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Proton Transfer between Styrene Molecular Anion and Ethanol in Rigid Organic Matrices

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The proton transfer from ethanol to styrene molecular anion was studied by examining the yield of the anion and α-methylbenzyl radical generated in γ-irradiated 2-methyltetrahydrofuran–ethanol mixed matrix at 77 K by means of optical absorption measurements. The radical yield was found to increase in proportion to the ethanol fraction at the expense of the anion yield. The maximum radical yield, 2.2, was identical with the yield of scavengeable electron in ethanol matrix where no anion was observed. Upon photobleaching the anion was transformed into the radical in the matrix. The transformation efficiency was constant, *ca.* 0.6, for the ethanol fraction 0.3—0.9. It is concluded that the radical arises from the anion through the proton transfer from ethanol to the β-carbon of vinyl group of the styrene anion. The proton transfer occurs readily only when a specific solvent site around the anion is populated by ethanol molecules. Otherwise, the proton transfer does not occur at all because of the restricted translational motion in the rigid matrix.

The proton transfer to aromatic radical anions in alcoholic solutions has been studied by means of pulse radiolysis technique[1] and its rate constant has been found to depend on the nature of the anion as well as the solvent. The proton transfer generally proceeds slowly because of a small pre-exponential factor in the rate constant. It has been observed to occur also in rigid alcoholic matrices at 77 K.[2–4] A steric factor is expected to affect significantly the rate of the proton transfer in the rigid matrices, since the translational motion of reactants are highly restricted. Styrene molecular anion (styrene anion) is transformed into α-methylbenzyl radical *via* proton transfer in γ-irradiated alcoholic matrices,[2–4] whereas it is stably trapped in aprotic rigid matrix of 2-methyltetrahydrofuran (MTHF) at 77 K.[2] In order to elucidate microscopically the mechanism of the proton transfer to an anion radical we have studied the transformation of the styrene anion into the α-methylbenzyl radical in the rigid matrices of MTHF–ethanol mixtures. The anion and the radical give distinct optical absorption spectra distinguishable from each other, so that the transformation can advantageously be followed by the optical spectrophotometric method.

Experimental

MTHF was distilled several times and treated with Na-K alloy. GR grade ethanol (Tokyo Kasei Chemical Ind., Ltd.) was used without further purification. Styrene was washed with aqueous solution of NaOH, distilled, dried with CaH$_2$, dehydrated with baked BaO and stored. It was distilled in a vacuum immediately before use. Sample solutions were degassed by a freeze-pump-thaw technique, transferred to an optical absorption cell of quartz or an ESR sample tube of quartz and sealed off in a vacuum of 10^{-5} Torr. γ-Irradiation was carried out at 77 K at a dose rate of 2 Mrad/h or 1 Mrad/h mostly to a dose of 0.2 Mrad. Optical absorption spectra were recorded with a conventional recording spectrophotometer (Hitachi, ESP-3A or Shimadzu, MPS-50L) and electron spin resonance (ESR) spectra with a conventional X-band spectrometer (JEOL, JES-3M) both at 77 K. The samples were annealed, when necessary, above 77 K with a controlled flow of cold nitrogen gas.

Results and Discussion

Yield of Styrene Anion and α-Methylbenzyl Radical. When an MTHF matrix containing styrene is irradiated at 77 K with γ-rays, the styrene anion is generated through the electron attachment to styrene, giving optical absorption bands at 415 and 600 nm.[2,3,5] Shida and Hamill reported that when a matrix of ethanol dissolving styrene is irradiated, α-methylbenzyl radical is exclusively detected by its absorption band with a maximum at 320 nm. Formation of the α-methylbenzyl radical in the ethanol matrix was evidenced by means of the fluorescence spectrophotometric method: the observed emission spectrum with the 0-0 band at 470 nm and the excitation spectra in visible and UV regions are essentially the same as those for the α-methylbenzyl radical generated by dissociative electron attachment to (1-chloroethyl)benzene in γ-irradiated organic matrices.[6] Williams and his co-workers[2] demonstrated by ESR studies a two-step mechanism for the formation of the α-methylbenzyl radical from styrene in the ethanol matrix, an electron attachment to styrene followed by proton transfer from a solvent molecule. Based on this mechanism, the stable trapping of the styrene anion in the MTHF matrix is attributed to the nature of MTHF solvent which cannot act as a proton donor.

A typical optical absorption spectrum recorded for the irradiated matrix of MTHF–ethanol mixtures con-

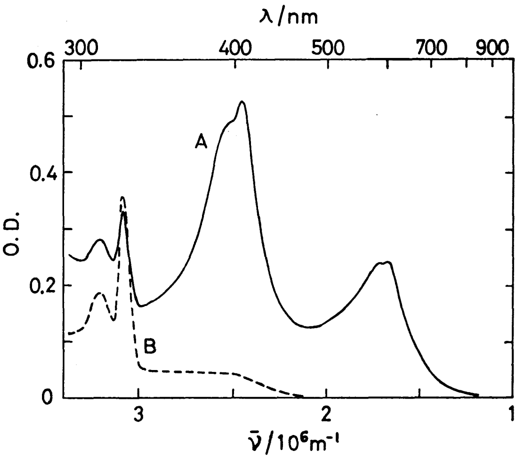

Fig. 1. Optical absorption spectra of a MTHF–ethanol mixed matrix (50 : 50 in mole) containing 50 mmol dm^{-3} styrene irradiated by γ-rays to 200 krad at 77 K (A) before and (B) after photobleaching with white light. Optical path-length: 0.2 cm.

taining styrene, for a solvent composition 50 : 50 in mole, is shown in Fig. 1A. The formation of trapped electron was completely depressed by 30 mmol dm^{-3} of styrene, the observed spectrum consisting of the band with the maximum at 320 nm due to α-methylbenzyl radical and the bands at 415 and 600 nm both due to the styrene anion. Figure 2 shows the relative yields of the radical and the anion monitored at 320 and 415 nm, respectively, as a function of the mole fraction of ethanol, X_{EtOH}, in the mixed matrix. The radical yield increases in proportion to X_{EtOH}, while the yield of the anion decreases linearly. This indicates, in accord with the two-step mechanism, that the radical is generated at the expense of the anion.

No transformation was observed from the anion into the radical after the irradiation as long as the matrix was kept at 77 K in the dark. This indicates that the proton transfer occurs so rapidly that it is completed during the course of γ-irradiation.

Proton Transfer in Rigid Matrix. The proton transfer reaction in a fluid solution is expected to follow the rate equation, $d[\mathrm{Radical}]/dt = k[\mathrm{Anion}][\mathrm{C_2H_5OH}]$. If we ignore subsidiary reactions such as ion recombination, the ethanol concentration would affect not the ultimate yield of the α-methylbenzyl radical but the rate of the radical formation. However, the proton transfer in the rigid matrix showed a different feature. The change in X_{EtOH} caused the change in the radical yield as shown in Fig. 2.

The translational motion of molecules is highly restricted in the rigid matrix. Only the anion with an ethanol molecule (or molecules) located properly around it might undergo the proton transfer, but not the anion having no ethanol molecule in a proper location. Assuming that at the maximum the solvent site can be adequately populated by n ethanol molecules for the reaction, the probability is given by $(1-X_{\mathrm{EtOH}})^n$ for the site being all populated by MTHF molecules, or for an anion not undergoing the proton transfer reaction.

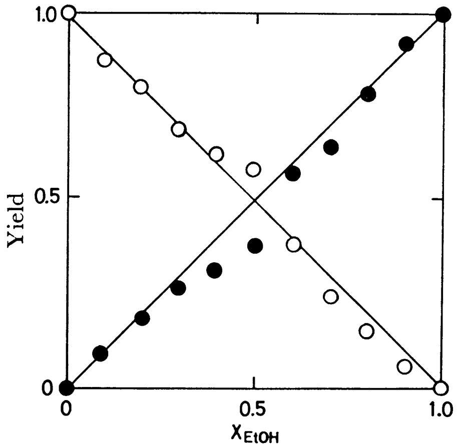

Fig. 2. Dependence of the yield of (○) styrene anion and (●) α-methylbenzyl radical upon the ethanol fraction in the MTHF–ethanol mixed matrix. The yields were corrected, so that their maximum value is 1.0. Straight lines indicate the dependence expected from Eq. 1 for $n=1$. Styrene concentration: 50 mmol dm^{-3}. γ-Irradiation: 200 krad.

Thus, the radical yield is given by $[\mathrm{Radical}] = [\mathrm{Anion}]_0 \cdot \{1-(1-X_{\mathrm{EtOH}})^n\}$, where $[\mathrm{Anion}]_0$ denotes the anion yield in the MTHF matrix or $X_{\mathrm{EtOH}}=0$. Since the *G*-value of scavengeable electrons is almost the same in the MTHF and ethanol matrices,[7] the dependence of the radical yield on X_{EtOH} is given by

$$\frac{[\mathrm{Radical}]}{[\mathrm{Radical}]_{\max}} = 1 - \frac{[\mathrm{Anion}]}{[\mathrm{Anion}]_0} = 1 - (1-X_{\mathrm{EtOH}})^n \quad (1)$$

where $[\mathrm{Radical}]_{\max}$ denotes the radical yield for $X_{\mathrm{EtOH}} = 1$.

If $n>1$, the radical yield *vs.* X_{EtOH} curve should be convex upward. For instance, $[\mathrm{Radical}]/[\mathrm{Radical}]_{\max}$ is calculated to be 7/8 for $n=3$ and $X_{\mathrm{EtOH}}=1/2$. The reaction in a fluid solution is an extreme case: an anion has a chance to encounter all the ethanol molecules present in the solution suitably for the proton transfer, so that n is effectively infinite, and that $[\mathrm{Radical}]/[\mathrm{Radical}]_{\max}=1$ except for $X_{\mathrm{EtOH}}=0$. The result shown in Fig. 2 can be interpreted by n of unity, indicating that the proton transfer to the styrene anion occurs from an ethanol molecule located very close to and specifically with respect to a reactive site of the anion. This is consistent with the pulse radiolysis result in fluid solution which shows that the slow proton transfer is associated with a small pre-exponential factor of the rate constant.[1] It is also indicated that the linear decrease in the anion yield with X_{EtOH} is entirely due to the transformation of the anion into the radical and not to the recombination between the anion and a cation.

Site of Proton Attachment. The attachment of a proton to the β-carbon of the vinyl group in the styrene anion directly results in the formation of α-methylbenzyl radical. Alternatively, the α-methylbenzyl radical could be generated, when the intramolecular hydrogen transfer occurs in the phenethyl radical primarily formed by the proton attachment to the α-carbon of the vinyl group. Such an intramolecular hydrogen transfer was suggested from the observation of α-methylbenzyl radical when dissociative electron attachment to (2-chloroethyl)benzene occurred in γ-irradiated rigid matrices.[6,8]

In order to confirm the possibility of the latter mode of α-methylbenzyl radical formation, the stability of the phenethyl radical was examined in the MTHF matrix by the ESR method. Upon photolyzing (2-bromoethyl)benzene in the matrix at 77 K with UV light, a seven-line spectrum extending over 15 mT was observed, distinctly differing from the spectrum assigned to α-methylbenzyl radical,[2] and probably due to the phenethyl radical. It was found to decay with no change in its spectral shape when warmed to 100 K.

When the MTHF matrix containing (2-bromoethyl)benzene was irradiated with γ-rays at 77 K, the observed spectral shape consisted of the superposition of the well-known spectrum of MTHF radical,[9] and that attributable to the phenethyl radical. The change in the spectral shape upon warming to 100 K was found to be due to the decay of only the latter spectrum by examining the difference in spectral shape before and after the warming. In this case the phenethyl radical seems to be formed by dissociative electron attachment to (2-bromoethyl)benzene.

From these photolysis and radiolysis studies it is obvious that the radical is too stable for the intramolecular hydrogen transfer to occur. Thus, the α-methylbenzyl radical is concluded to be generated exclusively by the direct mode of formation, the proton attachment to the α-carbon, the indirect mode being excluded. It is inferred that the proton transfer to the styrene anion in the mixed matrix occurs when an ethanol molecule happens to be properly located close to the β-carbon of the anion. Based on MO calculations, electron density is the highest as this carbon atom in the anion, so that it is expected to be the most reactive toward the proton attachment.

According to the present optical absorption study, the *G*-value of the α-methylbenzyl radical in the γ-irradiated ethanol matrix was determined to be 2.2 by using the extinction coefficient, 1.5×10^4 mol^{-1} dm^3 cm^{-1} at the absorption maximum for benzyl radical.[10] It is almost identical to the *G*-value of scavengeable electron in the ethanol matrix.[7] This coincidence of the *G*-values supports the view that the α-methylbenzyl radical arises from the styrene anion generated by the electron attachment to styrene, and that the proton transfer to the anion occurs almost exclusively to the β-carbon.

Photobleaching of Styrene Anion. Upon photobleaching with white light from an incandescent lamp (λ>400 nm), the styrene anion in the mixed matrix could be completely eliminated, being transformed partially into the α-methylbenzyl radical (Fig. 1B). The efficiency of this photoinduced transformation (the ratio of the increment of the radical yield to the yield of the photobleached anion) increases with increasing X_{EtOH} to reach a plateau value of *ca.* 0.6 (Fig. 3). The plateau could be determined by the competition for electrons photoreleased from the styrene anions between the dissociative electron scavenge reaction of ethanol[11,12] and the non-dissociative electron scavenge reaction of styrene associated with an ethanol molecule suitable for the proton transfer. Both the dissociative and non-dissociative scavenge reactions proceed at a rate proportional to the ethanol concentration in the mixed matrix, so that the transformation efficiency is independent of the ethanol concentration. The rate of non-dissociative scavenge reaction proportional to the ethanol concentration implies that only one ethanol molecule can be located in the solvent site adequate for the proton transfer, consistent with $n=1$ in Eq. 1.

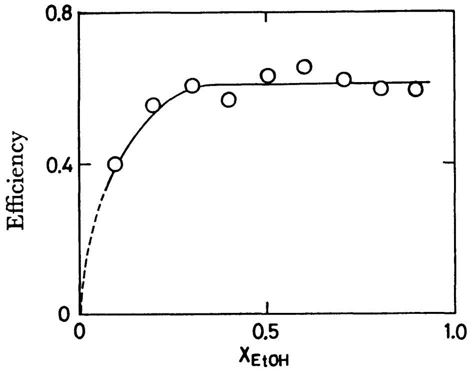

Fig. 3. Efficiency of photoinduced transformation of styrene anion into α-methylbenzyl radical as a function of the ethanol fraction in the MTHF-ethanol mixed matrix. Photobleaching was carried out with white light at 77 K after irradiating the matrices containing 50 mmol dm^{-3} styrene to the dose of 200 krad.

The fall of efficiency at low values of X_{EtOH} can be attributed to an increasing contribution of charge recombination reaction between the photoreleased electrons and positive ions, since the rate becomes low for both scavenge reactions.

So far the discussion has been given on the assumption that ethanol is perfectly missible in MTHF and *vice versa*, so that the mixed matrix is microscopically homogeneous. Sawai and Hamill studied the optical absorption spectra of trapped electrons in γ-irradiated MTHF–methanol mixed matrix and interpreted the spectral feature in terms of the microscopically homogeneous mixing of the two solvent components.[13]

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8) Dissociative electron attachment to (2-chloroethyl)-benzene leads to the formation of phenethyl radical. The observed α-methylbenzyl radical was therefore suggested to arise from the phenethyl radical.[6] However, the α-methylbenzyl radical was detected by the sensitive fluorescence spectrophotometric method, the formation of the phenethyl radical not being examined. It seems to us that the main product from (2-chloroethyl)benzene is the phenethyl radical and that the α-methylbenzyl radical is generated by a subsidiary reaction in the γ-irradiated matrices.

9) See for example, D. R. Smith and J. J. Pieroni, *Can. J. Chem.*, **43**, 876 (1965); T. Shida, T. Warashina, H. Yoshida, and S. Okamura, *Ann. Repts. Research Reactor Inst. Kyoto Univ.*, **3**, 19 (1970).

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