Radical Formation in the Radiolysis of Solid Isobutane as Studied by ESR Spectroscopy

Terunobu WAKAYAMA, Tetsuo MIYAZAKI, Kenji FUEKI and Zen-ichiro KURI
Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya

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Extensive studies have been made of the mechanism of radical formation in the radiolysis of hydrocarbons in condensed phases. Generally speaking, primary radicals can be produced from the neutralization reaction between positive ions and electrons, the ion-molecule reaction, and the decomposition of directly excited molecules or ions. It is of essential importance for understanding elementary processes in radiation chemistry to elucidate the mechanism of radical formation in irradiated systems. Most of the previous studies were based on the analysis of final products and not on the direct observation of radicals.

In the present work, we have made an ESR study of radicals produced in γ-irradiated isobutane with and without additives at 77°K. Figure 1(a) shows the ESR spectrum of pure isobutane, which is assigned to the isobutyl radical.[1] Figure 1(b) shows the ESR spectrum of isobutane containing 1 mol% carbon tetrachloride.
It is seen from a comparison of Fig. 1(a) and (b) that there is a drastic change in the spectrum. The absorption line (A) in Fig. 1(b) is attributed to the CCl_3 radical.[2] Figure 2 shows the relative yields of isobutyl radical and CCl_3 radical against the concentration of carbon tetrachloride. The yield of isobutyl radical decreases and that of CCl_3 radical increases with increaseing concentration of carbon tetrachloride.

We have also investigated the radical formation in γ-irradiated isobutane containing ethyl iodide. The ESR spectrum of ethyl radical was observed in this system, while the yield of isobutyl radical did not change significantly with increasing concentration of ethyl iodide. It can be said that the ethyl radical is produced by dissociative electron attachment to ethyl iodide. The addition of electron scavengers such as nitrous oxide and sulfur hexafluoride also did not cause a change in the yield of isobutyl radical.

These results indicate that in the radiolysis of solid isobutane the isobutyl radical is not produced from the neutralization reaction, but mainly from the decomposition of directly excited isobutane molecules or ions, and that energy transfer from isobutane to carbon tetrachloride plays a role in suppressing the decomposition of isobutane.

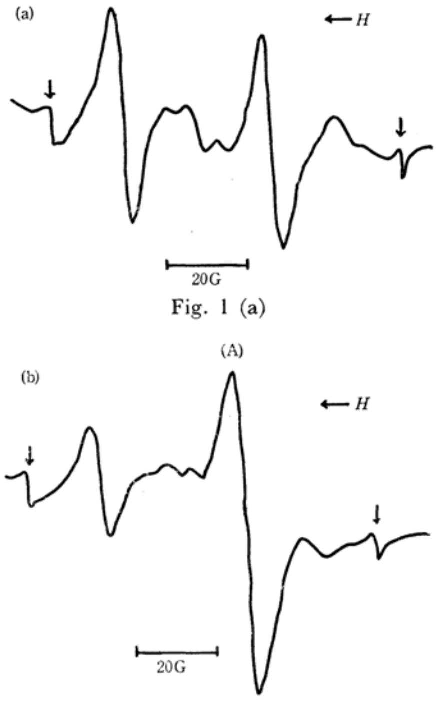

Fig. 1 (a)

Fig. 1 (b)

Fig. 1. (a) ESR spectrum of γ-irradiated isobutane at 77°K, (b) ESR spectrum of γ-irradiated isobutane containing 1 mol% carbon tetrachloride at 77°K. Irradiation dose: 1.7×10^5 rad. The arrow indicates signal of Mn^{2+}.

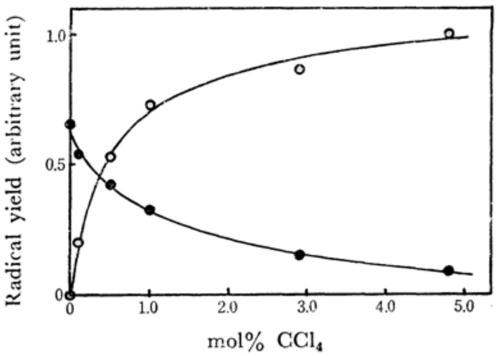

Fig. 2. Radical yields *vs.* concentration of carbon tetrachloride. —●— : isobutyl radical, —○— : CCl_3 radical. Irradiation dose: 1.7×10^5 rad. The yield of CCl_3 radical was obtained by subtracting the the contribution of solvent radical to the line (A).

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1) J. Lin and F. Williams, *J. Phys. Chem.*, **72**, 3707 (1968).

2) R. F. C. Claridge and J. E. Willard, *J. Am. Chem. Soc.*, **87**, 4992 (1965).