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Ion Radical Formation from α-Methylstyrene
in Irradiated Organic Glasses

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In order to study the ionic reactions of α-methylstyrene induced by ionizing radiations, 2-methyltetrahydrofuran and n-butyl chloride glasses containing a small amount of α-methylstyrene were irradiated by ^{60}Co γ-rays at 77°K and studied by means of electron spin resonance. In the former glass, the electron transfer occurs from the irradiated glass matrix to the solute, α-methylstyrene, giving anion radicals of α-methylstyrene. In the latter glass, on the other hand, the positive charge transfer from the glass matrix to the solute occurs and the cation radicals are formed. The anion radicals give an unresolved spectrum with the width (peak-to-peak in derivative curve) of 14 Gauss, which is bleached readily by visible lights. The cation radicals give a spectrum with the width of 35 Gauss. The observed shape of the spectra is in good agreement with that expected from the molecular orbital calculation.

INTRODUCTION

Recently electron spin resonance (ESR) technique was successfully employed to prove the formation of both anion radicals and cation radicals from styrene molecules in organic glasses irradiated by γ-rays at 77°K by charge transfer from the irradiated glass matrices to the solute styrene[1]. In n-butyl chloride glass, the electrons liberated from the matrix by radiation are stabilized by the electron capture of alkyl halide to form the halogen anion. Thus the positive charges of the cations of matrix molecule formed by radiation transfer to styrene molecules to form its cation radicals. On the other hand, in 2-methyltetrahydrofuran glass, the cationic intermediates are stabilized by the matrix molecules[2]. Thus the liberated electrons transfer to styrene molecules to form its anion radicals. The formation of the ion radicals from styrene was reported already by the optical absorption measurments by Shida and Hamill[3].

α-Methylstyrene is one of the typical monomers which polymerize under the influence of ionizing radiations, as styrene dose[4]. The ion radicals may perhaps be involved in the initiation processes of radiation-induced ionic polymerizations.

The radiation-induced polymerization of α-methylstyrene was studied by Hubmann and Williams[5], who found that the polymerization proceeded in the cationic propagation. On the contrary, Hirota *et al.* reported the anionic poly-

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merization[6] and the observation of anionic intermediates by the pulse radiolysis measurements which, they suggested, were involved in the initiation process of the polymerization[7]. In this respect, it is interesting to know the nature of α-methylstyrene in ionic reactions induced by radiations.

In the present investigation, the formation of the ion radicals from α-methylstyrene is examined in the γ-irradiated n-butyl chloride and 2-metylterahydrofuran glasses at 77°K by means of ESR, as in the case of the ion radicals from styrene reported previously[1].

EXPERIMENTAL

α-Methylstyrene, n-butyl chloride and 2-methyltetrahydrofuran were distilled three times, until the gas chromatographic tests proved their purity better than 99.99%. They were preliminarily dried by CaH_2. After the treatments above mentioned, the former two were dried in vacuum with BaO previously baked at 400°C for 24 hours. The latter one was dried several times with Na-K mirror in vacuum. The measured amount of these chemicals were transferred into ESR sample tubes of pure quartz (Spectrosil, Thermalsynd. Co.), cooled rapidly in liquid nitrogen to glassy state, and irradiated with γ-rays in the ^{60}Co irradiation facility at the Institute for Chemical Research, Kyoto University, at the dose rate of 3.5×10^{18} eV/g·min at 77°K in dark.

Photo-bleaching of the irradiated samples was done with a 150 watt tangsten lamp 25 cm apart from the sample through a filter (Toshiba, UV-46) which cut off lights shorter than 460 mμ.

ESR measurements were carried out with an X-band conventional type spectrometer at 77°K. Absolute intensity of the observed spectra was calibrated in reference to the spectral intensity of 1,1-diphenyl-2-picrylhydrazyl, of which purity was estimated by the iodometic method[8].

RESULTS

α-Methylstyrene in 2-Methyltetrahydrofuran glass

As previously reported[9], the irradiated 2-methyltetrahydrofuran glass gives the ESR signal as shown in Fig 1a which is the superposition of a central sharp spectrum and a broad seven-line spectrum. The former has the width (peak-to-peak, ΔH_{msl}) of 4.7 Gauss and is bleached readily with lights. These facts indicate that it is due to the electrons trapped in the glass. The latter is attributed to the free radicals formed from 2-methyltetrahydrofuran molecules[2].

The irradiated glass containing a small amount of α-methylstyrene gives the signal shape as shown in Fig. 1b as well as blue-purple color (in contrast to blue color in the absence of α-methylstyrene). The signal is composed of the seven-line spectrum due to the free radicals and a central broad spectrum in the place of the trapped electron spectrum. The broad central spectrum and the blue-purple color are bleached by the lights. The shape of the spectrum is obtained by subtracting the signal shape after the bleaching (dotted line) from that before

the bleaching (solid line of Fig. 1c). It extends to 48 Gauss, having the width, ΔH_{msl}, of 14 Gauss. It may be due to the anion radicals formed by the electron capture of α-methylstyrene. The remarkable saturation of the spectrum intensity by the increasing microwave power level suggests also that it is not due to some neutral hydrocarbon radicals.
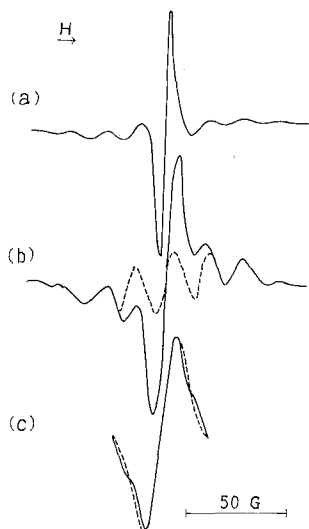

Fig. 1. ESR spectra of 2-methyltetrahy-
drofuran glasses irradiated by
γ-rays to the dose of 3.5×10^{18}
eV/g at 77°K. Measurements at
77°K. (a) Pure glass; (b) Glass
containing 5.31 mole% α-metyl-
styrene before (solid line) and
after (dotted line) photo-bleach-
ing; (c) Spectrum due to added
α-methylstyrene, observed shape
bleached by visible lights (solid
line) and expected shape simula-
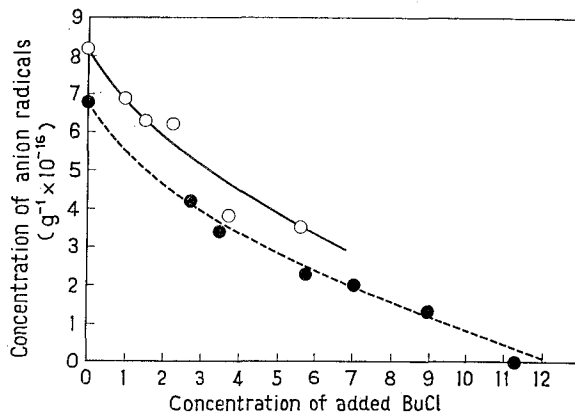ted from the MO calculation (dot-
ted line).

Fig. 2. Effect of the coexistence of n-butyl
chloride on the yield of anion ra-
dical formation from α-methylsty-
rene in the 2-methyltetrahydrofuran
glass irradiated to the dose of $3.5 \times$
10^{18} eV/g at 77°K. The abscissa
represents the ratio of the n-butyl
chloride concentration to the α-me-
thylstyrene concentration (1.0 mole
%). Results obtained for styrene[1]
are also shown by a dotted line
for comparison.

The above assignment of the broad spectrum due to the anion radicals of α-methylstyrene is supported by observing the competition between the electron transfer to α-methylstyrene and that to n-butyl chloride. Alkyl halides are known to scavenge electrons to form halogen anions. When a small amount of n-butyl chloride is added to the glass containing α-methylstyrene, the yield of the anion radicals is much suppressed as shown in Fig. 2.

In the absence of n-butyl chloride, the yield of the anion radicals is inde-pendent of the concentration of added α-methylstyrene in the range examined, i. e., 0.17~5.30 mole%. This fact indicates that the electron transfer occurs effi-ciently and all the electrons liberated from the glass matrix are captured by α-methylstyrene rather than recombine with positive ions. The yield increases linearly with the increasing radiation dose, which gives the G value of 2.1.

α-Methylstyrene in n-Butyl chloride glass

The irradiated n-butyl chloride glass is colored red-purple, giving a six-line spectrum as shown in Fig. 3a, which is assigned to be due to n-butyl radicals, as reported previously[1,10]. When the glass containing a small amount of α-methylstyrene is irradiated, the glass is colored green and the observed signal is the superposition of the six-line spectrum and the central broad spectrum, as shown in Fig. 3b. By subtracting the spectrum of the butyl radicals from the signal, the shape of the broad spectrum due to the added α-methylstyrene is obtained as shown in Fig. 3c (solid line). It extends to 61 Gauss, having the width, ΔH_{msl}, of 35 Gauss, and exhibits the more remarkable power saturation phenomenon than the butyl radical spectrum.
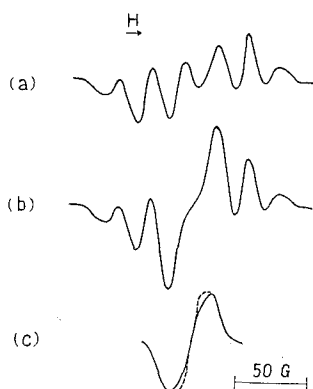

Fig. 3. ESR spectra of n-butyl chloride glasses irradiated by γ-rays to the dose of 3.5×10^{18} eV/g at 77 °K. Measurements at 77°K. (a) Pure glass; (b) Glass containing 0.69 mole% α-methyltsyrene; (c) Spectrum due to added α-methylstyrene, observed spectral shape (solid line) and expected shape simulated from the MO calculation (dotted line).
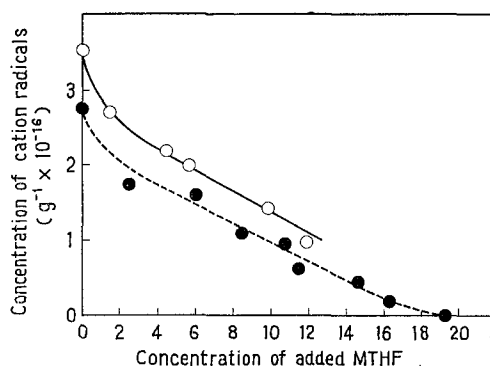
Fig. 4. Effect of the coexistence of 2-methyltetrahydrofuran on the yield of cation radical formation from α-methylstyrene in n-butyl chloride glass irraditated to the dose of 3.5×10^{18} eV/g at 77°K. The abscissa represents the ratio of the 2-methyltetrahydrofuran concentration to the α-methylstyrene concentration (1.0mole %). Results obtained for styrene[1] are also shown by a dotted line for comparison.

The spectrum due to the added α-methylstyrene is very much similar, except the difference in the width, to the spectrum of the anion radicals in the 2-methyltetrahydrofuran glasses. However, the nature of the n-butyl chloride glass suggests that the spectrum is due to the cation radicals formed from α-methylstyrene by the positive charge transfer from the cations of n-butyl chloride molecules (counterpart of the liberated electrons). The above assignment is supported, in this case also, by the observation of the competition between the positive charge transfer to α-methylstyrene and that to 2-methyltetrahydrofuran in the n-butyl chloride glass containing a small amount of both α-methylstyrene and 2-methyltetrahydrofuran, as shown in Fig. 4.

The yield of the cation radicals in the absence of the added 2-methyltetra-

hydrofuran increases with the increasing concentration of the added α-methyl-styrene, reaching to a plateau observed in the range of 0.25~3.10 mole%. In the range of 0.6~2.1 mole%, the yield increases linearly with the radiation dose, giving G=1.0.

DISCUSSION

Assignment of ESR Spectra

In order to make sure that the spectra due to α-methylstyrene added to the glasses are attributable to the cation and the anion radicals, the spin densities on the p_z-orbital of carbon atoms in the ion radicals are calculated by the simple LCAO MO treatment and then the shape of their spectra expected from the well known McConell's relation[11], $a_H = -Q\rho$ (Q=23 Gauss and ρ is the spin density), are compared with the observed spectra.

Parameters used in the calculation for the anion radicals and the obtained spin densities are as follows:
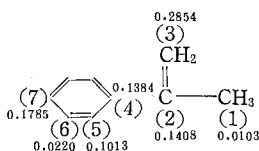
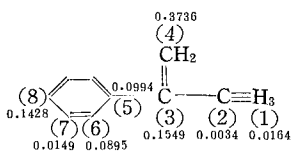Coulomb integrals

$$\alpha_{C(i)} = \alpha \text{ for } i=2\sim7$$

$$\alpha_{CH_3} = \alpha + 3\beta$$

Resonance integrals

$$\beta_{C-C} = \beta$$

The expected spectrum simulated by a computer is illustrated in Fig. 1c (dotted line), which is in good agreement with the observed spectrum. For the cation radicals, however, the similar treatment does not give the good agreement.

By taking the hyperconjugation of the methyl group, the spin densities in the cation radicals are calculated as follows:

Coulomb integrals

$$\alpha_H = \alpha - 0.5\beta$$

$$\alpha_{C(2)} = \alpha - 0.1\beta$$

$$\alpha_{C(i)} = \alpha \text{ for } i=3\sim8$$

Resonance integrals

$$\beta_{CH_3} = 2.5\beta$$

$$\beta_{C(2)-C(3)} = 0.7\beta$$

$$\beta_{C(i)-C(i+1)} = \beta \text{ for } i=3\sim7$$

The hyperfine coupling constant due to the methyl group is calculated by the Levy's formula[12]:

$$a = -(219.8\,\rho_{H_3} + 13.17\,\rho_{C(2)} + 107.7\sqrt{\rho_{H_3}\rho_{C(2)}} - 3.997\sqrt{\rho_{H_3}\rho_{C(3)}}$$
$$- 0.973\sqrt{\rho_{C(2)}\rho_{C(3)}} - 3.09\,\rho_{C(3)})$$

The simulated spectrum is illustrated in Fig. 3c (dotted line), which agrees well with the observed spectrum.
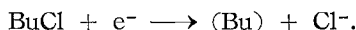
The above consideration of the spectral shapes supports strongly the assignment of the spectra described previously, though the reason why the hyperconjugation should be taken into account only for the cation radicals is not known.
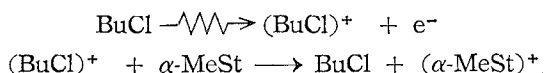
Formation Process of the Ion Radicals

The experimental results show that the formation processes of the anion radicals from α-methylstyrene in the irradiated 2-methyltetrahydrofuran glass are as follows:
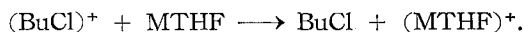
$$MTHF \longrightarrow\!\!\!\!\!\!\!\sim\!\!\!\!\!\!\!\longrightarrow e^- + (MTHF)^+$$
$$\alpha\text{-MeSt} + e^- \longrightarrow (\alpha\text{-MeSt})^-$$
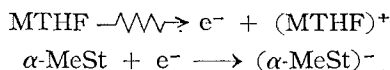
In the presence of n-butylchloride,

$$BuCl + e^- \longrightarrow (Bu) + Cl^-.$$

The cation radicals are formed in the irradiated n-butyl chloride glass as

$$BuCl \longrightarrow\!\!\!\!\!\!\!\sim\!\!\!\!\!\!\!\longrightarrow (BuCl)^+ + e^-$$
$$(BuCl)^+ + \alpha\text{-MeSt} \longrightarrow BuCl + (\alpha\text{-MeSt})^+$$

In the presence of 2-methyltetrahydrofuran,

$$(BuCl)^+ + MTHF \longrightarrow BuCl + (MTHF)^+.$$

These processes are completely analogous to those proposed for the ion radical formation from styrene in the irradiated glasses[1].

It is noted that the efficiency of the electron transfer to α-methylstyrene in comparison with the transfer to n-butyl chloride is very close to the efficiency of the electron transfer to styrene[1] as shown in Fig. 2. It is also the case for the positive charge transfer process (see Fig. 4). These facts may indicate that the efficiency of the charge (both negative and positive) transfer processes from the glass matrix to the solute molecules (such as styrene and α-methylstyrene) in the irradiated organic glasses is mainly determined by the charge migration rate rather than by the reactivity proper to the solutes as charge scavenger.

Apart from the results so far obtained by the pulse radiolysis technique, cationic intermediates are proved, in the present investigation, to be formed from α-methylstyrene. They are probably responsible for the radiation-induced cationic polymerization. The ESR study on the reactions of the ion radicals of α-methylstyrene is now in progress and will be soon reported elsewhere.

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