STABILITY OF RADIATION-INDUCED ORGANIC FREE RADICALS

DECAY BY HEAT

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ABSTRACT The rate of free radical decay was measured at various temperatures using electron paramagnetic resonance spectroscopy. Rate constants determined from first-order decay kinetics were used to determine the activation energy for the process of free radical decay. The similarity between the temperature dependence of free radical decay by heat and that of electrical conductivity has led us to consider the possibility that the two processes may be related. Mechanisms by which a population of electron-hole conducting states may lead to free radical decay are outlined and experimental data relating to these mechanisms are discussed.

INTRODUCTION

The sequence of events proceeding from the initial radiation-induced ionization of an organic molecule to the formation of a stable altered chemical product often involves one or more free radical intermediates. In the solid state, these intermediates may be trapped and studied by electron paramagnetic resonance (EPR) spectroscopy. The initial free radical ion produced by the irradiation is normally not stable at room temperature and, therefore, its detection involves irradiation and observation at very low temperatures. After several successive free radical conversion processes, the stable species obtained most often is a neutral free radical resulting from the breakage of a covalent bond. These free radicals can be observed at room temperature and are sometimes quite stable, exhibiting no noticeable decay for months or even years.

Heating the samples above room temperature may cause further conversion to a different free radical species (1) or more commonly may cause the free radicals to decay to non-radical species (2, 3). Any theory applied to this mechanism must take into consideration the fact that a free radical can only decay by reaction with another species having an unpaired electron. If this other species were an identical free radical the decay kinetics would be second-order. However, it is experimentally

observed that the decay process is apparently first-order. This implies that the interaction is with some species whose properties and concentration within the solid are different from those of the observed free radical. Such a species, if transient or in low concentration, would be unobservable by EPR.

In the present investigation we have attempted to gain some information about the nature of heat decay by measuring the activation energy of this process for several organic free radicals. The similarity between the temperature dependence of free radical decay by heat and that of electrical conductivity as measured by other workers (4–6) has led us to consider the possibility that the two processes may be related. Mechanisms by which a population of electron-hole–conducting states may lead to free radical decay are outlined and experimental data relating to these mechanisms are discussed.

EXPERIMENTAL PROCEDURE

Polycrystalline samples were irradiated in air at room temperature in a cobalt-60 source at a dose rate of 1.07×10^6 R/hr. A 20 mg sample irradiated to a total dose of 10^7 R was placed in an EPR tube and evacuated to 0.1 torr to prevent reactions with oxygen upon subsequent heating. After evacuation, three-quarters of an atmosphere of nitrogen was introduced to avert loss of free radicals by sublimation of the sample. A number of compounds were found to be unsuitable for kinetic analysis, notably those containing water of hydration and those for which the EPR spectrum changed with increasing temperature.

The temperature of the sample was controlled inside the EPR sample cavity by employing the Varian variable temperature control unit (Varian Associates, Palo Alto, Calif.). The temperature at the position of the sample in the cavity was measured prior to and following a series of spectra using a precalibrated thermistor placed in an EPR sample tube.

The EPR measurements were made with a Varian spectrometer operating at X-band microwave frequencies. Quantitative measurements of the relative number of spins in samples were made by comparison with a standard sample of pitch in KCl. A dual cavity operating in the TE_{104} mode, with separate modulating coils for each half of the cavity, was used for this purpose. Although the absolute number of spins in the unknown sample was not determined, the relative concentration at a given temperature and time could be ascertained quite accurately. Measurements were made on spectral lines for which the shape and width did not change during decay. Relative spin concentrations were obtained by measuring peak-to-peak heights from first-derivative spectra. Care was taken to avoid power saturation of the samples during the experiments.

RESULTS AND DISCUSSION

Kinetics and Energy of Activation

At any one temperature, the free radical population remaining in an irradiated sample at time t displayed kinetics which can best be described by the first-order decay equation:

$$\ln (N/N_0) = -k_1 t. \tag{1}$$

In this equation, N is the free radical population at time t, N_0 is the population at

time $t = 0$, and k_1 is the temperature-dependent decay constant with units of sec^{-1}. Fig. 1 demonstrates the heat-response curve at six different temperatures for D-tartaric acid.

The activation energy for the process of free radical decay was determined by plotting the values of k_1 according to the Arrhenius equation:

$$\ln k_1 = -(E_a/RT) + \ln A. \tag{2}$$

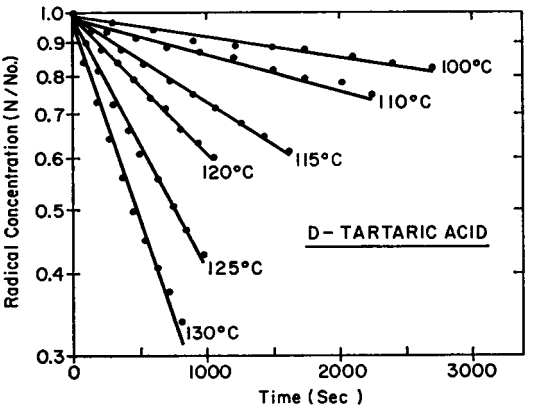

FIGURE 1 Heat-response curve for the decay of free radicals produced in D-tartaric acid with cobalt-60 γ-rays. Radical concentrations are normalized to the concentration at $t = 0$. Dots are experimental points while solid lines represent the least-squares computer fit to Equation 1.

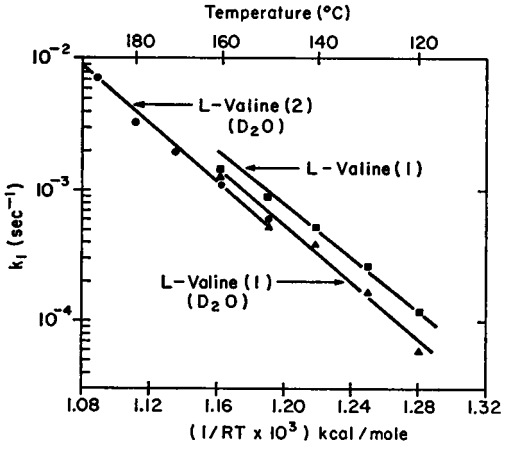

FIGURE 2 Arrhenius plot for determination of activation energy. Decay constants were obtained from plots such as those in Fig. 1. Solid lines represent the least-squares computer fit of Equation 2 to points. L-Valine (1) refers to the principal radical formed in this compound, which has been characterized by Shields et al. (14). L-Valine (2) refers to a peroxy radical whose presence is detectable only after most of the principal radicals have decayed.

In this equation, E_a is the activation energy, R is the gas constant, T is the absolute temperature, and A is the frequency factor. In Fig. 2, Arrhenius plots for three free radicals are shown, and a series of experimentally determined values for nine free radicals is tabulated in Table I.

Free Radical Decay and Electrical Conductivity: Similarities in Temperature Dependence

Activation energy comparisons between charge carriers and free radical concentrations in organic solids have been attempted previously (4, 7). Most of the research

thus far has centered around charge transfer complexes having relatively small energy gaps. A close correlation between activation energy for conduction and for spin concentration has been reported for pyrene-$2I_2$ and 2(perylene)-$3I_2$ complexes by Kommandeur (8), who considered the close correlation strong evidence that the observed unpaired spins are charge carriers.

In contrast, Eley (4) reported that for one series of charge transfer complexes, the free radical concentration increased as the conductivity decreased (band gap$\sim$0.5 ev). Furthermore, while the temperature had a marked effect on the conductivity, no effect could be observed on the EPR data.

In this investigation, the initial free radical concentration was produced by ionizing radiation to a level less than one free radical per 10^3 parent molecules. However, heating the sample does not increase the unpaired spin concentration as in the case

TABLE I

CONSTANTS FOR FREE RADICAL DECAY IN POLYCRYSTALLINE SAMPLES

Compound	Activation Energy E_a	Frequency Factor	Experimental Error	Activation Energy E_a	Energy Gap ϵ
	kcal/mole	*A sec*$^{-1}$		*ev*	*ev*
DL-Alanine	24.3	1.9×10^8	5.0%	1.06	2.12
L-Alanine	30.3	2.5×10^{11}	2.4%	1.31	2.62
D-Alanine	25.9	1.2×10^9	2.0%	1.12	2.24
DL-Valine	22.6	8.9×10^7	4.7%	1.00	2.00
L-Valine (1)	23.6	1.9×10^9	2.8%	1.05	2.10
L-Valine (1) (deuterated)	25.5	7.9×10^9	3.5%	1.10	2.20
L-Valine (2) (deuterated)	25.3	7.8×10^8	2.2%	1.11	2.22
D-Tartaric Acid	32.0	3.4×10^{14}	3.4%	1.39	2.78
Dihydrothymine	24.5	5.5×10^8	2.0%	1.07	2.14

of Kommandeur, but rather causes a decrease in the radical concentration. The temperature dependence of the free radical decay is in fact analogous to the temperature dependence of electrical conductivity in organic semiconductors (4–11).

The experimental conductivity is directly related to the number of charge carriers (holes and electrons) and varies with temperature according to the following relationship (9):

$$\ln \sigma = -(\epsilon/2kT) + \ln \sigma_0 \tag{3}$$

where σ is the electrical conductivity, ϵ is the energy in electron volts required to excite an electron from the highest energy level in the "valence band" to the lowest energy level in the "conduction band," k is the Boltzmann constant, and σ_0 is a constant. The factor of $\frac{1}{2}$ arises in conductivity measurements because the possible distributions of holes in the valence band are completely independent of the electron distributions in the conduction band (9). If one is measuring the energy of an acti-

vated state of a molecule (e.g., a triplet state), the factor of $\frac{1}{2}$ does not appear (12) because the hole distribution is determined by the electron distribution. Table II lists a few examples of the energy gap for electrical conductivity.

In the original calculations of free radical decay, an Arrhenius equation was used because there was no reason at first to suspect that free radical decay may be related to the number of current carriers present. However, the similarity in temperature dependence between free radical decay and electrical conductivity suggests that a comparison between the two systems could be made by calculating the activation energy for free radical decay using an equation of the form of Equation 3. By comparing the converted values from Table I, column 6, with the electrical conductivity values in Table II, it can be seen that even though alanine is the only compound

TABLE II

ELECTRICAL CONDUCTIVITY DATA ON ORGANIC SOLIDS

Compound	Energy Gap ϵ	Reference
	ev	
Alanine	2.16	6
Tyrosine	2.2	6
Polyglycine	3.12	6
Hemoglobin	2.75	6
Glycine	2.5	4
Glycine (deuterated)	2.6	4
Leucylglycylglycine	3.1	4
Leucylglycylglycine (deuterated)	3.1	4

common to both systems, the energy gap range observed for electrical conductivity is similar to that observed for free radical decay. It is also noted that deuteration has no appreciable effect on the energy gap in either system. The energy gap for electrical conductivity in both glycine and leucylglycylglycine was independent of deuteration. The same behavior was also noted for free radical decay in deuterated and nondeuterated L-valine. The frequency factors are included in Table I for completeness; their physical interpretation is not clear to us at the present time.

On the basis of these observations and comparisons, we suggest that the rate-limiting process in free radical decay by heat may involve production of electron-hole pairs giving rise to electrical conductivity. Thus, this work indicates a correlation between free radical decay and electrical conductivity but not the same behavior as observed in the pyrene-$2I_2$ charge transfer complexes (7, 8).

MECHANISMS FOR FREE RADICAL DECAY BY HEAT

In general, covalent bond breakage in a molecule AB produces two radical species A· and B·. To discuss the mechanisms of decay, we consider the case when only one

of these, say A·, is stable at room temperature. The concentration of A· relative to AB is usually 10^{-2} or less, depending on the compound and the radiation dose.

We assume the presence of a population of electron-hole pairs in equilibrium with the parent molecules AB. The concentration of these electron-hole pairs, which give rise to electrical conductivity, is a function of temperature (Equation 3).

Since organic semiconductors exhibit very little molecular overlap, Fox (12) suggests that both the charge carriers are in fact associated with the molecules. Therefore, the mechanisms to be discussed in the following paragraphs treat the positive charge carrier as a positive free radical ion $(AB^+)\cdot$ and the negative charge carrier as a negative free radical ion $(AB^-)\cdot$. Furthermore, the classical "hopping

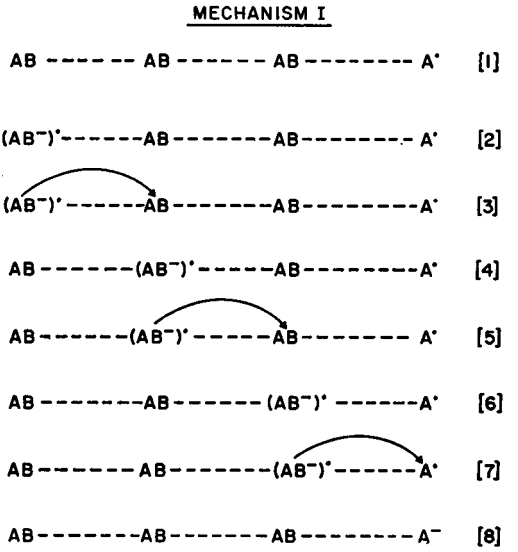

FIGURE 3 Mechanism I. A mechanism for free radical decay by heat which involves the formation of a negative free radical ion $(AB^-)\cdot$ from a parent molecule and migration of its site to a free radical A·. The electron-accepting free radical decays to a negative *non*radical ion.

model" of Fox (12) in which the charge carriers "jump" from molecule to molecule is used to describe migration within the crystal lattice. The quantum mechanical method of transfer (tunneling through or over a barrier, Eley (4), etc.) is not considered in this discussion. The concentration of $(AB^+)\cdot$ and $(AB^-)\cdot$ is so low in unirradiated solids that they are not detectable by EPR, and we presume their concentration to be much less than that of the neutral radical A· in the irradiated solid.

The first classical mechanism to be discussed is characterized in Fig. 3. Line [1] is a schematic representation of the irradiated organic sample containing a free radical A· and parent molecules AB in the crystal. A negative free radical ion $(AB^-)\cdot$ formed at some distance from A· by thermal production of charge carriers is shown in line [2]. The site of $(AB^-)\cdot$ migrates at random through the crystal (lines [3] through [5]) by the "hopping" of an electron to a neighboring molecule until recombination with $(AB^+)\cdot$ occurs. For decay of a free radical to occur, the site of

$(AB^-)\cdot$ must come close to $A\cdot$, as shown in line [6], before recombination takes place. It should be noted that, since migration of $(AB^-)\cdot$ is random, the probability of this close proximity occurring is proportional to the concentration of $A\cdot$ so that decay kinetics would follow Equation 1. The actual decay itself is shown in line [7], where the electron is transferred to or captured by the free radical $A\cdot$. This transforms $A\cdot$ to a nonradical negative ion A^- (line [8]) which is presumed to be stable within the lattice. The probability of electron transfer from $(AB^-)\cdot$ to $A\cdot$ is not necessarily unity, but as long as this probability is constant once the close proximity has occurred (line [6]), the decay kinetics observed will still obey first-order analysis.

Mechanism II, schematically described in Fig. 4, begins with the thermal production of charge carriers from a free radical (line [2]). The free radical becomes a positive *non*radical ion and the acceptor molecule is transformed into a negative

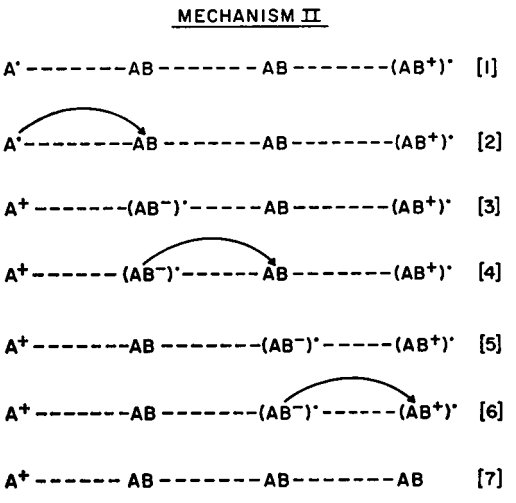

FIGURE 4 Mechanism II. A mechanism for free radical decay by heat which involves the formation of $(AB^-)\cdot$ on AB by acceptance of an electron from $A\cdot$. The site of $(AB^-)\cdot$ migrates to a hole $(AB^+)\cdot$. The electron-donating free radical decays to a positive *non*radical ion.

free radical ion (line [3]). The site of $(AB^-)\cdot$ now migrates randomly from molecule to molecule via the "hopping model" (12) (lines [4] and [5]) until it recombines with either A^+ or $(AB^+)\cdot$. Recombination of $(AB^-)\cdot$ with $(AB^+)\cdot$ results in a net free radical decay if it is assumed that A^+ is stable within the lattice. At elevated temperatures, the concentration of $(AB^+)\cdot$ is increased, thereby giving rise to a greater free radical decay rate. The kinetics of this mechanism would be first-order if the formation of A^+ and $(AB^-)\cdot$ were the rate-limiting factor. It is also of interest to note that since this mechanism begins with free radical donation of electrons, the energy gap for free radical decay within a given crystal will depend entirely upon the free radical species in question.

A third mechanism (Fig. 5) can be visualized which includes processes from I and II. A free radical $A\cdot$ becomes a positive *non*radical ion by donating an electron to a neighboring AB, forming $(AB^-)\cdot$, the site of which moves through the crystal by

the "hopping model" (9, 12, 13). Instead of recombining with $(AB^+)\cdot$, as in II, it comes in close proximity to another radical A· (line [5]). Recombination of $(AB^-)\cdot$ and A· proceeds as in Mechanism I, so that A· is transformed into a negative *non*-radical ion (line [7]). This mechanism would most likely be important only at high

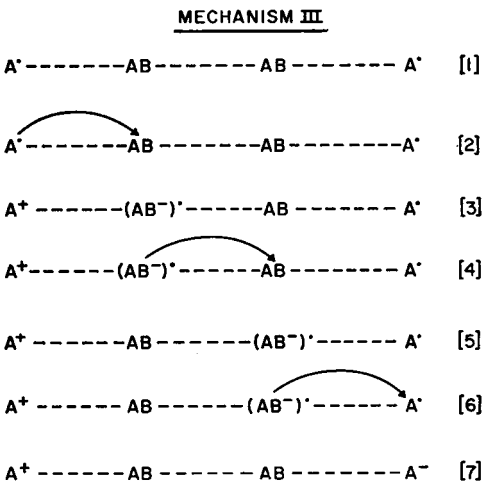

FIGURE 5 Mechanism III. A mechanism for free radical decay by heat which involves the formation of $(AB^-)\cdot$ on AB by acceptance of an electron from one free radical A·. The site of $(AB^-)\cdot$ migrates to another free radical A·. The electron-donating free radical decays to a positive *non*radical ion and the electron-accepting free radical decays to a negative *non*radical ion.

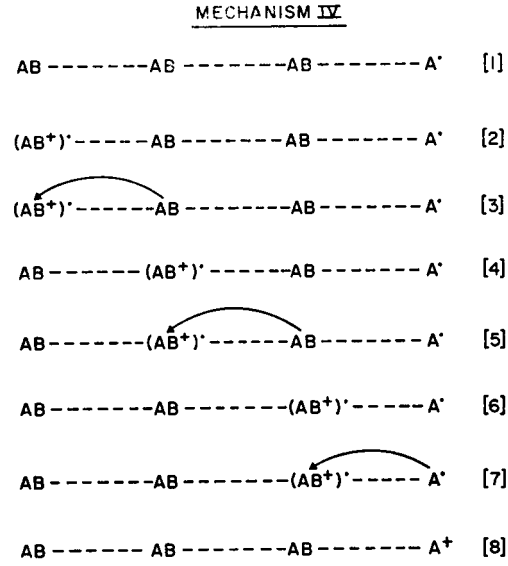

FIGURE 6 Mechanism IV. A mechanism for free radical decay by heat which involves the formation of a hole $(AB^+)\cdot$ from a parent molecule AB and migration of its site to a free radical A·. The electron-donating free radical decays to a positive *non*radical ion.

concentrations of A·, where the probability that $(AB^-)\cdot$ encounters A· before encountering $(AB^+)\cdot$ is significant. If the rate-limiting step for this mechanism were the production of A^+ and $(AB^-)\cdot$ from A·, or the recombination of $(AB^-)\cdot$ and A· to form A^-, the decay kinetics observed would be first-order. As in the case of

Mechanism II, the energy gap for free radical decay within a given crystal will depend entirely upon the free radical species in question.

Mechanism IV (Fig. 6) is different from Mechanism I only in that holes are the species responsible for decay of the free radicals. This mechanism is initiated by the formation of a positive free radical ion $(AB^+)\cdot$ from AB. The site of $(AB^+)\cdot$ migrates through the lattice by the "hopping model" (12) until recombination with either $(AB^-)\cdot$ or $A\cdot$ occurs. For this mechanism, the decay kinetics observed would be first-order and the energy gap dependent only on the crystal lattice properties, for the same reasons as discussed in Mechanism I.

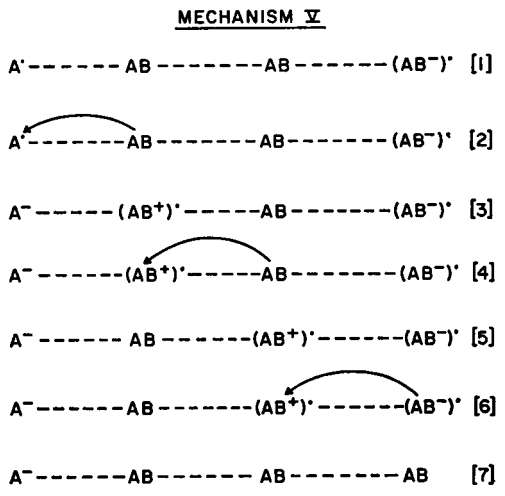

FIGURE 7 Mechanism V. A mechanism for free radical decay by heat which involves the formation of a hole $(AB^+)\cdot$ by donation of an electron to the free radical $A\cdot$. The site of $(AB^+)\cdot$ migrates until recombination with $(AB^-)\cdot$. The electron-accepting free radical decays to a negative *non*radical ion.

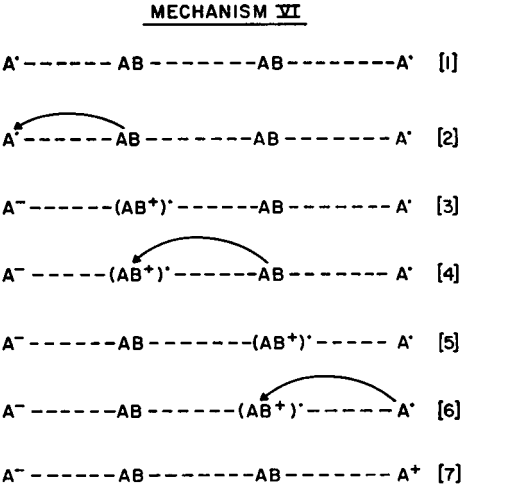

FIGURE 8 Mechanism VI. A mechanism for free radical decay by heat which involves the formation of $(AB^+)\cdot$ on AB by donation of an electron to one radical $A\cdot$. The site of $(AB^+)\cdot$ migrates to another free radical $A\cdot$. The electron-accepting free radical decays to a negative *non*radical ion and the electron-donating free radical decays to a positive *non*radical ion.

Mechanism V (Fig. 7) is different from Mechanism II only in that the free radical

$A\cdot$ accepts an electron from a nearby parent molecule AB to become a negative *non*radical ion A^-. The site of $(AB^+)\cdot$ migrates until recombination with either A^- or $(AB^-)\cdot$ occurs. For this mechanism, the energy gap would be radical-dependent and the decay first-order for the same reasons as discussed in Mechanism II.

The sixth mechanism to be described (Fig. 8) includes processes from IV and V. A radical $A\cdot$ becomes a negative *non*radical ion by accepting an electron from a neighboring AB, forming $(AB^+)\cdot$, the site of which migrates through the lattice until recombination with another $A\cdot$ occurs. The net result of this mechanism is the production of A^- and A^+ from two radicals. The arguments concerning kinetics, energy gap, and significance of this mechanism are the same as for Mechanism III.

DISCUSSION OF MECHANISMS

All six mechanisms for free radical decay by heat presented in the previous section involve in some manner the charge carriers which give rise to electrical conductivity. For Mechanisms I and IV, the initial, rate-limiting step is the production of an electron-hole pair at a site in the lattice some distance from the free radical itself. All other mechanisms involve the radical in the initial step. Our measurements of the energy gaps for free radical decay are consistent with Mechanisms I and IV; the other mechanisms are not precluded, however, since the energy gap for the rate-limiting steps might also be near that for electrical conductivity. Perhaps the most direct piece of evidence favoring either Mechanism I or IV over the others comes from the measurements of the energy gap for decay of two radical species in the same crystal lattice. Two different radical species in deuterated L-valine, indicated as (1) and (2) in Table I, were found to have energy gaps which were the same within experimental error. This would be expected for Mechanisms I and IV, but in general would not be expected for the other mechanisms in which the decaying radical species is involved in the initial step. The different values of the frequency factor (see Table I) for the two free radicals in L-valine could arise from a different probability of reaction of $(AB^-)\cdot$ [or $(AB^+)\cdot$] with the different free radicals after close proximity is reached.

Mechanism III (or VI) involves two radicals in the over-all process, and would, therefore, be most likely to occur at high free radical concentrations when there is a large probability that $(AB^-)\cdot$ [or $(AB^+)\cdot$] reacts with a second radical before recombining with $(AB^+)\cdot$ [or $(AB^-)\cdot$]. It should be noted that a combination of Mechanisms III (or VI) and II (or V), both of which are first-order, could give kinetics which would not appear to be first-order. This is because the relative contributions of the two mechanisms to the total decay process depend on the concentration of free radicals, which changes as decay proceeds.

Although our comparison between the activation energy for free radical decay and the energy gap for electrical conductivity assumes that either Mechanism I or IV is the mechanism involved, it is conceivable that both mechanisms could occur

simultaneously. If this were the case, one electron-hole pair would lead to the loss of two free radicals. The decay kinetics observed would still be first-order, even though the free radicals decayed in pairs, because the rate-limiting step is a single event, namely the production of the electron-hole pair, rather than the reaction of the electron and hole with the free radicals.

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