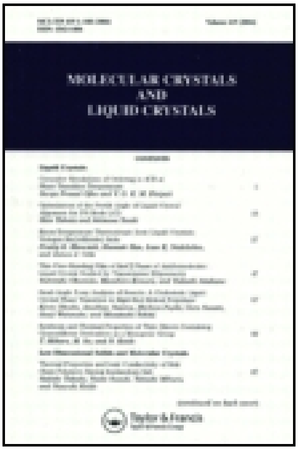

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Generation and Study of Reaction Intermediates in Organic Solids

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Generation and Study of Reaction Intermediates in Organic Solids

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Abstract—This paper reviews: (1) methods by which bond rupture, and ionization, can be produced in organic solids; (2) methods of detecting trapped reaction intermediates; (3) illustrative experiments dealing with the yields and the decay of trapped electrons and free radicals. Factors to be considered in deciding whether trapped electrons and radicals decay by random reaction with potential reacting partners, by combination with sibling partners, or by combination with other predestined partners are discussed. It is shown that radical decay rates do not show consistent correlation with viscosity.

1. Introduction

It is my assignment this morning to review some of the ways in which chemical bonds can be broken in organic solids, the nature of the reactive species formed, conditions controlling their trapping, and the present state of knowledge as to the mechanisms of their removal.

To the chemist concerned about the mechanisms of reactions of organic free radicals and ions, organic solids offer a means to an end. They allow otherwise transient species to be trapped and studied at leisure. In turn the chemical events may be revealing as to charge migration, diffusion and relaxation processes of the matrix. This paper seeks to give a perspective on the present state of such investigations.

The references presented are illustrative; they are not meant to provide a comprehensive coverage of the literature. Further information may be found in two recent review chapters.[2,3]

2. Production of Reaction Intermediates

GENERAL

As in gases or liquids, the production of radicals or ions in organic solids depends on delivering energy in excess of the binding energy to a chemical bond or an electron in a molecule. Most organic compounds melt at temperatures too low for thermal activation to cause significant bond rupture. Therefore to dissociate such molecules in the solid state, it is necessary to inject energy in the form of photons or particles capable of penetrating appreciably into the solid, but having a significant absorption coefficient. The most commonly used radiations which meet these criteria are visible, ultra-violet, X-ray and γ-ray photons, high energy electrons, and neutrons. Examples to illustrate the types of fragmentation they initiate are given in Figs. 1–4.

BY PHOTOLYSIS

Photochemical bond rupture in the solid state is severely limited by the cage effect,[21] i.e. recombination of the fragmenting partners is favored by the fact that their escape from each other is hindered by the close-packed surrounding molecules. This effect is greater the larger and heavier the fragments. Even with H atoms with 1–2 eV of kinetic energy, produced by absorption of a 2537 Å photon by HI in 3-methylpentane (3MP) glass at 77 °K (Fig. 1), it reduces the quantum yield from unity, as found in the gas phase to about 0.3, of which 0.2 results from attack of the hot H atoms on molecules in the cage wall and only 0.1 is attributable to thermalized atoms which escape the parent cage.[4,5] Conservation of momentum requires that the H atom from HI carry nearly all of the kinetic energy in excess of that required for bond rupture. Thus H-escape from HI is a particularly favorable case. Attempts to observe ethyl radicals from the photolysis of C_2H_5I and 3-methylpentyl radicals from the photolysis of each of the four 3-methylpentyl iodides by photolysis of either the pure glasses or their dilute solutions in 3MP at 77 °K have given negative results,[9,22,23] but the methyl radical esr signal has been detected following photolysis of CH_3I in 3MP[6]. Although photolysis of an iodide in an organic matrix does not (except in the case of CH_3I) produce trapped radicals

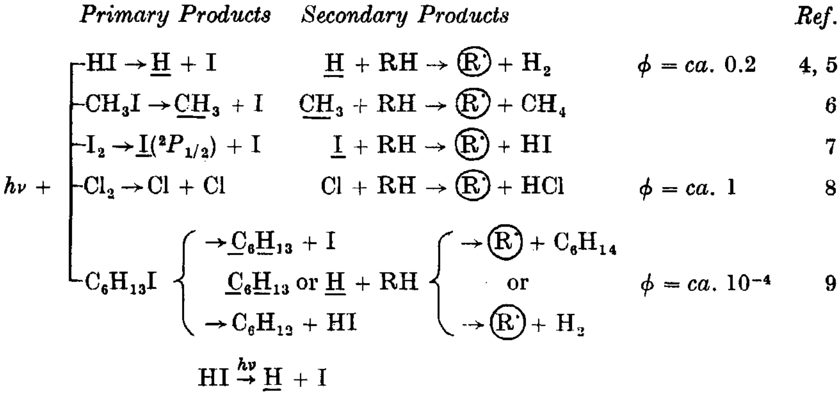

Figure 1. Examples of primary and secondary products from photolytic bond rupture of solutes in a solid hydrocarbon matrix.

Underlined species are " hot ", i.e., born with energy in excess of thermal equilibrium energies. Circled species have been observed experimentally. The primary products of bond rupture are shown in the parentheses.

derived from the iodide, it does produce, in low quantum yield, radicals formed by abstraction of H from the matrix. These must result either from hot radical reactions or from photolysis of HI which has been formed from the iodide (Fig. 1, $C_6H_{13}I$ example).

By Photoionization and Photosensitization

Photoionization of various amines[10,24] (Fig. 2) and other organic

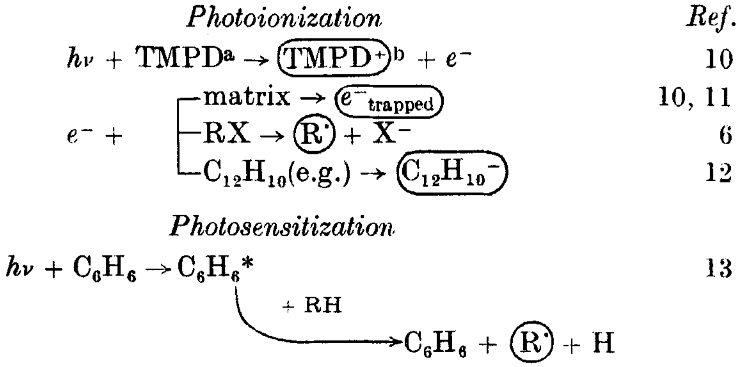

Figure 2. Examples of primary and secondary products from photoionization and photosensitization in organic solids.

[a] N,N,N′,N′-tetramethyl-p-phenylenediamine.

[b] Circled species have been observed experimentally.

compounds can be caused by near ultraviolet light. It is a convenient method of producing electrons and known cations in an organic matrix. Such electrons may be physically trapped,[10,11] cause dissociative capture by additives such as alkyl halides[6] or form anions by attachment to additives such as biphenyl.[12]

Light absorbing solutes which are not themselves decomposed by the radiation absorbed (of which benzene is given as an example in Fig. 2) are often able to transfer their energy, causing decomposition of matrix molecules or other solvent molecules.[13]

By Ionizing Radiation

The production of reaction intermediates by photolysis, photoionization or photosensitization, as discussed above, requires an organic matrix or solute with a significant absorption coefficient for UV or visible radiation in an energy region capable of causing bond rupture. By contrast, ionizing radiation (X-rays, γ-rays and energetic charged particles) is not discriminating. To a good approximation the amount of energy deposited per gram of material is proportional to the number of electrons per gram and independent of the nature of their chemical binding (except for the dependence on atomic number for absorption of electromagnetic radiation by the photoelectric effect and pair production).

Varied sources of ionizing radiation are available including naturally radioactive elements, synthetic radioactive isotopes, X-ray machines and particle accelerators. For production of intermediates in a solid it is commonly desirable to use radiation sufficiently penetrating so that the density of energy deposition does not vary greatly through the mass of the sample. Except for very thin samples, this excludes alpha particles from naturally radioactive sources, and low energy beta particles such as those from ^{14}C, and ^{3}H (unless the radioactive atoms are dispersed throughout the sample). A much used and convenient type of radiation is the γ radiation (1.1 and 1.3 MeV) from ^{60}Co. This has an absorption half-thickness of about 11 g/cm^{-2}. It is absorbed predominantly by Compton scattering, which is not influenced by atomic number.

Figure 3 depicts the types of events which occur as a result of γ-irradiation of a solid hydrocarbon, with or without a solute.

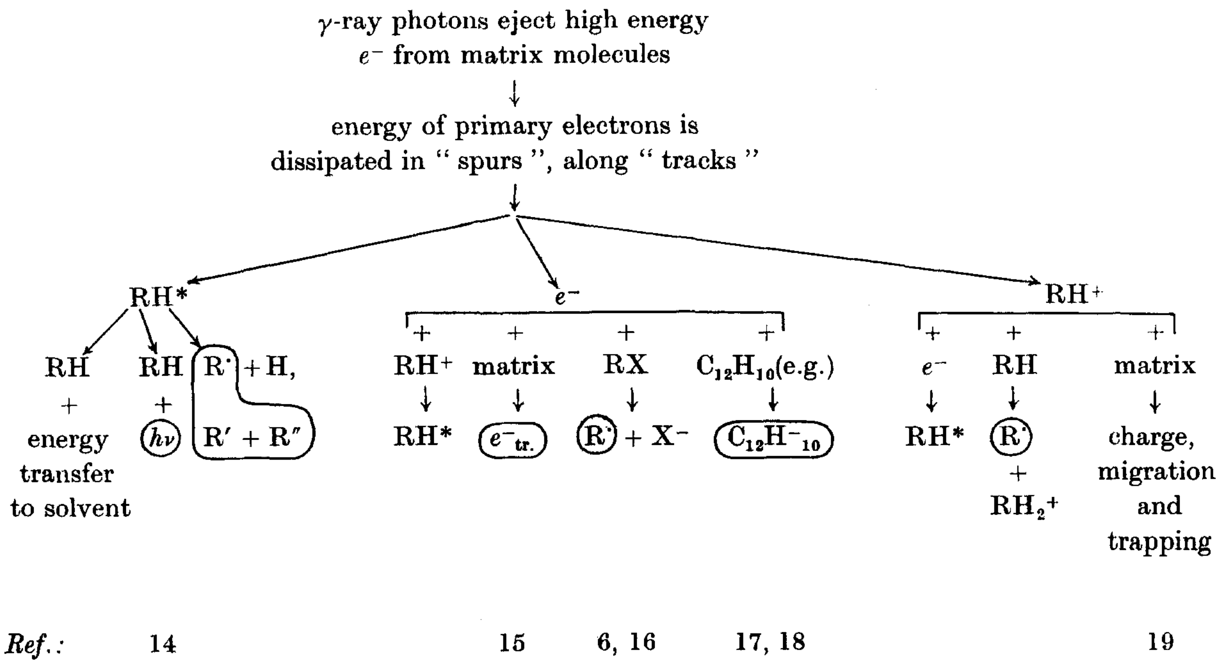

Figure 3. Examples of primary and secondary products from radiolysis of solid hydrocarbon. Circled species have been observed experimentally.

A large fraction of the γ rays pass through the sample unaffected. Each photon which interacts gives a substantial fraction of its energy to the electron ejected (about 500,000 eV on the average for a 1 MeV γ ray), with the remainder being carried by the scattered γ ray. This event forms only one ion-pair. Approximately 15,000 more are formed by the subsequent processes in which the high energy electron (primary electron) imparts energy to the electrons of molecules along its track, ejecting secondary electrons (of about 100 eV energy) which, in turn, eject several more electrons. In the course of these events an amount of energy approximately double that expended in ionization is expended in excitation of molecules without ionization. The ionization and excitation occurs along the " track " of the primary electron in " spurs " caused by the secondary electrons. These small regions of the order of tens of angstroms radius have a much higher concentration of excited and ionized species than the average of the medium.

G (ion pairs)[25] in gas phase radiolyses, measured by ion collection techniques, is about 3 for most materials. The primary ion pair yields in condensed states are presumably the same but G(e^-) in liquid hydrocarbons is only 0.1–0.2[26] as determined by electrical conductivity methods. This lowering of the observable ion-pair yield results from the fact that in condensed media electrons are slowed to thermal energies at a distance from their sibling positive ions such that the energy of coulomb attraction exceeds thermal energies and prompt recombination may occur.[27] In a variety of non-polar organic solids G($e^-{}_{\text{trapped}}$) has been demonstrated to be 0.5 to 1[28] and values as high as 2.6 have been reported for 2-methyltetrahydrofuran,[29] indicating that the solid matrix has the ability to stabilize the electron against recombination. As indicated in Fig. 3 free radicals may be formed by dissociative electron attachment reactions with solutes, and anions by stable attachment to other molecules. These processes compete with neutralization and physical trapping.

The positive hydrocarbon ions, which do not undergo prompt neutralization may be trapped at the site of formation or may undergo charge transfer by electron transfer or by proton transfer until neutralization occurs or a stable trapping site is found.

Molecules formed in excited electronic and vibrational states

(RH* in Fig. 3) may dissipate energy as thermal energy to the solvent, rupture bonds or lose energy by photon emission.

By Neutron Irradiation

Fast neutrons (Fig. 4) give energy to organic media by collisions with H atoms. These, when projected with high energy, become ionized, and thereafter lose their energy primarily by coulombic interactions. The velocity of a proton is much less than that of an electron of equal energy and hence the density of ionization and excitation along its track is much greater, thus increasing the probability of prompt combination of fragments, and increasing the " temperature " in the track.

Fast neutrons

$n + \mathrm{RH} \rightarrow \mathrm{R}^{\cdot} + \text{fast } \mathrm{H}^{+}$

↓

track of high density
ionization and excitation

Thermal neutrons[20]

$n + \mathrm{I}^{127} \rightarrow \mathrm{I}^{128} + \gamma$

I^{128} (1) has high kinetic energy from recoil;
(2) emits cascade of low energy Auger electrons producing " hot spot " of dense ionization and excitation

$n + \mathrm{U}^{235} \rightarrow$ fission products with high kinetic energy

↓

high density of ionization and excitation

$n + \mathrm{Li}^{6} \rightarrow \mathrm{He}^{4} + \mathrm{H}^{3}$, both with high kinetic energy

↓

high density ionization and excitation

Figure 4. Activation by neutrons

Thermal neutrons can impart chemically effective energy to a system only indirectly, by undergoing a nuclear reaction. Three examples of such processes are given in Fig. 4. They are of specialized usefulness when it is desired to produce ionization and excitation with a particularly high density in small " hot spots ". The energies per event for the (n, γ), fission and (n, α) processes listed are of the order of 10^2, 10^8 and 10^5 eV respectively.

3. Observation of Reaction Intermediates By Electron Spin Resonance

ESR has proved a valuable tool for the detection, identification and determination of yields of reaction intermediates in organic solids when these have unpaired electrons. As an example, Fig. 5 shows the esr spectrum from γ-irradiated 3-methylpentane glass at 77 °K. The low 6-peak signal is given by the sec-3-methylpentyl[9] radical and the sharp singlet by the trapped electron.[28a]

In the solid state esr line widths are usually broadened. This often obscures hyperfine splittings and lessens the possibility of unique identification of species. In some cases (e.g. I atoms) the broadening is so great that the signal is completely lost. When two or more radicals are present in approximately equivalent quantities, it is difficult to distinguish the species unless the signals are of much different width, or have much different rates of decay. When the radicals are generated from two different molecular species

Figure 5. ESR spectrum of 3-methylpentane glass following γ-irradiation at 77° K. Center singlet is the trapped electron signal. Six-line signal is the sec-3-methylpentyl radical spectrum.

in a solution, use of the deuterated form of one of them, causing it to yield a radical with much narrower signal, can be of value. In many systems of interest a single radical predominates and the above difficulties are of minor importance. In a few systems esr line saturation characteristics have been used to estimate the proximity to each other of reaction intermediates with unpaired spins.[30, 31]

By UV-Visible-Infrared Absorption

Trapped electrons in alcohols, methytetrahydrofuran and 3-methylpentane show broad absorption peaks which shift in the red direction with decreasing polarity, that for CH_3OH being at 5250 Å and that in 3MP at 16,000 Å.[15j] Free radicals do not in general show absorption at accessible optical wave lengths, but a 0.1 mole fraction solution of C_4H_9I in 3MP glass which has been gamma irradiated at 77 °K gives the series of peaks illustrated in Fig. 6. These are believed to be due to ions and charge transfer complexes.[19c,19d] Scavengers for positive charge and for negative charge have been used in determining which peaks are caused by positively charged species and which by negatively charged.

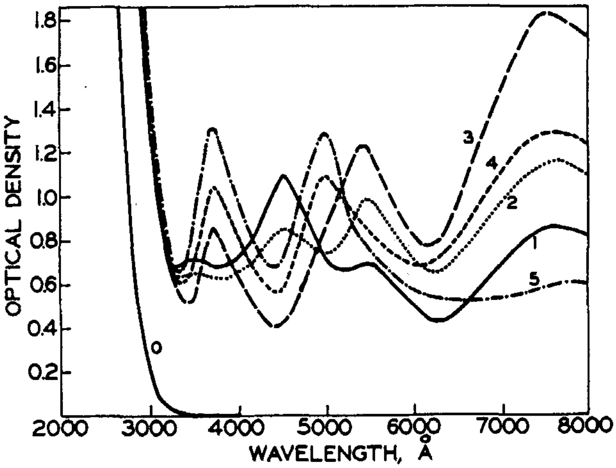

Figure 6. Spectra of γ-irradiated n-C_4H_9I in 3-MP at 80 °K as a function of time after irradiation: (0) before irradiation, (1) immediately after irradiation, (2) 10-min standing at 80 °K, (3) 30-min standing at 80 °K, (4) 120-min standing at 80 °K, (5) 400-min standing at 80 °K. $[n\text{-}C_4H_9I] = 1.1 \times 10^{-2}$ mf; dose $= 1 \times 10^{19}$ eV g^{-1}. (See reference 19c.).

By Electrical Conductivity

A plot of electrical conductivity vs. temperature following γ-irradiation of an organic solid shows the temperature at which trapped charges become mobile. It is thus capable of distinguishing between populations of charge carriers which are present in traps of different depths.[32] When such experiments are carried out with electron scavengers present during irradiation, they are capable of determining whether each charge population consists of electrons or of heavy ions. Variations in the concentration of scavenger give information on the distance electrons travel before trapping. Measurements of photo-induced conductivity of γ-irradiated matrices[31] and matrices where electrons have been released by photoionization of solutes can also be informative.[10]

Measurement of electrical conductivity *during* γ-irradiation is complicated by the ionization of air and insulation. It should be possible to avoid this difficulty by using tritiated samples undergoing self-irradiation.

By Luminescence

Luminescence accompanies the combination of electrons with positive ions during warming of γ-irradiated organic matrices. Its onset as a function of temperature can, like electrical conductivity, yield information on the presence of different types of trapping sites.[14] In another kind of experiment the direction of polarization of luminescence resulting from neutralization of $TMPD^+$ following photoionization with polarized light has been used to seek information on whether electrons return to their sibling partner ions.[33]

There would be interest in determining the intensity of luminescence, if any, due to the prompt neutralization processes which occur *during* γ-irradiation of samples, and there is preliminary evidence that it can be measured. Care must be taken to use exciting radiation of sufficiently low energy to avoid the production of Cerenkov radiation.

By Analysis for Stable Products

Some types of chemical processes in organic solids are detectable only by deducing them from final products found on analysis after melting or dissolving the sample. Thus the production of CH_4 when electrons are generated in a dilute solution of CH_3I in 3MP at 77 °K indicates that some of the CH_3 radicals produced by dissociative electron capture ($CH_3I + e^- \rightarrow CH_3 + I^-$) attack the solvent, abstracting H in a hot reaction.[16b] The fact that the hydrogen produced by the radiolysis of $CH_4 - CD_4 - Ar$ mixtures at 20 °K is primarily H_2 and D_2 requires the process $CH_4 \rightarrow CH_2 + H_2$.[34] The production of $CD_2HCD_2CD_2H$ from the radiolysis of cyclopropane-d_6 in 3 MP, and the increase of the yield by electron scavengers, is strong evidence for the reaction $C_6H_{14}^+ + (CD_2)_3 \rightarrow C_6H_{12}^+ + C_3D_6H_2$.[35]

4. Some Current Knowledge About Reaction Intermediates Produced by Radiation in Organic Solids

The purpose of this section is to indicate some emerging generalizations about radiation-induced reactions in organic solids. Illustrative examples will be given, with no attempt at comprehensive coverage. Many unsolved problems and significant observations not mentioned are reviewed elsewhere.[2,3]

CHARGE TRAPPING

Infrared absorption spectra, esr spectra, electrical conductivity and luminescence all reveal the presence of physically trapped electrons in γ-irradiated organic glasses at 77 °K.

The wavelength threshold for photobleaching of trapped electrons (i.e. for neutralization of ion pairs) in 3MP is 0.7 eV[36] or greater and that in MTHF is 1.4 eV.[29a] However, substantial thermal decay at 77 °K occurs within a few minutes in the dark and decay is complete within a few hours.[29a,29c,36] It appears, therefore, that there is a lower energy pathway for spontaneous thermal neutralization of ion pairs than for photoactivated neutralization. If the thermally activated process required 0.7 eV or more, spontaneous decay at 77 °K would require years.

Extensive evidence indicates that 50% or more of the electrons trapped in γ-irradiated 3MP or MTHF glass at 77 °K are in sufficiently close proximity to a positive ion so that when they are released from their traps either thermally or by absorption of light they are unequivocally committed to combining with that particular partner.

Convincing proof is that the initial decay rates are directly proportional to the γ-dose received rather than to the square of the dose.[29a,29c,36] When normalized for the dose, the decay curves are superimposable for the first 50% of decay or more. Thus the decay of each electron is by a process which is independent of the number of positive charges in the system. Further proof of this conclusion is the fact that the quantum yields (electrons removed per photon absorbed) for photobleaching of the electrons are independent of γ-dose over the ranges tested in both 3MP and MTHF glasses.[2,29a]

Although at least the first 50% of the e^- decay curves in γ-irradiated 3MP or MTHF show rates which are superimposable if normalized for dose, the decay is not exponential as required for a single type of first order decay. This indicates that there must be many configurations of ion pairs (space-wise or solvation-wise) with varying probabilities per unit time of mutual neutralization of the partners. We term this " composite " first order decay.

The fact that a trapped electron in one of the γ-irradiated glasses is predestined to combine with a particular positive ion, rather than randomly, does not require that it combine with its geminate partner, or even with an ion from the parent spur. Evidence on the effectiveness of scavengers in competing with traps for the electrons which would otherwise be trapped suggest that, on the average, these travel hundreds or thousands of molecular diameters before trapping. As little as 0.1% of various additives is sufficient to capture all the electrons that can be detected by any one of the several methods of observation,[29a,29b,31,32,36]

As a working model[3] it is envisioned that, in non-polar hydrocarbon glasses, trapping occurs at an imperfection in the matrix which is favorable in size and geometry for stabilization by a cage of induced dipoles. Positive charge which can migrate[2] from its point of origin by electron transfer or proton transfer becomes trapped adjacent to the electron in a similar polarized cage. The threshold energy for photochemical bleaching is that required to transfer the electron to the positive charge over the potential barrier of the dipole cages. Thermal decay at 77 °K results from chance thermal reorganization of the matrix molecules (coupled with the influence of the coulomb attraction) giving a lower energy pathway for the neutralization of the ion pair. It is noteworthy that search for trapped electrons in γ-irradiated polycrystalline hydrocarbons at 77 °K has thus far given negative results.

A question of interest is whether the electron in a hydrocarbon glass may be trapped by " digging its own hole ", i.e. by orienting a cage of induced dipoles around itself at random in the matrix, or whether trapping can occur only at a limited number of sites of a specialized type frozen into the matrix on cooling. Recent evidence[15j,37] indicates that in three glassy hydrocarbons tested (methylcyclohexane, 3-methylpentane, and 3-methyloctane) the matrix contains only a limited number of trapping sites. In these matrices the concentration of electrons increases with increasing γ-dose, passes through a maximum, and then *decreases*. This is contrary to the expectation that the concentration should reach a steady state at which the rate of thermal and " radiation catalyzed " neutralization of ion pairs is equal to their constant rate of production. It seems to indicate (1) that the number of trapping sites is limited; (2) that electrons trapped in these sites are vulnerable to reaction with some product of the irradiation; (3) that when such reaction occurs the site is either removed or remains occupied in such a way that it cannot trap another electron. It is suggested that H atoms may react with the trapped electrons producing H^- ions which preempt the traps. In MTHF glass at 77 °K, which is a more polar matrix than the hydrocarbons, the electron concentration reaches a plateau with increasing dose but does not decrease up to doses several times those at which the maxima appear with the hydrocarbons.

FREE RADICAL REACTIONS

(a) *Production; Selectivity of Bond Rupture.* Extensive exploratory investigations have been made of the production of free radicals in solid organic matrices by γ-irradiation. It is established, for example, that all of the glassy alkyl halides and some of the polycrystalline halides yield predominantly the radical which results from rupture of the carbon-halogen bond.[38,39,40,41] The polycrystalline iodides with even number of C atoms do not yield significant amounts of this radical but give an esr signal indicating an iodine-containing radical.[39,40,41]

γ-Irradiation of straight chain paraffin hydrocarbons[42,43,44] and doubly branched hydrocarbons[42] at 77 °K produces mixtures of radicals whose overlapping esr spectra make identification difficult. By contrast, the glasses of singly branched hydrocarbons which have been γ-irradiated at 77 °K yield a single predominant radical.[9,22] When branching is in the 3 position, the radical formed is that resulting from loss of an H atom from the secondary position nearest the end of the longest chain. Quite surprisingly, the same radical is selectively formed by attack by hot H atoms or hot radicals, when these are produced by photolysis of HI[45] or RI in the matrix.[9,22] Hot radical attack on 3MP in the gas phase[46,47] is much less selective; it produces nearly equal numbers of radicals resulting from attack on the primary, secondary and tertiary bonds. It therefore appears that the steric constraints on the singly branched hydrocarbon molecules in glasses at 77 °K significantly alter the relative vulnerability of the various bonds to attack and rupture.

Processes to be considered as the source of free radicals in γ-irradiated hydrocarbons include: (1) $RH^* \rightarrow R^\cdot + H$; (2) $RH^+ + RH \rightarrow R^\cdot + RH_2^+$ and (3) $RH^+ + e^- \rightarrow R^\cdot + H$. New evidence, available as this manuscript goes to press[48], indicates that H atoms (processes (1) and (3)) are not produced in the radiolysis of solid hydrocarbons. It has previously been shown[16b] that process (3) does not occur when trapped electrons are released by thermal or photobleaching of γ-irradiated 3MP at 70°K, and that the yield of 3-methylpentyl radicals is the same with or without an electron scavenger present.

(b) *Yields.* In those cases where radical yields from the γ-irradiation of hydrocarbons in the liquid phase have been compared with those in the glassy state at 77 °K the latter are lower. Thus G (radicals) from the radiolysis of 3MP glass is about 1.6[16b], whereas G values of 6 to 10 are observed for radical production from liquid hydrocarbons.[49]

G(R) from dissociative electron capture ($RX + e^- \rightarrow R^\cdot + X^-$) by dilute alkyl halide solutes in γ-irradiated hydrocarbon glasses increases with increasing RX concentration up to about 0.8 mole %, and then remains constant, indicating that all the electrons which can be captured in competition with prompt recombination are captured at this concentration. $G(R^\cdot) = G(e^-$ that can be captured) = 1.1 in 3MP.[16b]

(c) *"Radiation-Catalyzed" Removal of Radicals.* The rate of growth of concentration of radicals and other intermediates produced by γ-irradiation of organic solids frequently decreases with increasing dose until a plateau is reached where the rate of removal of radicals is equal to the rate of production. The rate of thermal decay of the radicals observed after termination of the radiation is often very slow compared to the rate of production during irradiation, which is known from the initial slope of the growth curve. These facts require that trapped radicals must be activated to recombine by energy deposited in the matrix at some distance from the radicals. They are illustrated and discussed elsewhere.[50,51]

(d) *Thermal Decay of Radicals.* When methyl radicals are produced from CH_3Cl, CH_3Br, CH_3I, or CD_3Br in 3MP glass at 77 °K by dissociative electron attachment using either electrons from photoionization of TMPD or from γ-radiolysis, 90% or more decay by a pure first-order exponential process (Fig. 7) with a 16 min half-life.[6] This is also true for CH_3 formed by the photolysis of CH_3I with 2537 Å radiation.[6] Decay does not occur by abstraction of H atoms from the hydrocarbon matrix. This is precluded at this temperature by activation energy requirements. Its absence is verified

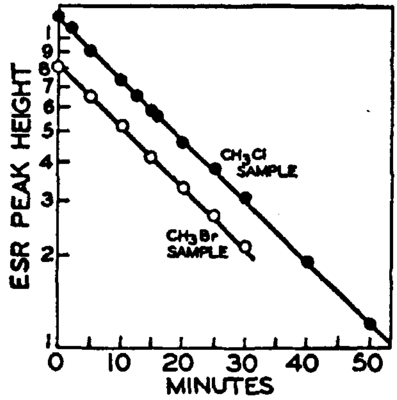

Figure 7. Log (esr. peak height) *vs.* time for decay of methyl radicals. Points show the observed peak height minus the long-lived background: ●, radicals from irradiation of 3-MP-TMPD-CH_3Cl; ○, radicals from irradiation of 3-MP-TMPD-CH_3Br. (See reference 6.)

by the fact that 3-methylpentyl radicals are not produced as the methyl radicals disappear. It appears that each CH_3 radical must be caged in the parent-solvent envelope with its sibling partner (X^- or I), and predestined to combine with it, uninfluenced by the presence of other radicals in the system. The lifetime of minutes for the recombination of reactive fragments must result from constraints on the CH_3 radical by the matrix which prevent the radical from gaining the configuration necessary for combination except occasionally. These constraints decrease with increasing temperature and increase with decreasing temperature, as indicated by changes in the half-life. Larger radicals have longer half-lives (that of C_2H_5 in 3MP at 77 °K is > 3 hr) and decay by " composite " first-order rather than " pure " first-order, that is, the decay is not exponential but the decay curves for samples having different concentrations as the result of different doses are superimposable.[6] Composite first-order decay is also typical of CH_3 radicals in several matrices other than 3MP which have been tested.[52] This is interpreted to mean that these radicals are trapped with a variety of configurations which have widely different probabilities per unit time of reorganization to the configuration necessary for recombination with the sibling partner.

The viscosities of a series of hydrocarbon glasses used as trapping matrices have been determined[53] as a function of temperature over the viscosity range of 10^6 to 10^{13} poise, in order to determine whether there is a correlation between viscosity and the decay rates of trapped radicals. Major deviations from such correlation are found.[52]

(e) *Hot Radical Reactions.* Observation of CH_4 formed when dissociative electron capture by CH_3I occurs in 3MP at 77 °K[19c] indicates that the CH_3 radicals are born with sufficient energy to abstract H from the matrix. The ratio of CH_4 formation to CH_3 trapping when the radicals are formed during γ-radiolysis is 0.6.[16b] When they are formed during photoionization of TMPD, it is 3.8.[52]

Other hot radicals formed by dissociative capture also abstract H, but with decreasing yields as the radicals become more complex. It is possible that complexing of the alkyl halides with TMPD may account for the fact that the ratio of H abstraction to trapping when it is used is different from that when γ-radiolysis is used.[6]

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