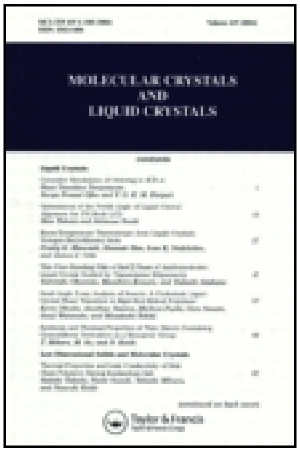

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Radical Recombination in Anthracene Single Crystals

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Abstract—A study of the relationship between radical recombination kinetics, as determined by electron paramagnetic resonance annealing studies, and molecular motion in anthracene single crystals is presented. Although the initial stages of annealing are complicated by a number of effects, the latter stages clearly proceed by a diffusion controlled mechanism which is identical to bulk self-diffusion. From such kinetics, one can estimate self-diffusion coefficients at much lower temperatures than can be done by sectioning techniques.

Introduction

Electron paramagnetic resonance (EPR) techniques have been used extensively in the last 20 years for the study of recombination of radicals produced in both organic and inorganic solids by UV, X-ray, γ irradiation, or bombardment with fast electrons.[1–5] The kinetics of such recombinations[5] have invariably been complex, with interference being caused by a number of effects such as correlated recombination of associated radical pairs, accelerated recombination in " spurs ", recombination at lattice point defects or line defects, and the presence of several radical species or other " frozen in " molecular fragments. In spite of such complicating factors, second-order reaction kinetics are observed over a fairly large change in radical concentration in many cases.

These bimolecular recombination kinetics, however, have not always been found to be rate controlling over large concentration ranges. In many studies[2,6,7] the radical concentration has been found to decrease bimolecularly and then level off at some constant radical concentration, a further decrease being obtained only on increasing the temperature of the sample. This type of behavior appears to be associated with samples which are rapidly quenched in liquid nitrogen. The largest body of work in this field has been carried out by such Russian workers as Buben, Molin and Voeyvodskii who have observed this "stepwise" recombination in a large number of organic materials ranging from aliphatic alcohols and amines to aromatic hydrocarbons. In discussing the kinetic model for such processes, they concluded that the recombination mechanism in the solid phase is obscure and that, of the various hypotheses advanced involving diffusion,[1,8] thermal chain[9] and migration[10] mechanisms, no single one could adequately explain the experimental data.

In another study Szwarc[2] studied what appeared to be an ideal system, cyclohexane, in an effort to clarify the role of various parameters affecting the recombination of γ induced radicals. In this study, however, a similar "stepwise" recombination was observed and the kinetics were very dependent on the thermal history of the sample. His conclusions were that self-diffusion was important only above the first-order phase transition at 186 °K, and that the low temperature recombination phenomena was due to rapidly freezing in an unstable cubic structure instead of the normal monoclinic structure.

Most of the previous studies suffer from having been performed on materials of undefined purity and crystal perfection (mainly glasses and polycrystalline samples). Samples in general were frozen rapidly in liquid nitrogen before irradiation. The present study was therefore undertaken on the relationship between radical recombination kinetics and molecular motion in anthracene single crystals, a material in which purity can be controlled fairly precisely and on which information can be obtained dealing with physical perfection of the crystal.[11,12]

Anthracene crystals appear particularly suitable for such an investigation for the following reasons: (1) stable radicals can be introduced by X-ray or γ irradiation at room temperature and only one species is formed; (2) the radical structure has been investigated and is believed to be caused by a simple hydrogen addition at the 9 position, hence the radical will be similar in shape and size to the parent molecule;[13] and (3) several workers have studied the self-diffusion of anthracene by radio-tracer techniques.[12,14,15]

Experimental

Two types of crystals were employed; type A were single crystals obtained from Harshaw Chemical Company; type B were melt-grown single crystals prepared in the following manner. Eastman X480 anthracene was twice vacuum sublimed, melted into a zone refining tube, given 50 zone passes and melted into a crystal growing tube for growth in a Bridgmann oven. All operations were carried out under the following furnace conditions: upper temperature = 238°, lower temperature = 191°, temperature gradient = 20°/cm, growth rate = 0.9 mm/hr. The crystal was slowly cooled from 190° to room temperature over 3 days. The physical perfection of these crystals was confirmed by X-ray diffraction studies, dislocation density measurements, and measurement of charge carrier lifetimes. Gas chromatography was used to assay purity.[12]

Crystals of suitable size for EPR studies were cut from the same section of each crystal and weighed approximately 10–20 mg. They were placed a few mm from the window of an X-ray tube and were irradiated at room temperature in air for periods of 15–19 hours with 50 KVP X-rays at 10 ma, with a total dose of approximately 5×10^8 rad. In this region, the G value for radical production[17] is approximately 5×10^{-4}, and Fig. 1 illustrates the rate of radical growth as a function of X-ray dose. The radical spectrum obtained was identical to that obtained by Blum *et al.*[18] and Harrah and Hughes[13] which corresponds to the proposed 2,3,5,6,-dibenzcyclohexadienyl radical.[13]

Annealing studies were carried out on a Varian E-3 spectrometer, the crystals being annealed in situ using a Varian temperature controller. The annealing curve was obtained by monitoring the decrease in the maximum peak height of the EPR signal setting the pen scan to repeat at 30 minute intervals. Periodically the background level was checked by turning the field dial off the resonance by approximately 200 gauss and then returning to the set position. A total of 6 annealing measurements were made on type A crystals and 8 on type B crystals.

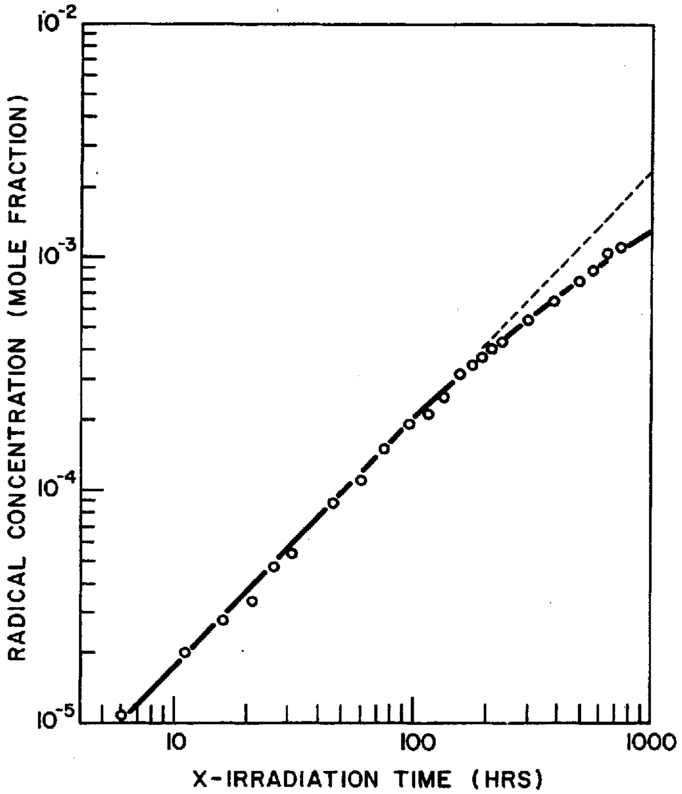

Figure 1. Radical production in anthracene single crystals.

Results and Discussion

Three typical annealing runs which illustrate the temperature dependence of the kinetics are shown in Fig. 2.

At all temperatures in the range 155–210° (m.p. 217°), the EPR signal was followed until it had less than 10% of the original signal intensity. There was no sign in any experiment of a constant spin concentration being reached. The radical spectrum was identical at the beginning and end of an experiment indicating that only one radical species was being annealed. In Fig. 2 it can be seen that all deviations from biomolecular kinetics occur

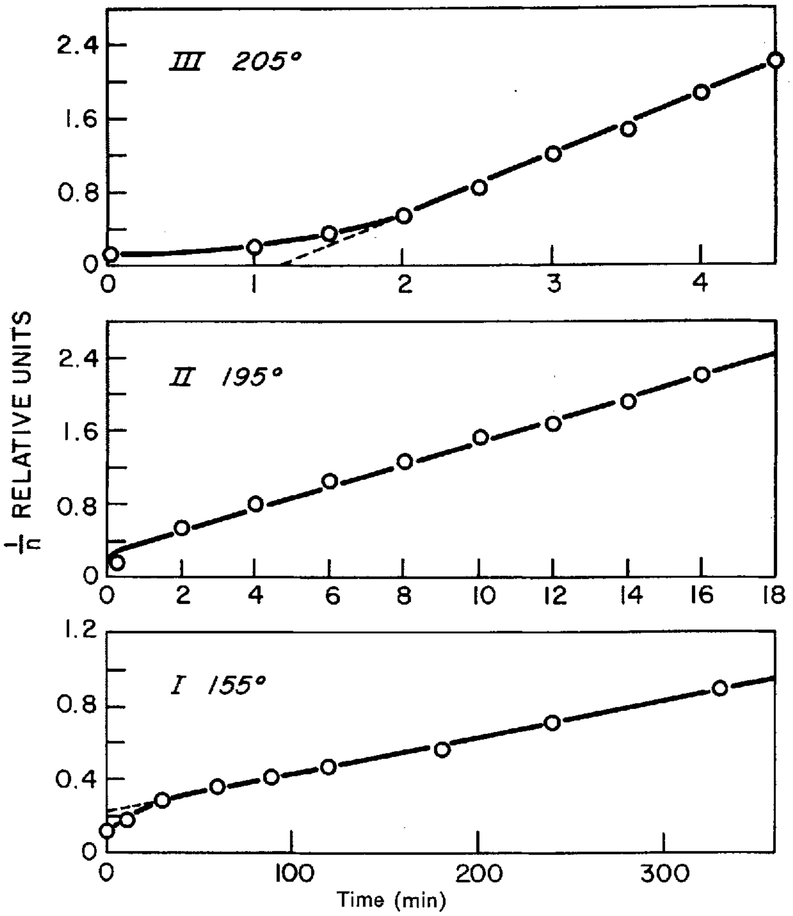

Figure 2. Second-order rate plots (relative units) for radical recombination in anthracene single crystals.

at the beginning of the anneals; these can be explained in each case as follows:

Case I: At low temperature, where molecular volume diffusion is slow, a large fraction of the recombination of radicals occurs by correlated recombination in " spurs " and thermal spike regions of the crystal. It is only after these high energy regions have been depleted that true bulk recombination becomes rate controlling. Hence the best representation of bulk diffusion controlled radical recombination is obtained in the latter stages of the anneals.

Case II. At this temperature, bulk diffusion is now so fast that correlated recombination in spurs is no longer rate controlling.

Case III. Here the apparent initial lag in annealing rate is simply the time lag necessary to heat the whole crystal to the annealing temperature, approximately 1 minute.

The absolute radical concentrations were obtained by comparing their intensity with that of freshly prepared α,α-diphenyl β-picrylhydrazyl and the Varian standard " weak pitch " signal. The accuracy of this method is estimated to be $\pm 50\%$. Since there is this large inaccuracy in measuring the radical concentration, the absolute rate constants were not calculated for each temperature. Instead the relative rate constants were obtained in consistent units, and an Arrhenius plot of these data is shown in Fig. 3. The approximate value of the rate constants range from $k = 10^2 \,\mathrm{l\,mole^{-1}\,sec^{-1}}$ at 195° to $0.5 \,\mathrm{l\,mole^{-1}\,sec^{-1}}$ at 155°.

Several points should be noted from Fig. 3. In general, the rate constants obtained for Harshaw crystals (type A) were higher and less self consistent within the set. Both sets of data tend to merge at high temperature. The data for melt grown (type B) crystals can be fairly well represented by the following equation over the temperature range of 55° studied:

$$k = k_0 \exp\left[\frac{-50{,}000 \pm 2{,}000}{RT}\right]$$

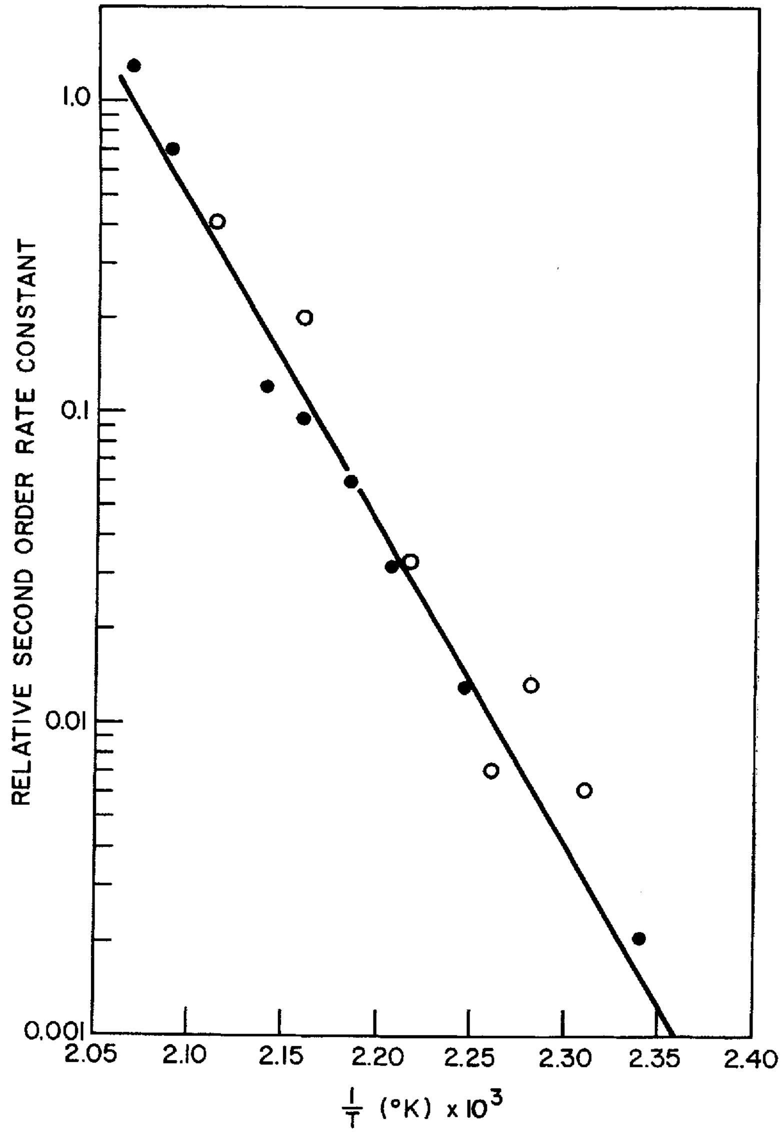

Figure 3. Temperature dependence of rate constants for radical recombination in anthracene single crystals. ○, Harshaw crystals (Type A). ●, Melt-grown crystals (Type B).

Type A crystals can be represented by the same equation but with a larger error associated with the measurements. It would appear at first sight that this activation energy is very large for a diffusion controlled recombination. It can be pointed out, however, that in a similar study carried out by Ermolaev *et al.*[1] on amorphous glycerine, the following expression for the recombination constant was obtained:

$$k = 10^{10.5} \exp\left[\frac{-30{,}500}{RT}\right]$$

This value was only obtained for " large dose " irradiation (300 Mrad). When a " small dose " (10–30 Mrad) was used, the expression

$$k = 10^{10.5} \exp\left[\frac{-20{,}000}{RT}\right]$$

was obtained. A possible explanation is that under the " large dose " condition vitrification takes place to a great extent, and recombination then corresponds more closely to that in a crystalline lattice. The lower E_A value was shown to correspond to the potential barrier for self-diffusion in amorphous glycerine, 25 kcal mole^{-1}.[19]

Shepp[20] and Ayscough [21] have shown that the activation energy for recombination is approximately zero, and therefore the activation energy must represent that for radical diffusion through the matrix. Two pieces of evidence can be presented which corroborate this statement. Sherwood[22] has carried out self-diffusion studies in anthracene and other aromatic hydrocarbons using the radioactive tracer technique and finds that the self-diffusion process in anthracene has an $E_A = 56$ kcal mole^{-1}, in reasonable agreement with the value obtained here, although it would not be expected that the radical would behave exactly like the parent molecule. Another equally convincing piece of evidence is to compare the actual diffusion coefficient of the radical with the self-diffusion coefficient obtained by tracer studies.

For a second-order radical recombination reaction the following equation holds to a good approximation:[23]

$$\frac{1}{n} - \frac{1}{n_0} = Z\nu t$$

where n_0 = initial mole fraction of radicals
n = mole fraction of radicals remaining after time t, sec
Z = coordination number of molecule on a lattice site
ν = jump frequency of radical, Hz

Taking the value for anthracene at 195° in the latter stages of annealing and assuming $Z = 6$, we can calculate ν.

$$\nu = 112 \text{ Hz}$$

From diffusion theory,[24] the diffusion coefficient of a species with jump frequency ν is given by the equation:

$$D = \gamma a^2 \nu$$

where γ = geometrical constant
ν = jump frequency
a = jump distance

Substituting in this equation $\nu = 112\,\text{Hz}$, $a = 5 \times 10^{-8}$ cm, $\gamma = 1/6$ gives $D = 0.4 \times 10^{-13}$ cm^2 sec^{-1}. This value is in fairly good agreement with the self-diffusion coefficient obtained in this laboratory:[12] $D = 2 \times 10^{-13}$ cm^2 sec^{-1}, at 191° for diffusion perpendicular to the (001) plane in crystals prepared in the same way as those used for the EPR study. The inaccuracies involved in this calculation are principally in obtaining a value for the mole fraction of radicals present and the choice of jump distance, a, which can range from 5 Å, the smallest distance between two molecules to 11 Å, the largest lattice dimension. Here the smallest value was used, but the larger the value taken the better the agreement would be. It should also be noted that the EPR technique gives the averaged isotropic diffusion coefficient which should differ from the anisotropic one obtained by the sectioning technique.

The agreement in both the activation energy and the absolute diffusion coefficient indicate that in the latter stages of annealing radical recombination proceeds by a diffusion controlled mechanism which is identical to that of bulk self-diffusion. Radical recombination studies may then offer a means of extending self-diffusion measurements below the limit set by conventional sectioning techniques of 10^{-13}–10^{-14} cm^2 sec^{-1}. For example, in the case of anthracene at 155°, the self-diffusion coefficient estimated from radical recombination studies is approximately 5×10^{-16} cm^2 sec^{-1}. A measurement of this self-diffusion coefficient is not practical by sectioning techniques, but the estimate can be made by the radical recombination study in only a few hours.

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