

THE SIMPLEST FREE RADICALS

F. S. DANTON

University of Nottingham, University Park, Nottingham, U.K.

INTRODUCTION

Every lexicographer knows that the meaning of a word is time dependent, and, in favour of the argument that it is also dependent on latitude and longitude, the perverse amongst us would cite Oscar Wilde's dictum, "England and America are two countries separated by a common language". Certainly the word *radical* has changed its meaning for chemists who originally thought of it as part of a molecule which remained unaltered through a series of chemical processes.

The man the centenary of whose birth we celebrate today inaugurated the 20th century by teaching us that such molecular fragments can exist as separate entities for finite periods, though they may react rapidly with a wide variety of substances, including themselves. Today a free radical is accepted as being either an atom or a group of covalently linked atoms having one or more unpaired electrons. It may be electrically charged, or electrically neutral. On this definition free radicals would include monatomic species such as $H\cdot$, Li , O , $O^{\cdot-}$, as well as polyatomic species such as H_2^+ , $\cdot OH$, $O_2^{\cdot-}$, $O_3^{\cdot-}$, and the more familiar large stable organic radicals like DPPH and galvinoxyl. The *mass* of the free radical does not alter its essential qualities though it may alter the time scale of the reactions into which it may enter. For this reason, I should prefer to regard the simplest free radical as an electron, which obviously satisfies the basic criterion. If you will bear with me in this further stage of evolution of the meaning of the term 'free radical', I should like first to describe the chemistry of the electron as a reactive entity, and then mention briefly some newer aspects of the chemistry of $H\cdot$, OH and HO_2 radicals. This order is appropriate because many of the techniques used for the study of the electron and many of the principles which its behaviour illustrates are equally applicable to other radicals, and in the last half decade or so an immense amount of new information about simple inorganic radicals has been accumulated, which has greatly illuminated some hitherto dark, but important, areas of chemistry. We also recall that the free electron is the simplest chemical entity and by definition also the simplest and most powerful reducing agent†. It is also the species which is exchanged between two partners in a very wide range of chemical reactions, namely redox and exchange reactions between identical groups, or between ions in different valency states, or between molecules.

The advances made in recent years have been so numerous that it is impossible, in the space available, to be comprehensive. I shall do no more

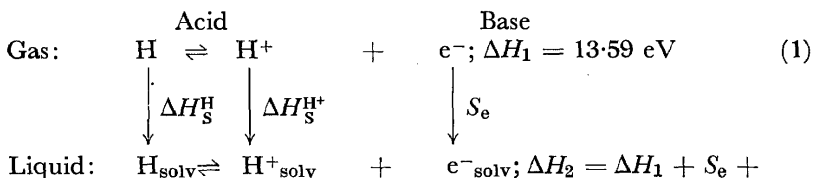
† As will be shown later, the solvated electron may be so stabilized by the solvent that it is a less powerful reducing agent than an alkali metal.

than draw attention to the methods used and the general nature of the results obtained.

A. THE CHEMISTRY OF THE ELECTRON IN AQUEOUS AND NON-AQUEOUS RIGID AND FLUID MEDIA

1. Preliminary thermodynamic considerations

It is convenient to begin by considering certain thermodynamic relationships illustrated in the cycle linking equations (1) and (2), where the enthalpy changes are clearly indicated. The known values of ΔH_1 , the near identity



$$\Delta H_S^{\text{H}^+} - \Delta H_S^{\text{H}} \quad (2)$$

of the entropies of H and H^+ in the gas phase and the small value of the entropy of the gaseous electron indicate that the equilibrium constant of reaction (1) is minute. A different situation arises when this reaction is carried out in a polarizable medium. We may reasonably suppose that, because of the small size and lack of polarity of the hydrogen atom, the heat and entropy of solution of this species, like that of the rare gases, will both be close to zero. In contrast, when hydrogen ions are "dropped" into a polarizable liquid, electrostatic forces ensure that both polarizable molecules and molecules having a permanent dipole moment will become oriented around the hydrogen ion in such a way as to minimize energy. When these molecules also have a high proton affinity, as in the case of water, alcohols, and ethers, the magnitude of $\Delta H_S^{\text{H}^+}$ may become very large and negative; for example, in water it is -12.3 eV .

The situation is somewhat similar when an electron is imagined to be "dropped" into a liquid, except for the fact that the motions of the solvent molecules (mainly rotational) are so slow relative to the motion of the electron that it is impossible to treat the solvation of an electron in the same quantitative way as the solvation of a more massive positive or negative ion. If, however, the electron moves into a region where the solvent molecules are not totally randomly oriented the electrical forces may be just sufficient to confine the electron to that small group of molecules. Its localization in this way will, in its turn, increase the orientation polarization of the surrounding molecules and the electron may then be regarded as bound within a potential well, the shape and depth of which will depend upon the molecules of the medium. This is illustrated in *Figure 1*. Several quantitative treatments of this kind of model have been given¹, and lead to various predictions about the relationship of the spectrum to the dielectric constant of the medium, temperature, and added electrolytes. It follows that S_e is also a negative quantity and therefore ΔH_2 is likely to be considerably less than ΔH_1 . Although the entropy of solution of H^+ is large and negative, and that

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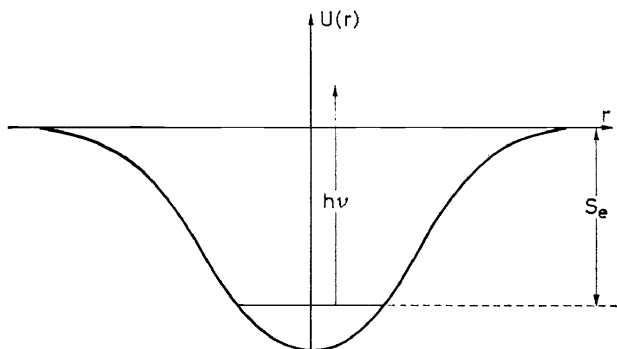


Figure 1. Schematic potential well of an electron in a continuous dielectric

of the electron is not expected to be large, the contribution which they make to the free energy changes will be small, consequently we expect $K_2 \gg K_1$, and it is also possible that in sufficiently polar media K_2 , though less than unity will yet be large enough to be measured and for the chemistry of e^-_{solv} to be studied.

Electrons can also be bound to particular sites in solids, and these sites may comprise the well-known defect sites in crystals, e.g. anion vacancies, or in vitreous solids they may be in zones in which the molecules are sufficiently oriented for the electron to be bound to a group of molecules. Whatever the nature of the site, once bound, the electron will be incapable of movement through the solid provided the temperature is low enough. Electrons immobilized in solids in this way will be referred to as e^-_t .

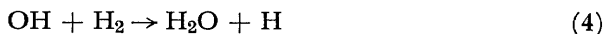
Equation (2) illustrates that the hydrogen atom is the simplest acid in either the Lowry-Brønsted or Lewis definitions, and the electron is the simplest base. As a corollary we would expect hydrogen atoms to react with hydroxide ions according to equation (3) to form the hydrated electron,



and from the known values of the electron affinity of the hydroxyl radical, the solvation energy of the hydroxide ion, the heats of formation of liquid water and the hydroxyl radical, it would be expected that ΔH_3 would equal $1.9 \text{ eV} + S_e$. It will be shown later that S_e in water is about 1.7 eV , so that it is expected that $\Delta G_3 = - \sim 5 \text{ kcal}$.

2. Preparation of e^-_{solv} and e^-_t

There are two basic methods by which solvated or trapped electrons may be prepared. The first depends upon the achievement of reaction (3) by generating hydrogen atoms in a highly basic medium. The hydrogen atom may be produced by flowing hydrogen gas through a discharge into the solution. Alternatively, they may be provided by some reaction [e.g. reaction (4)]



or by a chemical substance to which the hydrogen atom is only weakly bound, [e.g. as in reaction (5)], or by direct attack of the basic form of the



hydroxyl radical on a hydrogen molecule [reaction (6)].



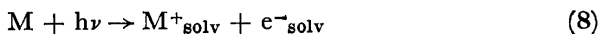
The second group of methods is based upon detachment of the electron, either from molecules in the bulk of the solution or from a surface. The latter method, though recently used², will not be considered further here, because it inevitably results in production of electrons in an inhomogeneous distribution so that the procedures appropriate to homogeneous kinetics cannot be applied.

Electrons may be detached from molecules in three ways, thermally, photochemically, and radiation-chemically. The thermal method requires the dissolution in the water of molecules, which spontaneously lose an electron to the water because the rate and energetics of reaction (7) are favourable. The species coming into this category include the alkali and the

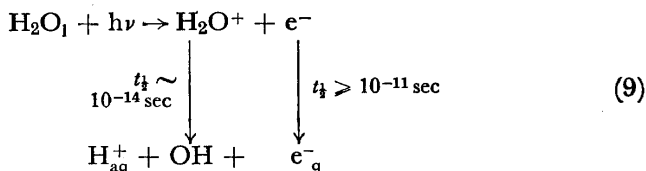


alkaline earth metals, and recent experiments by Hughes and Roach and by Walker and Schraebe² on the products formed when mercury amalgam of the alkali metals are brought into contact with aqueous solutions containing diagnostic reagents for the solvated electron have shown that this sort of reaction indubitably occurs. Moreover, optical reflectance spectra and e.s.r. spectra of alternate multi-molecular layers of water molecules and sodium atoms prepared in the rotating cryostat by Bennett, Mile and Thomas², have shown that e^-_{t} is present.

When reaction (7) is too slow to be achieved thermally, it is sometimes possible for an electron to be photodetached from a molecule M, according to equation (8). In principle, this should be possible for the solvent mole-



cules themselves. For example, in the case of water, equation (9) would represent the relevant reaction, and the H_2O^+ ion initially formed



would react rapidly to form the hydroxonium ion and the hydroxyl radical. However, the ionization potential of water is 12.56 eV and there is no reason to think that significantly less energy would be involved in the photo-ionization of liquid water as compared with gaseous water, since the large hydration energies of the proton and the electron would not be available during the absorption of the photon. Consequently the wavelength of the light required for this process would lie in the vacuum u.v. region, and it would be technically difficult to achieve this photo-ionization. Furthermore, any

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added solute, for which it was desired to study its reaction with an electron would almost certainly have a strong absorption band in the same region, and therefore exert a powerful inner filtration effect.

It is therefore necessary to look for reducing solutes which have relatively low ionization potentials. These include cations, anions, and neutral molecules³, and some relevant quantum yields of selected systems are given in *Table 1*. The same method is also applicable for producing trapped electrons. The only disadvantage associated with this method is that, after a short period of illumination, the solution contains significant amounts of both the oxidized and reduced forms of the solute and it is likely that the electron will react rapidly with one or both these species, a complication which it is preferable to avoid.

Table 1. Electron detachment quantum yields³

<i>Donor</i>	Br ⁻	Cl ⁻	OH ⁻	SO ₄ ²⁻	I ⁻	Fe(CN) ₆ ⁴⁻	Fe ²⁺	φNH ₂	φOH
λ(Å)	1849	1849	1849	1849	2537	2537	2537	2537	2537
φ(e ⁻ _{aq})	0.34	0.43	0.11	0.71	0.23	0.67	0.06	0.16	0.025

By far the most convenient method is to irradiate the substance with ionizing radiation, e.g. gamma-rays, beta-particles, electron beams. The method depends upon the fact that when a fast charged particle passes near a molecule the Coulombic interactions between the fast charged particle and an electron in a molecule ensure that, subject to certain quantum restrictions, energy is transferred from the particle to the electron. Molecules are thus electronically excited, and in some cases ionized, as illustrated in *Figure 2*. In the case of water, the reactions following ionization are precisely those described in equation (9). There are numerous advantages to this method, namely;

1. No competing solutes for the electron need be present other than H⁺ and OH which are produced by the radiation in yields comparable to that of the electron.

2. The radiation is non-selectively absorbed and therefore the presence of solutes chosen to react with the electron will in no way affect the primary act.

3. Since the mechanism of deposition of the energy is entirely independent of the translucency of the medium or of its state of aggregation, the method can be applied to coloured, crystalline, or amorphous solids as well as to liquids, and therefore the technique of matrix isolation (for later study of the intermediates by either optical or magnetic spectroscopy) can easily be applied.

4. Possibly the greatest merit of this particular method is that it is now possible to give high dose pulses of very short duration, and therefore the technique of pulse radiolysis, entirely analogous to flash photolysis, but with even shorter pulse duration times can be applied to measure the absolute rate constants of reactions of the intermediates e⁻_{aq} and OH.

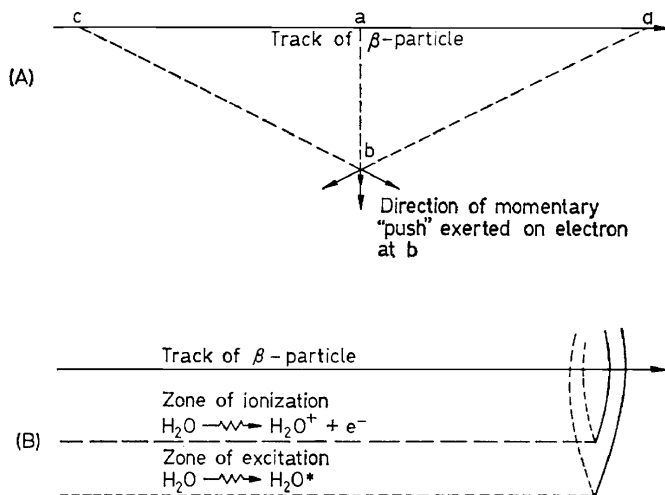


Figure 2. Interaction between a fast charged particle and molecules of water. [A 0.5 MeV β -particle will traverse a distance cd in Fig. (A) = about 40 Å in about 10^{-17} seconds. Within this time an electron at b attached to a water molecule will experience repulsion along cb and db . The components of these forces parallel to cd will cancel whilst those along ab reinforce one another. The electron at b therefore receives a sharp "push" perpendicular to the track. When the distance ab is short enough the kinetic energy gained by the electron in this way is sufficient to eject it from the water molecule. At greater distances the water molecule may be electronically excited but unionized and beyond a certain distance will be unaffected (see Fig. (B))]

3. Proof of the formation of e^-

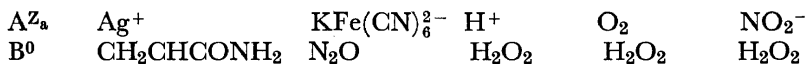
Until eight years ago, it was always assumed that any electrons formed in water would, within $\sim 10^{-11}$ sec, decompose into a hydrogen atom and an hydroxide ion [reverse of reaction (3)]. However, in the late 1950s a number of experimental results seemed to suggest that if this were the case then the hydrogen atom had some rather unusual properties. Thus, it appeared to react with chloracetic acid to liberate chloride ion preferentially, rather than to form hydrogen, and certain relative rates of reaction of the supposed hydrogen atom with two solutes appeared to be markedly dependent on pH in a way which suggested that one form of hydrogen atom was readily protonated in acid solution⁴. Possible pairs of forms of hydrogen atoms could clearly only be either H_2^+ and $H\cdot$ or $H\cdot$ and e^- . The first proof that it was the latter was obtained independently in Brookhaven and Leeds⁵ in 1962. The method used in each laboratory was to allow two solutes, A of charge Z_a , and B of zero charge, to react competitively for the electron according to reactions (10) and (11). According to the Brønsted-Bjerrum theory of ionic reactions equation (12) should express the



$$\log_{10} (k_{10}/k_{11})^{25^\circ C} = \text{constant} + 1.02 Z_e Z_a \mu^{1/2} / (1 + \mu^{1/2}) \quad (12)$$

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dependence of the relative rates of reactions (10) and (11) on the ionic strength μ of the medium. The pairs of solutes chosen are shown below. The results shown in *Figure 3* leave no doubt that the entity with which the



two solutes react has a unit negative charge and therefore must be presumed

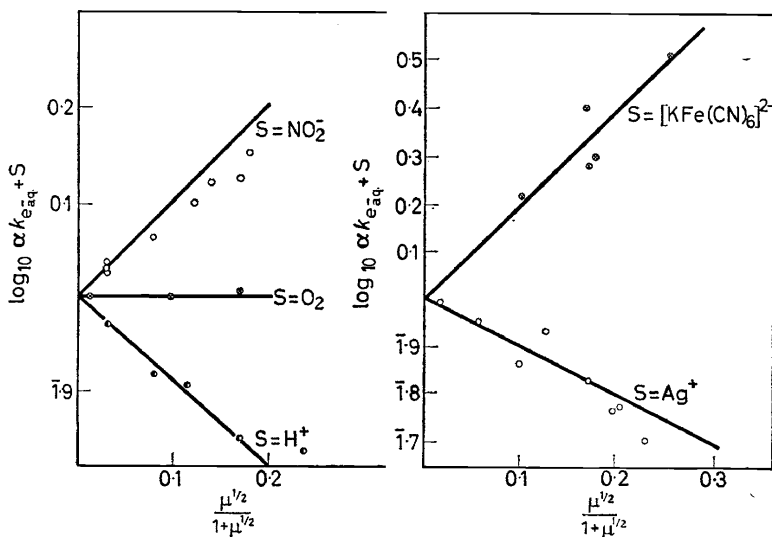


Figure 3. The effect of ionic strength on the relative rates of reaction of a charged solute [Ag^+ , $KFe(CN)_6^{2-}$, H^+ or NO_2^-] and an uncharged solute ($CH_2CHCONH_2$, N_2O or H_2O_2) with the hydrated electron⁵

to be the electron. It is of interest that theory predicts that the slope of these lines should be inversely proportional to $D^{3/2}$. Consequently, for methanol the slope of the line should be 3.6 and recent experiments in which $A = Ag^+$ or H^+ and $B = N_2O$ have confirmed this⁶. Measurements by the pulse radiolysis technique of the effect of ionic strength on individual reactions of the electron, e.g. with ferricyanide⁷ and cobaltous ions⁸ have confirmed these findings.

In the same year that the electron was identified by its charge, Boag and Hart⁹ pulse-radiolysed water, which had been carefully deaerated, and observed a strong absorption band with a peak at about 7000 Å which was rapidly quenched by the presence of small amounts of electron scavengers, such as H^+_{aq} , N_2O , H_2O_2 , and $CH_2CHCONH_2$. Furthermore, the optical density was increased in alkaline solution containing a high concentration of hydrogen¹⁰ due to the conversion of hydroxyl radicals to hydrogen atoms via reaction (4) followed by the formation of additional electrons in reaction (3). The spectrum is shown in *Figure 4*.

The extinction coefficient ($1.58 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$) at $\lambda_{\text{max}} = 7200 \text{ Å}$

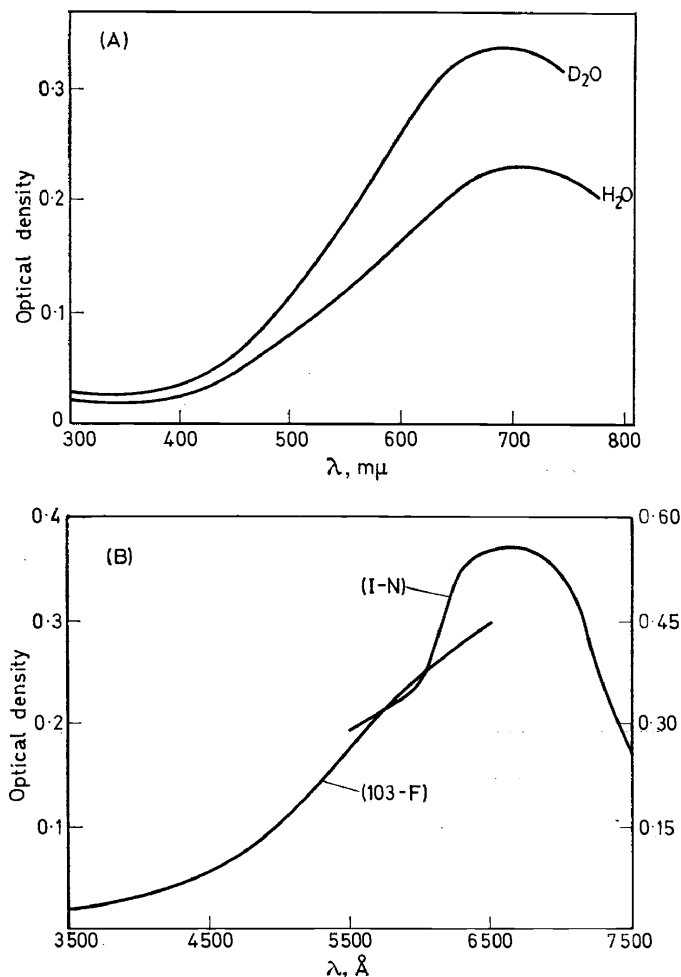


Figure 4. The spectrum of the hydrated electron generated (A) by ionizing radiation¹¹, and (B) photochemically from chloride ion¹²

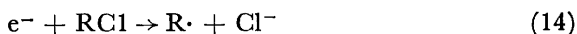
is so large that it is possible to observe the absorption at this wavelength, when a carefully deaerated aqueous solution is irradiated with gamma-rays at a dose-rate of only $3 \times 10^{19} \text{ eV l.}^{-1} \text{ sec}^{-1}$ provided that the solution is saturated with hydrogen¹³.

The spectrum of the solvated electron in a variety of media has been intensively studied in order to elucidate more precisely the nature of the electron trap. Arai and Sauer¹⁴ have investigated the effect of temperature and composition of the mixture on the position and shape of the spectrum and their results seem to indicate that a solvated electron interacts with a considerable number of solvent molecules as required by the theory of Jortner¹. Although λ_{max} is markedly shifted to shorter wavelengths at lower temperatures, the half-width of the absorption peak is unaffected.

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For several aliphatic alcohols, the magnitude of the shift (in energy units) is related to the static (D_s) and optical (D_{op}) dielectric constants according to the Davydov equation¹⁵. Measurement of the temperature coefficient of the spectrum enables the orbital radius of the solvated electron to be measured. For water, Gottschall and Hart¹⁶ found this to be 2.9\AA .

When electrons are generated either photochemically or by ionizing radiation in glasses, marked coloration occurs¹⁷. Since the absorption band has the expected shape and position and its intensity is diminished by the presence of solutes which can react with the electron, e.g. alkyl halides which react according to equation (14), this coloration is ascribed to trapped



electrons. Typical spectra are shown in *Figure 5*.

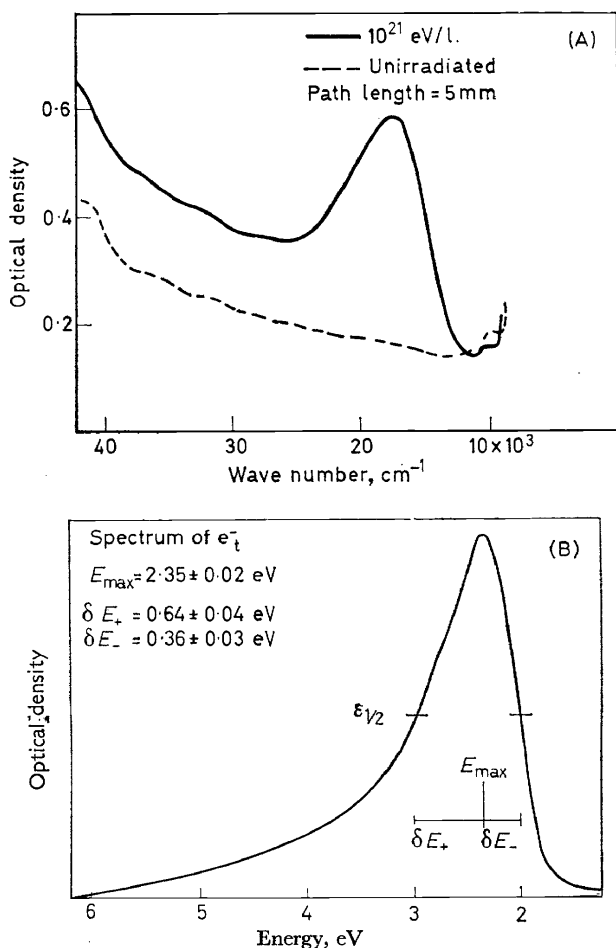
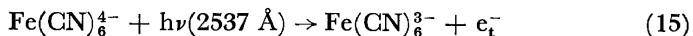


Figure 5. The absorption spectra of e_t^- in (A) 6 N NaOH and (B) methanol glasses^{17(a)} at 77°K ^{17(b)}

A free electron is expected to have a singlet electron spin resonance band and this band is shown in *Figure 6* for the electron produced by γ -irradiation or by the reaction (15) in an alkaline glass. The spectra of the γ -irradiated



glasses contain the contribution from the other odd electron species which is always produced, but the two signals can often be distinguished by their different susceptibilities to power saturation. A somewhat similar spectrum was also observed by Bennett, Mile and Thomas² when sodium and water

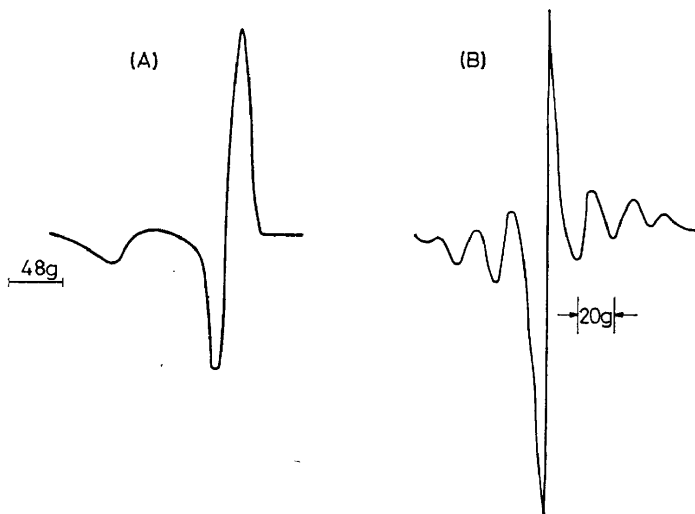


Figure 6. E.s.r. spectra of e^- and associated radical in (A) alkaline aqueous glass^{17(a, b)}, and (B) in a methyl tetrahydrofuran glass¹⁸

were allowed to react at 77°K. On warming, this singlet gave seven equally spaced lines which these authors attributed to the orientation in a symmetrical octahedral way of six hydrogen atoms forming part of six adjacent water molecules. Such a configuration is consistent with a trap radius of about 2.8 Å units.

4. Other physical properties of e^-

Recently, Schmidt and Buck¹⁹ have measured the changes of conductivity which occur during and after pulse radiolysis of a dilute solution of barium hydroxide, and have concluded that the equivalent ionic conductance of the hydrated electron is 170 mhos. This is almost exactly one half that of the hydroxonium ion in water and corresponds to a diffusion constant of $4.5 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$. It is interesting that this direct measurement is very close to the value for the diffusion constant of the hydrated electron which it has been necessary to assume to account for its reactivity.

The magnitude of the diffusion constant and the equivalent conductance indicate that the hydrated electron in water behaves almost as a normal ion,

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and suggest that it moves through the solution sufficiently slowly for its ion atmosphere to retain its equilibrium distribution, a conclusion which is confirmed by the normal primary salt effect, which is observed for ionic reactions in which the hydrated electron is one component. However, as we shall see later, many of the reactions of the hydrated electron are diffusion controlled and have bimolecular rate constants larger than $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. This raises the possibility that, by increasing the solute concentration, the hydrated electron may react before it has had time to establish its ion atmosphere. Under these conditions, it behaves as a reagent whose activity coefficient is independent of the ionic strength and the activated complex will have the ion atmosphere appropriate to the ion A^{Z_a} whilst the actual algebraic charge on the centre of the activated complex will be $Z_a - 1$. The consequence of this situation is that the rate constant of the reaction shows a diminished dependence on ionic strength²⁰. In the particular case of $Z_a = -1$ the expected dependence is given by equation (16).

$$\log_{10} k^{25^\circ\text{C}} = \text{constant} + 0.51 \mu^{1/2} / (1 + \mu^{1/2}) \quad (16)$$

Therefore for a fixed ionic strength the value of $\log_{10} k$ should diminish by approximately $\mu^{1/2}/2$ as the solute concentration is increased so that the half-life of the reaction becomes less than the ionic atmosphere relaxation time, τ . The observed value of τ is in good agreement with the Debye-Hückel-Falkenhagen theory. This effect is illustrated in *Figure 7*.

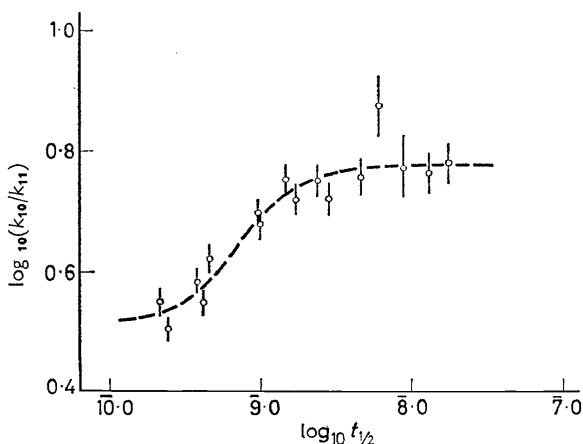


Figure 7. The variation of $\log_{10} (k_{10}/k_{11})$ with the half-life of the hydrated electron before reaction²⁰. A = I_3^- , B = N_2O

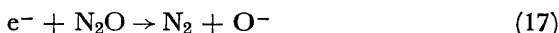
The physical properties of the solvated electron are summarized in *Table 2*.

Table 2. Physical Properties of e^-_{solv} and e^-_t

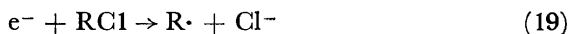
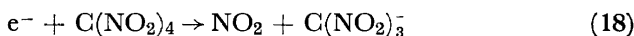
No.	Property	Values and comments
1. Charge on e^-_{solv}		For water and alcohols it is -1 .
2. Spectrum		Broad continuum half width $0.9\text{--}1.5\text{eV}$, $\lambda_{\text{max}} (= 7200\text{\AA})$, for e^-_{aq} , undergoes blue shift as temperature decreases, ϵ_{max} in range 1 to $2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ and oscillator strength in range $0.6\text{--}0.9$.
3. E.s.r. signal of e^-_t		Sharp singlet generally at $g = 2.003$
4. Diffusion constant		$D(e^-_{\text{aq}}) = 4.5 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ in water
5. Equivalent conductance		170 mho in water
6. Ion atmosphere relaxation time (τ)		For e^-_{aq} at $\mu = 0.23 = 3 \times 10^{-9} \text{ sec}$
7. Cavity radius		$r_{e^-_q} \simeq 3\text{\AA}$

5. Specific reagents for e^- and H: Acid-base relationships

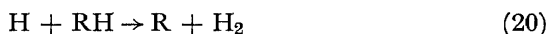
There are several reagents which react very rapidly with the electron and only sluggishly with the hydrogen atom, e.g. N_2O in equation (17). There



are others which react rapidly with the electron to form a highly coloured product, e.g. the nitroform anion in reaction (18); and yet other reagents which produce a permanent product, e.g. chloride ion in reaction (19)



which is not formed to any great extent by the attack of a hydrogen atom on the alkyl halide. Finally there are also reagents which react with hydrogen atoms to form hydrogen as in equation (20). Such electron and hydrogen atom



scavengers can be used to measure the total yield of electrons or hydrogen atoms emerging from either a primary photochemical process or a primary radiation chemical process as shown in Figure 8. Tetranitromethane is an extremely useful indicator for the presence of hydrated electrons, because when applied in conjunction with pulse radiolysis, the optical density of the hydrated electrons can be directly related to the optical density of the equivalent amount of the nitroform anion which they produce and, in this way, an absolute value of the extinction coefficient of the hydrated electron was obtained²². Similarly, reaction (19) has been used to confirm the presence of electrons in irradiated glasses^{17b}, since the presence of alkyl halides not only diminishes the blue colour, but results in the formation of an alkyl radical which may be identified either by its e.s.r. or optical spectrum.

The particular utility of reagents of this kind is that they can be used as indicators to explore the interconversion of the hydrogen atom and the hydrated electron, for instance the yield of nitrogen for a fixed dose of light

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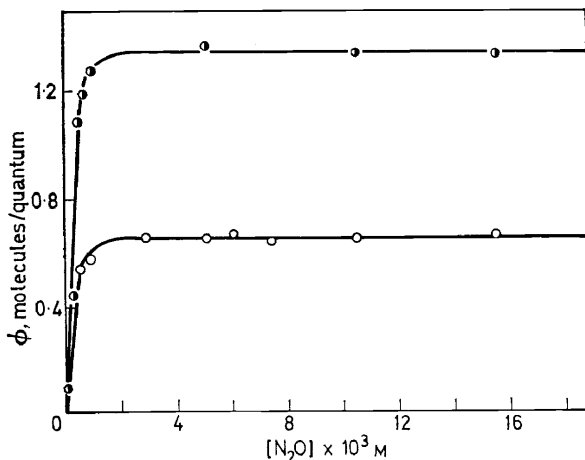


Figure 8. $\phi(N_2)$ (open circles) and $\phi(\text{ferricyanide})$ (half-filled circles) as a function of $[N_2O]$ for $10^{-3} \text{ M } K_4Fe(CN)_6$ solution illuminated with light of wavelength 2537 \AA ²¹

or ionising radiation delivered to an aqueous solution of nitrous oxide will diminish sigmoidally as the pH is decreased and electrons converted via reaction (— 2) to hydrogen atoms, to which nitrous oxide is relatively inert. Figure 9 illustrates one example of this. Mirror images of this kind of curve are, of course, obtained for hydrogen yields from aqueous solutions containing solutes such as alcohols²³. From curves of this kind, relative reactivities of the hydrogen ion in the chosen solute towards the electron are obtained by one of the following two procedures: in the case of the first example, the quantum yield of nitrogen should be given by equation (21), and therefore a plot of the reciprocal quantum yield against the

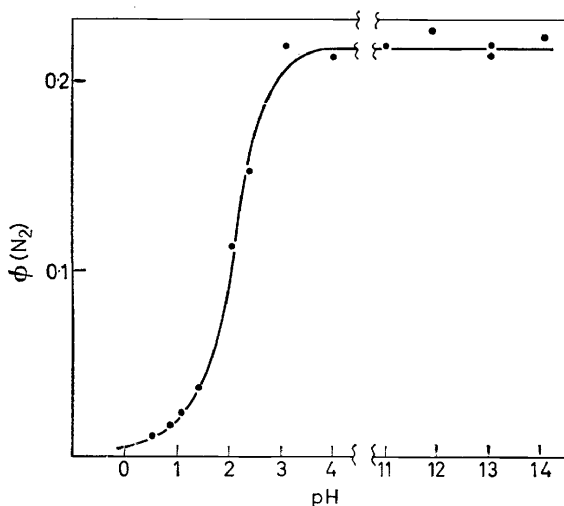


Figure 9. Variation with pH of $\phi(N_2)$ for aqueous solutions of KI containing N_2O and illuminated with 2537 \AA light²⁰

$$\phi(\text{N}_2) = \phi_e - k_{17} [\text{N}_2\text{O}] / \{k_{17} [\text{N}_2\text{O}] + k_{-2} [\text{H}^+]\} \quad (21)$$

ratio of hydrogen ion concentration to N_2O concentration should give a straight line, from the intercept and slope of which k_{17}/k_{-2} may be obtained. The alternative procedure is to have a second solute present which can react with the hydrogen atoms to form a distinctive product. *Figure 10* illustrates that when nitrous oxide and hydrogen ions are in competition for electrons in a medium which contains sufficient methanol to scavenge all hydrogen atoms by reaction (22), the results fit the expected equation (23).



$$\phi(\text{H}_2)/\phi(\text{N}_2) = k_{17}[\text{N}_2\text{O}]/k_{22} [\text{H}^+] \quad (23)$$

Using the production of chloride ion in reaction (19) as a diagnostic test for electrons, the forward reaction in equation (3) was elegantly verified by Jortner and Rabani²⁵. These authors passed a stream of hydrogen gas containing hydrogen atoms into a solution containing chloroacetic acid. As expected, no chloride ions were formed in the solution until the pH exceeded 10, when there was a sudden increase in yield so that, at $\text{pH} \geq 13.5$, one chloride ion was formed for each hydrogen atom injected into the solution.

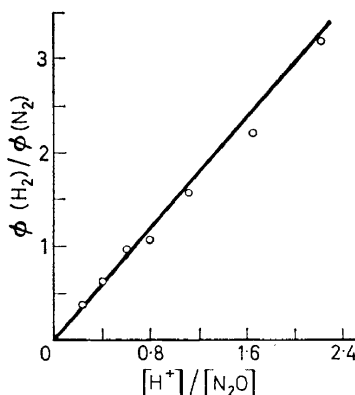
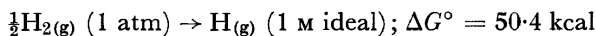


Figure 10. The dependence of $\phi(\text{H}_2)/\phi(\text{N}_2)$ on $[\text{H}^+]/[\text{N}_2\text{O}]$ for aqueous solutions containing $[\text{Cl}^-] = [\text{CH}_3\text{OH}] = 2 \times 10^{-2} \text{M}$ and illuminated with 1849 Å light²⁴

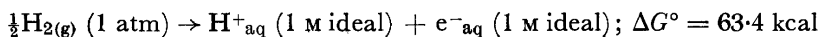
Pulse radiolysis methods may be used to determine the absolute values of the forward and back reactions in some of these acid-base equilibria. Thus solutions equilibrated with 100 atm of hydrogen contain about 0.1 M H_2 which is a sufficient concentration to ensure that all hydroxyl radicals are quickly converted to hydrogen atoms. From the rate of increase of optical absorption due to the electron in this solution at pH 11.6 Matheson and Rabani²⁶ found that $k_3 = 2 \times 10^7 \text{M}^{-1} \text{sec}^{-1}$, which was later confirmed by Hart, Gordon and Fielden²⁷, who also found that the half-life for first order decomposition of the electron in this system is 880 μsec . Assuming that the latter refers to the reverse of reaction (3), we obtain $k_{-3} = 800 \text{sec}^{-1}$ and therefore $K_3 = 2.5 \times 10^4 \text{M}^{-1}$ and $\Delta G^\circ_3 = -6.0 \text{kcal}$. Combining K_3 with the value of the ionic product of water the acid dissociation constant

THE SIMPLEST FREE RADICALS

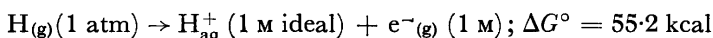
of the hydrogen atom $K_2 = [\text{H}^+_{\text{aq}}] [\text{e}^-_{\text{aq}}]/[\text{H}_{\text{aq}}]$ is found to be $10^{-9.6} \text{ M}$, and $\Delta G^\circ_2 = 13.0 \text{ kcal}$. From the known standard free energies of $\text{H}_{(\text{g})}$ and $\text{H}_{2(\text{g})}$ at 1 atm, we can obtain



which, together with $\Delta G^\circ_2 = 13.0 \text{ kcal}$ leads to



corresponding to a redox potential of -2.75 V (international scale). The hydrated electron is thus 0.56 V more strongly reducing than the hydrogen atom. In this calculation it has been assumed that there is no free energy change on dissolving gaseous hydrogen atoms in water, but if in fact this change, like that for the inert gases, is positive ΔG° will be slightly less than 63.4 and $|E_0^h|$ slightly less than 2.75 V . Noyes⁴⁰ has calculated ΔG° for the ionization



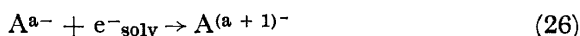
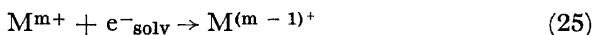
When this is combined with $\Delta G^\circ_2 = 13.0 \text{ kcal}$, and allowance made for the change in standard state of $\text{H}_{(\text{g})}$ from 1 atm to 1 M the free energy of hydration of the electron becomes -40.4 kcal , and Jortner and Noyes and co-



workers⁴⁰ have pointed out that this decrease is much smaller than that for hydration of any other univalent anion indicating much greater delocalization of the charge of the hydrated electron. Furthermore, if Noyes' semi-empirical formula for ΔG° (hydration) is applied, the radius of the charge distribution is close to 3 \AA and would be expected to correspond to a hydration entropy of about $+3 \text{ cal deg}^{-1} \text{ mole}^{-1}$ and hence to an enthalpy loss on hydration of about $39 \text{ kcal mole}^{-1}$, which is almost identical with ch/λ_{max} , where λ_{max} is 7200 \AA .

6. Rates and mechanisms of reaction of e^-_{aq}

The large oscillator strength of the hydrated electron and the relative slowness of its decomposition are two factors that greatly facilitate the determination of its rate of reaction with added solutes, and in the last four years the specific rate constants of about 400 bimolecular reactions involving the hydrated electron have been measured. These include dissociative reactions, e.g. (17), (18) and (19); and non-dissociative processes such as the capture of electrons by cations and anions [equations (25) and (26)] which in



some cases, e.g. $\text{M}^{m+} = \text{Fe}^{2+}$ and $\text{A}^{a-} = \text{ferricyanide}$, are the reverse of photodetachment processes. All these reactions have been reviewed in detail by several authors²⁸ and it will suffice here merely to draw attention

to salient features, some of which are illustrated in *Figures 11 and 12*. It is notable that a considerable number of the reactions have rate constants of about $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. This seems to suggest diffusion control of these reactions and although the temperature dependence of them has not been

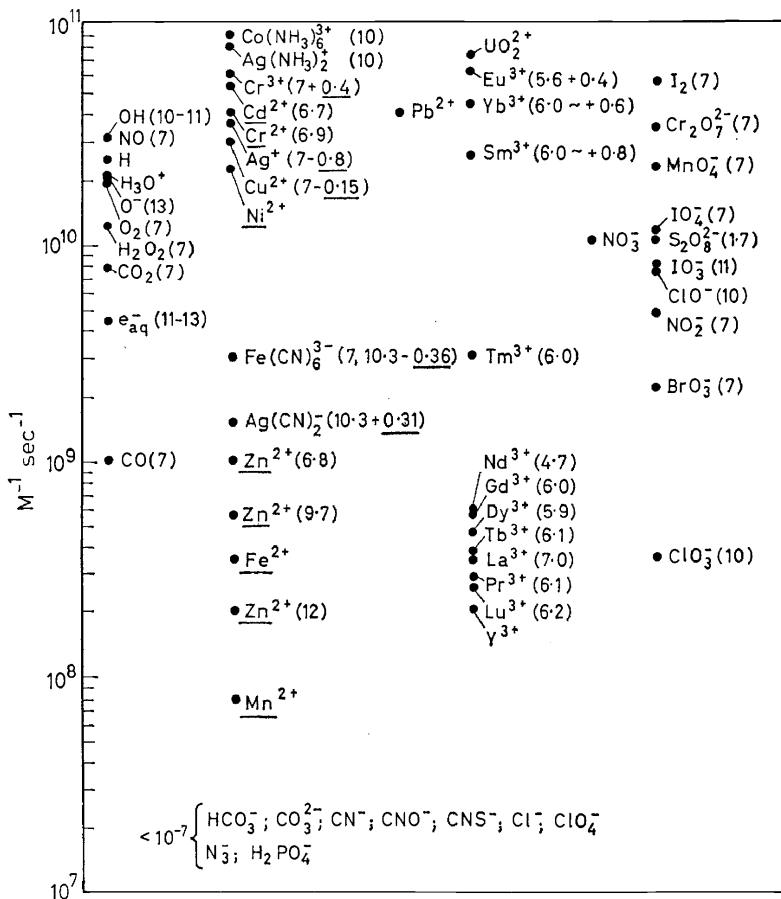


Figure 11. Rate constants for reactions of e^-_{aq} with inorganic solutes³⁰.

thoroughly studied, there are indications that the rate constant is adequately represented (a) by the Schmoluchovsky formula²⁹ given in equation (27), provided that the other reactant is an uncharged species, and (b) by the Debye equation (28) when the reactant is the species A with a charge Z_a .

$$k = 4\pi\sigma DN/1000 \text{ M}^{-1} \text{ sec}^{-1} \quad (27)$$

$$k = 4\pi Z_e Z_a / 1000 k\epsilon T \{e^{Z_e Z_a / \sigma k\epsilon T} - 1\} \quad (28)$$

In these equations D is the sum of the diffusion constants of the two reactants, σ is the mean collision diameter, Z_e is the charge on the electron, Z_a

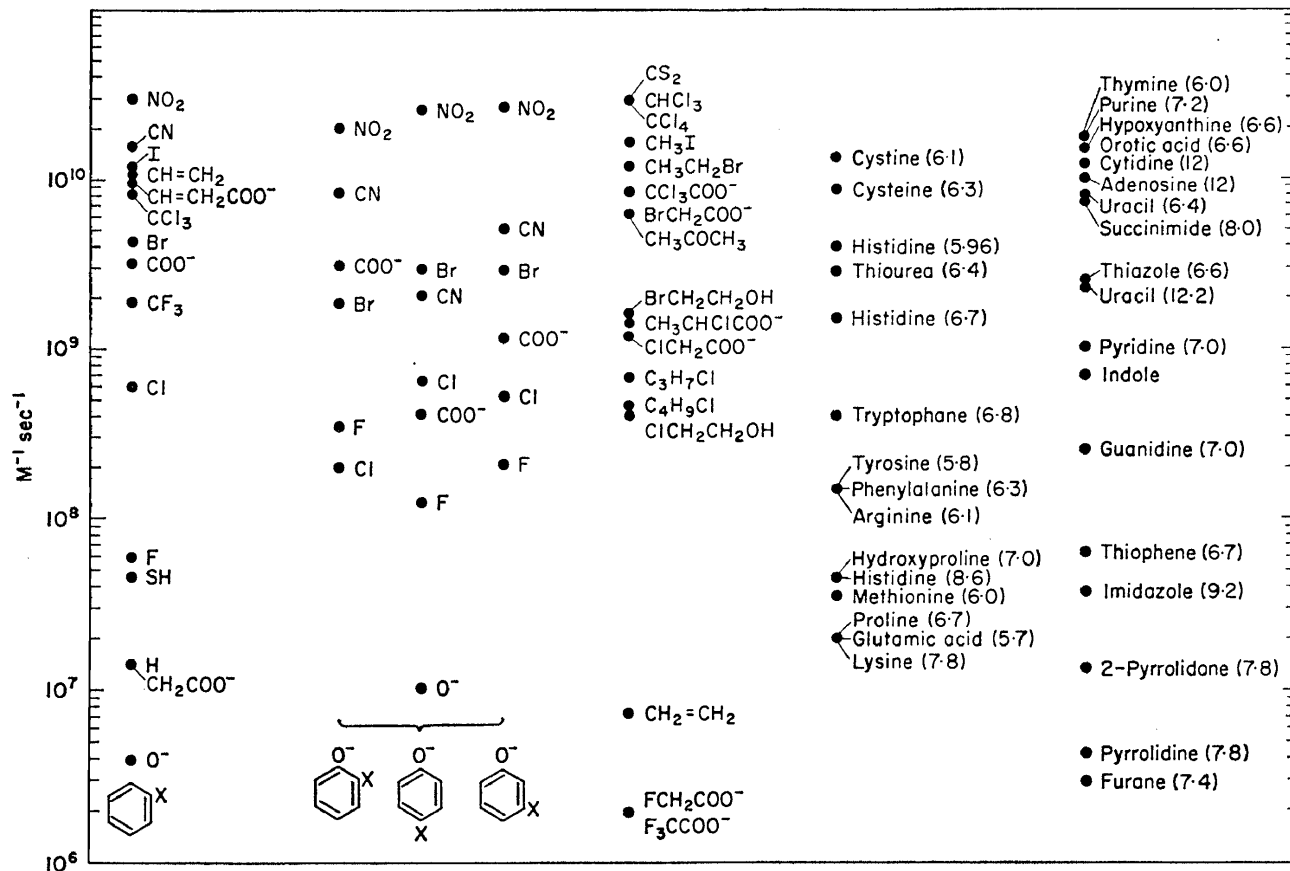


Figure 12. Rate constants for reactions of e^-_{aq} with organic solutes³⁰

the charge on the charged reactant, k is Boltzmann's constant and ϵ is the dielectric constant of the medium. Applying these equations to reactions which have k values greater than $10^{10} \text{ M}^{-1}\text{s}^{-1}$, σ may be found. When that part of σ attributable to the reagent is subtracted, the residue gives a measure of the reaction radius of the electron which emerges as being a variable quantity. This is another way of saying that our understanding of these reactions is imperfect at present. However, it does seem clear that even some of the reactions with rate constants in this region are not diffusion controlled, for example k_{-2} has a value that is smaller than would be expected on the basis of the known radius of the hydrated proton and assuming a radius for the hydrated electron of 3 Å units. Indeed, it is noticeable that the bimolecular rate constants of a hydrated electron are about one order of magnitude smaller than those of reactions of hydrated protons which Eigen and co-workers^{31a} have shown may often lie in the range 10^{11} to 10^{12} , and for which it has been suggested that proton tunnelling through the hydrogen bonded medium is taking place. Evidently, electron tunnelling is not a major factor influencing the rate of reactions of the hydrated electron. Instead, the electron is more conveniently regarded as bound to a group of water molecules, many of which *may* move with it during its diffusive displacements.

That the reactions of the hydrated electron may be encounter-controlled, requiring little or no activation energy is supported by the observation that they can occur readily at low temperatures. Thus, when alkaline aqueous glasses in which electrons have been trapped are slightly warmed, the electrons become mobile but can possess only very low kinetic energies. Nonetheless, they can react efficiently with solutes which they encounter.

Figures 11 and 12 show that not all bimolecular reactions are encounter-controlled and there is apparently an element of chemical selectivity. Not all acids react with the electron at the same rate and weak acids, such as NH_4^+ , H_2PO_4^- and HCO_3^- react more slowly than the hydronium ion. Again, even in the simple process of non-dissociative electron capture by cations there appears to be emerging a pattern in which those ions of which the hyper-reduced form, e.g. Mn^+ , La^{2+} is so unstable as to be unknown in conventional chemistry, react a good deal slower with the electron than ions such as Ag^+ , Eu^{3+} , Sm^{3+} , of which the reduced forms are well-known chemical entities. Broadly speaking when ΔG°_{25} is negative the reaction is rapid, but many other factors, including the nature of the ligand, the extent to which the d shell is already full, etc., also influence the rate.

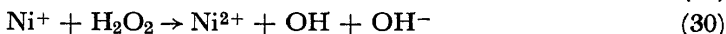
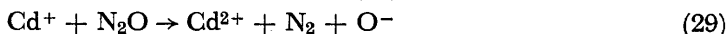
Progress on the theoretical front is less rapid, but Marcus^{31b} has already been able to show how his theory of electron-transfer reaction can be combined with polaron theory to give some insight into the detailed mechanism of reaction (25).

In many cases, the product of reaction (25) has a characteristic spectrum which is also formed when acid aqueous glasses containing salts of the ion M^{m+} are irradiated with γ -rays at 77°K ³². The assignment of this spectrum to the species $\text{M}^{(m-1)+}$ rests on the facts (a) that it is sometimes possible,

† When $\Delta G^\circ_{25} > \sim 5 \text{ kcal}$ the species $\text{M}^{(m-1)+}$ should spontaneously lose an electron to water at a rapid rate. This condition is satisfied for all the alkali metals for which $m = 1$, and it is of interest that all these elements rapidly decompose cold water and that their ions M^+ appear inert to e^-_{aq} .

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as for example in the case where $M^{(m-1)+} = Ag^{\circ}$, to identify $M^{(m-1)+}$ unambiguously by e.s.r. spectroscopy³³ and (b) that isoelectronic products e.g. In^{2+} , Cd^{+} and Ag° have absorption spectra in the region expected for $5^1S_{\frac{1}{2}} \rightarrow 5^2P_{\frac{1}{2}}$ transition or the C.T.T.S. band. These ions are powerful reducing agents and their intense absorption is particularly useful in that it enables the rates of the electron transfer reactions between them and added solutes to be determined easily by pulse radiolysis³⁴. Typical reactions of this kind are shown in equations (29) and (30).



Perhaps the most interesting aspect of selectivity arises from the fact that the electron is the simplest nucleophilic reagent and is, therefore, a sensitive probe of the regions of positive charge in molecules. *Figure 12* shows how reaction rate varies with structure of the organic reagent. Evidently alkanes are virtually unreactive, alkenes a little more reactive unless the ethylenic link is conjugated to an activating group such as CN, $CONH_2$, $COOH$, C_6H_5 . The reactions of the hydrated electron with aromatic compounds have been particularly closely studied. Benzene is relatively unreactive and no enhancement of reactivity occurs when *o*- or *p*-directing groups are introduced, whereas *m*-directing groups produce a vast increase in rate constant. These effects have been quantified by Anbar and Hart³⁵

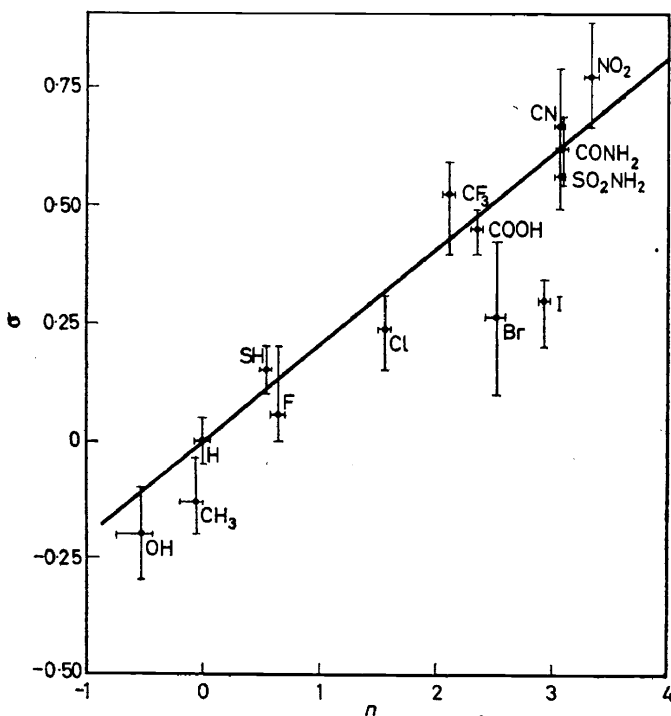


Figure 13. The effect of substituent X on the rate of the reaction of e^{-}_{aq} with C_6H_5X . $\log \{k(e^{-}_{aq} + C_6H_5X)/k(e^{-}_{aq} + C_6H_6)\}$ plotted against the Hammett σ function³⁵

for e^-_{aq} and by Sherman³⁶ for e^- in methanol and 2-propanol. Both authors find that log of the rate constant for the reaction of the electron with substituted benzene increases linearly with the Hammett σ functions. An example of this is shown in *Figure 13*.

7. Solvated electrons in organic media

It was mentioned earlier that electrons may be readily generated in organic solvents. The reactivity of the solvated electron with solutes follows a similar pattern in these media to the pattern which holds in water, but limitations of solubility of inorganic compounds has meant that comparatively few inorganic reactions have been studied in organic media, and likewise a very considerable number of organic electron scavengers have been used in organic solvents. However, to give but one example of each of the types of non-dissociative and associative electron capture, it has been observed that metal ions will attach electrons with great facility, that alkyl halides liberate halide ions and form a free alkyl radical which can be isolated in the glassy matrix.

Polynuclear hydrocarbons, their derivatives and aromatic ketones have frequently been used as solutes and here there is clear evidence of electron attachment. For example, diphenyl (D) in aprotic liquids³⁷ and glasses³⁸ very readily forms the diphenyl anion D^- by the reaction (31). Very similar



behaviour is observed for benzophenone (BP). The more polar the aprotic rigid or liquid solvent the more likely is the molecular anion to be formed, but in non-polar media such as benzene, and to a less extent in cyclohexane, triplet states of the solutes may also be produced. In the protic solvents, such as the alcohols, the molecular anion has a very short life and rapidly reacts with the solvent to extract a proton from it [equation (32)].



The rate constants of reactions of this type have been measured by Arai and Dorfman³⁹, and generally lie in the range 10^4 to $10^5 \text{ M}^{-1} \text{ sec}^{-1}$ so that in these solvents $t_{1/2}$ for D^- is generally $< 1 \mu\text{sec}$. Protonation of the molecular anion occurs much more rapidly by reaction with the alkyloxonium ion, equation (33), rate constants greater than $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ generally being observed.



Entirely similar reactions are found in organic glasses, thus the radical $\dot{N}H$ (N = naphthalene) appears in methanolic glasses containing naphthalene^{17c}, and Hamill³⁸ has made extensive use of the scavenging power of arenes and halides to investigate the detailed chemistry of many organic glasses.

B. THE HYDROGEN ATOM

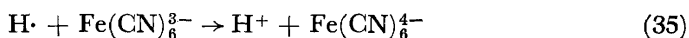
In the preceding section (A.2), considerable reference has been made to certain aspects of the chemistry of the hydrogen atom including methods of preparation, and its acid-base relationship to the electron. It follows from this

relationship that whenever an electron is generated in a glass which has a large concentration of proton donating groups, there is a high probability that when the electrons become thermalized they will react with these groups and form hydrogen atoms. This expectation is amply fulfilled and, indeed, the most convenient method of generating trapped hydrogen atoms is to γ -irradiate, at 77°K, aqueous glasses containing high concentrations (5 M–12 M) of mineral acids, such as sulphuric acid, phosphoric acid, hydrochloric acid, and perchloric acid. On rapid cooling of these water–acid mixtures, short chain polymers are formed either by hydrogen bonding, as in the case of HF and HClO₄, or polycondensation, as in the case of H₂SO₄ or H₃PO₄, when the polymeric anhydrides H(SO₃)_nOH and H(P₂O₅)_nOH are formed. The reaction for formation of these hydrogen atoms may then be written as equation (34), where HA_{gl} denotes an acid group at the end or along the chain⁴¹. The trapped hydrogen atoms may

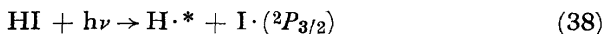


be recognized by their well-defined doublet e.s.r. spectrum, or, if fully deuterated glasses are used, by the characteristic triplet signal⁴¹.

A good deal of interest has centred on the reactivity of hydrogen atoms, and in *Figure 11* some values of the rate constants for reactions of this entity are given. In aqueous media, they undergo the expected reactions of reduction by (i) electron donation, e.g. equation (35), or (ii) addition to unsaturated compounds such as alkenes or aromatic systems to form well-characterized alkyl or cyclohexadienyl radicals, [equations (36) and (37)], which often have characteristic spectra



Hydrogen atoms may also exert an oxidative function, e.g. when they extract a hydrogen atom from CH bonds, as illustrated in equation (20). There is a good deal of evidence to suggest that the hydrogen atoms formed by irradiation of organic liquids and solids initially have high kinetic energy and are sometimes referred to as “hot” hydrogen atoms. Kupperman⁴² has recently devised a very elegant method for making mono-energetic “hot” hydrogen atoms. This is based on the fact that the photodissociation of hydrogen iodide, equation (38) is known to result in the formation of hydrogen atoms



and iodine atoms in their electronic ground states. Since these atoms cannot have vibrational or rotational energy, the difference between the energy of the incident quantum and the bond dissociation energy of hydrogen iodide must appear as kinetic energy of the two atoms partitioned according to Newton's laws, i.e. the kinetic energy of the “hot” hydrogen atom will be equal to $127(h\nu - D_{\text{HI}})/128$. By use of monochromatic light, it is therefore possible to study the rate at which hydrogen atoms of known kinetic energy react with molecules, and already the transition state theory of reaction (39)

has been tested and it has been shown that the threshold energy of the



hydrogen atom for reaction to occur is precisely that required by theory.

C. THE HYDROXYL RADICAL

The hydroxyl radical is the simplest diatomic radical, and in recent years a very great deal has been learnt about its chemistry.

1. Preparation

Hydroxyl radicals in useful concentrations were first prepared by Bonhoeffer, who passed an electrical discharge through gaseous mixtures of steam and oxygen, and observed the characteristic spectrum of the hydroxyl radical⁴³. From a detailed examination of these so-called "water" bands, Oldenberg⁴³ was able to identify hydroxyl radicals as products of various reactions both in the upper atmosphere and in the laboratory. Very recently, J. Polanyi⁴⁴, McKinley and his colleagues⁴⁵, have made use of this spectrum to determine vibrational and rotational temperatures of hydroxyl radicals emerging from reactions such as (40) and (41), and experiments of this kind

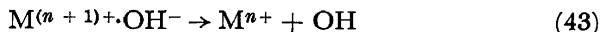


are giving new insights into the molecular dynamics of simple reactions.

One of the most convenient methods of preparing hydroxyl radicals is by direct photodissociation of hydrogen peroxide, [equation (42)], and numerous measurements, with various hydroxyl radical scavengers⁴⁶, have established that, for light of wavelength 2537 Å, for every pair of radicals formed

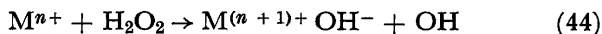


in the primary act in liquid water, about 0.9 escape the solvent cage. Another frequently used method in aqueous solutions is the photochemical electron transfer reaction (43). In the typical case of $\text{M}^{(n+1)+} = \text{Fe}^{3+}$, the number of



hydroxyl radicals escaping the aqueous cage, when 3130 Å light is used, is 0.17⁴⁷. This is a particularly useful reaction, because the rate of production of ferrous ions can be very simply related to the rate of formation of hydroxyl radicals.

Simple thermodynamic considerations suggest that powerfully oxidizing ions might spontaneously oxidize hydroxide ions, but in practice this method of thermal electron transfer has been very little used compared with the other type of reaction between reducing ions and hydrogen peroxide, the so-called Fenton reaction, [equation (44)]. This reaction has been extensively



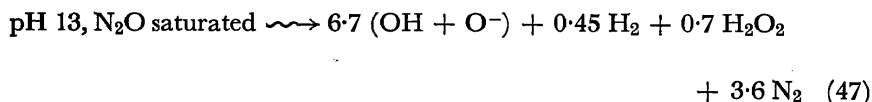
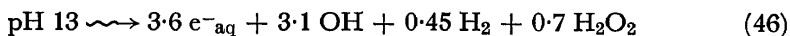
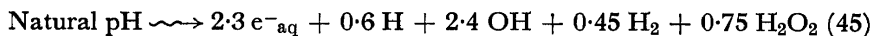
studied for the case where $\text{M} = \text{Fe}^{48}$, and has proved to be an unusually

THE SIMPLEST FREE RADICALS

convenient source of hydroxyl radicals used either for the initiation of polymerization⁴⁹, or for studying relative rates of reaction of the hydroxyl radical with two competing solutes⁵⁰.

The dissociation of water by light can also be used, but the longest possible wavelength is 1849 Å, so that the method is not very convenient, and it is better to generate the hydroxyl radicals from water by allowing ionizing radiation to fall on it. In the case of gamma-rays, the yields under three

γ-IRRADIATION OF DE-AERATED WATER



conditions are listed in equations (45), (46), and (47). The high efficiency of reaction (17) means that N₂O is a very useful reagent for converting electrons to hydroxyl radicals⁵¹.

2. Physical properties

Provided that the pH is less than 11 (see section 3 below) the hydroxyl radical remains undissociated. Consequently, the rates of its reactions with ions are unaffected by ionic strength⁵². The e.s.r. spectrum of hydroxyl radicals trapped in aqueous glasses has frequently been measured^{53, 17a}. Thus γ-irradiation of an alkaline glass gives a doublet attributed to the OH radical, a broad singlet attributed to the O⁻ radical (formed as described in section 3 below), and if D₂O is used instead of H₂O, the expected triplet is observed. The e.s.r. spectrum of the hydroxyl radical is not observed when acid glasses are irradiated, because the hydroxyl radical so formed readily oxidises the matrix, e.g. when 5.3 M sulphuric acid glass is irradiated, OH reacts with the sulphate groups to form a trapped³² sulphate radical $\cdot\text{SO}_4^-$.

The optical spectrum of hydroxyl radicals in the gas phase has a well-defined band system, from which the dissociation energy of the hydroxyl radical can be found to be 103.9 kcal. Continuous spectra attributed to the hydroxyl radical are found when ice⁵⁴ and alkaline glasses⁵⁵ are irradiated at liquid nitrogen temperatures (see *Figure 5a*), and pulse radiolysis of liquid water gives rise to a weak absorption beginning about 3000 Å and extending to shorter wavelength with increasing intensity⁵⁶. Whilst there can be little doubt that this absorption band is due to the hydroxyl radical it is not possible to get a precise value of the extinction coefficient. Thus, Thomas finds $G\epsilon = 900$ at 2600 Å and Brown *et al.* find $G\epsilon = 1120 \pm 260$ at 2750 Å⁵⁶.

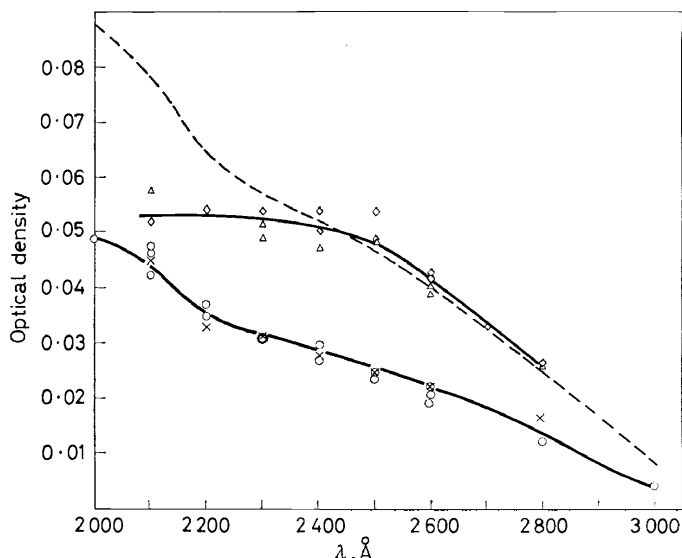


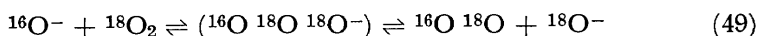
Figure 14. The absorption spectrum of the hydroxyl radical in water (Taken from Thomas *et al.*⁵⁶)

3. Acid-base relationships

Like the hydrogen atom, the hydroxyl radical can behave as a weak proton donor, [equation (48)]. This was first suggested by Gordon, Hart



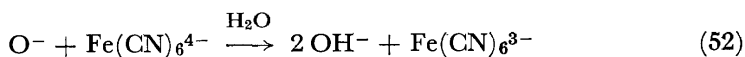
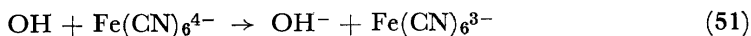
and Hutchison⁵⁷, who observed a very sharp increase in the rate of isotopic exchange between $^{18}\text{O}_2$ and light water, when the latter was γ -irradiated and the pH increased above 12. This was attributed to the high rate of reaction (49), made possible through the intermediate formation of a



hypothetical intermediate O_3^- as compared with the corresponding process $\text{HO} + \text{O}_2 \rightleftharpoons \text{HO}_3$ in which no exchange occurs. This hypothesis has since received full experimental verification. Further evidence for the existence of O^- came in 1962, when Schulte-Frohlinde and his colleagues were able to identify the broad singlet absorption band in γ -irradiated alkaline glasses (see Figure 6) as due to the O^- ion produced in reaction (50)^{17a}. Two years



later, Matheson and Rabani⁵⁸ used the pulse radiolysis technique to study the effect of pH on the rate constant for oxidation of ferrocyanide ion by hydroxyl radicals in the presence of scavengers such as N_2O , CCl_4 , H^+ or air to eliminate e^-_{aq} . They found that the rate diminished sharply and



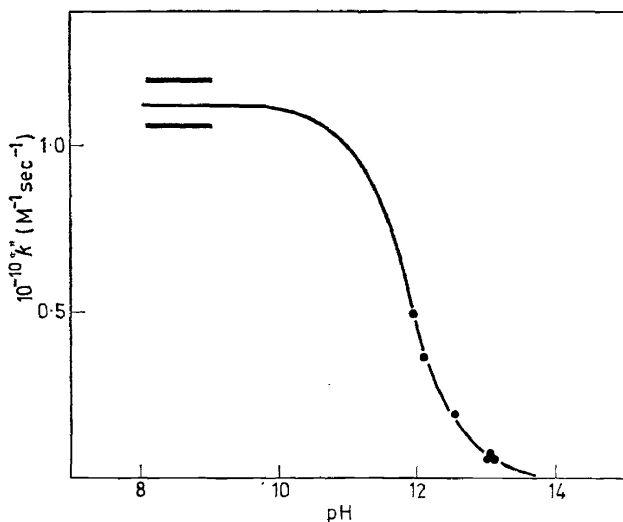
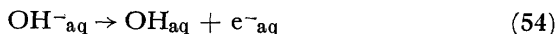
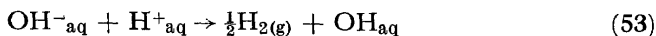
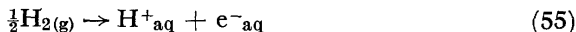


Figure 15. The dependence on pH of the apparent rate constant "k" of oxidation of ferrocyanide

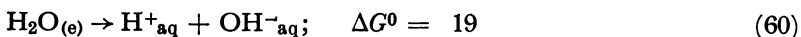
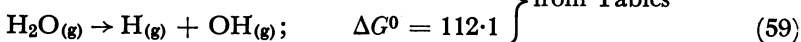
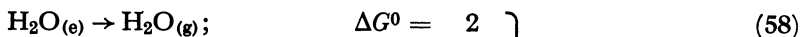
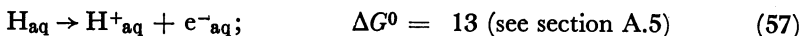
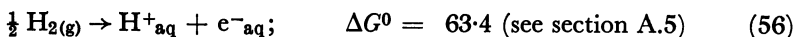
sigmoidally from a limiting value in neutral solution to another low limiting value at pH 13 (see Figure 15). From the value of the pH at the half-wave value, they calculated $pK = 11.9 \pm 0.2$. By similar experiments, but using thiocyanate ion and oxygenated solutions, Adams *et al.*⁵⁹ obtained a value of 11.9 ± 0.15 . The derived free energy values are $\Delta G_{48}^0 = 16$ and $\Delta G_{50}^0 = -3$ kcal. The standard oxidation potential of the hydroxyl radical in basic solution is obtained from the free energy of reaction (53), which may be



obtained in two ways. First there is Latimer's method⁶⁰, which is based on the tabulated standard free energies of formation of the hydroxyl radical (8.53 kcal) and the hydroxide ion in water (-37.6 kcal) and the assumption that the free energy change in dissolving a hydroxyl radical in water is negligible. Combining this with a free energy change for reaction (55)



which is conventionally regarded as zero, $\Delta G_{53}^0 = +46.1$ kcal, and hence the oxidation potential for the basic solution on the hydrogen scale is -2.0 V. Alternatively, the free energy change may be found from the actual free energy changes listed below, and assuming the free energy of the solution of the hydrogen atom and the hydroxyl radical are both zero. This leads to the value $\Delta G_{53}^0 = +44.6$, and an oxidation potential of -1.95 V in basic solution and therefore in one normal acid of -2.77 V. Evidently, the hydroxyl radical is just about as powerful an oxidant as the electron is a reductant.

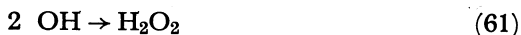


} from Tables

4. Measurement of the absolute rates of reaction of hydroxyl radicals

There are basically two ways of achieving this. The first is indirect, and relies upon the application of the diffusion theory of radiation chemical processes to the dependence of the yield of hydrogen peroxide formed by the combination of two hydroxyl radicals, on either dose-rate or on the concentration of some solute which reacts rapidly with hydroxyl radicals. This method will not be further elaborated here; suffice it to say that the results are in broad agreement with those obtained by the direct methods.

The most obvious direct method is to apply the techniques which have been used in determining the rates of reaction of the hydrated electron, but, as mentioned earlier, the hydroxyl radical absorbs light in the u.v. region and it, therefore, becomes difficult to measure the rate of reaction of the hydroxyl radical with chosen solutes, many of which also absorb in this region. Moreover, the extinction coefficient of the hydroxyl radical spectrum is not known with any high precision. Nevertheless, Thomas⁵⁶ has measured the rate of disappearance of the OH radical spectrum in N₂O-saturated water at 2600 Å. In neutral solution the early stages of the decay are almost entirely governed by the recombination of the hydroxyl radicals [equation (61)], whereas in acid solution the electrons are converted to hydrogen atoms

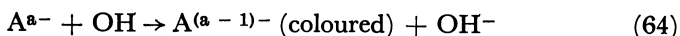


and two more processes, (62) and (63), also influence the rate of decay of the hydroxyl radicals. By this means Thomas found $k_{61} \simeq 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$



and, using the same method, Bradley has obtained a slightly lower value⁶¹.

A more widely applicable method of finding the rate constant for reactions of hydroxyl radicals is to use a solute designated A^{a-} which reacts with hydroxyl radicals, according to equation (64), to form an intensely coloured



product. Solutes of this kind include thiocyanate ion, carbonate ion, iodide ion, and selenate ion. The principle of the method is to have a sufficiently low concentration of this solute for a negligible amount of reaction to occur during the pulse, so that the build-up of the coloured product can be measured. It is easily shown that this should follow equation (65). Once

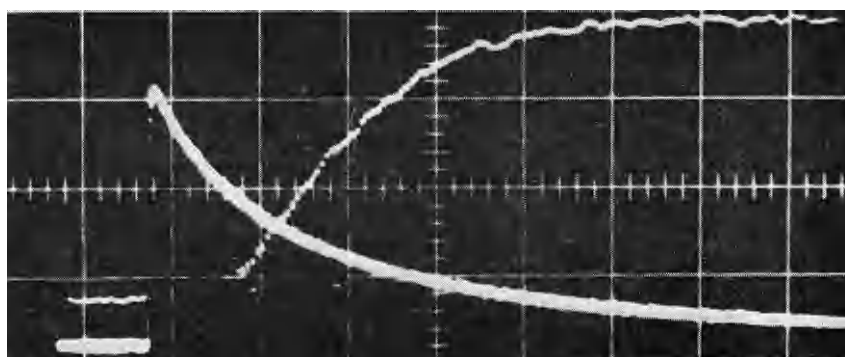


Figure 16. The growth of [SCN] after pulsing N_2O -saturated solutions 10^{-3}M KCNS solution at pH 13.5

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$$[A^{(a-1)-}]_t = [A^{(a-1)-}]_{t=\infty} \{1 - e^{-k_{64}t}\} \quad (65)$$

k_{64} has been determined further pulse experiments are carried out with solutions containing higher concentrations of both A^{a-} and the second competing solute, B, which reacts according to equation (66). When Pr_b



does not absorb in the same region as $A^{(a-1)-}$ the ratio of the optical density of the solution in the absence of the second solute, B, to the optical density when B is present, is plotted against the ratio of the concentrations of B to A^{a-} , a straight line should result, from the slope of which k_{66}/k_{64} , and hence the absolute value of k_{66} can be obtained. These methods have been used by Thomas⁵⁶ and Adams, Boag and Michael⁶². Examples of this method are illustrated in Figures 16 and 17.

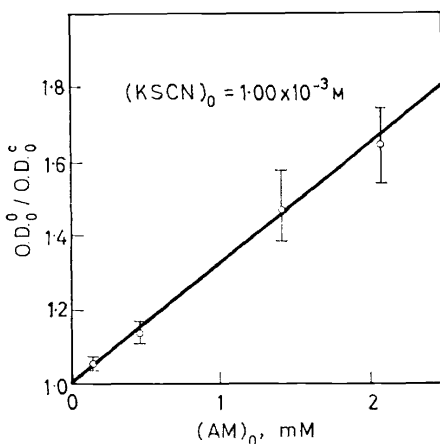
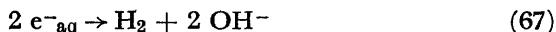


Figure 17. Competition between SCN^- and $CH_2:CH.CONH_2$ for OH

An extremely important reaction of the ionized hydroxyl radical is reaction (6), the rate constant of which was determined by Matheson and Rabani⁶³. These authors adjusted the hydrogen pressure in alkaline solutions (pH 13) to a value at which, just at the end of a pulse, the rate of formation of e^-_{aq} in reaction (6) is exactly balanced by its rate of destruction in reaction (67), i.e. $k_6[O^-]_0[H_2] = k_{67}[e^-_{aq}]^2$. In this way k_6 was found to be $1.6 \times 10^8 M^{-1} sec^{-1}$.



5. Comments on the reactions of OH and O^-

A very large number of rate constants of hydroxyl radicals have been measured by the pulse radiolysis technique, and a few have been measured by the flash photolysis method. In general, it is found that the reactions of hydroxyl radicals in water at room temperature are slightly more rapid than the reaction with the same reagent in the gas phase. Examples of this

are shown in *Table 3*. For the first two of these, the products from the aqueous reaction may differ from those in the gas reaction, for all of which

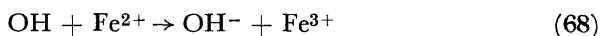
Table 3. Comparison of rate constants of OH radical reactions in gas and solutions

Reagents	GAS ^a			AQUEOUS	
	$k^{300^\circ\text{K}}$ ($\text{M}^{-1}\text{sec}^{-1}$)	$E(\text{kcal})$	Products	$k^{300^\circ\text{K}}$ ($\text{M}^{-1}\text{sec}^{-1}$)	Products
OH + OH	1.5×10^9	?	H ₂ O + O?	1.2×10^{10}	H ₂ O ₂
OH + CO	1.1×10^8	0.6	CO ₂ + H	4×10^8	COOH or CO ₂ + H
OH + H ₂	4×10^6	5.2	H ₂ O + H	4×10^7	H ₂ O + H

^a Taken from Dixon-Lewis, Wilson and Westenberg⁶⁴.

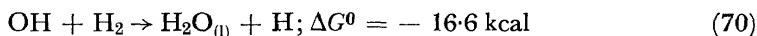
the process is a disproportionation. It is, therefore, not surprising that the combination of hydroxyl radicals and liquids should have a value which seems to be diffusion controlled, whereas the corresponding reaction in the gas phase, which probably involves bond breakage, is slower. It is less certain that comparable arguments may be applied to the second of these reactions.

Wherever comparisons are made between the ratio of the absolute rate constants as determined by pulse radiolysis and the same ratio obtained by competition under conditions where a steady state concentration of hydroxyl radicals prevails, the agreement is generally good, for example, the value of



k_6/k_{68} obtained by pulse radiolysis is 0.17 and that obtained by competitive experiments in which the hydroxyl radicals are generated by Fenton's reagent is 0.16⁵⁰.

The reaction of the ionized form of the hydroxyl radical with hydrogen is usually written in the form of equation (69), in which the products are a hydrogen atom and a hydroxide ion. An alternative formulation is that given in equation (6), in which the product is represented as the hydrated electron. There is a persuasive thermodynamic argument in favour of the latter formulation. From the free energies of formation of the hydroxyl radical, water and a hydrogen atom, we evaluate the free energy change for reaction (70). From the pK of the hydroxyl radical we obtain ΔG_{71} and from

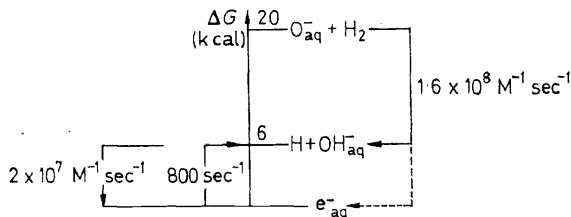


the ionic product of water ΔG_{72} , whence we may calculate $\Delta G_{69}^0 = -14$ kcal and combining this with $\Delta G_{73}^0 = -6.0$ kcal we see that the free energy



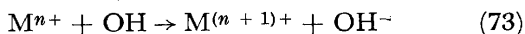
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relationship between the three "isomeric" species indicated in the diagram, together with the relevant rate constants. If we adopt the reasonable

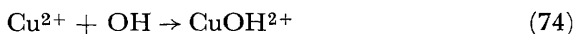


assumption that, because the decrease in free energy is larger if reaction (6) proceeds as written, rather than as written in equation (69), then we may also conclude that the rate constant for decomposition of the electron into O^- and H_2 , i.e. the reverse of reaction (6), is given by $k_{-6} \simeq 10^{-7} \text{ sec}^{-1}$.

Since the hydroxyl radical is such a powerful oxidant, it is possible to make easily cations of higher unstable valency states, the general type of reaction being given by equation (73). Thus $Ag(I)$ is readily oxidized to $Ag(II)$, $Mn(II)$ to $Mn(III)$, and $Cu(II)$ to $Cu(III)$, but in the last-named



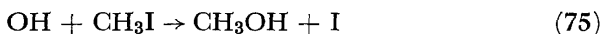
case, Baxendale and co-workers found that this is not so much an electron transfer oxidation as a combination of the cupric and hydroxyl radicals according to equation (74)⁶⁵. Anions may similarly undergo oxidation to



products which often possess very intense absorption spectra. The use of these for determining the absolute rates of hydroxyl radical reactions is mentioned in section C.4. It obviously also permits the study of the chemistry of the radicals which are produced, for example, the combination of thiocyanate radicals to form thiocyanogen. Many of these reactions proceed with high speed, and even take place freely in low temperature glasses, e.g. acid glasses containing either potassium chloride or potassium bromide on γ -irradiation give very clear evidence of the formation of the molecular anions Cl_2^- and Br_2^{--66} , the atomic precursors of which were surely Cl and Br (see *Figures 18 and 19*).

Hydroxyl radicals can, of course, oxidize by hydrogen atom abstraction. The absolute rates of these have been measured, and the controlling influences have been thoroughly discussed by Adams *et al.*⁵⁹. The rate constants are generally in the region of 10^8 to $10^9 \text{ M}^{-1} \text{ sec}^{-1}$, and appear to be able to take place with great ease even at liquid nitrogen temperatures.

A rather unusual metathetical reaction (75) has recently been discovered by Thomas⁶⁷. Radical displacement reactions are rather rare, and if this one should be verified it would be very interesting to see whether optical inversion of the carbon atom occurs during the reaction.



Very many addition reactions of the hydroxyl radical have been investigated. In nearly all of these, it behaves in a very similar manner to a halogen

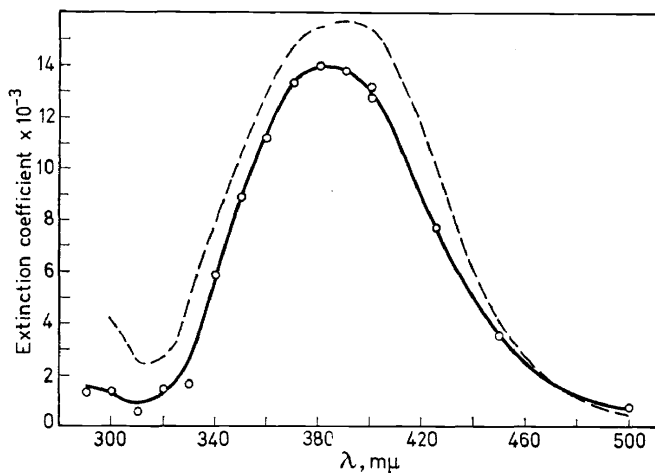


Figure 18. Spectra of I_2^- formed on pulse radiolysis of aqueous KI solution

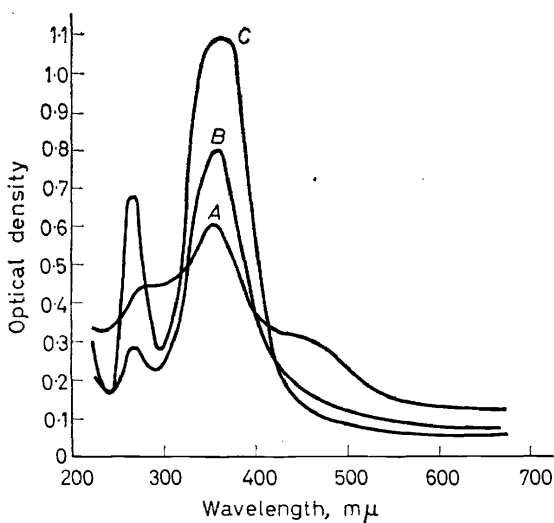
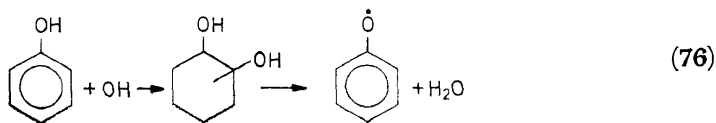


Figure 19. Absorption spectra produced in de-aerated 0.4 M NaBr, 5.4 M H_2SO_4 by γ -irradiation (1.14×10^{19} eV ml^{-1}) at 77°K. Curves A, B, and C are the absorptions at 77°, 132° and 143°K

atom; for example it reacts very rapidly with vinyl compounds to form substituted hydroxy-ethyl radicals, which are the initiating species for addition polymerization⁶⁸. The addition reactions to aromatic compounds have been particularly well studied. Dorfmann⁶⁹ shows that the hydroxyl radical first adds to the ring to form a hydroxycyclohexadienyl radical. If the aromatic ring already contains a hydroxyl radical then the ultimate reaction is one of oxidation, but it proceeds through an intermediate hydroxyl adduct, which, as later proved by Adams⁷⁰, then spontaneously dehydrates, as

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illustrated in equation (76). A further indication that the rate controlling



step is one of addition rather than bond breakage is shown by the fact that fully deuterated benzene reacts with hydroxyl radicals at the same rate as light benzene. Perhaps one of the most interesting reactions is that of addition of the basic form of the hydroxyl radical to the oxygen molecule to form species O_3^- (49). This reaction occurs very rapidly, and the ozonide ion has a very intense absorption at 4300 Å.

CONCLUSION

In this lecture I have concentrated on the simplest species which has free radical properties, i.e. the electron, the simplest monatomic free radical, and the simplest diatomic free radical. It is appropriate that these should have primacy of place in this Symposium, because they all react so very rapidly with a wide variety of molecules, in each case giving rise to new radicals of greater complexity. The recent explosive growth in our knowledge of the chemistry of these simple entities has been made possible principally by the development of more sophisticated techniques, (1) pulse radiolysis, (2) flash photolysis, (3) matrix isolation, and (4) electron spin resonance spectroscopy. By these means, much quantitative information about the structure and the reactivity of these species has become available, and many new questions have been raised, the answers to which are likely to have far-reaching consequences for physical, inorganic, organic and theoretical chemists alike.

In conclusion, I should like to acknowledge the very considerable debt to many students and colleagues who have tried to teach me more than I have been able to learn.

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