

Contributions of Pulse Radiolysis to Chemistry

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1 Introduction

The understanding of the primary chemical changes which occur when high-energy radiation (X - and γ -radiation, fast electrons, *etc.*) is absorbed in many pure liquids and gases is now fairly well developed, and the primary species which are responsible for the ultimate products are known for a variety of simple molecules, so much so that there is now much more activity in the use of these radiations to generate such species for chemical studies than in the effects of the radiation *per se*.

As with photochemistry there are two experimental approaches, *viz.* the continuous-irradiation or steady-state technique and the very short high-intensity pulsed-radiation technique. In this review we aim to give a broad account of how the latter has been applied in various areas of chemical research and has made valuable contributions. We shall be concerned with liquid-phase and a little with gas-phase systems and in almost all cases we shall be dealing with the chemistry of the solute in dilute liquid systems or as a minor component in a gas mixture. The reason for this is that most applications of the technique depend mainly on the reactions of the ions, atoms, free radicals, and excited states which are formed extremely rapidly on the absorption of the radiation. In a dilute mixture of two components such as a dilute solution, these species derive almost entirely from the major component, *i.e.* the solvent, since the radiation is absorbed by each component approximately in proportion to the mass fraction of the component. Hence, for example, in a 0.1 mol dm⁻³ solution composed of average-sized molecules the solvent will absorb about 99% of the incident energy and will provide about the same proportion of the primary reacting species which can react with the solute. Thus any chemical effects on the solute are produced indirectly. The primary species are themselves short-lived and their reactions frequently give short-lived products. The pulse radiolysis technique, which incorporates rapid monitoring methods, is used to follow both.

2 Primary Processes¹

Excitation and ionization (usually approximately equal amounts per unit of

¹ A more detailed treatment of the background radiation chemistry including the primary processes involved is to be found in (a) A. J. Swallow, 'Radiation Chemistry', Longmans Green, New York, 1973; (b) J. W. T. Spinks and R. J. Woods, 'An Introduction to Radiation Chemistry', 2nd Edn., Wiley, New York, 1976; and in the specialist articles in (c) 'Advances in Radiation Chemistry', ed. M. Burton and J. L. Magee, Wiley, New York, Vols. 1—6, 1959—1976.

energy absorbed) follow absorption of energy and for simple gaseous molecules the details of the ionization process can sometimes be found using high-pressure mass spectrometry and the total amounts of ions formed per unit of energy absorbed can be measured using ionization chambers. In general for γ - or fast-electron radiation 3–4 ion pairs are produced per 100 eV absorbed in gases, and to a first approximation this generally applies also to liquids but cannot always be assumed. Frequently these ions react with the parent molecules and the nature and rates of such reactions can often be established by mass spectrometry.

The approximate time-scale of the events which occur in an aqueous solution between the absorption process and the involvement of a minor component in chemical reaction is as follows:

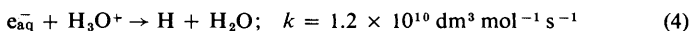
Ionization by photon	10^{-18} s
Excitation or ionization by fast electrons	10^{-16} – 10^{-15} s
Ion–molecule reactions with solvent	10^{-14} s
Electrons thermalized	10^{-13} s
Electrons and cations solvated	10^{-11} s
Chemical reactions by diffusion begin	10^{-10} s

The details of the chemically important final stages would be:



The major reactive species available for reaction with solutes are found to be OH and e^- which is rapidly solvated to e_{aq}^- . Minor amounts of H, H_2 , and H_2O_2 are also detectable at the early stages, the molecules being formed largely by dimerization of e_{aq}^- and/or H and of OH.

In acid solution e_{aq}^- rapidly gives H:



It is clearly essential to simplify a system by restricting reactions to those of H, OH, or e_{aq}^- only. Reactions of H atoms can be isolated by using acid solutions to remove e_{aq}^- quickly and adding t-butyl alcohol, which reacts with OH to give an unreactive butanol radical. The latter usually disappears by dimerization or dismutation. Reactions can be restricted to those of e_{aq}^- by using neutral solutions containing t-butyl alcohol. A small amount of H atoms remains but can usually be ignored or accounted for. If a solution saturated with N_2O is used e_{aq}^- is rapidly removed:



and OH reactions can be isolated.

Thus in irradiated aqueous systems there is available a very strong oxidizing species in the radical OH ($E^\circ = 1.9$ V), an equally potent reducing species in e_{aq}^- ($E^\circ = -2.9$ V), and H atoms, any one of which can be produced in nanoseconds using a pulsed electron beam and whose reactions with a large variety of organic

and inorganic solutes have been studied on time-scales of this order. The elucidation of processes involved at initial and subsequent stages is facilitated by a knowledge of the initial concentration of the primary species. These can be calculated from the energy input per electron pulse and the yield per unit energy, usually expressed by the symbol G , or sometimes g , which indicates the number of species per 100 eV absorbed. Thus in neutral water $G(\text{OH}) = 2.7$ radicals per 100 eV $G(\text{H}) = 0.55$, and $G(e_{\text{aq}}^-) = 2.7$.

The processes described above for water have analogies in other polar liquids and it may be generally stated that in liquids with a moderately high static dielectric constant the products of initial ionization exhibit separate chemical existence. With low dielectric constant liquids, however, ion recombination is usually very rapid and although added solutes do show evidence of electron-capture or charge-transfer processes with primary ions observed ion-yields are lower than in water, and need much higher solute concentrations for complete scavenging. Nevertheless the pulse radiolysis technique is a very convenient way of generating and following the reactivities of molecular cations and anions in, for example, a hydrocarbon liquid.

In the case of liquid aromatics (benzene, toluene, *etc.*) initial ion recombination leads to the formation of molecular excited states of the solvent in high yield. These serve as convenient sensitizers for production and observation of solute excited states.

The transfer of charge to a particular solute from primary ions, or excitation from primary excited solvent states, is governed, where thermodynamically feasible, only by the solute concentration. It is therefore possible, for example, to populate one solute anionic species and observe electron transfer to another low-concentration solute of higher electron affinity. In this way pulse radiolysis studies allow observation of the approach to equilibrium in electron-charge or energy-transfer reactions.

3 Experimental Methods²

A. Radiation Sources.—Although pulsed X-ray sources have been used, because of the higher deposition energies possible, the most common and convenient sources are pulsed electron accelerators. Three types are in current use, *viz.* Van de Graaff, microwave, and Febetron field emission machines. The time range over which investigations are possible is determined by the shortest pulse duration available which can deposit sufficient energy to produce measurable changes in a system. All these machines can be designed to deliver usable pulses of a few nanoseconds and in the particular case of the microwave linear accelerator (LINAC), because such pulses have a microstructure corresponding to the microwave

² Fuller descriptions of machines and pulse radiolysis techniques are given in (a) M. S. Matheson and L. M. Dorfman, 'Pulse Radiolysis', M.I.T. Press, Cambridge, Mass., and London, 1959; (b) L. M. Dorfman, 'Investigations of Rates and Mechanisms of Reactions, Part II', in 'Techniques of Chemistry' VI Series, ed. A. Weissberger, Wiley-Interscience, New York, 1974; and in articles in (c) ed. G. E. Adams, E. M. Fielden, and B. D. Michael, 'Fast Processes in Radiation Chemistry and Biology', Wiley, Bristol, 1975.

frequency, pulses of tens of picoseconds duration are available. Energy input per pulse, and therefore product concentration, is determined by the electron-beam current and the effective acceleration voltage. Van de Graaff machines commonly operate at 2 MeV and 2 A, LINACs at 4—12 MeV and 2—12 A, and the Febetron field emission machine at 2 MeV and up to several thousand A, although at a longer pulse length of *ca.* 30 ns. Energies much lower than 2 MeV become inconvenient since the electrons are not absorbed uniformly in liquids or solids over an appreciable depth of material. This introduces problems into the optical monitoring process and can complicate kinetic analysis owing to lack of homogeneity in the distribution of species.

Usually the machine output is chosen so that a single pulse gives $1\text{--}10 \times 10^{-5}$ mol dm⁻³ products, the particular value being chosen to suit the aims of the experiment and the monitoring equipment being used.

B. Detection and Measurement of Species Produced.—The three principal techniques used to investigate the species and reactions which occur following the absorption of an electron pulse are optical spectroscopy (emission and absorption), conductivity, and electron spin resonance. Of these, optical absorption spectrometry is by far the commonest. The optical detectors in current use for fast monitoring cover the wavelength range from 3 to 0.2 μm . Photomultipliers are used from 0.2 to 0.8 μm , silicon photodiodes from 0.4 to 1.0 μm , germanium diodes from 0.7 to 1.5 μm and an indium arsenide diode from 1 to 3 μm . Apart from the last of these, the response time of these detectors with their associated amplifiers can be as low as a few nanoseconds.³ The signal/noise characteristics of the solid-state detectors are such that meaningful measurements can be made on absorption signals as low as 0.1 % absorption even though the signal decays in tens of nanoseconds. For measurements in the picosecond time range special and ingenious experimental arrangements have been devised which do not require the use of exceptionally fast detectors.⁴

Conductivity is used in two areas. One is the study of the kinetics of reactions and mobility characteristics of the ions—electrons and cations—produced in hydrocarbon systems. The other is in aqueous systems where, in addition, the ionization characteristics of transient species are followed. In the former a straightforward d.c. method is used in which potentials up to several kV are applied to a simple conductivity cell and the current changes which follow the absorption of an electron pulse are monitored. In hydrocarbons, where electrons have mobilities up to 10^5 times as great as in water, this is a very fast and sensitive monitoring system which can be used to follow the behaviour of *ca.* 10^{-8} M electrons on nanosecond time-scales.⁵ In aqueous systems the background conductivity and problems associated with polarization have led to the use of the a.c. bridge. The time response is therefore limited but response times approaching 0.1 μs have

³ J. H. Baxendale, C. Bell, and J. Mayer, *Internat. J. Radiat. Phys. Chem.*, 1974, **6**, 117.

⁴ J. W. Hunt, *Adv. Radiat. Chem.*, 1976, **5**, 185.

⁵ J. H. Baxendale, J. P. Keene, and E. J. Rasburn, *J.C.S. Faraday I*, 1974, **70**, 718.

been attained and micromolar concentration changes can be followed.⁶ Another approach to conductivity measurements has been the use of microwave absorption.⁷ A recent development has been the application of time-resolved polarography^{8,9} to investigate the transient species produced following electron absorption. In this way information on the oxidation-reduction properties of free radicals, transient ions, *etc.* has been documented.

A technique designed to observe degradation in macromolecular systems utilizing changes in intensity of scattered light as a consequence of electron-beam irradiation has been described.⁹ The time dependence of chain fission and fragment separation has been followed with this technique both for synthetic polymers⁹ and for DNA solutions.¹⁰

The signals generated in the detection circuits described above are displayed and recorded either with a fast oscilloscope plus Polaroid camera combination or, more recently, using a digital signal analyser which converts the analogue waveform into a set of amplitude-time co-ordinates which can be directly read into an on-line computer for analysis.

In addition to the long-standing application of e.s.r. in the identification of very long-lived free radicals produced in solids or in frozen liquid systems at liquid nitrogen temperatures, it is now possible to apply the technique to transient species having lifetimes greater than a few microseconds.¹¹ Using repetitive pulsing and sweeping the field incrementally, spectra of the species can be built up, and in addition by observing a signal at a fixed field concentration changes can be followed with time. This technique has the obvious advantage of being able, in general, to identify positively the free radicals observed.

4 Inorganic Chemical Reactions and Species

In inorganic chemistry the technique of pulse radiolysis has been applied mainly to aqueous systems and in particular to oxidation and reduction reactions. As outlined above the species produced in neutral water by high-energy radiation are OH and e_{aq}^- in about equal amounts together with a smaller amount of H atoms and hydrogen peroxide. Figure 1 shows a composite absorption spectrum of the transient species formed in aerated water. In acid solutions e_{aq}^- is rapidly transformed into H by reaction with H_{aq}^+ . Reactions of OH, e_{aq}^- , and H with a wide variety of inorganic solutes have given information on reaction rates, new reactions, and previously unknown species. Many of the latter have been characterized by their optical absorption spectra, lifetimes, and e.s.r. spectra and some can now be seen to be intermediates in reactions previously investigated by less incisive techniques.

⁶ K.-D. Asmus, ref. 2c, p. 40.

⁷ P. R. Infelta, M. P. de Hass, and J. M. Warman, *Internat. J. Radiat. Phys. Chem.*, in press.

⁸ (a) A. Henglein, *Electroanalyt. Chem.*, 1975, 9, 163; (b) M. Grätzel, K. M. Bansal, and A. Henglein, in 'Radiation Research: Biomedical Chemical and Physical Perspectives', ed. O. F. Nygaard, H. I. Adler, and W. K. Sinclair, Academic Press, New York, 1975, p. 493.

⁹ G. Beck, J. Kiwi, D. Lindenau, and W. Schnabel, *European Polymer J.*, 1974, 10, 1069.

¹⁰ D. Lindeman, U. Hagen, and W. Schnabel, *Z. Naturforsch.*, 1976, 31c, 484.

¹¹ R. W. Fessenden, ref. 2c, p. 60.

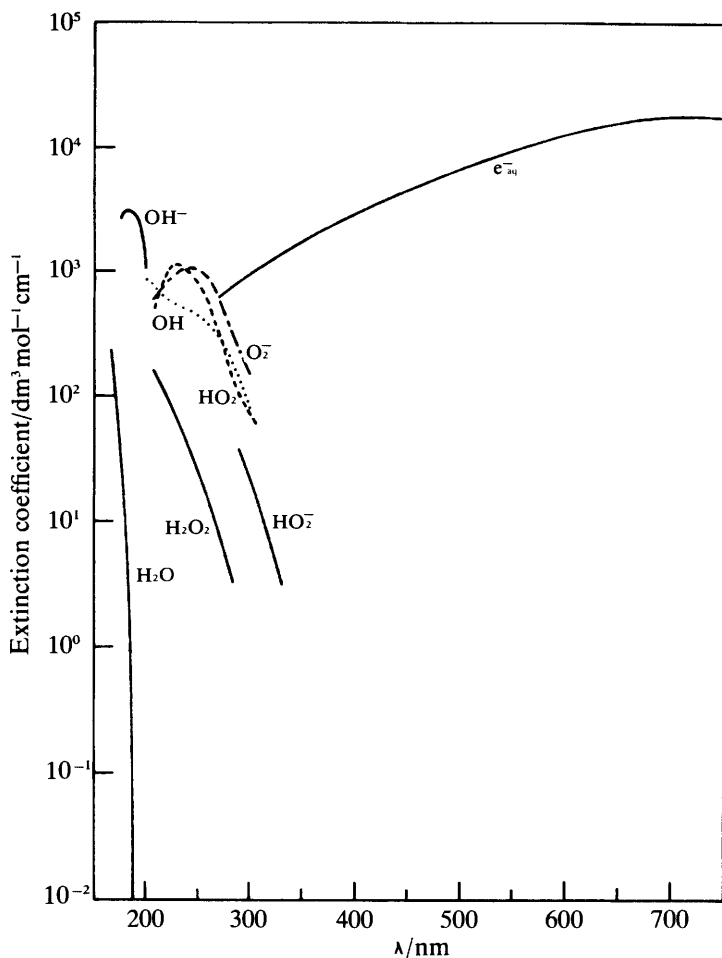


Figure 1 Absorption spectra of the species involved in water radiolysis

(Reproduced by permission from 'Pulse Radiolysis', ed. M. S. Matheson and L. M. Dorfman, M.I.T. Press, Cambridge, Mass., and London, 1959)

A. Reactions of OH.¹²—This is a well established species whose existence in aqueous solution was deduced many years ago from the behaviour of systems containing hydrogen peroxide and whose reactions have been studied using Fenton's reagent or photolytic techniques. The more powerful pulse radiolysis technique has considerably extended this field. The OH radical itself can be observed in absorption ($\lambda_{\max} = 230$ nm), as can its ionized form O^- ($\lambda_{\max} = 240$

¹² L. M. Dorfman and G. E. Adams, 'Reactivity of the Hydroxyl Radical in Aqueous Solution', *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, 1973, Vol. 46.

nm). For the ionization $pK_a = 11.9$ at 298 K and the heat of ionization is 40 kJ mol⁻¹. Both species are very reactive in electron or hydrogen abstraction reactions but in general O⁻ is less effective than OH, owing, no doubt, to its lower electron affinity.¹²

(i) *Metal ions.* The oxidation of most simple aquated metal ions whose next higher valency states are stable have been followed,¹³ e.g. Fe²⁺, Co²⁺, Ag⁺, Mn²⁺, Ce³⁺, Eu²⁺, and Sm²⁺. Oxidation of Cu²⁺ to the much less stable Cu^{III} has also been observed,¹⁴ and the acid-base equilibria involving [CuOH]²⁺, [Cu(OH)₂]⁺, and Cu(OH)₃ have been identified by spectral and conductivity measurements.¹⁵ Ions such as Tl⁺ and Cr³⁺ requiring two or more equivalents to produce the next stable state give transient intermediate states Tl^{II} and Cr^{IV} which decay by dismutation to the upper and lower states.¹⁶

All these reactions occur with rate constants ca. 10⁸ dm³ mol⁻¹ s⁻¹.

(ii) *Metal ion co-ordination complexes.* Oxidation to the next higher state almost invariably occurs by outer-sphere electron transfer, giving a product which may be stable, e.g. [Fe(CN)₆]³⁻ or [Ag(NH₃)₂]²⁺, or unstable to various degrees. In the latter case the subsequent reaction is frequently dismutation again, as with¹⁷ the transient [Ru(NH₃)₆]⁴⁺, various Ni^{III} ammine complexes, and [Pt(en)₃]³⁺. Sometimes the higher state is not stable with the ligand configuration of the lower state, so that ligand loss or rearrangement rapidly follows the oxidation step. This apparently occurs¹⁸ when [Au(CN)₂]⁻ is oxidized to the Au^{II} state and [PtCl₄]²⁻ to the Pt^{III} state and is very obvious when the stable [Ru(NH₃)₅(N₂)]²⁺ is oxidized to [Ru(NH₃)₅(N₂)]³⁺. Here the Ru^{III} state decays over about 10 ms, the dinitrogen ligand being replaced by OH⁻.

An alternative reaction path to electron transfer from the metal to OH is the reaction of OH with a ligand. A typical example is benzoatopenta-ammine-Co^{III}, which gives an intermediate formed by the addition of OH to the benzoate ring—a reaction which also occurs with benzoate itself.¹⁹ Following the addition, the intermediate apparently may react either in a second-order dismutation step to give presumably new Co^{III} complexes which have oxidized and reduced benzoate ligands or undergo intramolecular electron transfer to the metal to give a Co^{II}

¹³ (a) G. G. Jayson, B. J. Parsons, and A. J. Swallow, *J.C.S. Faraday I*, 1973, **68**, 2053; (b) G. V. Buxton, R. M. Sellers, and D. R. McCracken, *ibid.*, 1976, **72**, 1464; (c) J. Pukies, W. Roebke, and A. Henglein, *Ber. Bunsengesellschaft phys. Chem.*, 1968, **72**, 842; (d) D. M. Brown, F. S. Dainton, D. C. Walker, and J. P. Keene, 'Pulse Radiolysis', Academic Press, London, 1965, p. 221; (e) J. C. Muller, C. Ferradini, and J. Pucheault, *J. Chim. phys.*, 1966, **63**, 232; (f) A. K. Pikaev, G. K. Sibirskaya, and V. F. Spitsyn, *Doklady Phys. Chem.*, 1973, **209**, 339.

¹⁴ J. H. Baxendale, E. M. Fielden, and J. P. Keene, ref. 13d, p. 217.

¹⁵ (a) D. C. Barker and P. Fowles, *Trans. Faraday Soc.*, 1970, **66**, 1661; (b) D. Meyerstein, *Inorg. Chem.*, 1971, **10**, 638.

¹⁶ (a) B. Cercek, M. Ebert, and A. J. Swallow, *J. Chem. Soc. (A)*, 1966, 612; (b) J. Barrett and J. H. Baxendale, unpublished results.

¹⁷ (a) J. H. Baxendale, M. A. J. Rodgers, and M. D. Ward, *J. Chem. Soc. (A)*, 1970, 1246; (b) J. Lati and D. Meyerstein, *Inorg. Chem.*, 1972, **11**, 2393, 2397; (c) D. K. Storer, W. L. Waltz, J. C. Brodovitch, and R. L. Eager, *Internat. J. Radiat. Phys. Chem.*, 1975, **7**, 693.

¹⁸ (a) A. S. Ghosh-Mazumdar and E. J. Hart, *Adv. Chem. Ser.*, 1968, No. 81, p. 193; (b) G. E. Adams, R. K. Broszkiewicz, and B. D. Michael, *Trans. Faraday Soc.*, 1968, **64**, 1256.

¹⁹ M. Z. Hoffman and M. Simic, *J. Amer. Chem. Soc.*, 1970, **91**, 5533.

complex with an oxidized benzoate ligand. This rapidly dissociates to Co^{2+} and free ligands. Aliphatic ligands with abstractable hydrogens may also be attacked, as are ethylenediamine complexes of Cu^{II} and other metals.²⁰ The subsequent reactions here lead to the deamination of ethylenediamine.

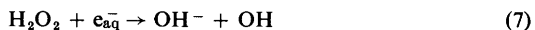
(iii) *Non-metallic anions.* Oxidation of NO_2^- , N_3^- , AsO_2^- , and SeO_3^{2-} by OH occur readily, but unexpected oxidations which have been shown to occur are those of SO_4^{2-} , HCO_3^- , and CO_3^{2-} , which by simple electron transfer¹² give SO_4^- , HCO_3 , and CO_3^- . These transient species absorb in the visible and have themselves been studied as oxidizing radicals with a range of potency.²¹ Halide-ion oxidations have been shown to produce the species Cl_2^- , Br_2^- , and I_2^- which were observed previously using flash photolysis, but the more recent pulse radiolysis work has shown that they are formed through intermediates of the type ClOH^- . The analogous products from CNS⁻ oxidation,²² $(\text{CNS})_2^-$ and SCNOH^- , had not been observed previously, nor had mixed ions²³ of the type ICNS^- . All exist in equilibrium with the free radical and ion, and equilibrium constants have been determined for most of them.

The reaction of the ionized form O^- with O_2 ,



has proved a very convenient way of producing the ozonide ion for studies of its stability and reactivity.²⁴ The corresponding reaction of OH is not known.

B. Reactions of Hydrated Electrons.²⁵—These may give three types of product, *viz.* anions by addition, *e.g.* to oxygen to give O_2^- , free radicals by a bond-scission reaction as with hydrogen peroxide,



or lower oxidation states as in the reactions of many metal ions (including Np and Pu ions) and their co-ordination complexes. Most interesting of the latter are the many transient aquated oxidation states made observable for the first time.²⁶

(i) *Metal ions.* Reactions having diffusion-controlled rate constants occur with the fairly easily reducible ions such as Ag^+ , Cr^{3+} , or Cu^{2+} . A detailed study of the reduction of Ag^+ to Ag^0 has shown that the latter subsequently gives Ag_2^+ , Ag_3^+ , and Ag_2 as intermediates in a reaction sequence leading to the formation of colloidal silver.²⁷ Ti^+ also gives²⁸ Ti^0 , which with Ti^+ gives Ti_2^+ . Electron

²⁰ D. Meyerstein, *Inorg. Chem.*, 1971, **10**, 2244.

²¹ P. Neta, V. Madhavan, J. Zemel, and R. W. Fessenden, *J. Amer. Chem. Soc.*, 1977, **99**, 163.

²² D. Behar, P. L. T. Bevan, and G. Scholes, *J. Phys. Chem.*, 1972, **76**, 1537.

²³ M. Schonshofer and A. Henglein, *Ber. Bunsengesellschaft phys. Chem.*, 1970, **74**, 393.

²⁴ B. H. J. Bielski and J. M. Gebicki, *Adv. Radiat. Chem.*, 1970, **2**, 177.

²⁵ (a) M. Anbar, *Adv. Chem. Ser.*, 1965, No. 50, p. 55; (b) M. Anbar, *Adv. Phys. Org. Chem.*, 1969, **7**, 115; (c) M. Anbar, M. Bambenek, and A. B. Ross, 'Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution: 1, Hydrated Electron', Nat. Stand. Ref. Data Ser. Nat. Bur. Stand., 1973, Vol. 43, and Supplement, 1975.

²⁶ J. H. Baxendale, E. M. Fielden, and J. P. Keene, *Proc. Roy. Soc.*, 1965, **A286**, 320.

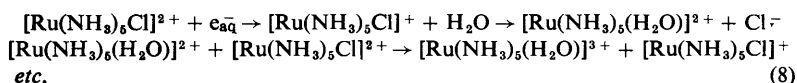
²⁷ J. Pukies, W. Roebke, and A. Henglein, *Ber. Bunsengesellschaft phys. Chem.*, 1968, **72**, 842.

²⁸ B. Cercek, M. Ebert, and A. J. Swallow, *J. Chem. Soc. (A)*, 1966, 612.

reduction is a very convenient way of preparing Cu^+ and Cr^{2+} . In the former case it has been used²⁹ to study the formation of Cu^+ complexes with acrylamide, maleic acid, and fumaric acid, and in the latter³⁰ the reaction of Cr^{2+} with oxygen, where an intermediate CrO_2^+ was observed and characterized.

Electron reduction can be used to give the aquated forms of unstable lower oxidation states of many metals which cannot be made using conventional reduction methods. These are short-lived species but can be prepared and investigated by pulse radiolysis. The univalent Co^+ , Mn^+ , Zn^+ , Cd^+ , and Pb^+ were the first to be observed²⁶ and have received most attention, but Cr^+ , Tm^{2+} , and Sm^{2+} have also been characterized^{31,32} spectroscopically and most of the other lanthanides have been shown to give the bivalent ion. The above univalent ions all absorb strongly in the near u.v. and this has been used to compare reactivities and follow their reactions with a variety of oxidants.^{33,13b} In these it is found, for example, that M^+ forms complexes with olefins and free radicals, gives MO_2^+ with oxygen, and $\text{MO}^+ + \text{N}_2$ with N_2O .

(ii) *Metal ion co-ordination complexes.* When these compounds react with e_{aq}^- they almost invariably do so at diffusion-controlled rates.²⁵ The immediate products, which are very often the lower oxidation state of the metal, may be stable, as with $[\text{Fe}(\text{CN})_6]^{3-} \rightarrow [\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Ru}(\text{NH}_3)_6]^{3+} \rightarrow [\text{Ru}(\text{NH}_3)_6]^{2+}$, but frequently have only transient existence. Their reactions to the final stable state have been followed in a variety of cases and have revealed some interesting reactions. The simplest perhaps is that of e_{aq}^- -reduced $[\text{Ru}(\text{dipy})_3]^{3+}$. The corresponding Ru^{II} complex is produced in an excited state which undergoes a fluorescent transition to the ground state³⁴ and is the same species as has been formed and investigated photochemically. The unstable $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^+$ formed from the corresponding Ru^{III} compound initiates a chain reaction^{17a} involving the latter which leads to its complete transformation into $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$:



Many complexes simply shed the ligands from the reduced metal as in the case of the multitude of Co^{II} amines which have been investigated.²⁵ An interesting development here is that the rate at which some of the ligands are lost can be measured using the conductivity technique.³⁵ Thus from $[\text{Co}(\text{NH}_3)_6]^{2+}$ three NH_3 ligands are lost too rapidly to be measured, but the rest come off with rate constants 6×10^4 , 1×10^4 , and $1.5 \times 10^3 \text{ s}^{-1}$. $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$, one of the first dinitrogen complexes to be prepared, is stable in solution but e_{aq}^- readily reduces it to Ru^{I} . The latter dismutates to the original Ru^{II} and Ru^0 , which rapidly

²⁹ D. Meyerstein, *Inorg. Chem.*, 1975, 14, 1716.

³⁰ R. M. Sellars and M. G. Simic, *J. Amer. Chem. Soc.*, 1976, 98, 6145.

³¹ H. Cohen and D. Meyerstein, *J.C.S. Dalton*, 1974, 2559.

³² M. Faraggi and Y. Tendler, *J. Chem. Phys.*, 1972, 56, 3287.

³³ D. Meyerstein and W. A. Mulac, *Inorg. Chem.*, 1970, 9, 1762.

³⁴ J. E. Martin, E. J. Hart, A. W. Adamson, H. Gaffney, and J. Halpern, *J. Amer. Chem. Soc.*, 1972, 94, 9238.

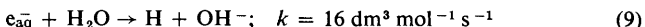
³⁵ M. Simic and J. Lilie, *J. Amer. Chem. Soc.*, 1974, 96, 291.

loses its ligands.³⁶ $[\text{Ni}(\text{CN})_4]^{2-}$ gives $[\text{Ni}(\text{CN})_4]^{3-}$, which after losing CN^- dimerizes³⁷ to the stable $[\text{Ni}_2(\text{CN})_6]^{4-}$.

Compounds with aromatic ligands present another possibility, *viz.* the addition of e_{aq}^- to the ligand prior to ultimate intramolecular transfer to the metal. This occurs with Co^{III} and Cr^{III} trisbipyridyls³⁸ and with nitrobenzoatopentammine Co^{III} .³⁹ Such reactions provide useful background information on intramolecular electron transfer which is useful in the interpretation of electron-transfer reactions in general.

Some biological metal complexes, *e.g.* Fe-cytochromes and haemoglobins, have also been investigated and although there are discrepancies between the observations from different laboratories it would appear that intramolecular electron transfer and slow conformational changes can be seen following the initial e_{aq}^- reaction.⁴⁰

(iii) *Non-metallic compounds.* In aqueous solutions an important reaction of e_{aq}^- is with the solvent,



which determines the maximum lifetimes of e_{aq}^- in the absence of other reactions.⁴¹ It is also important in conjunction with the reverse reaction, whose rate constant is also known, as a basis for calculating thermodynamic parameters for e_{aq}^- .⁴²

Simple addition of e_{aq}^- occurs with O_2 and CO_2 . The former reaction to give O_2^- (and HO_2 at lower pH) has proved a very convenient source of HO_2 for study by pulse radiolysis. Its acid-base properties ($\text{p}K_{\text{a}} = 4.5$), heat of ionization, and spectral characteristics have been measured and its reactivity investigated with a variety of compounds.²⁴ It is of interest biologically since specific enzymes, superoxide dismutases, exist to catalyse its decomposition to $\text{O}_2 + \text{H}_2\text{O}_2$, which is normally rather slow. These dismutases are Cu-, Fe-, and Mn-containing compounds. Pulse radiolysis studies have shown that they react by being alternately oxidized and reduced by O_2^- in cycles of reactions involving the metal in two or more oxidation states.⁴³

The ion CO_2^- although also readily prepared by electron addition to CO_2 is more conveniently produced by the oxidation of formate ion with OH. It absorbs in the u.v.⁴⁴ and has had many applications as a reducing agent, in which role it

³⁶ J. H. Baxendale and Q. G. Mulazzani, *J. Inorg. Nuclear Chem.*, 1971, **33**, 823.

³⁷ Q. G. Mulazzani, M. D. Ward, G. Semerano, S. S. Emmi, and P. Giordani, *Internat. J. Radiat. Phys. Chem.*, 1974, **6**, 187.

³⁸ (a) J. H. Baxendale and M. Fiti, *J.C.S. Dalton*, 1972, 1995; (b) M. Z. Hoffman and M. Simic, *J.C.S. Chem. Comm.*, 1973, 640; (c) M. Z. Hoffman and M. Simic, *J. Amer. Chem. Soc.*, 1972, **94**, 1757.

³⁹ M. G. Simic, M. Z. Hoffman, and N. V. Brezniak, *J. Amer. Chem. Soc.*, 1977, **99**, 2166.

⁴⁰ (a) A. Shafferman and G. Stein, *Biochim. Biophys. Acta*, 1975, **416**, 287; (b) E. J. Land and A. J. Swallow, *Biochem. J.*, 1976, **157**, 781.

⁴¹ E. J. Hart, S. Gordon, and E. M. Fielden, *J. Phys. Chem.*, 1966, **70**, 150.

⁴² (a) J. H. Baxendale, *Radiat. Res. Suppl.*, 1964, **4**, 139; (b) *ref. 1a*.

⁴³ (a) E. M. Fielden, P. B. Roberts, R. C. Bray, D. J. Lowe, G. N. Mautner, G. Rotilio, and L. Calabrese, *Biochem. J.*, 1974, **139**, 49; (b) M. Pick, J. Rabani, F. Yost, and I. Fridovich, *J. Amer. Chem. Soc.*, 1974, **96**, 7239.

⁴⁴ J. P. Keene, Y. Raef, and A. J. Swallow, *ref. 13d*, p. 99.

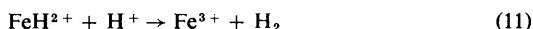
is not as potent as e_{aq}^- but is sufficiently so to reduce Cd^{2+} and, for example, $[Ni(CN)_4]^{2-}$ to $[Ni(CN)_4]^{3-}$ among many other complex ions.³⁷

Reaction of N_2O is the most commonly used of the bond-fission reductions brought about by e_{aq}^- because it is a source of OH. In the same way $S_2O_8^{2-}$ and other peroxy ions react $S_2O_8^{2-} + e_{aq}^- \rightarrow SO_4^- + SO_4^{2-}$ and have been used to study SO_4^- and analogous species.²⁷

C. Reactions of Hydrogen Atoms.—The hydrogen atom is much less reactive than e_{aq}^- which probably accounts for the less extensive attention paid to its reactions. Although like e_{aq}^- it reduces metal ions²⁸ such as Ce^{IV} , Tl^+ , and Cu^{2+} it cannot produce the univalent species from Co^{2+} , Ni^{2+} , Mn^{2+} , Cd^{2+} , and Pb^{2+} nor is it capable of reducing complex ions such as the cobalt(III) ammines. However, an interesting series of reactions uncovered using pulse radiolysis involves its behaviour as an oxidizing agent towards certain reducing ions such as Fe^{2+} , Cr^{2+} , and Ti^{III} .⁴⁵ Here the overall reaction is



but intermediate hydrides such as FeH^{2+} have been detected through their absorption spectra and these presumably react



$[Ni(CN)_4]^{2-}$, which is reduced to $[Ni(CN)_4]^{3-}$ by e_{aq}^- , gives $H[Ni(CN)_4]^{2-}$ with H, which then by a bimolecular reaction gives the original product and H_2 .³⁷

5 Electrons in Liquids⁴⁶

The suggestion that solutions of 'free' or 'excess' electrons could be prepared in some liquids is almost as old as the first observation of electrons in the gas phase.⁴⁷ The study of alkali-metal-ammonia solutions on which the suggestion was based did not progress very quickly beyond the work of Kraus until magnetic susceptibility measurements⁴⁸ established beyond doubt that, when dilute, these were indeed fairly stable solutions of electrons and metal ions. However, even now examples of this type of system are limited to a few alkali and alkaline earth metals in ammonia, some amines, and a few ethers. A recent review testifies to the current interest in this field.⁴⁹

By definition, ionizing radiation produces free electrons in all liquids but in most cases, unlike the ammonia systems, recombination with the concomitant cations or reaction with the liquid itself makes their existence transient. Only in

⁴⁵ G. G. Jayson, J. P. Keene, D. A. Stirling, and A. J. Swallow, *Trans. Faraday Soc.*, 1969, **65**, 2453.

⁴⁶ (a) 'Solvated Electron', ed. R. F. Gould, *Adv. Chem. Ser.*, 1965, No. 50; (b) E. J. Hart and M. Anbar, 'The Hydrated Electron', Wiley-Interscience, New York, 1970; (c) W. F. Schmidt, 'Electron Migration in Liquids and Glasses', Hahn-Meitner Institute, HMI-B156, 1974; (d) M. S. Matheson, 'Physical Chemistry', Vol. 7 'Reaction in Condensed Phases', ed. H. Eyring, Academic Press, New York, 473, 1975; (e) F. S. Dainton, *Chem. Soc. Rev.*, 1975, **4**, 323.

⁴⁷ C. A. Kraus, *J. Amer. Chem. Soc.*, 1908, **30**, 1323.

⁴⁸ S. Freed and N. Sugarman, *J. Chem. Phys.*, 1943, **354**, 11.

⁴⁹ M. C. R. Symons, *Chem. Soc. Rev.*, 1976, **5**, 537.

1958 was good evidence produced, in the form of specific chemical reactions, for their presence and importance in aqueous systems. Since 1962, when the pulse radiolysis technique was introduced, it has been possible to observe them by optical absorption and conductivity in a wide variety of liquids.

Pulse radiolysis studies have shown that in pure polar liquids, such as water and alcohols, the optimum electron lifetime is determined by its rate of reaction with the solvent, and that this varies from tens of milliseconds in water to a few microseconds in alcohols.⁵⁰ In aliphatic hydrocarbons, which are inert to electrons, the lifetime depends on the electron concentration since it is governed by the rate of recombination with the concomitant cation. However, it also varies considerably with the hydrocarbon, since electron diffusion (or mobility) is strongly influenced by the liquid structure.⁴⁶ Thus in n-hexane the ion recombination rate constant is *ca.* $5 \times 10^{13} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at room temperature and in iso-octane it is $5 \times 10^{15} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, so that to persist for several hundred nanoseconds concentrations must be kept below *ca.* $10^{-7} \text{ mol dm}^{-3}$ in n-hexane and *ca.* $10^{-9} \text{ mol dm}^{-3}$ in iso-octane.

The study of electrons in liquids by pulse radiolysis has been mainly in the areas of chemical reactions and optical properties, although measurements of mobilities in various liquids have also received attention.⁴⁶

(i) *Chemical reactions of electrons.* Not surprisingly aqueous systems have received most attention and a compilation²⁵ of reaction rate constants lists more than 600 compounds which have been studied. A much smaller collection of similar data on reactions in alcohols is also available.⁵¹ These reactions are easy to follow optically since, in polar media, electron absorption is high at wavelengths which are readily monitored, *e.g.* $[\epsilon_{\text{aq}}^-] = 1.06 \times 10^3 \text{ mol m}^{-2}$ at 578 nm. Also diffusion coefficients, *e.g.* $5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ in water, are not much greater than those of normal ions, so that even when reacting at diffusion-controlled rates ($k \approx 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) reaction times can be arranged to be in the range of microseconds.

Reactions are of two types, *viz.* simple electron additions to solutes and additions with bond scission.²⁵ Examples of both of these in inorganic systems have been given above. With organic solutes additions occur to ketones, quinones, aromatic hydrocarbons and substituted derivatives, and nitro-compounds. They give the corresponding anions—ketyl, semiquinone, *etc.*—whose spectral properties and subsequent reaction behaviour have usually been reported. Addition with bond scission invariably occurs with aliphatic halides to give the halide anion and the organic free radical. This is a very convenient method of preparation of the latter for subsequent investigation. Diperoxides, mercaptans, and alcohols react in this way, giving respectively the oxyradical and oxyanion, the hydrosulphide anion and hydrogen atom, and the oxyanion and hydrogen atom. Disulphides, important in biological systems, react analogously to diperoxides.

In polar solvents these reactions almost invariably have rates which are of the

⁵⁰ J. H. Baxendale and P. Wardman, *Chem. Comm.*, 1971, 429.

⁵¹ 'Selected Specific Rates of Reaction of the Solvated Electron in Alcohols', *Nat. Stand. Ref. Data Series, Nat. Bur. Stand.*, 1972, Vol. 42.

order expected for diffusion-controlled processes as calculated from the diffusion coefficients. Many of the latter have been determined from conductivity changes following pulse radiolysis.⁵² The rate constants are found to follow the Debye equation when charged solutes are involved, and also the Brønsted-Bjerrum application of the Debye-Hückel equation to such reactions when they occur in the presence of inert electrolytes.

In water the reaction with the solvent and its reverse, which can be observed by pulse radiolysis in alkaline solution, *viz.*



have been used to calculate⁴² the equilibrium constant for the above system, and hence the solvation energy of the electron in water (1.7 V) and the E° for e_{aq}^- (-2.9 V). The potent reducing capacity consequent upon the latter has already been referred to above.

Reactions of electrons in hydrocarbons are technically more difficult to follow optically since lifetimes are short at concentrations which are measurable and absorptions are only appreciable beyond 1000 nm. Liquids in which electron mobilities are low offer the best opportunity and some rates have been obtained in n-hexane using this technique.⁵³ Those in other hydrocarbons have been measured using conductivity.⁴⁶ The results reveal a range of very high rate constants from *ca.* $10^{12} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in n-hexane to *ca.* 10^{14} in tetramethylsilane. Electron mobilities, μ_e , are correspondingly high but for a particular solute in different hydrocarbons the rate constants do not change as would be expected from the changes in mobility.⁵⁴ Thus for n-hexane, iso-octane, and neopentane μ_e is 0.09, 7, and $7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively, whereas for reaction with SF_6 the rate constants are 2×10^{12} , 5.8×10^{13} , and $2.1 \times 10^{14} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, *i.e.* a smaller range than for μ_e . In some cases, *e.g.* $\text{C}_2\text{H}_5\text{Br}$, the rate constants actually pass through a maximum along the series.

The reason for this behaviour is not yet completely understood but an important factor appears to be V_0 , the electron binding energy of the liquid, or in other words the energy required to eject an electron into a vacuum from the liquid. V_0 has been determined for many hydrocarbons and may be positive or negative. In the above series the values are +0.04, -0.18, and -0.4 V respectively.⁵⁵

(ii) *Spectral characteristics of electrons in liquids.* The strong optical absorption of electrons in liquids in the red or near infrared has provided a convenient method of observing them, but in addition the absorption itself has been the subject of much theoretical work aimed at understanding the state of electrons in liquids.⁴⁶ Absorption spectra in a range of liquids—water, ammonia, alcohols, amines, ethers, hexamethylphosphoramide, and hydrocarbons—have been obtained.⁴⁶ They are all very broad: *e.g.* in water the band half-width is about 200 nm, and $\lambda_{\text{max}} = 700 \text{ nm}$. In general λ_{max} moves to longer wavelengths (see Figure 2) with

⁵² (a) G. C. Barker, D. Fowles, D. C. Salmon, and B. Stringer, *Trans. Faraday Soc.*, 1970, **66**, 1498; (b) G. C. Barker and P. Fowles, *ibid.*, p. 1661; (c) K.-D. Asmus, *ref. 2c*, p. 40.

⁵³ J. H. Baxendale and E. J. Rasburn, *J.C.S. Faraday I*, 1974, **70**, 705.

⁵⁴ A. O. Allen, T. E. Gangwer, and R. A. Holroyd, *J. Phys. Chem.*, 1975, **79**, 25.

⁵⁵ R. A. Holroyd and M. Allen, *J. Chem. Phys.*, 1971, **54**, 5014.

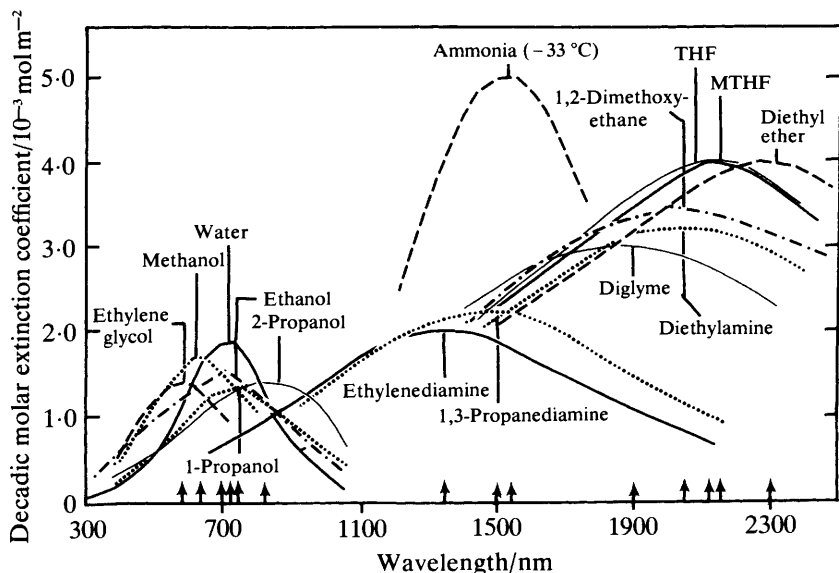


Figure 2 Transient absorption spectra of solvated electrons in liquids of varying polarity (Reproduced by permission from L. M. Dorfman, 'Investigations of Rates and Mechanisms of Reactions, Part II', in 'Techniques of Chemistry' VI Series, ed. A. Weissberger, Wiley-Interscience, New York, 1974)

decreasing solvent polarity although there are exceptions to this. The energy of λ_{\max} is generally assumed to be a measure of the depth of the potential well formed by the oriented solvent molecules. Theoretical treatments of the geometry and energy of such trapping and the optical transitions possible have been partially successful⁴⁶ in the case of water and ammonia, but an understanding of the large bandwidths of the absorptions is still lacking.

The solvated electron system has also provided a means by which the solvation process itself may be observed and quantified using the pulse radiolysis technique. This possibility was first demonstrated in liquid alcohols at low temperatures,⁵⁶ where spectra due to solvated electrons were found to take time to develop to the usual broad absorption with a maximum in the red. Immediately (*i.e.* nanoseconds) after production in the liquids, the electron absorptions are much further into the i.r., with maxima beyond 2000 nm. The spectral changes with time are attributed to the transformation of the electron environment from a random distribution of polar molecules to an oriented configuration of the molecular dipoles, brought about by the field of the electron. This change from a shallow to a deeper potential well causes the spectrum to shift towards the blue. The time-scales for this process have been related to those for solvent relaxation obtained

⁵⁶ J. H. Baxendale and P. Wardman, *J.C.S. Faraday I*, 1973, **69**, 586.

from dispersion measurements, and with the extension of the observations to room temperature using picosecond methods⁵⁷ a comparison can now be made over a large temperature range.

An analogous use of differences in absorption spectra between polar and non-polar environments has been used to indicate the molecular structure of mixtures such as alcohols and hydrocarbons. Spectral and conductivity measurements support the ideas of clusters of the polar component and can give an idea of their size.⁵⁸

Interestingly, no absorption spectra due to trapped or solvated electrons in aromatic liquids have been reported although observations over the range 300–1600 nm have been made. Since the yield of escaped electrons in, *e.g.*, benzene is not much lower than in *n*-hexane where transient spectra have been clearly observed,⁵³ their non-appearance must be due to lower extinction coefficients in the observation region. Pulse radiolysis studies on electrons in benzene and toluene have been performed⁵⁹ using conductivity detection. Kinetic parameters and mobilities resemble those in hexane.

6 Solution Chemistry of Radical Ions

At some time after ejection and thermalization, an electron may encounter a substrate having favourable cross-section for capture to occur:



or

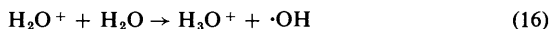


Many chemical substances act as acceptors of electrons, ranging from O₂, H₃O⁺, and hydrated transition-metal ions through carbonyls, aromatic hydrocarbons, quinones, and nitro-compounds to metal complexes and biological macromolecules.

Meanwhile the positive species, if stable towards fragmentation and the ion-molecule reaction with a neighbour, can relax to a solvated parent cation and undergo charge-transfer reactions with added solutes having lower ionization potential:



Substances which commonly react in this way are condensed-ring aromatic hydrocarbons, amines, and inorganic ions which are easily oxidized (*e.g.* I⁻ or SCN⁻). In some liquids (H₂O and aliphatic alcohols) the product of the ion-molecule reaction also has strong oxidizing properties:



⁵⁷ N. J. Chase and J. W. Hunt, *J. Phys. Chem.*, 1975, **79**, 2835.

⁵⁸ (a) J. H. Baxendale and P. H. G. Sharpe, *Chem. Phys. Letters*, 1976, **41**, 440; (b) J. H. Baxendale, *Canad. J. Chem.*, 1977, **55**, 1996.

⁵⁹ A. J. Robinson and M. A. J. Rodgers, *J.C.S. Faraday I*, 1975, **70**, 378.

These processes, which can be made to occur within the duration of the electron pulse, allow the production of oxidized or reduced species whose properties with respect to reaction with other added substances can be studied.

In the remainder of this section we detail some investigations which have used the pulse radiolysis technique to good effect in this way.

A. Radical Anions in Organic Liquids.—The study of the chemistry of radical anions of aromatic hydrocarbons has been pursued actively over the past twenty years.⁶⁰ These stable but reactive species are produced when the appropriate molecule is added to a solution of an alkali metal in an ether or other inert solvent.



This technique has been used extensively but suffers from the disadvantage that the alkali-metal cation produced concomitantly modifies the properties of the anion.⁶¹ Using electron capture in a pulse radiolysis experiment, however, an 'infinite-dilution' anion is formed, the properties of which can be monitored by time-resolved absorption spectrophotometry.⁶²

In this way electron-transfer equilibria,



have been studied⁶³ for a variety of donor-acceptor pairs. The data have been examined⁶³ by the Marcus theory of electron transfer with good results in a number of cases.

The kinetics of cation-anion associative pairing has also been studied by pulse radiolysis.⁶⁴ Capture of solvated electrons by benzophenone in solution in tetrahydrofuran or dioxan in the presence of added alkali-metal ions (as tetraphenylboronate salts) was used to give initially free ketyl radical anions which subsequently equilibrated with the cations present to form a population of ion pairs. Differences between the absorption spectra of the ion pairs and the free ions⁶⁵ were followed as a function of time ($< 1 \mu\text{s}$) after the free ketyl ions were produced. The rate constant for the forward step in the equilibrium



was found to be close to the diffusion limit.

There has been a recent awakening of interest in measuring the relaxation of solvent molecules around charge centres in an attempt to understand more fully the microscopic nature of the liquid state. Although pulse radiolytically produced electrons have most widely been used (see above), a recent study⁶⁶ showed that

⁶⁰ N. Hirota, in 'Radical Ions', ed. E. J. Kaiser and L. Kevan, Wiley, New York, 1963, p. 35.

⁶¹ M. Szwarc, in 'Carbanions, Living Polymers and Electron Transfer Processes', Wiley-Interscience, New York, 1968.

⁶² S. Arai and L. M. Dorfman, *J. Chem. Phys.*, 1964, **41**, 2190.

⁶³ J. R. Brandon and L. M. Dorfman, *J. Chem. Phys.*, 1970, **53**, 3849.

⁶⁴ D. Beaumont and M. A. J. Rodgers, *Trans. Faraday Soc.*, 1969, **65**, 2973.

⁶⁵ D. G. Powell and E. Warhurst, *Trans. Faraday Soc.*, 1962, **58**, 953.

⁶⁶ S. Arai, M. Hoshino, and M. Imamura, *J. Phys. Chem.*, 1975, **79**, 702.

the ketyl radical anions of acetophenone, benzophenone, and some derivatives undergo analogous spectral shifts due to solvation. The time dependence of such shifts was measured and showed two relaxation stages which were interpreted as being due to a rapid formation of a primary solvent shell followed by a slower outer-shell formation.

B. Radical Cations in Organic Liquids.—Although less extensively studied than radical anions, the cations formed by charge transfer from solvent positive ions to, *e.g.*, aromatic hydrocarbons have received some attention. For example, studies on the charge-transfer process between solvent cation and aromatic acceptor (*e.g.* biphenyl or pyrene) in dichloroethane⁶⁷ acetone,⁶⁸ and cyclohexane⁶⁹ show bimolecular rate constants in excess of those calculated from the Debye theory. The differences are most marked for pyrene in cyclohexane⁶⁹ and constitute evidence of movement of positive holes throughout bulk liquid by a resonance charge migration in addition to molecular diffusion.

As with radical anions, so cations can undergo charge exchange with molecules of lower ionization potential. Absolute rate constants for biphenyl to pyrene, biphenyl to *p*-terphenyl, and *p*-terphenyl to anthracene have been obtained⁶⁷ and shown to be diffusion-controlled. No evidence for back reactions was obtained.

A further example of the importance of charge-exchange studies is provided in recent work⁷⁰ in which the transfer of positive charge between chlorophyll-*a* and carotenoid pigments has been the subject of a pulse radiolysis investigation. A primary reaction in photosynthesis is thought to be loss of an electron by a chlorophyll-containing centre on photoexcitation, followed by a neutralization of the chlorophyll cation by charge transfer to a carotenoid auxiliary. It was found⁷⁰ that in a homogeneous liquid only charge transfer in the *reverse* direction can occur. Recently the radical cations and anions of several carotenoid pigments were generated and characterized using the pulse radiolysis technique.⁷¹ The wavelength maxima were found to be linearly dependent on the number of conjugated double bonds, in general agreement with a theoretical description using Hückel and PPP techniques.

An interesting property of aromatic radical cations is their tendency to add a neutral molecule to build up a sandwich-type dimer species, analogous to excimer formation by excited states of the same molecules, *e.g.*



This phenomenon was first observed⁷² in glassy matrices subjected to γ -radiolysis followed by slight softening. Such studies provided spectroscopic

⁶⁷ N. E. Shank and L. M. Dorfman, *J. Chem. Phys.*, 1970, **52**, 4441.

⁶⁸ M. A. J. Rodgers, *J.C.S. Faraday I*, 1972, **68**, 1278.

⁶⁹ E. Zador, J. M. Warman, and A. Hummel, *Chem. Phys. Letters*, 1973, **23**, 363.

⁷⁰ J. Lafferty, E. J. Land, and T. G. Truscott, *J.C.S. Chem. Comm.*, 1976, 70.

⁷¹ J. Lafferty, A. C. Roach, R. S. Sinclair, T. G. Truscott, and E. J. Land, *J.C.S. Faraday I*, 1977, **73**, 416.

⁷² B. Badger, B. Brocklehurst, and R. D. Russell, *Chem. Phys. Letters*, 1967, **1**, 122.

characteristics of dimer cations. Kinetic data for the monomer–dimer equilibrium have been obtained from pulse radiolysis experiments⁷³ in which the decay of the monomer cation and formation of dimer cation were monitored using absorption spectrometry with nanosecond time resolution. Thermodynamic data were obtained from temperature studies of these processes⁷⁴ which led to a binding energy of the pyrene dimer cation $\Delta H = -40 \text{ kJ mol}^{-1}$ with an overall entropy change of $\Delta S = 88 \text{ J K}^{-1} \text{ mol}^{-1}$, both values very similar to those for the pyrene excimer. For naphthalene and 2,6-dimethylnaphthalene, however, the binding energies obtained^{74a} were approximately one half of the corresponding excimer values ($\Delta H = -25 \text{ kJ mol}^{-1}$). For these same radical ions the entropy change in the dimerization step was close to $\Delta S = 8 \text{ J K}^{-1} \text{ mol}^{-1}$, indicating an overall gain in entropy on dimerization, presumably accounted for by a change in solvent ordering in the neighbourhood of the charge centre.

C. Electron Transfer Equilibria and Redox Potentials.—The transfer of a single electron from one molecular species to another in a consecutive reaction sequence is connected to the respiratory metabolism of glucose in mitochondria and the release of stored energy. The species involved in this respiratory chain are flavoproteins, cytochromes, NAD, and oxygen and in order to obtain a complete understanding of the mechanisms involved, quantitative details of the oxidation–reduction behaviour of the various molecular stages must be determined. Conventional polarographic techniques for the measurement of single electron redox data usually are inapplicable to biologically relevant media because of the short lifetimes of the radicals involved, which create irreversibilities. The pulse radiolysis technique has recently been put to effective use for overcoming such problems by allowing a quantity of a singly reduced substrate to be produced rapidly in aqueous phase by reaction with hydrated electrons:



Subsequently X^- comes to equilibrium with a second electron acceptor (A) present in lower concentration:



The time required for attainment of equilibrium depends on the individual rate constants and the acceptor concentration but is typically complete in $100 \mu\text{s}$. Then if the radicals X^- and A^- are stable for only milliseconds and their optical absorptions are sufficiently well separated for unambiguous measurement of equilibrium concentrations, the equilibrium constant for the transfer process can be determined and thence the one-electron redox potential of one of the couples, if the other is known.

This technique was used for measuring the potentials of several quinone–

⁷³ (a) M. A. J. Rodgers, *Chem. Phys. Letters*, 1971, **9**, 107; (b) A. Kira, S. Arai, and M. Imamura, *J. Chem. Phys.*, 1971, **54**, 489.

⁷⁴ (a) M. A. J. Rodgers, *J.C.S. Faraday I*, 1972, **68**, 1278; (b) S. Arai, A. Kira, and M. Imamura, *J. Chem. Phys.*, 1972, **56**, 1777.

semiquinone systems, the O_2/O_2^- couple,⁷⁵ and nitro-aromatic and nitro-heterocyclic single-electron potentials⁷⁶ against duroquinone and 9,10-anthroquinone 2-sulphonate standards. Parallel measurements of the spin densities on the nitro-groups of the radical anions using *in situ* radiolysis–e.s.r. found a linear correlation between spin density and redox potential in spite of wide structural variations. This technique has similarly been applied to determining the one-electron reduction potential of riboflavin⁷⁷ as a function of pH. Values ranging from $E_h = -0.24$ V at pH 5.9 to $E_h = -0.46$ V at pH 11.9 were found; the pH dependence followed the curve calculated from known pK_a values of riboflavin and its semi-reduced form. Recently, Marcus theory has been applied⁷⁸ to the rate constants of the forward and reverse reactions, resulting in good agreement between experimental and theoretical values. An exhaustive series of nitro-imidazole couples have been studied using the pulse radiolysis method⁷⁹ in an attempt to demonstrate that the one-electron potential determines the efficiency of such molecules in sensitizing hypoxic mammalian cells (cells having oxygen levels below physiological requirement) to ionizing radiation.

Recently, transient absorption spectra and lifetimes (several μ s) of carbonium ions, *e.g.* $PhCH_2^+$, Ph_2CH^+ , and Ph_3C^+ have been determined in halogenocarbon solvents.⁸⁰ Rate constants for reaction with halide ions and tertiary amines were measured and found to approach the diffusion limit.

7 Chemistry of Excited Molecules

Although the properties of electronically excited molecules are generally studied using photoexcitation techniques, several situations exist where such methods are less useful than pulse radiolysis. Such investigations have served to supplement the photoexcitation studies and have contributed new fundamental knowledge to all aspects of excited-state chemistry. In this section we have made a selection of topics for brief exposition to highlight the wide-ranging use of the technique.

A. Monomer Singlet States.—In certain cases, high-energy excitation will produce fluorescent molecular states not readily produced by the conventional spark sources of fluorometry. For example, the kinetic properties of fluorescent states of cyclohexane and other aliphatic hydrocarbons were monitored by following the decay of electron-pulse-induced emission at 260 nm.⁸¹ This fluorescence is thought to arise from a radiative transition from a $\sigma^*-\sigma$ state populated either by direct excitation or rapid charge recombination.

Similarly a fluorescent state of the cyclic ether dioxan was first reported⁸² in a

⁷⁵ D. Meisel and G. Czapski, *J. Phys. Chem.*, 1975, **79**, 1503.

⁷⁶ D. Meisel and P. Neta, *J. Amer. Chem. Soc.*, 1975, **97**, 5198.

⁷⁷ D. Meisel and P. Neta, *J. Phys. Chem.*, 1975, **79**, 2459.

⁷⁸ D. Meisel, *Chem. Phys. Letters*, 1975, **34**, 263.

⁷⁹ P. Wardman and E. Clarke, *J.C.S. Faraday I*, 1976, **72**, 1379.

⁸⁰ (a) R. L. Jones and L. M. Dorfman, *J. Amer. Chem. Soc.*, 1974, **96**, 5715; (b) J. R. Suidak, R. L. Jones, and L. M. Dorfman, *ibid.*, 1976, **98**, 4875.

⁸¹ J. H. Baxendale and J. Mayer, *Chem. Phys. Letters*, 1972, **17**, 458.

⁸² J. H. Baxendale, D. Beaumont, and M. A. J. Rodgers, *Chem. Phys. Letters*, 1969, **4**, 3.

pulse radiolysis study. The spectrum showed a maximum at 280 nm and the time constant for fluorescence was *ca.* 2 ns.

B. Excited Dimer States.—The large bulk of knowledge on excimers and exciplexes has been accumulated⁸³ from photostimulated fluorescence studies which allow the kinetic properties of the dimeric species to be characterized. The spectroscopic properties of such species as derived from fluorescence measurements are restricted to those states involved in radiative process, ${}^1D_1 \rightarrow {}^1D_0$. Kinetic absorption spectrophotometry, using pulse radiolysis, allows the ${}^1D_1 \rightarrow {}^1D_n$ electronic transitions to be observed, thereby supplying experimental support for the calculations of theoretical spectroscopists.

The first excimer absorption spectrum obtained was that of benzene in a pulse radiolysis experiment.⁸⁴ This showed a broad absorption band with $\lambda_{\max} = 520$ nm which was attributed⁸⁵ to the $B_{1g} \rightarrow E_{1u}$ excimer transition which was calculated to have the appropriate energy at an interplanar separation of 0.33 nm.⁸⁶

Transient absorption spectra measurements become increasingly important in studies of weakly or non-fluorescent species. The anthracene excimer is especially relevant: the S_1 state of anthracene is subject to encounter-controlled, ground-state quenching to yield a photodimer bonded between the 9- and 10-positions:



Clearly this reaction should proceed *via* an excimer state which, by analogy with excimers of other aromatic hydrocarbons,⁸³ would exist as a weakly bound 'sandwich' structure with the two 9- and 10-positions opposite each other. Unlike other excimers, however, no fluorescence from an anthracene species had been observed in fluid medium, presumably because the relaxation to photodimer occurred too rapidly. This was shown to be the case in pulse radiolysis experiments⁸⁷ on anthracene in benzene in which anthracene (S_1) was populated by diffusion-controlled energy transfer from benzene (S_1) under conditions where ground-state quenching was marked. A new species absorbing in the near i.r. ($\lambda_{\max} = 1200$ nm) was observed which had kinetic properties consistent with anthracene excimer. Other condensed-ring aromatic hydrocarbons have excimer absorption spectra in the near i.r. in agreement with calculations.⁸⁸ The lifetime of the anthracene excimer in benzene was less than 2 ns,⁸⁷ as expected if facile σ -bond formation followed.

C. Triplet States.—The measurement of the activity parameters of molecular excited triplet states necessitates the monitoring of $T_1 \rightarrow T_n$ absorptions since the

⁸³ J. B. Birks, 'Photophysics of Aromatic Molecules', Wiley-Interscience, London, 1970.

⁸⁴ (a) R. Cooper and J. K. Thomas, *J. Chem. Phys.*, 1968, **48**, 5097; (b) J. K. Thomas and I. Mani, *ibid.*, 1969, **51**, 1834.

⁸⁵ J. B. Birks, *Chem. Phys. Letters*, 1968, **1**, 625.

⁸⁶ M. T. Vala, I. H. Hillier, S. A. Rice, and J. Jortner, *J. Chem. Phys.*, 1967, **44**, 23.

⁸⁷ M. A. J. Rodgers, *Chem. Phys. Letters*, 1972, **12**, 612.

⁸⁸ M. F. M. Post, J. Langelaar, and J. D. W. van Woorst, *Chem. Phys. Letters*, 1976, **42**, 133.

$T_1 \rightarrow S_0$ transition, being spectroscopically forbidden, usually restricts phosphorescence measurements to rigid phases where diffusion, and therefore reaction, is obviated. Flash photolysis and pulse radiolysis excitations are both useful in this context. Which technique is better depends upon certain criteria which have to be met:

(i) The exciting flash must be able to populate a sufficient concentration of S_1 (depends on extinction coefficients of ground state and lamp/laser output spectrum). Further, intersystem crossing must effectively populate sufficient T_1 states.

(ii) If not, a sensitizer having a triplet state of sufficient energy to participate in an energy-transfer reaction with the molecule in question must be found which can satisfy criterion (i).

The pulse radiolysis technique largely over-rides these considerations in that energy is deposited initially in the solvent phase, becoming very rapidly localized in a solute *via* energy-transfer or ion-recombination processes.

The utility of the method is best shown by the work characterizing the triplet states of biologically active molecules such as carotenes and visual pigments,⁸⁹ porphyrins,⁹⁰ and isoprenoid benzoquinones⁹¹ in addition to a number of simple aromatics.⁹²

Any systematic study of excited-state molecules requires measurement of the quantum efficiencies of the various decay modes open to molecules in an upper level. To measure intersystem crossing, $S_1 \rightarrow T_1$, it is necessary to count the triplets formed, which in an absorption experiment requires knowledge of the T_1-T_n extinction coefficients (ϵ_{T-T}). An extremely useful method for determining such data has been developed.⁹³ An energy-transfer technique is used which fundamentally consists of comparing the absorption due to a triplet of known ϵ_{T-T} with that of the unknown one: two experiments are performed, one with the donor molecule alone in solution (benzene or cyclohexane), another with both donor (at the same concentration as before) and acceptor (at about 1% of the donor concentration). The solvent energy is first intercepted by the donor molecule which can transfer all or some to the acceptor, the partition depending on the relative rates of donor decay (measured in the first experiment) and energy transfer (measured as the rate of acceptor triplet formation in the second). The optical density due to the acceptor triplet is measured at the end of the transfer process and corrected for the amount of donor triplet lost to natural decay modes using the two measured rates. The ratio of the optical density to the donor triplet in the

⁸⁹ (a) T. G. Truscott, E. J. Land, and A. Sykes, *Photochem. and Photobiol.*, 1973, **17**, 43; (b) R. V. Bensasson, E. J. Land, and T. G. Truscott, *ibid.*, p. 53.

⁹⁰ S. J. Chantrell, C. A. McAuliffe, R. W. Munn, A. C. Pratt, and E. J. Land, *J. Luminescence*, 1976, **12/13**, 887.

⁹¹ R. V. Bensasson, C. Chachaty, E. J. Land, and C. Salet, *Photochem. and Photobiol.*, 1972, **16**, 27.

⁹² (a) E. J. Land, *Trans. Faraday Soc.*, 1969, **65**, 2815; (b) R. V. Bensasson, E. J. Land, T. Lafferty, R. S. Sinclair, and T. G. Truscott, *Chem. Phys. Letters*, 1976, **41**, 333; (c) E. J. Land, E. McAlpine, R. S. Sinclair, and T. G. Truscott, *J.C.S. Faraday I*, 1976, **72**, 2091.

⁹³ (a) E. J. Land, *Proc. Roy. Soc.*, 1968, **A305**, 457; (b) R. V. Bensasson and E. J. Land, *Trans. Faraday Soc.*, 1971, **67**, 1904.

absence of acceptor to the corrected acceptor optical density is equal to ϵ_{T-T} (donor)/ ϵ_{T-T} (acceptor), whence ϵ_{T-T} (acceptor) can be evaluated.

This technique was used initially to measure ϵ_{T-T} for several condensed-ring aromatic species^{93a} and show the solvent dependence^{93b} of both spectral shape and intensity. More recently the method has been utilized in characterizing the spectral features and reactivity parameters for a diverse range of molecular triplet states⁸⁹⁻⁹² and it is now widely recognized as a straightforward, convenient way of obtaining extinction coefficient data.

8 Surfactants and Micellar Systems⁹⁴

Aqueous solutions of amphiphilic molecules (surfactants) can exist in at least two well-defined states. At low concentration the dispersion is largely one of monomeric surfactants in water; at higher concentrations supramolecular aggregates (micelles) form in which the hydrophobic paraffin chains are inwardly disposed with the hydrophilic polar head groups at the surface layer. Micellar shapes can be roughly spherical or cylindrical. Above a critical micelle concentration (c.m.c.) monomers and micelles co-exist in dynamic equilibrium. Since micelle stability results from the same molecular interactions which stabilize bio-membranes and tertiary protein structures, micelles have been extensively studied as model biological entities. In recent years the pulse radiolysis technique has been added to the conventional means of probing such systems.

Early experiments using pulse radiolysis concentrated on measuring the reactivity of primary radicals (e_{aq}^- , $\cdot OH$ and $\cdot H$) with surfactant molecules and micelle-solubilized substrates.⁹⁵ For common surfactants such as cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulphate (SDS), and Igepal (a polyoxyethylene), bimolecular rate constants with $H\cdot$ atoms range between 10^8 and 10^9 $dm^3 mol^{-1} s^{-1}$; for OH radicals the range is 10^9 — 10^{10} $dm^3 mol^{-1} s^{-1}$. These surfactants are most unreactive to e_{aq}^- as may be anticipated from the lack of reactivity of saturated hydrocarbons.

The interaction of hydrated electrons with micelles or micelle-bound substrates is severely modified by the micellar surface charge. For example cetylpyridinium chloride (CPC) reacts efficiently with e_{aq}^- (rate constant of 7×10^9 $dm^3 mol^{-1} s^{-1}$) below the c.m.c. This rate constant is increased to 5×10^{12} $dm^3 mol^{-1} s^{-1}$ on micelle formation.⁹⁶ In addition, when CPC was added to CTAB micelles (unreactive to e_{aq}^-) at a level of one per micelle, very rapid micelle-micelle hopping by e_{aq}^- was observed to occur.⁹⁷

Reactions of primary water radicals with substrates adsorbed at a micelle sur-

⁹⁴ Accounts of pulse radiolysis studies of micellar systems can be found in (a) J. H. Fendler and E. J. Fendler, 'Catalysis in Micellar and Macromolecular Systems', Academic Press, New York, 1975; (b) 'Reaction Kinetics in Micelles', ed. E. Cordes, Plenum Press, New York, 1973; (c) J. K. Thomas, *Accounts Chem. Res.*, 1977, **10**, 133.

⁹⁵ (a) J. H. Fendler and L. K. Patterson, *J. Phys. Chem.*, 1970, **74**, 4608; (b) R. M. Bansal, L. K. Patterson, E. J. Fendler, and J. H. Fendler, *Internat. J. Radiat. Phys. Chem.*, 1971, **3**, 321; (c) J. H. Fendler, G. W. Bogan, E. J. Fendler, G. A. Infante, and P. Jirathana, ref. 2b, p. 53.

⁹⁶ M. Grätzel, J. K. Thomas, and L. K. Patterson, *Chem. Phys. Letters*, 1974, **29**, 393.

⁹⁷ L. K. Patterson and M. Grätzel, *J. Phys. Chem.*, 1975, **79**, 956.

face or solubilized within its interior have proved instructive. Thus the rate constant for e_{aq}^- reacting with benzene shows a ten-fold increase in the presence of CTAB micelles on which the benzene is adsorbed.^{95c} Other rate-constant enhancements have been measured for polycyclic aromatic hydrocarbons,⁹⁸ ketones and benzoquinones,⁹⁹ and nucleic acid bases.¹⁰⁰ Such enhancements have been variously attributed^{94a} to distortion by the micellar surface charge of the substrate π -system, thereby assisting nucleophilic attack, or to a purely electrostatic effect on the diffusion rate. Whatever the real reason, it is clear that reactivities of charged species with lipid-associated substrates at membrane sites cannot be confidently extrapolated from data obtained in dilute aqueous solution.

Equilibrium constants for the binding of transition metals to SDS micelles have been evaluated¹⁰¹ using pulse radiolysis to generate e_{aq}^- , which probes the concentration of metal ion in bulk solution. An interesting recent development has been the observation¹⁰² of the dismutation of Br_2^- species produced by the reactions



where the Br^- ions are in the diffuse double layer of CTAB micelles. Two kinetic processes involving Br_2^- dismutation were observed, one governed by normal diffusion through the inter-micellar region and the other resulting from diffusion restricted to the micellar surface by electrostatic forces. Such two-dimensional diffusion has obvious relevance to biochemical processes occurring in the vicinity of charged surfaces. There is no doubt that the study of micellar systems by the pulse radiolysis technique is rapidly expanding and future work will concentrate more on using the primary water radicals as probes for learning more about micellar structure and the location of adsorbed or solubilized substrates.

9 Organic and Biological Free Radicals

This heading covers probably the largest body of information which has resulted from pulse radiolysis studies of aqueous systems and it would be impossible in this article to attempt even a partial coverage of the field. Fortunately a number of comprehensive review articles have appeared recently¹⁰³ to which reference can be made for detail; our aim will be to attempt an overview of the subject punc-

⁹⁸ (a) S. C. Wallace and J. K. Thomas, *Radiat. Res.*, 1973, **54**, 49; (b) J. H. Fendler, H. A. Gillis, and N. V. Klassen, *J.C.S. Faraday I*, 1974, **70**, 145.

⁹⁹ Ref. 1a, Ch. 8.

¹⁰⁰ C. L. Greenstock and I. Dunlop, *Internat. J. Radiat. Phys. Chem.*, 1973, **5**, 231.

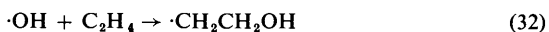
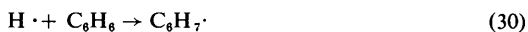
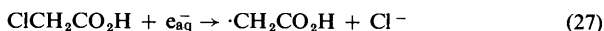
¹⁰¹ M. Grätzel and J. K. Thomas, *J. Phys. Chem.*, 1974, **78**, 2248.

¹⁰² A. J. Frank, M. Grätzel, and J. J. Kozak, *J. Amer. Chem. Soc.*, 1976, **98**, 3317.

¹⁰³ (a) P. Neta, in 'Advances in Physical Organic Chemistry', ed. V. Gold and D. Bethell, Academic Press, London, Vol. 12, 1976; (b) G. E. Adams, in 'Advances in Radiation Chemistry', ed. M. Burton and J. L. Magee, Wiley-Interscience, New York, Vol. 3, 1972; (c) M. Simic, in 'Fast Processes in Radiation Chemistry', ed. G. E. Adams, E. M. Fielden, and B. D. Michael, Wiley, London, 1975; (d) P. Wardman, in 'Reports on Progress in Physics', 1977, in press.

tuated with examples to describe the general aspects of free-radical properties which can be obtained from pulse radiolysis experiments.

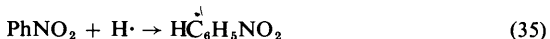
Organic free radicals are generated in pulse radiolysis by reaction of the primary water radicals with organic substrates; according to the selected conditions the organic substrates may be oxidized or reduced, *e.g.*



Monitoring of free radicals and their subsequent reactions has been carried out largely by time-resolved optical absorption spectroscopy supplemented by conductivity, polarography, and *e.s.r.* measurements following pulse radiolysis generation.^{103a} Absorption spectra are especially useful where the primary radical can react at different sites on the substrate, *e.g.*



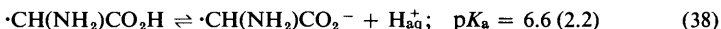
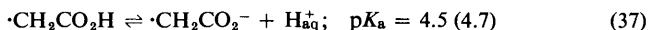
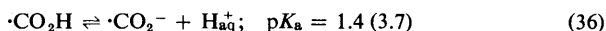
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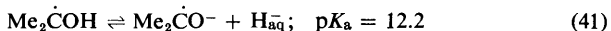
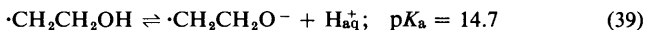
The two product radicals in this and other cases have sufficiently different absorption maxima to allow determination of the mode of $\text{H}\cdot$ reaction. In general, absorption spectra of carbon σ -radicals are in the low u.v. region and of low extinction coefficient, which makes their observation difficult. π -Bonded systems usually have absorption maxima in more accessible regions: the more extensive the conjugation, the more red-shifted the absorption becomes. Compilations of free-radical spectra have been published.¹⁰⁴

A particularly useful feature of optical absorption spectra of many free radicals is a shift in λ_{max} with pH. Utilization of this fact has made possible the determination of pK values of a multitude of free radicals, *e.g.*

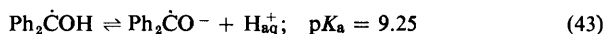
(i) Carboxylic acid dissociation (parent acid value in parenthesis)



(ii) Hydroxy-group dissociation

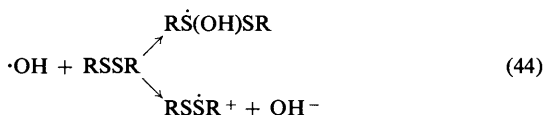


¹⁰⁴ (a) A. Habersbergerova, I. Janovski, and P. Kourim, *Radiat. Res. Rev.*, 1968, 1, 109; (b) A. Habersbergerova, I. Janovski, and J. Teply, *ibid.*, 1972, 4, 123.



An extremely large number of radicals have been characterized in this way¹⁰⁵ and the changes in pK_{a} with degree and nature of substitution have been correlated with empirical Taft and Hammett relationships.^{103a}

The time-resolved conductivity technique has been used to good effect where ionic concentrations undergo change as a result of radical formation (*e.g.* ionic dissociation or hydrogen halide elimination). Recently, interesting chemistry of oxidized dialkyl disulphides has been followed using combined optical and conductivity observations,¹⁰⁶ *viz.*



Formation of RSSR^+ results in a decrease in conductivity of the solution since the OH^- formed rapidly removes H_3O^+ ions from the solution, *i.e.* the highly mobile proton is replaced by a less mobile RSSR^+ ion. The dimethyl disulphide cation is found to react with reductants such as $[\text{Fe}(\text{CN})_6]^{4-}$ and Fe^{2+} , the former with a bimolecular rate constant of $1.5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ the latter of $5.2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Whereas the rate constant for reduction by ferrocyanide was diffusion-controlled for increasingly hindered disulphides, the reduction by ferrous ions became less efficient as the alkyl groups varied in the series Me, Et, Pr^i , Bu^t . Not only $\cdot\text{OH}$ radicals but also pulse-radiolytically produced radicals such as Ag^{2+} , $[\text{Ag}(\text{OH})]^+$, Ti^{2+} , HCO_3^- , and $\text{Br}_2^{\cdot-}$ caused oxidation of RSSR species.¹⁰⁷

Electron spin resonance studies of free radicals generated by electron pulses have been particularly useful in characterizing radical structures and yields.¹¹ In addition, time-resolved e.s.r. experiments following pulse radiolysis have demonstrated that non-equilibrium concentrations of spin-states are produced.¹⁰⁸ Kinetic information is also available from such experiments.^{109,11}

The ultimate decay mode of free radicals is by a bimolecular reaction involving either dismutation or dimerization. By and large, the rate constants governing such processes for organic radicals are in the range of $10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and are largely independent of structure.^{103a} Some radicals undergo unimolecular changes prior to the bimolecular decay. Thus hydroxyl radical addition to phenols and hydroquinone,¹¹⁰

¹⁰⁵ E. Hayon and M. Simic, *Accounts Chem. Res.*, 1974, 7, 114.

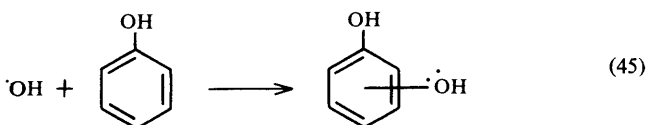
¹⁰⁶ M. Bonifacic, K. Schäfer, H. Möckel, and K.-D. Asmus, *J. Phys. Chem.*, 1975, 79, 1496.

¹⁰⁷ M. Bonifacic and K.-D. Asmus, *J. Phys. Chem.*, 1976, 80, 2426.

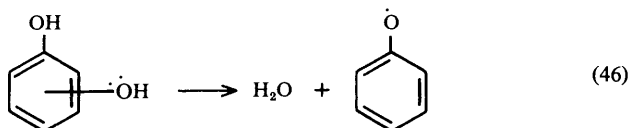
¹⁰⁸ (a) E. C. Avery, J. R. Remko, and B. Smaller, *J. Chem. Phys.*, 1968, 49, 951; (b) R. W. Fessenden, *ibid.*, 1973, 58, 2489.

¹⁰⁹ G. Nucifora, B. Smaller, J. R. Remko, and E. C. Avery, *Radiat. Res.*, 1972, 49, 96.

¹¹⁰ (a) E. L. Land and M. Ebert, *Trans. Faraday Soc.*, 1967, 63, 1181; (b) G. E. Adams and B. Michael, *ibid.*, p. 1171.



is followed by water elimination,



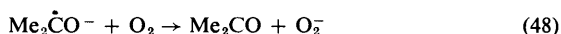
with eventual formation of phenoxy-radicals. Similar H₂O elimination has been demonstrated for ·OH adducts of anilines,¹¹¹ toluene,¹¹² pyrroles, and imidazoles.¹¹³ Kinetic parameters for many free-radical reactions have been collected and tabulated.¹¹⁴

An important bimolecular reaction of most organic free radicals is with oxygen. Two modes of reaction are possible:

(i) addition



(ii) electron transfer



These processes are of particular importance in the biological effects of free radicals in oxygenated systems.^{103c} For example, the killing of cells by ionizing radiation has been shown to be enhanced in the presence of oxygen.^{103b} This oxygen enhancement has been shown to involve (in part) free-radical intermediates in bacterial spores.¹¹⁵ Experiments using electron pulses quickly following oxygenation of cells in a rapid-mix system aim to characterize the time-scale of the oxygen effect.¹¹⁶ An understanding of this phenomenon and of the molecular mechanisms for cellular sensitivity to free-radical-induced processes has stimulated much effort into the study of organic free radicals, both as isolated systems and as components of macromolecules, *e.g.* proteins and DNA.

The involvement of radicals in general,^{103b} and peroxy-radicals in particular,^{103c} in biological effects has been reviewed. It would seem that a logical picture has emerged, *viz.* characterization of the reactivities and spectra of radicals derived from amino-acids and simple peptides by pulse radiolysis coupled to observations

¹¹¹ H. Christensen, *Internat. J. Radiat. Phys. Chem.*, 1972, 4, 311.

¹¹² H. Christensen, K. Sehested, and E. J. Hart, *J. Phys. Chem.*, 1973, 77, 983.

¹¹³ A. Samuni and P. Neta, *J. Phys. Chem.*, 1973, 77, 1629.

¹¹⁴ A. J. Swallow, in 'Progress in Reaction Kinetics', ed. R. B. Cundall and K. R. Jennings, Pergamon Press, in press.

¹¹⁵ E. L. Powers, in 'Electron Spin Resonance and Effects of Radiation on Biological Systems', Nuclear Science Series, Report No. 43, National Academy of Sciences, Washington D.C., 1966.

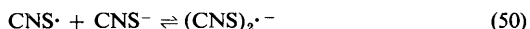
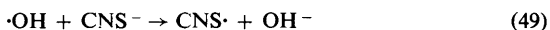
¹¹⁶ B. D. Michael, G. E. Adams, H. B. Hewitt, W. B. G. Jones, and M. E. Watts, *Radiat. Res.*, 1973, 54, 239.

of proteins and enzymes. Likewise the radical properties of nucleic acid bases, nucleosides, and nucleotides have been obtained in order to help an understanding of the response of DNA to free-radical attack.

The simple aliphatic amino-acids lose $H\cdot$ from the α -carbon when attacked by $\cdot OH$ or $H\cdot$ but are of low reactivity towards e_{aq}^- .^{103b} Sulphur-containing amino-acids are very reactive towards both $\cdot OH$ and e_{aq}^- . Amino-acids with aromatic residues are very reactive to e_{aq}^- and moderately so to $\cdot OH$.^{103b} Transient spectra of the $\cdot OH$ adducts of tyrosine and tryptophan have been characterized; a comprehensive study of the latter¹¹⁷ has shown that $\cdot OH$ adds to the C-2 and C-3 portions of the heterocyclic ions and to a site on the benzenoid nucleus with about equal efficiency.

Capture of e_{aq}^- by the disulphur bridges in cystine is very efficient ($k = 1.3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)¹¹⁸ and produces an anionic radical species absorbing strongly in the visible region. Studies¹¹⁹ using enzymes, lysozyme, papain, chymotrypsin, and ribonuclease show similar spectra on reaction with e_{aq}^- . It was suggested that e_{aq}^- attacks an enzyme at multiple reactive loci, following which the electron is rapidly passed through the protein intramolecularly to be localized eventually on the disulphide bridge.^{103b}

Free radicals have been successfully used to probe the active site of enzymes. Thus, $\cdot OH$ radicals have been shown to inactivate lysozyme in aqueous solution; hydroxyl radical scavengers, except thiocyanate ions, protect against inactivation; hence the $(CNS)_2^{\cdot -}$ ion formed by



must also deactivate lysozyme.¹²⁰ It was found that $(CNS)_2^{\cdot -}$ reacts with the enzyme with a rate constant of $6.6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Of the 20 amino-acids which make up lysozyme only tryptophan was found to react with $(CNS)_2^{\cdot -}$ at a significant rate. Subsequently tryptophan-108 was confirmed as being responsible for the activity.¹²⁰ This use of free radicals generated by pulse radiolysis suggests that such species may be more widely used as specific probes for identifying reaction centres.

The free bases of nucleic acids, nucleosides, and nucleotides are all very reactive towards $\cdot OH$ radicals and, with a few exceptions, hydrated electrons.^{103b} Much effort has been expended in identifying the loci of attack and the nature of radicals formed.¹²¹ The reaction of oxygen with the product radical (including DNA \cdot) has been shown to be extremely efficient¹²² ($> 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). The intense

¹¹⁷ R. G. Armstrong and A. J. Swallow, *Radiat. Res.*, 1969, **40**, 563.

¹¹⁸ R. Braams, *Radiat. Res.*, 1966, **27**, 319.

¹¹⁹ (a) J. V. Davies, M. Ebert, and R. J. Shalek, *Internat. J. Radiat. Biol.*, 1968, **14**, 19; (b) G. E. Adams, R. B. Cundall, and R. L. Willson, in 'Chemical Reactivity and Biological Role of Functional Groups in Enzymes', ed. R. M. S. Smellie, Academic Press, New York, 1970.

¹²⁰ J. E. Aldrich, R. B. Cundall, G. E. Adams, and R. L. Willson, *Nature*, 1969, **221**, 1049.

¹²¹ J. F. Ward, in 'Advances in Radiation Biology', ed. Lett and Adler, Academic Press, New York, Vol. 5, 1975.

¹²² R. L. Willson, *Internat. J. Radiat. Biol.*, 1970, **17**, 349.

interest in the oxygen enhancement of radiation damage in living systems has led to searches for O₂-mimics, *i.e.* substances which also enhance radiation sensitivity. Many are now known, some interesting ones being stable nitroxyl free radicals, *e.g.* triacetoneamine-*N*-oxyl (TAN). Pulse radiolysis studies of the reactivity of TAN with deoxyribonucleotides and DNA have been performed.¹²³ Recently, pulse radiolysis techniques have been used to investigate the redox properties of many radiation sensitizers (see above).

The reactivity of the radicals (CSN)₂^{•-}, Br₂^{•-}, e_{aq}⁻, and CO₂^{•-} with biological macromolecules has been used to probe macromolecule-substrate binding. Thus e_{aq}⁻ produced by pulse radiolysis in the presence of protein (*e.g.* serum albumin) undergoes addition and the rate of loss of e_{aq}⁻ can be followed absorptiometrically. When a drug molecule (*e.g.* penicillin) is bound to the protein, this reactivity is modified and measurements of the rate constants can lead to evaluation of the concentrations of free and bound drug and hence to equilibrium constants and, *via* a temperature dependence, to binding energies.¹²⁴ Similar experiments have been performed for observing the binding of detergents and proteins¹²⁵ and drugs by DNA and dye-DNA intercalation.¹²⁶

10 Gas-phase Chemistry

Early studies on gases were limited because of technical difficulties which derive from the fact that owing to the lower densities compared with liquids the energy absorption from a radiation pulse, and therefore the concentration of species produced, is much lower. However, the use of multiple reflection cells and the development of fast sensitive detection equipment has now made it possible to make observations comparable with those in liquid systems. Since an authoritative and detailed review of the pulse radiolysis of gases has recently been published¹²⁷ it will suffice for present purposes to outline the scope of these studies.

The work has covered the reactions of atoms, free radicals, electrons, ions, and excited states, using measurements of optical absorption and emission and, in the case of electrons, microwave conductivity.

Among the atom reactions those of oxygen have received most attention. In particular the formation of O₃ in oxygen by the three-body reaction



has been analysed in great detail. It proceeds by two steps:



¹²³ R. L. Willson and P. T. Emmerson, in 'Radiation Protection and Sensitization', ed. Moroson, Quintiliani, Taylor, and Francis, London, 1970.

¹²⁴ (a) G. O. Phillips, D. M. Power, C. Robinson, and J. V. Davies, *Biochim. Biophys. Acta*, 1970, **215**, 491; (b) G. O. Phillips, D. M. Power, and J. T. Richards, *Israel J. Chem.*, 1973, **11**, 517; (c) J. S. Moore, G. O. Phillips, D. M. Power, and J. V. Davies, *J. Chem. Soc. (A)*, 1970, 1115.

¹²⁵ C. V. Eadsforth, D. M. Power, E. W. Thomas, and J. V. Davies, *Internat. J. Radiat. Biol.*, 1976, **30**, 449.

¹²⁶ (a) D. W. Whillans, *Biochim. Biophys. Acta*, 1975, **414**, 193; (b) C. L. Greenstock and G. W. Ruddock, *ibid.*, 1975, **383**, 464.

¹²⁷ M. C. Sauer, 'Advances in Radiation Chemistry', Vol. 5, Wiley, New York, 1976, p. 97, which contains detailed references to all the work quoted in this section.



Rate constants for the deactivation step have been obtained for a variety of M, and at low pressures absorptions due to O_3^* in various states of vibrational excitation have been observed. The reactions of O (obtained from Ar + CO_2 or Ar + N_2O mixtures) with benzene and a range of substituted benzenes have been followed and the absorption characteristics of the adducts obtained.

Reactions of hydrogen atoms (from H_2 or Ar + H_2) with a range of aromatics and with O_2 , CO, NO, and C_2H_4 have been measured using either the optical absorption of the products or of H itself with Lyman α -radiation as monitoring light.

Using the identifiable absorptions of the radicals themselves, reactions of NH_2 (from NH_3), SH (from H_2S), CH (from CH_4), and CN (from C_2N_2) with a variety of inorganic and organic molecules have been studied and in the latter case the effect on reaction rates of having CN in various vibrational states has been examined.

Both absorption and emission have been used to study the excited states of Ar, Kr, and Xe. In argon the four $1s$ excited states have been observed in absorption and their decay characteristics obtained. Also, their appearance as a result of emission from the corresponding $2p$ states has been established. I.r. absorptions, which are assigned to excited dimers formed from the $1s$ states, are present in all three irradiated gases and have been used to measure the excimer lifetimes.

In nitrogen the behaviour of vibrationally and electronically excited states has been investigated. The lifetimes of $\text{N}_2(A^3\Sigma_n^+)$, $\text{N}_2(B^3\Pi_g)$, and $\text{N}_2(a^1\Sigma_u^-)$ in various states of vibronic excitation have been obtained using the absorption of the excited species. The kinetics of the emission from $\text{N}_2(C^3\Pi_u)$ have been shown to be consistent with its production by the neutralization reaction $e^- + \text{N}_4^+$. Other studies of emission from electronically excited states of species such as O_2^+ , CO_2^+ , CH, and CO as well as N_2 have given rates of collisional deactivation by various inert gases. Excited states of aromatics can be produced by energy transfer from, *e.g.*, excited argon, or by reaction of the aromatic cation with electrons or with the corresponding anion formed by electron capture. Using emission from the excited singlet to monitor the reactions with anthracene, rate constants of 2×10^{15} and $2 \times 10^{14} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ have been obtained.

Electron capture by a variety of organic halides is found to occur with rate constants which vary from about 10^8 (EtBr) to 10^{14} (CCl_4) $\text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Detailed examination of the CCl_4 reaction has shown effects of gas pressure which arise from the time required for the electrons to be thermalized; for example, this requires milliseconds in argon at 1 Torr but nanoseconds in hydrocarbons, N_2O , NH_3 , *etc.* at the same pressure.