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An Electron Spin Resonance Study of the Carbonization of Acenaphthylene

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Many Electron Spin Resonance (ESR) studies have been made on charred materials.[1-3] Since most of these experiments were carried out on solid state, however, only one signal was observed, and consequently the intermediate radicals produced in the process of carbonization could not be identified by the signal. Recently, Singer and Lewis[4-6] investigated the carbonization of acenaphthylene, 9,9′-bifluorene, and so forth in *m*-quinquephenyl, which is a high-boiling and inert solvent. They reported in their first paper[4] that the signal due to the perinaphthenyl radical is observed at the early stage of the pyrolysis of acenaphthylene and suggested that the 4,6-dimethylperinaphthenyl radical also appears during the carbonization. However, their discussion was chiefly confined to the identification of these radicals. The present investigation, therefore, was undertaken in order to clarify the reaction mechanism of the pyrolysis of acenaphthylene at from 200 to 500 °C on the basis of the variation in the signal intensity for the radicals identified by Singer and Lewis.[4] In this connection, decacyclene in *m*-quinquephenyl was carbonized in the same manner as acenaphthylene.

Experimental

The acenaphthylene was purified by recrystallization from ethanol. The decacyclene and *m*-quinquephenyl were purchased from the Aldrich Chem. Co. Inc. and K & K Laboratories, Inc., respectively. Samples were prepared by adding acenaphthylene to *m*-quinquephenyl at a weight ratio of 1: 10 and then by degassing them at room temperature. These samples were heated in a furnace for 5 min at 30 °C intervals in the range from 200 to 500 °C. All of the ESR spectra were measured at 150 °C because *m*-quinquephenyl begins to melt at 125 °C. The ESR apparatus was a Japan Electron Optics Laboratory JES-ME-3X-type spectrometer with a temperature-varying attachment.

Results and Discussion

When the temperature of acenaphthylene dissolved in *m*-quinquephenyl was raised to 290 °C, the well-

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[1] D. J. E. Ingram and J. E. Bennett, *Phil. Mag.*, **45**, 545 (1954).

[2] L. S. Singer, W. J. Spry, and W. H. Smith, Proc. Third Carbon Conf., Pergamon Press (1959), p. 121.

[3] S. Toyoda, S. Sugawara, and T. Furuta, *Carbon* (Oxford), **8**, 473 (1970).

[4] L. S. Singer and I. C. Lewis, *ibid.*, **2**, 115 (1964).

[5] I. C. Lewis and L. S. Singer, *ibid.*, **5**, 373 (1967).

[6] I. C. Lewis and L. S. Singer, *ibid.*, **7**, 93 (1969).

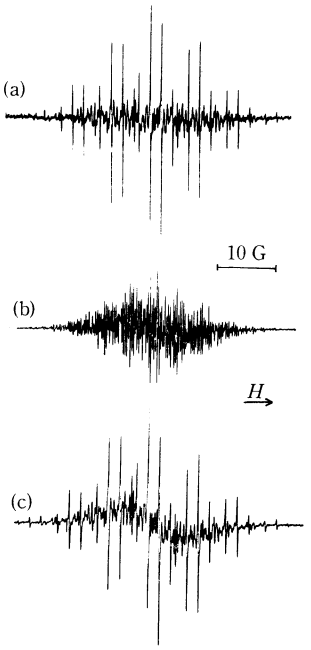

Fig. 1. ESR spectra of acenaphthylene in *m*-quinquephenyl heat-treated up to (a) 320 °, (b) 440 °, and (c) 500 °C.

resolved ESR spectrum shown in Fig. 1(a) was observed. It consists of two hyperfine structures; one structure is due to six equivalent protons, with a coupling constant of 6.32 gauss, and the other to three equivalent protons, with a constant of 1.81 gauss. It agrees closely with the spectrum observed by Singer and Lewis.[4] Thus, the substance in the solution can be identified as the perinaphthenyl radical (V).[7] Further heat-treatment up to 440 °C brings about the formation of a new radical, as may be seen in Fig. 1(b). The spectral lines derived by subtracting the signal due to the (V) radical from the spectral lines of Fig. 1(b) correspond to the 4,6-dimethylperinaphthenyl radical (VI) assigned by Singer and Lewis.[4] Though the spectral intensity due to the (V) radical is weak at this temperature, it increased again when the sample was heated to 500 °C. In addition, the broad line of 5 gauss became more intense. The variation in the spectral intensity of the (V) and (VI) radicals is represented in Fig. 2 as a function of the heat-treatment temperature. Since *m*-quinquephenyl boils near 540 °C, the samples were not heated above 500 °C. When the temperature of the sample was maintained at 500 °C, the signal intensity for the (V) radical decreased. Hence, the spectral intensity is probably lowered above 500 °C.

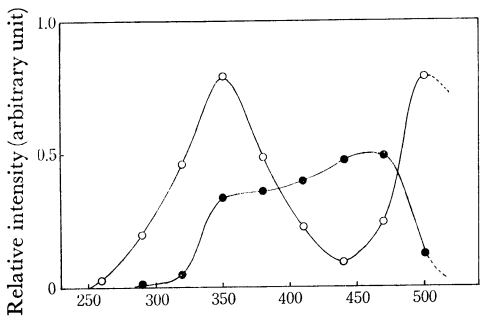

Fig. 2. The relation between the signal intensity and heat-treatment temperature.
○: Perinaphthenyl radical
●: 4,6-Dimethylperinaphthenyl radical

Acenaphthylene is well known to polymerize with pyrolysis at *ca.* 200 °C and then to decompose near 350 °C, resulting in biacenaphthylidene (II) (or dinaphthylenebutadiene), decacyclene (IV), and fluorocyclene (III).[8] Mueller[8] studied the acenaphthylene pyrolysis by thin-film chromatography and found that biacenaphthylidene (II) and fluorocyclene (III) disappear above 350 °C, while decacyclene (IV) is stable at 450 °C. On the basis of these facts, the increase in the radical concentrations of (V) and (VI) up to 350 °C may be explained in terms of the pyrolysis of biacenaphthylidene (II) and fluorocyclene (III). When the sample was heated at higher temperatures, the signal due to the (VI) radical remained almost constant, while that due to the (V) radical gradually decreased. Such a difference may be interpreted as follows: the (V) radical generally exists in equilibrium with its diamagnetic dimer.[9] Accordingly, a decrease in the amount of the (V) radical seems to be responsible for the dimerization. On the contrary, because of the steric hindrance, the (VI) radical is less mobile and less subject to dimerization than the (V) radical. Therefore, the (VI) radical may be thought to be present even at higher temperatures.

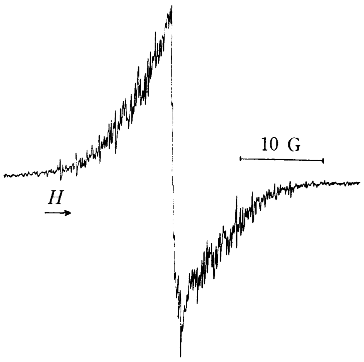

Fig. 3. ESR spectrum of decacyclene in *m*-quinquephenyl heat-treated up to 500 °C.

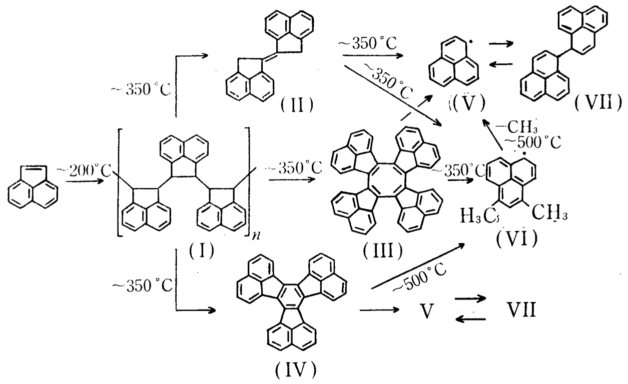

Fig. 4. The carbonization of acenaphthylene.

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7) This number is shown in Fig. 4.

8) K. Mueller, Ph. D. Thesis, Karlsruke University, W. Germany, 1967.

9) F. Gerson, *Helv. Chim. Acta*, **49**, 1463 (1966).

When decacyclene (IV) dissolved in *m*-quinquephenyl was heated, the faint signals due to the (V) and (VI) radicals began to appear at from 440 to 470 °C. However, the signals were significantly weaker than those obtained from carbonized acenaphthylene and were superposed by a spectral line, the linewidth of which was *ca.* 2.5 gauss (Fig. 3). Therefore, it seems unreasonable to regard the increase in the radical concentration of (V) at from 440 to 500 °C as caused by decacyclene (IV) alone. According to the results of Madison and Roberts,[10] the liquid-phase pyrolysis of an alkyl-substituted aromatic compound leads to a cleavage of the alkyl group at *ca.* 470 °C. In this case, it is clear that the (VI) radical decomposes to produce the (V) radical and methane. With this view, the high value of concentration for the (V) radical at 500 °C may be concluded to be due not only to decacyclene (IV), but also to the (VI) radical. Figure 4 shows a reaction scheme for acenaphthylene proposed on the basis of the results mentioned above. However, the formation of zethrene described by Ruland[11] should also be taken into account in the pyrolysis of acenaphthylene, although it cannot be detected by the ESR technique.

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[10] J. J. Madison and R. M. Roberts, *Ind. Eng. Chem.*, **50**, 237 (1958).

[11] W. Ruland, *Carbon* (Oxford), **2**, 365 (1965).