Effect of Phase on the Primary Process of the Formation of Butyl Radicals in the Radiolysis of Solid Isobutane-2-d_1

Yoshiyuki SAITAKE, Terunobu WAKAYAMA, Toyoaki KIMURA,
Tetsuo MIYAZAKI, Kenji FUEKI, and Zen-ichiro KURI
Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya
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We have studied the radiolysis of organic compounds in the solid state and have proposed that two important problems must be solved in order to elucidate the mechanism of the solid-phase radiolysis. One is the problem of the extent to which the formation of an exciton plays an important role;[1] the other is how the condition of the solid matrix affects the reaction of the exciton.[2,3] It was recently reported that the i-C_4H_9 radical is formed in the radiolysis of isobutane in the crystalline state, while the t-C_4H_9 radical is formed in the glassy state.[2] The possibility that the phase effect may be attributed to an isomerization of butyl radicals, such as i-$C_4H_9 \rightleftarrows t$-$C_4H_9$, was not completely excluded in the previous study.

In order to determine whether or not the phase change affects the primary process of the C–H bond rupture or the isomerization of butyl radicals, the radiolysis of $(CH_3)_3CD$ has been investigated by ESR spectroscopy at 77°K. $(CH_3)_3CD$ was prepared by the reaction of t-butyl magnesium bromide with D_2O. The ESR spectrum of γ-irradiated isobutane, which is polycrystalline at 77°K, is shown in Fig. 1a. The spectrum can be assigned to the $(CH_3)_2CHCH_2\cdot$ radical. The ESR spectrum of γ-irradiated pure $(CH_3)_3CD$ in the polycrystalline state is shown in Fig. 1b. The spectrum in Fig. 1b is quite different from that in Fig. 1a; it consists of three broad lines, with a splitting constant of 22.7G. The splitting constants of the α-proton and the β-proton of the $(CH_3)_2CHCH_2\cdot$ radical have been reported to be 22 and 35 G respectively.[4] Since the splitting due to a deuteron is about 15% of that due to a proton, it is expected that the spectrum of the $(CH_3)_2CDCH_2\cdot$ radical is split into three lines by two α-protons, with a slitting constant of 22 G, and that each line is then split further into three lines by a β-deuteron with a splitting constant of 5 G. Since the splitting due to a deuteron is, however, very small, the poorly-resolved spectrum in the solid state may consist of three broad lines with a splitting constant of 22 G. Thus, the spectrum in Fig. 1b coincides well with the spectrum expected for the $(CH_3)_2CDCH_2\cdot$ radical. An $(CH_3)_3$-CD sample containing methylcyclohexane (5.7 mol%) can be frozen to a clear glass by rapid cooling at 77°K. Upon the γ-irradiation of the mixture in the glassy state, the ESR spectrum shown in Fig. 1c was obtained. The spectrum is the same as that[2] obtained in the radiolysis of isobutane in the glassy state at 77°K; it can be assigned to the $(CH_3)_3C\cdot$ radical. Therefore, the bond rupture in the radiolysis of $(CH_3)_3CD$ in the solid state may be represented as follows:

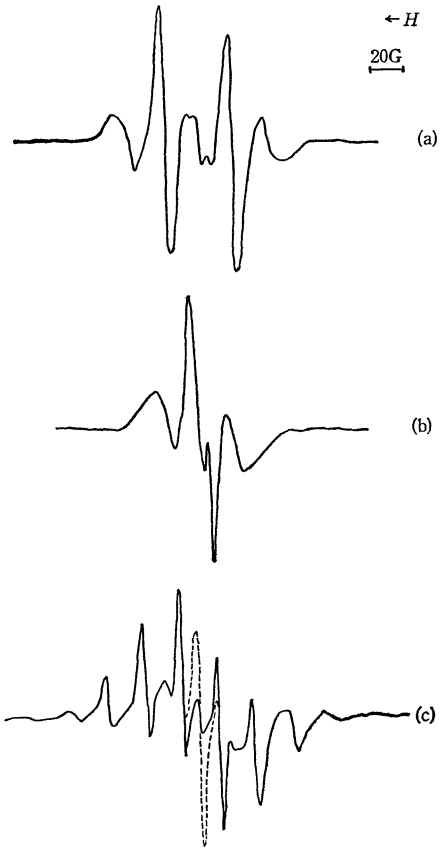

Fig. 1. (a) ESR spectrum of γ-irradiated i-C_4H_{10} in the polycrystalline state.
(b) ESR spectrum of γ-irradiated $(CH_3)_3CD$ in the polycrystalline state.
(c) ESR spectrum of γ-irradiated $(CH_3)_3CD$ containing methylcyclohexane (5.7 mol%) in the glassy state.
A dotted line represents the spectrum of trapped electron which is easily bleached by the illumination with visible light.
Irradiation dose: 2×10^5 rad.
Irradiation temperature: 77°K

$$(CH_3)_3CD \xrightarrow[\text{polycrystal}]{\sim\sim} (CH_3)_2CDCH_2\cdot + H \quad (1)$$

$$(CH_3)_3CD \xrightarrow[\text{glass}]{\sim\sim} (CH_3)_3C\cdot + D \quad (2)$$

It can be concluded that the phase change affects the primary process of the C–H bond rupture.

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