BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1230—1233 (1971)

ESR Study of Adsorbed Monomer and Dimer Cation Radicals of Benzene and Its Methyl Derivatives

Siro Nagai, Shun-ichi Ohnishi, and Isamu Nitta

Osaka Laboratory for Radiation Chemistry, Japan Atomic Energy Research Institute, Neyagawa City, Osaka

(Received September 14, 1970)

Benzene, toluene, *o*-, *m*-, *p*-xylene, and mesitylene adsorbed on silica gel were γ-irradiated at −196°C. ESR spectra observed at −196°C for these systems at low contents of the methylbenzenes were assigned to the respective monomer cations. Dimer cations of benzene, toluene, and *p*-xylene were produced on γ-irradiation at −196°C of the adsorbed systems at higher contents and also by the reaction of monomer cations and neutral molecules at higher temperature than −160°C.

Edlund *et al.*[1] reported that the monomer and dimer cations of benzene were produced in γ-irradiated benzene-silica gel system and these authers[2] studied the formation of these cations, as well as neutral radicals, as functions of adsorption amount and irradiation dosage. Tanei[3] also observed these cations adsorbed on silica gel by ultraviolet irradiation. In the present paper, we describe results of our study on γ-irradiated methylbenzenes adsorbed on silica gel. From the analysis of the ESR spectra, we determined the structure of the radicals produced on the gel and followed reactions of the radicals on raising the temperature.

Experimental

Silica gel (Mallinckrodt Chemical Works, 100 mesh) was heated *in vacuo* at 500—550°C for 10 hr before use. The BET surface area determined by N_2 adsorption was 500 m^2/g. Chemicals were obtained from commercial sources; spectrograde benzene from Merck and toluene, *o*-, *m*-, *p*-xylene, and mesitylene from Nakarai Chemical Co., Ltd. (reagent grade). These reagents were used without further purification. Adsorbed samples were prepared by adding methylbenzene gas of known volume to silica gel in a vacuum line at room temperature, and a part of them (*ca.* 300 mg) was transferred *in vacuo* to spectrosil tube for ESR measurement. Amount of adsorption was determined with a Hg manometer, and was limited in the present study to the low coverage region, from 1.0×10^{-5} mol/g to the amount of monolayer. The amount of monolayer (coverage) was estimated from the area occupied by an adsorbed methylbenzene molecule[4] and the BET surface area. The obtained value was approximately 2×10^{-3} mol/g for benzene and its methyl derivatives.

γ-Irradiation was carried out at −196°C with a 2,000 Ci Co-60 source to a dose of 5.0×10^{5}R. ESR spectra were recorded using a Varian V-4500 spectrometer and variable temperature accessorries at various temperatures from −196°C to room temperature. The ESR signal from the γ-irradiated silica gel did not contribute significantly to the observed spectra for the methylbenzene-silica gel system.

Results and Discussion

ESR Spectra of Irradiated Adsorbed Aromatic Compounds. ESR spectrum of the adsorbed benzene was dependent on the amount of adsorption as reported by Edlund *et al.*[2] The adsorbed methylbenzenes also showed quite similar dependence. When the adsorbed amount was about 1/100 of the monolayer coverage, the ESR spectra shown in Figs. 1 to 5 were observed. For benzene, the observed spectrum (Fig. 1a) was the same as that reported by Edlund *et al.*[2]; the seven lines with

---

[1] O. Edlund, P.-O. Kinell, A. Lund, and A. Shimizu, *J. Chem. Phys.*, **46**, 3678 (1967).

[2] O. Edlund, P.-O. Kinell, A. Lund, and A. Shimizu, "Advances in Chemistry Series," Vol. 82, ed. by R. F. Gould, American Chemical Socеity Publications, Washington, D.C. (1968), p. 311.

[3] T. Tanei, This Bulletin, **41**, 833 (1968).

[4] R. N. Smith, C. Pierce, and H. Cordes, *J. Amer. Chem. Soc.*, **72**, 5595 (1950).

asymmetric individual lines, the splitting value being $a_{\mathrm{H}}=4.4$ gauss. Toluene gives the 5-line spectrum of $a_{\mathrm{H}}=14.0$ gauss with additional splitting of 3 gauss (Fig. 2a). The spectrum of *p*-xylene consists of seven lines ($a_{\mathrm{H}}=14.5$ gauss) with additional 3 gauss splitting (Fig. 3a). The splitting values for *m*-xylene, *o*-xylene, and mesitylene are 11.0 gauss, 11.0 gauss with additional splitting of 6 gauss, and 8.0 gauss, respectively.

When the amount of adsorption was increased, but still smaller than the monolayer coverage, the spectra for benzene, toluene, and *p*-xylene changed into those having splitting values a'_{H} equal to one half of a_{H}. No half-field resonances were observed for benzene. Benzene gives the 13-line spectrum with $a'_{\mathrm{H}}=2.2$ gauss (Fig. 1b), in agreement with the result by Edlund *et al.*[1] The spectra for toluene and *p*-xylene have the splitting values $a'_{\mathrm{H}}=7.0$ gauss, and 7.5 gauss, respectively. For *m*-xylene, *o*-xylene, and mesitylene, on the other hand, no such spectra with $a'_{\mathrm{H}}=a_{\mathrm{H}}/2$ were observed. Instead, the spectra became broadened, as shown in in Fig. 4 for *m*-xylene.

On increasing the adsorption amount further, close to and larger than the monolayer coverage, all the samples gave broad spectra which can be assigned to the cyclohexadienyl type radicals. These types of spectra were observed as trace background also for the lower coverage samples.

Assignment of the Spectra. ESR spectra observed

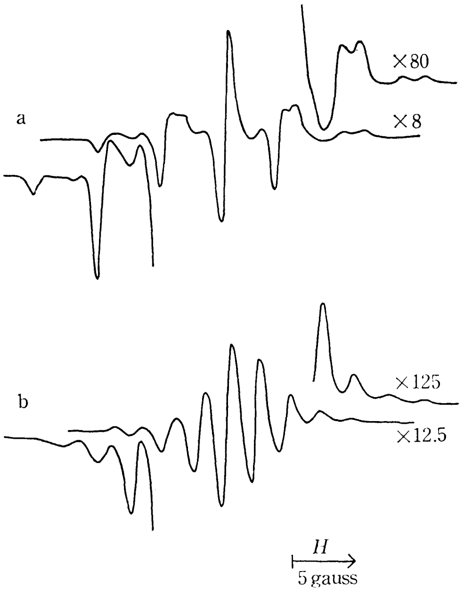

Fig. 1. ESR spectra from γ-irradiated benzene-silica gel at benzene content
(a) 2.4×10^{-5} mol/g, (b) 6.0×10^{-5} mol/g.

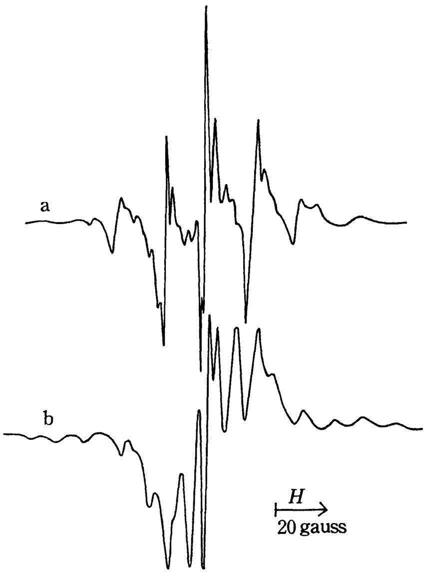

Fig. 3. Typical spectra from *p*-xylene-silica gel
(a) 2.1×10^{-5}mol/g, (b) 7.7×10^{-5} mol/g.

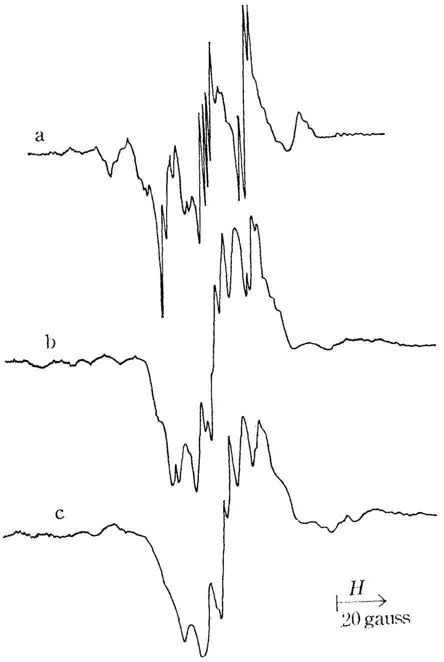

Fig. 2. ESR spectra from toluene-silica gel at toluene content
(a) 3.7×10^{-5} mol/g, (b) 7.5×10^{-5} mol/g, (c) 1.3×10^{-4} mol/g.

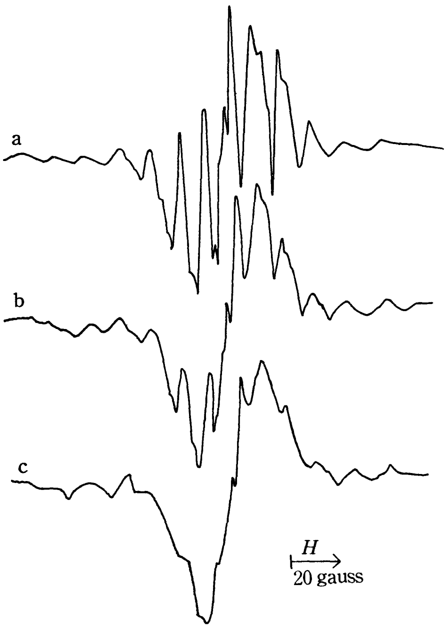

Fig. 4. ESR spectra from *m*-xylene-silica gel at *m*-xylene content
(a) 1.9×10^{-5} mol/g, (b) 4.1×10^{-5} mol/g, (c) 7.3×10^{-5} mol/g.

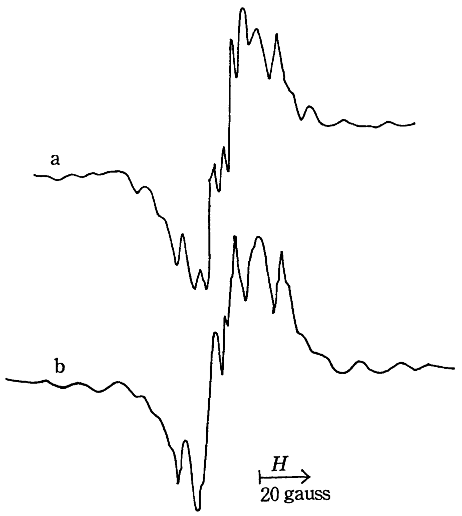

Fig. 5. ESR spectra from *o*-xylene and mesitylene-silica gel systems at low contents.
(a) *o*-xylene, (b) mesitylene

for the adsorbed compounds with the lowest coverages can be assigned to the respective monomer cations. Theoretical hyperfine splitting values are calculated by the simple Hückel MO method. The splitting values of the methyl protons, taking $Q_{\mathrm{H}}^{\mathrm{CCH_3}}=44$ gauss obtained for the cation of durene,[5)] are 14.7 gauss for the cations of toluene and *p*-xylene, 11.0 gauss for *o*- and *m*-xylene, and 7.3 gauss for mesitylene. These theoretical values agree well with the observed values. The additional splittings are due to the ring protons and the observed equal splittings for toluene and *p*-xylene are reasonable, in view of the same spin density (1/12) at the 2,3,5,6-ring carbon atoms of the two methylbenzenes.

Difference in the spectra for *o*-xylene and *m*-xylene cannot be explained by the simple Hückel theory. With the perturbation calculation,[6)] however, this difference could be explained; the 4,5-protons in *o*-xylene would have smaller splitting values than the 4,6-protons in *m*-xylene.

ESR spectra of toluene and *p*-xylene at the intermediate coverages can be asigned to the respective dimer cations, in view of the half splitting values a_{H}'.

Formation of Dimer Cations

ESR spectra of the adsorbed benzene, toluene, and *p*-xylene became those of the dimer cations, through intermediate composite spectra, as the adsorption amounts were increased.

This change of monomer to dimer was studied for benzene as a function of absorption amount and temperature. At −196°C, the formation of dimer cation began at the benzene content as low as 2×10^{-5} mol/g and the dimer increased at the expense of monomer, as the adsorption amount became larger (Fig.6).

The monomer spectrum was stable at −196°C for several weeks. At about −160°C, the seven-line spectrum began to change and the 13-line spectrum appeared. The latter spectrum became predominant at −140°C and at still higher temperatures it began to decay, the individual lines of the spectrum becoming sharp. Formation of the dimer at higher temperatures was studied with benzene by following spectral change at a constant temperature −155°C (Fig. 7). The result suggests that the dimer cations are produced from the monomer cations. The temperature for this conversion depends on the heat-treatment of silica gel. On a silica gel heat-treated at 850°C, the conversion occurs even at −196°C, while it hardly occurs at about −140°C with a silica gel heated at 200°C.

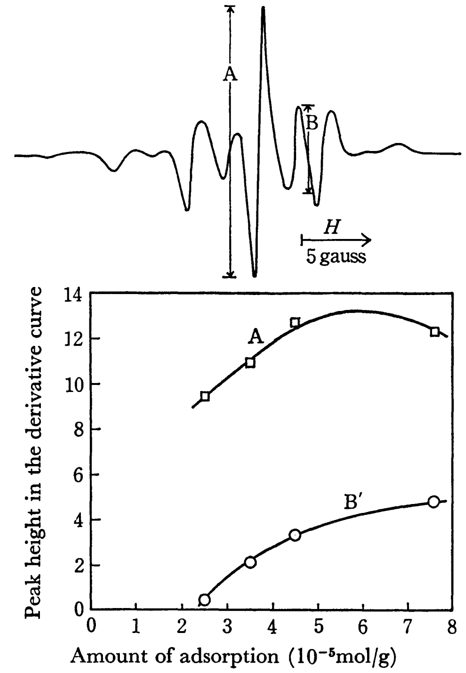

Fig. 6. Formation of the dimer cation as a function of the benzene content. The peak height B', which is the peak height B multiplied by the binomial ratio 924/792, was plotted against the content. The peak A is a superposition of the peaks of the spectra of the monomer and the dimer cations.

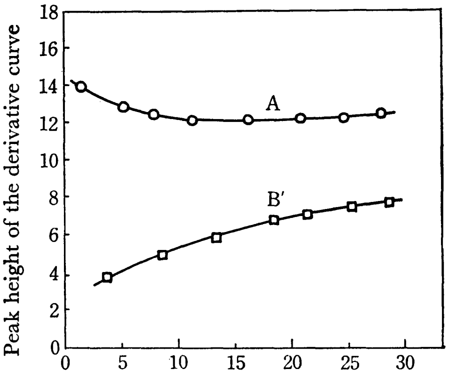

Fig. 7. Change in the concentration of the dimer cation at −155°C. The peak height B′=B×(924/792) was plotted against storage time at −155°C. See legend to Fig. 6 as for other notations.

At −196°C, the adsorbed benzene as well as the monomer cation radicals produced by irradiation does

---

5) R. Hulme and M. C. R. Symons, *J. Chem. Soc.*, **1965**, 1120.

6) T. H. Brown, M. Karplus, and J. C. Shug, *J. Chem. Phys.*, **38**, 1749 (1963).

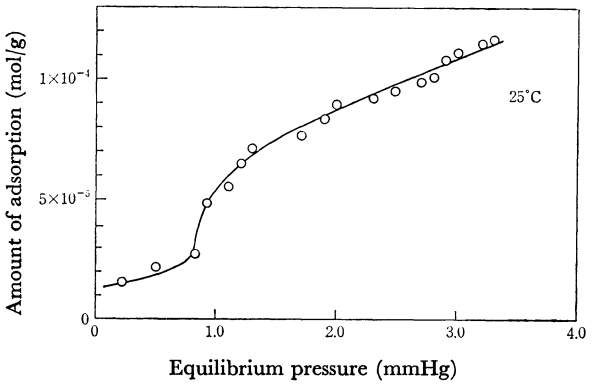

Fig. 8. Adsorption isotherm of benzene on silica gel at 25°C.

not have sufficient mobility to come close to form the dimer cation radicals. When the adsorption amount exceeds 2×10^{-5} mol/g, there seems to occur a certain change in the mode of adsorption as evidenced from the adsorption isotherm (Fig. 8). Adsorptions as benzene dimer might occur and these species would give the dimer cation on irradiation. The slower rates of motions of the monomer and dimer cations at −196°C can be noted from the asymmetry of the individual lines of the 7-line spectrum and the line-widths variation of the 13-line spectrum depending on the total nuclear quantum numbers.

At higher temperatures, the adsorbed monomer cations and molecules become mobile to come close to form the dimer cations. Such mobilization can be seen from the spectral changes and the decay. Different behavior for the monomer-to-dimer conversion with silica gels subjected to different heat-treatments suggests alterations in mobility of adsorbed benzene on silica gel heat-treated at various temperatures.

The same mechanism would also hold for the dimer formation of toluene and *p*-xylene. At higher temperatures, the spectra of dimer cations were observed.

For the cases of *o*-xylene, *m*-oxylene and mesitylene, such clear evidence for the dimer formation was not obtained from ESR spectra. At higher temperatures, however, the adsorbed molecules become also mobile in view of decay of the signals. The spectra also change to the broad spectra, which might be responsible for the dimer cation radials.