BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1934—1935 (1972)

ESR Study of γ-Irradiated Isobutylene-Silica Gel System

Siro NAGAI, Shun-ichi OHNISHI, and Isamu NITTA
Osaka Laboratory for Radiation Chemistry, Japan Atomic Energy Research Institute, 508 Mii, Neyagawa-shi, Osaka

(Received December 14, 1971)

In a previous paper,[1] we reported that monomer and dimer cations of some methylbenzenes are produced in the adsorbed states upon γ-irradiation. Isobutylene is known to be a vinyl monomer polymerizing through a cationic mechanism. The present study was undertaken to examine the possibility of observing isobutylene radical cation. A detailed study of the nature of the adsorbed radicals seems to be of importance.

We describe our ESR study of free radicals produced in the γ-irradiated isobutylene-silica gel system. It is seen that the well-resolved spectra observed under certain conditions not only make the identification of radicals possible but also show the phenomena of asymmetric linewidth variation of the hf lines.

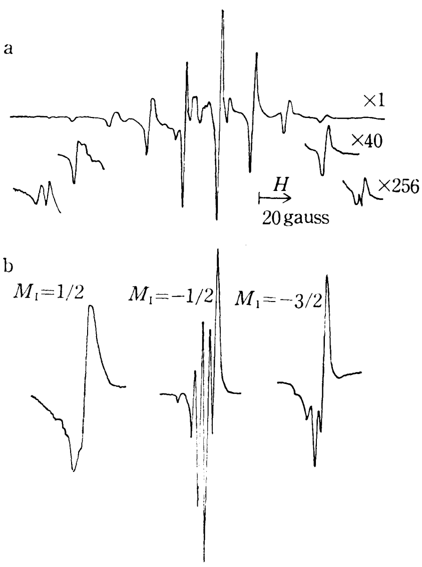

Fig. 1. a; ESR spectrum of γ-irradiated isobutylene-silica gel at -196°C. b; Second-order structures of the central three lines of the *t*-butyl radical spectrum observed at -80°C.

Experimental

Silica gel was the same as that reported.[1] Isobutylene (99.0%) was obtained from Takachiho Trading Co. Ltd., and was used without further purification. All experimental procedures were the same as described.[2] The isobutylene contents in the adsorbed samples were in the range 1—20% of the monolayer value.

Results and Discussion

A typical spectrum of adsorbed isobutylene observed at -196°C consists of 10 lines with 22.4 gauss splitting and of several weak lines as shown in Fig. 1a. The 10-line spectrum was assigned to *t*-butyl radical $\dot{C}(CH_3)_3$ from the hyperfine splitting constant.

It should be noted that the linewidths of individual hf lines differ from each other. The $M_I=-1/2$ line is the narrowest of the 10 lines throughout the whole temperature range investigated, and gives the partially resolved second-order structure even at -196°C. At higher temperatures, the structures of the other two lines, $M_I=1/2$ and $-3/2$ become observable (Fig. 1b). The spacings of the second-order components of the $M_I=-1/2$ line at -60°C are 0.70, 0.50, 0.39, and 0.25 gauss which agree with the data in liquid phase.[3] The asymmetric linewidth variation can be explained in terms of a modulation of the anisotropic hyperfine and g-tensor interactions.[4]

The ESR spectrum becomes well-resolved at higher temperatures. The main part of the spectrum (±70 gauss) is shown in Fig. 2a. In this region 6 lines of the 10-line spectrum of the *t*-butyl radical appeared.

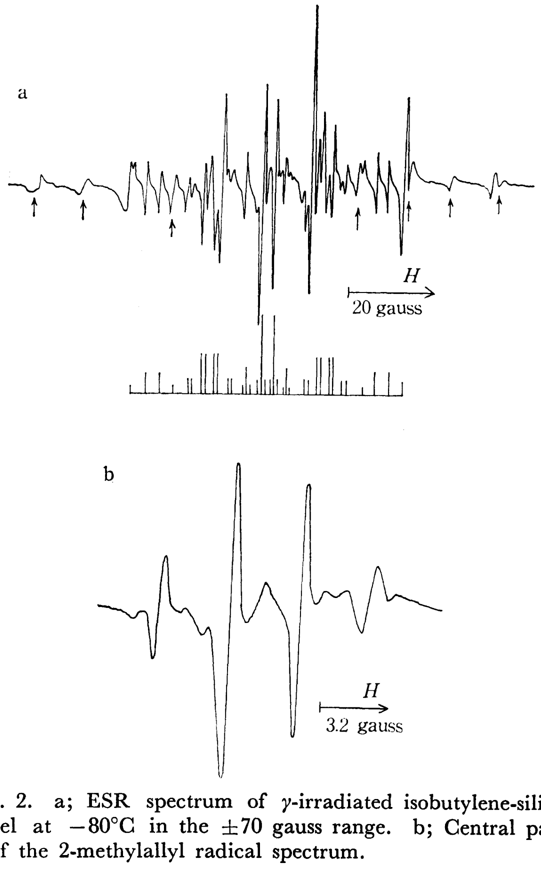

Fig. 2. a; ESR spectrum of γ-irradiated isobutylene-silica gel at -80°C in the ±70 gauss range. b; Central part of the 2-methylallyl radical spectrum.

---

[1] S. Nagai, S. Ohnishi, and I. Nitta, This Bulletin, **44**, 1230 (1971).

[2] S. Nagai, S. Ohnishi, and I. Nitta, *Chem. Phys. Lett.*, **13**, 379 (1972).

[3] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

[4] J. H. Freed and G. K. Fraenkel, *ibid.*, **39**, 326 (1963).

The weak signals at −196°C (Fig. 1a) are well-resolved and the 36 lines (3×3×4) drawn by sticks were assigned to 2-methylallyl radical $CH_2 \dot{=} C(CH_3) \dot{=} CH_2$. The hf splitting constants measured at −80°C were $a(CH_2)=13.8$ gauss, $a'(CH_2)=14.6$ gauss and $a(CH_3)=3.2$ gauss. The splitting values of methylenic protons show a good correspondence with $a(CH_2)=13.93$ gauss and $a'(CH_2)=14.83$ gauss of the unsubstituted allyl radical.[3]

The asymmetric linewidth variation is appreciable in the spectrum due to the 2-methylallyl radical (Fig. 2b). Qualitative examination of the spectrum shows that the methyl proton lines are broader on the high-field side of the spectrum than on the low-field side. The behavior may be explained on the basis of the theory of ESR linewidth developed by Freed and Fraenkel,[4] provided that the theory is applicable to the spectra of adsorbed radicals. Detailed analyses, however, have not been made because of overlapping of the hf lines with those of two other radicals.

In addition to the 36-line spectrum, we note other lines indicated by arrows in Fig. 2a. The widths of the lines are broader than those of the other two radicals. They may be regarded as a part of the spectrum of the propagating radical $\dot{C}(CH_3)_2\text{–}CH_2\text{–}R$ on the basis of the approximate hf splitting values of 22 gauss for methyl protons and 12 gauss for methylene protons. A similar propagating radical on silica gel was found from adsorbed ethylene.[5] From the fact that the signal intensity decreases with the rise of temperature, the propagating radicals are considered to be formed at −196°C during irradiation. It is reasonable to assume that the condensation of isobutylene molecules occurs inhomogeneously on the surface of silica gel before irradiation. The related phenomena were observed in the formation of benzene dimer cations from adsorbed benzene,[1,6] and also in that of benzene monomer cations from adsorbed acetylene.[2]

ESR spectra from the samples with amounts of adsorption less than 2.0 cc STP/g are mainly due to positive holes in irradiated silica gel.[7] With the rise of temperature, the intensity of the spectrum of the *t*-butyl radical is found to increase slightly at the expense of the silica gel signal, suggesting the formation of the *t*-butyl radical partly through a cationic mechanism.

---

[5] P. O. Kinell, A. Shimizu, O. Edlund, and A. Lund, *J. Polym. Sci.*, Part B, **6**, 133 (1968).

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

[7] N. F. Shamonia, A. G. Kotov, and S. Ya. Pshezhetskii, *Khimiya Vysokikh Energii*, **4**, 43 (1970).