

Rate Constants for Reactions of Aliphatic Carbon-Centered Radicals in Aqueous Solution

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Absolute rate constants for reactions of aliphatic carbon-centered radicals in aqueous solutions have been compiled and evaluated from the literature. Rate constants are included for reactions of radicals with inorganic and organic compounds and for decay by radical-radical reactions. The radicals were generated by radiolysis, photolysis, or other techniques, and their rate constants were determined generally by kinetic spectrophotometry. The tables include data for over 2,500 reactions of 373 radicals from 740 literature references.

Key words: Alkyl radicals; aminoalkyl radicals; aqueous solution; benzyl radicals; chemical kinetics; haloalkyl radicals; hydroxyalkyl radicals; photolysis; radiolysis; rate constants.

1. Introduction

Alkyl radicals and substituted alkyl radicals are important reactive intermediates formed in certain reductions and oxidations of organic and biological materials. Because of their importance in biological systems, in atmospheric reactions, and in industrial processes, they have been the topic of numerous investigations. Earlier studies have been discussed in several reviews^{1,2} and the kinetic results were summarized in several compilations.^{3,4} Many direct measurements of absolute rate constants for reactions of carbon-centered radicals in solution have been reported. The present compilation is intended to evaluate the available rate constants in aqueous solution and to present them in a concise and readily accessible form. The tables include over 2,500 reactions of 373 radicals, compiled from 740 literature references. The data presented here are also included in the NDRL/NIST Solution Kinetics Database.⁵ A brief description of the methods of production of the radicals and of determination of their rate constants, as well as the general patterns of radical reactions, are given below.

2. Production of Aliphatic Carbon-Centered Radicals

2.1. Radiolysis

Alkyl and substituted alkyl radicals are produced in irradiated aqueous solutions by the reactions of e_{aq}^- , H^\bullet , or $\cdot\text{OH}$ radicals with various organic compounds. If the $\cdot\text{OH}$ radical is to be used, the solutions typically contain N_2O to convert the e_{aq}^- into $\cdot\text{OH}$, thus increasing the yield of the desired alkyl radical and reducing possible complications arising from other reactions of the electron.



If the hydrated electron is to be used to produce the desired alkyl radical, the $\cdot\text{OH}$ radical cannot be converted readily to the hydrated electron, but often can be converted to a reducing radical capable of producing more of the

desired alkyl radical. Otherwise, if the $\cdot\text{OH}$ is scavenged by an additive to form a non-reducing radical, the secondary products arising from the $\cdot\text{OH}$ must be taken into account in the kinetic analysis.

(a) Many alkyl radicals have been formed by hydrogen abstraction from a solute upon reaction with $\cdot\text{OH}$ and $\text{H}\cdot$.



This can result in a mixture of several alkyl radicals, depending upon the structure of the solute and the selectivity of the reacting radicals. The $\cdot\text{OH}$ radical is very non-selective and is used primarily to produce radicals from simple precursors, for example methanol, acetone or acetonitrile, each of which produces only one alkyl radical. For 2-propanol, which is slightly more complex, 86% of the alkyl radicals will be secondary while 13% will be primary. When $\cdot\text{OH}$ is allowed to react with precursors containing unsaturated bonds or aromatic moieties, the situation may be even more complex, with the formation of OH-adduct radicals along with radicals formed by abstraction. Rate constants for a large number of hydroxyl radical reactions are summarized in a recent compilation⁶ and in the Solution Kinetics Database.⁵ Hydrogen atoms are somewhat more selective than $\cdot\text{OH}$ radicals in their reaction at different sites of a solute molecule, but because of their lower yield in the radiolysis of water they have a smaller contribution to the total yield of radicals.

(b) Certain carbon-centered radicals were produced by the addition of $\text{H}\cdot$ or $\cdot\text{OH}$ to unsaturated aliphatic compounds.



This method was used in a limited number of cases and suffers from two restrictions: (1) to produce a single radical the compound has to be symmetric about the double bond, and (2) if the molecule contains reactive sites such as allylic or doubly allylic, hydrogen abstraction may occur with a substantial yield to form a different radical. Reaction of $\cdot\text{OH}$ with a triple bond forms a hydroxyvinyl radical which isomerizes to an oxoalkyl radical.

(c) Many simple alkyl radicals can be formed by the reaction of $\cdot\text{OH}$ with alkyl sulfoxides via an addition/fragmentation mechanism.⁷



Since the rate constants for reaction of $\cdot\text{OH}$ with the sulfoxides are $>10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ and the lifetimes of the OH-adducts are $<200 \text{ ns}$, the radicals $\text{R}\cdot$ are produced in $<1 \times 10^{-6} \text{ s}$ after the pulse in 0.01 mol L^{-1} sulfoxide solutions. With the higher alkyl sulfoxides, a fraction of the $\cdot\text{OH}$ radicals may react via H-abstraction.

(d) Alkyl radicals are also produced by reaction of e_{aq}^- with halogenated organic compounds, leading to reductive elimination of a halide ion. The $\cdot\text{OH}$ radicals can be removed by scavenging them with 2-PrOH, Eq. (9), or with formate ions, Eq. (10).



The radical from 2-PrOH will reduce some halogenated compounds (such as CCl_4 or CH_3I) to produce more of the

desired radical.⁸



Many halogenated compounds, however, do not react rapidly with $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$. The reaction of $\text{CO}_2^{\bullet-}$ with halogenated compounds is slow, even that with CCl_4 .

(e) Alkyl radicals have been produced also by reaction of e_{aq}^- with alkylammonium derivatives, a reaction that proceeds by reductive elimination of ammonia.⁹



Elimination of ammonia occurs only when the amino group is protonated and the α -carbon bears an electron withdrawing group such as carbonyl or phenyl. However, the process is not always quantitative; diphenylmethylammonium deaminates to 95%, but benzylammonium undergoes deamination corresponding to only 70% of the e_{aq}^- . The rest of the hydrated electron reactions occur via ring addition and protonation to give an H-adduct.

(f) Hydroxyalkyl radicals have been produced also by the addition of e_{aq}^- to a carbonyl group, followed by protonation.



2.2. Photolysis

The main photochemical method for production of alkyl radicals, employed in the studies summarized here, is the photolysis of alkyl-metal complexes,¹⁰ e.g.



Other photochemical methods include the reductive quenching of triplet ketones with an alcohol, amine or phenol,¹¹⁻¹³ e.g.



and



followed by,



Other methods which have been used are oxidative decarboxylation of benzoic acid photosensitized by uranyl ion,¹⁴ photolysis of 2,4-dihydroxy-2,4-dimethyl-3-pentanone¹⁵ and the photolysis of H_2O_2 followed by reaction of $^\bullet\text{OH}$ with an organic solute.¹⁶

2.3. Chemical Methods

Chemical methods also have been used to produce certain alkyl radicals. These include Fenton-like systems, where Fe^{II} or Ti^{III} ions react with H₂O₂ to produce [•]OH radicals, which then react with organic solutes to form other radicals. Alkyl radicals have also been generated by thermal homolysis of organometallic compounds, such as certain chromium species¹⁷ containing alkyl or substituted alkyl groups attached to the chromium by a carbon-metal bond.

3. Determination of Rate Constants

3.1. Time-Resolved Methods

Most of the rate constants compiled here were determined by kinetic spectrophotometric methods, i.e. by following the increase in the optical absorption of a product (p.b.k.) or the decrease in the optical absorption of a reactant (d.k.), either the radical or the reacting molecule. In those cases where neither the reactants nor the products exhibit sufficient absorption in a range that can be monitored under the applied conditions, the rate constants were determined by one of the following methods. Another reactant is added as an indicator molecule, or a probe, which is an absorbing species that can be monitored, or which reacts to yield an absorbing species that is readily monitored. When the indicator is present at a constant concentration and the reactant of interest is added at various concentrations, one can derive the rate constant from a linear plot of the observed rate vs concentration.¹⁸ Alternatively, the rate constants were determined by competition kinetics (c.k.), where a reference reactant (R), that reacts with a known rate constant (k_R) and yields an absorbing species, is added as a competitor and the optical absorbance after the reaction is determined at various concentrations of the two reactants. From the absorbance in the absence (A_0) and in the presence (A) of various concentrations of a compound (S) one calculates its rate constant (k_S) from the equation: $A_0/A - 1 = (k_S[S])/(k_R[R])$.^{17,19,20}

A number of rate constants were determined by using other monitoring techniques. Several studies utilized the esr signal of a radical to follow its formation or decay.^{21,22} In several cases, changes in the conductance of the solution were monitored. This method is particularly suitable for reactions that involve changes in concentration of the strongly conducting species H⁺ and OH⁻.^{23,24}

3.2. Other Methods

The time-resolved methods outlined above utilize optical absorption, conductance, or esr signals to follow the changes in concentration as the reaction progresses. The initial concentration of radicals in these methods generally is in the micromolar range or higher, so that radical-radical reactions may have a significant contribution and may limit the ability to monitor relatively slow radical-molecule reactions. Rate constants for such reactions often have been determined or estimated from steady-state experiments, where the radical concentration is relatively low. Rate constants were determined from yields of products based on competition kinetics using a reference compound or based on competition with radical-radical termination reactions. In some of these studies, the steady-state concentration of a radical was obtained from esr measurements and the rate constant derived from the assumed mechanism and the termination rates.

4. Reactions of Aliphatic Carbon-Centered Radicals

All of the radicals included in this compilation are short-lived and react relatively rapidly with other molecules present in solution or with each other. Most radical-radical reactions take place with rate constants generally in the range of 10⁸ to 10⁹ L mol⁻¹ s⁻¹, except for highly charged species which decay more slowly due to electrostatic repulsion. Therefore, reactions of radicals with solutes can be observed only if they effectively compete with the second-order decay. In the pulse radiolysis and flash photolysis experiments used in most of the studies compiled here, the radical concentrations that can be monitored generally are between 10⁻⁶ and 10⁻⁴ mol L⁻¹ so that their half lives are in the microsecond to millisecond time range. Considering that the concentration of the reacting solute may be limited due to solubility or to prevent undesired reactions, the lower limit of the rate

constants that can be measured by these methods is generally $10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ or higher. Only a few rate constants lower than this have been reported and they have been measured or estimated by other techniques.

4.1. Reactions With Oxygen

Most of the radicals included here react very rapidly with O_2 with k of the order of $10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. In most cases the reaction is via addition to form a peroxy radical, but in the case of $\text{CO}_2^{\bullet-}$ the reaction may be via electron transfer to yield O_2^- directly.



Certain hydroxyalkyl and aminoalkyl radicals react with O_2 by addition to form peroxy radicals, but these are unstable and eliminate $\text{O}_2^{\bullet-}$.

4.2. Reduction of Substrate

The majority of the rate constants reported in this compilation are for reduction of inorganic and organic compounds by the strongly reducing radicals $\text{CO}_2^{\bullet-}$, $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$, $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ and similar radicals derived from methanol and ethanol. In general, alkyl radicals that have a hydroxy or an amino group²⁵ on the same carbon as the unpaired electron have reduction potentials in the range of -1 to -2 V vs NHE²⁶ and thus can reduce many compounds (quinones (Q), nitro compounds, porphyrins, higher oxidation state metal ions and complexes, etc.), e.g.



The reduction was assumed to take place in general via electron transfer, but in a number of cases it has been shown to occur via an addition-elimination mechanism.^{24,27}

4.3. Hydrogen Abstraction

H-abstraction was reported mainly for weakly bonded H atoms, such as those in SH groups.²⁸



These reactions are generally slower than the reductions mentioned above.

4.4. Addition to Substrate

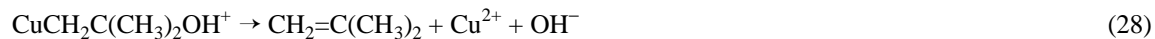
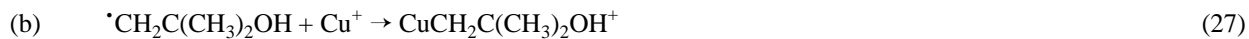
Alkyl radicals also react by addition to unsaturated bonds.²⁹



These reactions are generally slow. Alkyl radicals react rapidly with many reduced metal ions via addition to form organometallic compounds. Some of these adducts are relatively stable whereas others may decompose rapidly by various mechanisms.³⁰



$$k(25) = 5 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}, k(26) = 1.5 \text{ s}^{-1} \text{ at pH } 5 \quad (31)$$



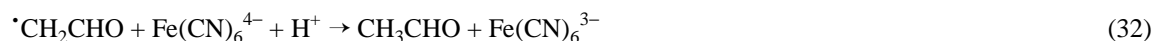
$$k(27) = 4.5 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}, k(28) = 2.2 \times 10^5 \text{ s}^{-1} \text{ at pH } 2.7 \quad (32)$$



$$k(29) = 1.5 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}, \text{ and } k(-29) = 1.2 \times 10^5 \text{ s}^{-1} \quad (33)$$

4.5. Oxidation of Substrate

Carbon-centered radicals containing a carbonyl group at position β , such as $\cdot\text{CH}_2\text{CHO}$, due to partial spin density on the oxygen, are oxidants toward phenoxide ions, TMPD (*N,N,N',N'*-tetramethyl-*p*-phenylenediamine), ascorbate, ferrocyanide and other reductants.^{34,35}



5. List of Abbreviations and Symbols

<i>A</i>	frequency factor
abs.	absorption
abstr.	abstraction
ABTS	2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonate)
Ac	acetyl
AcOH	acetic acid
addn.	addition
alk.	alkaline
anal.	analysis
bpy	2,2'-bipyridine
bpz	2,2'-bipyrazine
BuOH	butanol
<i>tert</i> -BuOH	<i>tert</i> -butyl alcohol (2-methyl-2-propanol)
calcd.	calculated
chem.	chemical
c.k.	competition kinetics
condy.	conductivity
contg.	containing
cor.	corrected
CTAB	hexadecyltrimethylammonium bromide
cyclam	1,4,8,11-tetraazacyclotetradecane
detd.	determined
4,11-dieneN ₄	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene
d.k.	decay kinetics
dmg	dimethylglyoxime
DMSO	dimethyl sulfoxide
ϵ	extinction coefficient (molar absorptivity)
E_a	activation energy
EDTA	ethylenediaminetetraacetate
elec.	electrolysis, electrochemical method
<i>e</i> -r.	electron radiolysis
esr	electron spin resonance
estd.	estimated
Et	ethyl
EtOH	ethanol
formn.	formation
f.p.	flash photolysis
f.p./rq	flash photolysis/reductive quenching
f.p./oq	flash photolysis/oxidative quenching
γ -r.	gamma radiolysis
<i>G</i>	radiation yield (molecules per 100 eV)
ΔH^\ddagger	activation enthalpy
<i>I</i>	ionic strength
J	joules (4.184 J = 1 cal)
<i>K</i>	equilibrium constant
<i>k</i>	rate constant
k_f	rate constant of the forward reaction
k_r	rate constant of the reverse reaction
L	ligand
MB	methylene blue
meas.	measured

MeOH	methanol
MV ²⁺	methyl viologen (1,1'-dimethyl-4,4'-bipyridinium)
NTA	nitrilotriacetate
obs.	observed
opt.	optical absorption
Pa	pascals (N m ⁻²)
p.b.k.	product buildup kinetics
phen	1,10-phenanthroline
phot.	photolysis
pK _a	negative logarithm of the acid dissociation constant, where AH + H ₂ O ⇌ A ⁻ + H ₃ O ⁺
PNAP	<i>p</i> -nitroacetophenone
PANBCo ^{III}	<i>p</i> -nitrobenzoato(pentaammine)cobalt(III) ion
p.r.	pulse radiolysis
prod.	product
PrOH	propanol
py	pyridine
Q	1,4-benzoquinone
redn.	reduction
rel.	relative
resp.	respectively
ΔS [‡]	activation entropy
satd.	saturated
SDS	sodium dodecylsulfate
s.f.	stopped-flow
soln.	solution
TAN	2,2,6,6-tetramethyl-4-piperidone <i>N</i> -oxyl
TEOA	triethanolamine
TNM	tetranitromethane
TPPS	tetrakis(4-sulfonatophenyl)porphine
ΔV [‡]	activation volume
X-r.	X-radiolysis

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