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Radical Conversions in γ-Irradiated 3-Methylpentane-Isobutene Systems

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Radical conversions in γ-irradiated 3-methylpentane-isobutene systems were observed by means of the electron spin resonance method after keeping the sample at -196°C for a few days, or by subjecting it to ultraviolet irradiation. One of the changes was caused by hydrogen atom abstraction from neighboring molecules by original free radicals. The other change was attributed to dissociation of the free radicals from 3-methylpentane by ultraviolet irradiation.

There have been several studies on photoinduced radical conversions. Among them the photoinduced dissociations of alcohol radicals are well known.[1,2] Recently several authors reported photoinduced conversions of hydrocarbon radicals; photoinduced conversions of allyl radicals to alkyl radicals in γ-irradiated polyethylene by Ohnishi *et al.*,[3] isomerization of *t*-butyl radicals to isobutyl radicals in γ-irradiated isobutyl bromide,[4] a similar isomerization in γ-irradiated polypropylene by Iwasaki *et al.*,[5] and the photoinduced conversion of allylic radicals to other allylic radicals in γ-irradiated 2-methylpentene-1 (2MP-1) by Smith and Pieroni.[6] Smith *et al.*[7] also observed radical conversions in a γ-irradiated 3-methylpentane (3MP)-2MP-1 (15 mol%) mixture by storing the sample for 24 hr at -196°C and ultraviolet irradiation. After receiving a 1 Mrad dose from Co-60 γ-rays, the 3MP-2MP-1 mixture became blue and the ESR spectrum consisted of a narrow intense singlet superimposed on the central line of the spectrum of the 3-methylpentyl radical $CH_3CH_2\dot{C}(CH_3)CH_2$-$CH_3$. The ESR singlet and blue color were easily eliminated by visible light illumination. After keeping the sample for 24 hr at -196°C, the spectrum converted to that of an allylic radical. Upon subsequent UV photolysis, the ESR spectrum changed to that which has been attributed to the 3-methylpentyl radical.[8] It was concluded[7] that ultraviolet light induces the allylic radical from 2MP-1 in 3MP to abstract a hydrogen atom from a neighboring 3MP molecule.

We have reported[9] that $\dot{C}(CH_3)_2$-CH_2-R radicals with two different conformations and relatively

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5) M. Iwasaki, T. Ichikawa and K. Toriyama, *J. Polymer Sci.*, **B5**, 423 (1967).
6) D. R. Smith and J. J. Pieroni, *J. Phys. Chem.*, **70**, 2379 (1966).
7) D. R. Smith, F. Okenka and J. J. Pieroni, *Can. J. Chem.*, **45**, 833 (1967).
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stable trapped electrons were observed in γ-irradiated 3MP-isobutene (IB) systems. The latter was easily bleached out by visible light illumination, and only neutral free radicals remained. In the present investigation we report that these neutral free radicals convert to other ones by keeping the sample at -196°C for a few days or by ultraviolet irradiation as in the 3MP-2MP-1 mixtures.[7]

Experimental

Commercial 3-methylpentane was distilled over sodium after passing through activated alumina. It was dried four times with Na-K alloy. Isobutene was dried with Na-K alloy after passing through potassium hydroxide.

Samples were made in ESR sample tubes by vacuum distillation and sealed off after evacuating to about 10^{-4} mmHg. Irradiation was carried out by γ rays from Co-60 (6×10^5 R/hr). Ultraviolet photolysis was carried out at -196°C with a high pressure mercury lamp (Toshiba Electric Company, Ltd., H-400-p, 400W).

A conventional X band ESR spectrometer was used with 100 Kc field modulation. Microwave power was less than 1 mW. γ-Irradiations and ESR measurements were carried out at -196°C in the dark.

Results

A mixture of 3MP-IB (2.4 mol%) forms a transparent colorless glass at -196°C. When it was irradiated to a dose of 2×10^5 R in the dark at -196°C, it turned blue and gave the ESR spectrum shown in Fig. 1a, which consists of an eight-line spectrum with a hyperfine separation of 23 gauss and a sharp singlet spectrum at the center. The former is attributed probably to the free radical $R\text{-}CH_2\text{-}\dot{C}(CH_3)_2$ with a certain conformation.[9] The sharp singlet spectrum and blue color were easily bleached out by visible light illumination, and they were attributed to trapped electrons.[9] The intensities of both the singlet and eight-line spectra are proportional to dose up to 3×10^5R. After photolysis with visible light, only the eight-line spectrum (Fig. 1a dotted line) remained, and after 7 days, this converted at -196°C to the other spectrum shown in Fig. 1b, where the five-line spectrum with a coupling constant of about 13 gauss due to allylic radicals (arrow marks) and another spectrum (maybe 6 lines) were observed. This spectrum further changed by subsequent ultraviolet irradiation into the spectrum shown in Fig. 1c without any decrease of radical concentration; both six- and four(arrow marks)-line spectra were observed, and the latter decayed out at -168°C as shown in Fig. 1d. The coupling constant of the six-line spectrum is about 22 gauss, and the

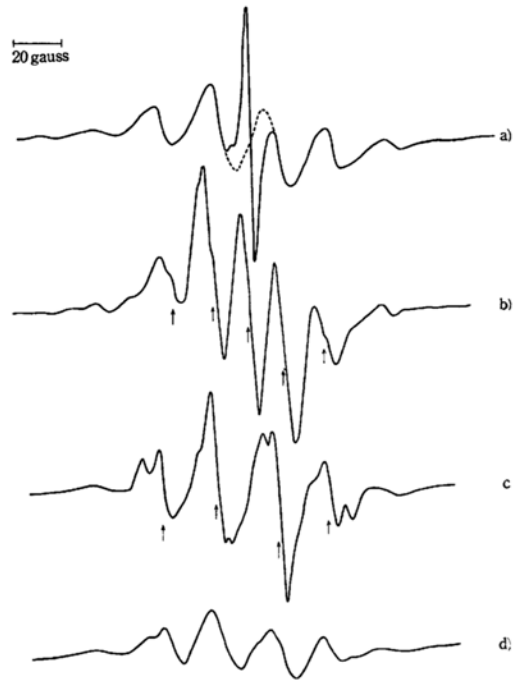

Fig. 1. ESR spectra of 3MP-IB (2.4 mol%) irradiated to a dose of 2×10^5 R at -196°C.
a) immediately after γ-irradiation (solid line); after bleaching with visible light (dotted line).
b) after keeping the sample at -196°C for 7 days; arrow marks represent a five-line spectrum due to allylic radicals.
c) after subsequent ultraviolet irradiation of the sample b) for 45 min. Arrow marks represent a four line spectrum due to methyl radicals.
d) same sample as c) measured at -168°C.

spectrum is the same as that produced by γ-irradiation of 3MP. Thus this spectrum is attributed to the free radicals produced from 3MP($CH_3\text{-}CH_2\text{-}\dot{C}(R)\text{-}CH_2\text{-}CH_3$, R=H or CH_3). The four-line spectrum is attributed to methyl radicals because of its coupling constant (23 gauss) and intensity ratio (1 : 3 : 3 : 1). Methyl radical production, however, was slow and methyl radical concentration seemed to saturate at a certain ratio to that of 3MP radicals.

A mixture of 3MP-IB (61 mol%) made an apparent transparent glass at -196°C. After γ-irradiation, only a fifteen-line spectrum was obtained, and neither a sharp singlet nor blue color were observed. The fifteen-line spectrum shown in Fig. 2a has been attributed to the free radicals $\cdot C(CH_3)_2\text{-}CH_2\text{-}R$ formed with two conformations.[9] This spectrum did not change by keeping the sample at -196°C for a few days, but converted

9) K. Tsuji, H. Yoshida, K. Hayashi and S. Okamura, *J. Polymer Sci.*, **B5**, 313 (1967).

to the five-line spectrum due to allylic radicals by subsequent ultraviolet irradiation as shown in Fig. 2b. The intensity of the allylic radicals decreased with the increase of the time of irradiation,

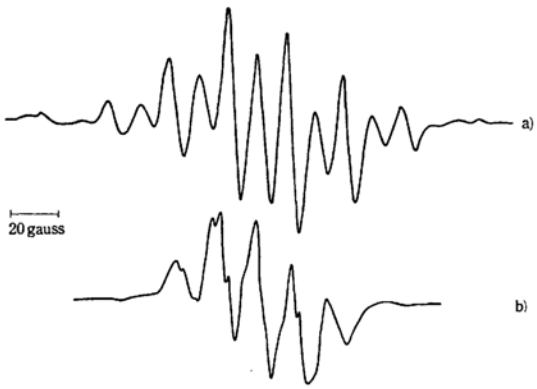

Fig. 2. ESR spectra of 3MP-IB (61 mol%) irradiated to a dose of 2×10^5R at -196°C.
a) immediately after γ-irradiation.
b) after subsequent ultraviolet irradiation for 15 min.

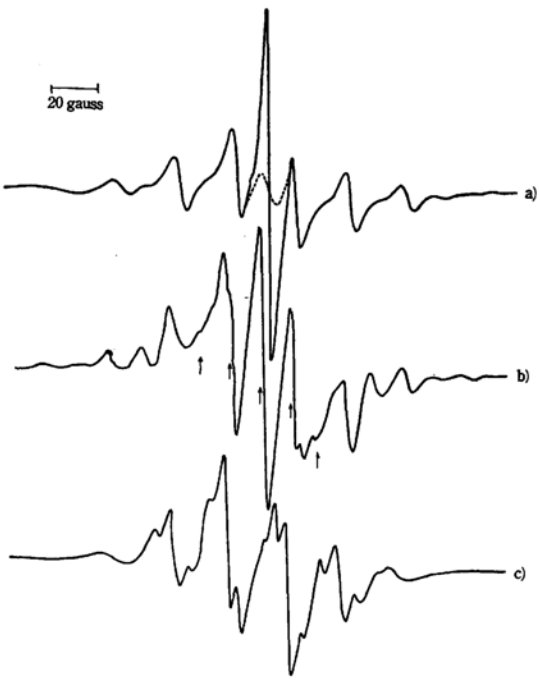

Fig. 3. ESR spectra of 3MP-IB (12 mol%) irradiated to a dose of 2×10^5 R at -196°C.
a) immediately after γ-irradiation (solid line); after bleaching with visible light (dotted line).
b) after keeping the sample at -196°C for two days; arrow marks represent a five-line spectrum due to allylic radicals.
c) after subsequent ultraviolet irradiation for 45 min.

but no methyl radicals were observed.

For an intermediate case 3MP-IB (12 mol%), an eight-line spectrum and a sharp singlet were initially observed after γ-irradiation as shown in Fig. 3a. The sharp singlet at the center was removed by visible-light illumination (Fig. 3a dotted line), but the eight-line spectrum remained unchanged. After keeping the sample at -196°C for a few days, however, the eight-line spectrum changed into the superposition of 15 lines observed for 3MP-IB (61 mol%) and five lines (arrow marks) due to allylic radicals as shown in Fig. 3b. By subsequent ultraviolet irradiation, the spectrum converted to the same one as observed for 3MP-IB (2.4 mol%), the radical concentration remaining constant.

Discussion

We observed two kinds of radical conversions. One proceeds by keeping the sample at -196°C for a few days, and the other by subsequent ultraviolet irradiation. They could be explained by intermolecular reactions with original free radicals and by dissociation of the free radicals.

When IB concentration in 3MP is low (2.4 mol%), radical conversions were observed at -196°C without UV irradiation, and the five-line spectrum due to allylic radicals and the other spectrum which seemed to be attributed to the free radicals from 3MP were obtained. This could be explained in terms of hydrogen atom abstraction by the original free radicals from both neighboring IB and 3MP molecules.

$$\cdot\mathrm{C}(\mathrm{CH_3})_2\mathrm{-CH_2-R} \begin{cases} + \text{ IB} \rightarrow \mathrm{CH(CH_3)_2\text{-}CH_2R} \\ \qquad + \mathrm{CH_2{=}C(CH_3)\text{-}\dot{C}H_2} \qquad (1) \\ + \text{ 3MP} \rightarrow \mathrm{CH(CH_3)_2\text{-}CH_2R} \\ \qquad + \mathrm{CH_3\text{-}CH_2\text{-}\dot{C}(R')\text{-}CH_2\text{-}CH_3} \\ \qquad (\mathrm{R'{=}H \text{ or } CH_3}) \qquad (2) \end{cases}$$

These reactions might be caused by the mobility of free radicals in the glass. Reaction (1) is very similar to that observed in the 3MP-2MP-1 system,[7] although the original free radicals were 3-methylpentyl radicals in this case. It seems reasonable to conclude that a hydrogen atom is abstracted more readily from IB than from 3MP, since even at low concentrations of IB, allylic radicals were produced and at higher concentration only allylic radicals were produced. This might be caused by the stability of allylic radicals.

Methyl radicals were produced by subsequent ultraviolet irradiation. Since 3MP does not absorb UV light, any reactions through an excited 3MP molecule can be ruled out. In fact although unirradiated 3MP gave methyl radicals and other free

radicals by ultraviolet irradiation under the same conditions employed for the γ-irradiated 3MP-IB systems, the intensity was negligible compared with the present intensity. Methyl radical production is thought to be caused by dissociation of the free radical from 3MP(CH_3–CH_2–$\dot{C}$(R)–CH_2–CH_3), since the same change was observed for γ-irradiated 3MP.[10]

$$CH_3\text{–}CH_2\text{–}\dot{C}(R)\text{–}CH_2\text{–}CH_3 \rightarrow CH_3\text{–}CH_2\text{–}C(R)=CH_2 + \cdot CH_3 \quad (3)$$

Allylic radicals disappeared by ultraviolet irradiation and new alkyl radicals (CH_3–CH_2–$\dot{C}$(R)–CH_2–CH_3) were observed, besides methyl radicals. This result is consistent with that reported for 3MP-2MP-1 systems,[7] and could be explained in terms of intermolecular hydrogen abstraction by allylic radicals from neighboring 3MP molecules. In the case of irradiated polyethylene, allyl radicals converted to alkyl radicals by UV irradiation. This was, however, explained by intramolecular hydrogen atom shift.[3] But it may also occur by an intermolecular hydrogen atom abstraction mechanism.

Some of the free radicals CH_3CH_2–$\dot{C}$(R)–CH_2CH_3 produced in the course of UV photolysis of allylic radicals would be photolyzed to produce methyl radicals by the mechanism (3). The concentration of methyl radicals, however, was not so large and no significant increase was observed with longer time of irradiation. This might be caused by the recombination of methyl radicals.

When IB concentration was high (61 mol%), no change in the spectrum was observed by keeping the sample at −196°C for a few days in contrast to the systems with lower IB concentration (2.4 mol%). This seems to be due to a smaller mobility of free radicals as the glass of this mixture is close to the polycrystalline state, as could be supposed from the fact that no trapped electrons were observed.[11]

A spectrum change was observed by subsequent ultraviolet irradiation, and only allylic radicals were observed. This is caused by hydrogen atom abstraction only from an IB molecule. It is reasonable to expect that hydrogen atom abstraction by UV irradiation proceeds only from IB molecules as IB molecules are present close to the parent free radicals because of high IB concentration, and because IB is more reactive than 3MP for hydrogen abstraction.

It should be noted that the eight-line spectrum gradually converted to the fifteen line spectrum when the sample with intermediate IB concentration (12 mol%) was stored at −196°C for a few days. According to our tentative interpretation,[9] this is caused by changes in the conformations of the free radicals. Therefore the conversion from the eight-lines to the fifteen lines seems to be a kind of relaxation process. On the other hand, if the two conformations have an intimate relation with the chain length,[9] a spectrum change could be caused by the propagation of post-polymerization at −196°C.

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