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An ESR Study of Intermediates in γ-Irradiated Methylcyclohexane and Isobutane Containing Benzene

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The present work was undertaken in order to examine intermediates from benzene and toluene in γ-irradiated glassy methylcyclohexane (MCH) and polycrystalline isobutane matrices at 77°K. The γ-irradiation of MCH containing low concentrations of benzene gave an ESR spectrum with a good hyperfine resolution, which can be ascribed to the benzene anion, while at higher concentrations of benzene it gave an ESR spectrum with a poor resolution, which is attributable to the benzene monomer and dimer anions. On the contrary, the γ-irradiation of polycrystalline isobutane containing benzene did not yield an ESR spectrum which can be attributed to the benzene anion. However, the γ-irradiation of a mixed glass of isobutane and 4 mol% MCH containing benzene gave an ESR spectrum which is attributable to the benzene anion. The yield of trapped electrons in this system was three times as large as that in pure γ-irradiated MCH. Such a difference in the results between glassy MCH and polycrystalline isobutane matrices gives evidence of a phase effect on the radiolysis of solid hydrocarbon.

In a previous paper,[1] we reported a study of radiation-induced intermediates from toluene in solid isobutane in which the electron spin resonance technique was used. The ESR spectrum observed consisted of five lines, with a splitting constant of 4.2 G; it was ascribed to the toluene anion. These results indicated that toluene has some electron scavenging ability in a hydrocarbon matrix at 77°K. However, γ-irradiated polycrystalline isobutane containing benzene did not give an ESR spectrum which is attributable to the benzene anion. Recently, it was found by optical absorption spectroscopy that a γ-irradiated glassy matrix of 3MP containing low concentrations of benzene yielded the benzene anion and cation, while at higher concentrations of benzene it yielded the dimer anion and cation.[2] We have investigated, by the ESR method, radiation-induced intermediates from benzene in glassy matrices of MCH and of isobutane- 4 mol% MCH, independently of the optical study referred to above. In this paper, we will report the ESR results on the reaction intermediates and will attempt to compare these results with the optical results.

Experimental

The isobutane, methylcyclohexane (MCH), and 3-methylpentane (3MP) were more than 99.9% pure. The gas-chromatographic analysis did not show any detectable impurities. These materials were used after degassing and distillation on a vacuum line. The

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[1] T. Wakayama, T. Kimura, T. Miyazaki, K. Fueki and Z. Kuri, This Bulletin, **43**, 1017 (1970).

[2] A. Ekstrom, *J. Phys. Chem.*, **74**, 1705 (1970).

benzene and toluene (99.9%) were used after vacuum distillation. The nitrous oxide and sulfur hexafluoride were of a high purity, while the cyclohexene was 99.9% pure and was used after vacuum distillation.

The samples were irradiated with γ-rays from Co-60 at a dose rate of 4.2×10^5 rad/hr. The photobleaching of γ-irradiated samples was carried out at 77°K with light from an infrared or tungsten lamp.

The ESR measurements were made on a JES-3BX ESR spectrometer. The G-value of the benzene anions was determined by assuming $G(\text{radical}) = 1.6$ for radicals produced in γ-irradiated 3MP at 77°K.[3]

Results and Discussion

A) Intermediates Produced at Lower Concentrations of Benzene.

When 0.05 mol% benzene in MCH glass is γ-irradiated at 77°K, a species is formed which displays an ESR spectrum with a good hyperfine resolution. This ESR spectrum consists of five lines whose splitting constant is 3.8 G, and it can be bleached by exposure to infrared light for a few minutes (Fig. 1(A)).

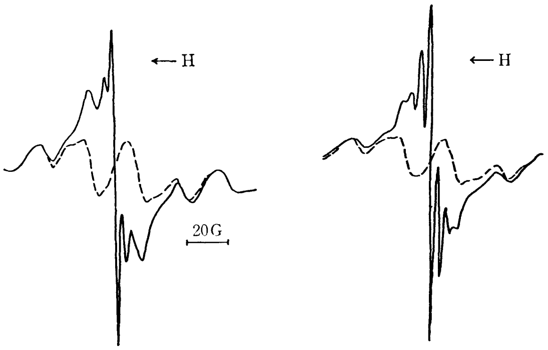
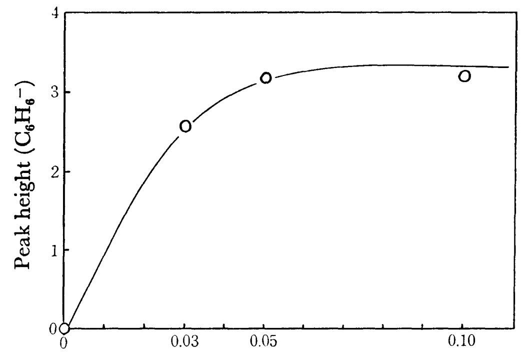


Fig. 1. A Fig. 1. B

A) ESR spectrum of γ-irradiated MCH containing 0.05 mol% benzene at 77°K.
——, after γ-irradiation.
------, after 5 min illumination with infrared light.
Dose, 1.7×10^5 rad.

B) ESR spectrum of γ-irradiated MCH containing 0.05 mol% benzene and 1.0 mol% cyclohexene at 77°K.
——, after γ-irradiation.
------, after 5 min illumination with infrared light.
Dose, 1.7×10^5 rad.

As the benzene concentration in MCH matrix is increased, the intensity of the five-line spectrum at first increases, and then reaches a plateau at 0.05 mol% benzene concentration (Fig. 2).

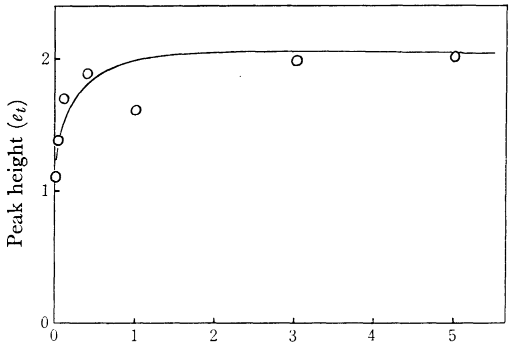


Concentration of C_6H_6 (mol/100mol MCH)

Fig. 2. Effect of benzene concentration in MCH glass on the yield of the benzene anion at 77°K. Dose, 1.7×10^5 rad.

In order to determine whether the species produced in γ-irradiated MCH containing benzene is the benzene anion or the benzene cation, we used SF_6 and N_2O as electron scavengers, and cyclohexene as a cation scavenger. Since the hyperfine splitting constants for the benzene anion and cation have been reported to be 3.75[4] and 4.2 G[5] respectively, it is difficult to distinguish between the anion and the cation by their ESR spectra under our experimental conditions.

It is known that when olefin is added to hydrocarbon matrices, the yield of trapped electrons in γ-irradiated hydrocarbons increases.[6] Such a result was obtained for γ-irradiated MCH containing cyclohexene in the present study (Fig. 3). Cyclohexene may stabilize trapped electrons, since a charge transfer from MCH to cyclohexene would suppress cation-electron recombination by trapping the positive charge.



Concentration of C_6H_{10} (mol/100mol MCH)

Fig. 3. Effect of cyclohexene concentration in MCH glass on the yield of the trapped electron at 77°K. Dose, 1.7×10^5 rad.

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[3] M. Shirom and J. E. Willard, *J. Phys. Chem.*, **72**, 1702 (1968).

[4] S. P. Solodovnikov, *Zh. Strukt. Khim.*, **2**, 282 (1961).

[5] J. R. Bolton, A. Forman and L. E. Orgel, *Mol. Phys.*, **5**, 43 (1962).

[6] M. Irie, K. Hayashi, S. Okamura and H. Yoshida, *J. Chem. Phys.*, **48**, 922 (1968).

$$\mathrm{MCH} \rightsquigarrow \mathrm{MCH}^+ + e^- \qquad (1)$$

$$\mathrm{MCH}^+ + C_6H_{10} \longrightarrow \mathrm{MCH} + C_6H_{10}^+ \qquad (2)$$

When 0.05 mol% benzene in MCH glass containing 1.0 mol% cyclohexene as a cation scavenger is γ-irradiated at 77°K, a species is formed which displays an ESR spectrum with a good resolution (Fig. 1(B)). This spectrum consists of seven lines, and its splitting constant is 3.8 G. It can be bleached by exposure to infrared light for a few minutes.

γ-Irradiated MCH containing 0.07 mol% benzene and 0.07 mol% SF_6 displays a very different ESR spectrum from that of γ-irradiated MCH containing 0.07 mol% benzene and 0.4 mol% SF_6 (Fig. 4(A)). The former spectrum has a seven-line component with a hyperfine splitting constant of 3.8 G and is attributed to the benzene anion, while the latter does not have a seven-line component and indicates only MCH radicals. This result can be interpreted in terms of the following competitive reactions:

$$e^- + C_6H_6 \longrightarrow C_6H_6^- \qquad (3)$$

$$e^- + SF_6 \longrightarrow SF_6^- \qquad (4)$$

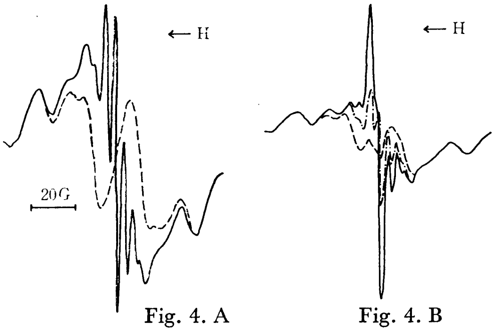

Fig. 4. A Fig. 4. B

A) ESR spectrum of γ-irradiated MCH containing 0.07 mol% benzene in the presence of SF_6 at 77°K.

——, 0.07 mol% SF_6.

------, 0.4 mol% SF_6.

B) ESR spectrum of γ-irradiated MCH containing 0.07 mol% benzene and 0.07 mol% N_2O at 77°K.

——, after γ-irradiation.

-·-·-, after 1 sec illumination with infrared light.

------, after 40 sec illumination with infrared light.

Dose, 1.7×10^5 rad.

Figure 4(B) shows the ESR spectrum, obtained after γ-irradiation, of MCH, containing 0.07 mol% benzene and 0.07 mol% N_2O, as an electron scavenger. The center line in the spectrum may be ascribed to the electron trapped near the N_2O superimposed on the spectrum of the benzene anion and the solvent radical. The narrow side lines are due to the benzene anion. The center line does not saturate so easily upon an increase in the microwave power as does the trapped electron in pure MCH. A similar result is obtained upon microwave saturation and the photobleaching of the trapped electron (ESR singlet with $\Delta H_{\mathrm{msl}}=4.1$ G) produced in MCH containing N_2O.[7] The ESR spectra obtained by illuminating the preceding sample with infrared light for 1 sec and for 40 sec are shown in Fig. 4(B). As can be seen in Fig. (4B), the spectrum of the trapped electron decreases remarkably in intensity upon illumination, while that of the benzene anion does not change very much. This result indicates that the trapped electron can be photobleached more efficiently than the benzene anion.

Thus, the seven-line spectrum may be attributed to the benzene anion, and the *G*-value of the benzene anion in MCH containing 0.05 mol% benzene and 1.0 mol% cyclohexene is 1.3. This value is in accordance with the *G*-value of the biphenyl anion in a γ-irradiated hydrocarbon containing biphenyl.[8] The results presented above indicate that benzene has some electron scavenging ability at low concentrations.

B) Intermediates Produced at Higher Concentrations of Benzene.

When 3MP glass, MCH glass, or isobutane-4 mol% MCH glass containing 5 mol% benzene is γ-irradiated at 77°K, a species is formed which displays an ESR spectrum with a poor resolution. This ESR spectrum has a hyperfine splitting constant of 3.8 G, and it can be bleached by exposure to infrared light for a few minutes (Fig. 5(A)). The formation of this species is suppressed by the presence of N_2O as an electron scavenger in 3MP. On the contrary, the species produced in MCH is not suppressed by the presence of 1 mol% N_2O or SF_6, and in this case the ESR spectrum can not be

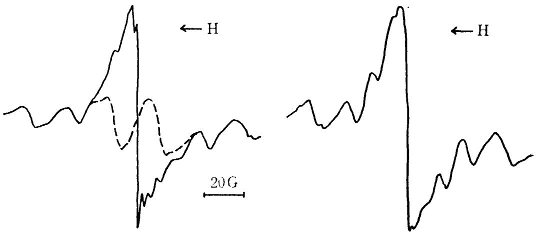

Fig. 5. A Fig. 5. B

A) ESR spectrum of γ-irradiated MCH containing 5 mol% benzene at 77°K.

——, after γ-irradiation.

------, after 5 min illumination with infrared light.

B) ESR spectrum of γ-irradiated MCH containing 5 mol% benzene and 1 mol% N_2O at 77°K.

Dose, 1.7×10^5 rad.

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[7] A similar effect of N_2O on the trapped electron in 3-methylhexane was reported by Yamazaki *et al.* at the 22nd Annual Meeting of the Chemical Society of Japan, 1969, Tokyo, Japan.

[8] J. Lin, K. Tsuji and F. Williams, *J. Amer. Chem. Soc.*, **90**, 2766 (1968).

bleached by exposure to a tungsten light (Fig. 5(B)).

These results suggest that an anion is produced in γ-irradiated 3MP, MCH, and isobutane- 4 mol% MCH containing 5 mol% benzene, while the species produced in γ-irradiated MCH containing 5 mol% benzene and 1 mol% N_2O or SF_6, is a cation. Recently Ekstrom suggested, in an optical absorption study, that the species produced in γ-irradiated 3MP could be attributed to the benzene monomer anion and cation, or to the benzene dimer anion and cation, depending on the benzene concentration. We would also like to suggest that the ESR spectra obtained at higher concentrations of benzene in the hydrocarbons may be ascribed to the benzene monomer and dimer anions, while the species produced in γ-irradiated MCH containing 5 mol% benzene and 1 mol% electron scavengers may be ascribed to the benzene monomer and dimer cations. Our results indicate that the dimer anion is formed at benzene concentrations above about 1 mol%, a value which is in good agreement with the optical values.[2]

TABLE 1. EFFECTS OF THE HYDROCARBON MATRIX ON THE FORMATION OF BENZENE AND TOLUENE ANIONS

	Benzene	Toluene
MCH	Benzene anion	No
Isobutane	No	Toluene anion
Isobutane- 4 mol% MCH	Benzene anion	Toluene anion

C) Effects of the Hydrocarbon Matrix on the Formation of Benzene and Toluene Anions.

Table 1 shows the anionic species produced in γ-irradiated hydrocarbon matrices (MCH, isobutane, and isobutane- 4 mol% MCH) containing 3 mol% benzeene or toluene at 77°K. The benzene anion is produced in a MCH matrix, but not in an isobutane matrix. On the contrary, the toluene anion is produced in an isobutane matrix, but in a MCH matrix. Both the benzene and toluene anions, however, can be produced in a mixture of isobutane- 4 mol% MCH.

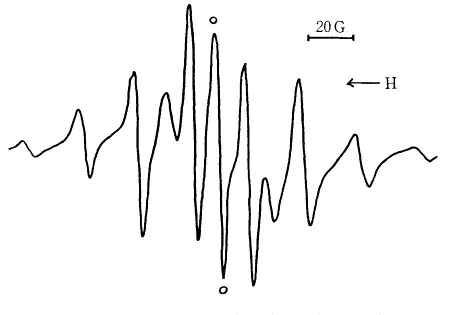

Fig. 6. ESR spectrum of γ-irradiated isobutane- 4 mol% MCH at 77°K. ○ represents a signal of the trapped electron. Dose, 0.7×10^5 rad.

It is found by ESR measurements that the species produced in γ-irradiated pure isobutane, which is polycrystalline at 77°K, is the isobutyl radical, while the species produced in a γ-irradiated mixture of isobutane- 4 mol% MCH, which is glassy at 77°K, consists of the isobutyl and t-butyl radicals and trapped electrons (Fig. 6). The yield of t-butyl radicals in this system is much greater than that of isobutyl radicals, and the yield of trapped electrons in a γ-irradiated mixture matrix is three times as large as that in γ-irradiated pure MCH.

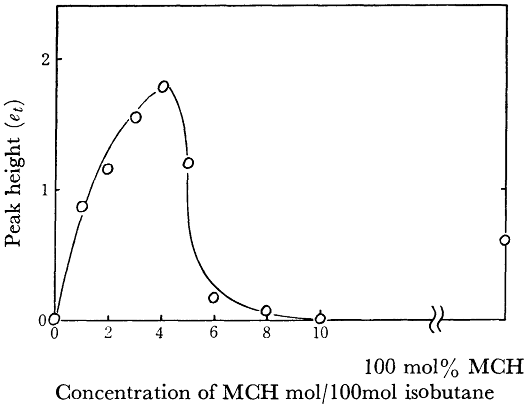

Fig. 7. Effect of MCH concentration in isobutane on the yield of the trapped electron at 77°K. Dose, 0.7×10^5 rad.

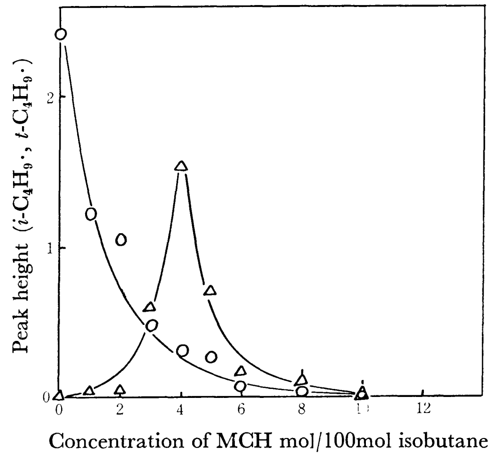

Fig. 8. Effect of MCH concentration in isobutane on the yields of the i-butyl radical and of the t-butyl radical at 77°K.
○, isobutyl radical. △, t-butyl radical.
Dose, 0.7×10^5 rad.

Figures 7 and 8 show the dependence of the yields of trapped radicals and electrons on the concentration of MCH. As the concentration of MCH in isobutane is increased, the yields of both t-butyl radicals and trapped electrons increase, while the yield of isobutyl radicals decreases. The yields of t-butyl radicals and trapped electrons decrease in the range of MCH concentrations above

4 mol%, where the matrix becomes so soft that the radicals and electrons are not trapped in the matrix. As the concentration of MCH increases, the matrix becomes glassy, so benzene and toluene dissolve easily in the matrix; both the benzene and toluene anions may be trapped in an isobutane-4 mol% MCH mixture.

Accordingly, the results presented above indicate that the viscosity of a matirx has an important influence upon the formation of trapped anions, cations, electrons, and radicals in the matrix.