_3)_3\text{C}\dot{\text{O}} + p\text{-ClC}_6\text{H}_4\text{CH}_3 \xrightarrow{h\nu} (\text{CH}_3)_3\text{COH} + p\text{-ClC}_6\text{H}_4\dot{\text{C}}\text{H}_2$	Phot. of $(\text{CH}_3)_3\text{COCl}$ RS	Freon 113	297	$2k_t/k_a^2 \approx 150 \text{ Ms}$	67 Car 2
$2(\text{CH}_3)_3\text{C}\dot{\text{O}} \xrightarrow{h\nu} \text{OO-dimer}$ $(\text{CH}_3)_3\text{C}\dot{\text{O}} + p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_3 \xrightarrow{h\nu} (\text{CH}_3)_3\text{COH} + p\text{-CH}_3\text{C}_6\text{H}_4\dot{\text{C}}\text{H}_2$	Phot. of $(\text{CH}_3)_3\text{COCl}$ RS	CCl_4 Freon 113	297	$2k_t/k_a^2 = 3.6 \text{ Ms}$ $= 2.1$	67 Car 2
$2(\text{CH}_3)_3\text{C}\dot{\text{O}} \xrightarrow{h\nu} \text{OO-dimer}$ $(\text{CH}_3)_3\text{C}\dot{\text{O}} + \text{C}_6\text{H}_5\text{C}(\text{CH}_3)_3 \xrightarrow{h\nu} (\text{CH}_3)_3\text{COH} + \text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\dot{\text{C}}\text{H}_2$	Phot. of $(\text{CH}_3)_3\text{COCl}$ RS	Freon 113	297	$2k_t/k_a^2 \approx 150 \text{ Ms}$	67 Car 2
$2(\text{CH}_3)_3\text{C}\dot{\text{O}} \xrightarrow{h\nu} \text{OO-dimer}$ $(\text{CH}_3)_3\text{C}\dot{\text{O}} + (\text{C}_6\text{H}_5)_3\text{CH} \xrightarrow{h\nu} (\text{CH}_3)_3\text{COH} + (\text{C}_6\text{H}_5)_3\dot{\text{C}}$	Phot. of $(\text{CH}_3)_3\text{COCl}$ RS	CCl_4	297	$2k_t/k_a^2 = 4.3 \text{ Ms}$	67 Car 2

⁷⁾ A value of 0.77 had been reported earlier [66 Wal 1].
⁸⁾ A value of 0.73 had been reported earlier [66 Wal 1].

⁷⁾ A value of 0.77 had been reported earlier [66 Wal 1].⁸⁾ A value of 0.73 had been reported earlier [66 Wal 1].