Electron Spin Resonance Spectra in Benzene UV-Irradiated at 77°K

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An ESR spectrum, consisting of six lines with a splitting value of 6 gauss and with an intensity ratio of approximately 1 : 1.8 : 2.6 : 2.6 : 1. 8 : 1 (see Fig. 1(a)), was observed when benzene was irradiated by ultraviolet light from a high-pressure mercury lamp (Toshiba 400W) at 77°K.

As the samples, Dotite spectrosol benzene manufactured by the Dojindo Research Laboratories Co., Ltd., and Merck's spectrograde benzene were used. These samples were treated with Na-K alloy *in vacuo* for 1 to 30 days and then vacuum-distilled into quartz ampoules and sealed after having been frozen and thawed repeatedly. Recrystallized benzene was also used after it had been purified according to the method of Kanda *et al.*1) ESR spectra were recorded at 77°K on a Varian V-4560 EPR spectrometer with 100Kc modulation. The same six-line spectrum was observed from samples purified differently. The spectrum due to the cyclohexadienyl radical2,3) was not observed in specimens of the purified benzene. When thiophene was added to the purified benzene at a concentration of 0.1 mol/*l*, the six-line spectrum in Fig. 1(a) became unsymmetrical because of the overlapping of the thiophene radicals component. However, when the concentration of thiophene was less than 0.1 mol/*l*, no effect on the spectrum appeared. Merck's hexadeuterobenzene gave only a singlet spectrum with a ΔH_{msl} value of 7 gauss upon ultraviolet irradiation (see Fig. 1 (b)). Using filters (Toshiba UV-25, UV-D25 and UV-29), the effective wavelength for the spectrum was found in the region from 2300 Å to 2600 Å. The effectiveness of light shorter than 2000 Å was not examined. The rate of radical formation was found nearly proportional to the square of the photo-intensity.

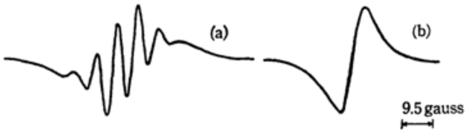

Fig. 1. ESR spectra of UV irradiated benzene (a) and hexadeuterobenzene (b) at 77°K. Ultraviolet irradiation was performed with a high-pressure mercury lamp at 77°K, for 120 min (a) and 250 min (b).

The six-line spectrum can be interpreted as a phenyl radical in which the two ortho protons have a hyperfine coupling constant of 12 gauss and in which the para proton gives a 6 gauss splitting, while the meta protons seem to contribute only negligibly.

Several papers have been published on the ESR spectrum of the phenyl radical. In earlier studies,3,4) a singlet spectrum with ΔH_{msl} values of 20 to 25 gauss was assigned to the phenyl radical. Tolkachev *et al.*5) observed a spectrum by photolysing iodobenzene adsorbed on silica gel and claimed that it consisted of a triple-triplet. However, their spectrum does not resolve very well. More recently, Benett *et al.*6) have succeeded in observing the spectra of the phenyl radical produced by chemical reaction of iodobenzene with metallic sodium. In the matricies of benzene, hexadeuterobenzene, and water, a triple-triplet spectrum was obtained, with the largest splitting, (18 gauss) due to two ortho protons, and a minor splitting, (7 gauss) due to meta protons. However, in the matricies of xenon and iodobenzene, only broad, poorley-resolved spectra were observed. They ascribed this very apparent difference to the effects of the matrix.

As for the hyperfine coupling constants of the phenyl radical, two theoretical papers have been published. Morokuma *et al.*,7) basing their work on the valence bond method, have shown that the ortho and meta protons would give hyperfine splitting values of −12.1 and −6.3 gauss respectively. On the other hand, Dixon8) has predicted somewhat different results, his ortho protons giving a 23.3 gauss splitting, and his para proton, a 17.9 gauss splitting, on the basis of the molecular orbital calculation. The present spectrum seems to agree with Dixon's prediction with respect to the order of magnitude of the hyperfine coupling constant.

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