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Electron Spin Resonance Study on Ultraviolet Light Irradiated Benzene Adsorbed on Silica Gel and Alumina

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Benzene adsorbed on silica gel was irradiated at 77°K with ultraviolet light. Three kinds of samples, with different degree of adsorption, were examined. ESR spectra were strongly dependent on the amount of benzene adsorbed and three different spectra were observed; (1) six-line spectrum with a splitting value of 6 gauss, assigned to phenyl radical, (2) seven-line spectrum with a splitting value of 4.5 gauss, assigned to benzene cation radical, and (3) apparent nine-line spectrum with 2.4 gauss splitting due to benzene dimer cation radical. Upon raising temperature, benzene cation radical was found to transform into benzene dimer cation radical. In UV-irradiated benzene-alumina system, cyclohexadienyl radicals were observed in addition to the ion radicals. It is suggested that the above reaction may be occurred by two photon absorption process involving the excitation of triplet benzene.

Photochemical studies on benzene have been carried out in various organic rigid glasses, mainly by optical spectroscopic methods. Gibson *et al.*1) showed an evidence that benzene was photochemically decomposed in the rigid glasses of EPA and 3-methyl perfluoropentane to produce hexatriene-1,3,5 and diphenyl, respectively. Subsequently, Porter2) and Leach *et al.*3) independently investigated these reactions and led to a conclusion of the formation of substituted hexatriene. Migirdicyan4) made an attempt to observe photochemical intermediates of benzene in organic rigid glasses by the method of electron spin resonance, but failed to observe any intermediate signal from benzene.

In the previous paper,5) we reported that an ESR spectrum, consisting of six lines with the splitting value of 6 gauss, was observed from benzene irradiated with ultraviolet light from high-pressure mercury lamp at 77°K. In relation to this investigation, the present work was undertaken in order to obtain more insight in unstable photochemical intermediates from UV-irradiated benzene and to examine its reaction mechanism, using the method of ESR. We obtained an evidence that benzene adsorbed on silica gel can be photoionized by UV-irradiation at 77°K and that, when alumina is used as an adsorbent, hydrogen addition reaction to benzene ring can take place in addition to photo-ionization. A subsequent conversion reaction of benzene cation radical has also been investigated. On the basis of these experimental results, a photochemical reaction mechanism of benzene has been presented.

Experimental

Materials. Benzene was obtained from two commercial sources, Dotite spectrosol benzene manufactured by the Dojindo Research Laboratories Co., Ltd., and Merck's spectro-grade benzene. These samples were purified by recrystallization according to the method of Kanda *et al.*6) In some experiments, benzene was purified in the presence of Na-K alloy through repeated freezing and thawing *in vacuo*. Hexadeuterobenzene of Merck (purity: 99%) was used without further refining. Silica gel from Mallinckrodt Chemical Works (100 mesh silica gel) was heated *in vacuo* for about 5 hr at 413 to 773°K. In some experiments, the silica gel was washed with special grade concentrated hydrochloric acid and distilled water, immediately before its use. Silica powder was obtained from ground quartz ampoules. Activated alumina for chromatographic adsorption from Nakarai Chemical Company Ltd. was used without further refining. It was heated *in vacuo* at 573°K for about 5 hr.

Adsorption Procedures. The adsorption apparatus was made modifying a vacuum transfer apparatus by Lewis *et al.*7) and was connected to vacuum line. All samples were treated in the adsorption apparatus and subsequently the vapor was led to adsorbent in the ESR ampoule. The amount of adsorption of

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benzene was not measured, but controlled by the following three procedures. 1) ESR quartz ampoule was cooled by liquid nitrogen for a moment (Sample-1). 2) Silica gel was exposed to benzene vapor for about 5 to 10 min at room temperature (Sample-2). 3) Sample-2 was pumped off at 323 to 333°K for about 2 to 3 hr (Sample-3).

Light Source and Irradiation. Either high-pressure mercury lamp (Toshiba 400W) or low pressure mercury lamp (Toshiba germicidal lamp) was used. As the filters were used Toshiba UV-25, UV-D25 and UV-29, respectively. γ-Irradiation was performed with Co-60 (700 Ci) at 77°K.

ESR Measurement. Spectra were recorded on a Varian V-4560 EPR spectrometer with 100kc modulation at 77°K and at higher temperatues up to about 173°K by using the Varian liquid nitrogen and variable temperature accessories.

Results

Benzene-Silica Gel Adsorption System. ESR spectra of UV-irradiated Sample-1, Sample-2 and Sample-3 are shown in Fig. 1. The effective wavelength to produce these spectra was found in the region from 2300 Å to 2600 Å by using filters. It is demonstrated that the spectra are strongly dependent on apparent amount of adsorption of benzene. UV-Irradiated hexadeuterobenzene, corresponding to Sample-2 and Sample-3, gave only a singlet spectrum with ΔH_{msl} value of 3.4 gauss (see Fig. 2). Irradiated silica gel without adsorbed benzene gave no ESR signal, nor did adsorbed benzene without irradiation.

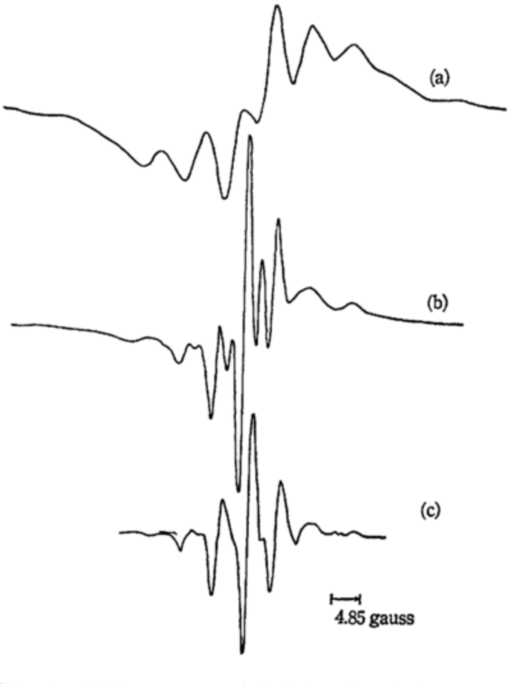

Fig. 1. ESR spectra of UV-irradiated benzene adsorbed on silica gel. The alphabetical marks in the figure, (a), (b) and (c), corresponds to Sample-1, Sample-2 and Sample-3 (see Experimental in this paper), respectively. UV-irradiation was performed for 100 min at 77°K.

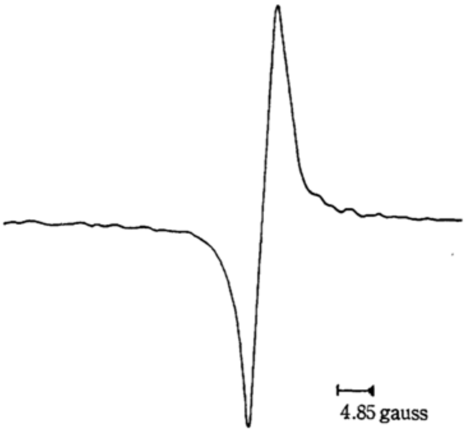

Fig. 2. ESR spectrum of UV-irradiated hexadeuterobenzene adsorbed on silica gel. UV-irradiation was performed for 100 min at 77°K.

On raising temperature, these spectra change as shown in Figs. 3 to 5. In the spectrum of Sample-1 (see Fig. 3), a sharp component of the splitting 2.4 gauss appears in the central part. The seven-line spectrum of Sample-3 (see Fig. 5) gradually disappears and an apparent nine-line spectrum, with the intensity ratio of 1 : 2 : 5 : 8 : 14 : 8 : 5 : 2 : 1 and the splitting value of 2.4 gauss, appears, when the sample was kept at dry ice - methanol temperature. The behavior of Sample-2 (see Fig. 4) is also analogous to those of Sample-1 and Sample-3.

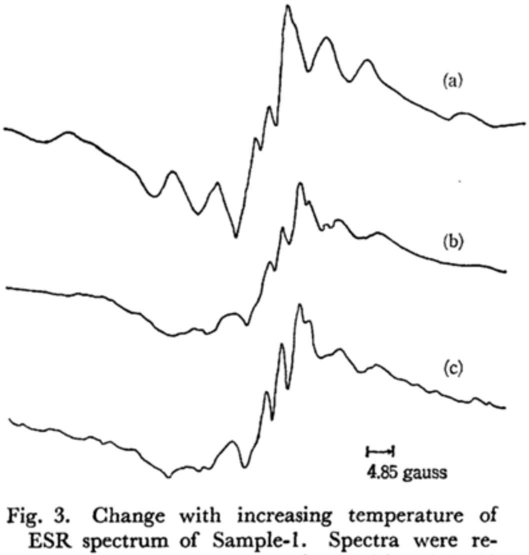

Fig. 3. Change with increasing temperature of ESR spectrum of Sample-1. Spectra were recorded at the temperatures of 77°K (a), 123°K (b) and 153°K (c).

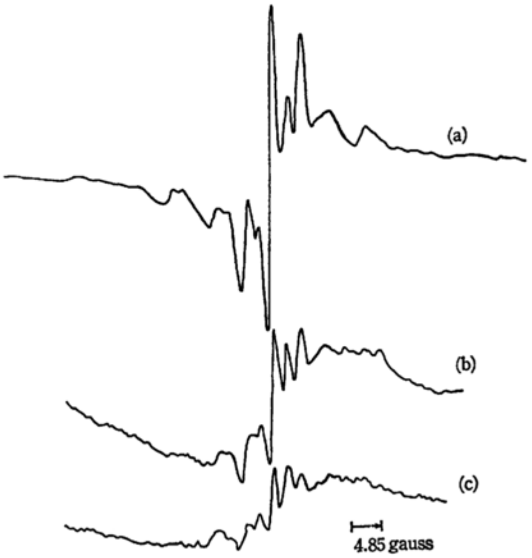

Fig. 4. Change with increasing temperature of ESR spectrum of Sample-2. Spectra were recorded at the temperatures of 77°K (a), 128°K (b) and 173°K (c).

The spectrum of Sample-1 mainly consists of six lines with the splitting value of 6 gauss (see Fig. (1 a)), which is essentially the same as the six-line spectrum[5] observed from UV-irradiated polycrystalline benzene at 77°K. The spectrum of Sample-2 is a superposition of the six-line spectrum and some sharp line spectrum in the central part, with the splitting value of 2.4 gauss (see Fig. 1(b)). The spectrum of Sample-3 is a sharp seven-line one, with the intensity ratio of 1 : 5 : 16 : 24 : 15 : 4.5 : 1, and its splitting value is approximately 4.5 gauss (see Fig. 1(c)).

From the UV-irradiated mixture of benzene with ground silica powder was observed a poorly resolved six-line spectrum, with the splitting value of 6 gauss, which is quite similar to the six-line spectrum of UV-irradiated polycrystalline benzene.

To summarize, we have observed three different spectra from UV-irradiated benzene adsorbed on silica gel. One is the six-line spectrum of 6 gauss separation (Fig. 1(a)). The second one is the seven-line spectrum of 4.5 gauss splitting (Fig. 1(c)) and the third one is the apparent nine-line spectrum of 2.4 gauss splitting (Fig. 5(c)).

Benzene-Alumina Adsorption System. The ESR spectrum of UV-irradiated benzene-alumina system (see Fig. 6) consists of a triplet of about 47 gauss splitting, each component with further quartet splitting of about 10.5 gauss, and in addition, it has a six-line component analogous to the benzene-silica gel system in the central part. The triplet spectrum of about 47 gauss splitting can be ascribed to the cyclohexadienyl radical.[8,9]

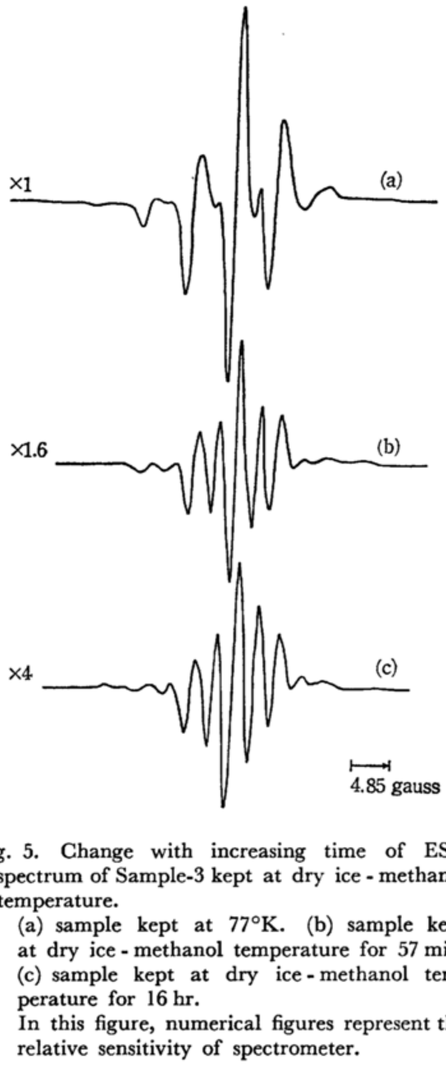

Fig. 5. Change with increasing time of ESR spectrum of Sample-3 kept at dry ice - methanol temperature.
(a) sample kept at 77°K. (b) sample kept at dry ice - methanol temperature for 57 min. (c) sample kept at dry ice - methanol temperature for 16 hr.
In this figure, numerical figures represent the relative sensitivity of spectrometer.

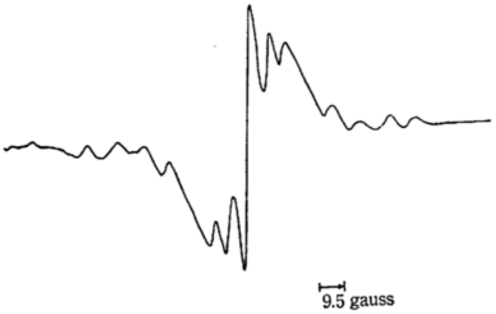

Fig. 6. ESR spectra of UV-irradiated benzene adsorbed on alumina. This sample corresponds to Sample-2. UV-irradiation was performed for 75 min at 77°K.

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Appearance of this triplet component is in contrast with the benzene-silica gel system. Upon subsequent γ-irradiation at 77°K, increase in triplet component was observed.

Discussion

Interpretation of ESR Spectra. According to the presentation in the preceding paper,[5] the six-line spectrum of 6 gauss splitting in Fig. 1(a) can be interpreted as the phenyl radical. The seven-line spectrum of 4.5 gauss splitting (Fig. 1(c)) can be assigned to the benzene cation radical. The splitting value is found to be 25% larger than that of the benzene anion radical. The difference between negative and positive ion radicals of alternant aromatic hydrocarbons has been studied by many workers from experimental and theoretical points of view.[7,10–17] Bolton *et al.*[12] have predicted that proton hyperfine coupling constants of positive ions should be larger than those of corresponding negative ions as a result of difference in charge density and obtained the following equation.

$$a_{\mathrm{H}}\pm = (Q\rho \pm K\rho^2) \tag{1}$$

a_{H}: the hyperfine coupling constant between electron and an aromatic proton

ρ: the spin density on the adjacent carbon atom

Q: a constant charateristic for an aromatic C–H bond

K: excess charge density

Lewis *et al.*[7] have measured the proton coupling constants of cation radicals of alternant aromatic hydrocarbons and concluded that hyperfine coupling constants of cation radicals are 25% larger than those of corresponding anion radicals. Their empirical values of Q and K in the Eq. (1) are 32.2 and 16, respectively.

The experimental result in the present work is found to agree quite well with the general tendency ascertained as for the difference between corresponding anions and cations. However, we have to use a different set of Q and K values. Namely, Q should be 25 and K be 15, in the Eq. (1). Most recently, in an independent work of the present study, Edlund *et al.*[18] have observed the ESR spectrum of the benzene cation radical from γ-irradiated benzene adsorbed on silica gel. Their splitting value is found to be in accord with the present value.

As shown in Fig. 5, benzene cation radical gradually decays and changes to show an apparent nine-line spectrum, on being preserved at dry ice-methanol temperature. The splitting value of nine-line spectrum corresponds to one half of that of benzene cation radical. On the basis of these data, it seems the most reasonable to assume that the apparent nine-line spectrum is responsible for the benzene dimer cation radical $(C_6H_6)_2{}^+$, in which the spin density on carbon atom should be 1/12 and its theoretical spectrum should consist of 13 lines with the intensity ratio of 1 : 12 : 66 : 220 : 495 : 792 : 924 : 792 : 495 : 220 : 66 : 12 : 1. The above ratio indicates that the intensities of outer peaks become almost negligible as compared with those of the central part. Therefore, its relation seems to be consistent with the experimental fact that only the nine lines, with the intensity ratio of 1 : 2 : 5.4 : 8.1 : 14 : 8.1 : 5.4 : 2 : 1, were observed from the benzene dimer cation radical. The central intensity ratio in the experimental nine-line spectrum, however, seems to be rather higher in comparison with the theoretical intensity ratio. Its difference is probably due to the overlapping of the initial seven-line spectrum still just remaining in the central part of the nine-line spectrum. Edlund *et al.*[18] have also observed this nine-line spectrum from γ-irradiated benzene adsorbed on silica gel.

The spectrum shown in Fig. 1(b) can be interpreted as an overlapping of six-line spectrum in Fig. 1(a), seven-line spectrum in Fig. 1(c) and nine-line spectrum in Fig. 5(c).

In benzene-alumina system (Fig. 6), one can interpret that cyclohexadienyl radicals are produced in addition to phenyl and benzene ion radicals.

Bubnov *et al.*[19] have observed ESR spectra from ultraviolet light irradiated "benzene-phosphoric acid matrix" (benzene concentration; 2×10^{-2} mol/*l*) at 77°K. And very recently, Carter *et al.*[20] have observed the seven-line and nine-line spectrum from UV-irradiated "benzene-sulfuric acid matrix" and the six-line spectrum from UV-irradiated polycrystalline benzene, while we are preparing the present manuscript.

Photochemical Reactions of Adsorbed Benzene. Photo-ionization of benzene derivatives has been observed in various media by many

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workers[21-25] and its mechanism has been interpreted by two photon absorption process involving an excitation of triplet state. In the case of photoionization of adsorbed benzene, the absorption of one photon, with the energy of 4.75 to 5.37 eV, would be energetically insufficient to photoionize benzene, because the first ionization potential of benzene corresponds to 9.2 eV. In the radiolysis of hydrocarbons adsorbed on silica gel, an increase in G values has been confirmed.[26] Moreover, it has also been reported that some catalytic sites are generated in silica gel irradiated with ionizing radiation.[27] In the photolysis, however, such a phenomenon has never been reported. Accordingly, it seems reasonable to assume that silica gel, generally well known as a physical adsorbent, would only act as a trapping site for very unstable paramagnetic species. As a trapping site in silica gel, one can suppose OH group, by which π-type hydrogen bond can be formed between benzene and silica gel surface.[28,29] From such a point of view, the photochemical reactions in benzene - silica gel system could be interpreted in terms of the following processes involving an excitation of triplet state benzene.

$$C_6H_6(\mathrm{ads}) \xrightarrow{2h\nu} C_6H_6^+ + e \qquad (2)$$

$$C_6H_6^+ + C_6H_6 \rightarrow \{C_6H_6\cdots C_6H_6\}^+ \qquad (3)$$

In the process (2), photo-ionization is induced by two photon absorption to lead to the formation of benzene cation radical. Namely, two photon absorption mechanism in benzene could be attained through transitions between the following excited states.

$${}^1A_{1g} \xrightarrow{h\nu} {}^1B_{2u}(4.84\,\mathrm{eV}) \quad {}^1B_{2u} \rightarrow {}^3B_{1u}(3.7\,\mathrm{eV})$$

$${}^3B_{1u} \xrightarrow{h\nu} {}^3E_{2g}(8.4\,\mathrm{eV})$$

In fact, triplet-triplet absorption in benzene has been successfully observed in organic rigid glasses of isopentane and 3-methyl-pentane at 77°K by Godfrey *et al.*[30] in recent years. Furthermore, the experimental fact that UV-irradiation at dry ice-methanol temperature gave no paramagnetic species and the emittance of phosphorescence at 77°K seem to suggest that the photo-excitation of ${}^3B_{1u}$ state plays a very important role in photoionization of benzene. The energy of ${}^3E_{2g}$ state, theoretically calculated by Pariser,[31] is approximately comparable to the benzene ionization potential energy.

Benzene cation radical is known as very unstable paramagnetic species. In the process (3), benzene cation, weakly adsorbed in polylayer state, and with more mobility, is followed by dimerization with surrounding benzene molecules to produce benzene dimer cation.

The process of the phenyl radical formation can not be reasonably explained from the present experimental results, although Carrington *et al.*[32] have suggested a possibility of phenyl radical being produced from benzene cation by ring proton detachment. According to the prediction by Carrington *et al.*,[32] the six-line spectrum of Fig. 1(a) can be responsible for the phenyl radical, the unpaired electron being localized on the carbon σ orbital.

The observation of cyclohexadienyl radicals in benzene-alumina system is rather different from the result in benzene - silica gel system, where cyclohexadienyl radicals can hardly be observed. This phenomenon can be reasonably interpreted as being responsible for the catalytic activity of alumina for the hydrogenation.[33]

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