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Radiation Induced Paramagnetic Centers in Anthracene and Deuterated Anthracene*

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Abstract—EPR Studies of radiation damage in anthracene $C_{14}H_{10}$ and deuterated anthracene ($C_{14}D_{10}$) powders have been made up to a dose of 7×10^8 rad. Interpretation of the spectra is consistent with that resulting from the hyperfine interaction of three equivalent protons. Excessive breadth of the spectrum of the radical produced in $C_{14}D_{10}$ is attributed to a high concentration of incompletely deuterated radical resulting from the presence of $C_{14}D_9H$.

Introduction

The centers introduced by high energy irradiation of anthracene may be chemical or physical in nature.[1, 2, 3] A physical type consists of defects reparable by annealing or recrystallization. The other type, chemical defects, may consist of stable decomposition products or dimers. By measuring the radiation damage by different methods, different G-values for the radiation damage centers are obtained.[1–3, 6–10] Thus, various defects are produced.

A model of one physical defect has been proposed recently by Blum *et al.*[4] They interpret the 4-line EPR spectra, intensity distribution 1:3:3:1, associated with a radiation induced, annealable defect in crystalline anthracene as resulting from the hyperfine interaction of 3 equivalent protons on a linear segment of a dimeric

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anthracene radical. If such a species is indeed produced, then it may be anticipated that the paramagnetic center produced on irradiation of deuterated anthracene will have a considerably narrower 7-line structure with intensity distribution of 1:3:6:7:6:3:1. Our results on polycrystalline deuterated anthracene are consistent with Blum's *et al.* interpretation of three equivalent protons.

Experimental

Eastman X-480 anthracene, Eastman H-480 synthetic anthracene, and Volk/Isotopes deuterated anthracene were used without further purification. The composition of the deuterated anthracene is specified by Volk/Isotopes to contain 91.77% anthracene $C_{14}D_{10}$ and 8.23% anthracene $C_{14}D_9H$. Irradiations were performed with a 2700 curie Cobalt-60 source. Dose rates were of the order 2×10^5 rads/hr. Measurements on the powdered anthracenes were made for doses from 10^5 to 10^8 rads in unirradiated Suprasil tubes on a Varian E-3 Spectrometer. All spectra were obtained under conditions of minimum power saturation. The concentrations of the paramagnetic centers were determined by comparison of the areas of spectra with areas of known galvinoxyl concentrations under identical instrument conditions.

Results and Discussion

Figure 1 (a) shows the derivative spectra of the paramagnetic centers produced in anthracene powder. The spectra obtained from anthracene X-480 was identical to that from H-480. No changes in the spectra were observed on rotation of the sample tube. Nor were changes observed in the spectra of samples which were allowed to stand for times up to one month after removal from the radiation source. However, samples which had been exposed to the air for times as great as one year developed a very strong line, located slightly below the center point of the spectra, possibly the result of oxygen diffusion into the crystal and resultant peroxy radical formation.[5] Detailed analysis of the spectra under highest resolution conditions showed no changes in the spectra other than intensity up to a maximum dose of 7 × 10^8 rad. The estimated spacing of the lines is approximately 20 gauss for the paramagnetic center in H-480 or X-480. The width of the integrated signal at half maximum intensity is 37 gauss.

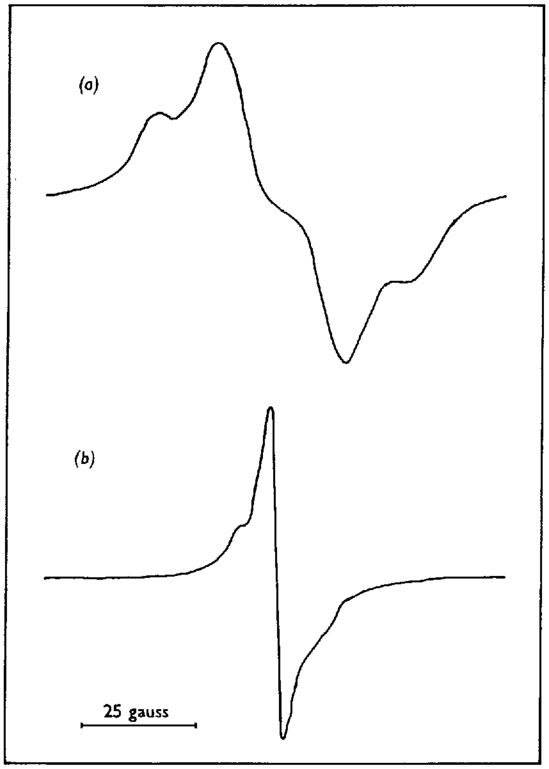

Figure 1. (a) ESR spectrum of gamma irradiated anthracene. Dose: 6.6 × 10^8 rads. (b) ESR spectrum of gamma irradiated deuterated anthracene. Dose: 9.8 × 10^7 rads. In both cases the spectrum is centred at $H = 3381$ gauss and $\nu = 9.53$ gigacycles. The modulation for (a) is 0.5 gauss and for (b) is 1 gauss.

The paramagnetic center associated with the deuterated anthracene seen in Fig. 1(b) shows so much anisotropic broadening that it is impossible to estimate spacing or number of lines. The width at half maximum intensity of the integrated signal is 16 gauss. While this value is considerably less than that of the paramagnetic center produced in anthracene, it is still larger than would have been anticipated from the interactions of three equivalent deuterons.

One possible cause of excessive breadth of EPR signal in a powder is that due to anisotropy in the hyperfine interactions. The intensity of an EPR line is a function of both the isotropic and anisotropic components of the hyperfine interaction tensor. These components are very much smaller for a deuterated radical than the corresponding protonated radical. Consequently, the broadening experienced by a deuterated radical would be less than in a protonated radical. Since the spectral extent of the radical in powder anthracene is not broadened more than that of methyl radical in solution, (see for example, Fig. 2), then it follows that the breadth of the deuterated radical in powdered anthracene will not be greater than that of a deuterated methyl radical. Hence, it is unlikely that anisotropic broadening is a major cause of the excessive breadth of the deuterated anthracene radical signal. On the

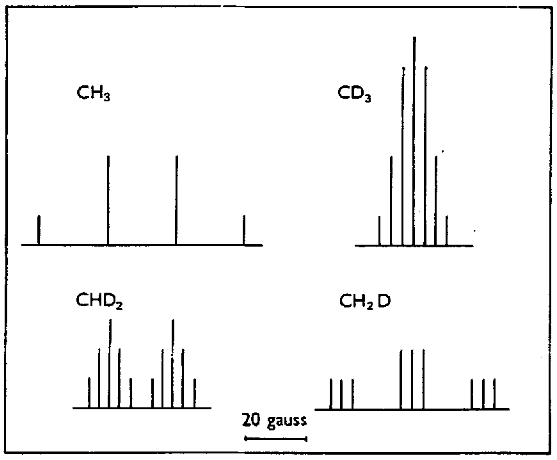

Figure 2. Spectra of methyl and partially deuterated methyl radicals based on measured splitting constants of Fessenden and Shuler[6,5].

basis of the line spectra of methyls radicals, based upon data of Fessenden and Shuler[6, 5], it can be argued that the radical produced in deuterated anthracene has an extent less than one-third that of the protonated radical.

The area of the integrated signal of the deuterated radical spectrum outside of one-third of the extent of the spectrum of the protonated radical corresponds to 6% of the total. This is very close to the percentage of $C_{14}D_9H$ nominally present in the sample. A radical produced by radiolysis of this impurity may have spectral extent corresponding to CHD_2, Fig. 2. Since $C_{14}D_9H$ has only one proton, and at this concentration all nearest neighbors in the crystal lattice would be fully deuterated, the resultant radical could have no more than one proton. The spectrum of a mixture of deuterated and partially deuterated radicals would be broadened,

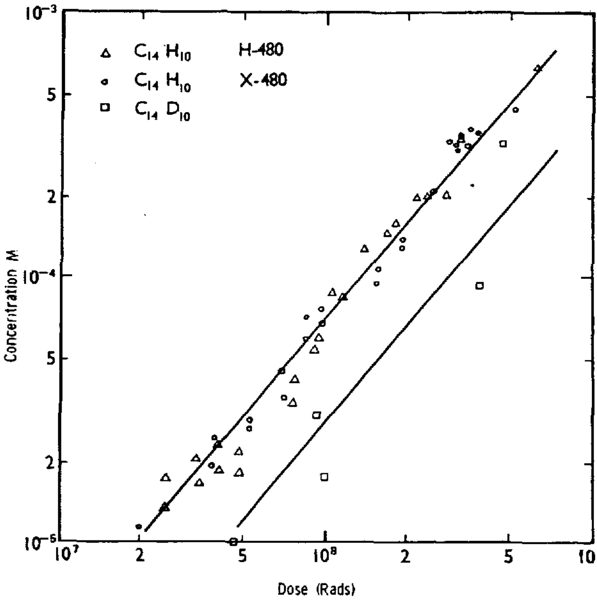

Figure 3. Concentration of radiation induced centers in anthracene and deuterated anthracene vs radiation dose. Galvinoxyl was used for the calibration of concentration.

hence it could explain our results. Studies of the EPR spectra produced by irradiation of selectively deuterated anthracene is anticipated to provide even greater insight into the nature of the γ-ray induced paramagnetic centers in anthracene.

Figure 3 shows concentration of these centers vs. dose. The concentration depends linearly upon dose, and is unaffected by the purity of the sample. The G value for the production of these paramagnetic centers in $C_{14}H_{10}$ is $7 \times 10^{-4}/100$ eV and $3 \times 10^{-4}/100$ eV in $C_{14}D_{10}$. These values are lower than our previously reported G values for production of singlet excitons quenching centers[7] ($G = 5/100$ eV) for triplet exciton quenching centers[7] ($G = 6 \times 10^{-2}/100$ eV) and for carrier traps[8] ($G = 10^{-2}/100$ eV). They do agree with a previously reported value[9] for the production of paramagnetic centers in $C_{14}H_{10}$ ($G = 4 \times 10^{-4}/100$ eV).

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