Reactivity of the Hydroxyl Radical in Aqueous Solutions

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NSRDS

Foreword

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The System now includes a complex of data centers and other activities in academic institutions and other laboratories. Components of the NSRDS produce compilations of critically evaluated data, reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data. The centers and projects also establish criteria for evaluation and compilation of data and recommend improvements in experimental techniques. They are normally associated with research in the relevant field.

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Reliable data on the properties of matter and materials is a major foundation of scientific and technical progress. Such important activities as basic scientific research, industrial quality control, development of new materials for building and other technologies, measuring and correcting environmental pollution depend on quality reference data. In NSRDS, the Bureau's responsibility to support American science, industry, and commerce is vitally fulfilled.

RICHARD W. ROBERTS, *Director*

Contents

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The reaction rate data of the hydroxyl radical in aqueous solution are compiled and evaluated in this critical review. The values are reported in a series of tables covering addition, hydrogen abstraction, inorganic electron transfer and radical reactions. Rate constants for the hydroxyl radical with biological molecules are included. In addition, the rate constant data for the oxide radical ion are given. Physical properties are listed and the experimental methods employed in OH radical chemistry are reviewed. An analysis involving rate constant data comparisons is made.

Key words: Abstraction reactions; addition reactions; aqueous solution; biological molecules; electron transfer reactions; hydroxyl radical; oxide radical ion; radical reactions; rate constants; reference data.

Chapter I. Introduction

Water is the most important single solvent in which the physical and chemical processes that can occur are of broad importance in so many areas of the natural sciences. As a result, the rates and equilibria of chemical reactions in aqueous solution have been the subject of countless investigations of almost every conceivable chemical system of substances soluble in water. Among the important chemical reactions occurring in water are those of the free hydroxyl radical, OH, a reactive decomposition product of water which exhibits strong oxidizing properties. Indeed, it is one of the strongest of chemical oxidizing agents.

Hydroxyl radical reactions are of importance in both chemical and biological systems. In chemical systems, such reactions may be fundamental steps in the hydroxylation and oxidation of aquo-organic systems, in the oxidation of inorganic ions and ion complexes, and in the initiation of polymerization. In aqueous solutions which have been exposed to ionizing radiation, the hydroxyl radical is one of the two principal reactive species formed in the decomposition of the water. Subsequent oxidation reactions are the result of its formation. It is, in fact, the application of fast reaction methods in radiation chemistry which has provided the major part of the new information on the reactivity of the hydroxyl radical, to which this monograph is directed.

In radiation biology, since 80 percent of the cell consists of water, reactions of the hydroxyl radical as a reactive transient are important in biological damage. The effects are indirect and evidence has recently been accumulated which shows that a substantial part of this indirect damage to the cells, in many systems, is due to oxidative effects which may be attributable to the hydroxyl radical. Information from such studies, moreover, has a bear-ing on our understanding of molecular processes in biological systems in general.

The chemical reactions of the hydroxyl radical in water may be classified as four different types. These are:

(a) Addition

$$OH + C_6H_6 = (OH)C_6H_6 \cdot \qquad (1)$$

in which the hydroxyl radical adds to an unsaturated compound, aliphatic or aromatic, to form a free radical product. The addition to aromatic compounds, from which various cyclohexadienyl radicals are formed, is typical;

(b) Hydrogen Abstraction

$$OH + CH_3OH = \cdot CH_2OH + H_2O \qquad (2)$$

to form a free radical and water;

(c) Electron Transfer

$$OH + [Fe(CN)_6]^{4-} = [Fe(CN)_6]^{3-} + OH^- \qquad (3)$$

to form ions in a higher valence state, or an atom or free radical if a mononegative ion is oxidized, and the hydroxide ion;

(d) Radical Interaction

$$OH + OH = H_2O_2 \qquad (4)$$
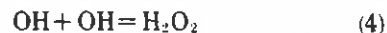
in which the hydroxyl radical reacts with another hydroxyl radical, or with an unlike radical, to combine or to disproportionate to form a stable product.

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A subclassification of these four reaction types exists since the hydroxyl radical has more than one form. OH behaves like a weak acid, ionizing in very strongly basic solution to form O^-, a species whose reactivity differs substantially from that of OH.

Many separate reactions of each type have been investigated and the specific reaction rates determined. Precise quantitative information has been developed principally through the application of the pulse radiolysis technique. Since the radiolysis of water, the mechanism of which is fairly completely understood, produces hydroxyl radicals in known yields, the use of this fast reaction method has been most fruitful in determining the chemical reactivity of OH.

The observation of the spectra of cyclohexadienyl radicals by Dorfman and his co-workers [1–3][1], and their determination of rate constants for several addition reactions of OH, led to subsequent measurements of such rate constants for a large number of organic compounds. The work of Rabani and Matheson [4, 5] on the reactivity of the hydroxyl radical with ferrocyanide ion, provided an example of electron transfer in a reaction which has proved useful as a reference reaction. The generality of such electron transfer reactions of OH with inorganic anions and complexes was demonstrated by Adams and Boag [6, 7] who observed the formation of optically absorbing transients from anions of Group 4–7 of the periodic table. A large part of the work which has provided the information contained in this monograph has evolved from studies of this type.

A critical appraisal and compilation of available data constitutes the substance of this monograph. Any quantitative model for a reacting system rests on a knowledge of the individual rate constants for the elementary reactions of the reactive transient species. Most satisfactory tests of the validity of such models require a knowledge of these individual rate constants. It is our hope that the contents of this critical compilation will prove useful in different areas of research.

Explanation of Tables

The information contained in these tables represents a critical evaluation as well as a compilation. Accordingly, the tables contain not only the values and the cogent parameters of the system, but also brief notations about the method used in each case and the particular experimental conditions which may be crucial in establishing the validity of the results obtained. In the case of many of the rate constants determined on a relative basis, the values presented in these tables will be found not to coincide with the values suggested by the original authors. Such values have been corrected to bring them into accord with the most reliable values available for the rate constants of reference reactions

which have been used in the determination of these relative values. The following notation has been used to distinguish the characteristics of the values wherever possible:
- *, absolute values—which do not depend upon the value of a rate constant for some reference reaction used in competition studies;
- †, most reliable values—values of which the accuracy (within the stated experimental uncertainty or lacking such a statement, within ± 30%) seems least open to question considering such factors as the scatter, or in some cases the paucity of the experimental results or, more commonly, the complexities in interpretation of the data.

The selection has the following basis: Values merit the confidence implied by the designation "most reliable" when they are obtained by methods:
- (a) which are as direct as possible,
- (b) which involve only few, well-established assumptions about mechanism, and
- (c) from which the evaluation of the data follows from a closed analytical solution of the rate equations for such a mechanism, or from a computer analysis of these rate equations. Accordingly it is not surprising that most of the values so designated have been determined absolutely by pulse radiolysis, or in competition kinetics by pulse radiolysis rather than by analysis of stable products.

It may be helpful to point out that, conversely, the following negative criteria have, in general, been applied in excluding the † designation for many of the data whenever:
- (a) the system involves a complex mechanism which may not be clearly established, or more particularly,
- (b) the relationship between the species monitored and the reaction of the hydroxyl radical is not clearly established, or
- (c) the degree of scatter of the results is so great as to raise a question about the meaningfulness of the average, or
- (d) the variation of appropriate physical parameters covers too small a range to constitute a satisfactory test of validity of the kinetic analysis, or
- (e) insufficient information has been provided to judge whether the criteria for inclusion have been met. Data from the thiocyanate competition method, for example, have not been designated most reliable because of uncertainties about the mechanism; nor have values for the reactions with aromatic compounds obtained by carbon dioxide analysis because of the uncertainty in relating the yield of this stable product to the rate of the elementary reaction in question.

The designation of most reliable values should be viewed as an attempt to provide some guidance to the reader who is not familiar with the details of the methods. It is *not* bestowed as an accolade.

[1] Figures in brackets indicate the literature references at the end of each chapter. References are numbered independently for each chapter.

Although we may have erred in selecting too few values as "most reliable", it is clear to us that the inclusion of such a designation enhances the value of the compilation.

Glossary of Abbreviations

The following abbreviations have been used in the tables to conserve space:

abs.	absorbed
addit.	addition
calc.	calculated or calculation
comp.	competition or competitive
comput.	computer
conc.	concurrent
corr.	correction or corrected
ϵ	molar extinction coefficient
ferrocyan.	ferrocyanide
form.	formation
G	radiation chemical yield (molecules reacting or forming per 100 eV absorbed)
irrad.	irradiation
IP	2-propanol
neut.	neutral
obs.	observed or observation
PNBA	p-nitrobenzoate ion
PNDA	p-nitrosodimethyl aniline
prod.	product
P	pulse
R	radiolysis
reac.	reaction
rel.	relative
RT	room temperature
S	steady
scav.	scavenger or scavenged
thiocyan.	thiocyanate

Chapter I. References

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Chapter II. Experimental Methods

Several different methods of generating hydroxyl radicals in water, or in aqueous solutions, have been used. Among these are: (1) radiation chemical methods in which water is decomposed by ionizing radiation, as, for example, by electrons, (2) photochemical methods in which hydroxyl radicals are formed from water by the absorption of light in the vacuum ultraviolet, or from hydrogen peroxide in solution by the absorption of light in the ultraviolet, and (3) chemical methods in which the hydroxyl radical is formed in a chemical reaction as in Fenton's reaction, or the reaction of titanous ion with hydrogen peroxide.

The determination of the specific reactivity of hydroxyl in its elementary reactions further requires that the method of generation permits the isolation and observation of individual elementary reactions, preferably by fast reaction methods. The pulse radiolysis method [1–5] has proved to be by far the most effective fast reaction technique for the study of hydroxyl radical kinetics and it is from such investigations that the bulk of the data tabulated here have originated.

The brief description of the experimental methods which follows, is in no way intended to be a manual of technique. It is simply a brief summary, intended to provide the general reader with some understanding of the method of generating hydroxyl radicals and of observing their reactions and determining from such observations, the individual rate constants. It is intended to give the reader some appreciation of the complexities which are encountered in arriving at the final results.

Radiation Chemical Methods

The decomposition of water as a result of the absorption of energy from ionizing radiation passing through it produces some stable products and some reactive intermediates, the identity of which has been well established by investigations extending over three decades [6–8]. The principal reactive intermediates are the hydroxyl radical, which exhibits oxidizing properties and the hydrated electron (along with a smaller yield of hydrogen atom) which exhibits reducing properties. The radiation chemical decomposition of neutral water may be represented as:

$$H_2O \longrightarrow OH, e_{aq}^-, H, H_2, H_2O_2, H_3O_{aq}^+, OH_{aq}^- . \quad (1)$$
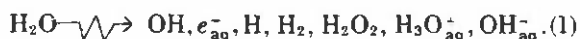
In addition to the oxidizing species, OH, and the reducing species, e_{aq}^- and H, there is a smaller yield of molecular products, hydrogen and hydrogen peroxide. These are thought to be formed, at least in part, in local regions of high concentration of the primary species resulting from the spatially inhomogeneous initial distribution of energy in the system, in regions called spurs and blobs (depending on their size). These have spherical radii which are initially less than 100 Å. The hydronium ion is formed in the rapid ion molecule reaction which forms the hydroxyl radical:

$$H_2O^+ + H_2O = H_3O^+ + OH \quad (2)$$
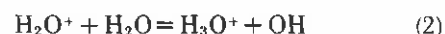
This reaction occurs in a time shorter than the dielectric relaxation time and thus, before the H_2O^+ is solvated. Hydrated electrons are formed in less than 10^{-11} s as the secondary electrons in the system approach thermalization. Both OH and e_{aq}^- are thus formed in times shorter than 10^{-11} s. The hydroxide ion, indicated in reaction (1), is formed by interaction of a hydrated electron with hydroxyl radical in the spurs.

The yields of these transient species are a function of radiation quality and of pH. For neutral solutions and with electrons of energy greater than about 1 MeV the yields [6, 9–12] (represented by the symbol G) are: $G_{OH} = 2.8$, $G_{e_{aq}^-} = 2.8$, $G_H = 0.55$, $G_{H_2} = 0.45$, $G_{H_2O_2} = 0.7$, $G_{H_3O^+} = 2.9$ and $G_{OH^-} = 0.1$ molecules/100 eV. With regard to the study of the kinetics of the hydroxyl radical then, irradiated water may be regarded as essentially a two-radical system of OH and e_{aq}^-, with H amounting to only 9 percent of the total initial concentration of reactive radicals. It is also possible to convert the hydrated electrons into hydroxyl radicals by the use of nitrous oxide as an electron scavenger. The occurrence of the overall reaction

$$e_{aq}^- + N_2O + H_2O = N_2 + OH + OH^- \quad (3)$$
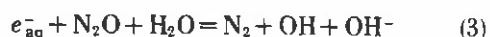
the nature of which will be discussed in a subsequent chapter, thus creates very nearly a one-radical system of OH in water, with the initial concentration ratio $[OH]_0/[H]_0 \cong 10$.

It should be pointed out that it is the nature of the process of energy loss by the ionizing radiation that makes the radiolysis of water the most convenient method for generating hydroxyl radicals in aqueous solutions. The energy loss process, resulting in ionization and excitation of the absorber system by electron impact, is one of coulomb interaction of incident electrons with the system electrons and depends roughly on the electron density of the

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components of the system. In dilute solutions of any solute, therefore, it is the water which absorbs almost all the energy, leaving the solute molecules relatively unaffected. This is in contrast to the partition of incident energy in the photolysis of dilute solutions, where the high energy photons necessary for the decomposition of water or hydrogen peroxide will also be absorbed quite strongly by most solutes of interest even at low concentration.

It should also be understood that the energy of the incident electrons is not a physical parameter fundamental to the investigations since a continuous electron energy degradation spectrum exists in the system.

Although the initial spatial distribution of the reactive transients in irradiated water is nonhomogeneous and has itself been the subject of direct investigation [13] on a time scale of 10^{-11} s, this heterogeneity is short-lived. The spurs have a lifetime on the order of 10^{-9} to 10^{-8} s, after which the distribution of the reactive transients becomes homogeneous by diffusion. Most kinetic investigations of hydroxyl radical reactivity have been carried out on a time scale greater than 10^{-8} s. The hydroxyl radicals generated in this way are in the ground electronic state and, presumably, in the ground vibrational state since collisional de-excitation in condensed phase would be very rapid.

Since the radiolysis of water provides such a convenient means of producing hydroxyl radicals, the development of the pulse radiolysis technique furnished an ideal fast reaction method for the study of their reactivity. In this method, the radiation is delivered to the solution in a single pulse, the duration of which may range from 10^{-11} to 10^{-6} s. Most investigations of hydroxyl radical reactivity have utilized electron pulses ranging from 50 ns to 1 μs in duration.

The source of the electron pulse in such studies may be any one of a number of different types of electron accelerators. Microwave linear accelerators, with energies ranging from about 2 to 30 MeV, are used most extensively in such applications. Van de Graff accelerators, modified to store charge and deliver a single, high current electron pulse, usually at 2 or 3 MeV, have been used in several laboratories. The Febetron[2], an impulse machine utilizing a capacitor bank with a Marx surge circuit to deliver a pulse of fixed length at 2 MeV, is a convenient source for pulse radiolysis. X rays have been used infrequently because of the conversion loss and have not been applied in any of the work on hydroxyl radicals. Detailed characteristics of most of the sources used have been presented in a recent book [4] on this subject.

The characteristics of the electron pulse, which are of importance in fast reaction studies are its duration and time-profile and its amplitude. Pulse

lengths ranging from 1 ns to 1 μs or longer are readily available; pulse lengths of less than 20 ps, from the fine structure of a microwave linac pulse, have been used in a special application [14]. The pulses with a duration greater than a few nanoseconds are fairly well represented as a square waveform. Thus, the Van de Graaff at Argonne National Laboratory, with which pulses as short as 1 ns have been used, has a pulse with rise time and decay time of less than 0.5 ns. The microwave linac at the Ohio State University, with which pulses generally longer than 10 ns have been used, has rise and decay times of 5 ns. It is an important convenience in the interpretation of kinetic data that the time-profile of the pulse approximates to a square wave—particularly that the falling edge is represented by a step function.

The pulse current must be high enough so that a single pulse delivers sufficient power to the system in order to produce an observable concentration of the transient species of interest. With the shortest electron pulses, currents in the range of several amperes to several tens of amperes have been used; with the longer pulses, currents are generally of the order of 0.1 A to almost 1 A. In any event, the magnitude of the product of current, duration, and voltage of the pulse is such that, in most applications, a single pulse will deliver in the range of 0.02 to 5 J. With most systems, this is a sufficient power level to produce an "instantaneous" concentration of transient species in the range of $10^{-7} M$ to almost $10^{-4} M$. Such a concentration is readily detectable by a variety of methods.

The solution into which this energy perturbation is injected is generally contained in a quartz cell of rectangular or cylindrical design with a volume generally larger than a few ml, and, perhaps, up to several tens of ml, depending upon the electron beam energy. The power level is insufficient, therefore, to produce any significant temperature rise in the system.

The reaction of interest may be observed by monitoring one of the properties of either the reactive intermediate or of a product formed directly in the elementary reaction, over an appropriate period of time following the electron pulse. Properties which have been used are: optical absorption, optical emission if this occurs, electron spin resonance absorption if the requirement of time resolution permits, and electrical conductivity if the species is charged. Optical absorption is the most versatile of these methods and has proved to be by far the most extensively used. In this case, the optical absorption of a monitoring light beam passing through the reaction cell is measured by fast spectrophotoelectric recording at an appropriate wavelength, starting at, or before, the time of the pulse and extending after it for several half-times of the observed reaction. A typical rate curve for the formation of a product in a hydroxyl radical reaction is shown in figure 1. The identity of the absorbing species may, in some cases, be known from previous work in which the spectrum
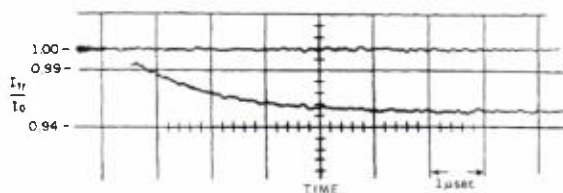
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FIGURE 1. *Rate curve for the reaction of the oxide radical ion, O⁻, with ethanol obtained by observing the formation of the · C₂H₄O⁻ radical ion at 360 nm following a 300 ns electron pulse in an aqueous solution at pH 13.92 containing 4.3 × 10⁻⁴ M ethanol.*

The fraction of the light transmitted is shown as a function of time at a sweep speed of 1 μs/cm on the oscilloscope. Data taken from reference [7], chapter IX.

has already been assigned; in others, it may be the subject of some speculation in the event the identity is based on the chemical behavior of the system.

Rate constants for reactions of the hydroxyl radical, with the exception of the combination reaction and the reaction with molecular hydrogen, have not been determined by observing OH directly. An optical absorption in the far uv [15, 16a] thought to be that of the hydroxyl radical in water, is too weak, and in a spectral region too readily obscured by most solutes to be used for this purpose. Instead, the rate curves for product formation have been used.

In many cases, as will be explained, rate constants have been determined by competition, in which the relative concentration, rather than the rate, of a product formed is determined. Such competition methods may utilize a steady radiation source such as a Co⁶⁰ γ-ray source rather than a pulsed electron source and will, in that case, involve the relative concentration of a stable product rather than that of an intermediate.

Another radiation chemical method which has been used effectively for the determination of rate constants of two important reactions of OH, is the equivalent of the rotating sector method. A pulsed Van de Graaff accelerator, in which the pulse duration and period could be varied, was used.

Photochemical Methods

Water vapor absorbs strongly in the vacuum ultraviolet region of the spectrum, the continuum extending from about 145 to 200 nm. This absorption was, at first, thought to result in the photodissociation reaction:

$$H_2O \longrightarrow [H_2O^*] \longrightarrow H_2 + O. \qquad (4)$$

However, it was argued, on energetic grounds, that the dissociation is not possible for wavelengths longer than about 180 nm and that the primary dissociation step is:

$$H_2O \longrightarrow [H_2O^*] \longrightarrow H + OH. \qquad (5)$$

The absorption spectrum in liquid water is displaced slightly to longer wavelength. The first indica-

tion that reaction 5 also occurs in the liquid phase, was the demonstration that ferric ion is formed in the flash photolysis of aqueous solution of ferrous ion with light of wavelength below 200 nm [16b]. In an extension of this work [17], the observation that H₂O₂ is a major product in the flash photolysis of deaerated water, provided fairly reliable confirmation that this reaction takes place. There is no experimental evidence that solutes, certainly at concentrations less than 1 M, interact with the primary excited state of water. Although liquid water does not absorb above 200 nm, some mercury photosensitized decomposition has been observed in aqueous solution, although the quantum yields are rather low [18].

It was reported [19] that hydroxyl radicals are formed by the photodecomposition of hydrogen peroxide with light of wavelength 253.7 nm:

$$H_2O_2 \longrightarrow OH + OH. \qquad (6)$$
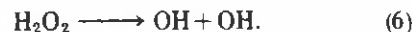
Under some conditions the quantum yields for H₂O₂ removal can be extremely high, suggesting the occurrence of chain processes, although, at high light intensities, the chain length decreases. A study of the kinetics of H₂O₂ photodecomposition indicated, initially, a primary quantum yield of unity [20]. However, a subsequent investigation [21] of the photo-oxidation of formic acid in solution containing H₂O₂ showed that the true quantum yield is 0.5. The kinetic behavior of the decomposition product is identical to that of the oxidizing species formed in the γ-radiolysis of water [22] and there is now little doubt that it is the free hydroxyl radical.

The fast-flow technique has been used in an ESR study [23] of the structure of radicals formed by reaction of OH produced by H₂O₂ photolysis. In this technique, which, in some respects, is similar to that used in the fast flow ESR studies with the Ti³⁺/H₂O₂ reagent described below, H₂O₂ solution is photolyzed just before it is passed through the cavity of the ESR spectrometer. Under appropriate conditions, radicals formed by reaction of OH with a second solute are sufficiently long-lived to permit their ESR spectra to be recorded. As with the other flow experiments, the strength of this technique lies in its suitability for studying the structures of radicals formed by reaction of OH.

Although attempts have been made to use H₂O₂ photolysis as a source of OH radicals for kinetic studies [24, 25], its usefulness is restricted to those few systems where the absorption of the solute at this wavelength is low relative to that of H₂O₂.

It has been shown [26] that solutions of ferric ion can initiate vinyl polymerization when irradiated with light of wavelength 365 nm and oxidize aromatic compounds, including benzene itself [27], to the corresponding phenols. The evidence is strong that the primary photochemical reaction involves an internal electron transfer reaction in a ferric ion complex which leads to ejection of the hydroxyl radical from the solvation shell:

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$$Fe\ OH^{2+} \rightarrow Fe^{2+} + \ OH. \qquad (7)$$
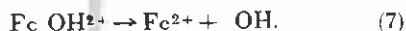
In the case of benzene, the primary quantum efficiency for light of wavelength 313 nm is 0.13 [27]. There are no reports of this system being used for determining any OH reactivities.

Chemical Methods

The Fenton Reaction

In 1894, Fenton [28] reported that a variety of α-hydroxy acids could be oxidized by mixtures of hydrogen peroxide and ferrous salt. Subsequently, it was shown that polyhydric alcohols, sugars, amino compounds, and phenols were similarly oxidized while, at higher temperatures, some simple aliphatic alcohols also reacted. The reactions appeared to be specific to ferrous ion and were dependent upon pH.

In the thirties, the classic work of Haber and Weiss, continued later by Weiss, led to the postulation of the hydroxyl radical as an intermediate in the Fenton reaction [29]. This did much to clarify the mechanisms of the many oxidation processes initiated by this reagent.

To explain the observation that ferrous ion was a much better catalyst than the ferric ion in the dehydrogenation of various substrates by hydrogen peroxide, it was proposed that the initial step is the reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-. \qquad (8)$$

Adequate confirmation of the OH radical as an intermediate, obtained first from an investigation of the chain polymerization of olefins [30] was provided by evidence from a variety of other systems [31–34].

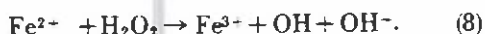The mechanism of oxidation of organic substrates by the Fenton reagent can be complex. An initial examination of the kinetics of oxidation of a range of compounds [33, 34] appeared to indicate that the reactions could be classified into "chain" and "non-chain" processes. It was proposed that OH radicals formed in acid solution by reaction (8) react with an oxidizable substrate RH, by hydrogen abstraction to form the radical R $\cdot$. Since H_2O_2 is present this radical may react in a chain propagation step to regenerate OH:

$$R \cdot + H_2O_2 \rightarrow ROH + OH \qquad (9)$$

In such cases, low concentrations of ferrous ions could initiate the chain oxidation of an excess of organic solute. If, however, reaction (9) were slow, chain termination could occur by radical-radical reaction by oxidation by Fe III. Since ferrous ion can compete with the substrate for OH, it was proposed that kinetic analysis of the data should yield the rate constant ratio for these two reactions. A large number of relative rate constants were obtained by this method, although it is now known

that the mechanisms proposed are incomplete. No account was taken of either the reaction of the organic radical with oxygen or the formation of HO_2 in the chain propagation step:

$$OH + H_2O_2 \rightarrow HO_2 + H_2O. \qquad (10)$$
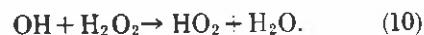
The overall reaction mechanism is sensitive, therefore, to the relative concentrations of the various solutes. Nevertheless, the kinetic data are interesting from the historical viewpoint in that they represent the first systematic study of OH reactivity generally.

Although the Fenton reaction has been used in more recent years for a study of some OH rate constants [25] the complexities of the oxidation mechanisms seriously limit its reliability as a general kinetic method. As is the case with the titanium/ H_2O_2 system described below, the usefulness of the Fenton reaction lies more in its application in fast-flow/ESR techniques where the emphasis is on the structure of the radicals formed by reactions of OH rather than on the kinetics of the processes.

Titanous Ion

Titanous ion, Ti^{3+}, reacts with H_2O_2 in a process analagous to the Fenton reaction, although it has been reported that the reaction is faster [35].

$$Ti^{3+} + H_2O_2 \rightarrow Ti^{4+} + OH + OH^-. \qquad (11)$$
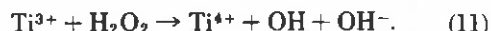
A convenient and fruitful method of studying reactions of the OH radical generated by this reaction has been used [36, 37] in which the reactants, titanous ion, H_2O_2, and an organic substrate, RH, are mixed in a rapid-flow apparatus. The combined solution is then passed through the cavity of an electron spin resonance spectrometer a short time after mixing and the ESR spectra of the transient free radicals formed by reaction of OH with the substrate are recorded.

The mechanism of the titanous ion/H_2O_2 reaction is undoubtedly complex. The OH radical produced in (11) reacts with both Ti^{3+} and H_2O_2 forming, respectively, Ti^{4+} and HO_2 radicals. The relative efficiency with which OH can react with an added substrate then depends on the relative solute concentrations. However, further complications arise from the existence of complexes between H_2O_2 and the Ti^{4+} ions formed in the reaction. In the ESR spectrum observed after mixing Ti^{3+} and H_2O_2, two singlet lines are observed which have been attributed to separate species in view of the different time constants for the decay [38, 39]. There is little doubt that the singlets are due to complexes of titanium ions and oxyradicals [40, 41] and recent evidence [42] indicates that the radical involved in both complexes is HO_2.

It has been suggested [40] that the reactive agents in the oxidation of organic substrates are complexes containing titanium ions and OH radicals and not free OH and that they are responsible for

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the singlet spectra. Double mixing experiments have shown. however. that this is not so [43].

When Ti^{3+} and H_2O_2 are brought together a short time before an organic reactant is added, both singlets are still observed. They are not quenched and are certainly due to relatively unreactive species. As would be expected, unless an oxidizable organic substrate is available for reaction immediately the OH radical is formed, OH will react with other species in the system. However, there seems little doubt that, despite the complexity of the reaction when such a compound is available at the time of mixing, the reacting species is the free, uncomplexed hydroxyl radical. This is confirmed further by the considerable data concerning the nature of the radicals formed from various organic substrates. Where comparisons are possible, agreement with pulse radiolysis data on radical assignments are good. Examples of reactions studied by the flow method include addition of OH to aromatic [44] and various unsaturated aliphatic compounds [45, 46].

The strength of the fast flow/ESR method lies in the facility for determining the structure of the radicals produced by reaction of OH. However, the limitations imposed by the time resolution available with the method and the complexities of the mechanisms involved, make it less suitable for the quantitative measurement of the kinetics of OH reactions.

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Chapter III. Kinetic Analysis

The rate constants in this compilation have been determined by one or another of the following methods, for which the kinetic analysis will be indicated and some of the requirements and pitfalls mentioned. Three of these methods lead to absolute values for the rate constant, while a fourth, very commonly used, leads to relative values in which only the ratio of the rate constant to that of a competing reference reaction is known.

Direct Observation of Product Formation

Direct observation of the rate curve for the formation of a product is feasible if the product, P, has a sufficiently strong and accessible optical absorption,

$$OH + X = P. \qquad (1)$$

P may be an adduct free radical, where X represents a stable molecule or ion, a free radical formed by abstraction of hydrogen, or a radical or ion-product of the oxidation of an ion. If no concurrent reaction of hydroxyl radical such as

$$OH + OH = H_2O_2 \qquad (2)$$

is competitive with reaction (1), a condition that will obtain if the ratio $k_1[X]_0/k_2[OH]_0$ is sufficiently large, say, greater than 50, the rate equation for product formation is, simply,

$$\frac{d[P]}{dt} = k_1[OH][X], \qquad (3)$$

which reduces, for the condition $[X]_0 \gg [OH]$ to

$$\frac{d[P]}{dt} = k_1'[OH]. \qquad (4)$$

Since the formation of P and the disappearance of OH are complementary, the integrated form of this equation, in terms of the optical density, D_t, of P at any time, is:

$$\log(D_\infty - D_t) - \log D_\infty = -0.4343 k_1' t \qquad (5)$$

k_1', the first order rate constant, may then be obtained from the slope of a plot of $\log(D_x - D_t)$ versus time, which should be linear. The absolute value for k_1, the bimolecular rate constant, is then obtained from

$$k_1 = k_1'/[X]_0 \qquad (6)$$

In this application, P must be the only species absorbing at λ_1, the monitoring wavelength, whose concentration changes sensibly during the observation. It is generally not satisfactory, because of the insensitivity of log plots, to rely on a linear plot at only a single concentration of X, but rather more desirable to demonstrate constancy of k_1, with variation of $[X]_0$ over a reasonable range. If several products are formed concurrently from OH and X in reaction (1), k_1 will be equal to the sum of the rate constants for the individual reactions.

If the rate of reaction (2) is not negligible relative to that of (1), some deviation from linearity will be observed and the occurrence of (2) must be taken into account in the treatment of the data. This can be done quite readily by analog or digital computer calculation since the value for k_2, as will be seen, is known absolutely. In some cases the reaction of e_{aq}^- and of H will not interfere in the foregoing direct determination of k_1. In others where one or other may result in the formation with a rate constant differing from k_1' of a product also absorbing at λ_1, it is necessary to convert e_{aq}^- into OH by means of reaction (3) chapter II, and to take into account the reactivity of H, the concentration of which then amounts to only 10 percent of that of OH.

An experimental condition which has occasionally been overlooked in such rate constant determinations and which can result in small, but significant, errors, is the nonuniformity of the radiation flux throughout the cell volume. A variation of the initial concentration of reacting species along the path of the analyzing light has no effect [1, 2] upon rate constants for first order reactions and only a small effect in the case of second order reactions. Variation across the light path in the direction of the electron beam, if these are at right angles, has a small effect on first order constants and may have a significant effect upon second order constants, as has been indicated with numerical examples [1, 2].

A considerable number of absolute rate constants for reactions such as addition to aromatic molecules, electron transfer from anions, and a special case of hydrogen abstraction, have been determined by such observation of product formation in pulse radiolysis. Included are some reactions which may be used as reference reactions in competition methods. With proper attention to the experimental conditions and care in analysis of the data, absolute rate constants have been obtained with an uncertainty as low as ±10 percent in the accuracy, which represents very nearly the best attainable.

Direct Observation of the Hydroxyl Radical Disappearance

This method, which is, in principle, the most desirable one, has proved feasible [3-5] for only two reactions, the recombination, reaction (2), and the reaction with molecular hydrogen. As will be seen in chapter IV, a weak optical absorption at wavelengths below 280 nm, seen in irradiated water under appropriate conditions, is thought to be that of the hydroxyl radical. By monitoring this absorption in the presence of a sufficient concentration of hydrogen, an approximate value for the rate constant of the reaction

$$OH + H_2 = H_2O + H \qquad (7)$$
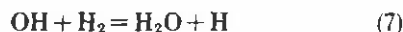
known more accurately from other methods, was determined. In this case for the condition $[H_2]_0 \gg [OH]_0$, the integrated form of the differential rate equation, in terms of the optical density of OH, is

$$\log D_t - \log D_0 = -0.4343 k_7' t. \qquad (8)$$

k_7 may then be obtained absolutely from the slope of the straight line resulting from a plot of $\log D_t$ versus time, if $[H_2]_0$ is known.

With N_2O present to convert e_{aq}^- to OH, the rate constant for reaction (2) was determined. If (2) were the only reaction occurring, the integrated form of the differential rate expression for the disappearance of OH, in terms of its optical density, would be:

$$1/D_t - 1/D_0 = \left(\frac{2k_2}{\epsilon_{OH}^\lambda l} \right) t, \qquad (9)$$

where ϵ_{OH}^λ is the molar extinction coefficient of the hydroxyl radical at the wavelength, λ, of observation. ϵ_{OH}^λ may be determined provided the dose is known, since the yields of OH and of e_{aq}^- are accurately known. The absolute value for k_2 may then be determined from the slope of a straight line plot of $1/D_t$ versus time. Since there is some contribution from the reaction

$$OH + H = H_2O, \qquad (10)$$

this was taken into account in evaluating k_2.

The limitation on the application of this method stems from the fact that the absorption of OH is very weak and is in a region of the spectrum in which most solutes as well as HO_2, an intermediate formed in the radiolysis, absorb rather strongly.

Competition Kinetic Measurements

Here only a relative rate constant can be determined.

Stationary State Systems

While it is true that the pulse radiolysis technique has provided most of the accurate OH-rate data now available, much of the basic information concerning the general mechanisms of reaction of OH has derived from the considerable effort directed to the study of the stationary-state radiolysis of aqueous solutions. In such systems, irradiated at the dose rates available with conventional x- or γ-ray sources, the duration of the irradiation is many orders of magnitude greater than the lifetime of the OH radical formed under these conditions. Consequently, throughout the course of the radiolysis, this species is present at a constant, but extremely low, concentration. Its reactions cannot be observed directly and the determination of the reaction mechanisms depend entirely on the qualitative and quantitative estimation of the final, stable reaction products.

In aqueous solutions, therefore, the reactivity of the OH radical must be obtained by analysis of the yields and distribution of these final products. It can only be expressed relative to some other reference rate constant which itself has to be determined absolutely by some other method. The reliability of rate data so determined is dependent, therefore, on the accurate knowledge of the overall reaction mechanism. However, in spite of these difficulties, useful rate data have been obtained from stationary state kinetic competition analysis.

In principle, two general methods are employed for the determination of a relative rate constant for for reaction of OH with a given solute. In the first method, the kinetic analysis is based upon the effect of an additive on the yield of a stable product which results from reaction of OH with the solute. In the second, the competition is measured by the effect of the additive on the rate of removal or modification of the original solute.

The formic acid system [6] is an example of the former method. OH radicals react with this solute to form the carboxyl radical, COOH:

$$OH + HCOOH \rightarrow H_2O + COOH. \qquad (11)$$
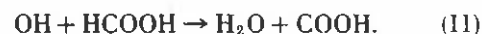
In the presence of ferric ion, at low pH, carboxyl radicals are oxidized to CO_2 which can be collected and measured after the radiolysis is complete:

$$COOH + Fe^{3+} \rightarrow CO_2 + Fe^{2+} + H^+. \qquad (12)$$
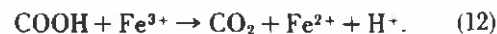
With a second solute present, which reacts competitively with OH, the yield of CO_2 will decrease.

If $G(CO_2)$ is the radiation yield of carbon dioxide resulting *entirely* from reaction (12), then the effect on this yield of an added solute is given by the equation:

$$\frac{1}{G(CO_2)} = 1 + \frac{k_x[X]}{k_{11}[HCOOH]}, \qquad (13)$$

where [X] is the concentration of the added solute and k_x and k_{11} are the respective rate constants for reaction of OH with each solute. The relative rate constant ratio k_x/k_{11} is obtained from the data expressed graphically according to eq (13).

Examples of the second type of stationary state competition system includes those in which the highly-colored compound, paranitrosodimethylaniline, PNDA [7], and the pyrimidine base, thymine [8–10], are used as reference solutes.

The compound PNDA has an intense optical absorption band with a maximum at 440 nm where the molar extinction coefficient is $3.42 \times 10^4 M^{-1}$ cm^{-1}. The reaction product of OH with PNDA, believed to be an adduct radical, has a much weaker absorption at this wavelength. Consequently, irradiation of an aqueous solution of this compound leads to bleaching of the solution. In the presence of a second solute which can compete effectively for the OH radical, the extent of the bleaching is reduced. Simple kinetic analysis of the data yields the relative rate constant ratio for reaction of OH with the two solutes.

The thymine method is similar in principle to that employing PNDA as the reference solute. The presence of the 5:6 double bond in this molecule gives rise to a strong optical absorption band at 264 nm ($\epsilon = 7.95 \times 10^3 M^{-1}$ cm^{-1}). It is well established that OH radicals add to the 5:6 double bond in thymine and, since this reaction destroys the chromophore, reaction of OH can be followed by direct measurement of the radiation-induced bleaching. Provided that the ultimate product of reaction of OH with a competitive solute does not contribute to the final absorption (or, if so, the extent of the contribution must be known) the relative rate constant for the solute can be determined.

Although both these competition methods have been used extensively, their reliability depends ultimately on the validity of the overall mechanisms assumed for the competition. Both solutes have been used, however, as reference standards for competition studies in pulse radiolysis where less emphasis need be placed on knowledge of the *overall* reaction mechanism. This is discussed later in chapter XI.

Pulse Radiolysis Methods

Several competition methods are available where the pulse radiolysis technique is used for obtaining relative OH rate data, although, as before, the validity of *absolute* rate constants derived from the data depends upon the accuracy with which the reactivity of OH with the reference solute can be determined.

As with the stationary state systems, two general spectrophotometric methods are available. In the event that the reference solute has suitable optical absorption properties, the reaction of OH radicals can be measured by observation of the bleaching of this absorption. The reaction of a competitive solute is indicated by a reduction in the extent of the bleaching, provided the transient product has a weaker absorption in the relevant region of the spectrum. Alternatively, the reference solute may react with OH to form a transient product with a much stronger absorption than the stable solute.

In this case, provided the product of OH reaction with the competitive solute does not absorb strongly in the same region, the competition is followed by measurement of the suppression of the transient absorption.

The competition kinetics of such systems are as follows: A solution containing a reference solute, A, of concentration [C] and a concentration [S] of a test solute B is irradiated by a short electron pulse. The OH radicals then react with either solute in proportion to the products of the concentration and rate constant of the respective reactions:

$$OH + A \xrightarrow{k_a} \text{absorbing product}$$

$$OH + B \xrightarrow{k_b} \text{nonabsorbing product.}$$
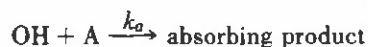
If A_o is the optical density of the absorbing product when solute B is absent and A is the optical density when solute B is present, then it follows that

$$\frac{A_o}{A} = 1 + \frac{k_b[S]}{k_a[C]} . \tag{14}$$

A plot of A_o/A against the ratio of solute concentrations is linear with the slope equal to k_b/k_a.

The rate constant k_b can be derived, assuming that the reference rate constant, k_a, can be measured directly.

The carbonate radical, CO_3^{2-} was the first reference system used in pulse radiolysis for the determination of OH rate data [11, 12]. The carbonate ion reacts with OH to form the transient radical, CO_3^-, which has an absorption maximum at 600 nm. Reaction of OH with a competitive solute suppresses this absorption band. An advantage of this system is that it can be used in aerated solution, although the drawbacks include the rather low extinction coefficient ($\epsilon^{500} = 1.8 \times 10^3 M^{-1}$ cm^{-1}) and the obvious restriction to alkaline solutions.

Other systems were introduced in which the extinction coefficient of the reference absorption band is much higher. These include the halide and pseudohalide radicals, I_2^- [4], and $(CNS)_2^-$ [12], which have absorption maxima at 390 nm and 480 nm respectively. The serious disadvantage with systems of this type, which, in some cases may invalidate the method, is due to the fact that the reference absorptions are not formed in a one-step process. In the thiocyanate system, for example, the absorbing radical, $(CNS)_2^-$, is formed according to

$$OH + CNS^- \rightarrow CNS , \tag{15}$$

$$CNS + CNS^- \rightleftharpoons CNS_2^-. \tag{16}$$

It has been shown [13] that reaction (16) is somewhat slower than reaction (15) and is thus rate determining. Since the measured rate constant (6.6×10^9 M^{-1} s^{-1}) for the formation of the absorption refers

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to reaction (16), rate constants for other solutes measured by competition using this value are too low. Nevertheless, as will be discussed later, the large amount of published rate data for this system can be successfully normalized by arbitrary fitting with apparent self-consistency. Added kinetic complications which would arise if competition reactions of the uncomplexed CNS radical were to occur, seem to be unimportant in this system.

In similar competition studies where the Br_2^- absorption, formed from OH oxidation of bromide ions is used as the reference absorption, these complications are probably present [12]. The competition between carbonate and bromide ions for OH can be followed either by monitoring the CO_3^- absorption or that due to Br_2^-. In either case, the rate constant for reaction of OH with Br^- was found to be 1.8×10^8 M^{-1} s^{-1}. However, the value obtained from direct observation of Br_2^- formation is considerably larger. Pulse radiolysis systems in which the competition is measured by the effect of the second additive on the OH-induced bleaching of an absorbing reference solute, have been used fairly successfully. Both the thymine and paranitrosodimethyl aniline methods, used originally under steady state conditions, have been adapted for use in pulse radiolysis experiments. As discussed previously, the validity of the stationary state experiments depends on the validity of the reaction mechanism assumed. However, in pulse radiolysis, since the competition is followed by *direct* observation of the extent of reaction between OH and the reference solute, subsequent radical reactions which could complicate the *overall* mechanism, become irrelevant.
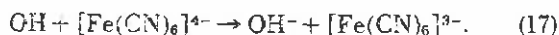
A pulse radiolysis reference system which has much to commend it, is that in which ferrocyanide ion is used as the reference solute [14, 15]. The ion is oxidized by OH rapidly and quantitatively in the simple, one-electron transfer reaction:

$$OH + [Fe(CN)_6]^{4-} \rightarrow OH^- + [Fe(CN)_6]^{3-}. \quad (17)$$

The product, ferricyanide ion, is stable and has a characteristic absorption band with a maximum at 410 nm ($\epsilon^{410} = 1000$ M^{-1} cm^{-1}). Further, it can be used over the entire range of pH. Although radicals produced by reaction of OH with the competitive solute may, in some cases, react rapidly with the ferricyanide ion formed in (17) at the radiation doses which may be used in this technique, the rate of such reactions are still too slow to prevent accurate measurement of the initial values of the absorption.

Intermittent Irradiation

Intermittent irradiation [16] may be employed with application of the rotating sector method [17]. An absolute value for k_7 and a value for k_2 relative to k_7 have been determined by this method. The intermittency was provided by a pulsed, 1.5 MeV Van de Graaff accelerator, with variable pulse length and variable frequency (although the off/on

ratio was fixed at 7.5) with the period for a cycle variable from 10^{-5} to 5 s. The product, of which the yield was measured, was hydrogen peroxide at steady state, $[H_2O_2]_{ss}$, using intermittent irradiation and with a steady beam, $[H_2O_2]_b$. Data were presented of $[H_2O_2]_{ss}/[H_2O_2]_b$ as a function of τ, the pulse duration. With a risetime of 1 μs the pulse has a square waveform which simplifies the interpretation of rotating sector data.

A modification of the kinetic analysis normally used in the rotating sector method (in which product formation rate is proportional to the average concentration of the rate controlling transient) was necessary, since the concentration of measurable products here is at steady state. The analysis involves the overall mechanism for the water radiolysis. The experimental quantity, $[H_2O_2]_{ss}/[H_2O_2]_b$, is a complex function of (a) τ and the off/on ratio, (b) the beam intensity, (c) the relative rate and, hence, rate constants of the individual reactions, (d) the ratio $[O_2]/[H_2O_2]$ under steady beam conditions and, (e) the yield of OH and of H_2. The function is solved by trial and error by fitting to a curve of $H_2O_{2ss}/[H_2O_2]_b$ versus $k_2[H_2O_2]_b$ τ from which the value for k_2 is found. Notwithstanding the complexity of the function used, the uncertainty in k_7 is only ± 10 percent. Since $k_2/k_7^{\frac{1}{2}}$ is also obtained in this experiment, a relative value for the recombination rate constant is determined. The reader is referred to the original papers for the detailed interpretation of the data.

Chapter III. References

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Chapter IV. Physical Properties and Chemical Equilibrium

Those physical properties of the hydroxyl radical in water which pertain most directly to its chemical reactivity are the pK for its ionic dissociation, which has been accurately determined, and its diffusion coefficient, which has been estimated. Several other properties, such as the optical absorption spectrum, electron paramagnetic resonance absorption spectrum, and electron affinity which are also known, are given here.

The hydroxyl radical is a neutral free radical. The determination that it bears zero charge when formed in water radiolysis was made in two ways, by comparison of the reactivity [1] of OH produced in radiolysis with that produced photochemically and by the use of tests of the kinetic salt effect [2]. In the former, the chemical behavior of photolytic and radiolytic OH was shown to be the same; in the latter experiments the absence of any kinetic salt effect showed that the oxidizing species in water radiolysis bore zero charge. This conclusion was an important step in identifying the species as OH. The formation of hydroxyl radicals in irradiated ice and in various irradiated hydrated crystals, has also been shown [3, 4] from its ESR spectrum at 4.2 K and 77 K. This spectrum consists of an asymmetric doublet in accord with the interaction of the unpaired electron with the hydrogen atom. The isotropic hyperfine splitting in ice was -26.3 Oe compared with -26.7 Oe in the vapor phase [5] and a calculated value [6] of -24.2 Oe. This observation of OH in irradiated ice further supports the conclusion that it is formed in water, but to the best of our knowledge, the ESR spectrum has not been observed in the liquid phase, very likely because of the low steady state concentration and short lifetime.

The electron affinity of the hydroxyl radical in the gas phase does not appear to be known accurately, and experimental estimates cover a substantial range. A value [7, 8] of about 2 eV or slightly higher, seems to be correct. The heat of hydration of the hydroxide ion is estimated [9] to be about 88 kcal/mol. The sum of this value and the electron affinity of OH in the gas phase would then place the electron affinity of OH in water at about 5.8 eV.

The hydroxyl radical behaves like a weak acid, undergoing ionic dissociation in strongly basic solution:

$$OH + OH^- \rightleftharpoons O^- + H_2O. \qquad (1)$$
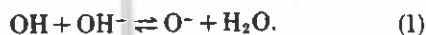
The pK for this equilibrium is 11.9 ± 0.2. Since O^-, the basic form of the hydroxyl radical, exhibits substantially different chemical reactivity than the more familiar form, OH, we may expect the apparent reactivity of the hydroxyl radical to show a marked pH-dependence in the region of pH from about 10.5 to 13.

This difference in reactivity was, in fact, used [10] to determine the pK in the following way. The reactivity of OH with ferrocyanide is much greater that that of O^-.

$$OH + [Fe(CN)_6]^{4-} = OH^- + [Fe(CN)_6]^{3-}, \qquad (2)$$

$$O^- + [Fe(CN)_6]^{4-} \overset{H_2O}{=} 2 OH^- + [Fe(CN)_6]^{3-}. \qquad (3)$$
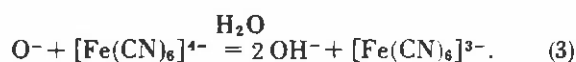
This rate of formation of ferricyanide ion was observed by pulse radiolysis as a function of pH in the appropriate range. With $k_2 \gg k_3$, the following equation holds:

$$\log (k_2/k - 1) = pH - pK \qquad (4)$$

where k is the apparent rate constant for reaction of both OH and O^-. The data gave $pK = 11.9 \pm 0.2$. This was also confirmed in later experiments in which the reactivity of hydroxyl with carbonate ion was studied [11], which gave $pK = 11.8 \pm 0.2$ and with thiocyanate ion [12] which gave $pK = 11.9 \pm 0.15$.

The reverse of (1), the reaction of O^- to form OH, involves a water molecule rather than the hydronium ion which is present in very low concentration at such high pH.

The reactions of OH and of O^- are listed in separate chapters in this compendium, where the difference in reactivities may be readily compared. These differences in reactivity with compounds such as oxygen and aromatic molecules are so large as to be qualitative.

The hydroxyl radical in water appears to show a weak optical absorption in the far ultraviolet, which has been recorded in pulse radiolysis studies [13–15]. In the gas phase, OH exhibits a series of fairly strong absorption bands [16] at 280 to 306 nm. In water, a weak absorption, which is thought to be that of the hydroxyl radical, is seen, starting at about 300 nm and increasing at shorter wavelengths to 200 nm, the limit of measurements made. This absorption, which seems to be continuous, is shown in figure 2 in which data from two groups of investigators is included. If any fine structure existed, it would not likely be seen in such spectrophotometric measurements with a relatively large band pass. The identification of this absorption with OH is based upon two observations:

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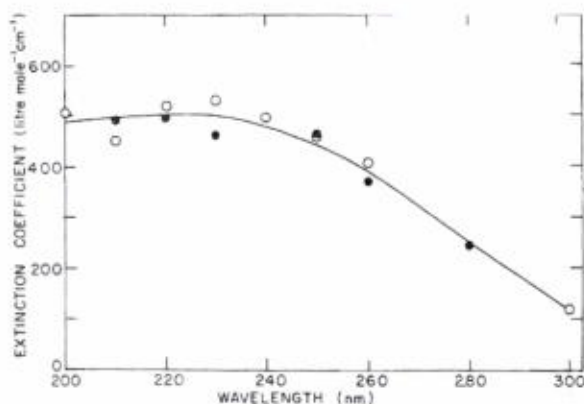
FIGURE 2. *The absorption spectrum attributed to the hydroxyl radical in water obtained by pulse radiolysis of aqueous solutions containing either N_2O or H_2O_2 to scavenge the hydrated electron.*

The molar extinction coefficient is plotted against wavelength. ○ Data from reference [15], chapter IV, in which the solution contains 2 mM N_2O, and the absorption is corrected for H_2O_2, H and OH^-. ● Data from reference [13], chapter IV, in which the solution contains either 1 mM N_2O or 0.2 mM H_2O_2, and the absorption is corrected for H_2O_2.

(1) with N_2O present, the optical density is doubled in accord with the conversion of e_{aq}^- to OH and, (2) the decay kinetics of the absorption in this system in which $[OH]_0/[H]_0 \cong 10$, and there are, ostensibly, no other radicals present, gives values for k_{OH+OH} and k_{OH+H_2} in quite good agreement with the values obtained by other methods. Molar extinction coefficients of 370 M^{-1} cm^{-1} at 260 nm [13] and 530 M^{-1} cm^{-1} at 230 nm [15], in fairly good agreement, have been reported from the two laboratories. The suggestion has been made [15] that this absorption is a red-shift of the water continuum resulting from a partial electron transfer from the first excited singlet state of water to a neighboring OH radical.

It should be understood that experiments in this spectral region, involving as they do a weakly absorbing transient, are difficult and complex in that there are overlapping absorptions from species such as H, OH^-, and H_2O_2. However, appropriate corrections [15] have been made and the agreement in the observation lends confidence to the validity of the assignment. The existence of the absorption maximum reported [15], does, however, depend upon the optical density measurement at a single wavelength. A somewhat similar absorption thought to be that of O^- has been observed [17] in strongly basic solution, but no definitive evidence for the assignment has been obtained.

The diffusion coefficient of the hydroxyl radical in water was estimated [18] from the value determined for the rate constant of the reaction of hydroxyl radical with catalase, which is 8.3×10^{10} M^{-1} s^{-1} at 25 °C. The diffusion coefficient was obtained from this value and from the Smoluchowski [19] equation on the assumption that the reac-

tion was diffusion-controlled and that the catalase was stationary, with OH being the only diffusing partner. With the reasonable approximation that the sum of the radii of interaction is equal to the molecular radius of the catalase molecule, a value of 2.3×10^{-5} cm^2 s^{-1} at 25 °C was estimated for the diffusion coefficient. The assumption is also inherent in taking the rate constant to be diffusion-controlled, that no factor of geometry is involved in the value for the specific rate. If this were not the case, the value determined would then represent a lower limit for the diffusion coefficient of OH.

Table 1 summarizes these physical properties of OH.

TABLE 1. *Physical properties of OH in water*

Optical absorption	at $\lambda \leq 300$ nm
Molar extinction coefficient	$\begin{cases} \epsilon^{260} = 370 \ M^{-1} \ cm^{-1} \\ \epsilon^{230} = 530 \ M^{-1} \ cm^{-1} \end{cases}$
pK	11.9 ± 0.2
Diffusion coefficient	2.3×10^{-5} cm^2 s^{-1}
ESR spectrum (ice)	Doublet
Electron affinity (gas phase)	2 eV
Electron affinity (aqueous-calc.)	5.8 eV
Heat of ionization[20]	0.44 eV

Chapter IV. References

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TABLE 2. *Addition reactions*

Reactant	$k(M^{-1} s^{-1})$	$T(°C)$	pH	Ref.	Method	Comments
acetanilide	5.0×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH + PNDA} = 1.25 \times 10^{10}$
acetophenone	$\dagger^*(6.5 \pm 0.7) \times 10^9$	RT	7	[8]	PR prod. form.	Absolute. N_2O added. H-corr.
	4.8×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH + PNDA} = 1.25 \times 10^{10}$
	5.2×10^9	RT		[17]	PR comp. with ferrocyan	Rel. to $k_{OH + ferrocyan.} = 9.3 \times 10^9$
	$^*5.4 \times 10^9$	RT		[17]	PR prod. form.	Absolute. N_2O added
acrylamide	$(3.3 \pm 0.6) \times 10^9$	18–25	10.7	[10]	S irrad. $^{14}CO_2$ form. from benzoic acid	Rel. to $k_{OH + benzoate} = 5.6 \times 10^9$ with ratio $= 0.59$, e_{aq}^- scav. by O_2
	$(3.3 \pm 0.8) \times 10^9$	20 ± 3	6	[11]	PR comp. with OH + CNS$^-$	Rel. to $k_{thiocyan}^{rel} = 1.1 \times 10^{10}$
	4.7×10^9	RT		[17]	PR comp. with ferrocyan	Rel. to $k_{OH + ferrocyan.} = 9.3 \times 10^9$
	$^*6.8 \times 10^9$	RT		[17]	PR prod. form.	Absolute. N_2O added
aniline	$(6.9 \pm 0.9) \times 10^9$	18–25	10.7	[10]	S irrad. $^{14}CO_2$ form. from benzoic acid	Rel. to $k_{OH + benzoate} = 5.6 \times 10^9$ with ratio $= 1.24$, e_{aq}^- scav. by O_2
	8.9×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH + PNDA} = 1.25 \times 10^{10}$
N,N-dimethyl aniline	8.9×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH + PNDA} = 1.25 \times 10^{10}$
anisole	$\dagger^*(1.2 \pm 0.3) \times 10^{10}$	RT	7	[8]	PR prod. form.	Absolute. N_2O added. H-corr.
	6.0×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH + PNDA} = 1.25 \times 10^{10}$
benzamide	4.4×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH + PNDA} = 1.25 \times 10^{10}$
benzene	$\dagger^*(7.8 \pm 1.1) \times 10^9$	RT	7	[8]	PR prod. form.	Absolute. N_2O added. H-corr.
	$(6.7 \pm 0.7) \times 10^9$	18–25	10.5	[10]	S irrad. $^{14}CO_2$ form. from benzoic acid	Rel. to $k_{OH + benzoate} = 5.6 \times 10^9$ with ratio $= 1.2$. e_{aq}^- scav. by O_2
	$(4.7 \pm 0.8) \times 10^9$	18–25	3	[10]	S irrad. $^{14}CO_2$ form. from benzoic acid	Rel. to $k_{OH + benzoic} = 4.3 \times 10^9$ with ratio $= 1.1$
	$^*(3.3 \pm 0.8) \times 10^9$	25	3	[12]	PR prod. form.	Absolute. No H-scav. used, $\therefore$ conc. H-addit.
	3.2×10^9	RT	7	[13]	PR comp. with I_2^- form.	Rel. to k_{OH+I^-} with ratio $= 0.31$, but doubtful since $I + I^-$ may be rate limiting.
	5.0×10^9	RT	6–7	[14]	PR comp. with OH + CNS$^-$	Rel. to $k_{thiocyan}^{rel} = 1.1 \times 10^{10}$ with ratio $= 0.45$
	$(4.8 \pm 0.5) \times 10^9$	RT	2.0–2.2	[15]	PR comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$ with ratio $= 1.02$
	$(4.3 \pm 0.9) \times 10^9$	23	neut.	[1]	PR prod. form.	Absolute. No H-scav. used, but may be trace O_2 present.
	$\dagger(7.6 \pm 1.9) \times 10^9$	RT	neut.	[16]	PR comp. with PNBA$^-$ ion	Rel. to $k_{OH + PNBA} = 2.6 \times 10^9$ e_{aq}^- removed by scav.
benzene-d_6	$(4.7 \pm 0.9) \times 10^9$	23	neut.	[1]	PR prod. form.	Absolute. No H-scav. used, but may be trace O_2 present.
benzene-sulfonamide	2.8×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH + PNDA} = 1.25 \times 10^{10}$ or $k_{OH + C_3H_7OH} = 1.85 \times 10^9$
benzene-sulfonate ion	3.0×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH + PNDA} = 1.25 \times 10^{10}$
	$\dagger^*(4.7 \pm 0.6) \times 10^9$	RT	7	[8]	PR prod. form.	Absolute. N_2O added. H-corr.

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TABLE 2. *Addition reactions*—Continued

Reactant	$k(M^{-1}\,s^{-1})$	$T(°C)$	pH	Ref.	Method	Comments
benzoate ion	4.2×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	†*$(6.0 \pm 0.7) \times 10^9$	RT	6–9.4	[8]	PR prod. form.	Absolute. N_2O added. H-corr.
	†*$(5.7 \pm 0.2) \times 10^9$	RT		[17]	PR prod. form.	Absolute. N_2O added. No H-corr.
	5.5×10^9	RT	6–7	[14]	PR comp. with OH + CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	5.4×10^9	RT		[17]	PR comp. with ferrocyan.	Rel. to $k_{OH+ferrocyan.} = 9.3 \times 10^9$
p-aminobenzoate ion	7.9×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
p-bromobenzoate ion	3.1×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
p-chlorobenzoate ion	†*$(5.0 \pm 0.8) \times 10^9$	RT	6–9.4	[8]	PR prod. form.	Absolute. N_2O added. H-corr.
	3.2×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
p-fluorobenzoate ion	3.5×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
p-hydroxy-benzoate ion	*$(9 \pm 2) \times 10^9$	RT	7	[8]	PR prod. form.	Absolute. N_2O added. H-corr.
	5.4×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
p-methoxy-benzoate ion (anisate ion)	5.0×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
p-methylbenzoate ion (4-toluate ion)	4.4×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
p-nitrobenzoate ion	†*$(2.6 \pm 0.4) \times 10^9$	RT	6–9.4	[8]	PR prod. form.	Absolute. N_2O added. H-corr.
	2.0×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
benzoic acid	†*$(4.3 \pm 0.8) \times 10^9$	25	3	[3]	PR prod. form.	Absolute. N_2O added. H-corr.
	*$(2.1 \pm 0.3) \times 10^9$	25	3	[12]	PR prod. form.	Absolute. No H-scav. used .: conc. H-addit.
	$(5.6 \pm 1.1) \times 10^9$	18–25	3	[10]	S irrad. ¹⁴CO_2 form. from benzoic acid.	Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$ with ratio = 1.0, e_{aq}^- scav. by O_2
benzonitrile	†*$(4.9 \pm 0.6) \times 10^9$	RT	neut.	[8]	PR prod. form.	Absolute. N_2O-added. H-corr.
	3.3×10^9	18–25	10.7	[10]	S irrad. ¹⁴CO_2 form. from benzoic acid	Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$ with ratio = 0.59, e_{aq}^- scav. by O_2
	3.6×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	*8.5×10^9	RT	6.3	[39]	PR prod. form.	Absolute. N_2O added. No corr. H-atom
benzyl alcohol	*$(8.4 \pm 1.2) \times 10^9$	RT	neut.	[8]	PR prod. form.	Absolute. N_2O-added. H-corr.
carbon monoxide	5.4×10^6	25	7	[18]	Phot. H_2O_2 sol.	Rel. to $k_{OH+H_2O_2} = 4.5 \times 10^7$
	7.1×10^6	20–25	1	[19]	Fenton's reagent comp.	Rel. to $k_{OH+Fe^{2+}} = 3.3 \times 10^8$ with ratio = 2.14
carbon dioxide	$< 10^6$	RT	neut.	[20]	PR prod. form.	Absence of transient prod. sets limit
chlorobenzene	$(6.2 \pm 0.7) \times 10^9$	18–25	10.7	[10]	S irrad. ¹⁴CO_2 form. from benzoic acid	Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$ with ratio = 1.1, e_{aq}^- scav. by O_2
1,3-cyclohexadiene	†$(9.8 \pm 2.5) \times 10^9$	RT	neut.	[16]	PR comp. with PNBA⁻ ion	Rel. to $k_{OH+PNBA} = 2.6 \times 10^9$ e_{aq}^- removed by scav. H abstraction amounts to 30 percent

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TABLE 2. *Addition reactions — Continued*

Reactant	$k(M^{-1} s^{-1})$	$T(°C)$	pH	Ref.	Method	Comments
1,4-cyclohexadiene	†$(7.7 \pm 1.9) \times 10^9$	RT	neut.	[16]	PR comp. with PNBA⁻ ion	Rel. to $k_{OH+PNBA^-} = 2.6 \times 10^9$ e_{aq}^- removed by scav. H-abstraction amounts to 45 percent
cyclohexene	$(8.8 \pm 2.2) \times 10^9$	RT	neut.	[16]	PR comp. with PNBA⁻ ion	Rel. to $k_{OH+PNBA^-} = 2.6 \times 10^9$ e_{aq}^- removed by scav.
dimethylsulfoxide	7.1×10^9	RT	neut.	[20]	PR comp. with OH + CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
dimethylthioether	8.7×10^9	RT	neut.	[20]	PR comp. with OH + methanol	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$ with ratio = 0.79, as secondary standard
dioxane	2.4×10^9	RT	7	[13]	PR comp. with I_2^- form.	Rel. to k_{OH+I^-} with ratio = 0.23, but doubtful since $I + I^-$ may be rate limiting
	1.7×10^9	RT	2.0–2.2	[15]	PR comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$ with ratio = 0.37
ethylene	1.8×10^9	RT	neut. and acid	[21] [22]	PR comp. with OH + CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$ Calc. although details not given
p-hydroxynitro-benzene (p-nitro-phenol)	†*$(3.8 \pm 0.6) \times 10^9$	RT	1.3	[23]	PR prod. form.	Absolute. N_2O added. Evidence indicates reac. is not addition, but with nitro group
hydroquinone	2.1×10^{10}	RT	6–7	[14]	PR comp. with OH + CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
nitrobenzene	†*$(3.2 \pm 0.4) \times 10^9$	RT	neut.	[8]	PR prod. form.	Absolute. N_2O added. H-corr.
	3.4×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	2.2×10^9	18–25	10.5	[10]	S irrad. ¹⁴CO₂ form. from benzoic acid	Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$ with ratio = 0.39. e_{aq}^- scav. by O_2
	†*$(4.7 \pm 0.5) \times 10^9$	RT	1	[5]	PR prod. form.	Absolute. O_2 to scav. e_{aq}^-
nitromethane	$< 9 \times 10^8$	*RT	neut.	[24]	PR comp. with OH + CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$ Upper limit only
nitromethane anion	†*$(8.5 \pm 1.5) \times 10^9$	RT	neut.	[25]	PR prod. form.	Absolute. Addit. reac. with anionic form of molecule
nitrosobenzene	1.9×10^{10}	RT	neut.	[26]	PR comp. with OH + CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$ Reac. is not addit. to ring, but nitroso group
p-nitroso-N,N-di-methylaniline	1.25×10^{10}	22–25	9	[27]	S irrad. using PNDA bleaching	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$ with ratio = 6.8
	*1.8×10^{10}	RT	9	[28]	PR of PNDA bleaching	Absolute. N_2O added. Authors question use of PNDA as ref. reac.
	†*1.25×10^{10}	RT	neut.	[29]	PR prod. form.	Absolute. N_2O added. No H-corr. Low pulse intensity recommended
phenate ion	9.1×10^9	18–25	10.7	[10]	S irrad. ¹⁴CO₂ form. from benzoic acid	Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$ with ratio = 1.62. e_{aq}^- scav. by O_2

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TABLE 2. *Addition reactions*—Continued

Reactant	$k(M^{-1} s^{-1})$	$T(°C)$	pH	Ref.	Method	Comments
phenol	†*$(1.4 \pm 0.3) \times 10^{10}$	19–23	7.4–7.7	[4]	PR prod. form.	Absolute. N_2O added. No corr. for H-addit.
	8.6×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	6.0×10^9	18–25		[10]	S irrad. $^{14}CO_2$ form. from benzoic acid	Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$ with ratio = 1.08, e_{aq}^- scav. by O_2
	1.8×10^{10}	RT	6–7	[14]	PR comp. with OH+CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$ with ratio = 1.6
β-phenylacetate (2-phenylethanoate)	†*$(7.9 \pm 1.1) \times 10^9$	RT	6–8	[8]	PR prod. form.	Absolute. N_2O added. H-corr.
	4.4×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
phenylacetate	5.0×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
phenylhydroxylamine	†*1.5×10^{10}	RT	3.7–11.5	[30]	PR prod. form.	Absolute. N_2O added. No H corr.
	2.0×10^{10}	RT		[30]	PR comp. with OH+CNS⁻	Rel to $k_{thiocyan}^{rel.} = 1.1 \times 10^{10}$
pyridine	$(3.1 \pm 0.6) \times 10^9$	RT	neut.	[31]	PR comp. with OH+CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	*1.8×10^9	21	7	[33]	PR prod. form.	Absolute. N_2O added. No H-corr.
pyridinium ion	$(3.4 \pm 0.6) \times 10^7$	RT	1	[31]	PR comp. with OH+CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
2,2'-dipyridyl	*6.2×10^9	21	9.3	[33]	PR prod. form.	Absolute. N_2O added. No. H-corr.
4,4'-dipyridyl	*5.3×10^9	21	9.3	[33]	PR prod. form.	Absolute. N_2O added. No H-corr.
salicylate ion	5.6×10^9	18–25	10.7	[10]	S irrad. $^{14}CO_2$ form. from benzoic acid	Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$ with ratio = 1.0, e_{aq}^- scav. by O_2
	†*1.2×10^{10}	RT	7	[32]	PR prod. form.	Absolute. N_2O added. H-corr.
	$(2.0 \pm 0.2) \times 10^{10}$	RT	7	[32]	PR comp. with OH+CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$(9.4 \pm 0.1) \times 10^9$	22–25	9	[27]	S irrad. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
terephthalate ion	3.2×10^9	25	9	[7]	S irrad. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
toluene	*$(3.0 \pm 0.7) \times 10^9$	25	3	[12]	PR prod. form.	Absolute. No H-scav. used. ∴ conc. H-addit

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Chapter V. References

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Chapter VI. Hydrogen Abstraction Reactions

Fully saturated organic compounds and many unsaturated molecules such as aldehydes and ketones react with hydroxyl radicals by simple hydrogen abstraction to form water and a carbon radical

$$RH + OH = R \cdot + H_2O \tag{1}$$
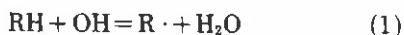
In some cases, however, the possibility exists that the detailed mechanism of reaction involves, initially, electron abstraction to form a cationic species which then rapidly deprotonates

$$RH + OH = RH^+ + OH^- \tag{2}$$

$$RH^+ = R \cdot + H^+ \tag{3}$$
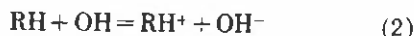
Since OH is a strong electrophile, rate constants for hydrogen abstraction are, in general, particularly sensitive to the influence of inductive effects in the structure. In addition to effects on the overall reaction rate, such effects influence the actual site of the hydrogen abstraction process. This is well illustrated by the data for mono- and polyhydric alcohols given in table 3 of this chapter.

For the primary straight chain alcohols, the rate constants increase progressively from $8 \times 10^8 \ M^{-1}s^{-1}$ for methanol to about $5-6 \times 10^9$ for alcohols containing five or more carbon atoms. This latter value probably represents a diffusion-controlled limit for reactions of these compounds. The trend undoubtedly illustrates the effect of the inductive effect of the aliphatic carbon chain on the electron density at the α-carbon atom, although there is evidence that OH attack becomes multifocal as the chain length increases [1, 2]. Information from experiments where OH is generated either by pulse radiolysis or by photolysis of hydrogen peroxide indicates that the proportion of α-carbon attack decreases from 100 percent in methanol to 37 percent in normal butanol. However, as might be expected, chain branching increases the probability of reaction at this position. In isopropanol, about 95 percent of OH radicals react at the α-carbon atom compared with only 66 percent in normal propanol. In the polyhydric alcohols, the effect of carbon chain length on the overall reactivity is less evident.

In the carboxylic acids (tables 4 and 5), the OH reactivities are generally lower than those for the alcohols. Further, there is a pronounced effect of pH on the rate constants, the values for the anions being usually greater than those for the unionized structures. It would be expected that resonance stabilization in the carboxyl group would tend to hinder OH attack at this group and if, therefore, the β, or more distant, carbon atoms were the only available reaction sites, it is not surprising that the rate constants are lower than those for the corresponding alcohols. Formic acid is an exception since an α-hydrogen is available in this molecule and is, therefore, more reactive than acetic acid. Substitution of an OH group in the α-position has a marked effect on reactivity due to the effect on the electron density at this site. Lactic acid is about 20–25 times more reactive than acetic acid. The effect of halide substitution at this position is less, although it is still evident.

Data for carboxylic esters (table 6) are more limited, although where multiple determinations are available, e.g., methyl acetate, the agreement is good. As might be expected the overall reactivities of the esters lie between those of the aliphatic alcohols and acids from which they are derived. It can be seen that trends exist in the data. For a given ester group, the rate constants increase with chain length in the acid stem, e.g. butyrate > propionate > acetate. As has been pointed out [3] ethyl formate is an exception to the trend, although, in this instance, the reactivity is increased considerably by the presence of the α-hydrogen atom. For the various acetates, the rate constants also increase with chain length, the value for the n-propyl derivative is an order of magnitude greater than that for methyl acetate.

Electrophilic attack by OH on the carbonyl group is most unlikely in these esters. Although it is difficult to draw definite conclusions as to the site of attack, the apparent effect on the rate constants of the chain lengths of both the acid and the ester stems suggests that both regions of the molecules are reaction sites. This aspect has been discussed in more detail elsewhere [3].

In the ethers (table 7), where the results of several determinations are available, the agreement is generally good. As would be expected, the data for both diethyl ether and dioxan indicate that the OH reactivities of ethers are generally unaffected by variation in pH.

Rate constants for reactions of OH with miscellaneous carbonyl compounds are given in table 8. Understandably, acetone is the ketone for which the most data are available. The agreement between the values obtained by relative methods using five different reference solutions is clearly excellent, the overall spread between the separate mean values being less than 10 percent. As is the case with the alcohols and esters, the increasing influence of the inductive effect of the alkyl group is again evident in the four simple monoketones. However, the value for acetone seems abnormally low, since the increase from acetone to methylethyl ketone is

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much greater than that observed in the corresponding alcohols. This may be due to the greater influence in acetone of keto-enol tautomerization.

Aldehydes appear to be more reactive, as might be expected, since, in solutions, these compounds have some gem-diol character which should increase the electron availability at the α-carbon atom.

The effect of miscellaneous substitutents is indicated in table 9.

Table 10 contains rate data for miscellaneous nitrogen compounds. Information on amino compounds is scarce. However, there has been a systematic study of aliphatic amides [4], which has shown that, in general, these compounds are very reactive. The compound, $CH_3CO\ N(CH_3)CH_2CH_2N(CH_3)CO\ CH_3$ has been isolated from irradiated acetamide solution [4] showing that the principle site of OH attack on this molecule occurs at an N-methyl group.

TABLE 3. *Aliphatic alcohols*

Reactant	$k(M^{-1}\ s^{-1})$	pH	Ref.	Method	Comments
methanol	7.35×10^8	2.0	[3]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	$(7.6 \pm 0.5) \times 10^8$	2.0	[5]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	8.6×10^8	6	[6]	S irrad. comp. with Br⁻	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	4.7×10^8	neut.	[7]	PR comp. with I⁻	Rel. to $k_{OH+I} = 1.02 \times 10^{10}$ (uncertain)
	†8.0×10^8	neut.	[8]	PR comp. with benzoate	Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$
	†8.3×10^8	neut.	[8]	PR comp with phenylacetic acid	Rel. to $k_{OH+PA} = 7.9 \times 10^9$
	†8.4×10^8	neut.	[8]	PR comp. with pNO₂ benzoate	Rel. to $k_{OH+PNBA} = 2.6 \times 10^9$
	8.02×10^8	7.0	[3]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	†9×10^8	neut.	[9]	PR comp. with Cu²⁺	Rel. to $k_{OH+Cu^{2+}} = 3.5 \times 10^8$
	†8.6×10^8	neut.	[10]	PR comp. with ferro cyanide	Rel. to $k_{OH+ferrocyan.} = 9.3 \times 10^9$
	1.08×10^9	9	[11]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	1.00×10^9	9	[12]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	8.6×10^8	6	[6]	S irrad. comp. with Br⁻	Rel. to $k_{OH+ethanol} = 1.85 \times 10^9$
	9.5×10^8	10.5	[13]	S irrad. comp. with benzoate	Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$
methanol-d_3	4.2×10^8	6	[6]	S irrad. comp. with BR⁻	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
ethanol	1.64×10^9	2	[3]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	$(1.75 \pm 0.15) \times 10^9$	2	[5]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	$(1.7 \pm 0.2) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	7.2×10^8	neut.	[7]	PR comp. with I⁻	Rel. to $k_{OH+I} = 1.02 \times 10^{10}$
	1.59×10^9	3	[13]	S irrad. comp. with benzoate	Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$
	$(1.55 \pm 0.2) \times 10^9$	5	[14]	S. irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	1.15×10^9	6.6–10.5	[15]	S irrad. comp. with ferrocyan.	Rel. to $k_{OH+ferrocyan} = 9.3 \times 10^9$
	1.8×10^9	7	[3]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	1.8×10^9	7	[16]	PR comp. with H₂O₂	Rel. to $k_{OH+H_2O_2} = 4.5 \times 10^7$
	†1.73×10^9	neut.	[8]	PR comp. with benzoate	Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$
	†1.83×10^9	neut.	[8]	PR comp. with phenylacetic acid	Rel. to $k_{OH+phenyl.A} = 7.9 \times 10^9$
	†1.81×10^9	neut.	[8]	PR comp. with pNO₂ benzoate	Rel. to $k_{OH+PNBA} = 2.6 \times 10^9$
	†1.85×10^9	neut.	[10]	PR comp. with ferrocyan	Rel. to $k_{OH+ferrocyan.} = 9.3 \times 10^9$
	†1.8×10^9	neut.	[9]	PR comp. with Cu²⁺	Rel. to $k_{OH+Cu^{2+}} = 3.5 \times 10^8$
	$(1.82 \pm 0.1) \times 10^9$	9	[11]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	1.54×10^9	10.5	[13]	S irrad. comp. with benzoate	Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$
ethanol d_3	1.14×10^9	6	[6]	S irrad. comp. with Br⁻	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
β-bromoethanol	7.7×10^8	9	[17]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
β-chloroethanol	9.2×10^8	9	[17]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
2-ethoxyethanol	1.68×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
n-propanol	$(2.8 \pm 0.3) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	$(2.6 \pm 0.3) \times 10^9$	5	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	2.45×10^9	7	[3]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	†2.7×10^9	neut.	[10]	PR comp. with ferrocyan.	Rel. to $k_{OH+ferrocyan.} = 9.3 \times 10^9$
	2.72×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$

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TABLE 3. *Aliphatic alcohols* — Continued

Reactant	$k(M^{-1} s^{-1})$	pH	Ref.	Method	Comments
isopropanol	$(1.82 \pm 0.15) \times 10^9$	2	[5]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	2.2×10^9	6	[6]	S. irrad. comp. with Br^-	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	$(2.0 \pm 0.2) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	$(2.0 \pm 0.2) \times 10^9$	5	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	1.74×10^9	neut.	[7]	PR comp. with I^-	Rel. to $k_{OH+I^-} = 1.02 \times 10^{10}$
	†2.01×10^9	neut.	[10]	PR comp. with ferrocyan	Rel. to $k_{OH+ferrocyan} = 9.3 \times 10^9$
	$(2.13 \pm 0.1) \times 10^9$	9	[11]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	2.0×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	1.84×10^9	?	[18]	PR comp. with CNS^-	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
αD isopropanol	1.44×10^9	6	[6]	S irrad. comp. with Br^-	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
n-butanol	$(4.0 \pm 0.4) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	$(4.0 \pm 0.4) \times 10^9$	5	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	†4.0×10^9	neut.	[10]	PR comp. with ferrocyan.	Rel. to $k_{OH+ferrocyan.} = 9.3 \times 10^9$
	3.7×10^9	7	[3]	PR comp. with CNS^-	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	3.7×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
isobutanol	$(3.3 \pm 0.3) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	3.3×10^9	7	[3]	PR comp. with CNS^-	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	3.5×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
secondary butanol	$(2.3 \pm 0.25) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	3.1×10^9	7	[3]	PR comp. with CNS^-	Rel. to $k^{rel.}_{thiocyan.}$ 1.1×10^{10}
	2.4×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
t-butanol	$(6.3 \pm 0.7) \times 10^8$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	†5.2×10^8	neut.	[10]	PR comp. with ferrocyan.	Rel. to $k_{OH+ferrocyan} = 9.3 \times 10^9$
	4.2×10^8	7	[3]	PR comp. with CNS^-	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	4.7×10^8	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
n-amyl-alcohol	4.7×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
t-amyl-alcohol	1.8×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
n-pentanol	$(4.5 \pm 0.5) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	$(4.8 \pm 0.5) \times 10^9$	5	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
n-hexanol	5.2×10^9	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
n-heptanol	$(5.4 \pm 0.5) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
n-octanol	$(5.6 \pm 0.7) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
allyl-alcohol	1.97×10^9	7	[3]	PR comp. with CNS^-	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
ethylene glycol	$(1.5 \pm 0.15) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	1.14×10^9	6	[6]	S irrad. comp. with Br^-	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	1.44×10^9	7	[3]	PR comp. with CNS^-	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	†1.47×10^9	neut.	[10]	PR comp. with ferrocyan.	Rel. to $k_{OH+ferrocyan.} = 9.3 \times 10^9$
	1.51×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
1,2-propanediol	$(1.6 \pm 0.15) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	1.58×10^9	6	[6]	S irrad. comp. with Br^-	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	1.68×10^9	7	[3]	PR comp. with CNS^-	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	1.66×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$

TABLE 3. *Aliphatic alcohols*—Continued

Reactant	$k(M^{-1} s^{-1})$	pH	Ref.	Method	Comments
1,3-propanediol	2.9×10^9	6	[6]	S irrad. comp. with Br$^-$	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	2.4×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
diethylene glycol	2.0×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
glycerol	$(1.64 \pm 0.16) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	1.59×10^9	7	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$\dagger 1.9 \times 10^9$	neut.	[10]	PR comp. with ferrocyan	Rel. to $k_{OH+ferrocyan.} = 9.3 \times 10^9$
	2.04×10^9	9	[11]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	1.85×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
1,3-butane-diol	2.2×10^9	7	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	2.3×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
2,3-butane-diol	1.35×10^9	7	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
1,4-butane-diol	3.2×10^9	7	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	3.0×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
erythritol	2.0×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
pentaerythritol	3.2×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
ribose	2.1×10^9	9	[19]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
D-glucose	$(1.9 \pm 0.15) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
ascorbic acid	1.2×10^{10}	1	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
sucrose	2.4×10^9	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$

TABLE 4. *Saturated aliphatic acids* – (Monobasic)

Reactant	$k(M^{-1} s^{-1})$	pH	Ref.	Method	Comments
Formic acid	1.36×10^9	1.0	[7]	PR comp. with I$^-$	Rel. to $k_{OH+I^-} = 1.02 \times 10^{10}$
	1.25×10^8	1	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	1.53×10^8	acid	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$ (interpolated from pH curve)
	1.2×10^8	0.05 M H$_2$SO$_4$	[20]	S irrad. comp. with isopropanol	Rel. to $k_{OH+IP} = 2.0 \times 10^9$
	2.45×10^9	neut.	[7]	PR comp. with I$^-$	Rel. to $k_{OH+I^-} = 1.02 \times 10^{10}$
	4.2×10^7		[21]	S irrad. comp. with H$_2$O$_2$	Rel. to $k_{OH+H_2O_2} = 4.5 \times 10^7$
	3.1×10^9	neut.	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$ (interpolated from pH curve)
	2.7×10^9	7	[20]	S irrad. comp. with isopropanol	Rel. to $k_{OH+IP} = 2.0 \times 10^9$
	$\dagger 2.8 \times 10^9$	neut.	[10]	PR comp. with ferro	Rel. to $k_{OH+ferrocyan} = 9.3 \times 10^9$
	4.0×10^9	9	[11]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	3.5×10^9	10.7	[13]	S irrad. comp. with benzoate	Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$
	1.2×10^9	13	[20]	S irrad. comp. with isopropanol	Rel. to $k_{OH+IP} = 2.0 \times 10^9$

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TABLE 4. *Saturated aliphatic acids — (Monobasic) — Continued*

Reactant	$k(M^{-1}\,s^{-1})$	pH	Ref.	Method	Comments
acetic acid	2.3×10^7	1.0	[3]	PR comp. with CNS⁻	Rel. to $k_{\text{thiocyan}}^{\text{rel.}} = 1.1 \times 10^{10}$
	*$(9 \pm 0.4) \times 10^6$	1.0	[7]	PR disappearance of OH spectrum	Absolute
	1.4×10^7	1.0	[7]	PR comp. with I⁻	Rel. to $k_{OH+I^-} = 1.02 \times 10^{10}$
	2.0×10^7	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+\text{thymine}} = 4.7 \times 10^9$
	†7×10^7	neut.	[10]	PR comp. with ferrocyan.	Rel. to $k_{OH+\text{ferrocyan}} = 9.3 \times 10^9$
	†*8.5×10^7	neut.	[10]	PR prod. form.	Absolute measurement N_2O added No corr. for H reaction
	$(8.8 \pm 0.5) \times 10^7$	9	[11]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	7.2×10^7	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	6.2×10^7	10.7	[13]	S irrad. comp. with benzoate	Rel. to $k_{OH+\text{benzoate}} = 5.6 \times 10^9$
bromoacetic acid	4.4×10^7	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
chloracetic acid	4.3×10^7	1	[3]	PR comp. with CNS⁻	Rel. to $k_{\text{thiocyan}}^{\text{rel}} = 1.1 \times 10^{10}$
	$(7.0 \pm 0.7) \times 10^7$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+\text{thymine}} = 4.7 \times 10^9$
	5.5×10^7	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
fluor-acetic acid	3.0×10^7	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
methoxy-acetic acid	6.0×10^8	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
cyano-acetic acid	1.54×10^7	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
ethylene-diamine tetracetic acid	3.5×10^9	9	[19]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
trimethyl acetic acid	1.4×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^{10}$
propionic acid	$(4.6 \pm 0.5) \times 10^8$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH-\text{thymine}} = 4.7 \times 10^9$
	7.9×10^8	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
α-bromo-propionic acid	2.2×10^8	8.5	[17]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
pyruvic acid	3.2×10^7	9	[19]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
β-bromo propionic acid	2.3×10^8	8.5	[17]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
α-chloro-propionic acid	2.4×10^8	8.5	[17]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
β-chloro-propionic acid	3.2×10^8	8.5	[17]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$

TABLE 4. *Saturated aliphatic acids — (Monobasic) — Continued*

Reactant	$k(M^{-1} s^{-1})$	pH	Ref.	Method	Comments
n-butyric acid	$(1.64 \pm 0.2) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	1.85×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
iso butyric acid	1.26×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
cyclobutane carboxylic acid	3.02×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5 OH} = 1.85 \times 10^9$
α-amino-n-butyric acid	$(3.3 \pm 0.3) \times 10^8$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
β-amino-n-butyric acid	$(6.8 \pm 0.7) \times 10^7$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
γ-amino-n-butyric acid	$(1.9 \pm 0.2) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
2-methyl butyric acid	2.4×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
3-methyl butyric acid	2.2×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
3,3-dimethyl butyric acid	1.66×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
n-valeric acid	2.9×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
n-caproic acid	3.9×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
cyclo-pentane carboxylic acid	4.0×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
cyclo-hexane carboxylic acid	5.4×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$

TABLE 5. *Polybasic and hydroxy-carboxylic acids*

Reactant	$k(M^{-1} s^{-1})$	pH	Ref.	Method	Comments
oxalic acid	$(8 \pm 3) \times 10^6$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	1.03×10^7	7	[22]	S irrad. comp. with methanol and ethanol	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	$(8.4 \pm 1.5) \times 10^6$	9	[11]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
malonic acid	$(1.7 \pm 0.15) \times 10^7$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	3.0×10^8	6–7	[3]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	5.5×10^7	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
succinic acid	$(1.2 \pm 0.1) \times 10^8$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
glutaric acid	$(6.1 \pm 0.5) \times 10^8$	2	[14]	S. irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
adipic acid	$(1.5 \pm 0.15) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$

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TABLE 5. *Polybasic and hydroxy-carboxylic acids* – Continued

Reactant	$k(M^{-1} s^{-1})$	pH	Ref.	Method	Comments
pimelic acid	$(2.6 \pm 0.3) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
suberic acid	$(3.5 \pm 0.4) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
azelaic acid	$(4.0 \pm 0.5) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
sebacic acid	$(4.7 \pm 0.5) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
citric acid	5×10^7	1	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$(4.7 \pm 0.3) \times 10^8$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
glycolic acid	$(4 \pm 0.3) \times 10^8$	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	7.2×10^8	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
lactic acid	4.3×10^9	1	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$(5.6 \pm 0.5) \times 10^8$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
malic acid	$(4.7 \pm 0.5) \times 10^8$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
tartaric acid	$(5.2 \pm 0.5) \times 10^8$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	6.8×10^8	9	[19]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
tetrahydroxy-succinic acid	1.3×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
thioglycolic acid	6.0×10^9	1	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$

TABLE 6. *Aliphatic carboxylic esters*

Reactant	$k(M^{-1} s^{-1})$	pH	Ref.	Method	Comments
ethyl formate	3.8×10^8	6–7	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
methyl acetate	1.3×10^8	2	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	1.2×10^8	6–7	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	1.1×10^8	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
ethyl acetate	$(2.4 \pm 0.2) \times 10^8$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	4.0×10^8	6–7	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
isopropyl acetate	4.3×10^8	2	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	4.5×10^8	6–7	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
n-propyl acetate	1.4×10^9	6–7	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
methyl propionate	4.5×10^8	6–7	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
ethyl propionate	8.7×10^8	6–7	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
methyl butyrate	1.7×10^9	6–7	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
ethyl butyrate	1.6×10^9	6–7	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
diethyl malonate	6.5×10^8	6–7	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
diethyl succinate	7.8×10^8	6–7	[3]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$

TABLE 7. *Ethers*

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
diethyl ether	3.9×10^9	neut.	[7]	P comp. with I⁻	Rel. to $k_{OH+I^-} = 1.02 \times 10^{10}$
	1.36×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	$(2.4 \pm 0.2) \times 10^9$	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	2.3×10^9	0.05 M H₂SO₄	[20]	S irrad. comp. with isopropanol	Rel. to $k_{OH+IP} = 2.0 \times 10^9$
	2.4×10^9	7	[20]	S irrad. comp. with isopropanol	Rel. to $k_{OH+IP} = 2.0 \times 10^9$
	1.74×10^9	~13	[20]	S irrad. comp. with isopropanol	Rel. to $k_{OH+IP} = 2.0 \times 10^9$
dioxane	2.35×10^9	neut.	[7]	PR comp. with I⁻	Rel. to $k_{OH+I^-} = 1.02 \times 10^{10}$
	1.74×10^9	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	1.85×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
1,3,5-trioxane	4.9×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
tetrahydrofuran	2.7×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
2,3,6-trimethyl -1,3,5-trioxane (paraldehyde)	1.00×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
diethyleneglycol diethylether	3.2×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
diethoxyethane	2.2×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
ethyleneglycol monomethyl-ether	1.3×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
dimethoxy-ethane	1.56×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$

TABLE 8. *Carbonyl compounds*

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
formaldehyde	~2×10^9		[23]	PR comp. with H₂O₂	Rel. to $k_{OH+H_2O_2} = 4.5 \times 10^7$
acetone	6.6×10^7	2	[14]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^7$
	7.7×10^7	neut.	[7]	PR comp. with iodide	Rel. to $k_{OH+I^-} = 1.02 \times 10^{10}$
	9.7×10^7	6–7	[3]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	7.3×10^7	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	12×10^7	9	[10]	PR comp. with ferrocyan	Rel. to $k_{OH+ferrocyan} = 9.3 \times 10^9$
	~7×10^7	9	[19]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	$(9 \pm 4) \times 10^7$	10.7	[13]	S irrad. comp. with benzoate	Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$
acetoin	8.5×10^8	2	[3]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	1.5×10^9	neut.	[24]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
diacetyl	1.7×10^8	neut.	[24]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
butyraldehyde	3.5×10^9	2	[3]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
methylethyl ketone	9×10^8	6–7	[3]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
diethylketone	1.35×10^9	6–7	[3]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
methyl *n*-propyl ketone	1.9×10^9	6–7	[3]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$

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TABLE 9. *Substituted hydrocarbons*

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
methane	2.4×10^8	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
ethane	1.2×10^9	1.2	[25]	S irrad. comp. with formic acid	Rel. to $k_{OH+HCOOH} = 1.2 \times 10^8$
chloroform	1.4×10^7	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
cyanomethane	5.5×10^6	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
diethoxyethane	1.55×10^9	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
dimethoxyethane	5.7×10^8	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
nitromethane	3.1×10^8 †*$(8.5 \pm 1.5) \times 10^9$	9 10.5	[6] [26]	S irrad. comp. with PNDA PR prod. form.	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$ Absolute N$_2$O added. no correct. for H addit.

TABLE 10. *Nitrogen compounds*

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
methylamine	1.9×10^7 1.8×10^8 2.4×10^9 1.15×10^{10}	5 neut. 12 12	[69] [27] [6] [27]	S irrad. comp. with PNDA PR comp. with CNS⁻ S irrad. comp. with PNDA PR comp. with CNS⁻	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$ Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$ Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$ Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
ethylenediamine	1.0×10^9	5	[28]	S irrad. comp. with isopropanol	Rel. to $k_{OH+isopropanol} = 2.0 \times 10^9$
formamide	$< 5 \times 10^8$	5.5	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
acetamide	1.9×10^8 1.3×10^7	5.5 9	[29] [6]	PR comp. with CNS⁻ S irrad. comp. with PNDA	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$ Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
acrylamide	$(3.3 \pm 0.8) \times 10^9$ $(3.3 \pm 0.2) \times 10^9$	neut. 10.7	[30] [13]	PR comp. with CNS. S irrad. comp. with benzoate	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$ Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$
acetonitrile	3.5×10^6	9	[6]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
N-methylformamide	1.2×10^9	5.5	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
N-dimethylacetamide	1.7×10^9	5.5	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
N-methylacetamide	1.6×10^9	5.5	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
N-dimethylacetamide	3.5×10^9	5.5	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
dimethylacetamide	1.6×10^9	5–6	[4]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
trimethylacetamide	1.4×10^9	5–6	[4]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
N-methyldimethyl acetamide	1.9×10^9	5–6	[4]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
N-methyltrimethyl acetamide	2.4×10^9	5–6	[4]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$

TABLE 10. *Nitrogen compounds*—Continued

Reactant	$k\,(M^{-1}\mathrm{s}^{-})$	pH	Ref.	Method	Comments
N-dimethyl trimethyl acetamide	4.0×10^{9}	5–6	[4]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
N-tert. butylacetamide	1.1×10^{9}	5–6	[4]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
propionamide	7.0×10^{8}	5–6	[4]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
N-methyl propionamide	1.4×10^{9}	5–6	[4]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$

Chapter VI. References

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Chapter VII. Inorganic Electron Transfer Reactions

This chapter lists rate constants for reactions of OH with neutral and charged inorganic compounds. With few exceptions, reactions of this type involve simple electron transfer of OH to form the hydroxide ion with a corresponding change in the valency state of the donor.
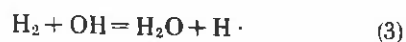
$$M^{n+} + OH = M^{(n+1)+} + OH^- \qquad (1)$$

or

$$M^{n-} + OH = M^{(n-1)-} + OH^- \qquad (2)$$
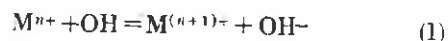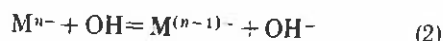
The data in table 11 are listed according to the periodic classification of the elements.

Although H_2 is listed here, the isotope effect evident in the significant difference between the OH reactivities of hydrogen and deuterium indicates that the reactions probably involve direct hydrogen transfer

$$H_2 + OH = H_2O + H \cdot \qquad (3)$$

rather than the formation of an intermediate H_2^+ ion:

$$H_2 + OH = H_2^+ + OH^- \qquad (4)$$
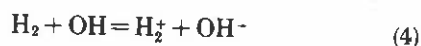
However, for convenience, the data for H_2 and D_2 are given in this chapter and not in Chapter VI.

For the group I metal cations, Ag^+ [1] and Au^+ [2], and, presumably, Cu^+ react with OH to form higher valency states. Surprisingly, the oxidation of cupric ion to a form of Cu III also proceeds at a rate which is only an order of magnitude lower than that for a diffusion-controlled reaction [3].

Interest in the reaction of OH with the powerful reducing agent, borohydride ion, centered on its possible value as a means of converting OH into the highly reducing hydrogen atom [4].

$$BH_4^- + OH = BH_4 + OH^- \qquad (5)$$

$$BH_4 = BH_3 + H \cdot \qquad (6)$$
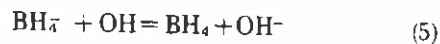
Preliminary studies indicated, however, that the BH_4 intermediate is sufficiently stable to dissociation to permit it to react with other solutes.

There are some data for reaction of OH with cations and complex anions of metals of the transition series. With the exception of ferrous ion and

thallous ion, data are sparse for the transition complex cations. For the three complexes listed, there is no change in the coordination number following OH oxidation, although this is not the case for a complex of Pt II, $[Pt\ Cl_4]^=$. The one-electron oxidation state of this anion, a complex of Pt III, is unstable and the reaction proceeds to the ultimate formation of a 6-coordination complex of Pt IV. The initial reaction is *not* electron transfer and involves addition of OH to form an intermediate platinum complex of coordination number five [5].

There are adequate data for the reaction of OH with carbonate ion. Agreement is good, although there is a pH effect on the rate constant due to the carbonate-bicarbonate ionic equilibrium. The CO_3^- radical ion formed in the reaction gives rise to a strong transient absorption spectrum with a maximum at 600 nm. For this and other reasons, the reaction has been used as a reference system in pulse radiolysis competition experiments for the measurement of a large number of OH rate constants. We recommend that a value of 4.1×10^8 be used for the reference rate constant in such determinations.

As would be expected, the reactivity of the reducing oxy-anions of the three-valent Group 5 and the four-valent Group 6 elements approach diffusion-limited values. Where multiple determinations are available, the agreement is generally quite good.

There is a considerable amount of data available on the reactivity of the halide ions of Group 7; reactivities for the pseudo-halide, thiocyanate ion, CNS, are also included in this section. For both Cl^- and Br^- there is a strong effect of acid pH on the reactivity and for chloride, the effect is particularly marked due to the complex nature of the overall oxidation process [6]. There are numerous determinations of the reactivity of bromide ion with, apparently, good agreement at both acid and neutral pH.

Oxidation of a halide ion, X^-, proceeds in two stages:

$$OH + X^- = X \cdot + OH^-, \qquad (7)$$

$$X \cdot + X^- \rightleftharpoons X_2^-. \qquad (8)$$
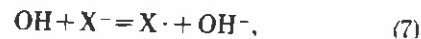
In competition experiments designed to measure the OH-reactivity of a second solute, the possibility exists, therefore, of competitive reaction of the intermediate species, $X \cdot$, with both solutes. If this occurs, relative rate data determined by such methods could be misleading. Rate constants

measured in pulse radiolysis experiments by direct observation of the rate of formation of the complex radical X_2^- depend for their validity on the assumption that, in the overall process, reaction (7) is rate-determining. Experiments have been carried out [7] which show that this assumption is *not* valid. Kinetic analysis of the reaction sequence in the thiocyanate system indicated that the rate constant of reaction (7) is greater than that of reaction (8). In view of the frequency with which the CNS$^-$ system has been used as a reference system in kinetic competition studies, the validity of the rate data so determined is discussed in detail in the final chapter.

TABLE 11. *Inorganic electron transfer reactions*

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
H$_2$	*$(6.0\pm2)\times10^7$	neut.	[8]	PR removal of OH spectrum	Absolute
	4.2×10^7	7	[9]	S irrad. comp. with H$_2$O$_2$	Rel. to $k_{OH+H_2O_2}=4.5\times10^7$
	4.5×10^7	7	[10, 27]	Intermittent irradiation	Rel. to $k_{OH+H_2O_2}=4.5\times10^7$
D$_2$	1.5×10^7	0.1 N HClO$_4$	[11]	Comp. with Fe^{2+} (Fenton)	Rel. to $k_{OH+Fe^{2+}}=3\times10^8$
Cu^{2+}	*3.5×10^8	7	[3]	PR product form.	Absolute, N$_2$O added
Au$^+$	*$(4.7\pm0.8)\times10^9$	7	[2]	PR product form.	Absolute
BH$_4^-$	*1.2×10^{10}	11	[4]	PR product form.	Absolute
	* $<4\times10^8$	12.8	[4]	PR product form.	Absolute (O$^-$ rate constant)
Vanadium IV VO^{++}	$(5.0\pm1.5)\times10^8$	0.1	[12]	S irrad. comp. with H$_2$	Rel. to $k_{OH+H_2}=4.5\times10^7$
Cr^{3+}	$(3.2\pm1)\times10^8$	....	[13]	S irrad. comp. with H$_2$	Rel. to $k_{OH+H_2}=4.5\times10^7$
Mn^{2+}	* $\geq1.4\times10^8$	neut.	[14]	PR product form.	Absolute. N$_2$O added
Fe^{2+}	* $>10^8$	0.1	[15]	PR product form.	Absolute
	3.0×10^8	1	[16]	S irrad.	Rel. to $k_{OH+H_2}=4.5\times10^7$
	3.2×10^8	1.6	[17]	S irrad. comp. with H$_2$	Rel. to $k_{OH+H_2}=4.5\times10^7$
	5.0×10^8	2	[18]	Fenton reaction, OH comp. with PNDA	Rel. to $k_{OH+PNDA}=1.25\times10^{10}$
	2.6×10^8	2.1	[17]	S irrad. comp. with H$_2$	Rel. to $k_{OH+H_2}=4.5\times10^7$
[Fe(CN)$_5$NO]$^{2-}$	1.2×10^7	neut	[19]	PR comp. with bicarbonate	Rel. to $k_{OH+HCO_3^-}=5.5\times10^7$
[Fe(CN)$_6$]$^{4-}$	1.7×10^{10}	neut.	[20]	PR comp. with I$^-$	Rel. to $k_{OH+I^-}=1.02\times10^{10}$
	†*$(1.1\pm0.2)\times10^{10}$	neut.	[21]	PR product form.	Absolute. N$_2$O added
	8.7×10^9	7	[22]	PR comp. with ethanol	Rel. to $k_{OH+C_2H_5OH}=1.85\times10^9$
	†*9.3×10^9	neut.	[23]	PR product form	Absolute N$_2$O added
	$(1.25\pm0.2)\times10^{10}$	9	[24]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA}=1.25\times10^{10}$
[Ru(NH$_3$)$_5$N$_2$]$^{2+}$	*4.8×10^8	neut.	[25]	Product form.	Absolute. N$_2$O added
Ce^{3+}	7.2×10^7	0.1	[26, 27]	S irrad. comp. with formic acid	Rel. to $k_{OH+H_2O_2}=4.5\times10^7$
Tl$^+$	2.7×10^9	0.1	[27, 28]	S irrad. comp. with Ce^{3+} ion	Rel. to $k_{OH+H_2O_2}=4.5\times10^7$
	$(0.9\pm0.3)\times10^{10}$	0.1	[12]	S irrad. comp. with H$_2$	Rel. to $k_{OH+H_2}=4.5\times10^7$
	†*$(7.6\pm1)\times10^9$	6.5	[29]	PR product form.	Absolute. N$_2$O added

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TABLE 11. *Inorganic electron transfer reactions* — Continued

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
$[PtCl_4]^{2-}$	*8×10^9	7	[30]	PR product form.	Absolute. N_2O added
	*8×10^9	>13	[30]	PR product form.	Absolute. N_2O added
$[Pt(CN)_4]^{2-}$	1.0×10^{10}	2	[30]	PR comp. with methanol	Rel. to $k_{OH+CH_3OH} = 8.5 \times 10^8$
CO_3^-	†*4.2×10^8	10.8	[31]	PR product form.	Absolute. N_2O added
	4.5×10^8	10.5	[32]	S irrad. comp. with benzoate	Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$
	3.8×10^8	10.7	[33]	PR comp. with methanol and ethanol	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	†*3.65×10^8	11	[34]	PR product form.	Absolute. N_2O added
HCO_3^-	*1.0×10^7	6.5	[35]	PR prod. form.	Absolute. CO_2 added
	*1.5×10^7	8.4	[31]	PR prod. form.	Absolute. N_2O added
CO	4.5×10^6	neut.	[36]	PR comp. with H_2O_2	Rel. to $k_{OH+H_2O_2} = 4.5 \times 10^7$
CN^-	$(4.5 \pm 0.3) \times 10^9$	9	[24]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
$C(NO_2)_3^-$	*3×10^9	neut.	[37]	PR bleaching of solute	Absolute. N_2O added
Sn^{++}	$(2.5 \pm 0.3) \times 10^9$	0.1	[38]	S irrad. comp. with Fe^{2+}	Rel. to $k_{OH+Fe^{2+}} = 3.5 \times 10^8$
NO_2^-	5×10^9	neut.	[39]	S irrad. comp. with H_2	Rel. to $k_{OH+H_2} = 4.5 \times 10^7$
	1.3×10^9		[40]	PR of NO_3^- solutions	Computer analysis of reactions
	7.1×10^9		[41]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	$(8.1 \pm 0.4) \times 10^9$	9	[24]	PR comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	7.4×10^9	10.7	[33]	PR comp. with CO_3^-	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
	8.1×10^9	11	[42]	PR comp. with CO_3^-	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
NO	$(8.8 \pm 1.1) \times 10^9$	7	[43]	S irrad. comp. with alcohols	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
azide	$(1.08 \pm 0.05) \times 10^{10}$	9	[24]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
hypophosphite	1.9×10^9	10.7	[33]	PR comp. with CO_3^-	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
phosphite	3.9×10^9	10.7	[33]	PR comp. with CO_3^-	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^9$
HPO_4^{2-}	$< 10^7$	neut.	[20]	PR comp. with iodide	Rel. to $k_{OH+I^-} = 1.02 \times 10^{10}$
	$< 5 \times 10^6$		[44]	PR comp. with CO_3^-	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
PO_4^{3-}	$< 10^7$		[44]	PR comp. with CO_3^-	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
$P_2O_7^{4-}$	$< 4 \times 10^6$		[44]	PR comp. with CO_3^-	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
arsenite (AsO_2^-)	$(7.6 \pm 0.3) \times 10^9$	9.0	[24]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	9.5×10^9	10.7	[33]	PR comp. with CO_3^-	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$

TABLE 11. *Inorganic electron transfer reactions* – Continued

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
H_2O_2	1.2×10^7	3	[45]	Prod. analysis. High dose rate radiolysis	Comp. with radical-radical reactions in $H_2O/O_2/H_2O_2$
	4.5×10^7	neut.	[27]	Prod. analysis. High dose rate radiolysis	Comp. with radical-radical reactions in $H_2O/O_2/H_2O_2$
	2.25×10^7	neut.	[20]	PR comp. with I^-	Rel. to $k_{OH+I^-} = 1.02 \times 10^{10}$
H_2S	1.83×10^{10}	6	[46]	PR comp. with CNS^-	Rel. to $k^{rel}_{thiocyan} = 1.1 \times 10^{10}$
H_2SO	3.5×10^5	0.1	[27, 28]	S irrad. comp. with Ce^{3+}	Rel. to $k_{OH+H_2O_2} = 4.5 \times 10^7$
	$(4.5 \pm 0.5) \times 10^5$	< 0.4	[12]	S irrad. comp. with H_2	Rel. to $k_{OH+H_2} = 4.5 \times 10^7$
	$(1.2 \pm 0.3) \times 10^6$	0.3–2.0	[47]	S irrad. comp. with Safranine T	Rel. to $k_{OH+C_6H_6} = 7.9 \times 10^9$
$KHSO_4$	1.5×10^6	neut.	[48]	PR comp. with methanol	Rel. to $k_{OH+CH_3OH} = 8.5 \times 10^8$
HSO_5	3.9×10^9		[49]	PR comp. with CO_3^-	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
$S_2O_8^-$	$< 10^6$		[49]	PR comp. with CO_3^-	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
selenite SeO_3^-	4.6×10^9	7	[33]	PR comp. with methanol	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
tellurite TeO_3^-	3.9×10^9	10.7	[33]	PR comp. with CO_3^-	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
Cl^-	see original paper	acid and alkal.	[6]	PR product form. and comp. with methanol and ferrocyanide	Rate constant depend. on pH, Cl^- concentration and overall ionic strength
	*$(1.5 \pm 0.3) \times 10^{10}$	0.8–3.4	[50]	PR prod. form	Absolute. Obs. Cl_2^-
	10^6	9	[24]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
ClO_2	1.1×10^9	5.8–6.0	[51]	S irrad. comp. with Br^-	Rel. to $k_{OH+Br^-} = 1.1 \times 10^9$
Br^-	1.02×10^{10}	1.3	[52]	S irrad. comp. with ethanol	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	*5.0×10^9	2	[53]	PR prod. form	Absolute. Obs. Br_2^-
	$(1.0 \pm 0.15) \times 10^{10}$	2	[47]	S irrad. comp. with Safranine T	Rel. to $k_{OH+C_6H_6} = 7.8 \times 10^9$
	3.9×10^9	0.05 N H_2SO_4	[54]	S irrad. comp. with isopropanol	Rel. to $k_{OH+IP} = 2.0 \times 10^9$
	7.2×10^9	2.7	[52]	S irrad. comp. with ethanol	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	$(5.0 \pm 0.7) \times 10^9$	3	[47]	S irrad. comp. with Safranine T	Rel. to $k_{OH+C_6H_6} = 7.8 \times 10^9$
	$(2.2 \pm 0.3) \times 10^9$	5.5	[47]	S irrad. comp. with Safranine T	Rel. to $k_{OH+C_6H_6} = 7.8 \times 10^9$
	1.17×10^9	6	[55]	S irrad. comp. with ethanol	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	1.1×10^9	6	[52]	S irrad. comp. with ethanol	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	*1.0×10^9	7	[53]	PR prod. form.	Absolute. Obs. Br_2^-
	1.14×10^9	7–10.5	[32]	S irrad. comp. with benzoate	Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$
	*$(1.2 \pm 0.15) \times 10^9$	7	[56]	PR prod. form.	Absolute. Obs. Br_2^-
	1.08×10^9	8	[55]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	$(1.1 \pm 0.06) \times 10^9$	9	[24]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$

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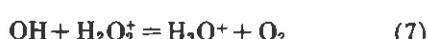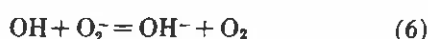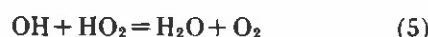TABLE 11. *Inorganic electron transfer reactions* — Continued

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
hypobromite BrO$^-$	4.4×10^8	11	[57]	PR comp. with carbonate	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
	1.9×10^9	13	[57]	PR comp. with carbonate	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
I$^-$	1.38×10^{10}	0.05 N H$_2$SO$_4$	[54]	S irrad. comp. with isopropanol	Rel. to $k_{OH+IP} = 2.0 \times 10^9$
	$(1.13 \pm 0.16) \times 10^{10}$	2	[47]	S irrad. comp. with Safranine T	Rel. to $k_{OH+C_6H_6} = 7.8 \times 10^9$
	*3.4×10^{10}	2–7	[7]	PR prod. form.	Absolute, Analysis of $I + I^- \rightleftharpoons I_2^-$ equilibrium
	$(7.5 \pm 1.1) \times 10^9$	3–5.5	[47]	S irrad. comp. with Safranine T	Rel. to $k_{OH+C_6H_6} = 7.8 \times 10^9$
	1.6×10^{10}	7	[54]	S irrad. comp. with isopropanol	Rel. to $k_{OH+IP} = 2.0 \times 10^9$
	*$(1.02 \pm 0.13) \times 10^{10}$	neut.	[20]	PR product form.	Absolute N$_2$O added
	1.2×10^{10}	9	[42]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	$(1.09 \pm 0.06) \times 10^{10}$	9	[24]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	1.37×10^{10}	10.5	[32]	S irrad. comp. with benzoate	Rel. to $k_{OH+benzoate} = 5.6 \times 10^9$
	7.3×10^9	11	[42]	PR comp. with CO$_3^-$	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
	3.4×10^{10}	1.0 M NaOH	[51]	S irrad. comp. with isopropanol	Rel. to $k_{OH+IP} = 2.0 \times 10^9$
thiocyanate	8.6×10^9	2	[58]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	1.13×10^{10}	2	[33]	PR comp. with C$_2$H$_5$OH	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	*$(7.5 \pm 0.5) \times 10^9$	2–10	[59]	PR prod. form.	Absolute N$_2$O added
	*2.8×10^{10}	2–9	[7]	PR prod. form.	Absolute. Analysis of CNS$ + CNS^- \rightleftharpoons CNS_2^-$ equilibrium.
	9.2×10^9	5	[60]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
	1.13×10^{10}	7	[33]	PR comp. with C$_2$H$_5$OH	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	*6.6×10^9	7	[35]	PR form. of (CNS)$_2^-$	Absolute N$_2$O added
	1.19×10^{10}	9	[18]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	*$(1.08 \pm 0.1) \times 10^{10}$	neut.	[61]	PR prod. form.	Absolute. N$_2$O added.

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Chapter VIII. Radical Reactions

Rate constants for the reaction of the hydroxyl radical with another hydroxyl, or with other free radicals (notably those formed in the radiolysis of water) have proved to be among the most difficult of the hydroxyl rate constants to determine accurately. Nevertheless, values have been obtained, in one case by several methods, for the following radical-radical reactions of OH as well as for three analogous reactions of the deuteroxy radical, OD, the latter in deuterium oxide, rather than in water.

$$OH + OH = H_2O_2 \tag{1}$$

$$OH + O^- = HO_2^- \tag{2}$$

$$OH + H = H_2O \tag{3}$$

$$OH + e_{aq}^- = OH^- \tag{4}$$

$$OH + HO_2 = H_2O + O_2 \tag{5}$$

$$OH + O_2^- = OH^- + O_2 \tag{6}$$

$$OH + H_2O_2^+ = H_3O^+ + O_2 \tag{7}$$

$$OD + OD = D_2O_2 \tag{8}$$

$$OD + D = D_2O \tag{9}$$

$$OD + e_{D_2O}^- = OD^- \tag{10}$$

k_1 has been determined, as pointed out in chapter III, by a method analogous to the rotating sector technique. k_1 and k_3 have been determined by pulse radiolysis observation of the hydroxyl radical directly. The molar extinction coefficient must be known for this calculation, and it should be noted that there is a weak overlapping absorption of H-atoms. Several of these rate constants have been determined by computer fitting of over-all product yields in pulsed and steady irradiations, relative to the rate constant for hydrogen atom recombination. These values, dependent as they are upon a fit to many parameters, must be regarded as approximate. An accurate value for k_2 has been determined by pulse radiolysis, in competition with the ferrocyanide ion oxidation by OH. For the reactions of OD, there is some uncertainty, since the pK for OD is not precisely known, concerning the extent of involvement of O^- in the reactions. The values, as well as a brief indication of the method used along with other pertinent factors, are given in table 12.

TABLE 12. *Radical reactions*

| Reaction	$k(M^{-1} s^{-1})$	$T(°C)$	pH	Ref.	Method	Comments
$OH + OH = H_2O_2$	$\dagger(4.0 \pm 1.0) \times 10^9$	RT	neut.	[1]	P rot. sector	Relative to $k_{OH+H_2} = 4.5 \times 10^7$ Mechanism dependent
	$\dagger(5.5 \pm 0.8) \times 10^9$	23	acid and neut.	[2]	PR	Relative to $k_{OH+ferrocyan} = 0.93 \times 10^{10}$
	$*(5.3 \pm 0.5) \times 10^9$	RT	neut.	[3]	PR direct obs. of OH	Dependent on ϵ_{OH}. Absolute. Corr. made for H + OH.
	$*(5.3 \pm 0.5) \times 10^9$	RT	3	[4]	PR direct obs. of OH	Dependent on ϵ_{OH}. Absolute.
	6×10^9	RT	acid	[6]	Prod. yields in P and S irrad.	Comput. fit to over-all mechanism with $k_{H+H} = 6 \times 10^9$
	7×10^9	RT	acid	[8]	Prod. yields in P and S irrad.	Comput. fit to over-all mechanism with $k_{H+H} = 6 \times 10^9$
$OH + O^- = HO_2^-$	$\leqslant 2.0 \times 10^{10}$	23	basic	[2]	PR	Relative to $k_{OH+ferrocyan} = 0.93 \times 10^{10}$
$OH + H = H_2O$	7×10^9	RT	3	[4]	PR direct obs. of OH	No corr. for overlapping abs. of H
	1.2×10^{10}	RT	acid	[6]	Prod. yields in P and S irrad.	Comput. fit to over-all mechanism with $k_{H+H} = 6 \times 10^9$
	3×10^{10}	RT	acid	[8]	Prod. yields in P and S irrad.	Comput. fit to over-all mechanism with $k_{H+H} = 6 \times 10^9$
$OH + e_{aq}^- + OH^-$	$*(3.0 \pm 1.0) \times 10^{10}$	23	basic	[5]	PR obs. of e_{aq}^-	Mechanism dependent. Absolute.

TABLE 12. *Radical reactions* — Continued

Reaction	$k(M^{-1}s^{-1})$	$T(°C)$	pH	Ref.	Method	Comments
$OH + HO_2^- = H_2O + O_2^{--}$	6×10^9	RT	acid	[6]	Prod. yields in P and S irrad.	Comput. fit to over-all mechanism with $k_{H+H} = 6 \times 10^9$
	7.1×10^9	25	acid	[7]	Prod. yields in P irrad.	Comput. fit of $G(H_2O_2)$ with $k_{OH+OH} = 6 \times 10^9$
	1.4×10^{10}	RT	acid	[8]	Prod. yields in P and S irrad.	Comput. fit to over-all mechanism with $k_{H+H} = 6 \times 10^9$
$OH + O_2^- = OH^- + O_2$	1.01×10^{10}	25	> 2.74	[7]	Prod. yield in P irrad.	Comput. fit of $G(H_2O_2)$ with $k_{OH+OH} = 6 \times 10^9$
$OH + H_2O_2^+ = H_3O^+ + O_2$	1.27×10^{10}	25	< 1.51	[7]	Prod. yield in P irrad.	Comput. fit of $G(H_2O_2)$ with $k_{OH+OH} = 6 \times 10^9$
$OD + OD = D_2O_2$	4.00×10^9	23	basic	[9]	PR obs. of e_{aq}^-	Concurrent with $OD + e_{aq}^-$ Uncertainty about O^-
$OD + D = D_2O$	2.00×10^{10}	23	basic	[9]	PR obs. of e_{aq}^-	Concurrent with $OD + e_{aq}^-$ Uncertainty about O^-
$OD + e_{D_2O}^- = OD^-$	2.80×10^{10}	23	basic	[9]	PR obs. of e_{aq}^-	Uncertainty about amount of O^-

Chapter VIII. References

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Chapter IX. Reactions of the Oxide Radical Ion

The chemical reactivity of the basic form of the hydroxyl radical, O^-, differs markedly from that of OH in many reactions. Since the pK is 11.9 for the equilibrium

$$OH + OH^- \rightleftharpoons O^- + H_2O, \qquad (1)$$
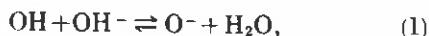
all chemical reactions of the oxide radical ion have been studied in strongly basic solution. The difference in reactivity of O^-, compared with OH, may be seen in the following reactions. Whereas the hydroxyl radical is unreactive toward oxygen, the oxide radical ion adds readily to form the ozonide ion:

$$O^- + O_2 = O_3^-. \qquad (2)$$

While the hydroxyl radical adds readily to aromatic molecules, the reactivity of O^- toward aromatic compounds is lower by at least three orders of magnitude in the specific rate constant. The OH radical is much more effective than is the oxide radical ion in oxidizing a number of inorganic anions. Coulombic repulsion of O^-, which undoubtedly accounts for part of this difference, is not great enough to account for all of it, and the larger part of the effect may be the result of a lower electron affinity of O^- compared with that of OH. Hydrogen abstraction reactions of O^-, on the other hand, exhibit a specific reactivity only slightly lower than that of OH:

$$O^- + C_2H_5OH - OH^- + C_2H_4OH \qquad (3)$$
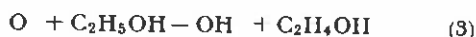
Rate constants for reactions of O^- have been determined in a few cases by direct observation of a transient product in pulse radiolysis. Thus the ozonide ion, formed in reaction (2), has a strong optical absorption with a maximum [1, 6] at 430 nm, which has been used [3] to determine k_2 absolutely. Similarly, k_3 has been determined absolutely [7] by observing the formation of the α-ethanol radical, of which the ionic form [8, 9] present at high pH has a conveniently observable optical absorption in the uv.

In other cases, rate constants have been determined in flash photolysis and in pulse radiolysis by competition kinetic studies [3, 6, 10, 14] using reaction (3), or some other process as the reference reaction. Where the desired result is obtained by monitoring O_3^-, the interpretation of the data is usually quite complex, involving as it does not only the equilibrium constant for the pH-dependent equilibrium (1), and the forward and reverse rate constants for the thermal equilibrium (2), as well as the rate constant for the reaction of interest, but also the rate constant for the analogous competing reaction of OH. Notwithstanding the complexity, competition kinetics with ozonide formation is a feasible method, since the formation rate constant, k_2, is reasonably accurately known and the decomposition constant, k_{2r}, has been determined [10] as 3.3×10^3 s^{-1} at 25 °C.

Table 13 lists the rate constants for reactions of O^-, among which are to be found examples of addition, hydrogen abstraction, and reaction with other radicals and radical ions, notably those formed in the radiolysis of water.

TABLE 13. *Reactions of the oxide radical ion*

Reaction	$k(M^{-1} s^{-1})$	$T(°C)$	pH	Ref.	Method	Comments
$O^- + O_2 = O_3^-$	†*2.5 × 10⁹	RT	13	[3]	PR prod. form.	Absolute. Observ. O_3^- Single concen. of O_2
	*2.5 × 10⁹	RT	13–13.7	[6]	Flash. phot. prod. form.	Absolute. Observ. O_3^- in H_2O_2 phot. No data given
	†*(3.6 + 0.4) × 10⁹	20–25	11 & 13	[11]	PR prod. form.	Absolute. Observ. of O_3^- form.
	4 × 10⁹	23	11.9	[17]	PR prod. form.	Absolute. Approximate
$O^- + C_6H_5COO^-$	< 6 × 10⁶	25	13	[4]	PR comp. with O_3^- form.	Rel. to $k_{O^- + O_2} = 2.5 \times 10^9$. Complex kinetics. May be very much lower.

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TABLE 13 *Reactions of the oxide radical ion*—Continued

Reaction	$k(M^{-1} s^{-1})$	$T(°C)$	pH	Ref.	Method	Comments
$O^- + H_2O = OH + OH^-$	5.5×10^2 $(3.0 \times 10^4 s^{-1})$	RT	13-13.7	[6]	Flash phot.	Rel. to $k_{O^-+O_2} = 2.5 \times 10^9$
	1.7×10^6 $(9.2 \times 10^7 s^{-1})$	20-25	11	[12]	PR comp. with $O^- + CO_3^{2-}$	Rel. to $k_{O^-+C_2H_5OH} = 1 \times 10^9$
	2×10^7	25	13	[10]	Calculated	Based on equilibrium consts. and $k_{OH+OH} = 4 \times 10^9$
$O^- + H_2 = OH^- + H$	$(8 \pm 4) \times 10^7$	23	13	[13]	PR observ. of e_{aq}^-	Comput. fit with other rate consts. and depend. upon $\epsilon_{e_{aq}^-}$
$O^- + HO_2^- = OH^- + O_2^-$	$(7 \pm 3) \times 10^8$	25	13	[4]	PR observ. of O_2^-	Rel. to $k_{O^-+O_2} = 2.5 \times 10^9$
	8.1×10^8	20-25	11	[11]	PR comp. with $OH + CO_3^{2-}$	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
	$(5.0 \pm 1.7) \times 10^8$	RT	13-13.7	[6]	PR observ. of O_2^-	Rel. to $k_{O^-+O_2} = 2.5 \times 10^9$
	2.74×10^8	24	12-13.5	[21]	PR comp. with $O^- + O_2$	Rel. to $k_{O^-+O_2} = 2.5 \times 10^9$ Corr. to zero ionic strength
$O^- + CH_3OH$ $= \cdot CH_2OH + OH^-$	$\dagger(5.2 \pm 1.0) \times 10^8$	25	13	[10]	PR observ. of O_2^- decay	Rel. to $k_{O^-+O_2} = 2.5 \times 10^9$
	$\dagger^*(5.8 \pm 0.8) \times 10^8$	25	> 13.3	[7]	PR prod. form.	Absolute. Observ. of alcohol radical form.
$O^- + C_2H_5OH$ $= \cdot C_2H_4OH + OH^-$	$\dagger 8.9 \times 10^8$	RT	> 13	[14]	PR observ. of O_2^-	Rel. to $k_{O^-+O_2} = 2.5 \times 10^9$
	$\dagger(8.4 \pm 1.6) \times 10^8$	25	13	[10]	PR observ. of O_2^- decay	Rel. to $k_{O^-+O_2} = 2.5 \times 10^9$
	$\dagger^*(1.13 \pm 0.17) \times 10^9$	25	> 13.3	[7]	PR prod. form.	Absolute. Observ. of alcohol radical form.
$O^- + C_2O_4^{2-}$ $= CO_2 + 2OH^- + CO_2^-$	1.6×10^7	24	12-13.5	[15]	S irrad. CO_2 form.	Rel. to $k_{O^-+O_2} = 2.5 \times 10^9$
$O^- + [Fe(CN)_6]^{4-}$ $\overset{H_2O}{=} [Fe(CN)_6]^{3-} + 2OH^-$	$< 7 \times 10^7$	23	13.5	[17]	PR comp. with OH + ferro-cyanide	Approx. upper limit
$O^- + CO_3^{2-} \overset{H_2O}{=} CO_3^- + 2OH^-$	$< 10^7$	23	10.6-13.5	[16]	PR prod. form.	Absolute. Approx. limit.
$O^- + HCO_2^-$ $\overset{H_2O}{=} HCO_2 + 2OH^-$	1.4×10^9	20-25	11	[11]	PR comp. with $OH + CO_3^{2-}$	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
$O^- + NO_2^- \overset{H_2O}{=} NO_2 + 2OH^-$	2.8×10^8	20-25	11	[11]	PR comp. with $OH + CO_3^{2-}$	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
$O^- + I^- \overset{H_2O}{=} I + 2OH^-$	9.6×10^8	20-25	11	[11]	PR comp. with $OH + CO_3^{2-}$	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
$O^- + CNS^-$ $\overset{H_2O}{=} CNS + 2OH^-$	1.0×10^9		> 12	[19]	PR comp. with $O^- + O_2$	Rel. to $k_{O^-+O_2} = 2.5 \times 10^9$

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TABLE 13. *Reactions of the oxide radical ion* — Continued

| Reaction	$k(M^{-1} s^{-1})$	$T(°C)$	pH	Ref.	Method	Comments
$O^- + O^- = O_2^{2-}$	5.8×10^9	RT	13	[3]	PR comp. with O_2^- form.	Rel. to $k_{O^- + O_2} = 2.5 \times 10^9$. N_2O added
	2×10^9	23	12–13	[18]	PR comp. with OH + ferro-cyanide	Rel. to $OH + [Fe(CN)_6]^{4-}$
	$< 1.8 \times 10^9$	23	12–13	[17]	PR comp. with OH + ferro-cyanide	May be much less
	$< 8 \times 10^8$	23	13	[20]	PR comp. with OH + ferro-cyanide	Recalculated from ref. [17]
$O^- + OH = HO_2^-$	$< 2.6 \times 10^{10}$	23	12–13	[17]	PR comp. with OH + ferro-cyanide	May be 4-fold lower
$O^- + e_{aq}^- \overset{H_2O}{=} OH^-$	$(2.2 \pm 0.6) \times 10^{10}$	23	> 13	[13]	PR observ. of e_{aq}^-	Comp. fit with other rate constants
$O^- + O_2^- \overset{?}{\rightarrow}$	5×10^8	25	13	[10]	PR observ. of O_2^- decay	Rel. to $k_{O^- + O_2} = 2.5 \times 10^9$

Chapter IX. References

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# Chapter X. Reactions With Biological Molecules

There is an extensive literature on the reactions of the OH radical with compounds relevant to, or involved in, many biochemical and biological processes. Reactions studied include oxidative deamination of aliphatic amino acids; addition to the free bases, nucleotides, and nucleosides derived from the nucleic acids; hydrogen abstraction involving the thiol group in cysteine and other sulfur-containing compounds and carbohydrates; and also, various investigations of OH-oxidation of biologically-active macromolecules including enzymes and nucleic acid itself. In this chapter the data for the compounds are presented in separate tables grouped according to general biochemical type.

Amino Acids

It is now well established that oxidative and reductive deamination are major processes in the radiolysis of dilute aqueous solutions of simple aliphatic amino acids such as glycine and alanine [1]. It is believed that OH attack on amino acids of this type, represented as $NH_3^+CH(R)COO^-$, occurs mainly at the carbon atom alpha to the carboxyl or amino group.

$$OH + NH_3^+CH(R)COO^- = H_2O + NH_3^+\dot{C}(R)COO^- \quad (1)$$
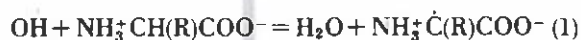
Dependent upon experimental conditions, the α-amino radical may react by dismutation to form an intermediate imino-cation which hydrolyzes to yield ammonia and a keto acid:

$$2NH_3^+C(R)COO^- = NH_3^+CH(R)COO^-$$
$$+ NH_2 = C(R)COO^- \quad (2)$$

$$NH_2^+ = C(R)COO^- + H_2O = NH_4 + RCOCOO^-$$
$$(3)$$
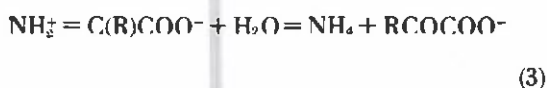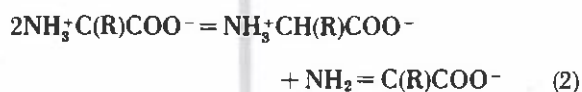
Although there is an approximate 1:1 stoichiometry between OH disappearance and ammonia production, this is not so for aliphatic amino acids containing longer side chains. For example, in the radiolysis of such amino acids in dilute aqueous solution, the efficiency of ammonia production falls with increasing length of the aliphatic side chain [2]. This is due to the reduction in the yield of the α-amino radical relative to that of radicals formed by OH attack elsewhere in the molecule.

Oxidative deamination is not a major process following the reaction of OH with the ring-containing amino acids, e.g. tyrosine, phenylalanine, tryptophan, and histidine. As might be expected by analogy with other aromatic and heterocyclic compounds, OH radicals react predominantly by addition to the ring. In the case of tyrosine, the hydroxycyclohexadienyl radical formed in this reaction undergoes a unimolecular elimination reaction in which a molecule of water is lost from the structure [3].

$$(4)$$
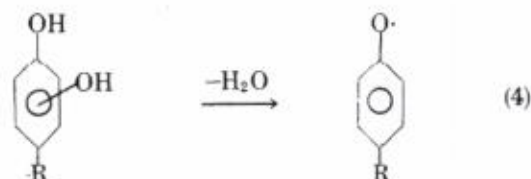
The reaction is acid-base catalyzed.

The rate constants for OH addition to the ring-amino acids are an order of magnitude or more larger than those for the non-ring amino acids, with the exception of the sulfur-containing compounds. For this reason therefore, the ring structures in enzymes are particularly vulnerable to OH radical attack, reactions which may lead, in some cases, to loss of biological activity.

In the heterocyclic amino acid, tryptophan, there is evidence of multifocal attack by OH. This is based on the analysis of the stable products following radiolysis of aqueous solutions [4] and also, on a study of the reactions of OH generated in the Fenton reaction [5]. A detailed pulse radiolysis study of tryptophan and related substituted indoles not only confirmed that multifocal attack occurs but has also provided information on which sites in the ring are involved [6]. The transient absorption maximum due to the OH-adduct has three subsidiary maxima at 310, 325, and 345 nm. The spectrum was compared with those obtained by OH addition to indoles in which substituent groups were present at various positions in the structures. It was found that the relative intensities of the three subsidiary maxima are dependent upon the position of the substituent. It was argued that substitution of a methyl group on various positions of the indole ring should restrict electrophilic attack by OH at that position. Complications arising from changes in the electron density distribution in the molecule due to the inductive effect of the methyl group appear to be negligible since the molecular spectrum of indole is not very different from those of the substituted indoles. It was concluded that the effect of substitution on the relative intensities of the subsidiary maxima in

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the transient spectra reflect the lowering of the probability of OH attack at the substituted position. Kinetic data indicated that the OH reactivities at the three sites in tryptophan were of the same order of magnitude, from which it was concluded that the three OH-adducts are formed in approximately equal yield.

It is evident from table 14, that the sulfur-containing amino acids react extremely rapidly with OH. Cysteine (RSH) is oxidized to cystine through the formation of the intermediate radical RS which results from abstraction of a hydrogen atom from the thiol group

$$RSH + OH = RS\cdot + H_2O \qquad (6)$$

It has been shown by pulse radiolysis studies on cysteine-related compounds including H_2S and simple mercaptans [7, 8], that under nonacidic conditions, the intermediate RS radical complexes with a solute molecule to form the ion-radical RSSR⁻ according to the equilibria
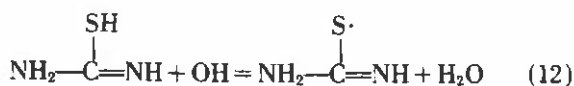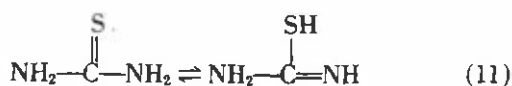
$$RSH \rightleftharpoons RS^- + H^+ \qquad (7)$$

$$RS + RS^- \rightleftharpoons RSSR^-. \qquad (8)$$

Cystine is probably formed by dimerization of the uncomplexed RS radicals

$$RS + RS = RSSR. \qquad (9)$$

In the presence of oxygen, the high efficiency for the oxidation of RSH indicates the occurrence of a chain reaction [9]. It has been suggested that the RS radicals formed in (6) react with oxygen to form the RSO_2 radical which propagates the chain by the H-atom transfer reaction

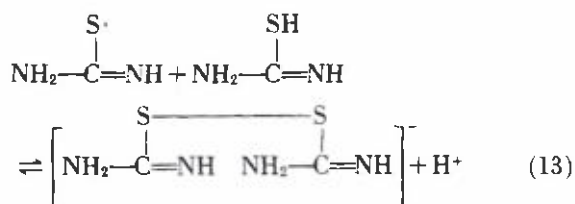$$RSO_2 + RSH = RSO_2H + RS. \qquad (10)$$

The chain termination step is dimerization of RS radicals to from cystine. Thiourea is rapidly oxidized by OH radicals [10]. It has been suggested that the reaction proceeds through a transient intermediate imino radical formed by hydrogen abstraction from the imino form of the solute.

$$\underset{NH_2—\overset{\overset{\displaystyle S}{\|}}{C}—NH_2}{} \rightleftharpoons \underset{NH_2—\overset{\overset{\displaystyle SH}{|}}{C}=NH}{} \qquad (11)$$

$$NH_2—\overset{\overset{\displaystyle SH}{|}}{C}=NH + OH = NH_2—\overset{\overset{\displaystyle S\cdot}{|}}{C}=NH + H_2O \qquad (12)$$

A strong transient absorption band with a maximum near 400 nm, is formed during the pulse radiolysis of thiourea solutions [10]. This was attributed originally to the imino-RS radical formed in reaction (11). However, more recent pulse radiolysis studies with the analogue selenourea [11], where a similar

absorption band is observed, indicate that the absorption band is due to a radical anion-dimer analogous to the species RSSR⁻ formed by OH oxidation of thiols.

$$NH_2—\overset{\overset{\displaystyle S\cdot}{|}}{C}=NH + NH_2—\overset{\overset{\displaystyle SH}{|}}{C}=NH$$

$$\rightleftharpoons \left[NH_2—\overset{\overset{\displaystyle S}{|}}{C}=NH \quad NH_2—\overset{\overset{\displaystyle S}{|}}{C}=NH\right]^- + H^+ \qquad (13)$$

Some trends are apparent in the rate constant data listed in the tables. Clearly the absolute reactivities of OH with amino acids (table 15) and simple peptides (table 16) vary considerably with the structure of the compound and also with pH, an effect which is due to the influence of the ionic equilibria in these solutes. With increasing pH, the net charge on amino acids changes from $+1$ in acid solution through zero to -1 in alkaline solutions which favors reaction with the electrophile OH.

The simple aliphatic amino acids, glycine and alanine, appear to be the least reactive although when OH groups or branched chains are present in the molecules, inductive effects tend to increase the reactivity. As discussed earlier, the ring-structured amino acids are among the most reactive due to the ease with which OH addition to the π-electron system can occur. Similar trends are apparent in the data for the simple peptides although the peptide linkage evidently increases the reactivity relative to that of the free amino acids. As might be expected, in peptides where the component amino acids have different reactivities in the free state, e.g., glutathione and glycyltyrosine, the rate constants are comparable in each case to that of the more reactive amino acid component.

Enzymes

Table 17 lists the available data for some relatively simple enzymes. In most cases, the rate constants are of the order of $10^{11}M^{-1}s^{-1}$, values which are calculated on the basis of the *total* molecular weight of the enzymes. Since these compounds contain in excess of 100 amino acids in their structure, the rate constants calculated on the basis of the total molarity of the individual component amino acids are of course considerably smaller. Although attempts have been made to calculate overall rate constants from a knowledge of the values for the single units, such calculations are of doubtful significance in view of the complex tertiary structure of enzymes and the varying degrees of accessibility to free radical attack of different regions in the molecules.

Overall rate constants have been measured by pulse radiolysis and stationary-state methods. Data obtained by competition techniques are less reliable than those determined by absolute methods due to

the problems of kinetic inhomogeneity encountered in systems containing very large macromolecules. Fortunately, rate constants can be measured quite conveniently by the absolute pulse radiolysis methods since OH attack on proteins gives rise to strong transient absorption bands in the ultraviolet region of the spectrum. These absorption bands are due to addition of OH to the ring-amino acids present in the structure.

Nucleic Acid Derivatives

The relationship between intracellular damage to DNA and the response of the cell (lethal or otherwise) to ionizing radiation is one of the most fundamental problems of radiobiology. It is not surprising therefore that much effort has been devoted to the study of the radiation chemistry of DNA and its constituent nucleotides, nucleosides, and free bases.

It is from this field of research that almost all of the available information on OH reactivities with these compounds derives. It is relevant therefore to discuss first some of the early work on the stationary-state radiation chemistry of these compounds.

Dilute aqueous solutions of simple pyrimidine bases, e.g., thymine, cytosine, and uracil are bleached by ionizing radiation [12, 13]. The chromophore in these solutions is the 5:6 double bond in the heterocyclic ring which gives rise to an absorption maximum at 260 nm and it was concluded therefore that the radiation-induced bleaching was due to saturation of this double bond. This was subsequently confirmed by measurement of residual double bonds by bromination with free bromine. In oxygenated thymine solutions, hydroperoxides are formed, and it was concluded therefore that OH radicals formed during the radiolysis add to the 5:6 double bond [14, 15]. The full reaction sequence is as follows:

(14)

This has since been confirmed in numerous experiments with thymine and other pyrimidines. By comparison with the *cis* and *trans* isomers of 5-hydroxy-6-hydroperoxythymine and 6-hydroxy-5-hydroperxoythymine, it was shown chromatographically [16, 17] that the radiation-induced peroxy compound is a mixture of the *cis* and *trans* isomers of the 6-hydroxy derivative. However, for uracil and dimethyluracil where hydroxyhydroperoxides are also produced, there are indications that both the 6-hydroxy and 5-hydroxy radicals are formed by OH attack in the bases [18].

An interesting application of the aerated thymine system, and of relevance to this monograph, is its use as a reference standard for the measurement of relative rate constants for reactions of OH with many different solutes [19a, 19b]. The method is based on kinetic analysis of the competition,

$$OH + thymine \rightarrow loss\ of\ chromophore \quad (15)$$

$$OH + solute \rightarrow products, \quad (16)$$
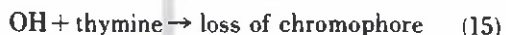
in which the extent of bleaching of the thymine chromophor is used to measure the relative rate constant ratio k_{16}/k_{15}. The application of this kinetic system is discussed more fully in the final chapter together with the normalization procedure used for obtaining absolute values of the rate constants determined by this method.

In the thymine, the site of OH attack changes gradually with increasing pH [20]. In solution of

pH > 9, 5-hydroxymethyluracil is one of the overall products of the oxidation, indicating that under these conditions some attack occurs at the 5-methyl group

(17)
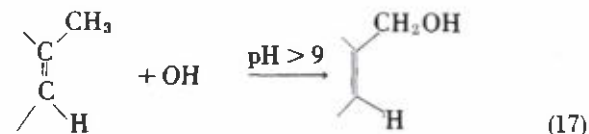
In the presence of cupric ion, the OH adduct of uracil is mainly oxidized directly to the vicinal glycol derivative [21]

(18)
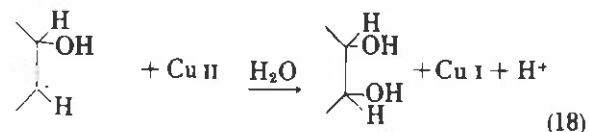
although isobarbituric acid is a minor product of the reaction

(19)
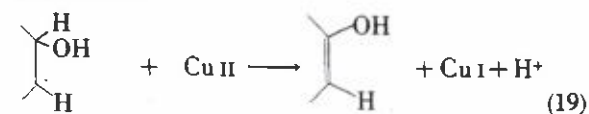
Compared with the pyrimidines, the mechanism of OH-induced oxidation of the purines has received considerably less attention. Early radiation chemical

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studies which showed that deamination and ring opening were important in the overall oxidation process were explained on the basis of OH-addition to the 4-5 double bond as the main initiating reaction [22, 23]

(21)
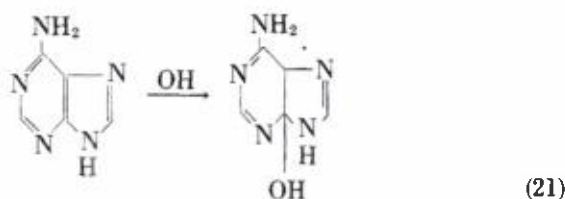
However there is some evidence [24] that OH attack can occur elsewhere in adenine since small yields of 8-hydroxyadenine and 4-5-6-triaminopyrimidine are formed in this system.

Further confirmation that the 4-5 double bond is a major locus of OH attack in purines was obtained from an analysis of the radiolysis products from several purine bases [25, 26]. It was argued from conventional purine chemistry that oxidation at the 4-5 position should give, on hydrolysis, 4-5 diketo products. The overall stoichiometry in the case of xanthine is given by the equation:

(22)
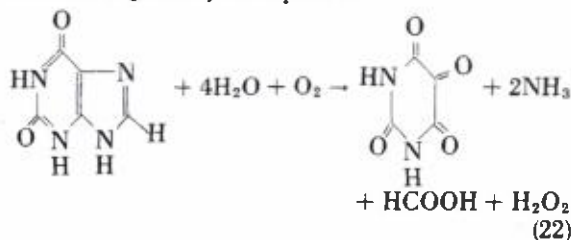
Analysis of irradiated oxygenated xanthine solution showed that alloxan and ammonia were formed in relative yields required by this stoichiometry. For other purines, the degradation products vary although OH addition at the 4-5 double bond is indicated as the main initiating reaction in each case.

Rate constants for reactions of OH with free bases, nucleosides, and nucleotides are listed in table 18. In general, the rate constants are near diffusion-limited values and unlike the reactivities with the strongly reducing entity, the hydrated electron, there appears to be little difference between free bases and the sugar phosphate derivatives. Where the data are available, it can be seen that the rate constants measured absolutely by direct observation of the rate of formation of the OH-adduct, agree well with those determined by measurement of the rate of bleaching of the chromophor. This again confirms that the 5-6 double bond in the pyrimidines is the locus of OH attack. Although there are occasionally very small changes in reactivity with change of pH, it is clear that, also unlike reaction with e_{aq}^-, there appears to be little general effect of tautomerism on the rate constants for reaction with OH.

DNA

Nucleoprotein in aqueous solution is itself fairly resistant to OH attack [27] which contrasts markedly with the sensitivity of free DNA even when present in solution with equimolar proportions of free protein. This apparent protection of DNA in nucleoprotein is consistent with the proposed structure for this molecule in which the double helix of DNA is enveloped by the protein chains. In aqueous solution therefore, OH radicals formed in the solvent have restricted access to the DNA core and must react preferentially with the protein sheath.

In solution, free DNA is inactivated by reaction with OH, a process which occurs mainly by attack at the base moieties. However, elimination of free bases also occurs due to OH attack on the sugar backbone [22]. The relative yield of free base measured after hydrolysis of the irradiated DNA, is about 20 percent of the total base damage. This is as might be expected since, in general, rate constants for reaction of OH with alcohols and polyhydric compounds (table 19), e.g., ribose, are about an order of magnitude lower than those for addition to pyrimidine and purine bases.

TABLE 14. *Sulfur and selenium compounds*

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
cysteamine	$(1.47 \pm 0.1) \times 10^{10}$	1.4–9	[8]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
cysteine	1.3×10^{10}	1	[20]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$(5.1 \pm 0.5) \times 10^9$	2	[19]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
cystine	$(4.8 \pm 0.5) \times 10^9$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
dimethylsulfide	$^*5.2 \times 10^9$	neut.	[30]	PR product. form.	Absolute. N$_2$O added. No corr. for H-atoms
dimethylsulfoxide	7.0×10^9	neut.	[30]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$

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TABLE 14. *Sulfur and selenium compounds* Continued

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
glutathione	1.47×10^{10}	1.0	[28]	PR comp. with CNS$^-$	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
glycylmethionine	$(4.0 \pm 0.3) \times 10^8$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
	$(1.1 \pm 0.25) \times 10^8$	2	[29]	PR comp. with CNS$^-$	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	$(2.2 \pm 0.3) \times 10^8$	5	[29]	PR comp. with CNS$^-$	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
hydrogen sulfide	1.84×10^{10}	6	[7]	PR comp. with CNS$^-$	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	9.0×10^9	alk.	[7]	PR comp. with CNS$^-$	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
hydrogen selenide	$(1.0 \pm 0.3) \times 10^{10}$	1.0	[31]	PR comp. with CNS$^-$ I$^-$ and Br$^-$	Mean value calculated three det. Rel. to $k_{OH+CNS^-} = 6.6 \times 10^9$
	5.5×10^9	8.5–11.5	[31]	PR comp. with CNS$^-$ I$^-$ and Br$^-$	$k_{OH+I^-} = 7.0 \times 10^9$ $k_{OH+Br^-} = 5.0 \times 10^9$
t-butylmercaptan	$(1.8 \pm 0.3) \times 10^{10}$	7	[32]	PR comp. with CNS$^-$	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
methylmercaptan	$(3.3 \pm 0.5) \times 10^{10}$	7	[32]	PR comp. with CNS$^-$	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	$(1.0 \pm 0.15) \times 10^{10}$	11	[32]	PR comp. with CNS	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
2-mercaptoethanol	8.5×10^9	6–7	[28]	PR comp. with CNS$^-$	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	$(2.7 \pm 0.4) \times 10^{10}$	7	[32]	PR comp. with CNS$^-$	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	†$(6.1 \pm 0.7) \times 10^9$	6.5	[33]	PR comp. with ferrocyanide	Rel. to $k_{OH + ferrocyan.} = 9.3 \times 10^9$
	†$(4.9 \pm 0.5) \times 10^9$	6.5	[33]	PR comp. with nitrobenzene	Rel. to $k_{OH + \Phi NO_2} = 4.7 \times 10^9$
	$(6.7 \pm 0.1) \times 10^9$	11	[32]	PR comp. with CNS$^-$	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
methionine	$(8.2 \pm 0.7) \times 10^9$	5.5–7	[29]	PR comp. with CNS$^-$	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	8.5×10^9	6–7	[28]	PR comp. with CNS$^-$	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	$(6.0 \pm 0.5) \times 10^9$	2–2.8	[29]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
selenourea	*6.9×10^9	neut.	[11]	PR bleaching of solute	Absolute
	*5.5×10^9	neut.	[11]	PR build-up	Absolute
	1.20×10^{10}	neut.	[11]	PR comp. with CNS$^-$	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	1.14×10^{10}	neut.	[11]	PR comp. with ethanol	Rel. to $k_{OH + C_2H_5OH} = 1.85 \times 10^9$
	1.17×10^{10}	neut.	[11]	PR comp. with methanol	Rel. to $k_{OH + CH_3OH} = 0.85 \times 10^9$

TABLE 15. *Amino acids*

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
alanine	$(4.4 \pm 0.2) \times 10^7$	2	[19]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
	4.65×10^7	6	[35]	S irrad. comp. with ferrocyanide	Rel. to $k_{OH + ferrocyan.} = 9.3 \times 10^9$
	$(7.7 \pm 0.6) \times 10^7$	5.5–6	[29]	PR comp. with CNS$^-$	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	6.6×10^8	9.75	[35]	S irrad. comp. with ferrocyanide	Rel. to $k_{OH + ferrocyan.} = 9.3 \times 10^9$
arginine	$(6.6 \pm 0.6) \times 10^8$	2	[29]	PR comp. with CNS$^-$	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	$(7.2 \pm 0.5) \times 10^8$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
	$(3.5 \pm 0.3) \times 10^9$	6.5–7.5	[29]	PR comp. with CNS$^-$	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
asparagine	3.1×10^7	2	[19]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
aspartic acid	$(2.1 \pm 0.2) \times 10^7$	6.8	[29]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
	$(7.5 \pm 1) \times 10^7$	2	[29]	PR comp. with CNS$^-$	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$

TABLE 15. *Amino acids*—Continued

Reactant	$k(M^{-1}\text{s}^{-1})$	pH	Ref.	Method	Comments
glutamic acid	$(1.3 \pm 0.1) \times 10^8$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
glutamine	1.5×10^8	2	[19]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
glycine	1.7×10^7	1	[28]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$(7.2 \pm 0.3) \times 10^6$	2.8	[29]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
	$(1.0 \pm 0.07) \times 10^7$	2.8	[29]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	4.5×10^6	5	[36]	S irrad. comp. with PNDA	Rel. to $k_{OH + C_2H_5OH} = 1.85 \times 10^9$
	$(1.7 \pm 0.17) \times 10^7$	5.8	[29]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	5.9×10^6	7	[35]	S irrad. comp. with ferrocyanide	Rel. to $k_{OH + ferrocyan.} = 9.3 \times 10^9$
	2.7×10^8	9.5	[35]	S irrad. comp. with ferrocyanide	Rel. to $k_{OH + ferrocyan.} = 9.3 \times 10^9$
	$(1.8 \pm 0.15) \times 10^9$	9.5	[29]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	2.6×10^9	10.5	[37]	S irrad. comp. with benzoate	Rel. to $k_{OH + benzoate} = 5.6 \times 10^9$
	3.8×10^9	10.5	[35]	S irrad. comp. with ferrocyanide	Rel. to $k_{OH + ferrocyan.} = 9.3 \times 10^9$
	2.0×10^9	12	[36]	S irrad. comp. with PNDA	Rel. to $k_{OH + C_2H_5OH} = 1.85 \times 10^9$
histidine	$(1.9 \pm 0.15) \times 10^9$	2	[29]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$(5.0 \pm 0.3) \times 10^9$	6–7	[29]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
hydroxyproline	$(3.3 \pm 0.15) \times 10^8$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
isoleucine	$(1.7 \pm 0.1) \times 10^9$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
leucine	$(1.8 \pm 0.1) \times 10^9$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
	$(1.6 \pm 0.1) \times 10^9$	2	[29]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$(1.6 \pm 0.1) \times 10^9$	5.5	[29]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$(3.8 \pm 0.5) \times 10^9$	9.8	[29]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
lysine	$(6.0 \pm 0.5) \times 10^8$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
norleucine	2.8×10^9	2	[19]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
norvaline	1.4×10^9	2	[19]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
ornithine	1.6×10^8	2	[19]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
phenylalanine	$(7.0 \pm 0.3) \times 10^9$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
	$(5.7 \pm 0.5) \times 10^9$	2	[29]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$(5.8 \pm 0.5) \times 10^9$	5.5–6	[29]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$\dagger 6.0 \times 10^9$	neut.	[38]	PR comp. with ferrocyanide	Rel. to $k_{OH + ferrocyan.} = 9.3 \times 10^9$
	$\dagger^* 6.6 \times 10^9$	neut.	[38]	PR product form.	Absolute. N_2O added. No corr. for H-addit.
	$(9.5 \pm 1.5) \times 10^9$	10.6	[39]	PR comp. with carbonate	Given rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
proline	$(2.9 \pm 0.15) \times 10^8$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$
serine	$(2.5 \pm 0.15) \times 10^8$	2	[29]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$(3.2 \pm 0.3) \times 10^8$	5.5–6	[29]	PR comp. with CNS$^-$	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
threonine	$(3.6 \pm 0.15) \times 10^8$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH + thymine} = 4.7 \times 10^9$

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TABLE 15. *Amino acids – Continued*

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
tryptophan	†*$(1.25 \pm 0.2) \times 10^{10}$	1	[6]	PR product form.	Absolute. N_2O added. No corr. for H-addit.
	$(1.1 \pm 0.25) \times 10^{10}$	2	[29]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$(7.0 \pm 0.6) \times 10^{9}$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^{9}$
	$(1.4 \pm 0.25) \times 10^{10}$	6.1	[29]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	†*$(1.2 \pm 0.3) \times 10^{10}$	8.8	[6]	PR product form.	Absolute. N_2O added. No corr. for H-addit.
tyrosine	$(2.2 \pm 0.5) \times 10^{10}$	10.6	[39]	PR comp. with CO_3^{2-}	Given rel. to $k_{OH+CO_3^{2-}} = 4.1 \times 10^{8}$
valine	$(6.6 \pm 0.5) \times 10^{8}$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^{9}$

TABLE 16. *Simple peptides*

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
acetylalanine	4.6×10^{8}	9.2	[41]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
acetylglycine	4.2×10^{8}	8.7	[41]	PR comp. with CNS	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
acetylglycylglycine	7.8×10^{8}	8.6	[41]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
alanylglycine	$(1.4 \pm 0.8) \times 10^{7}$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^{9}$
glycylalanine	$(1.7 \pm 0.15) \times 10^{8}$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^{9}$
	$(3.5 \pm 0.3) \times 10^{8}$	5.5–6	[29]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
glycylglycine	$(1.2 \pm 0.1) \times 10^{8}$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^{9}$
	$(1.6 \pm 0.1) \times 10^{8}$	2.2	[19]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	4.4×10^{8}	4.2	[41]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$(2.2 \pm 0.2) \times 10^{8}$	5.5–6	[29]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	2.7×10^{8}	6–7	[28]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	5.2×10^{9}	10.5	[41]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
glycylglycylglycine	$(1.4 \pm 0.07) \times 10^{8}$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^{9}$
	$(2.4 \pm 0.25) \times 10^{8}$	2.8	[29]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	7.3×10^{8}	5.4	[41]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$(3.3 \pm 0.7) \times 10^{8}$	5.5–6.0	[29]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$(1.75 \pm 0.15) \times 10^{9}$	8.5	[29]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	5.0×10^{9}	10.6	[41]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
glycylglycylglycylglycine	$(2.2 \pm 0.6) \times 10^{8}$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^{9}$
	$(3.5 \pm 0.3) \times 10^{8}$	2.4	[29]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$(4.5 \pm 0.5) \times 10^{8}$	5.5–6.0	[29]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$(1.2 \pm 0.1) \times 10^{8}$	7.7	[29]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
	$(3.0 \pm 0.1) \times 10^{9}$	9.5	[29]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
glycylisoleucine	$(2.7 \pm 0.15) \times 10^{8}$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^{9}$
glycylleucine	$(2.3 \pm 0.15) \times 10^{9}$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^{9}$
glycylpenylalanine	$(8.2 \pm 0.6) \times 10^{8}$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^{9}$

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TABLE 16. *Simple peptides* — Continued

Reactant	$k(M^{-1} s^{-1})$	pH	Ref.	Method	Comments
glycylproline	$(1.3 \pm 0.1) \times 10^9$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
glycylserine	$(5.3 \pm 0.3) \times 10^8$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
glycyltyrosine	$(9.0 \pm 0.6) \times 10^9$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
glycylvaline	$(1.1 \pm 0.1) \times 10^9$	2	[29]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
histidylhistidine	$(9.0 \pm 0.3) \times 10^9$	5.5–6.5	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$

TABLE 17. *Enzymes*

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
alcoholdehydrogenase (yeast)	1.6×10^{11}	9	[42]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	2.2×10^{11}	neut.	[43]	PR comp. with nitrobenzene	Rel. to $k_{OH+\Phi NO_2} = 4.7 \times 10^9$
catalase	1.4×10^{11}	basic	[44]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
lysozyme	†4.9×10^{10}	neut.	[45]	PR product form.	Absolute. N_2O added. No corr. for H-addit.
	5.1×10^{10}	neut.	[46]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
	1.86×10^{10}	9	[42]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
ribonuclease	4.3×10^{10}	6.8	[47]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	ª8.7×10^{10}	6.8	[47]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
trypsin	†$(8.2 \pm 0.7) \times 10^{10}$	7.1	[48]	PR prod. form.	Absolute. N_2O added. No corr. for H addit.
	$(1.6 \pm 0.1) \times 10^{11}$	7.4	[48]	PR comp. with glucose	Rel. to $k_{OH+glucose} = 1.9 \times 10^9$
trypsinogen	$(1.6 \pm 0.1) \times 10^{11}$	7	[48]	PR comp. with glucose	Rel. to $k_{OH+glucose} = 1.9 \times 10^9$

ª$T = 60$ °C

TABLE 18. *Nucleic acid derivatives*

Reactant	$k(M^{-1} s^{-1})$	pH	Ref.	Method	Comments
adenine	$(8.8 \pm 0.8) \times 10^8$	2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	$(3.8 \pm 0.15) \times 10^9$	5–5.5	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	$(2.8 \pm 0.5) \times 10^9$	6.5	[49]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	$(5.0 \pm 0.5) \times 10^9$	7.3	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
adenosine	$(1.75 \pm 0.15) \times 10^9$	2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	$(3.8 \pm 0.3) \times 10^9$	5.2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	$(4.2 \pm 0.4) \times 10^9$	7.6	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
adenosine-5-phosphate	$(1.25 \pm 0.12) \times 10^9$	2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	$(3.0 \pm 0.3) \times 10^9$	5.2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	4.0×10^9	9	[42]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
deoxyadenylic acid	$(1.37 \pm 0.12) \times 10^9$	2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$
	$(3.5 \pm 0.3) \times 10^9$	6.4	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.} = 1.1 \times 10^{10}$

TABLE 18. *Nucleic acid derivatives* — Continued

Reactant	$k(M^{-1}\,s^{-1})$	pH	Ref.	Method	Comments
cytosine	$(3.1 \pm 0.15) \times 10^9$	2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
	$(4.5 \pm 0.3) \times 10^9$	5–6	[29]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
	$(4.9 \pm 0.3) \times 10^9$	7.4	[29]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
cytidine	$(3.3 \pm 0.3) \times 10^9$	2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
	$(4.9 \pm 0.5) \times 10^9$	5.2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
	$(4.6 \pm 0.5) \times 10^9$	7.2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
cystosine-5-phosphate	$(2.5 \pm 0.25) \times 10^9$	2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
	$(4.4 \pm 0.5) \times 10^9$	7.4	[29]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
deoxycytidylic acid	$(3.0 \pm 0.15) \times 10^9$	2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
	$(3.8 \pm 0.3) \times 10^9$	4.3	[29]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
	$(5.0 \pm 0.3) \times 10^9$	6.7	[29]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
guanosine	7.6×10^9	9	[42]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
deoxyguanylic acid	$(4.7 \pm 0.5) \times 10^9$	2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
	$(6.8 + 0.5) \times 10^9$	6.5–7.0	[29]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
orotic acid	5.1×10^9	neut.	[54]	PR comp. with ferrocyanide	Rel. to $k_{OH+ferrocyan.} = 9.3 \times 10^9$
isoorotic acid	3.9×10^9	neut.	[54]	PR comp. with ferrocyanide	Rel. to $k_{OH+ferrocyan.} = 9.3 \times 10^9$
dihydroorotic acid	2.9×10^9	neut.	[54]	PR comp. with ferrocyanide	Rel. to $k_{OH+ferrocyan.} = 9.3 \times 10^9$
orotidine	3.9×10^9	neut.	[54]	PR comp. with ferrocyanide	Rel. to $k_{OH+ferrocyan.} = 9.3 \times 10^9$
thymine	$(3.7 \pm 0.2) \times 10^9$	0.7–7.0	[50]	S irrad. loss of chromophor	Rel. to ethanol taking $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	5.2×10^9	1	[28]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
	$(5.2 \pm 0.2) \times 10^9$	2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
	$(7.8 \pm 1.0) \times 10^9$	2	[19]	S irrad. loss of chromophor	Rel. to $k_{OH+C_2H_6} = 7.8 \times 10^9$
	$(5.0 \pm 0.2) \times 10^9$	5–5.5	[29]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
	$(5.3 \pm 0.2) \times 10^9$	7.2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} = 1.1 \times 10^{10}$
	*7.4×10^9	7	[51]	PR product form.	Absolute. N_2O added. No corr. for H addit.
	4.9×10^9	7	[52]	S irrad. loss of chromophor	Comp. with methanol and ethanol. Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
	†4.7×10^9	neut.	[38]	PR comp. with ferrocyanide	Rel. to $k_{OH+ferrocyan.} = 9.3 \times 10^9$
	†*5.1×10^9	neut.	[38]	PR bleaching chromophor	Absolute. N_2O and O_2 added
	$(7.6 \pm 1.1) \times 10^9$	neut.	[53]	PR comp. with CNS⁻	Rel. to $k^{rel}_{thiocyan.} \times 1.1 \times 10^{10}$
	*$(7-4 \pm 0.5) \times 10^9$	neut.	[53]	PR bleaching of chromophor	Absolute. No corr. for H-addit.
	*$(4.6 \pm 0.3) \times 10^9$	neut.	[53]	PR product form.	Absolute. No corr. for H-addit.
	6.2×10^9	9	[42]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
	†*3.9×10^9	11	[51]	PR product form.	Absolute. N_2O added. No corr. for H-addit.
	†*1.1×10^9	12.4	[51]	PR product form.	Absolute. N_2O added. No corr. for H-addit.

TABLE 18. *Nucleic acid derivatives* — Continued

Reactant	$k\,(M^{-1}\,s^{-1})$	pH	Ref.	Method	Comments
dihydrothymine	$(4.7\pm0.5)\times10^9$	neut.	[53]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
	†*2.2×10^9	neut.	[53]	PR product from.	Absolute. No corr. for H-addit.
	†*2.2×10^9	neut.	[51]	PR product form.	Absolute. N₂O added. No corr. for H-addit.
	*4×10^8	12.4	[51]	PR product form.	Absolute. N₂O added. No corr. for H-addit.
thymidine	$(4.6\pm0.5)\times10^9$	2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
	$(5.0\pm0.5)\times10^9$	5	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
	$(4.6\pm0.5)\times10^9$	7.4	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
	†*4.7×10^9	7	[51]	PR product form.	Absolute. N₂O added. No corr. for H-addit.
	†*2.1×10^9	12.4	[51]	PR product form.	Absolute. N₂O added. No corr. for H-addit.
thymidylic acid (amm. salt)	$(4.3\pm0.5)\times10^9$	2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
	$(5.3\pm0.5)\times10^9$	6.5–7.0	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
uracil	$(4.8\pm0.5)\times10^9$	2	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
	$(5.2\pm0.7)\times10^9$	5	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
	$(7.3\pm0.9)\times10^9$	6.5	[49]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
	†*$(7.4\pm1.0)\times10^9$	7	[49]	PR loss of chromophor	Absolute. No corr. for H-addit.
	$(7.3\pm0.9)\times10^9$	neut.	[53]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
	†*$(6.0\pm0.3)\times10^9$	neut.	[53]	PR loss of chromophor	Absolute. No corr. for H-addit.
	†*$(6.5\pm0.7)\times10^9$	neut.	[53]	PR product form.	Absolute. No corr. for H-addit.
	$(5.3\pm0.5)\times10^9$	7.3	[29]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
	6.8×10^9	9	[42]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA}=1.25\times10^{10}$
5-bromouracil	4.3×10^9	9	[42]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA}=1.25\times10^{10}$
	†*3.6×10^9	7	[40]	PR prod. form.	Absolute. N₂O added. No corr. for H-addit.
dihydrouracil	$(1.2\pm0.15)\times10^9$	neut.	[53]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
uridine	$(4.2\pm0.6)\times10^9$	neut.	[53]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
	†*$(6.0\pm0.3)\times10^9$	neut.	[53]	PR loss of chromophor	Absolute. No corr. for H-addit.
	†*$(6.5\pm0.7)\times10^9$	neut.	[53]	PR product form.	Absolute. No corr. for H-addit.
	$(4.3\pm0.6)\times10^9$	6.5	[49]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
uridine mono-phosphate (mixed)	$(5.1\pm0.8)\times10^9$	6.5	[49]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
	$(5.1\pm0.7)\times10^9$	neut.	[53]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
	†*$(4.6\pm0.3)\times10^9$	neut.	[53]	PR loss of chromophor	Absolute. No corr. for H-addit.
	†*$(4.0\pm0.4)\times10^9$	neut.	[53]	PR product form.	Absolute. No corr. for H-addit.
uridylyl 3′ → 5′ uridine (UpU)	$(5.3\pm0.6)\times10^9$	neut.	[53]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
	†*$(3.8\pm0.2)\times10^9$	neut.	[53]	PR loss of chromophor	Absolute. No corr. for H-addit. (calc. per unit base)
oligouridylic acid	$(4.0\pm0.6)\times10^9$	neut.	[53]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$
	†*$(4.3\pm0.2)\times10^9$	neut.	[53]	PR loss of chromophor	Absolute. No corr. for H-addit. (calc. per unit base)
polyuridylic acid	$(1.5\pm0.15)\times10^9$	neut.	[53]	PR comp. with CNS⁻	Rel. to $k^{rel.}_{thiocyan.}=1.1\times10^{10}$

TABLE 19. *Nucleic acid derivatives — Continued*

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
DNA	$^*6 \times 10^8$	7	[51]	PR product form.	Absolute. N_2O added. No corr. for H-addit. Based on mean nucleotide mol. wt. of 350
	$^*6 \times 10^8$	12.4	[51]	PR product form.	Absolute. N_2O added. No corr. for H-addit. Based on mean nucleotide mol. wt. of 350
	10^{13}	9	[42]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$ (mol. wt. $= 5 \times 10^6$)
	$^*1.3 \times 10^{13}$	7.5	[34]	PR product form.	Absolute. N_2O added. No corr. for H-addit. (mol. wt. $= 5 \times 10^6$)

TABLE 19. *Carbohydrates and related compounds*

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
ascorbic acid	1.20×10^{10}	1	[26]	PR comp. with CNS	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
2-acetamido-2-deoxy-D-glucose	3.07×10^9		[55]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
2-acetamido-2-deoxy-D-galactose	1.62×10^9		[55]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
N-acetylglucoseamine	3.07×10^9		[56]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
2-amino-2-deoxy-D-galactose (HCl)	1.77×10^9		[55]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
chondroitin-4-sulfate I	8.0×10^8		[55]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$ Conc. = mol. equiv./liter (1. equiv. = average mol. wt. of hexose unit)
chondroitin-6-sulfate I	6.8×10^8		[55]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$ Conc. = mol. equiv./liter (1. equiv. = average mol. wt. of hexose unit)
N-desulfated heparin	8.0×10^8		[55]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$ Conc. = mol. equiv./liter (1 equiv. = average mol. wt. of hexose unit)
2-deoxy-2-sulfo-amino-D-glucose	2.12×10^9		[55]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
erythrytol	2.0×10^9	9	[36]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
glucose	1×10^9		[57]	PR comp. with I⁻	Rel. to $k_{OH+I^-} = 1.0 \times 10^{10}$
	1.9×10^9	2	[19]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
glucuronic acid	3.09×10^9		[56]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
D-glucuronate (Na)	3.09×10^9		[55]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$
heparin	3.7×10^8		[56]	PR comp. with CNS⁻	Rel. to $k_{thiocyan.}^{rel.} = 1.1 \times 10^{10}$ Conc. = mol. equiv./liter (1 equiv. = average mol. wt. of hexose unit.)

TABLE 19. *Carbohydrates and related compounds—Continued*

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
hyaluronic acid	6.7×10^8		[56]	PR comp. with CNS⁻	Rel. to $k_{thiocyan}^{rel.} = 1.1 \times 10^{10}$ Conc. = mol. equiv./liter (1 equiv. = average mol. wt. of hexose unit.)
	$(1.34 \pm 0.07) \times 10^9$		[58]	PR comp. with CNS⁻	Rel. to $k_{thiocyan}^{rel.} = 1.1 \times 10^{10}$ Conc. = mol. equiv./liter (1 equiv. = average mol. wt. of hexose unit.)
hyaluronic acid (sulfated)	6.0×10^8		[55]	PR comp. with CNS⁻	Rel. to $k_{thiocyan}^{rel.} = 1.1 \times 10^{10}$ Conc. = mo. equiv./liter (1 equiv. = average mol. wt. of hexose unit.)
keratan sulfate	7.8×10^9		[59]	PR comp. with CNS⁻	Rel. to $k_{thiocyan}^{rel.} = 1.1 \times 10^{10}$ Conc. = mol. equiv./liter (1 equiv. = average mol. wt. of hexose unit.)
pentaerythrytol	3.2×10^9	9	[36]	S irrad. comp. with PNDA	Rel. to $k_{OH+C_2H_5OH} = 1.85 \times 10^9$
ribose	2.1×10^9	9	[42]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$
sucrose	$(2.5 \pm 0.3) \times 10^9$	2	[19]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$

TABLE 20. *Miscellaneous compounds*

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
benzene sulfonate	2.9×10^9		[56]	PR comp. with CNS⁻	Rel. to $k_{thiocyan}^{rel.} = 1.1 \times 10^{10}$
ethane sulfonate	1.0×10^7		[56]	PR comp. with CNS⁻	Rel. to $k_{thiocyan}^{rel.} = 1.1 \times 10^{10}$
glutamine	$(1.4 \pm 0.15) \times 10^8$	2	[19]	S irrad. comp. with thymine	Rel. to $k_{OH+thymine} = 4.7 \times 10^9$
poly(ethylene-sulfonate)	1.2×10^7		[56]	PR comp. with CNS⁻	Rel. to $k_{thiocyan}^{rel.} = 1.1 \times 10^{10}$
poly(styrene-sulfonate)	3.3×10^8		[56]	PR comp. with CNS⁻	Rel. to $k_{thiocyan}^{rel.} = 1.1 \times 10^{10}$
toluene sulfonate	3.0×10^9		[56]	PR comp. with CNS⁻	Rel. to $k_{thiocyan}^{rel.} = 1.1 \times 10^{10}$
nor-pseudo-peller-tierine-N-oxyl (NPPN)	$(7.4 \pm 1) \times 10^9$	alk.	[60]	PR comp. with CO_3^-	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
sodium sulfacetamide	8.1×10^9		[61]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$ (Values interpolated from data)
sulfanilic acid	6.3×10^9		[61]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$ (Values interpolated from data)
sulfanilamide	6.0×10^9		[61]	S irrad. comp. with PNDA	Rel. to $k_{OH+PNDA} = 1.25 \times 10^{10}$ (Values interpolated from data)
triacetoneamine-N-oxyl	$(4.3 \pm 0.5) \times 10^9$	alk.	[60]	PR comp. with CO_3^-	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$

TABLE 20. *Miscellaneous compounds*—Continued

Reactant	$k(M^{-1}s^{-1})$	pH	Ref.	Method	Comments
eosin	2×10^{10}	8.5	[62]	PR comp. with CO_3^-	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
eosin-Y	1.4×10^9	10.5	[63]	PR comp. with CO_3^-	Rel. to $k_{OH+CO_3^-} = 4.1 \times 10^8$
eosin dianion	*1.7×10^9 (i) *6×10^8 (ii)	9	[64]	PR product form.	Absolute. Computer analysis. (i) electron transfer reaction (ii) OH-addition
fluoroscein	*$(1.6 \pm 0.3) \times 10^9$ (i) *$(1.4 \pm 0.2) \times 10^9$ (ii)	9.2	[65]	PR product form.	Absolute computer analysis. (i) electron transfer reaction (ii) OH-addition
indole	$(1.37 \pm 0.5) \times 10^{10}$	9	[66]	S irrad. comp. with PNDA	Rel. to tryptophan $k_{OH+tryptophan} = 1.25 \times 10^{10}$
indoline	$(2.02 \pm 0.14) \times 10^{10}$	9	[66]	S irrad. comp. with PNDA	Rel. to tryptophan $k_{OH+tryptophan} = 1.25 \times 10^{10}$
1-methylindole	$(1.44 \pm 0.01) \times 10^{10}$	9	[66]	S irrad. comp. with PNDA	Rel. to tryptophan $k_{OH+tryptophan} = 1.25 \times 10^{10}$
2-methylindole	1.44×10^{10}	9	[66]	S irrad. comp. with PNDA	Rel. to tryptophan $k_{OH+tryptophan} = 1.25 \times 10^{10}$
3-methylindole	1.05×10^{10}	9	[66]	S irrad. comp. with PNDA	Rel. to tryptophan $k_{OH+tryptophan} = 1.25 \times 10^{10}$
1,2-dimethylindole	$(1.25 \pm 0.02) \times 10^{10}$	9	[66]	S irrad. comp. with PNDA	Rel. to tryptophan $k_{OH+tryptophan} = 1.25 \times 10^{10}$
1,3-dimethylindole	$(1.01 \pm 0.08) \times 10^{10}$	9	[66]	S irrad. comp. with PNDA	Rel. to tryptophan $k_{OH+tryptophan} = 1.25 \times 10^{10}$
2,3-dimethylindole	$(1.26 \pm 0.01) \times 10^{10}$	9	[66]	S irrad. comp. with PNDA	Rel. to tryptophan $k_{OH+tryptophan} = 1.25 \times 10^{10}$
5-methylindole	$(1.66 \pm 0.06) \times 10^{10}$	9	[66]	S irrad. comp. with PNDA	Rel. to tryptophan $k_{OH+tryptophan} = 1.25 \times 10^{10}$
5-chloroindole	$(1.91 \pm 0.06) \times 10^{10}$	9	[66]	S irrad. comp. with PNDA	Rel. to tryptophan $k_{OH+tryptophan} = 1.25 \times 10^{10}$
5-bromoindole	$(1.57 \pm 0.18) \times 10^{10}$	9	[66]	S irrad. comp. with PNDA	Rel. to tryptophan $k_{OH+tryptophan} = 1.25 \times 10^{10}$
5-hydroxyindole	$(1.67 \pm 0.10) \times 10^{10}$	9	[66]	irrad. comp. with PNDA	Rel. to tryptophan $k_{OH+tryptophan} = 1.25 \times 10^{10}$
5-methoxyindole	$(1.39 \pm 0.04) \times 10^{10}$	9	[66]	S irrad. comp. with PNDA	Rel. to tryptophan $k_{OH+tryptophan} = 1.25 \times 10^{10}$
5-amido indole	$(3.17 \pm 0.31) \times 10^{10}$	9	[66]	S irrad. comp. with PNDA	Rel. to tryptophan $k_{OH+tryptophan} = 1.25 \times 10^{10}$
5-nitroindole	$(1.25 \pm 0.24) \times 10^{10}$	9	[66]	S irrad. comp. with PNDA	Rel. to tryptophan $k_{OH+tryptophan} = 1.25 \times 10^{10}$
5-cyanoindole	$(1.06 \pm 0.24) \times 10^{10}$	9	[66]	S irrad. comp. with PNDA	Rel. to tryptophan $k_{OH+tryptophan} = 1.25 \times 10^{10}$
indole-5-acetic acid	$(0.79 \pm 0.07) \times 10^{10}$	9	[66]	S irrad. comp. with PNDA	Rel. to tryptophan $k_{OH+tryptophan} = 1.25 \times 10^{10}$

Chapter X. References

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constants, it is evident from table 21 that agreement with values determined by absolute methods is generally very good. There is little doubt attached to the authenticity of the absolute value of the reference rate constant and, in addition, the reference reaction is a one-electron transfer reaction in which both the reactant (ferrocyanide ion) and the product (ferricyanide ion) are stable chemical species. We consider, therefore, that the evidence to date justifies the acceptance of this method as a reliable competition method for the determination of OH rate constants.

Chapter XI. References

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