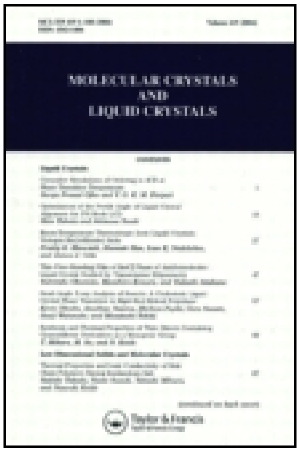

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Annealing Kinetics of Free Radicals in Irradiated Organic Crystals

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Abstract—Experiments are reported on the production, and annealing kinetics of free radicals in irradiated organic crystals. Both processes are shown to be well reproducible for nominally identical crystals although the annealing rate may be much slower in crystals damaged by previous irradiation and annealing. Free radical destruction was found in numerous instances to proceed by second-order kinetics, the only exception being crystals of acetylglycine where the reaction is third-order. Activation energies of the reactions are reported together with experimental investigation of the deuterium isotope effect. The significance of these results is discussed in relation to the existence of hydrogen atom jumping or " kenon diffusion " as an annealing mechanism.

Introduction

Since the early 1950s it has been known[1,2] that free radicals are produced in a variety of organic materials and in particular in organic single crystals when these substances are exposed to x-rays or γ-rays. In many cases the radicals are stably trapped and protected by their environment so that they survive indefinitely if stored at room temperature. Although it has often been noticed[3] that the free radicals are destroyed by annealing at a sufficiently high temperature, no quantitative studies have been made of the annealing process in single crystals. To date the most extensive studies of annealing kinetics are those of Dole and co-workers[4,5] who examined the thermal destruction of free radicals in irradiated polythene. This work for the first time raised the question of the existence of the hydrogen atom vacancy as a mobile defect

Owing to the requirements of spin conservation, the removal of free radicals must essentially involve the recombination of the unsatisfied valencies in pairs. It seems quite unlikely that diffusive motion of the aliphatic chains in polythene would provide sufficient mobility to bring this about. Thus one is forced to accept the concept of the mobility of the radical state through hydrogen atom jumping and the transfer of hydrogen atom vacancies. Again, because the free radicals are required to recombine in pairs one expects the kinetics of the reaction to be of second-order. In this regard, unfortunately, the ESR annealing studies on polythene indicate that the reaction does not conform to a simple hypothesis. In fact, there has even been some dispute[5,6] as to whether the reaction displays first or second-order kinetics. Under isothermal annealing it is found that the reaction, which initially proceeds rapidly, eventually ceases leaving a fraction of the radicals intact. Raising the temperature further causes the annealing process to proceed once more until again a certain fraction of the radicals are found to be resistant to destruction, and so on. It is a natural presumption that we have here a reaction system that is not homogeneous and this Dole attributed to a non-uniform distribution of free radicals arising from their production in clumps or " spurs." It seems to us more reasonable to regard the inhomogeneity of the system as arising from the inhomogeneity of the polythene itself, consisting as it does of regions of differing degrees of crystallinity.

For the elucidation of the microscopic processes involved in organic free radical annealing in solids it is preferable to choose materials which are better characterised than are polymers, i.e., to use organic single crystals. Several questions present themselves. Is the annealing of free radicals in irradiated organic single crystals a well-behaved reaction in the sense of obeying a particular order of kinetics? Is the annealing rate constant from crystal to crystal of a particular compound or is it " structure sensitive " in that it depends sensitively on the impurity and defect concentration of the crystal? Is the annealing rate affected by the irradiation and thermal history of the specimen? Can the activation energy of the annealing process be measured? Can the kinetic isotope effect be detected by comparison of the annealing rates of free radicals in deuterated and undeuterated crystals? In order to provide a partial answer to these questions, we have studied free radical production and annealing in crystals of glycine, succinic acid, malonic acid, alanine and acetylglycine, some in partially deuterated form.

Experimental

The ESR spectrometer used has been described previously.[7] To facilitate studies of isothermal annealing a heatable vacuum jacketed cavity was constructed to allow spectra to be taken at frequent intervals as annealing proceeded. It was found that adequate temperature stability for isothermal annealing experiments (vis. $\pm \frac{1}{2}\,°C$) was obtained by running resistance heaters, fixed to the cavity, from a variable regulated power supply, the cavity itself being thermally isolated on the end of a 40 cm length of German silver waveguide within the vacuum jacket. For kinetics studies, temperatures were chosen within a range where the reaction proceeded sufficiently slowly with respect to the time needed to bring the cavity to a steady operating temperature, yet not so slowly as to be inconvenient to observe. Complete spectra were taken continuously for times ranging between $\frac{1}{2}$ and 4 hours. To correct for any drift in spectrometer sensitivity a standard specimen was included in the cavity in a second specimen position provided. This took the form of a hollow PTFE rod containing powdered ZnSe : Mn whose spectrum of six equally spaced lines of uniform height fits comfortably around the hyperfine spectrum of most organic free radicals. The complete spectrum of both specimen and standard (Fig. 1(a)) was obtained repeatedly with a 4 min. sweep, yielding up to 30 charts per run from which the relative heights of specimen and standard spectra were obtained. When prolonged heatings were required the crystals were mounted in detachable cavities which were heated in a temperature controlled oven, the samples being protected from oxidation by a

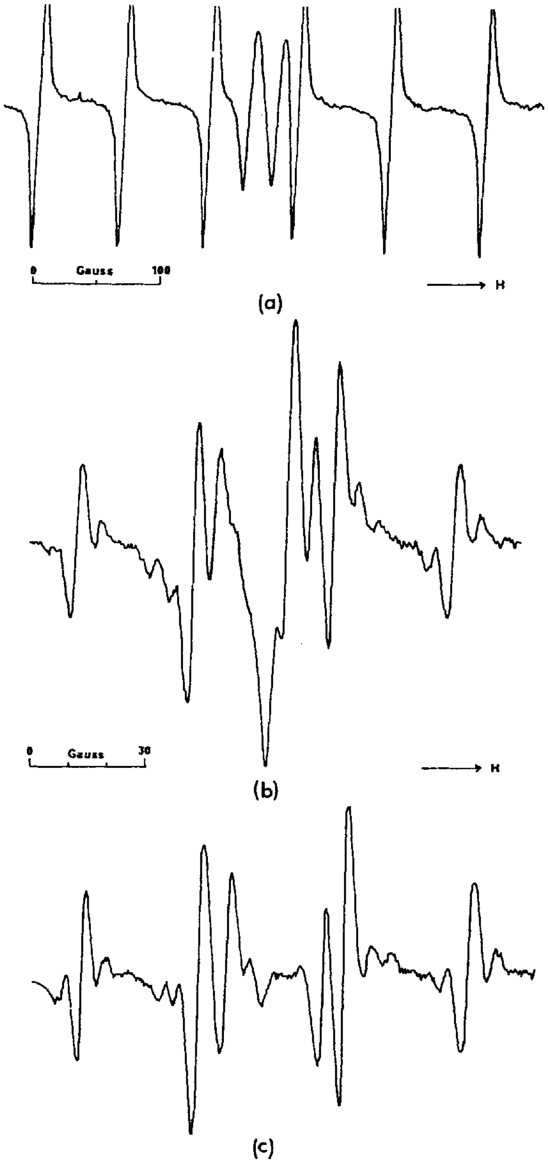

Figure 1. (a) Superimposed spectra of free radical $\mathrm{CH_3{-}CO{-}NH{-}\dot{C}H{-}COOH}$ in irradiated acetylglycine and of standard specimen of powdered ZnSe : Mn.

(b) Spectra of radical A, $\mathrm{HOOC{-}CH_2{-}CH_2{-}CO\dot{O}}$ (central line) and radical B, $\mathrm{HOOC{-}CH_2{-}\dot{C}H{-}COOH}$ in freshly irradiated succinic acid.

(c) Showing independent annealing of radical A after specimen is held for 2 h at 80 °C. Applied field perpendicular to crystal *b* axis and making 100° with a axis.

nitrogen atmosphere. Where the heating was performed *in situ* the crystal was protected in this regard by the evacuation of the cavity. In fact no effects were observed that could be attributed to the reaction of atmospheric oxygen with the free radicals even when air was admitted presumably because of the low permeability of these crystals to oxygen. The major hazards to the crystals arising from heating them are oxidation, fracture due to thermal stresses and in some cases, the evaporation of the crystal. This last difficulty can be very satisfactorily eliminated by coating the crystals with silicone grease.

It is important to maintain the orientation of the crystal unchanged throughout the experiment and this was achieved by slothing each into an individually cut PTFE rod of diameter chosen so as to be a firm push fit in a bush on the cavity wall. The particular orientation chosen for the crystal is of importance only when it is necessary to separate the lines due to two different radicals, as in the case of succinic acid, when the crystal was mounted with the magnetic field in the direction of the c* axis (Fig. 1(b) and (c)).

For accurate comparison of the free radical annealing rates in pairs of crystals a double cavity constructed after the fashion of Köhnlein and Müller[8] was used. Two soft iron discs attached to the outside of the cavity at one of the two sample positions shifted the spectrum of that crystal by about 100 gauss in terms of the applied field allowing the comparison of the virtually identical spectra of two similar crystals.

The crystals used were prepared from analytical reagent grade chemicals by slow evaporation from aqueous solutions. Large batches were grown in order to facilitate the choice of matched pairs of crystals of similar habit and appearance and of closely similar mass. No difficulty was found in obtaining pairs of crystals with masses equal to less than $\frac{1}{2}\%$ thus simplifying the comparison of free radical concentrations to that of comparing the total number of spins present in each specimen. Deuterated crystals were prepared by three recrystalizations from 99.75% D_2O, using a sufficiently large amount of the solvent so that the eventual degree of deuteration of exchangeable hydrogens reached essentially this value. Under mild conditions such as these, deuteration usually takes place only at polar hydrogens, in particular, in the compounds used, for the amino and carboxylic acid groups and at the amide hydrogens of dihydrothymine. In addition it should be noticed that treatment with heavy water effects the complete deuteration of malonic acid, even on the backbone positions.[9]

Irradiation of crystals was performed with x-rays from a Mo anode x-ray tube operated at 40 KVP. To aid in the uniform irradiation of the crystals, a matter of some importance for kinetic studies, the radiation was hardened by 0.005″ of Al foil and the crystals given equal doses from two opposite sides. The radiation so produced consists essentially of the $\kappa\alpha$ characteristic and consiedrable amounts of much more penetrating white radiation. Calculation shows that the above procedure should result in adequately uniform irradiation of typical organic materials up to 2 mm in thickness and crystals thicker than this were not used. Accurate dosemetry is not an easy problem with the radiation used. However, we believe that an adequate estimate of the doses used is provided by a comparison of rate of free radical production by our source with that in the Co^{60} gamma source at the Australian Institute of Nuclear Science and Engineering, Lucas Heights, N.S.W. The nominal doses we quote mean essentially a free radical concentration equal to that produced by a corresponding dose of Co^{60} gamma rays. The typical dose used for kinetic studies was about 5 Mrad nominal. It is perhaps worth remarking that wherever the experiments here described were repeated on gamma irradiated specimens, no detectable differences in behaviour were noticed.

Free Radical Production and Annealing Rates

Because pairs or sets of crystals of a given compound containing essentially the same concentration of free radicals were required for comparisons of annealing rates from crystal to crystal and for the obtaining of activation energies of free radical destruction, investigation was made as to how reliably this could be achieved by subjecting nominally similar crystals to the same dose of radiation. Selected crystals were irradiated in pairs or batches and the relative concentration of radicals resulting were determined by comparing successively with a copper sulphate standard. The findings may be summarised by stating that the production rate of free radicals in nominally similar crystals was always found to be the same to within the accuracy of measurement (Table 1, col. 3) which was about 5%, being limited principally by small errors in the alignment of the individual crystals. Even preirradiating a crystal with 5 Mrad and annealing out the radicals produced did not subsequently affect the efficiency of the radical production in it. More remarkably, it was found in five compounds studied (Table 6) that deuteration of the crystals did not cause any considerable change in the free radical production rate when effects due to the sharpening of the lines by the reduction of inhomogeneous broadening were accounted for by integrating the areas under the respective absorption spectra. These observations made us confident that in most cases crystals with equal free radical concentration or known multiple concentrations can be prepared by manipulation of the radiation dose, provided only the dosage saturation is avoided.

Using the double cavity five compounds (Table 1) were examined for the reproducibility of annealing rates between matched pairs of crystals. The crystals were irradiated in pairs to a dose of about 5 Mrad and the resulting small differences in radical concentration were taken into account in the comparisons of reaction rates as indicated in the table. This required a knowledge of the kinetic order of the reaction which was in fact second-order for all cases except N-acetylglycine where the reaction obeys third-order kinetics. Although the data gained from these rather tedious experiments is limited in extent it is clear that free radical annealing in organic crystals displays (e.g., Fig. 2(a)) a degree of reproducibility which is remarkable for reactions in the solid state.

Two different procedures were adopted to discover whether the

TABLE 1. Comparative Reaction Rates in Matched Irradiated Crystals

Compound	Radical(s)	Initial Rel. Conc. of Radicals	Rel. Fractional Decay Rates	Ratio of Rates Corrected for Diff. in Concs.
Glycine	$\mathrm{NH_3^+}$—$\dot{\mathrm{C}}$H—$\mathrm{COO^-}$ and Unknown	1.04	0.96	0.99
L-α-alanine	$\mathrm{CH_3}$—$\dot{\mathrm{C}}$H—R	1.04	1.08	1.12
Malonic Acid	$\dot{\mathrm{C}}\mathrm{H_2}$—COOH	1.04	1.07	1.11
Succinic Acid	HOOC—$\mathrm{CH_2}$—$\mathrm{CH_2}$—CO$\dot{\mathrm{O}}$	1.06	1.08	1.14
N-acetylglycine	$\mathrm{H_3C}$—CO—NH—$\dot{\mathrm{C}}$H—COOH	1.04	0.94	0.98

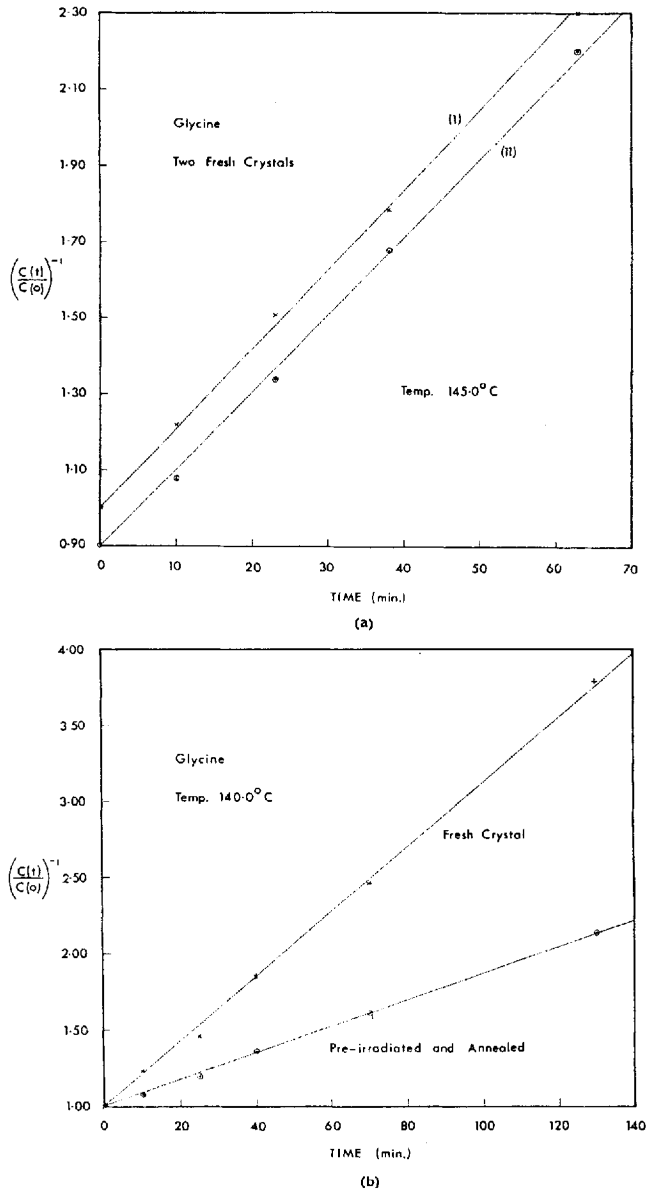

Figure 2. (a) Kinetic plots of second order decay of free radical signal on annealing of two nominally identical irradiated glycine crystals. The lower curve has been displaced vertically for clarity (b) showing the effect on annealing rate of damage produced by pre-irradiating and annealing.

annealing rate of free radicals is affected by the radiation dose that the crystal has received. A pair of crystals of a selected compound were prepared with free radical concentration different by a factor of about 2 by adjustment of their respective radiation doses. By comparison of their annealing rates in the double cavity and with a knowledge of the kinetic order obeyed by the reaction (the determination of which is described later) one can compare the observed relative annealing rate with that expected on the basis of the differing concentration. Since one crystal received about twice the radiation dose than the other and therefore about twice as much secondary damage, the equality of the annealing rates after correction for the difference in concentration would indicate that the annealing rate is essentially unaltered by the extra radiation dose. This was found to be the case for the two compounds examined in this way, namely L-α-alanine where the annealing kinetics of the free radicals was second-order and in acetylglycine where it was third-order (Table 2).

TABLE 2. Effect of Radiation Induced Impurities on the Reaction Rate

Compound	Relative Concentrations of Radicals	Rel. Fractional Decay Rates	Expected Rel. Rates
L-α-alanine	2.1	2.0	2.1
N-acetylglycine	2.2	4.5	4.8

For the other method of examining the effect of previous irradiation on annealing rates, a pair of crystals of the compound were selected, one of which was given a radiation dose of 5 Mrad, and then both crystals were annealed together at a temperature sufficient to destroy the free radicals produced in the irradiated member of the pair. Both crystals were then treated with a 5 Mrad dose at room temperature which produced equal free radical concentrations in each in accordance with the observations mentioned earlier. The relative annealing rates of the crystals were then compared in the double cavity. In marked distinction to the previous procedure it was found that the differing histories of the crystals resulted in widely different annealing rates yet with the annealing curve accurately obeying the expected kinetic law (Fig. 2(b)). In each case preirradiating, annealing and cooling remarkably reduced the annealing rate by as much as a factor of 4 in the case of acetylglycine (Table 3).

TABLE 3. Effect of Preirradiating and Annealing on the Reaction Rate of Free Radical Destruction

Compound	Conc. in Preirrad. Crystal / Conc. in Fresh Crystal	Rel. Fractional Decay Rates	Expected Relative Rates
Glycine	1.02	0.48	1.02
L-α-alanine	1.05	0.53	1.05
N-acetylglycine	0.98	0.25	0.96

The kinetic order for free radical destruction was mostly determined by measurements on the sample *in situ* in the variable temperature cavity. Spectra were taken continuously with the cavity containing the sample crystal and the standard maintained at a constant temperature. The height of the spectrum of the sample relative to the standard was plotted according to the hypotheses of first, second and third-order kinetics. In this way the reaction order was determined for the crystals of Table 4. In no case did deuteration of the crystal effect the reaction order, the reaction curves being always conformable to second-order kinetics except for acetylglycine (Fig. 3) and its deuterated analogue where the data can be fitted accurately with third-order kinetic curves. In most cases the determination of the kinetic order for the series of spectra is a quite straight forward matter especially where only one radical is present after irradiation, when measurement of the height of a prominent peak in the spectrum allows one to follow changes in the relative concentration of the free radicals. Where two radical species are present after irradiation as in malonic and succinic acid measurement of the decay curves

TABLE 4. Free Radical Destruction Reactions Studied to Determine the Kinetics of the Reactions

Compound	Formula	Radical(s)	Kinetics Determined	Temperature Convenient for Annealing	Reference
Glycine	$\mathrm{NH_3^+—CH_2—COO^-}$	$\mathrm{NH_3—\dot{C}H—COO^-}$ and Unknown Species	Apparently second-order (see text)	150 °C	Present work
D_3-glycine	$\mathrm{ND_3^+—CH_2—COO^-}$	(See text)	Second-order	150 °C	Present work
L-α-alanine	$\mathrm{CH_3—CH(NH_2)—COOH}$	$\mathrm{CH_3—\dot{C}H—R\ (R{=}COOH\ or\ COO^-)}$	Second-order	160 °C	Present work
dl-α-alanine	$\mathrm{CH_3—CH(NH_2)—COOH}$	$\mathrm{CH_3—\dot{C}H—R\ (R{=}COOH\ or\ COO^-)}$	Second-order	160 °C	Present work
Malonic acid	$\mathrm{HOOC—CH_2—COOH}$	$\mathrm{\dot{C}H_2—COOH}$	Second-order	65 °C	Present work
		$\mathrm{H\dot{O}OC—CH—COOH}$	Not determined	80 °C	Present work
D_4-Malonic Acid	$\mathrm{DOOC—CD_2—COOD}$	Two unknown radicals	Second-order (see text)	55 °C	Present work
β-Succinic Acid	$\mathrm{HOOC—CH_2—CH_2—COOH}$	$\mathrm{HOOC—CH_2—CH_2—CO\dot{O}}$ (Radical A)	Second-order	80 °C	Present work
		$\mathrm{HOOC—CH_2—\dot{C}H—COOH}$ (Radical B)	Second-order	105 °C	Present work
D_2-Succinic Acid	$\mathrm{DOOC—CH_2—CH_2—COOD}$	$\mathrm{DOOC—CH_2—CH_2—CO\dot{O}}$	Second-order	90 °C	Present work
		$\mathrm{DOOC—CH_2—\dot{C}H—COOD}$	Second-order	105 °C	Present work
N-Acetylglycine	$\mathrm{H_3C—CO—NH—CH_2—COOH}$	$\mathrm{H_3C—CO—NH—\dot{C}H—COOH}$	Third-order	125 °C	Present work
D_2-Acetylglycine	$\mathrm{H_3C—CO—ND—CH_2—COOD}$	$\mathrm{H_3C—CO—ND—\dot{C}H—COOD}$	Third-order	125 °C	Present work
n-Octadecyl Disulphide (polycrystalline)	$\mathrm{C_{18}H_{37}—S—S—C_{18}H_{37}}$	Alkyl Radical and $\mathrm{R\dot{S}}$ Radical	Second-order	20 °C	Truby, MacCallum and Hesse (1962)

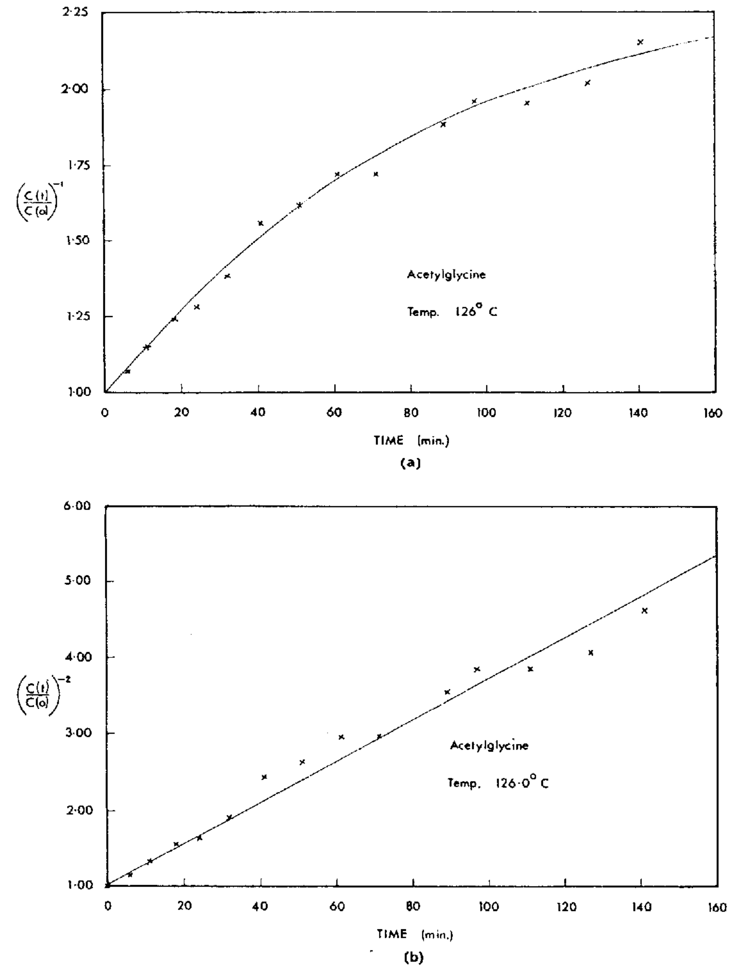

Figure 3. (a) Annealing of free radicals in acetylglycine plotted according to second order kinetic hypothesis (b) plotted according to third order kinetic hypothesis.

depended on choosing a crystal orientation such that absorption lines of each radical could be isolated free from overlap from the spectra of the other. This was achieved easily in succinic acid and with somewhat more difficulty in malonic acid. In succinic acid the radicals [10,11] ($HOOC—CH_2—CH_2—CO\dot{O}$ and $HOOC—CH_2—\dot{C}H—COOH$) anneal independently with second-order kinetics with life times of about 30 minutes at 80 °C and 110 °C respectively. It is evident that in this compound at least, that each radical species " destroys itself " with no sign of reaction between the dissimilar radical types (Fig. 1(b) and (c)). Similar remarks apply to observations made on deuterated succinic acid crystals. In malonic acid the situation is similar with the radicals[12] ($\dot{C}H_2—COOH$ and $HOOC—\dot{C}H—COOH$) annealing in the experimental time of 65 °C and 80 °C, respectively, again with second-order kinetics. In the deuterated compound, however, the spectrum of the irradiated crystal was very narrow making it impossible to isolate lines of the separate species which were obviously present as can be demonstrated from the change in the shape of the spectrum as the microwave power is varied, a characteristic of a sample containing at least two species with different spin-lattice relaxation times requiring differing power levels for saturation. It was observed, however, that the whole spectrum annealed with second-order kinetics at a lower temperature than for the undeuterated material, namely 55 °C. In glycine the only other crystal containing two radical species when freshly irradiated the situation is more complex and may be summarized as follows. The identity of these two radicals was the matter of some dispute[13,14] until they were shown[15] to be $\dot{C}H_2—COO^-$ and $NH_3^+—\dot{C}H—COO^-$ respectively. On storing the crystal for several weeks at room temperature or warming for a few hours at 40 °C the ESR spectrum alters[16] with the disappearance of the lines of the former radical and the appearance of the spectrum of a new and as yet unidentified radical. Integration of the ESR spectra shows that this change proceeds with no alteration in the total spin concentration. It is apparent that one of the radicals is converted more or less quantitatively into a new species. Investigation of the kinetics of this reaction presents some difficulty because in the complex spectrum one cannot isolate lines either of the parent or daughter. The kinetics were shown to be first-order by assertaining that the relaxation time of the reaction rate is independent of radical concentration. A pair of matched crystals were prepared with relative concentration of radicals in the ratio of 3 : 1 by adjustment of the irradiation doses. These were mounted separately in detachable cavities and annealed in parallel in the oven, their spectra being taken at frequent intervals. Careful measurement show that the parameters of the complex spectra, such as peak height ratios, etc., changed at the same rate for each specimen throughout the annealing. The further annealing of the glycine crystals resulting from this treatment showed more interesting features. At 145 °C the spectrum of the remaining radicals is annealed with little change in shape of the spectrum being apparent until the end, when a small residuum of the unidentified radical survives prolonged heating at this temperature. The decay follows second-order kinetics and looks deceptively like the familiar annealing of a single radical although observations of saturation verify that two radicals are present. It is apparent that we here observe the mutual destruction of two dissimilar radicals initially present in almost equal concentrations and displaying a true second-order reaction.

Activation Energies

When it was found that the rate of free radical annealing does not vary greatly from crystal to crystal, it was hoped to measure the activation energies by measuring the change in annealing rate with temperature using sets of matched crystals. For this purpose six selected glycine crystals were irradiated similarly and the decay curves of their ESR spectra were obtained as they were annealed at various temperatures from 135 °C to 155 °C. Unfortunately on the Arrhenius plot the points showed so much scatter that the best estimate that could be made of the activation energy was 1.0 ± 0.4 eV. It is apparent that the rate of annealing of the free radicals although tolerably similar in different crystals is still sufficiently variable to prevent accurate derivation of activation energies when the temperature variation of the rate is measured using different crystals for each temperature. It was found necessary to measure the temperature variation of the annealing rate by partially annealing the same crystal successively at two temperatures separated by a suitable temperature interval. To this end the crystal was mounted in the variable temperature cavity and maintained at such a temperature that the ESR absorption signal decayed to about half strength over an hour's observation, the spectra being taken at frequent intervals. The relative free radical concentrations thus obtained yielded, of course, a straight line plot when a graph is made of their reciprocals (or reciprocal squares) as a function of time and in effect the further annealing behaviour of the crystal if it were to be maintained at this temperature can be predicted by extrapolation. However, when sufficient points have been obtained to allow this to be done the annealing temperature is increased as rapidly as possible by about 10 °C and the experimental points for the further annealing were entered on the graph (e.g., Fig. 4) to give a new straight line of increased slope. Comparison of the two annealing rates yields the activation energy. Examination of the data leads one to estimate the error in the activation energy thus derived at about 10%. Activation energies were found with values ranging from 0.5 eV (D_3-glycine) to 2.7 eV (malonic acid) as shown in Table 5. It is noteworthy that the value of the activation energy in deuterated glycine is quite different from that of the undeuterated material. The extent of this difference is much more than can be attributed to the effect of deuteration on a particular chemical reaction, offering further evidence that in this case at least, deuteration of the crystal steers the course of post-irradiation chemical events into new channels.

The need to measure the activation energy from successive annealing experiments on one crystal which must be discarded after use, together with the limited temperature range over which rates of annealing are accessible to experimental study virtually

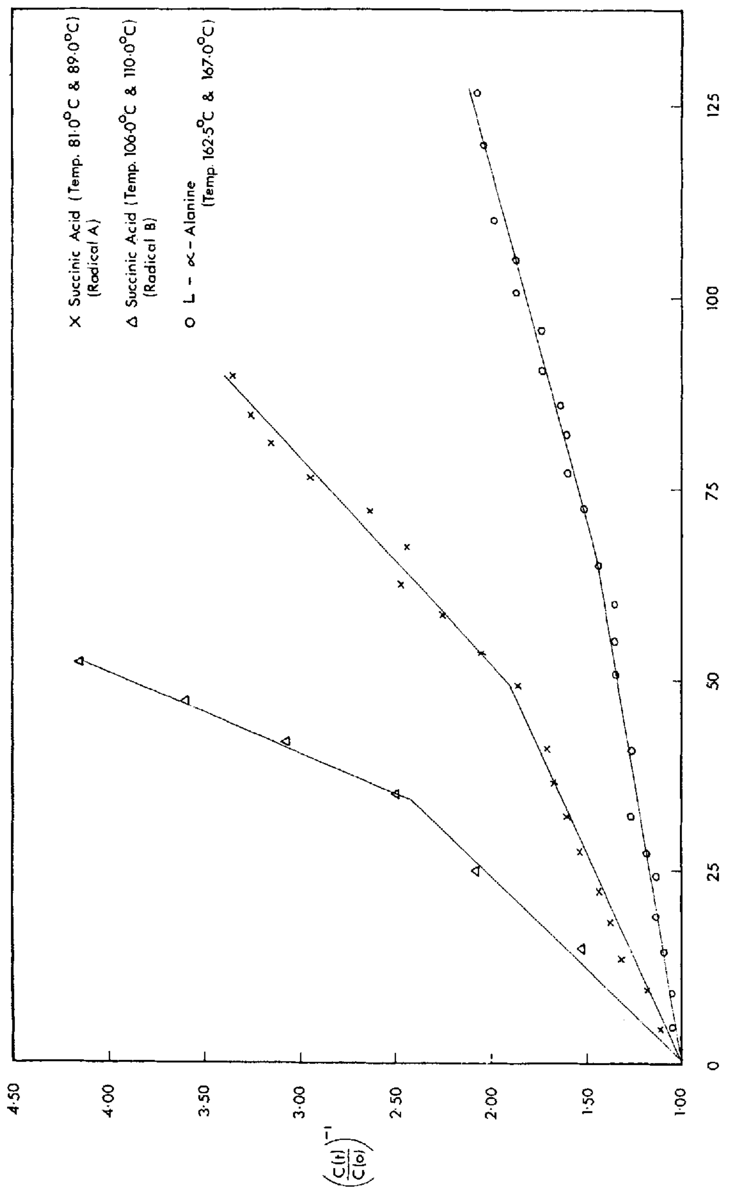

Figure 4. Typical annealing curves used for the derivation of activation energies.

TABLE 5. Activation Energies Determined for Free Radical Reactions

Compound	Radical	Activation Energy (eV)	Reference
Glycine	NH_3^+—$\dot{C}$H—COO$^-$ and Unknown	1.0	Present work
D_2-glycine	R—CO$\dot{O}$	0.5	Present work
L-α-alanine	CH_3—$\dot{C}$H—R	2.1	Present work
Malonic Acid	$\dot{C}H_2$—COOH	2.7	Present work
Succinic Acid	HOOC—CH_2—CH_2—CO$\dot{O}$ (Radical A)	1.0	Present work
	HOOC—$\dot{C}$H—CH_2—COOH (Radical B)	2.3	Present work
N-acetylglycine	H_3C—CO—NH—$\dot{C}$H—COOH	2.6	Present work
Dihydrothymine	$\dot{C}^6 \rightarrow \dot{C}^5$ (Conversion)	1.0	Bernhard and Snipes (1967)

precludes investigating whether the activation energy is constant with temperature.

Deuteration and the Kinetic Isotope Effect

The comparisons of the annealing rates necessary for the study of the deuterium isotope effect were made with the help of the detachable double cavity using oven heating. The pair of crystals, deuterated and undeuterated, were irradiated together before mounting in the cavity. Where the deuterium isotope effect was not present the spectra decayed together, but when present the isotope effect produces such a marked difference[17] in the annealing rates as to be unambiguously recognisable. The relative rate constants were derived from kinetic plots (e.g., Fig. 5) with appropriate allowance being made for any slight differences in initial concentrations in the free radicals in the pairs of crystals; these are shown in Table 6.

The case of glycine calls for comment in that the radicals present in deuterated glycine after irradiation and low temperature annealing to effect the conversion routine are obviously different in

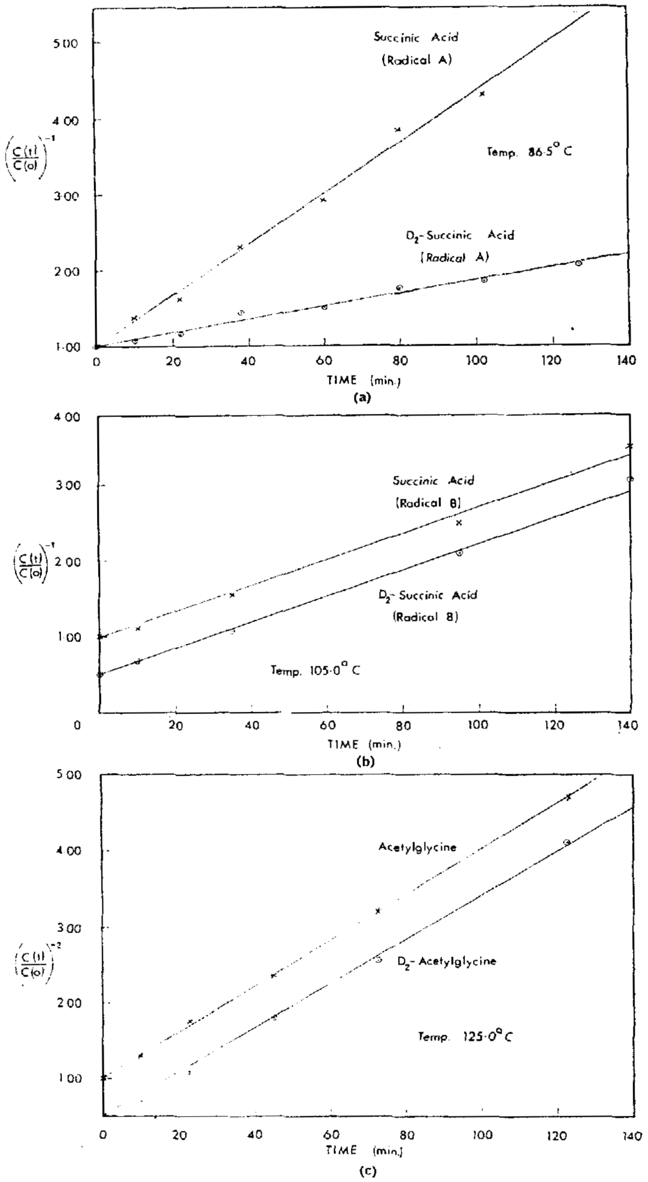

Figure 5. (a) Kinetic plots comparing the annealing rates of radical A in deuterated and undeuterated succinic acid, showing the presence of the deuterium isotope effect. (b) Similar plots for the annealing of radical B, showing the absence of an isotope effect. The lower curve has been displaced downward for clarity. (c) Kinetic plots showing the absence of isotope effect in acetylglycine, where the annealing kinetics are third order.

Table 6. Free Radical Reactions Studied for the Deuterium Isotope Effect

Compound	Radicals on which reaction rates were compared	Type of free radical reaction	Relative rate constant	Isotope effect
N-acetyl-glycine	H$_3$C—CO—NH—$\dot{C}$H—COOH and H$_3$C—CO—ND—$\dot{C}$H—COOD	Destruction	1·1	No
Malonic Acid	$\dot{C}$H$_2$—COOH and unknown radicals	Destruction	0·8	No
Succinic Acid	HOOC—CH$_2$—CH$_2$—CO$\dot{O}$ and DOOC—CH$_2$—CH$_2$—CO$\dot{O}$ (Radical A)	Destruction	4·5	Yes
	HOOC—CH$_2$—$\dot{C}$H—COOH and DOOC—CH$_2$—$\dot{C}$H—COOD (Radical B)	Destruction	1·0	No
Glycine	$\dot{C}$H$_2$—COO$^-$ and $\dot{C}$D$_2$—COO$^-$	Conversion	Not Determined	Yes (See Text)
Dihydrothymine	$\dot{C}_5$ and $\dot{C}_6$	Conversion	1·0	No

structure from those in ordinary glycine treated similarly, the spectrum contracting to a strong single line. It was however, observed that the deuterated crystals needed to be held at 55 °C to promote the conversion reaction at the same rate as in the undeuterated at 45 °C. In succinic acid it is found that not only do the two radicals observed anneal independently with second-order kinetics as stated earlier, but that one reaction (viz, that involving HOOC—CH$_2$—CH$_2$—CO$\dot{O}$, radical A), exhibits the deuterium isotope effect while the subsequent annealing of the radical HOOC—CH$_2$—$\dot{C}$H—COOH, radical B, does not.

Summary and Conclusions

The experimental observations indicate that the production of free radicals in organic crystals and their post-irradiation behaviour involve chemical processes which are remarkably reproducible when compared to what is usual for reactions in the solid state[18]. In the crystals of any particular compound the irradiation produces free radicals with closely similar efficiency which is unaffected by the selection of crystals from different batches or by subjecting them to different histories of preirradiation and annealing. It was even found in the cases studied that deuteration of the crystals did not noticeably alter the dosage efficiency of free radical production. The rates of post-irradiation annealing reactions of the free radicals were found to be reproducible within 10 to 15% from crystal to crystal. Comparison of annealing rates of crystals subjected to different radiation doses showed no differences in rates beyond those expected in nominally identical crystals. Although the dosage of radiation itself was found not to influence greatly the annealing rates, a history of irradiation followed by annealing was observed to markedly alter the annealing rate of the radicals produced by subsequent room temperature irradiation. Since this change can be due neither to the effects of irradiation nor of annealing (since this of course must occur anyway when the reaction rate is observed) it is apparent that the alteration is produced by the cooling of the crystal which has suffered both irradiation and annealing. Considering that unirradiated crystals when annealed at the experimental temperature and cooled exhibit rate constants for the annealing of subsequently produced free radicals which are similar to those of unannealed crystals, one can conclude that the combination of irradiation, annealing and cooling is necessary to produce the presumed damage to the crystal structure. In fact crystals so treated were frequently observed to have become brittle and opaque to various extents in distinction to crystals respectively subjected to irradiation or annealing alone, which always remained water clear and intact. It is reasonable to suppose that annealing of irradiated crystals allows the aggregation by diffusion of radiation-produced impurities, which cause the disruption of the crystal lattice when it is cooled. The experiments lead one to conclude that crystals of reduced perfection may exhibit markedly lower annealing rates and also that nominally identical water grown crystals behave essentially similarly in this regard.

On annealing the crystals the decay of the ESR spectrum was always found to be describable accurately by a simple kinetic law. For free radical destruction this was always unambiguously second-order except for normal and deuterated acetylglycine where third-order kinetics were obeyed. It need hardly be said that one, *a priori*, expects second-order kinetics for this reaction, involving as it does, the pairing of the unpaired electron spin of the free radical. The example of third-order kinetics discovered may be evidence of one free radical playing the role of catalyst in assisting the recombination of another two similar radicals. In any case it is interesting to speculate as to what transport mechanism is involved in bringing the radicals together so that they may combine. Whether the mechanism is that of diffusion of the whole radical or of the radical state alone, it is apparently impeded by damage to the crystal consequent on irradiation, annealing and cooling. The low temperature conversion reaction in glycine was found to follow first-order kinetics. This is in accordance with expectations as is the fact that it was observed to be uneffected by treatments affecting the crystal perfection.

Although annealing rates varied slightly from crystal to crystal of a particular compound to a sufficient extent to preclude accurate determination of activation energies using sets of crystals this quantity could be measured reasonably accurately from experiments on one crystal, the values being reproducible on repetition with fresh crystals. These covered a rather wide range, viz. 0.5 to 2.7 eV. Although it would be unwarranted at present to draw any firm conclusions on this data it is interesting to consider the relevance of activation energies to the problem of the nature of the transport mechanism involved in the free radical annealing. If the free radicals migrate bodily one would expect the activation energy of this process to be comparible with that for self diffusion in the molecular crystal. At present published data[19,20,21] on self diffusion in organic crystals is very limited and does not extend to hydrogen bonded crystals, let alone the particular compounds studied here. The data above, however, is potentially useful for making this comparison when activation energies for self diffusion in these crystals becomes available. The alternative transport mechanism, viz. radical state transfer by hydrogen atom jumping is in this context essentially a topochemically determined chemical reaction, the process having to proceed with the molecules constrained in particular spatial relations by the rigidity of the crystal structure. If the intermolecular geometry is favourable the transfer may proceed either with a very low or zero activation energy possible for free radical reactions, or if not with high or very high activation energies.

Of the six radicals examined for the isotope effect in annealing, one showed the deuterium isotope effect on annealing of a partially deuterated crystal, viz. $\mathrm{HOOC{-}CH_2{-}CH_2{-}CO\dot{O}}$ in succinic acid, while the others were just as unambiguously negative in this regard. If free radical destruction proceeds by way of hydrogen atom jumping then annealing of the fully deuterated crystal should certainly exhibit the deuterium isotope effect. Deuteration should have little effect on diffusive mobility of molecules and whole free radicals in the crystal, since their mass is thereby not greatly altered. The absence of the deuterium isotope effect in some partially deuterated crystals as observed above, of course provides little evidence either way although examination of a range of selectively deuterated crystals of a particular compound would be very interesting. In the case of the radical $\mathrm{HOOC{-}CH_2{-}CH_2{-}CO\dot{O}}$ in succinic acid the observed isotope effect indicates that at some stage of the annealing reaction the movement of a hydrogen atom constitutes the rate controlling step. Unfortunately, however, it is not permissible to regard this as proof of radical state transport by hydrogen atom jumping because the rate controlling step might well be that of the reaction of the radicals after they have arrived at adjacent sites, by whatever means this occurs. However, the present experiments show that it is easy to distinguish unambiguously the presence or absence of the deuterium isotope effect and thus obtain clear cut data extremely relevant to the central problem, viz. the existence of the hydrogen atom vacancy as a mobile crystal defect. For this hypothetical defect the present authors have coined the name "kenon."[22]

In summary free radical reactions in irradiated organic crystals are well behaved in the sense that a specific reaction order is accurately obeyed indicating the homogeneity of the reaction system, and production and reaction rates are closely similar in nominally identical crystals. Procedures which damage the crystal certainly affect the reaction rates while individual, similarly prepared crystals do not appear to differ greatly in crystal perfection in at least as far as free radical reaction rates are concerned. Activation energies of reaction are easily and fairly accurately measurable and it would appear that in most cases the presence or absence of the deuterium isotope effect can unambiguously be determined.

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