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ESR and ENDOR Study of the Carbonization of Rubrene

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Synopsis. An ESR spectrum of the radical produced during the carbonization of rubrene was measured and analyzed from an ENDOR spectrum and using computer simulations.

It is well-known that the initial thermal reactions of organic materials are of particular importance in determining the course of the subsequent carbonization and graphitization processes.[1-3] The reaction mechanism and the precursor of the carbon produced have been investigated by X-ray diffraction,[1] mass spectrometry,[3] chromatography,[4] *etc.* Singer and Lewis[5] have pointed out that the electron spin resonance (ESR) spectrometer is a powerful tool for obtaining information about the individual steps of the carbonization process when pyrolysis is carried out in an inert solvent such as *m*-quinquephenyl. In many cases, however, it appears rather difficult to analyze the many ESR spectral lines due to radicals of large molecular size.[6]

The purpose of the present study is to identify the radicals produced during initial carbonization by combining the ESR technique with electron nuclear double resonance (ENDOR) and to clarify the reaction process involving the mechanism of radical formation. This paper is concerned with the structure of the radical formed by the pyrolysis of rubrene, *i.e.*, 5,6,11,12-tetraphenylnaphthacene ($C_{42}H_{28}$), and with the associated reaction mechanism. The reason why rubrene was selected as the starting material is that the carbonization reaction rate is moderate compared with that of naphthacene.

Experimental

Rubrene and *m*-quinquephenyl were purchased from the Aldrich Chem. Co., Inc., and the K & K Laboratories, Inc., respectively. The preparation of the sample and the procedure for ESR measurement are described elsewhere.[6] The ENDOR spectra were obtained using a Japan Electron Optics Laboratory ES-EDX1 ENDOR spectrometer.

Results and Discussion

Rubrene dissolved in *m*-quinquephenyl in a weight ratio of 1 : 10 began to exhibit a large number of ESR spectral lines for pyrolysis at 450 to 470 °C. Figure 1(a) shows the spectrum observed at 150 °C for the heat treatment of rubrene at 500 °C for 5 min. This spectrum consists of about 57 lines with the same interval of 0.44 G, which are overlapped by a broad line. The spectrum illustrated in Fig. 1(a) is spread over about 25 G. The spin concentration is of the order of about 1.2 species per 1000 molecules of rubrene heat-treated at 450 °C. A similar spectrum was observed also when only rubrene was pyrolyzed at 425 °C for 1 h or at 450 °C for 10 min and then dissolved in *m*-quinquephenyl. Accordingly, it appears reasonable that the *m*-quinquephenyl used in this experiment does not participate in the rubrene carbonization.

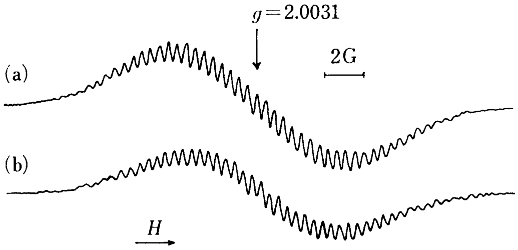

Fig. 1. (a) Experimental ESR spectrum of the radical produced when rubrene was heat-treated in *m*-quinquephenyl at 500 °C for 5 min. The spectrum was measured at 150 °C. (b) The calculated spectrum. Line spape is Gaussian, with a peak to peak linewidth of 0.35 G. The spectrum consists of 8 equivalent protons with $a^H=0.884$ G, 6 protons with 1.230, 4 protons with 1.724, 2 protons with 1.964, and 2 protons with 2.412.

When the rubrene was treated in *m*-quinquephenyl at 500 °C for a period longer than 5 min, the intensity of the broad line gradually increased but the relative intensity of the hyperfine spectral lines scarcely changed. Also, when the spectra were measured at various temperatures between 130 and 190 °C, the line widths became sharper with increasing temperature, whereas no significant variation of the intensity ratio was observed in this temperature range. Assuming a single radical on the basis of these observations, one can explain the odd lines of the hyperfine structure in terms of the interaction with even hydrogen nuclei.

An ENDOR spectrum was recorded at 150 °C for the sample heat-treated in *m*-quinquephenyl at 500 °C for 5 min (Fig. 2). Five pairs of lines which were reduced to hyperfine splitting constants of 0.884, 1.230, 1.724, 1.964, and 2.412 G, were observed above and below the free-proton frequency.

On the basis of the values of the splitting constants determined from the ENDOR signal, the ESR spectrum was simulated using the SESRS computer program of Stone and Maki.[8] As a result, two calculated spectra were found to fit the observed spectrum best by trial and error. One consists of 8 equivalent protons at $a^H=0.884$ G, 6 protons at 1.230, 4 protons at 1.724, 2 protons at 1.964, and 2 protons at 2.412. The other is composed of 8 protons at 0.884 G, 6 protons at 1.230, 4 protons at 1.724, 4 protons at 1.964, and 2 protons at 2.412. The former spectrum is represented in Fig. 1(b).

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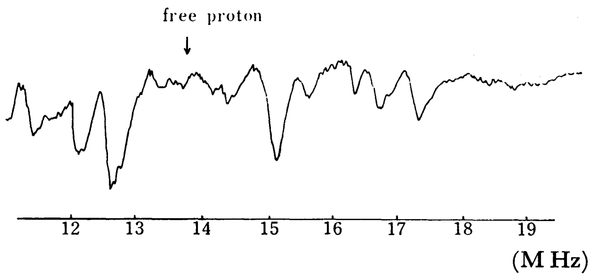

Fig. 2. ENDOR spectrum of the radical produced when rubrene was heat-treated in *m*-quinquephenyl at 500 °C for 5 min. The spectrum was measured at 150 °C.

π-Radicals, such as perinaphthenyl, are generally known to be stable at the intermediate stage of early carbonization.⁷⁾ These radicals always contain an odd number of carbon atoms. In this case, since carbon-carbon bond cleavage within the benzene and/or naphthacene ring in the rubrene is impossible at as low a temperature as 500 °C, the radical produced from the rubrene is considered to be located in the carbon-frame composed of 11 rings, such as bi-naphthacene.

In order to confirm the existence of a biradical, on the other hand, the lines due to the $\Delta M_s=\pm 2$ transition were examined and temperature variations of the spectrum were measured over the range 123—373 K, for which a single line was observed. No line corresponding to this transition was found at low field, but the absorption intensity significantly decreased with decreasing temperature. This result may suggest the existence of a biradical. Also, it can be considered that dimerization of the radical causes a reduction in the signal intensity.¹⁰⁾ But the large molecular size of the radical formed in the carbonization of rubrene may make dimerization difficult in the solid phase at the low temperature tested. Accordingly, identification of the radicals is expected after further experimentation.

As an approach to estimating the molecular weight of the reaction product, the mass spectrum of the sample carbonized at 450 °C with no solvent was observed. New intense peaks appeared in the range 608—684, in addition to a group of peaks at $m/e=532$, which were assigned to the unreacted parent molecular ion.⁹⁾ The thermal reaction of rubrene involves the elimination of substituted phenyl groups, subsequent polymerization and aromatization to a condensed aromatic layer. The development of such a plane as the precursor of carbon is thought to result in a well-ordered graphite product, the *c*-spacing of which is 3.356 Å.¹¹⁾

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