

Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals ($\cdot\text{OH}/\text{O}^-$) in Aqueous Solution

George V. Buxton

*University of Leeds,
Cookridge Radiation Research Centre,
Leeds, LS16 6QB, England*

and

Clive L. Greenstock

*Medical Biophysics Branch,
Whiteshell Nuclear Research Establishment,
Atomic Energy of Canada Limited Research Company,
Pinawa, Manitoba, Canada, ROE 1LO*

and

W. Phillip Helman and Alberta B. Ross

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

Kinetic data for the radicals $\text{H}\cdot$ and $\cdot\text{OH}$ in aqueous solution, and the corresponding radical anions, O^- and e_{aq}^- , have been critically reviewed. Reactions of the radicals in aqueous solution have been studied by pulse radiolysis, flash photolysis and other methods. Rate constants for over 3,500 reactions are tabulated, including reactions with molecules, ions and other radicals derived from inorganic and organic solutes.

Key words: Aqueous solution; chemical kinetics; critical review; data compilation; hydrated electron; hydrogen atom; hydroxyl radical; rate constants.

1. General Introduction

The development of aqueous radiation chemistry,¹ and especially the pulse radiolysis technique,² has provided chemists with a very simple and clean method of generating and studying the reactions of unstable species in aqueous solution such as organic and inorganic free radicals and metal ions in unusual oxidation states. This review comprises a critically evaluated compilation of the rate constants which have been measured for the reactions with solutes of the hydrated electron, e_{aq}^- , the hydrogen atom, $\text{H}\cdot$, the hydroxyl radical, $\cdot\text{OH}$, and its basic form, the oxide radical ion, O^- . A knowledge of these data enables the chemist to choose the appropriate conditions for generating the species of interest starting with these free radicals, and this knowledge has many applications in the whole field of chemistry in aqueous solution.

Many reviews, data compilations, and monographs have been published on the reactivity of transients from water.³⁻¹⁰ This compilation contains data published through 1986 and is a complete reevaluation and update of the earlier NSRDS-NBS reports⁸⁻¹⁰.

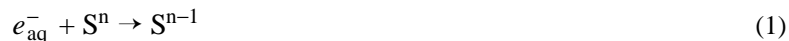
1.1. Properties of e_{aq}^- , H^\bullet , $\bullet\text{OH}$ and $\bullet\text{O}^-$

The properties of these species are listed in Table 1 and their optical absorption spectra are shown in Fig. 1.

1.1.1. The Hydrated Electron

The hydrated electron may be visualized as an excess electron surrounded by a small number of oriented water molecules and behaving in some ways like a singly charged anion of about the same size as the iodide ion. Its intense absorption band in the visible region of the spectrum makes it a simple matter to measure its reaction rate constants using pulse radiolysis combined with kinetic spectrophotometry.

As expected from its standard reduction potential^{22,29} of -2.9 V, the hydrated electron reacts rapidly with many species having more positive reduction potentials. Its mode of reaction can be generally represented as the one-electron transfer process



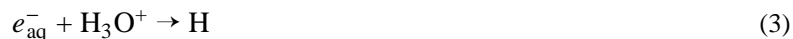
where n is the positive charge on the solute, although in some cases the electron adduct immediately dissociates. Its rate constants range from $\sim 10^1$ L mol⁻¹ s⁻¹ up to the diffusion controlled limit but the activation energies are invariably small and lie in the range 6-30 kJ mol⁻¹. This suggests that the dominant kinetic parameter is the availability of a vacant orbital of the solute into which the electron can transfer.

The hydrated electron acts as a nucleophile in its reactions with organic molecules, and its reactivity is greatly enhanced by electron-withdrawing substituents adjacent to alkene double bonds or attached to aromatic rings. Increased reactivity is also observed when organic molecules contain substituent halogen atoms, in which case the negative ion formed in Eq. (2) rapidly eliminates the halide ion.

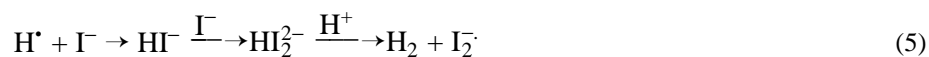
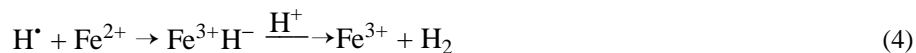


1.1.2. The Hydrogen Atom

The hydrogen atom is the conjugate acid of e_{aq}^- , and it is the major reducing species in acidic solution, Eq. (3).



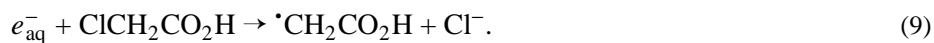
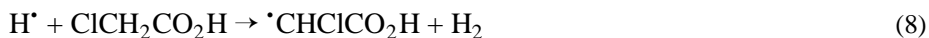
It absorbs only weakly in the ultraviolet so that its reactions are not readily measured by observing H^\bullet itself. With a reduction potential^{22,29} of -2.3 V the hydrogen atom is a slightly less powerful reducing agent than e_{aq}^- , but its chemistry is often quite different. It readily reduces inorganic ions having more positive reduction potentials than itself, but often at slower rates than e_{aq}^- . In some cases, in highly acidic solution, it effectively reacts as an oxidant, forming a hydride intermediate which decomposes to molecular hydrogen and the oxidized solute^{40,41}, for example,



The hydrogen atom reacts with organic compounds by abstracting H from saturated molecules and by adding to centers of unsaturation, for example,



In this respect it resembles the hydroxyl radical, although the latter is more reactive and less selective in abstraction reactions. A good illustration of the different chemistry of H^\bullet and e_{aq}^- is provided by their reactions with chloroacetic acid, as shown by Eqs. (8) and (9),



1.1.3. The Hydroxyl Radical

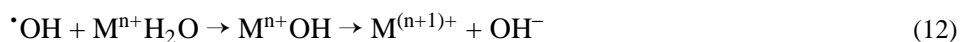
The hydroxyl radical is a powerful oxidant, having a standard reduction potential³¹⁻³³ of 2.7 V in acidic solution and 1.8 V in neutral solution where the free energy of neutralization of OH⁻ by H⁺ is not available. The reaction of [•]OH with ions is often represented as a simple electron transfer,



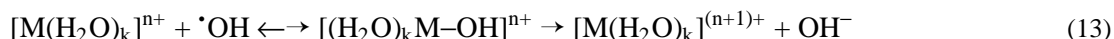
where n is the charge on the ion, but such a simple step is unlikely because of the large solvent reorganization energy involved in forming the hydrated hydroxide ion. Instead, it is suggested⁴² that an intermediate adduct is formed. Such an adduct is observed in the oxidation of halide and pseudo-halide ions,



Although there are several examples of [•]OH reacting with inorganic ions at the diffusion controlled rate, rate constants for oxidation of many aquated metal cations seem to be no more than $\sim 3 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$. A suggested reason⁴³ for this is that [•]OH abstracts H from a coordinated water molecule and this is followed by electron transfer from the metal to the oxidized ligand.



An alternative proposal⁴² is that [•]OH adds to the metal ion to increase its coordination number and oxidation takes place via an inner-sphere mechanism in the equilibrium stage.



It is known that Mⁿ⁺OH is indeed the initial product when Mⁿ⁺ = Tl⁺, Ag⁺, Cu²⁺, Sn²⁺, Fe²⁺ and Mn²⁺, and ligand substitution by [•]OH is ruled out because there is no correlation between rates of substitution and oxidation.

In strongly alkaline solution [•]OH is rapidly converted to its conjugate base [•]O⁻,



with $k_{14} = 1.2 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$, $k_{-14} = 10^8 \text{ s}^{-1}$ and $\text{p}K_a(^{\bullet}\text{OH}) = 11.9$. Thus equilibrium between [•]OH and [•]O⁻ is established when $k[\text{S}] < 10^7 \text{ s}^{-1}$ for [•]OH reactions. [•]O⁻ reacts much more slowly than [•]OH with several inorganic anions, and the rate is immeasurably slow with Br⁻, CO₃²⁻ and Fe(CN)₆⁴⁻ although these ions are all rapidly oxidized by [•]OH.

In its reactions with organic molecules [•]OH behaves as an electrophile whereas [•]O⁻ is a nucleophile. Thus [•]OH readily adds to unsaturated bonds but [•]O⁻ does not. Both forms of the radical abstract H from C-H bonds, and this can result in the formation of different products when the pH is raised to where [•]O⁻, rather than [•]OH, is the reactant. For example, if an aromatic molecule carries an aliphatic side chain, [•]O⁻ attacks there by H abstraction whilst [•]OH adds preferentially to the aromatic ring. As mentioned in section 1.1.2., hydroxyl radicals and hydrogen atoms undergo similar types of reaction with organic molecules, but in abstraction from C-H bonds [•]OH is more reactive and less selective than H[•] because the formation of the H-OH bond is 57 kJ mol⁻¹ more exothermic than the formation of the H-H bond.

2. Methods of Generation of e_{aq}⁻, H[•], [•]OH, and [•]O⁻

All of these radicals are most readily generated in the radiolysis of water, which is described in section 2.1. Although this is by far the most commonly used method, some of the radicals can also be generated in one or more of the following ways: (i) photolysis of an appropriate solute, (ii) production of H[•] by electric discharge in hydrogen gas, (iii) sonolysis of water, and (iv) Fenton-type reactions.

2.1. Radiolysis of Water

This is summarized in the scheme given in Fig. 2 where the numbers represent the G-value of each species in neutral water.

$$G = \frac{\text{no. of molecules formed}}{100 \text{ eV}} \quad (15)$$

This scheme represents the sequence of events initiated by a fast electron either injected from an accelerator or generated *in situ* by ⁶⁰Co γ-rays. Fast electrons are by far the most commonly used type of ionizing radiation.

The initial radiolysis products are generated in isolated volume elements called spurs. As the spurs expand through diffusion a fraction of the species react together while the remainder escape into the bulk solution. In water, 10^{-7} s is the lifetime of a radical reacting at the diffusion-controlled rate with a solute S, whose concentration is 10^{-3} mol L⁻¹, i.e. $k[S] = 10^7$ s⁻¹ where k is the bimolecular rate constant. Thus, under these conditions the yields (G) of e_{aq}^- , H^\bullet and $\bullet OH$ available are as shown in the scheme at 10^{-7} s. When $k[S] < 10^7$ s⁻¹ the available yields scarcely change provided $[S] \gg [\text{radicals}]$, but when $k[S] > 10^7$ s⁻¹ the yields can increase by 0.3-0.5 for each 10-fold increase in $k[S]$. This is an important consideration when evaluating, for example, the extinction coefficient of a reaction product.

In pure water there is scarcely any net decomposition because the radiolytic products undergo very efficient back reactions. The reactions which occur in pure water are listed in Table 2.

The great advantage of the radiolysis method over other methods for generating reactive intermediates lies in the fact that the amount of energy absorbed by any component of the system is proportional to its electron fraction. This means that in moderately dilute (≤ 0.1 mol L⁻¹) aqueous solution essentially all the energy is absorbed by the water so that the yields of the primary radicals, e_{aq}^- , H^\bullet and $\bullet OH$ are always well known.

2.2. Other Methods

These do not have wide applicability in the context of this review but can be useful in certain circumstances, for example in providing corroborative evidence for a particular reaction.

2.2.1. Photolysis

Examples of solutes which can be photolysed to generate some of the primary water radicals are listed below.



2.2.2. High Frequency Electric Discharge

This method can be used to produce H^\bullet atoms in pure H_2 gas which is then pumped through the vigorously stirred solution. Mass transfer of H^\bullet from the gas phase into solution has to be taken into account in the kinetic analysis.⁴⁴

2.2.3. Sonolysis

Like the electric discharge method, sonolysis of water saturated with an inert gas generates radicals in the gas phase, in this case due to decomposition of the water vapor at the very high temperatures and pressures generated in the gas bubbles by the ultrasound.⁴⁵ Direct evidence has been obtained recently⁴⁶ that the decomposition reaction is



2.2.4. Fenton-Type Reactions

These are used to generate $\bullet\text{OH}$, the main reactions used being



The first of these was widely employed⁴⁷ before the development of radiation chemistry; the second, being a much faster reaction, provides a convenient method for generating secondary radicals for study by e.s.r. using flow methods.⁴⁸

3. Kinetic Features of Reactions of Transient Species

By their very nature, transient species can only be measured using fast reaction techniques. These involve pulse methods in which either absolute rate constants are obtained by direct observation of the decay of the transient or the growth of its product, or, where only relative rate constants can be deduced, from measurements of product yields using the

competition method. The latter method is also used in continuous radiolysis, but here it is inherently less accurate unless the mechanism by which the measured products are formed is known completely.

3.1. Direct Method

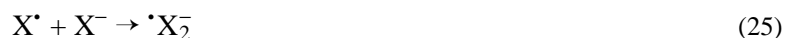
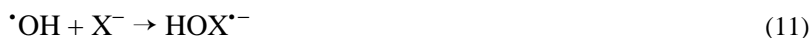
Ideally conditions are chosen such that only one primary radical is present and the concentration of the reactive solute is high enough to ensure that pseudo-first order kinetics are obeyed. As noted above, the reaction may be followed by monitoring the decay of the primary radical, which is generally the case for e_{aq}^- because of its very suitable absorption spectrum (see Fig. 1), or by monitoring the growth of the product, which is usual for H^\bullet , $\bullet OH$ and $\bullet O$ because their spectral properties are quite unsuitable for monitoring their decay. In all cases the concentration of the reactive solute should be varied to demonstrate that the pseudo-first order rate constant is proportional to the solute concentration. This eliminates error due to reaction of the primary radicals with themselves or with impurities in the solvent.

3.1.1. Sources of Error

One source of error arises when the conditions specified above are not, or cannot be, fulfilled. Reasons for this include limited solubility of the reactive solute, or poor observability of the product necessitating a higher than ideal dose per pulse, both of which can result in a fraction of the primary radicals reacting with themselves in competition with their reaction with the solute. These conditions are not always recognizable from the kinetics alone and so one should demonstrate that the yield of the reaction product matches the yield of the primary radical.

In most cases the reaction product is itself a free radical and so is an unstable species. Therefore, when the growth of such a transient product is being measured, corrections for its simultaneous decay should be applied. Again, it is not always obvious from the growth kinetics alone that such corrections are necessary, but measurements of the yield of the product and its relative stability will clarify the situation.

Sometimes there can be more than one step involved in the formation of the observed reaction product from the primary radical so that the rate of formation of this product is not a measure of the rate of reaction of the primary radical. Well known examples of this are the reactions of $\bullet OH$ with halide and pseudo-halide ions (X^-) where the first product is $HOX^{\bullet-}$ although the measured product is $\bullet X_2^-$.



Instrumental errors can arise in the kinetic spectroscopic detection and analysis of transient species, from the lack of adequate calibration of the detection equipment.⁴⁹ Oscilloscope, digitizer or streak camera time-base calibration, in particular, is essential for accurate half-life or decay rate determinations. In computer-automated or manual computation of transient decay curves or other kinetic results, the adequacy and validity of computer programs or analytical methods designed to assess kinetic order parameters, and curve fitting, goodness-of-fit criteria or regression curve analysis, will also influence the overall accuracy obtained. Other practical considerations include an assessment of the stability of the solute under pulse radiolysis conditions in particular by the intense illumination from the analyzing light source and any deleterious effects from the machine dark current or from multiple pulses of ionizing radiation to the solution.

3.2. Competition Kinetics

This method is used in pulse radiolysis when neither the primary radical nor the reaction product can be observed directly. The general scheme is shown below where R^\bullet represents the primary radical, S the solutes and P the products,



so that if P_1 is the observable product

$$\frac{G(R^\bullet)}{G(P_1)} - 1 = \frac{k_2[S_2]}{k_1[S_1]} \quad (28)$$

Ideally, concentrations of S_1 and S_2 are chosen so that reaction is complete during the pulse and $[S_2]/[S_1]$ is varied over a suitable range, but with $\sum k_i[S_i]$ kept constant so that $G(R)$ does not vary (see Section 2.1).

3.2.1. Sources of Error

Generally, conditions can be chosen to eliminate reactions of the primary radicals with themselves, but this should be checked by measuring $G(P_1)$ in the absence of S_2 , and by showing that G -values are independent of dose per pulse. Care should be exercised in the choice of the reference solute, S_1 ; in some cases where P_1 is not formed in a single step, e.g.



the intermediate species X may react with S_2 leading to an erroneous evaluation of k_2 . This situation has been identified when SCN^- is used as the reference solute,⁵⁰ and can be revealed by the use of more than one reference solute to measure k_2 . Indeed, it is good practice to use more than one competitor to measure the same rate constant. This also helps to reveal any errors in the reference rate constant.

Errors can arise, of course, through misinterpretation of the experimental data. This can happen particularly when reactions of $\cdot OH$ and/or $\cdot O^-$ are being measured in alkaline solutions where both forms are present in equilibrium, Eq. (14), under normal conditions.⁵¹ A typical fault is to assume, for example, that in 1 mol L⁻¹ OH⁻ solution the equilibrium in Eq. (14) lies wholly to the right and to attribute any measured rate constant to the reaction of $\cdot O^-$. However, in reality, the system comprises 1% $\cdot OH$ so that if the observed rate constant is 100-fold lower than that known for the reaction of $\cdot OH$ with the same solute, it means that $\cdot O^-$ must react at an even slower rate, if it reacts at all.

3.3. Steady-state Method

In principle the competition method can be used in steady-state experiments and, in fact, much reliable data has been obtained in this way. It is an inherent weakness of the steady-state method, however, that only the permanent reaction products can be measured and so considerable reliance has to be placed on an exact knowledge of the reaction mechanism leading to their formation from the primary radicals.

The most reliable systems are those where the measured product is formed in a single step from the primary radical and is itself unreactive towards other radicals. Thus relative rate constants of H^{\bullet} can generally be measured reliably by steady-state methods by choosing a pair of competing reactions where one produces H_2 and the other does not, for example,



where RH is a saturated organic molecule with a single kind of C-H bond and S is the solute whose rate constant is sought.

3.3.1. Sources of Error

Without doubt the greatest source of error in the steady-state method is the lack of mechanistic information. Because of the very much longer timescales and lower dose rates as compared with the pulse method (see Section 3.2), relatively unreactive secondary species can interfere, whereas they are essentially inert on the timescales of the pulse experiments.

4. Reaction Rates for the Hydrated Electron

4.1. Methods

4.1.1. Direct Method

Because of its intense optical absorbance in the visible and near infrared regions of the spectrum, e_{aq}^- is most conveniently and reliably observed directly using pulse radiolysis, and the majority of rate constants included in Table 6 have been measured by the method of decay kinetics (d.k.). When the hydrated electron is formed radiolytically it is produced concomitantly with the other radiolysis species H^{\bullet} and $\cdot OH$. Therefore care must be taken to ensure that competing side-reactions involving other reactive intermediates or impurities are minimized. One way commonly used to achieve this is to add a scavenger that removes, or converts to unreactive products, all but the reactive species under study. In the case of e_{aq}^- , the use of *tert*-butyl alcohol is generally accepted as an effective means of removing $\cdot OH$ and, to a lesser extent, the lower yield of H^{\bullet} .



It must be remembered that any experimental determination of e_{aq}^- rate constants, based on observing e_{aq}^- decay or the appearance of transient product species is subject to experimental errors and uncertainties, and necessitates certain assumptions and needs the correction of observed data for potential errors.

Corrections must be made for competing reactions, Eqs. (34-36), involving solute S, e_{aq}^- and any impurities I (including H^+ and O_2 for example).



The differential equation for the hydrated electron reaction is:

$$\frac{d[\text{S}^{\bullet-}]}{dt} \approx -\frac{d[e_{\text{aq}}^-]}{dt} = k_{34}[\text{S}][e_{\text{aq}}^-] + 2k_{35}[e_{\text{aq}}^-]^2 + k_{36}[\text{I}][e_{\text{aq}}^-] - k_{37}[\text{H}^{\bullet}][\text{OH}^-] \quad (38)$$

which can be integrated, but does not yield simple exponential decay of the hydrated electron. If reaction (34) is the dominant reaction, the decay approaches simple exponential and corrections for the ‘‘observed’’ rate constant can be derived for the limiting cases ($[\text{I}] \rightarrow 0$), ($[\text{H}^{\bullet}] \rightarrow 0$) and ($[e_{\text{aq}}^-] \rightarrow 0$).

In order to minimize errors associated with the radiation chemical conditions and design of the experiment, it is necessary to reduce the contribution from reactants other than the solute reacting with e_{aq}^- (i.e. by using pH buffers to control $[\text{H}^+]$ and degassing solutions to remove oxygen), reduce the contribution from other primary radicals by use of scavengers, controlling the temperature and/or ionic strength, reducing impurities, and operating at low doses to minimize the bimolecular reaction, Eq. (35). Each experimental rate constant determination should preferably be derived from results obtained for a series of different doses and solute concentrations.

4.1.2. Competition Kinetics

Data are also included in Table 6 in which the rate constants are obtained by steady-state or pulse radiolysis competition kinetics (c.k.). Less than 5% of the hydrated electron rate constants in Table 6 have been determined by this method. In competition kinetics, the rate constant k for the reaction of e_{aq}^- with a solute is determined relative to that with a competing solute whose rate constant k_{C} is known. This is generally done by monitoring the decrease in the yield of the product P of the reaction between e_{aq}^- and competitor with increasing solute concentration: See section 3.2, Eqs. (26-28). Competing reactants which have been successfully used to determine relative rate constants are listed in Table 3a.

4.2. Evaluation of the Data

Rate data were selected as suitable for inclusion in this listing on the basis of the best available direct determinations, preference being given to data derived from pulse radiolysis or other kinetic or time-resolved methods capable of monitoring either the e_{aq}^- decay or the formation of the transient product of its reaction with the solute. Also, high priority was given to those entries derived from publications containing the most comprehensive information concerning the experimental methodology, errors, conditions of the experiment, details of parameters needed for the unambiguous identification and characterization of the reactive species and nature of the reaction, and those factors influencing or controlling the reaction kinetics. Consideration was given to the date of publication and the consequent developments in physical and chemical techniques of production, detection and kinetic analysis of transients, and the uncertainty and errors associated with computing rate constant data.

4.2.1. Selected Rate Constants for e_{aq}^-

Reactants and their rate constants selected as reference values for competition kinetic studies are shown in Table 3a; those values have been listed in bold face at the head of the entries in Table 6. The reference values have been obtained from pulse radiolysis determinations and selected on the basis of internal consistency with values obtained by direct methods. The selected rate constant for the reaction of e_{aq}^- with H^+ is only strictly applicable at low ionic strength. For $I \geq 0.05$, the authors' values for $k(e_{\text{aq}}^- + \text{H}^+)$ have been used and are included in the Comment.

All rate constants measured relative to these reactants have been renormalized to the selected values. Other reactants that have been used with less reliable results in competition kinetic studies reported in Table 6 are: acetone, copper(II) ions,

and peroxydisulfate ions. Data judged acceptable for inclusion in the compilation, in the case of multiple entries for a given solute, have been averaged and the average is listed at the head of the values used to obtain the average. No average is given for multiple values that diverge by more than a factor of two nor those where different ionic strengths can lead to divergent values.

4.2.2. Ionic Strength Effects

Since e_{aq}^- is a negatively charged species, it will be influenced by electrostatic charges on the solute, and its reactivity will be dependent upon the ionic strength I of the solution:

$$I = \frac{1}{2} \sum_i Z_i^2 C_i \quad (39)$$

where C_i and Z_i are the molar concentration and the number of charges of the solute components i , respectively.

According to the Brønsted-Bjerrum equation:

$$\log \frac{k}{k_0} = \frac{1.02 Z_s I^{1/2}}{1 + I^{1/2}} \quad (40)$$

where k and k_0 are the rate constants at ionic strength I and zero, respectively.

Rate constants corrected for ionic strength have been quoted when reported by the authors and “ k cor. for I ” has been added to the comments; k_{obs} is also given in the comment, if available. The reviewers did not attempt to make corrections for ionic strength because of uncertainties such as actual charge on the ions, concentrations, etc.

5. Reaction Rates for the Hydrogen Atom

5.1. Methods

5.1.1. Direct Methods

Because the H^\bullet atom absorbs light only in the ultra-violet region of the spectrum, mainly below 200 nm, direct observation of decay of the transient using kinetic optical spectroscopy is not a suitable technique. Directly determined rate constants listed in Table 7 include those obtained from direct observation of the absorbing transient products of the H^\bullet atom reaction with the solute by optical methods. Rate constants have also been determined by direct observation of the H^\bullet atom generated by pulse radiolysis by esr or by competitive reduction of the esr signal due to the addition of solutes.^{19,20,52,53} Observation of the hydrogen atom esr signal is possible because of its enhancement by spin polarization effects and its decay is followed to give a pseudo-first order rate in the presence of a solute.

5.1.2. Competition Kinetics

Many H^\bullet atom rate constants have been determined indirectly by steady-state or pulse radiolysis using competition kinetic methods. Here the rate constant for the reaction of H^\bullet atoms with a solute S_2 is compared with the rate constant k_1 for the reaction with a competitive solute, S_1 . In competition kinetics, the relative yield of a product is monitored as a function of the ratio of solute to competitor concentration: See section 3.2, Eqs. (26-28). In addition to competition kinetics by product analysis, rate constants have been determined by the comparison of the decrease in the esr signal for the hydrogen atom in the presence of competing solutes in a steady-state experiment.

Competing reactants used to determine relative rate constants are listed in Table 3b. Other reactants, considered unreliable, that have been used in competition kinetic studies reported in the main table are: glucose, hydrogen peroxide, silver(I) ion, copper(II) ion, iron(II) ion, iron(III) ion, nitrate ion, nitrite ion, allyl alcohol, benzoquinone, methanol- d_3 , 2-methyl-1-propanol, *p*-nitrobenzoic acid and phenol.

5.2. Evaluation of the Data

The criteria used for evaluating H^\bullet atom rate constants for inclusion in this compilation are substantially the same as those outlined for e_{aq}^- data.

Emphasis is placed on recent determinations containing comprehensive information covering a wide range of conditions, quoting errors, and a consideration of the experimental design including the use of appropriate scavengers and corrections for secondary reactions and other complicating circumstances. Other requirements considered important are the evidence supporting first-order kinetics, the establishment of conditions for a single reaction between reactants and supporting evidence for or a means of identifying the species involved and the reaction scheme, rate data given for a range of solute

concentrations with matrix corrections for impurities, oxygen and self-reactions or secondary reactions (dose and dose-rate dependent), and the selection of appropriate chemical conditions (pH, dose, concentration, etc).

Rate constants for reactions of H[•] with metal complexes where atomized hydrogen was produced by electric discharge (see section 2.2.2) were included whenever other data were not available; the rate constants should be considered to have error limits of a factor of two.

5.2.1. Selected Rate Constants for H[•]

Several reactants and their values of k_1 have been selected as reference values for competition kinetics and are shown in Table 3b. These values have been obtained by pulse radiolysis using either optical or esr detection. Additional reference values have been selected for several reactants with rate constants determined relative to the primary reference values. All rate constants measured relative to these reactants have been renormalized to the selected values.

6. Reaction Rates for the Hydroxyl Radical and the Oxide Radical Ion

6.1. Methods

These have already been described in general terms in section 3.

6.1.1. Direct Method

In principle, the most reliable data are to be obtained using pulse radiolysis and observing directly the decay of [•]OH and/or the formation of product,



In practice, the decay of [•]OH generally cannot be followed because of its weak ultraviolet absorption spectrum, and of course the formation of P₁ can only be measured when it has a suitable absorption spectrum. This is the so-called method of product build-up kinetics (p.b.k.), and it generally requires the use of rather low concentrations of solute, S₁. It is important, therefore, either to choose conditions where reaction of [•]OH with itself is negligible and the product P₁ does not react further, or to make appropriate corrections when these conditions cannot be realized.

6.1.2. Competition Kinetics

This method (c.k.) is quite widely used to measure [•]OH reaction rate constants by pulse radiolysis. A number of suitable standard competitors are available (see Table 3c), and it is desirable to measure the unknown rate constant relative to more than one of these standards. The competition method has the advantage that higher concentration of solutes can be employed, thereby eliminating the possibility of [•]OH reacting with itself, and also shortening the timescale of observation and so minimizing the extent of reactions of the product. In using the competition method it is obviously important to state what value of the reference rate constant has been selected.

6.1.3. Steady-State Method

The steady-state method most frequently involves either γ -radiolysis or the use of the Fenton reaction to generate [•]OH. In either case rate constants are deduced from measurements of stable products. As mentioned earlier, the method necessarily requires that the mechanism of product formation be known completely, and whilst there are numerous examples to show that the steady-state method does give reliable results, there are many others that show just the opposite.

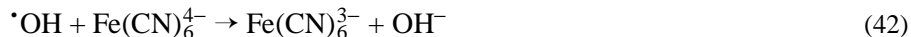
6.2. Evaluation of the Data

All reported values of [•]OH and [•]O⁻ rate constants have been examined with the aim of obtaining a set of valid data. For reasons discussed above, the more reliable data are considered to be those obtained by pulse radiolysis, and of these the most reliable are those concordant values which have been obtained by more than one method. Where concordant data have been obtained by both pulse radiolysis and steady-state methods, the latter have been omitted from Table 8 but are retained in Appendix C. In many cases only a single determination of a rate constant has been made and its value is listed in Table 8 regardless of the method of its measurement, provided that the value can be judged to be a reasonable one, for example by comparing it with data for similar compounds.

6.2.1. Selected Rate Constants for $\cdot\text{OH}$

Certain rate constants have been measured many times by various methods and their values are considered to be well established (Table 3c). These are recommended for use in the pulse radiolysis competition method.

To obtain a self-consistent set of selected values the following procedure has been adopted. The rate constant for reaction (42) has been chosen as the primary standard because it is measurable by direct observation of the formation of the stable product $\text{Fe}(\text{CN})_6^{3-}$.



Moreover, this reaction is almost certainly diffusion-controlled, so that if an intermediate adduct of $\cdot\text{OH}$ and $\text{Fe}(\text{CN})_6^{4-}$ is formed it must be very short-lived. Secondary standards were then chosen on the basis that their rate constants can be related directly or indirectly to k_{42} . Consider methanol as an example. The value of k_{43} for reaction (43)



has only been determined by the competition method, but the same value is obtained, within the usual error limits for kinetics measurements, using eight different competitors. It follows, therefore, that the rate constants for these eight compounds must be correct. In this way a set of selected rate constants has been built up whose values are mutually consistent.

6.2.2. Selected Rate Constants for $\cdot\text{O}^-$

The same procedure has been followed as for $\cdot\text{OH}$. The chosen primary standard in this case is the rate constant for reaction (44) between $\cdot\text{O}^-$ and 3-hexene-1,6-dioate ion which has been carefully measured⁵⁴ by the p.b.k. method.



6.2.3. Comments on Data for $\cdot\text{O}^-$

In general, reactions of $\cdot\text{O}^-$ are measured in alkaline solution ($\text{pH} > 13$), although reaction (45) has been exploited⁵⁵ to make such measurements in neutral solution.



In all cases it is important to remember that the equilibrium between $\cdot\text{OH}$ and $\cdot\text{O}^-$ is rapidly established so that corrections for the presence of $\cdot\text{OH}$ will generally be necessary. For the reaction scheme



the observed rate constant is given by Eq. (48),

$$k_{\text{obs}} = \frac{k_{46} + k_{47} \frac{K \cdot\text{OH}}{[\text{H}^+]}}{1 + \frac{K \cdot\text{OH}}{[\text{H}^+]}} \quad (48)$$

so that by choosing conditions where equilibrium (14) is maintained, and by varying the pH, one can evaluate both k_{46} and k_{47} unambiguously, provided that the reactivity of the solute S does not change in the pH range of interest.

Care is needed in obtaining rate constants for $\cdot\text{O}^-$ when the corresponding rate constants for $\cdot\text{OH}$ are an order of magnitude larger. A clear example of this is provided by the system " $\cdot\text{OH}$ " and " H_2O_2 " in alkaline solution, where $\text{p}K_{\text{a}}(\cdot\text{OH}) = 11.9$, Eq. (14), and $\text{p}K_{\text{a}}(\text{H}_2\text{O}_2) = 11.7$, Eq. (49).



For the reactions,



the observed rate constant,

$$k_{\text{obs}} = \frac{k_{50}}{\left[1 + \frac{K_{\cdot\text{OH}}}{[\text{H}^+]}\right] \left[1 + \frac{K_{\text{H}_2\text{O}_2}}{[\text{H}^+]}\right]} + \frac{k_{51}}{\left[1 + \frac{K_{\cdot\text{OH}}}{[\text{H}^+]}\right] \left[1 + \frac{[\text{H}^+]}{K_{\text{H}_2\text{O}_2}}\right]} \\ + \frac{k_{52}}{\left[1 + \frac{[\text{H}^+]}{K_{\cdot\text{OH}}}\right] \left[1 + \frac{K_{\text{H}_2\text{O}_2}}{[\text{H}^+]}\right]} + \frac{k_{53}}{\left[1 + \frac{[\text{H}^+]}{K_{\cdot\text{OH}}}\right] \left[1 + \frac{[\text{H}^+]}{K_{\text{H}_2\text{O}_2}}\right]} \quad (54)$$

Fig. 3 shows the experimental values of k_{obs} from five investigations^{56,57,58,59,60}. The solid lines show the contributions of the terms in Eq. (55) for k_{51} and k_{53} using the parameters taken from Table 2. The dominant term is that for k_{51} for $10^{-4} \leq [\text{OH}^-] \leq 10^{-1} \text{ mol L}^{-1}$. The term in k_{52} is negligible if $k_{52} < 5 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ and the term in k_{50} is also small, negligible for $[\text{OH}^-] \geq 10^{-3} \text{ mol L}^{-1}$. The contribution from the term in k_{53} becomes significant at $[\text{OH}^-] \geq 10^{-2} \text{ mol L}^{-1}$ and dominant at $[\text{OH}^-] \geq 10^{-1} \text{ mol L}^{-1}$. Above $10^{-1} \text{ mol L}^{-1} \text{ OH}^-$, the effect of ionic strength is illustrated using Rabani's value⁵⁷ ($k_{53}^0 = 2.74 \times 10^8$ at $I = 0$). The calculated dotted line shows the contribution from $k_{53} 10^{f(I)}$ in this region where,

$$f(I) = 1.02 \frac{I^{1/2}}{1 + I^{1/2}} \quad (55)$$

assuming the ionic strength is the same as the hydroxide concentration.

A number of reported rate constants for $\cdot\text{O}^-$ reactions have been omitted from Table 9 because their values become negligibly small when k_{obs} is corrected for the contribution from $\cdot\text{OH}$.

7. Data Fitting and Statistical Analysis

As is the case with recent compilations of extinction coefficients for triplet-triplet absorption⁶¹ and reactivity of singlet oxygen in solution⁶², the data in this compilation have been analysed mathematically as part of the effort to find the best value for each rate constant. For these data several different algorithms have been tried to find "best" values from a network of relative data, the values intercompared, and found to be in statistical agreement. The method has been used first to focus attention on cases in which there is disagreement between values, thus indicating that further evaluation is required, and second to recalculate rate constants from relative measurements bringing a measure of internal consistency to the values reported.

The method of data fitting used for these data is not a true least squares method, rather it is a restricted form of averaging. Primarily, the distinction is that values that are widely accepted or that are known to have been determined with unusual care and attention to details are not subjected to the random vagaries of the fitting procedures. Thus a set of reference values (see Tables 3a, 3b, and 3c) was fixed apart from the fitting procedure. The true least squares fitting would require that the rate constants for both competitors in relative rate measurements be adjusted; the designated reference rate constants, however, were not adjusted. Thus the fitting procedure used adjusts only the subset of rate constants that can not be objectively chosen. The fitting procedure gives a value for each rate constant, an average, and for reactants with more than one measured rate constant a standard deviation that gauges how well the measurements agree with each other. For all four fitting algorithms tested the results were similar.

The first use of these fittings was to flag problems that required resolution. One problem resulted when a global fitting gave a rate constant for a reaction that did not match the value that is widely accepted. Another problem occurred when measured values were far apart. After fixing several reference values, and omitting measurements thought to be less reliable, the fitting procedure gave acceptable results. These results were subjected to the same statistical tests as used by Carmichael *et al.*⁶¹ The deviations of the measurements relative to the fit values may be considered to be normally distributed such that

95% of the measurements will be within about 50% of the fit value. Specifically, 51% for hydrated electron rate constants, 46% for directly determined hydrogen atom rate constants, 62% for relative determinations of hydrogen atom rate constants, 63% for directly determined hydroxyl radical rate constants, and 47% for relative determinations of hydroxyl radical rate constants. These values suggest that the differences between rate constants reported from different laboratories exceed the typical quoted error estimates. This also forms the basis for not reporting an average if measurements differ by a factor of two.

For rate constants known to be determined relative to another rate constant, the ratio of the two rate constants, reported or implied, was used with the selected or averaged rate constant for the designated reference rate constant to recalculate the value reported in these tables. Recalculated rate constants have been rounded to two significant figures unless the original authors report only one significant figure, in which case we report only one. In some cases this leads to reporting an average which seems to be in error. The reason for that is the following. When we recalculate relative rate constants using our selected or averaged values, the rounding is not done until *after* the average is calculated. An example is the reaction of Hydrogen atom with 2-Methyl-1-propanol with two reported values, both relative to Benzoic acid, one value obtained by the esr method and the other value by the method of product yields in gamma radiolysis (see Table 7, entry 441). The value 6.4×10^7 was reported by the esr method assuming a value of 1.0×10^9 for Benzoic acid, thus $k(\text{H}^\bullet + (\text{CH}_3)_2\text{CHCH}_2\text{OH})/k(\text{H}^\bullet + \text{BzOH}) = 0.06400$. The value 5×10^7 was reported by the product yields method, also assuming 1.0×10^9 , thus the ratio is 0.05000. These ratios are multiplied by our selected value for $k(\text{H}^\bullet + \text{BzOH}) = 9.2 \times 10^8$. The calculated values, 5.888×10^7 and 4.600×10^7 , give an average of 5.244×10^7 . These round to 5.9×10^7 and 5×10^7 with the average rounded to 5.2×10^7 . tables.

8. Activation Energies

Kinetic spectroscopy is a convenient direct method to measure activation energies of the reactions of water radiolysis species, particularly e_{aq}^- . Such determinations are important not only in mechanistic studies^{63,64}, but also in such diverse areas of applied radiation chemistry as nuclear reactor coolant chemistry⁶⁵ and hyperthermia treatment of cancer⁶⁶.

Activation energies of e_{aq}^- , $\cdot\text{OH}$ and H^\bullet reactions have been measured by pulse radiolysis and competition kinetics for a wide range of reaction rate constants (Table 4). Diffusion controlled reactions of most solutes in water have activation energies (E_a) between 3 and 4 kcal mol⁻¹ (10 to 18 kJ mol⁻¹). In slower reactions, the measured activation energy approximates the enthalpy term ($H = E_a + RT$).

The most common method of determining activation energies is to measure a rate constant k for a given reaction at several temperatures (T) and to calculate the slope of the so-called Arrhenius plot of $\ln k$ against $1/T$ to fit the equation:

$$\ln k = \ln A - \frac{E_a}{R}T \quad (56)$$

where R is the gas constant and RT at room temperature is 2.4 kJ mol⁻¹.

Some Arrhenius plots such as the one for the decay of e_s^- in 10 mol L⁻¹ OH⁻ are non-linear⁶⁷, and it is necessary to obtain rate constant data over a wide temperature range in order to detect these anomalies. Some reasons for the non-linearity may be associated with steric factors, viscosity changes, complications from secondary or competing reactions, and tunneling or inhomogeneous diffusion kinetics. It may be possible to determine activation energies under such non-ideal conditions by using the modified Eq. (57):

$$\ln k = \ln A - \frac{E_a}{R(T - T_{\text{fixed}})} \quad (57)$$

9. Acknowledgements

The Radiation Laboratory at the University of Notre Dame is operated under contract DE-AC02-76ER0038 with the Department of Energy. The Radiation Chemistry Data Center is supported jointly by the Office of Basic Energy Sciences of the Department of Energy, the Armed Forces Radiobiology Research Institute, Defense Nuclear Agency and the National Bureau of Standards, Office of Standard Reference Data. This is Radiation Laboratory Document No. NDRL-2993.

10. References to Text

- ¹I.G. Draganic and Z.D. Draganic, *The Radiation Chemistry of Water* (Academic Press, New York, 1971).
- ²M.S. Matheson and L.M. Dorfman, *Pulse Radiolysis* (M.I.T. Press, Cambridge, Mass., 1969).
- ³E.J. Hart and M. Anbar, *The Hydrated Electron* (Wiley-Interscience, New York, 1970).
- ⁴A.K. Pikaev, *The Solvated Electron in Radiation Chemistry* (Izdatel'stvo "Nauka", Moscow, 1969).
- ⁵A.K. Pikaev and S.A. Kabakchi, *Reaction Rates for Primary Products of Water Radiolysis* (Energoizdat, Moscow, 1982).
- ⁶L.M. Dorfman and G.E. Adams, *Reactivity of the Hydroxyl Radical in Aqueous Solution*, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.A.), **46** (1973).
- ⁷P. Neta, *Chem. Rev.* **72**, 533 (1972).
- ⁸M. Anbar, M. Bambenek and A.B. Ross, *Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution. I. Hydrated Electron*, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.A.), **43** (1973, and supplement, 1975).
- ⁹M. Anbar, Farhataziz and A.B. Ross, *Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution. II. Hydrogen atom*, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.A.), **51** (1975).
- ¹⁰Farhataziz and A.B. Ross, *Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution. I. Hydroxyl Radical and Perhydroxyl Radical and their Radical Ions*, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.A.), **59** (1977).
- ¹¹J. Rabani and M.S. Matheson, *J. Am. Chem. Soc.* **86**, 3175 (1964).
- ¹²J.H. Baxendale, *Radiat. Res. Suppl.* **4**, 139 (1964).
- ¹³J. Jortner and R.M. Noyes, *J. Phys. Chem.* **70**, 770 (1966).
- ¹⁴K.H. Schmidt, and W.L. Buck, *Science* **151**, 70 (1966).
- ¹⁵R.M. Noyes, *Adv. Chem. Ser.* **81**, 65 (1968).
- ¹⁶R. Braams and M. Ebert, *Adv. Chem. Ser.* **81**, 464 (1968).
- ¹⁷E.C. Avery, J.R. Remko, and B. Smaller, *J. Chem. Phys.* **49**, 951 (1968).
- ¹⁸K.H. Schmidt and S.M. Ander, *J. Phys. Chem.* **73**, 2846 (1969).
- ¹⁹P. Neta, R.W. Fessenden and R.H. Schuler, *J. Phys. Chem.* **75**, 1654 (1971).
- ²⁰K. Eiben and R.W. Fessenden, *J. Phys. Chem.* **75**, 1186 (1971).
- ²¹J.H. Baxendale, M.D. Ward and P. Wardman, *Trans. Faraday Soc.* **67**, 2532 (1971).
- ²²A.J. Swallow, *Radiation Chemistry. An Introduction* (Wiley, New York, 1973).
- ²³H. Hotop and W.C. Lineberger, *J. Phys. Chem. Ref. Data* **4**, 539 (1975).
- ²⁴F.P. Sargent and E.M. Gardy, *Chem. Phys. Lett.* **39**, 188 (1976).
- ²⁵N.C. Verma and R.W. Fessenden, *J. Chem. Phys.* **65**, 2139 (1976).
- ²⁶H.M. Rosenstock, K. Draxl, B.W. Steiner and J.T. Herron, *J. Phys. Chem. Ref. Data* **6** (Suppl. 1), (1977).
- ²⁷S.W. Benson and P.S. Nangia, *J. Am. Chem. Soc.* **102**, 2843 (1980).
- ²⁸R.H. Schuler, A.L. Hartzell and B. Behar, *J. Phys. Chem.* **85**, 192 (1981).
- ²⁹H.A. Schwarz, *J. Chem. Educ.* **58**, 101 (1981).
- ³⁰G.L. Hug, *Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution*, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.A.), **69** (1981).
- ³¹W.H. Koppenol and J.F. Liebman, *J. Phys. Chem.* **88**, 99 (1984).
- ³²H.A. Schwarz and R.W. Dodson, *J. Phys. Chem.* **88**, 3643 (1984).
- ³³U.K. Klaning, K. Sehested and J. Holcman, *J. Phys. Chem.* **89**, 760 (1985).
- ³⁴W.H. Koppenol and J. Butler, *Adv. Free Radical Biol. Med.* **1**, 91 (1985).
- ³⁵B. Hickel and K. Sehested, *J. Phys. Chem.* **89**, 5271 (1985).
- ³⁶A.G. Ryabukhin, *Russ. J. Phys. Chem.* **51**, 573 (1977); transl. from *Zh. Fiz. Khim.* **51**, 968 (1977).
- ³⁷F. Busi, M. D'Angelantonio, G. Bettoli, V. Concialini, O. Tubertini, and G.C. Barker, *Inorg. Chim. Acta* **84**, 105 (1984).
- ³⁸V.A. Benderskii, A.G. Krivenko and A.N. Rukin, *High Energy Chem.* **14**, 303 (1980); transl. from *Khim. Vys. Energ.* **14**, 400 (1980).
- ³⁹A. Henglein, *Radiat. Phys. Chem.* **15**, 151 (1980).
- ⁴⁰G.G. Jayson, J.P. Keene, D.A. Stirling and A.J. Swallow, *Trans. Faraday Soc.* **65**, 2453 (1969).
- ⁴¹A.J. Elliot, S. Geertsen and G.V. Buxton, to be published.
- ⁴²D. Meyerstein, *J. Chem. Soc., Faraday Disc.* **63**, 203 (1977); *Acc. Chem. Res.* **11**, 43 (1978).
- ⁴³V.M. Berdnikov, *Russ. J. Phys. Chem.* **47**, 1547 (1973).
- ⁴⁴G. Czapski, J. Jortner and G. Stein, *J. Phys. Chem.* **65**, 956 (1961).
- ⁴⁵A. Weissler, *J. Acoust. Soc. Am.* **25**, 651 (1953).
- ⁴⁶K. Makino, M.M. Mossoba and P. Riesz, *J. Phys. Chem.* **87**, 1369 (1983).

- ⁴⁷W.A. Waters, *Chemistry of Free Radicals* (Oxford University Press, London, 1946).
- ⁴⁸W.T. Dixon and R.O.C. Norman, *J. Chem. Soc.*, 3119 (1963). 1702 (1973).
- ⁴⁹J.W. Hunt, C.L. Greenstock and M.J. Bronskill, *Int. J. Radiat. Phys. Chem.*, **4**, 87 (1972).
- ⁵⁰S.R. Logan and G.A. Salmon, *Radiat. Phys. Chem.* **24**, 593 (1984).
- ⁵¹G.V. Buxton, *Trans. Faraday Soc.* **66**, 1656 (1970).
- ⁵²B. Smaller, E.C. Avery, and J.R. Remko, *J. Chem. Phys.* **55**, 2144 (1971).
- ⁵³R.W. Fessenden and N.C. Verma, *Faraday Discuss. Chem. Soc.*, **63**, 104 (1977).
- ⁵⁴P. Neta and R.H. Schuler, *J. Phys. Chem.*, **79**, 1 (1975).
- ⁵⁵D. Zehavi and J. Rabani, *J. Phys. Chem.* **75**, 1738 (1971).
- ⁵⁶W.D. Felix, B.L. Gall and L.M. Dorfman, *J. Phys. Chem.*, **71**, 384 (1967).
- ⁵⁷J. Rabani, *Adv. Chem. Ser.*, **81**, 131 (1968).
- ⁵⁸G.V. Buxton, *Trans. Faraday Soc.*, **65**, 2150 (1969).
- ⁵⁹H. Christensen, K. Sehested and H. Corfitzen, *J. Phys. Chem.*, **86**, 1588 (1982).
- ⁶⁰D. Behar and G. Czapski, *Isr. J. Chem.*, **6**, 43 (1968).
- ⁶¹I. Carmichael, W.P. Helman and G.L. Hug, *J. Phys. Chem. Ref. Data*, in press.
- ⁶²F. Wilkinson and J. G. Brummer, *J. Phys. Chem. Ref. Data* **10**, 809 (1981).
- ⁶³M. Anbar, *Quart. Revs.* **4**, 578 (1968).
- ⁶⁴M. Anbar, *Adv. Phys. Org. Chem.* **7**, 115 (1969).
- ⁶⁵W.G. Burns and W.R. Marsh, *J. Chem. Soc. Faraday Trans. 1* **77**, 197 (1981).
- ⁶⁶J.P. Lowenthal, ed., *Workshop Conference on Hyperthermia in Cancer Treatment*, *Cancer Res. Suppl.* **44**, 4703-s (1984).
- ⁶⁷G.V. Buxton, F.C.R. Cattell and F.S. Dainton, *Trans. Faraday Soc.* **67**, 687 (1971).
- ⁶⁸pKs are taken from: R.C. Weast, *CRC Handbook of Chemistry and Physics*, 63rd ed. (CRC Press, Boca Raton FL, 1982). H.A. Sober, *CRC Handbook of Biochemistry*, Second ed. (Chemical Rubber Co., Cleveland, OH, 1970). D.D. Perrin, *Ionisation Constants of Inorganic Acids and Bases in Aqueous Solution*, Second ed., IUPAC Chemical Data Series No. 29 (Pergamon Press, Oxford, 1982). M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Translated by J.A. Franklin (Pergamon Press, Oxford, 1966). G. Kortum, W. Vogel and K. Andrussov, *Dissociation Constants of Organic Acids in Aqueous Solution* (Butterworths, London, 1961). E.P. Serjeant and B. Dempsey, *Ionisation Constants of Organic Acids in Aqueous Solution*, IUPAC Chemical Data Series No. 23 (Pergamon Press, Oxford, 1979). D.D. Perrin, *Dissociation Constants of Organic Bases in Aqueous Solution*, (Butterworths, London, 1965); and Supplement (1972).

Table 1. Properties of the primary water radiolysis species in aqueous solution, e_{aq}^- , H^\bullet , $\bullet OH$ and $\bullet O^-$

	e_{aq}^-	H^\bullet	$\bullet OH$	$\bullet O^-$
Absorption maximum ^a (nm)	720	<200	~225	240
Extinction coefficient ^a , ϵ (L mol ⁻¹ cm ⁻¹)	19000 (720 nm)	1620 (188 nm)	540 (188 nm)	240 (240 nm)
dhv/dT (0 to 100°C) (eV K ⁻¹ × 10 ³)	-2.9 ³			
Half-width (eV)	0.93 ³			
Oscillator strength	0.71 ³			
ESR g-factor	2.0002 ¹⁷ 2.00033 ²⁵ 2.0002, 2.0003 ²⁴	2.00210 ²⁰		
ESR line width (gauss)	<0.06 ²⁴ <0.15 ²⁹			
ESR hyperfine coupling constant (gauss)		503.0 ¹⁹ 503.2 ²⁰		
Charge	-1	0	0	-1
Radius (cm × 10 ⁸)	2.5 ≤ r ≤ 3.0 ³ 2.98 ^{1,13}		2.2 ¹⁶	
Primary yield ^b (molecules per 100 eV), pH 7	2.6	0.6	2.7	
Diffusion coefficient (cm ² s ⁻¹ × 10 ⁵)	4.90 ^{3,18} 4.75 ^{1,14}	8 ³⁷ 7 ³⁸	2.3 ^{6,23} 2 ¹⁶ 2.1 ³⁷	
Equivalent conductivity (mho cm ²)	190 ^{3,18}			
Mobility (cm ² V ⁻¹ s ⁻¹ × 10 ³)	1.98 ^{3,18} 1.8 ¹⁴			
Reduction potential (V)	-2.77 ^{c 3} -2.6 ^{c 1} -2.9 ^{c 22} -2.87 ^{c 29}	-2.1 ^{d 1} -2.3 ^{d 22,29}	1.77 ^{e 31} 1.89 ^{e 32} 1.91 ^{e 33} 2.59 ^{f 31} 2.72 ^{f 32} 2.74 ^{f 33} 11.9 ^{i 11} 42 ²¹	1.64 ^{g 31,34} 1.76 ^{g 32} 1.78 ^{g 33}
pK _a		9.6 ^{h 22}		
ΔH (ionization) (kJ mol ⁻¹)				
Electron affinity (eV)		0.776 ^{j 23}	1.83 ^{i,k 27,26}	
ΔG_f° (kJ mol ⁻¹)	276 ²⁹ 277 ^{1,35} -157 ¹³	222 ²⁹ 222 ¹⁵	13 ^{31,34} 25 ³² 27 ³³ 19 ²⁹ 35.7 ^{1,39}	96 ²⁹ 92 ³² 95 ³³ 93 ²¹ 81.2 ^{31,34} 103 ^{1,39}
ΔH_f° (kJ mol ⁻¹)	277 ^{1,35} -136.4 ^{m 35} -153 ¹³	213 ²⁹ 214 ¹⁵	-7 ²⁷ -4 ²⁹	38 ²¹ 13 ²⁹
S°_{298} (J mol ⁻¹ K ⁻¹)	13 ¹³ 65 ^{1,35} 69.8 ^{m 35} 65.2 ³⁶	38 ¹⁵	96 ²⁷	
ΔG (hydration) (kJ mol ⁻¹)	-156 ¹³	18 ²⁹	-10 ³² -21 ³¹	-438 ³¹ -415 ^{1,39}
ΔH (hydration) (kJ mol ⁻¹)	-159 ¹³ -167 ^{1,12} -142 ^{m 35}	-3 ²⁹	-42 ²⁹	-473 ²¹
ΔS (hydration) (J mol ⁻¹ K ⁻¹)	-7.9 ¹³ 49 ^{m 35}			

^aSee Fig. 1.³⁰

^bSee Section 2.1., Fig. 2.

^c(H₂O + e⁻ → e_{aq}⁻)

^d(H₂O + e⁻ + H⁺ → [•]H_{aq})

^e([•]OH + e⁻ → OH⁻)

^f([•]OH + e⁻ + H⁺ → H₂O)

^g([•]O⁻ + e⁻ + H⁺ → OH⁻)

^b(H[•] + H₂O → H₃O⁺ + e_{aq}⁻)

ⁱ([•]OH + H₂O → H₃O⁺ + [•]O⁻)

^jGas phase.

^k5.8 eV calcd. for aqueous phase⁶ based on gas phase value of 2 eV.

^lBased on convention that ΔH_f° , ΔG_f° , and S° for H_{aq}⁺ = 0.

^mBased on values for H_{aq}⁺: $\Delta H_f^\circ = 413$ kJ mol⁻¹, $\Delta G_f^\circ = 434$ kJ mol⁻¹, and $S^\circ = -4.89$ J mol⁻¹ K⁻¹.

Table 2. Reactions in the radiolysis of pure water

Reaction	k (L mol ⁻¹ s ⁻¹)
$e_{\text{aq}}^- + \text{H}_2\text{O} \rightarrow \text{H}^\bullet + \text{OH}^-$	1.9×10^1
$e_{\text{aq}}^- + e_{\text{aq}}^- \rightarrow \text{H}_2 + 2 \text{OH}^-$	$2k = 1.1 \times 10^{10}$ ^a
$e_{\text{aq}}^- + \text{H}^\bullet \rightarrow \text{H}_2 + \text{OH}^-$	2.5×10^{10}
$e_{\text{aq}}^- + \text{}^\bullet\text{OH} \rightarrow \text{OH}^-$	3.0×10^{10}
$e_{\text{aq}}^- + \text{}^\bullet\text{O}^- \rightarrow 2 \text{OH}^-$	2.2×10^{10}
$e_{\text{aq}}^- + \text{H}^\bullet \rightarrow \text{H}^\bullet$	2.3×10^{10} ^a
$e_{\text{aq}}^- + \text{H}_2\text{O}_2 \rightarrow \text{OH}^- + \text{}^\bullet\text{OH}$	1.1×10^{10}
$e_{\text{aq}}^- + \text{HO}_2^- \rightarrow 2 \text{OH}^- + \text{}^\bullet\text{OH}$	3.5×10^9
$e_{\text{aq}}^- + \text{O}_2 \rightarrow \text{O}_2^{\bullet-}$	1.9×10^{10} ^a
$e_{\text{aq}}^- + \text{O}_2^{\bullet-} \rightarrow \text{O}_2^{2-}$	1.3×10^{10}
$\text{H}^\bullet + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{}^\bullet\text{OH}$	1×10^1
$\text{H}^\bullet + \text{H}^\bullet \rightarrow \text{H}_2$	$2k = 1.55 \times 10^{10}$ ^a
$\text{H}^\bullet + \text{}^\bullet\text{OH} \rightarrow \text{H}_2\text{O}$	7.0×10^9
$\text{H}^\bullet + \text{OH}^- \rightarrow e_{\text{aq}}^-$	2.2×10^7 ^a
$\text{H}^\bullet + \text{H}_2\text{O}_2 \rightarrow \text{}^\bullet\text{OH} + \text{H}_2\text{O}$	9×10^7
$\text{H}^\bullet + \text{O}_2 \rightarrow \text{HO}_2^\bullet$	2.1×10^{10} ^a
$\text{H}^\bullet + \text{HO}_2^\bullet \rightarrow \text{H}_2\text{O}_2$	$\sim 10^{10}$
$\text{}^\bullet\text{OH} + \text{}^\bullet\text{OH} \rightarrow \text{H}_2\text{O}_2$	$2k = 1.1 \times 10^{10}$ ^a
$\text{}^\bullet\text{OH} + \text{}^\bullet\text{O}^- \rightarrow \text{HO}_2^-$	$\leq 2 \times 10^{10}$
$\text{}^\bullet\text{OH} + \text{H}_2 \rightarrow \text{H}^\bullet + \text{H}_2\text{O}$	4.2×10^7
$\text{}^\bullet\text{OH} + \text{OH}^- \rightarrow \text{}^\bullet\text{O}^- + \text{H}_2\text{O}$	1.3×10^{10}
$\text{}^\bullet\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^\bullet$ $\rightleftharpoons \text{O}_2^{\bullet-} + \text{H}^\bullet$	2.7×10^7
$\text{}^\bullet\text{OH} + \text{HO}_2^- \rightarrow \text{OH}^- + \text{HO}_2^\bullet$ $\rightleftharpoons \text{O}_2^{\bullet-} + \text{H}^\bullet$	7.5×10^9
$\text{}^\bullet\text{OH} + \text{H}_2\text{O}_2^+ \rightarrow \text{H}_3\text{O}^+ + \text{O}_2$	1.2×10^{10}
$\text{}^\bullet\text{OH} + \text{HO}_2^\bullet \rightarrow \text{H}_2\text{O} + \text{O}_2$	6×10^9
$\text{}^\bullet\text{OH} + \text{O}_2^{\bullet-} \rightarrow \text{OH}^- + \text{O}_2$	8×10^9
$\text{}^\bullet\text{O}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{}^\bullet\text{OH}$	1.8×10^6
$\text{}^\bullet\text{O}^- + \text{}^\bullet\text{O}^- \rightarrow \text{O}_2^{2-}$	^b
$\text{}^\bullet\text{O}^- + \text{H}_2 \rightarrow \text{H}^\bullet + \text{OH}^-$	8.0×10^7
$\text{}^\bullet\text{O}^- + \text{H}_2\text{O}_2 \rightarrow \text{O}_2^{\bullet-} + \text{H}_2\text{O}$	$\leq 5 \times 10^8$
$\text{}^\bullet\text{O}^- + \text{HO}_2^- \rightarrow \text{O}_2^{\bullet-} + \text{OH}^-$	4×10^8
$\text{}^\bullet\text{O}^- + \text{O}_2 \rightarrow \text{O}_3^-$	3.6×10^9 ^a
$\text{}^\bullet\text{O}^- + \text{O}_2^{\bullet-} \rightarrow 2 \text{OH}^- + \text{O}_2$	6.0×10^8

^aSelected value.^bNo reliable measurement.

Table 3a. Selected e_{aq}^- rate constants

Reactant	Rate Constant
Hydrogen ion	2.3×10^{10} ^a
Oxygen	1.9×10^{10}
Nitrous oxide	9.1×10^9
Nitrate ion	9.7×10^9
Chloroacetate	1.0×10^9
Bromophenol	7.0×10^9

^aLow $[\text{H}^+]$ or $I \rightarrow 0$.

Table 3b. Selected H^\bullet rate constants

Reactant	Rate Constant
Hydrogen atom	7.8×10^9
Ferricyanide ion	6.3×10^9
Hydroxide ion	2.2×10^7
Oxygen	2.1×10^{10}
Benzoic acid (BzOH)	9.2×10^8
Ethanol	1.7×10^7
Methanol	2.6×10^6
2-Propanol	7.4×10^7
Formate ion	2.1×10^8 ^a
<i>d</i> -Formate ion	2.9×10^7 ^a
Formic acid	4.4×10^5 ^a
2-Propanol-2 <i>d</i>	9.6×10^6 ^a
2-Propanol- <i>d</i> ₇	8.9×10^6 ^a

^aFitted values derived from a comparison with those values selected above.

Table 3c. Selected rate constants for $\cdot\text{OH}$ and $\cdot\text{O}^-$

Reactant	Rate Constant
<i>$\cdot\text{OH}$ Reactions</i>	
Bicarbonate ion	8.5×10^6
Thiocyanate ion	1.1×10^{10}
Carbonate ion	3.9×10^8
Ferrocyanide ion	1.05×10^{10}
Iodide ion	1.1×10^{10}
ABTS	1.2×10^{10}
Benzoate ion (BzO^-)	5.9×10^9
<i>N,N</i> -Dimethyl-4-nitrosoaniline (RNO)	1.25×10^{10}
Ethanol	1.9×10^9
Formate ion	3.2×10^9
Methanol	9.7×10^8
2-Methyl-2-propanol (<i>tert</i> -BuOH)	6.0×10^8
Nitrobenzene (NB)	3.9×10^9
4-Nitrobenzoate ion (PNBA^-)	2.6×10^9
2-Propanol	1.9×10^9
Thymine (5-MeU)	6.4×10^9
<i>$\cdot\text{O}^-$ Reactions</i>	
Oxygen	3.6×10^9
Ethanol	1.2×10^9
3-Hexene-1,6-dioate ion (3-HX)	6.3×10^8
Methanol	7.5×10^8
2-Propanol	1.2×10^9

TABLE 4. Activation energies

Reactant	E_a^a	$\log A^b$	k^c	ΔS_{\ddagger}^d	Ref. ^e	No. ^f
e_{aq}^- reactions						
$e_{aq}^- + e_{aq}^-$	23		5.		86A009	5.1.1
	22		7		85A373	
	22		5.5		80A187	
					81A370	
	18		5.0		76A250	
	22		6.3		670109	
Bromate ion	19		7.8		690567	6.31
Chlorate ion	13		0.22		690567	6.63
Cobalt(II) ions	24		12.		650044	6.65
$Co(NH_3)_6^{3+}$	18		90.		650044	6.81
$Co(NH_3)_5^{3+}$	13		58.	-3	670098	6.82
Hydrogen ion	11		22.		710580	6.230
					690567	
	10		28.		700243	
	13				640046	
	16		22.		650044	
	13		25.	-9	670098	
Manganese(II) ions	32		0.038		650044	6.265
Mn^{II} EDTA	17		0.0015		670299	6.269
Permanganate ion	13		44.		690567	6.279
Nitrite ion	7		3.4		690567	6.294
	14		3.4	-26	670098	
Nitrate ion	10		9.3		690567	6.295
	16		11.	-16	670098	
Ni^{II} NTA	22		0.6		690277	6.319
Ni^{II} EDTA	18				690277	6.321
Oxygen	13	12.5	18.		771174	6.331
Hydrogen peroxide	15		11.		690567	6.332
Water	19			-130	670532	6.334
	19				640046	
				-109	85A373	
Thiosulfate ion	16		0.6		690567	6.420
Thallium(I) ion	10		28.		710580	6.453
					690567	
Acetamide	15		0.035	-63	670098	6.493
Acetone	11	11.9	8.0	-18	85A282	6.498
	12	11.9	6.6	-16	79A117	
Acetonitrile	23	11.6	0.044	-22	79A117	6.500
Acrylamide	16		33.		690567	6.534
Allyl alcohol	24	11.8	0.072	-18	84A357	6.571
	14	9.7	0.020	-60	79A117	
2-Aminopyrimidine	15		7.6	-14	670098	6.584
Benzenesulfonate ion	15		1.2	-36	670098	6.625
Benzoate ion	15		3.6	-26	670098	6.630
Benzyl alcohol	15		0.18	-50	670098	6.644
4-Bromophenol	13		12.		690567	6.685
	13		12.	-15	670098	
5-Bromouracil	16		19.		690567	6.694
Carbon tetrachloride	15		24.		771041	6.716
Chloroacetate ion	12		0.89		670299	6.721
	16		1.1	-36	670098	
2-Chloroethanol	13		0.33		670299	6.739
3-Chloropropionate ion	15		0.44		670299	6.755

Cyclobutanone	15		8.2		761103	6.784
Cycloheptanone	16		6.0		761103	6.785
Cyclohexanone	15		7.8	-19	670098	6.789
	15		7.2		761103	
Cyclooctanone	15		4.3		761103	6.792
Cyclopentanone	15		7.4		761103	6.793
Ethyl acetate	16	10.5	0.046	-44	79A117	6.923
Formamide	13		0.033	-64	670098	6.953
5-Iodouracil	10		17.		690567	6.1107
Nitrobenzene	18	13.6	38.	16	85A282	6.1256
	19	13.9	40.	20	84A357	
	18	13.6	25.	15	84A200	
	15	13.3	42.	9	79A117	
	9.1		28.		690567	
4-Nitrophenol	11		36.		690567	6.1273
Phenol	15	10.0	0.021	-53	85A282	6.1315
	20	10.9	0.025	-36	84A200	
	15	9.8	0.016	-57	79A117	
Phenylacetate ion	14		0.032	-65	670098	6.1319
Phenylalanine	14		0.14	-51	670098	6.1321
	15 ^e		-0.3		80A064	
3-Phenylpropionate ion	15		-0.04		80A064	6.1337
Phthalate ion	13		4.6	-24	670098	6.????
Propargyl alcohol	18	11.4	0.21	-27	79A117	6.1351
Pyridine	19		3.7		690567	6.1365
	16		34.6	-25	670098	
Toluene	20	10.6	0.014	-42	85A282	6.1466
Tryptophan	21	12.3	0.32	-10	84A200	6.1489
Urea	14		0.00032	-105	670098	6.1496

***H reactions**

Silver(I) ion	90	19	27.		751197	7.1
Iron(II) ion	14	10.2	-0.05		760011	7.76
Manganese(II) ions	20	12.3	0.66		751197	7.99
Hydroxide ion	26		0.045	-25	85A373	7.117
α -Methylstyrene	10		0.45		751198	7.446
2-Propanol	16	11.0	0.14		751197	7.493
2-Propanol- <i>d</i> ₇	20	10.8			760011	7.495
	23	10.4			760011	

***OH reactions**

*OH + *OH	8				81A370	5.3.1
Bicarbonate ion	21.2	12.8	0.01		870901	8.18
Carbonate ion	23.6	10.8	0.4		870901	8.19
Thiocyanate ion	11		9.6		84A349	8.26
	13				84A349	
Copper(II) ions	13		0.31		80A187	8.67
Deuterium	23 ^h		0.017		590028	8.83
Iron(II) ion	9		0.43		81A370	8.85
Ferrocyanide ion	13		10		84A349	8.90
Hydrogen	19		0.035		83A015	8.104
	13		0.040		771079	
	20 ⁱ		0.032		590028	
Iodide ion	12		12.		84A349	8.109
Hydrogen peroxide	14		0.027		82A096	8.159
Formate ion	8.5		3.8		84A349	8.672
2-Methyl-2-propanol	10		0.66		84A349	8.954
2-Propanol	5		2.3		84A349	8.1090

^akJ mol⁻¹.^fEntry numbers in Tables 5-8.

^bA in L mol⁻¹ s⁻¹.

^cIn units of 10⁹ L mol⁻¹ s⁻¹, at room temperature.

^dJ K⁻¹ mol⁻¹

^eSee Section 13 for reference list following Tables 6-10.

^gDependent on pH.

^hA = 16 ± 6 rel. to A(*OH + Fe²⁺).

ⁱA = 14 ± 6 rel. to A(*OH + Fe²⁺).