

Effect of Phase on the Trapped Radical in the Radiolysis of Solid Isobutane as Studied by ESR Spectroscopy

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The solvent radicals observed in the radiolysis of solid hydrocarbons are mostly formed by the C-H bond rupture. Since the yields of the radicals are generally not affected by the addition of electron scavengers¹⁾ or by the photobleaching of trapped electrons,¹⁾ the mechanism of their formation cannot be explained simply in terms of charge neutralization reactions. Recently the present authors reported that the addition of carbon tetrachloride to solid isobutane suppresses the production of the solvent radicals.^{2,3)}

In this work we have observed that quite different radicals are trapped in the radiolysis of isobutane depending on whether it is in the glassy or the crystalline state. The ESR spectrum of γ -irradiated pure isobutane, which is polycrystalline at 77°K, is shown in Fig. 1a. The spectrum can be assigned to the isobutyl radical.⁴⁾ An isobutane (92 mol%)—3-methylpentane (8 mol%) mixture can be frozen to a clear glass by rapid cooling or to a polycrystal by slow cooling at 77°K. Upon the γ -irradiation of the mixture in the polycrystalline state, the ESR spectrum shown in Fig. 1b was obtained; it is the same as the spectrum obtained in the radiolysis of pure isobutane at 77°K. A quite different ESR spectrum, however, was obtained by the γ -irradiation of the mixture in the glassy state (Fig. 1c). The spectrum consists of ten equally-spaced lines with a coupling constant of 22.3G; the value is consistent with the value of 22.5G for the t -C₄H₉ radical.⁵⁾ The spectrum coincides with the



Fig. 1. (a) ESR spectrum of γ -irradiated isobutane at 77°K.

(b) ESR spectrum of γ -irradiated isobutane (92 mol%)—3-methylpentane (8 mol%) mixture in the polycrystalline state at 77°K.

(c) ESR Spectrum of γ -irradiated isobutane (92 mol%)—3-methylpentane (8 mol%) mixture in the glassy state at 77°K.

Irradiation dose: 3.7×10^5 rad, Spectrometer gain setting of figures a, b and c were 67 db.

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spectrum of t -C₄H₉ radicals produced by dissociative-electron attachment to t -C₄H₉Br in the radiolysis of 3-methylpentane containing 5 mol% t -C₄H₉Br at 77°K.

Such a phase effect in the radiolysis of solid hydrocarbons has not been reported previously. Further studies of this phenomenon are now in progress.