INTERMEDIATES IN RADIATION CHEMISTRY AT LOW TEMPERATURE

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Contents

I. Introduction

In recent years, considerable research has been directed toward a detailed study of the effects of high-energy radiation on simple molecules, and it has been through the application of techniques for studying fast reactions and for identifying reactive intermediates that a better appreciation of the overall chemical changes involved in radiation chemistry has evolved. Hence, in this review it is proposed to cover some of the features of this work as they pertain to simple organic systems and to aqueous systems in order to present a framework of concepts upon which current investigations are proceeding. Particular emphasis will be placed on results obtained from radiation experiments carried out at low temperatures, as studied by absorption spectroscopy and electron spin resonance (esr) spectroscopy, and mention will also be made of results obtained by pulse radiolysis where they are relevant.

II. Elementary Processes

Initially, the interaction of ionizing radiation involves a perturbation of the medium resulting from the passage of radiation through it. The radiation deposited in the medium is absorbed almost entirely by interaction with the electrons of the constituent molecules,[2] and the individual acts of energy transfer generally lead to the formation of electronically excited molecules. These processess, which occur within about 10^{-17} sec after the primary radiochemical act, have been described as "the physical stage of radiation damage" by Hart and Platzman,[2a] though from the chemist's point of view there is little detail available for a description of the processes that occur within them.[2b] However, these excited molecules do undergo their own characteristic chemistry which not only involves the formation of excited species[3] but also leads to subsequent ionization with the production of energetic secondary electrons and positive ions.[2a,4,5]

The secondary electrons, which arise from ionization processes caused by the passage of X-rays and γ-rays, are produced from the parent molecule by the process of photoelectric emission, but, when the incident photon energy occurs in the range 0.1–2 MeV, their production by concurrent Compton scattering also becomes important.[2a,4] These ejected electrons may themselves be sufficiently energetic to produce further ionization and excitation, the less energetic ones having only a short range and producing smaller clusters or spurs of excited and ionized species close to the center of the original ionization. On the other hand, the more energetic electrons, with energies greater than about 100 eV in the condensed phase, form tracks of their own and are, in fact, responsible for a significant proportion of the total number of ions produced in any radiation process. The spurs which contain these clusters of ions and excited species can be considered as the centers of the localized radiation damage and usually occur in discrete little pockets within the reaction medium—typically at intervals of about 10^4 Å and extending over an area of approximately 500 Å^2.[6,7]

The environment of the species trapped within the spur no doubt helps to determine the chemical processes which occur in a system, but it is the fate of the ejected electron and of the complementary positive hole (or positive ion subsequently formed from it) that will be discussed here.

By collision, the ejected electron and the secondary electrons, formed subsequently, rapidly lose their excess energy in condensed media (within approximately 10^{-10} sec) and then undergo a variety of reactions both by attachment and by dissociative processes. Their fate depends on the nature of the solvent, the extent of hydrogen bonding within the solvent, and the nature of any solute present. Indeed, Milliken,

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[1] Chemistry Division, Defence Standards Laboratories, Ascot Vale 3032, Victoria, Australia.

[2] (a) E. J. Hart and R. L. Platzman, Mechanisms in "Radiobiology," M. Errera and A. Forssberg, Ed., Academic Press, New York, N. Y., 1961, Chapter 2; (b) R. L. Platzman, "Radiation Research," G. Silini, Ed., John Wiley and Sons, Inc., New York, N. Y., 1966, p 20.

[3] S. L. Lipsky and M. Burton, *J. Chem. Phys.*, 31, 1221 (1959).

[4] F. Hutchison and E. C. Pollard in ref 2a, Chapter 1.

[5] J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964.

[6] A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, 21, 1080 (1953).

[7] J. L. Magee, *Ann. Rev. Phys. Chem.*, 12, 389 (1961).

Morgan, and Johnsen[8] have used this behavior to set up quite a satisfactory scheme to classify the different reactions that the trapped electrons undergo. This includes the following: (A) systems with hydrogen bonding, (B) systems without hydrogen bonding, and (C) systems containing molecules with low-lying empty orbitals.

This classification is quite useful, even though it is inevitable that some overlap between the categories must occur. The general features common to each category will be summarized directly and then a detailed examination of examples in each category will be presented in the next section.

In the "systems with hydrogen bonding," most of the information available comes from studies of the radiation chemistry of water and alcohols. For methanol and for ethanol, the following reactions satisfactorily account for the radiation processes

$$\mathrm{ROH} \rightsquigarrow\!\!\!\longrightarrow \mathrm{ROH}^+ + \mathrm{e_m}^- \qquad (1)$$

$$\mathrm{e_m}^- \longrightarrow \mathrm{e_t}^- \qquad (2)$$

$$\mathrm{ROH}^+ + \mathrm{ROH} \longrightarrow \mathrm{ROH_2}^+ + \text{radical} \qquad (3)$$

where $\mathrm{e_m}^-$ is a mobile electron and $\mathrm{e_t}^-$ is a trapped electron. Similar reactions have also been noted in water.

The radiation chemistry of "systems without hydrogen bonding" incorporates that of both aliphatic and aromatic hydrocarbons as well as that of alkyl and aryl halides. When a glass of a hydrocarbon, RH, containing a reactive solute, R′X, is irradiated at 77°K, the results can often be interpreted in terms of the following scheme

$$\mathrm{RH} \rightsquigarrow\!\!\!\longrightarrow \mathrm{RH}^+ + \mathrm{e_m}^- \qquad (4)$$

$$\mathrm{e_m}^- + \mathrm{R'X} \longrightarrow \mathrm{R'} + \mathrm{X}^- \qquad (5)$$

some details of which will be considered later.

The interaction of radiation on a system containing molecules with energetically low-lying empty orbitals often leads to the stabilization of positively and negatively charged ions within the system.

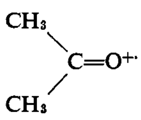
For instance, X- and γ-irradiation of disulfides at low temperature in the glassy state[8,9] and in the crystalline state[10] yields both positive and negative ions, according to the scheme

$$\mathrm{RSSR} \rightsquigarrow\!\!\!\longrightarrow \mathrm{RSSR}^+ + \mathrm{e_m}^- \qquad (6)$$

$$\mathrm{e_m}^- + \mathrm{RSSR} \longrightarrow \mathrm{RSSR}^- \qquad (7)$$

The charges are localized on the sulfur atoms, and the assignment is based on scavenging experiments[8] and on the analyses of the parameters of the esr spectra.[9,10]

When acetone glasses are irradiated at 77°K with $\mathrm{Co^{60}}$ γ-rays, two broad optical absorption bands are discerned, one due to the radical cation (i) and the other due to the radical anion (ii), an assignment verified by various scavenging experiments.[11] These species arise from a sequence of events akin to those described by eq 6 and 7.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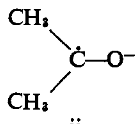
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Table I

Kinetic Data[a] for Some Reactions of Hydrated Electrons with Substrates

Reaction	*pH*	*Rate constant, k, $M^{-1}\ sec^{-1}$*	*Ref*
$\mathrm{e_{aq}}^- + \mathrm{H_3O^+} \rightarrow \mathrm{H} + \mathrm{H_2O}$	4.0	2.0×10^{10}	*b*
$\mathrm{e_{aq}}^- + \mathrm{H_2O} \rightarrow \mathrm{H} + \mathrm{OH^-}$	8–9	16 ± 1	*c*
$\mathrm{e_{aq}}^- + \mathrm{OH} \rightarrow \mathrm{OH^-}$	10–11	3.0×10^{10}	*b*
$\mathrm{e_{aq}}^- + \mathrm{e_{aq}}^- \rightarrow 2\mathrm{OH^-} + \mathrm{H_2}$	7–13	5.0×10^{9}	*b*
$\mathrm{e_{aq}}^-$ + alcohols	11	$<10^{5}$	*d*
$\mathrm{e_{aq}}^-$ + acetone	7	5.9×10^{9}	*e*
$\mathrm{e_{aq}}^- + \mathrm{CO_2}$	7	7.7×10^{9}	*e*
$\mathrm{e_{aq}}^-$ + benzene	11	1.4×10^{7}	*f*
$\mathrm{e_{aq}}^-$ + naphthalene	11	5.4×10^{9}	*f*
$\mathrm{e_{aq}}^-$ + ethylene		7.6×10^{6}	*g*
$\mathrm{e_{aq}}^-$ + acetic acid	5.4	1.8×10^{8}	*e*
$\mathrm{e_{aq}}^-$ + acetate anion	10	$<10^{8}$	*e*
$\mathrm{e_{aq}}^- + \mathrm{H_2PO_4}^-$	7	2×10^{7}	*h*
$\mathrm{e_{au}}^- + \mathrm{ClCH_2CO_2H}$	11	1×10^{10}	*i*
$\mathrm{e_{aq}}^-$ + amino acids (aliphatic)	6–6.5	10^{6}–10^{8}	*j*
$\mathrm{e_{aq}}^-$ + S-contg amino acids	6–6.5	10^{8}–10^{10}	*j*
$\mathrm{e_{aq}}^-$ + peptides	6–11.8	10^{6}–10^{8}	*k*
$\mathrm{e_{aq}}^-$ + ribonuclease	6	10^{9}	*j*
$\mathrm{e_{aq}}^-$ + purines, pyrimidines	7–12	10^{9}	*l*
$\mathrm{e_{aq}}^-$ + maleic acid	6.5	1.2×10^{9}	*e*
$\mathrm{e_{aq}}^-$ + succinic acid		10^{6}–10^{7}	*d*

[a] Kinetic data are for reaction, $\mathrm{e_{aq}}^- + \mathrm{S} \rightarrow \mathrm{S}^-$; the data usually refer to experiments at 25°, though this is often not stated in the references. [b] M. S. Matheson and J. Rabani, *J. Phys. Chem.*, **69**, 1324 (1965). [c] E. J. Hart, S. Gordon, and E. M. Fielden, *ibid.*, **70**, 150 (1966). [d] E. J. Hart, J. K. Thomas, and S. Gordon, *Radiation Res., Suppl.*, **4**, 74 (1964). [e] S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *Discussions Faraday Soc.*, **36**, 193 (1963). [f] M. Anbar and E. J. Hart, *J. Am. Chem. Soc.*, **86**, 5633 (1964). [g] J. H. Baxendale, *et al.*, *Nature*, **201**, 468 (1964). [h] A. Appleby, G. Scholes, and M. Simic, *J. Am. Chem. Soc.*, **85**, 3891 (1963). [i] M. Anbar and E. J. Hart, *J. Phys. Chem.*, **71**, 3700 (1967). [j] R. Braams, *Radiation Res.*, **27**, 319 (1966). [k] R. Braams *ibid.*, **31**, 8 (1967). [l] E. J. Hart, S. Gordon, and J. K. Thomas, *J. Phys. Chem.*, **68**, 1271 (1964).

Throughout this review, it should be noted that, unless stated to the contrary, samples irradiated at a particular temperature are studied at that temperature without warming being allowed to take place in the interim.

III. Classification of Reaction Systems

A. SYSTEMS WITH HYDROGEN BONDING

1. Water

The radiation chemistry of liquid water has been reviewed in detail just recently, and there is little need to amplify what has already been covered therein.[12,13] By the application of the techniques of pulse radiolysis, Hart and Boag[14,15] in 1962 observed and identified the absorption spectrum of the solvated electron in the radiolysis of water, and within a short period of

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(8) S. B. Milliken, K. Morgan, and R. H. Johnsen, *J. Phys. Chem.*, **71**, 3238 (1967).

(9) F. Truby, D. C. Wallace, and J. E. Hesse, *J. Chem. Phys.*, **42**, 3845 (1965).

(10) H. C. Box and H. G. Freund, *ibid.*, **41**, 2571 (1964).

(11) T. Shida and W. H. Hamill, *J. Am. Chem. Soc.*, **88**, 3683 (1966).

(12) D. C. Walker, *Quart. Rev.* (London), **21**, 79 (1967).

(13) A. K. Pikaev and B. G. Ershov, *Usp. Khim.*, **36**, 1427 (1967).

(14) E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.*, **84**, 4090 (1962).

(15) W. C. Gottschall and E. J. Hart, *J. Phys. Chem.*, **71**, 344 (1967).

time many aspects of the radiation chemistry of water were reassessed.[16,17] In essence, the following over-all reaction scheme is applicable

$$H_2O \rightsquigarrow H_2O^* \qquad (8)$$

where H_2O^* denotes the electronically excited water molecule formed in the elementary excitation reaction

$$H_2O^* \longrightarrow H + OH \qquad (9)$$

and, alternatively

$$H_2O^* \dashrightarrow e_{aq}^- + H_2O^+ \qquad (10)$$

where e_{aq}^- is the solvated electron in water

$$H_2O^+ \longrightarrow OH + H^+ \qquad (11)$$

$$e_{aq}^- + S \longrightarrow S^- \longrightarrow \text{products} \qquad (12)$$

the solvated electron, e_{aq}^-, being scavenged by many reactive substrates in reactions which in many instances very nearly conform to diffusion-controlled kinetics. A typical list of kinetic data is given in Table I.

Furthermore, recent calculations[18] suggest that relatively stable electron-hole pairs, $[H_2O^+, H_2O^-]$, are formed in radiation-damaged water; they exist in the form of triplet excitons and dissociate according to the reaction

$$[H_2O^+, H_2O^-] \longrightarrow H + OH + H_2O \qquad (13)$$

Such reactions, which may occur within the scope of reaction 9 and within the same spur, serve to define the over-all reaction mechanism more precisely.

At the same time as the radiation chemistry of liquid water has been developed through the use of pulse radiolysis, considerable information about the nature of the species formed in the radiolysis of ice has been obtained from electron spin resonance spectroscopy at low temperature and, depending on the nature of the solution under consideration, the following species have been observed and characterized: the trapped electron (e_t^-), the hydroxyl radical (OH), the oxygen radical anion (O^-), and the hydrogen atom (H), while the presence of the acid conjugate of OH (H_2O^+) has been suggested in acidic media, though its unambiguous identification still remains to be substantiated.

Since most of these species are also observed, either directly or indirectly, in the radiolysis of liquid water, it seems reasonable to assume that similar mechanisms are applicable in both liquid and solid (polycrystalline and glassy) phases, though medium effects may modify the individual details somewhat.

When neutral ice in the single crystal form is irradiated at 77°K, the resonance pattern consists of a multiplet of lines, asymmetrically centered about $g = 2.00$ in most orientations and spread over approximately 60 G. The reason for the complexity of the single-crystal spectra originates from the fact that naturally occurring ice has a hexagonal symmetry in which the oxygen atoms are hydrogen-bonded in a zinc sulfide (wurtzite) structure, each oxygen atom being surrounded by four tetrahedrally disposed hydrogen atoms—two covalently bound to the oxygen and the other two hydrogen-bonded to it.[19,20] However, from a very careful analysis of the single-crystal spectra, both Dibdin[21] and Brivati, *et al.*,[22] have identified and characterized the hydroxyl free radical as the principal free radical trapped in the crystal lattice. This species can be trapped at 24 distinct sites within the lattice, these sites differing from one another only with respect to their relative orientation, and, from a consideration of various tensor elements, it appears that the OH radical is flattened slightly with respect to its original configuration.

Oriented hydroxyl radicals have also been trapped at 77°K in γ-irradiated hydrated salts by Gunter,[23] who investigated $CaSO_4 \cdot 2H_2O$ and $LiSO_4 \cdot H_2O$, and by Aseltine and Kim,[24] who also investigated the latter compound. The esr parameters for the OH radical in these salts were very similar to those in oriented ice.

There is no evidence for the presence of H atoms trapped in these samples at 77°K, and it has been suggested that, in ice at 77°K, the H atoms formed in the radiolysis reaction diffuse away, reacting to give diamagnetic products. These results are consistent with observations of Siegel and coworkers,[25] who found that H atoms can be trapped upon irradiation of ice at 20°K but that they disappear very rapidly above 50°K, the kinetics of their disappearance being very complex. However, it is also worth mentioning in this regard that Kevan, Moorthy, and Weiss[26] have been able to observe trapped hydrogen atoms in nearly neutral γ-irradiated ices at 77°K in the presence of Brønsted acids, *viz.*, HSO_4^- and $H_2PO_4^-$, which presumably scavenge the mobile electron according to eq 12 and then dissociate. This suggests that the trapping sites for H atoms occur in a deeper potential well in these glasses, more so because, in both acidic and alkaline media, H atoms have been trapped upon irradiation of ices at 77°K, and these have been identified at leisure.[27]

For instance, Livingston and his associates[28,29] found that the esr spectrum of γ-irradiated aqueous glasses containing sulfuric acid in the concentration range 5–15 *M* consisted of two portions (the H-atom doublet and a central resonance pattern, centered at $g = 2.00$), and they concentrated their attention on the nature of the H-atom doublet.

The high-field component of the doublet was slightly broader than the low-field component, and each component of the doublet had a pair of satellites of weak intensity. These features were analyzed satisfactorily in terms of simultaneous changes occurring in both the spin state of nearby protons and the spin state of the electron, the satellite spacing corresponding to the proton magnetic resonance in the applied field. Similar satellites are also observed in the H-atom spectra of aqueous glasses of perchloric acid and of phosphoric acid at 77°K, though these were not studied in detail. Further to these studies, Kohnlein and Venable[30] looked closely at the esr spectrum of 6 *M* H_2SO_4 in water irradiated and observed

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(16) E. J. Hart, *Radiation Res., Suppl.*, 4, 215 (1964).

(17) I. A. Taub, M. C. Sauer, and L. M. Dorfman, *Discussions Faraday Soc.*, 36, 1 (1963).

(18) J. J. Weiss, *Nature*, 215, 150 (1967).

(19) K. Lonsdale, *Proc. Royal Soc.* (London), A247, 424 (1958).

(20) L. C. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(21) G. Dibdin, *Trans. Faraday Soc.*, 63, 2098 (1967).

(22) J. A. Brivati, M. C. R. Symons, D. J. A. Tinling, H. W. Wardale, and D. O. Williams, *ibid.*, 63, 2112 (1967).

(23) T. E. Gunter, *J. Chem. Phys.*, 46, 3818 (1967).

(24) C. L. Aseltine and Y. W. Kim, *J. Phys. Chem. Solids*, 28, 867 (1967).

(25) J. M. Flournoy, L. H. Baum, and S. Siegel, *J. Chem. Phys.*, 36, 2229 (1962).

(26) L. Kevan, P. N. Moorthy, and J. J. Weiss, *J. Am. Chem. Soc.*, 86, 771 (1964).

(27) T. Henriksen, *Radiation Res.*, 23, 63 (1964).

(28) R. Livingston, H. Zeldes, and E. Taylor, *Discussions Faraday Soc.*, 19, 166 (1955).

(29) G. T. Trammell, H. Zeldes, and R. Livingston, *Phys. Rev.*, 110, 630 (1958).

(30) W. Kohnlein and J. H. Venable, *Nature*, 215, 618 (1967).

at 77 °K, and they found that each component of the H doublet can be resolved into three sets of satellite peaks under conditions of very high resolution. On extending Livingston's calculations,[29] they proposed that there are at least three "nearest protons" surrounding the trapped H atom in their system, and these are located at distances within the range 1.79–1.85 Å from it, results which appear quite reasonable although such experiments do not define the nature of the H-atom trap in the matrix.

For this purpose, Zimbrick and Kevan[31] measured the paramagnetic relaxation times of several sulfuric acid solutions at 77 °K as a function of dose, and from their experiments they concluded that some of the H atoms do migrate away from the initial spur in which they are formed before they are trapped.

While these researchers were concerned with the features of the trapped H-atom doublet, Henriksen[27] was more interested in studying the behavior of the central pattern with respect to changing concentrations of the sulfuric acid solute in the frozen solution. A selection of these spectra is reproduced in Figure 1. He observed that, up to concentrations of 1 *M* solute, the central part of the esr pattern at 77 °K consists mainly of the familiar "water" pattern, attributable to the OH radical; however, this pattern disappears at high acidities (up to 10 *M* H_2SO_4) and is replaced by another pattern which consists of at least two lines and is possibly due to the acid, conjugate to OH, *viz.* H_2O^+. However, this assignment is only speculative.

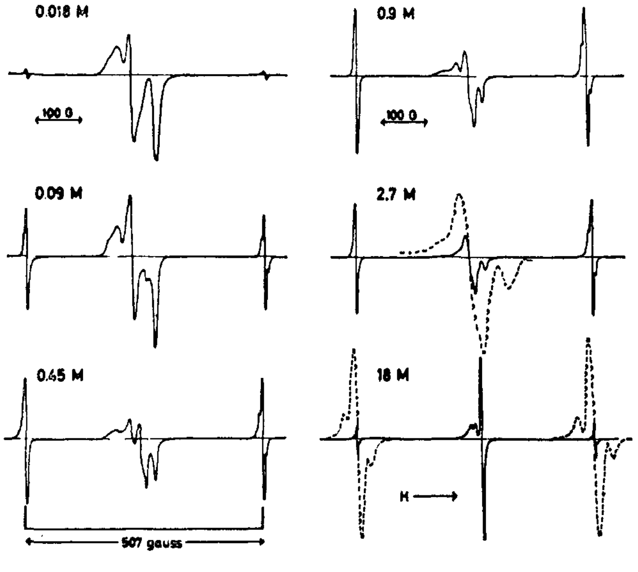

Figure 1. The qualitative esr spectra of H_2SO_4 solutions at different concentrations. The solutions were irradiated and measured at 77°K (radiation dose, 5 × 10^5 R). In order to study spectral details more closely, the central resonances of the 2.7 *M* spectrum and the two H-atom lines in the 18 *M* spectrum were recorded at higher gain and slower sweep rates, as reproduced by the dashed curves.

From these studies and those of Moorthy and Weiss,[32] it appears that in aqueous glasses of sulfuric acid at lower concentrations of acid at 77 °K, the following over-all reaction takes place

$$H_2O \rightsquigarrow H_2O^* \tag{14}$$

$$H_2O^* \longrightarrow H_2O^+ + e_m^- \tag{15}$$

$$e_m^- + H_3O^+ \longrightarrow H, H_2O \tag{16}$$

$$e_m^- + HSO_4^- \longrightarrow HSO_4^{2-} \longrightarrow H + SO_4^{2-} \tag{17}$$

$$H_2O^+ + HX \longrightarrow H_3O^+ + X \tag{18}$$

where HX = H_2O, HSO_4^-, H_2SO_4. Reaction 18 represents probable ion–molecule reactions involving the positive hole, H_2O^+. Consistent with this mechanism is the fact that in 10 *M* sulfuric acid glasses, a third pattern, which consists of a single sharp line, width 4.1 G and centered at $g = 2.003$, is indeed observed in the esr pattern in addition to the H atom doublet, and this may be ascribed to a species such as SO_4^-, from reaction 18. The relative extent of the scavenging reactions will depend on solute concentrations, but one should mention at this stage that, in sulfuric acid solutions where the concentration of sulfuric acid is very high, the initial act probably involves excitation and ionization of sulfuric acid molecules as well as water molecules.

It is also possible that reactions such as those summarized by eq 9 contribute to the over-all reaction, and the relative importance of such direct homolytic reactions is still to be assessed. Indeed, the presence of H atoms stabilized in aqueous solutions of sodium hydroxide (0.5 to 10 *M*) has been explained by such reactions,[27] although alternative pathways, as represented by eq 19 and 20, have not been ruled out.

$$e_m^- + H_2O \longrightarrow OH^- + H \tag{19}$$

$$H_2O^+ + e_m^- \longrightarrow H + OH \tag{20}$$

Nevertheless, the main interest in the radiation chemistry of alkaline hydroxide matrices has been in the study of the trapped electron, e_t^-. Both in neutral and acidic matrices[21–32] at low temperatures, there has been no evidence for the presence of trapped electrons *per se*,[33] but electrons produced by γ-irradiation in alkaline ices at 77°K in both the glassy and the polycrystalline phases can be trapped and are quite stable.[27,34–36]

At hydroxide concentrations greater than 0.5 *M*, e_t^- is characterized by a sharp esr singlet at $g = 2.001$ and a broad intense absorption band, λ_{max} 585 mμ,[34] which imparts an intense blue color to the irradiated ices. This esr spectrum and the broad blue absorption band are very similar to that reported for trapped electrons produced by the deposition of alkali metal atoms on ice and on alcohols at 77 °K,[37] though the most decisive evidence for this assignment comes from scavenging experiments. When the known electron scavengers,[38,39] nitrate (NO_3^-), nitrite (NO_2^-), and acetone, are added to alkaline solutions and the ices irradiated at 77 °K, the esr signal at $g = 2.001$ and the blue absorption band are no

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(31) J. Zimbrick and L. Kevan, *Nature*, 214, 693 (1967).

(32) P. N. Moorthy and J. J. Weiss, *ibid.*, 204, 776 (1964).

(33) A recent title, B. G. Ershov and A. K. Pikaev, "Stabilization of Electrons in Irradiated Neutral Glassy Solutions of Electrolytes," *Khim. Vysok Energii*, 1, 29 (1967), may shed some light on this subject.

(34) D. Schulte-Frohlinde and K. Eiben, *Z. Naturforsch.*, 18a, 199 (1963).

(35) B. G. Ershov, A. K. Pikaev, P. Ya Glazunov, and V. F. Spitsyn, *Dokl. Akad. Nauk SSSR*, 149, 363 (1963); *Chem. Abstr.*, 59, 2309c (1963).

(36) D. Schulte-Frohlinde in ref 2b, p 251.

(37) J. E. Bennett, B. Mile, and A. Thomas, *J. Chem. Soc., A*, 1393, 1399 (1967).

(38) P. B. Ayscough, R. G. Collins, and F. S. Dainton, *Nature*, 205, 965 (1965).

(39) J. Zimbrick and L. Kevan, *J. Chem. Phys.*, 47, 2364 (1967).

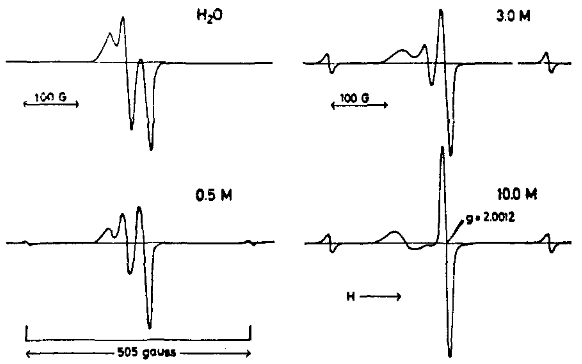

Figure 2. The qualitative esr spectra of water and aqueous solutions of NaOH at different concentrations. The solutions were irradiated and measured at 77°K (radiation dose, 5×10^5 R).

longer observed; instead, the esr pattern is characteristic of the interaction of an electron with the scavenger, thus indicating that the mobile electrons, which precede the formation of trapped electrons, have reacted with the scavenger.

However, in the esr spectrum from aqueous glasses of 3 *M* sodium hydroxide solution, X-irradiated at 77°K, three distinct patterns can be resolved[27] in the immediate vicinity of $g = 2.00$. These patterns are (a) the sharp, high-field line at $g = 2.001$, attributed to e_t^-; (b) an anisotropic doublet, overall splitting 40 G, located at $g = 2.01$ and characteristic of the hydroxyl radical; and (c) a broad, low-field anisotropic singlet, line width approximately 40–45 G, centered at $g = 2.06$ and associated with the base, conjugate to the hydroxyl radical, O^-.[40] From more concentrated solutions, the contribution of (c) relative to that of (b) predominates, a result consistent with the formulations proposed; in fact, in 6 *M* sodium hydroxide glasses, the esr pattern is described entirely in terms of that from O^- and e_t^-, and a reaction scheme similar to those previously written can be formulated.

Typical esr spectra illustrating the observed changes are presented in Figure 2.

Although e_t^- can be considered as a discrete species, located in a hydroxide anion vacancy,[40] it does interact with the medium in which it is trapped quite significantly.[38] Paramagnetic relaxation characteristics[39] of the esr signal attributed to e_t^- suggest that the anion vacancy in which the electron is trapped occurs within the radiation-produced spur and that the trapped electron relaxes by cross relaxation with the radical O^-. Line-width studies[41] indicated that the esr spectrum of e_t^- depends to a small, but appreciable extent (less than 25%), on which alkali-metal cation is present in the matrix and to a larger extent on the proton interactions from the solvent water. As the absence of any discernible hyperfine structure in the spectrum precludes significant electron–alkali metal and electron–proton Fermi contact interaction,[42] a theoretical analysis in terms of dipolar anisotropic interactions of the Gaussian line shapes has been carried out.

These results[39,41] suggest that the trapped electron interacts with approximately eight near-neighbor protons in its environment, a conclusion which indicates that the environment of the trapped electron found in radiation-damaged glasses differs somewhat from that produced chemically by a charge-transfer reaction in which the spectrum of the trapped electron displays some direct proton hyperfine interaction.[37] Furthermore, the number of sites which actually trap the mobile electrons within a particular spur of radiation damage in alkali metal glasses is not unlimited.[43] There is very good evidence to suggest that, at very high doses (greater than 10 Mrads), spin-paired centeres, corresponding to dielectrons $(e^-)_2$ are trapped within the same vacancy in irradiated sodium hydroxide (10 *M*) glasses at 77°K and that these centeres dissociate only on warming to 120°K or on photoactivation in which cases they acquire sufficient energy to escape the weak potential well in which they were originally associated.

2. *Methanol*

From pulse radiolysis studies on methanol at room temperature, absorption spectra attributable to both the solvated electron (λ_{max} 650 $m\mu$, half-life 2 μsec) and the hydroxymethyl radical, CH_2OH (λ_{max} 290 $m\mu$), have been detected, and these assignments have been verified by results from scavenging experiments.[44,45] However, when methanol is irradiated in the solid state at 77°K, the nature of the trapped products depends significantly on the physical state of the trapping matrix, a result which appears to be quite general.[46] For instance, when methanol in the opaque polycrystalline state is exposed to γ-irradiation, the matrix remains colorless, and the characteristic singlet in the esr spectrum at $g = 2.001$, attributed to the solvated electron, is missing. On the other hand, in methanolic glasses (made from methanol containing a small amount of water, approximately 5%), the matrix, after exposure to ionizing radiation, becomes intensely violet in color and the esr spectrum indicates the presence of the two species which are seen in pulse radiolysis of liquid methanol, the hydroxymethyl radical and the solvated electron, trapped in almost stoichiometric amounts.[45] The assignment of the solvated electron, trapped in the glassy matrix, e_t^-, is confirmed by scavenging experiments carried out in the presence of known electron scavengers: naphthalene, benzene, benzyl chloride, and carbon tetrachloride.[46–49]

Supporting evidence for these assignments has been obtained from absorption spectroscopy.[45] Two distinct absorption bands, each belonging to a different species are observed: one, λ_{max} 533 $m\mu$, belongs to the trapped electron, and the other, which extends into the ultraviolet, belongs to the free radical, CH_2OH; the response of these bands to various treatments parallels that observed for the two species as studied by esr spectroscopy. In passing, however, it should be mentioned that the difference in the absorption spectra observed for the solvated electron in liquid methanol (λ_{max} 650 $m\mu$) and the trapped electron in glassy methanol at 77°K (λ_{max} 533 $m\mu$) can be explained qualitatively in terms of the reorientation of the solvent required to trap the free electron in the solid phase.[37]

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While the evidence for the presence of e_t^- appears to be certain, there has been no evidence for the complementary methanol positive ion, $(CH_3OH)^+$, trapped in the matrix. However, both the trapped electron and the hydroxymethyl radical are formed in approximately stoichiometric amounts, and this suggests that their origin is closely related; indeed, it seems reasonable to assume that the hydroxymethyl radical arises from an ion–molecule reaction, involving an initially formed "hot ion," CH_3OH^+, and that this reaction proceeds as follows.

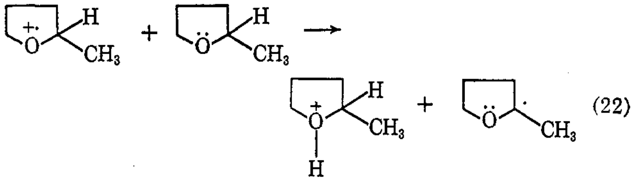
$$CH_3OH^+ + CH_3OH \longrightarrow CH_3OH_2^+ + \cdot CH_2OH \quad (21)$$

Based on this assignment of the reaction products, e_t^-, CH_2OH, and $CH_3OH_2^+$, trapped in γ-irradiated glasses of methanol, the chemistry associated with the production of ethane-1,2-diol and formaldehyde from γ-irradiated solutions of methanol at room temperature[50] and the production of hydrogen and carbon monoxide from the uv irradiation of γ-irradiated methanol glasses[51] can be explained quite simply.[45] Furthermore, this explanation of the origin of intermediates in the radiolysis of methanol can be extended to the observation pertinent to other alcohols,[50-52] and it has been suggested[45] that the reason for the different behavior of compounds of this type, when studied in the crystalline form or in the glassy state, stems from the fact that in the glassy state, there are a larger number of vacancies suitable (but undefined) to accommodate the intermediate species in the glass and these vacancies approximate those of the liquid solvent. As a result, it appears that the localized field of the electrons trapped at vacancies in alcohol glasses is then sufficiently strong to reorient at least some of the O–H bonds in the solvent in order to stabilize the charge,[46] this reorientation being achieved to a greater extent at 77°K than at 4.2°K.[48]

B. SYSTEMS WITHOUT HYDROGEN BONDING

1. 2-Methyltetrahydrofuran

The radiation chemistry of 2-methyltetrahydrofuran (MTHF) is characterized by a sequence of events similar to that observed for water, alcohols, and hydrocarbons; that is, the primary products following excitation correspond to the mobile electron, e_m^-, which is either trapped at a suitable site in the glassy matrix or scavenged, and the complementary positive hole, $(MTHF)^+$.[48,53,54] The positive hole then undergoes the usual ion–molecule reaction to yield the free radical and the cation,[53,55] according to eq 22, the structure of the free radical being characterized by its esr spectrum. Were these events the main features associated with MTHF, then the radiation chemistry of this compound would scarcely warrant inclusion in this review; however, it is the behavior of the trapped electron that is interesting.


(22)

In hydroxylic glasses irradiated at 77°K, the mobile electron is trapped in an environment located within the radiation-produced spur,[39] the immediate environment of the trapped electron being associated with several polarized O–H protons from the solvent.[40] However, in each of the following solvents, MTHF, 2-methylpentene-1 (a representative olefin which is not an efficient electron scavenger but is an effective reagent for H atoms),[56] and 3-methylpentane (a popular solvent used in the study of radiation damage in hydrocarbon glasses), the esr spectrum of the trapped electron, measured at 77°K, is very narrow (*ca.* 5 G)[48,57] in relation to that of the trapped electron in water, ethanol, and methanol (*ca.* 15 G),[39,48] and, from a comparison of the data calculated by Zimbrick and Kevan,[39] it appears that there is very little reorientation of the solvent and very little solvent–electron interaction in the nonhydrogen-bonding solvents.

Furthermore, the thermal decay of the trapped electron in methanol at 100°K proceeds with first-order kinetics with respect to the trapped electrons, a result which implies that either the rate-determining step in this thermal bleaching reaction is the rate at which solvent molecules disorient to give limited mobility to the trapped electron or that most electrons react with ions within the spur in which they are originally trapped.[45] However, in MTHF, thermal decay of the trapped electrons proceeds with second-order kinetics with respect to the trapped electrons,[54] a result which suggests that the mobile electrons so formed may be reacting in pairs with species from spurs other than those of their origin. From these studies and those done in mixed solvents,[58] it appears that the traps formed in each of these solvents are quite specific, though their formal description is still undefined.

2. Saturated Hydrocarbons

From an analysis of a large quantity of data on radiation yields and product analysis, the over-all picture associated with the action of ionizing radiation on saturated hydrocarbons in the gaseous phase appears to be relatively clear and has been reviewed in detail.[59-61]

However, there has also been considerable activity in the study of those chemical reactions which occur at low temperature (77 and 4.2°K) and which contribute to some of the steps associated with the formation of the stable products of radiolysis. Much of this work has been carried out in 3-methylpentane (3-MP), a compound which is easily purified,[48,62] forms very clear glasses when rapidly cooled in liquid air, and is an ideal matrix for both esr and optical absorption studies.[57]

When 3-methylpentane, very carefully purified and rigorously degassed, is γ-irradiated at 77°K, an analysis of the esr

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spectrum at very low incident microwave power[57] indicates that two paramagnetic species are trapped in the matrix: one, the methylpentyl free radical, $CH_3\dot{C}H\cdot CH(CH_3)C_2H_5$, is quite stable at 77°K; the other, characterized as the trapped electron, is thermally unstable at 77°K, with a half-life of *ca.* 25 min, and readily disappears when the matrix is illuminated with near-ir light. The esr signal of the trapped electron is microwave power-saturated very easily.[48,57]

On the other hand, when 3-methylpentane is only degassed incompletely, the esr spectrum of the irradiated matrix at 77°K appears similar to that from rigorously degassed samples, but, on more careful analysis under high resolution, it can be seen that this similarity around $g = 2.00$ is accidental.[57] In addition to the spectrum of the 3-methylpentyl radical, the spectra of two new species are observed: one represented by a doublet, splitting approximately 8 G, the identity of which has not been established; the other, represented by a single line, centered at $g = 2.0008$.

This latter signal is distinguishable from the signal attributed to the trapped electron by the fact that it decays less than 20% per day at 77°K in the dark, is observable up to higher microwave powers, and is not bleached by infrared radiation. In addition, in the presence of added carbon dioxide to the matrix, the intensity of the singlet increases considerably, suggesting that carbon dioxide is scavenging the mobile electrons released in the initial radiation-induced ionizations. Furthermore, these spectra are very similar to those observed by Johnson and Albrecht,[63] who identified the species $CO_2\cdot^-$ as the free radical responsible for the strong singlet, centered at $g = 2.001$, trapped in uv-irradiated matrices of tetramethyl-*p*-phenylenediamine (TMDA) in 3-methylpentane, incompletely degassed or to which CO_2 (and $^{13}CO_2$) was previously added. It appears definite that this free radical is also trapped in γ-irradiated 3-methylpentane prepared under similar conditions and emphasizes that, in systems where the trapped electron is believed to be present as a discrete species, the appearance of a sharp peak at $g = 2.001$ in the esr spectrum is not sufficiently definitive to permit this assignment.

As to the nature of the trapping site in irradiated 3-methylpentane, very little information is presently available. The fact that the esr signal at $g = 2.001$ is very readily microwave power saturated suggests that the interaction between the trapped electron and its medium is very weak, and this is confirmed by photobleaching experiments. In both aqueous and methanolic glasses at 77°K, the wavelength necessary to release the unpaired electron from its trap is approximately 7000 Å, while in 2-methyltetrahydrofuran and 3-methylpentane the threshold necessary for photobleaching is in the near-infrared, 12,000–16,000 Å,[64] the depth of the trap paralleling the interaction of the trapped electron with its medium.[48,53] However, results on the electrical conductivity[62] and on the thermoluminescence[65] of γ-irradiated glasses of 3-methylpentane indicate that there are several discrete energy levels in which both electrons and positively and negatively charged ions can be trapped within the matrix or within a particular spur, while scavenging experiments yield further insight into the nature of charge transfer within hydrocarbon matrices.

Although no direct evidence is available as to the nature of the positive hole formed from 3-methylpentane, *viz.* 3-MP$^+$, in the initial ionization step at 77°K, it can be inferred that this species undergoes both collisional deactivation and intermolecular charge migration through the matrix,[66] the net result being the production of the methylpentyl radical and a cationic species. In the presence of positive-hole scavengers, some interesting facts emerge; for example, when 3-methylpentane glasses containing isopropyl chloride (1%), an electron scavenger, in the presence of benzene (1%) and tetramethyl-*p*-phenylenediamine (1%) (both of which can act independently as positive-hole scavengers), are irradiated at 77°K, both tetramethyl-*p*-phenylenediamine cation radical (Wurster's blue cation), TMDA$^+$ (λ_{max} 950 mμ), and a radical tentatively described as the benzene cation radical, $C_6H_6^+$ (λ_{max} 630 mμ), are trapped in the matrix.[66,67] When this glass is exposed to infrared light, the band corresponding to $C_6H_6^+$ is bleached, whereas the intensity of that due to TMDA$^+$ is enhanced. Since the direct transfer of electronic charge from TMDA to $C_6H_6^+$ is not probable, it appears that charge migration probably proceeds through the solvent cation, 3-MP$^+$, which is then scavenged both by TMDA (to give TMDA$^+$) and Cl^- (formed by dissociative electron capture by *i*-PrCl in the electron-scavenging act), an observation which confirms the feasibility of intermolecular charge transfer through the matrix.

In the presence of solutes which have an ionization potential lower than that of the solvent 3-MP, for example, 2-methylpentene-1 (2-MP-1), the positive hole is transferred to the solute, a reaction which can be formally written

$$\text{3-MP}^+ + \text{2-MP-1} \longrightarrow \text{3-MP} + (\text{2-MP-1})^+ \qquad (23)$$

whereas, in the presence of those solutes whose ionization potentials are greater than or equal to that of the solvent, for example, 2-methyltetrahydrofuran (MTHF), the hole may be scavenged by proton transfer; thus

$$\text{3-MP}^+ + \text{MTHF} \longrightarrow \text{MTHF, H}^+ + \text{radical} \qquad (24)$$

Up to the present, we have stressed the role of charged species in the solid-state radiation chemistry of hydrocarbons, and, while their contribution is important, it should be realized that the results obtained should not be transferred verbatim into the radiation chemistry of liquid hydrocarbons and even extrapolated too far in the evaluation of the radiation chemistry of the solid state. Decomposition from excited states, formed either directly in the primary radiochemical act or by charge neutralization,[60,68] from charge transfer,[69] and from hot-atom reactions[70] are all pertinent to a proper evaluation of the mechanism of radiation damage, especially in hydrocarbons. For instance, in the radiolysis of liquid hydrocarbons at 77°K, as studied by esr spectroscopy,[71] the free radicals so formed probably arise from hot-atom hydrogen extraction reactions, while charge neutralization and energy transfer from subexcitation electrons[2] have been invoked to explain the formation of triplet-excited states of aromatic hydrocarbon so-

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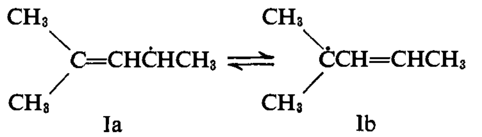
lutes in irradiated cyclohexane solutions.[72] There is still considerable basic work to be done in this area alone.

3. *Olefins*

Because of their relatively low ionization energy,[73,74] olefins have been found to be suitable traps for positively charged transient species in the radiation chemistry of various glasses at low temperature, and they are not generally regarded as electron scavengers.[75] When pure 2-methylpentene-1 (2-MP-1), is irradiated as a glass at 77 °K, the glass is intensely blue in color and the resulting esr spectrum is due to trapped electrons and free radicals, formed in approximately stoichiometric amounts; furthermore, when irradiated in the presence of biphenyl or naphthalene, known electron scavengers, the esr spectrum due to the trapped electron is replaced by that of the solute anion and the glass is colorless.[67,76] However, the ability of 2-MP-1 to act as a scavenger for positively charged species has been demonstrated through absorption spectroscopy.

After γ-irradiation at 77 °K, the absorption spectrum of 2-MP-1 is characterized by a maximum at 18,000 Å, due to the trapped electron, and a shoulder at 6800 Å, which has been assigned[75] to the radical cation (positive hole) of 2-methylpentene-1, $(\text{2-MP-1})^+$; both of these features disappear when the irradiated glass is exposed to light, wavelength 7500–10,500 Å, which mobilizes the trapped electron. Furthermore, upon irradiation of glasses of 2-MP-1 containing either biphenyl or naphthalene (0.05 mole %), the intensity of the 18,000-Å absorption band is reduced and that of the 6800-Å band increases,[75] since there is competition for the mobile electrons between the scavenging solute and the solvent radical cation or species derived from it. Still, the evidence from absorption spectroscopy does not really define the structure of the product which is responsible for this absorption band.

On the other hand, an analysis of the incompletely resolved hyperfine structure of the esr spectrum of the free radical trapped in the 2-methylpentene-1 matrix suggests that the stable moiety complementary to the trapped electron is the allylic radical (I) formed from the trapped positive hole by



Ia Ib

isomerization and a subsequent ion–molecule reaction,[76] according to the sequence

$$\text{2-MP-1} \rightsquigarrow (\text{2-MP-1})^+ + e_m^- \qquad (25)$$

$$e_m^- \longrightarrow e_t^- \qquad (26)$$

$$(\text{2-MP-1})^+ \longrightarrow (\text{2-MP-2})^+ \qquad (27)$$

$$(\text{2-MP-2})^+ + \text{2-MP-1} \longrightarrow \text{I} + (\text{2-MP-1})\text{H}^+ \qquad (28)$$

where $(\text{2-MP-2})^+$ is a positive hole, formally akin to 2-methylpentene-2. This scheme is quite an attractive one, though there are insufficient data available pertaining to the absorption spectra of trapped allyl radicals to comment on the over-all picture, at this stage; suffice it to say that, from a study of the absorption spectra of a variety of monoolefins irradiated in alkyl halide and alkane glasses,[77] it appears that a band intimately associated with the positive-charge scavenging reaction appears in the range 6800 ± 800 Å, and so this problem is definitely worth pursuing.

4. *Alkyl Halides*

Despite careful attempts to prepare glasses of carbon tetrachloride at 77 °K, it has been found that only polycrystalline matrices of pure carbon tetrachloride can be prepared. Despite this, it has been possible to study the radiation chemistry of this compound at 77 °K by absorption spectroscopy and to identify a species, $\lambda_{\max}$ 400 mμ, which is associated with the migration of positive charge through the matrix. This species has been tentatively assigned the structure CCl_4^+,[75,78] and the evidence for this appears reasonable though some recent work suggests that this assignment may be oversimplified.[79] A similar type of intermediate has been identified in irradiated *t*-butyl chloride glasses,[80] though in both of these studies no attempt was made to investigate the fate of the mobile electron released in the primary chemical step. However, it appears reasonable to assume that dissociative thermal attachment (eq 29) occurs.

When glasses of 3-methylpentane containing alkyl halides (10^{-4} *M*) are exposed to ionizing radiation at 77 °K, alkyl radicals, characteristic of the solute, are formed by dissociative thermal attachment,[78] thus

$$e_m^- + \text{RX} \longrightarrow (\text{RX})^- \longrightarrow \text{R}\cdot + \text{X}^- \qquad (29)$$

the alkyl halide, RX, acting as an electron scavenger. However, several metastable species are also trapped in the matrix, though in much smaller concentrations, when alkyl iodides (and alkyl bromides, too) are used as solutes[81–83] (among the products being RI^+, $(\text{RI})_n{}^+$, $(\text{RI}\cdot\text{I})$, I, and I_2^-), indicating that the over-all reaction is quite complex.

In addition, when alkyl iodide matrices are irradiated at 77 °K, the nature of the predominant product trapped in the matrix is determined by the nature of the matrix.[84] When the matrix is in the glassy state, free radicals having esr spectra consistent with C–I bond breaking are stabilized in the matrix at 77 °K, and these are only stable up to about 100–120 °K in these matrices. On the other hand, from the same alkyl halide in the form of a polycrystalline matrix, the esr spectrum is spread over several hundred gauss, centered at $g = 2.00$, and consists of many more lines; the most feasible explanation for this type of spectrum is through the formation of a free radical of the type RCHI, in which the unpaired electron interacts with the α-iodine nucleus, which has a nuclear spin of $^5/_2$ and a high nuclear magnetic moment, 2.794 nuclear mag-

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netons.[85] These radicals are also stable up to the melting point of the matrix (usually *ca.* 200 °K). The mechanism by which these radicals form also operates in the glassy state most likely but is much less important than the halogen-dissociating thermal electron attachment reaction. A possible mechanism for this behavior has been suggested by Voevodskii, though in the absence of satisfactory quantitative work it is best regarded as a tentative proposal.[86]

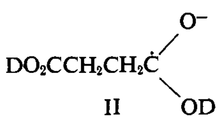
C. SYSTEMS CONTAINING MOLECULES WITH LOW-LYING ORBITALS

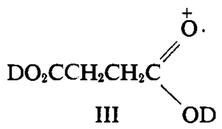
One feature common to all electron scavengers is that they have a relatively high electron affinity because they have empty, low-lying oribtals and yield a thermodynamically feasible anion; in the case of biphenyl and naphthalene, the radical anion itself is stable and has been identified and analyzed by esr and by absorption spectroscopy, the spectral characteristics of the radical anion formed by radiolysis being identical with that formed in dilute solution by standard chemical means.[87] In the case of alkyl halides, RCl, RBr, and RI, the radical anion has only a transitory existence at 77 °K and undergoes subsequent dissociation to more stable products as outlined in eq 29.

On the other hand, efficient positive charge scavengers, such as aromatic amines and olefins, are characterized by relatively low ionization potentials and can thereby accommodate a migrating positive hole yielding the corresponding radical cation by ion–molecule reactions.

In all the discussion thus far, we have directed our attention almost entirely to the radiation chemistry of solvents and solutes in glassy and polycrystalline matrices, as it relates to the characterization of the trapped intermediates. The same principles developed in this discussion also apply to the radiation chemistry of single crystals, and in this field the techniques of electron spin resonance spectroscopy have thrown considerable light. Most of the work that we shall discuss concerns the primary, chemically relevant radiation damage to organic compounds from which single crystals have been readily obtained (dicarboxylic acids, amino acids, and some sulfur-containing compounds), though these techniques have also been applied to inorganic systems. The structures of the free radical(s) initially formed have been identified from nuclear hyperfine interactions and from *g*-tensor analyses.

When succinic acid, recrystallized from deuterium oxide, is irradiated in the single crystal form at 4.2 °K,[88] the esr spectrum of the sample consists of two components: a four-lined spectrum, attributed to the negative ion II, which is stable up to temperatures greater than 77 °K, and a singlet peak, which is unstable at 77 °K and which shows a large variation in *g* value, suggesting that the unpaired electron is localized on oxygen; this singlet peak is ascribed to the positive ion radical III, or its resonance hybrid.


II


III

Evidence for the validity of the assignment of the four-lined spectrum to the radical anion II comes from a detailed analysis of the esr spectrum from C^{13}-carboxyl-enriched succinic acid irradiated at 77 °K[89a] and, more recently, from the very close similarity observed between the C^{13} and H esr hyperfine splitting components found from this species and those from "authentic" radical anions of selected carboxylic acids and esters, as prepared by the deposition of sodium atoms on films of these carbonyl compounds at 77 °K on a rotating cryostat drum.[89b] From the *g*-tensor analysis of the product from irradiated succinic acid at 77 °K, it appears that the unpaired electron is located in an orbital which has considerable p_π character and which lies in a plane which corresponds very closely to that of the C $2p_\pi$ orbital of the carbonyl group in the undamaged molecule. This suggests that only a minimum spatial rearrangement occurs around the carboxylic C atom. More definitive evidence comes from the analysis of the C^{13} hyperfine splitting tensor. This tensor is axially symmetric, and the isotropic part of the splitting which arises from the electron density at the carbon nucleus is 112 G (314 MHz, not 93 MHz as quoted in Table I of the original reference[89a]). The hyperfine splitting which would be observed if the unpaired electron were wholly in the carbon 2s orbital has been calculated to be in the range 1110 (3110 MHz) to 1180 G (3300 MHz),[42,89,90] the small variation arising from the type of wave function chosen to describe the orbital under consideration; hence, the spin density in the 2s state on the carbon atom bearing the unpaired electron in the free radical II is in the range 112/1110 (=0.101) to 112/1180 (=0.095), indicating that some rehybridization at the now-damaged carboxyl group in the original molecule has occurred. Were the radical center in a completely reoriented pyramidal sp^3 electronic configuration,[91] the per cent of s character associated with the spin density on carbon would have been 0.25; this suggests that, in the present instance, only partial reorientation occurs at 77 °K.

When the sample is allowed to warm up to room temperature, a further reaction or a rearrangement occurs and the structure of the free radical trapped in the crystalline matrix is the neutral free radical IV. The mechanism of this change

$$DO_2CCH_2\dot{C}HCO_2D$$
IV

is still to be worked out; however, in several cases, different stages in the transformation are discernible and these have been pointed out elsewhere.[92–97]

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Since this investigation, several other instances for ionic intermediates trapped in irradiated carbonyl derivatives at low temperature are recognizable in the earlier literature and, at the same time, extension of this work to other compounds has become topical.

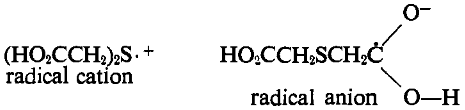
Thus, contributions from the esr spectra of the radical anion $R\dot{C}(O^-)OH$ can be recognized among the spectra of several polycrystalline amino acids, irradiated at 77°K,[98–101] while detailed single-crystal studies have also been carried out on the radical anions from glycine[94] and alanine.[92,93] Radical anions of this type have also been recognized in the esr spectra of cyclohexane-1-carboxylic acid, irradiated at 4.2°K,[102] and various 2-substituted malonic acids,[103] irradiated at 77°K, while a reinterpretation of the low-temperature spectra[103] from irradiated polycrystalline glycolic acid[104] indicates that this type of radical is also formed in irradiated hydroxy acids. The broad doublet observed at 77°K in X-irradiated single crystals of urea oxalate[105] most likely corresponds to that from the radical anion from oxalic acid, while from the ammonium salt of trifluoroacetic acid[106] the esr spectrum at 77°K corresponds to that of the radical anion $CF_3\dot{C}(O^-)OH$. Nevertheless, caution should be applied in extending these results too glibly; one recent report,[107] which claimed that the free radical trapped in (hydrated (?)) sodium acetate after irradiation at 77°K was, in fact, the radical anion $CH_3\dot{C}(O^-)_2\ Na^+$, is obviously in error when considered in the light of more detailed studies, using C^{13}-labeled compounds.[108] The free radical observed in this study is the methyl radical, $CH_3\cdot$.

For many instances, however, it should be mentioned that only the radical anion has been identified[89] from an analysis of the esr spectrum from irradiated carboxylic acids at low temperatures. However, in nearly all these cases, subspecies[89,96,97] which correspond to either the positive hole or to free radicals derived from it can be recognized or their presence inferred from the distorted line widths which are sometimes seen in the spectrum of the radical anion. Hence, it appears that the general picture of radiation damage, presented in the earlier section, applies to that observed in irradiated carbonyl compounds as the single crystals.

Nevertheless, these are not the only organic compounds in which ionic intermediates have been trapped at low temperatures and identified by esr techniques. Several sulfur-containing compounds have recently been studied and the results obtained have been quite interesting, not only in view of the role of disulfides and thiols in radiation biology but also because of the distribution of the unpaired electron within the bonding framework provided by the sulfur atom.

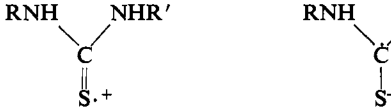
When the disulfides, cystine dihydrochloride[10,109] and dithiodiglycolic acid,[110] are irradiated at 4.2°K, both positive and negative ions are trapped in the crystal in stoichiometric amounts, the unpaired electron in the anion being in a σ^* (3p) molecular orbital embracing the disulfide bond, while the unpaired electron in the cation occupies the σ (3p) bonding molecular orbital. On warming, neutral free radicals of the type $R{-}CH_2{-}S\cdot$, having characteristics similar to those observed in the parent compound irradiated at room temperature, are formed.[111]

When thiodiglycolic acid, $S(CH_2CO_2H)_2$, is irradiated at room temperature, the free radical formed corresponds to that of the structure[112] $HO_2CCH_2S\dot{C}HCO_2H$. Similar free radicals of this form, $R'S\dot{C}HR$, are observed in other irradiated sulfides, for example, diethyl sulfide,[113] di(*n*-hexyl) sulfide,[113] and methionine.[114] However, when thiodiglycolic acid is irradiated at 4.2°K,[115] the esr spectra and endor spectra can be analyzed in terms of two free radicals



the thermalized electron being trapped on the most electronegative center[116–118] in the undamaged trapping molecule, the carboxylic acid group. This result is consistent with our notion that the most efficient electron scavengers have accessible, low-lying orbitals in which to accommodate the stabilizing negative charge.

The importance of the low temperature needed to stabilize the trapped ionic species is borne out in the case of irradiated thioureas.[119] When representative thioureas, which can assume a planar conformation in the crystal lattice, are irradiated at 77°K, no esr signal is observed. However, when these compounds are irradiated at 4.2°K, the esr spectra of both the positive and negative ions, which can be formally written as



a, R = H; R′ = H
b, R = CH_3; R′ = CH_3
c, R = allyl; R′ = H

are resolvable. It is on the basis of the behavior of the *g* values with changes in crystal orientation that the two species can be assigned. The *g* values of the positive ion are markedly anisotropic, having their minimum value near the free spin value of *g* and in the direction of the C–S bond;[109] on the other hand, the *g* values of the negative ion are approximately isotropic and centered around $g = 2.003$, and this behavior is consistent with that predicted for both species.[110]

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The same principles applied to the study of organic crystals at low temperature have also been applied to inorganic crystals, and the same results are obtained: species corresponding to the positive hole (or radical cation) and to the electron acceptor (or radical anion), or to species derived from them, are trapped in the crystalline matrix. All of the free radicals are identified by electron spin resonance spectroscopy.

When silver nitrate is irradiated at 77°K, Ag^{2+} and $AgNO_3^-$ are identified as the primary products;[120] when potassium nitrate is irradiated at 4.2°K,[121] NO_3 and NO_3^{2-} are trapped in the matrix, along with species NO_2^{2-}, NO_2, O, and NO, which can be derived from them. The radical ions, CO_3^- and CO_3^{3-}, obtained from single crystals of X-irradiated calcium carbonate at 77°K, are further examples of the type of radical pairs which can be trapped;[122] both species are formally radical anions, one being electron deficient and the other being electron rich with respect to their normal valencies.

Irradiation of single crystals of sodium sulfate decahydrate and of sodium thiosulfate pentahydrate[123] at 77°K yields, among the free radical products, the corresponding positive hole anions, SO_4^- and $S_2O_3^-$, each identified by the relation of its g tensor to the crystal structure of the undamaged parent molecule, an interesting result as it appears that, when lithium sulfate monohydrate is irradiated at 77°K,[23] the hydroxyl radical from the water of crystallization is the species formed.

Just recently, a comprehensive text[42] on the structure of inorganic radicals as studied by the techniques of esr spectroscopy was published, and the interested reader is referred to this text to supplement the content of this review as it pertains to this subject.

IV. Conclusion

From the application of techniques which enable one to identify reactive intermediates and, in some cases, to follow their reactions, a considerable amount of information has been obtained on the mode of breakdown of various irradiated molecules over the last few years. While a general pattern of behavior is slowly emerging, there is still much to be done, not only in unambiguous characterization of many of the intermediates postulated but also in the study of modes of excitation in the primary radiation process,[2a] in energy-transfer reactions,[68-70] and in ion–molecule reactions[124-126] in the gaseous phase, in solution, and in the solid state. In many instances, the reaction pathways postulated in radiation chemistry are really quite speculative in the sense that they are invoked to explain possible or probable reactions which can lead to the observed products; an example of this is that found in the sequence, eq 16–18, *inter alia.* The mechanistic implications of many of these proposals still remain to be tested. This is especially applicable for those reactions which involve the primary chemical species formed following excitation.

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