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ESR and Optical Studies of the Reaction Intermediates Produced from Phenyl Halides by Dissociative Electron Attachment in γ-Irradiated Organic Glasses at 77°K

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ESR and optical studies have been made of dissociative electron attachment by phenyl halides and reaction intermediates produced in γ-irradiated glassy solid matrices at 77°K. Dissociative electron attachment by phenyl halides is an efficient process and the ratio of cross sections $C_6H_5I/C_6H_5Br/C_6H_5Cl$ for this process in MTHF glass is 1.5/1.0/1.0. The phenyl radical produced abstracts a hydrogen atom from solvents (MTHF, 3MP) at 77°K and is stable in aqueous alkali-metal hydroxide glass. A part of 3MP radicals in a γ-irradiated solution of phenyl bromide in 3MP at 77°K disappear by a first-order process for which $k=4.3\times10^{-2}\ \text{min}^{-1}$. γ-Irradiated 3MP glasses containing phenyl halides exhibit the optical absorption spectra having characteristic absorption bands in the visible and UV region which are assigned to solute cations and hydrogen-adducts respectively.

Dissociative electron attachment by organic halides ($RX+e^-\rightarrow R+X^-$) has been shown by ESR[1,2] and optical[3] measurements to be an efficient process in glassy solid matrices whenever the electron affinity of X exceeds the bond dissociation energy of R-X. Consequently, low concentrations of organic halides may serve as electron scavengers in radiolytic systems. It is also expected that dissociative electron attachment could selectively yield the radical R from organic halides RX. Most of the previous studies are concerned with alkyl halides as solutes.

In the present work, a study was made of dissociative electron attachment by phenyl halides in γ-irradiated organic glasses and reaction intermediates produced in these systems at 77°K. ESR and optical absorption techniques were applied to detect the reaction intermediates.

Experimental

Materials. MTHF was purified by passing through an activated alumina column. 3MP and *n*-butyl chloride were purified by passing through a silica-gel column. Solvents were dried with calcium hydride. Commercially available purest phenyl halides were used with purification by vacuum distillation.

Sample Preparation. Phenyl halide was stored in vacuum and was distilled from the storage bulb, pipetted into an ESR tube or an optical absorption cell containing a known amount of solvent, then returned to the vacuum line and degassed by conventional vacuum techniques before sealing the tube or the cell.

Irradiations, ESR and Optical Measurements. Samples were prepared, γ-irradiated and measured in quartz ESR tubes (i. d. 5 mm) or optical absorption cells (1 cm × 1 cm), sealed in vacuum and immersed in liquid nitrogen prior to irradiation and subsequent measurements. They were examined using a JES-3BX ESR spectrometer and a Hitachi-Perkin-Elmer-139 UV-VS spectrophotometer. Doses were 2.3×10^5 rad and 8.0×10^4 rad for ESR and optical experiments, respectively. Photobleaching of γ-irradiated samples was performed with visible light from a tungsten lamp and using glass filters as needed.

Results

Phenyl Halides in MTHF. γ-Irradiated MTHF glasses containing phenyl halides displayed the ESR spectrum of trapped electron superimposed on that of MTHF radical, the intensity of their signals depending on solute concentration. Figure 1 shows the dependence of trapped electron or MTHF radical concentration on the concentration of phenyl iodide. It can be seen from Fig. 1 that the concentration of trapped electrons decreases and that of MTHF radicals increases with increasing phenyl iodide concentration. The concentration of MTHF radicals approaches to a limiting value of twice that of the radicals in pure MTHF at *ca.* 2 mol% solute concentration, while the concentration of trapped electrons is nearly zero at the same solution concentration.

A γ-irradiated MTHF glass containing 1.0 mol% phenyl iodide did not exhibit any absorption bands in the wavelength region $\lambda>300\ \text{m}\mu$ in

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[1] D. W. Skelly, R. G. Hayes and W. H. Hamill, *J. Chem. Phys.*, **43**, 2795 (1965).

[2] R. F. C. Claridge and J. E. Willard, *J. Am. Chem. Soc.*, **87**, 4992 (1965).

[3] J. B. Gallivan and W. H. Hamill, *J. Chem. Phys.*, **44**. 1279 (1966).

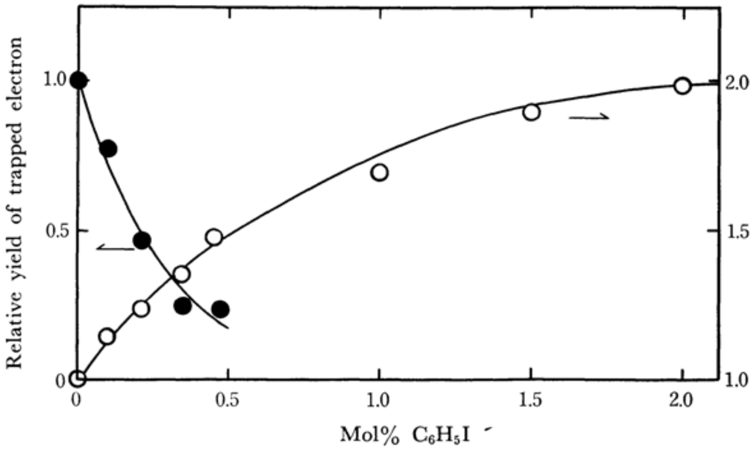

Fig. 1. Dependence of the yields of trapped electron and MTHF radical on phenyl iodide concentration in γ-irradiated solutions of phenyl iodide in MTHF at 77°K.

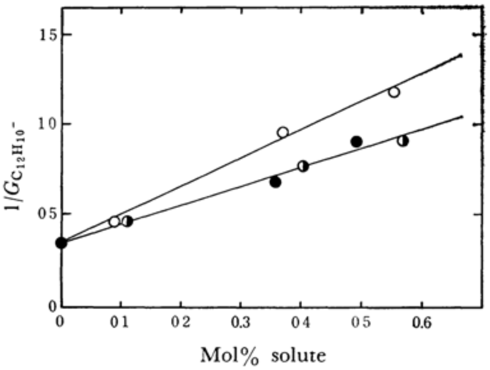

Fig. 2. $1/G_{C_{12}H_{10}^-}$ *vs.* mol% phenyl halides in γ-irradiated MTHF solutions containing 0.15 mol% biphenyl at 77°K.
○, C_6H_5I; ◑, C_6H_5Br; ●, C_6H_5Cl

the optical absorption spectrum. Figure 2 shows a plot of $1/G_{C_{12}H_{10}^-}$ *vs.* the concentration of phenyl halides (iodide, bromide, and chloride) in MTHF solutions containing 0.15 mol% biphenyl. $G_{C_{12}H_{10}^-}$ is the *G*-value for biphenyl anions formed. There are linear relationships between these quantities for all the solutes. Optical measurements were made for determination of the yield of biphenyl anion, in which the extinction coefficient for biphenyl anion was taken to be $3.7\times10^4\ l\ \mathrm{mol}^{-1}\cdot\mathrm{cm}^{-1}$ at 410 mμ.[4] As shown in Fig. 2, straight lines drawn through the experimental points can be extrapolated to the same point on the ordinate.

Phenyl Halides in 3MP. The ESR spectrum of γ-irradiated 3MP glass containing 0.2 mol% phenyl iodide was similar in shape to that of pure 3MP glass, indicating only the solvent radical (Fig. 3). However, the amount of solvent radicals produced in 3MP containing phenyl iodide was larger than that in pure 3MP under the same irradiation condition.

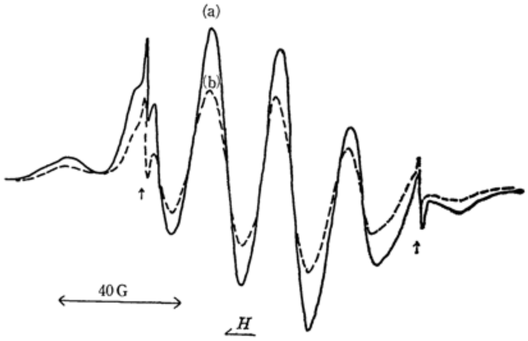

Fig. 3. ESR spectra of γ-irradiated 3MP solutions with and without phenyl iodide at 77°K. (a) 3MP containing 0.2 mol% phenyl iodide; (b) pure 3MP. Arrows indicate the signal of Mn.

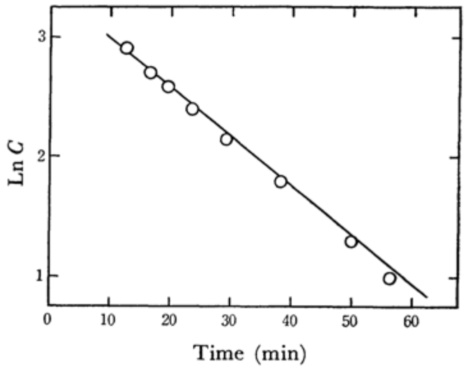

Fig. 4. First-order plot for the decay of 3MP radical in a γ-irradiated solution of 0.2 mol% phenyl bromide in 3MP at 77°K. *C*, concentration of 3MP radical in arbitrary unit.

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4) M. R. Ronayne, J. P. Guarino and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 4230 (1962).

In γ-irradiated 3MP glasses containing phenyl halides, a part of solvent radicals disappeared much rapidly than those in pure 3MP glass. A first-order plot for the decay of such 3MP radicals at 77°K is shown in Fig. 4. The decay rate for these radicals is obtained to be $k=4.3\times10^{-2}\ \mathrm{min}^{-1}$. After the rapidly decaying 3MP radicals had disappeared, residual 3MP radicals disappeared very slowly as those in pure 3MP.

3MP glasses containing phenyl iodide or bromide, after γ-irradiation, exhibited the optical absorption spectra as shown in Fig. 5 or 6. In a 3MP glass containing 0.2 mol% phenyl iodide, the absorption bands having $\lambda_{max}=300$, 560 and 710 mμ were observed in the spectrum obtained 0.5 hr after termination of the γ-irradiation. Although the 300 mμ band did not change with time, the 710 mμ band decreased in intensity and new absorption bands having $\lambda_{max}=410$ and 520 mμ appeared in the spectrum obtained 2 hr after termination of the γ-irradiation. In a 3MP glass containing 0.2 mol% phenyl bromide, the absorption bands having $\lambda_{max}=290$ and 620 mμ and a shoulder at 330 mμ were observed in the spectrum obtained 0.5 hr after termination of the γ-irradiation. The 620 mμ band decreased in intensity and the 330 mμ band increased in the spectrum obtained 1.5 hr after termination of the γ-irradiation, while the 290 mμ band did not change with time. In a 3MP glass containing phenyl chloride, the absorption band having $\lambda_{max}=580$ mμ was observed and other bands were too broad for their maxima to be discernible in the spectrum.

Phenyl Halides in *n*-BuCl. It was found by ESR measurements that the yield of solvent radicals produced in γ-irradiated *n*-BuCl glass containing 1.0 mol% phenyl iodide was nearly equal to that in pure *n*-BuCl glass under the same irradiation condition.

γ-Irradiated *n*-BuCl glasses containing 0.5 mol% phenyl iodide or bromide displayed the optical absorption spectra having an absorption band with $\lambda_{max}=710$ or 620 mμ, respectively, in addition to the bands attributable to the intermediates from *n*-BuCl.

Phenyl Halides in Aqueous Alkali-metal Hydroxide Glass. γ-Irradiated glassy aqueous solutions of 10 mol% NaOH containing a saturated concentration of phenyl iodide exhibited a narrow

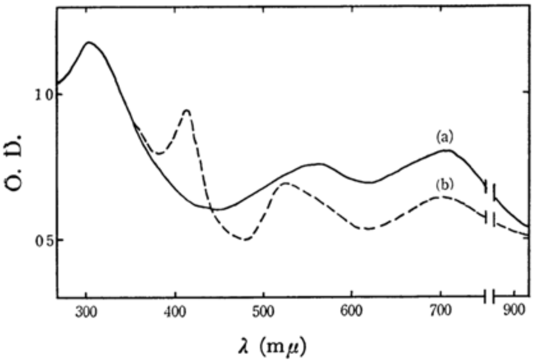

Fig. 5. Absorption spectra of a γ-irradiated solution of 0.2 mol% phenyl iodide in 3MP at 77°K. (a) 0.5 hr, (b) 2 hr after termination of the γ-irradiation.

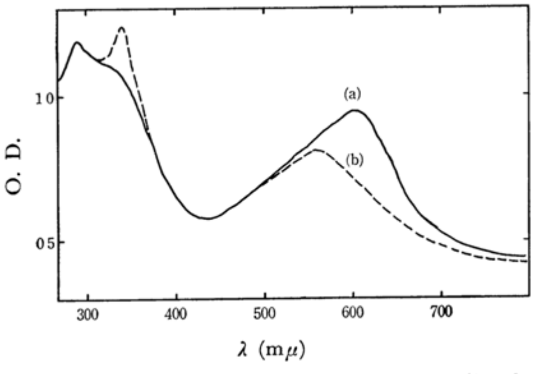

Fig. 6. Absorption spectra of a γ-irradiated solution of 0.2 mol% phenyl bromide in 3MP at 77°K. (a) 0.5 hr, (b) 1.5 hr after termination of the γ-irradiation.

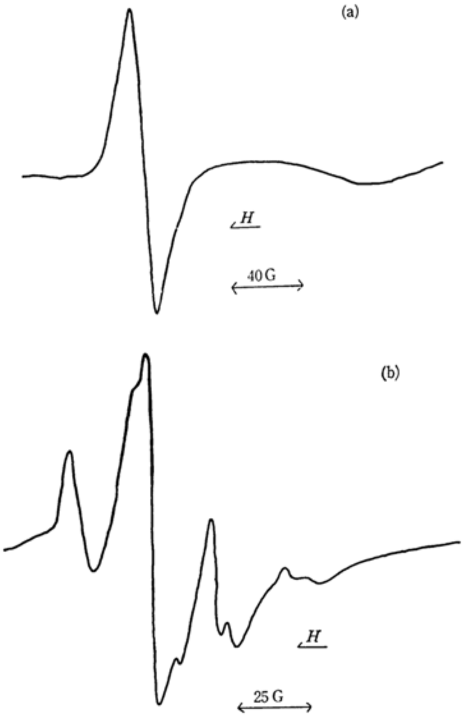

Fig. 7. ESR spectra of a γ-irradiated 10 mol% NaOH aqueous solution containing a saturated concentration of phenyl iodide at 77°K. (a) before photobleaching, (b) after photobleaching with visible light. The spectrum (b) was obtained using a 50 times greater sensitivity than the spectrum (a).

ESR singlet at $g=2.001$ and a broad singlet in the lower magnetic field (Fig. 7(a)). Photobleaching of the same sample as the preceding with visible light yielded the spectrum with the hyperfine structure as shown in Fig. 7(b).

Discussion

It is well known that trapped electrons are produced in γ-irradiated MTHF glass at 77°K.[4,5] The results that the yield of trapped electrons decreases in the presence of phenyl halides indicate that phenyl halides compete with the solvent for capturing electrons. Electrons are captured almost completely by phenyl iodide at *ca.* 2 mol% concentration in MTHF. On the other hand, the yield of MTHF radicals increases with phenyl iodide concentration, approaching to a limiting value of twice that of the radicals in pure MTHF. It is generally accepted that the MTHF radical is formed by the ion-molecule reaction $C_5H_{10}O^+ + C_5H_{10}O \rightarrow C_5H_{10}OH^+ + C_5H_9O$ in γ-irradiated pure MTHF.[6,7] The increase in the yield of MTHF radicals observed in MTHF solutions containing phenyl iodide is interpreted in terms of H-abstraction by phenyl radicals from the solvent. When electrons are captured completely by phenyl halides, the yield of phenyl radicals formed should be equal to that of MTHF cations. Therefore, at sufficiently high concentrations of phenyl iodide, the yield of MTHF radicals reaches twice that in pure MTHF.

The relative cross section for electron attachment is obtained by making use of competitive reactions for electrons between a reference solute and other solutes in MTHF. A simple kinetic treatment leads to the relation[8]:

$$\frac{1}{G_{Y^-}} = \frac{1}{G^\circ_{Y^-}} + \frac{1}{G^\circ_{Y^-}}\frac{\sigma_X[X]}{\sigma_Y[Y]} \qquad (1)$$

where Y is a reference solute of known anion spectrum, X any second solute, and σ_Y and σ_X are the respective electron attachment cross sections. G_{Y^-} and $G^\circ_{Y^-}$ are the G-values for formation of anion Y^- in solutions with and without the second solute respectively. A plot of $1/G_{Y^-}$ *vs.* $[X]$ with a fixed concentration of Y yields the relative cross section σ_X/σ_Y and extrapolation of this plot to $[X]=0$ gives $G^\circ_{Y^-}$ in Eq. (1). In the present study, in which biphenyl is used as the reference solute, $G^\circ_{Y^-}$ is obtained as 2.9 which is in agreement with the literature value.[4] The ratio of cross sections $C_6H_5I/C_6H_5Br/C_6H_5Cl$ for dissociative electron attachment in MTHF is 1.5/1.0/1.0.

The increase in the yield of 3MP radicals observed in 3MP glasses containing phenyl halides is also interpreted in terms of H-abstraction by phenyl radicals from the solvent.[*1] Such an interpretation is supported by the fact that the yield of benzene formed is equal to the decrease in hydrogen yield in the radiolysis of methylcyclohexane glass at 77°K.[9]

A part of 3MP radicals produced in a 3MP solution containing phenyl bromide at 77°K disappear rapidly by a first order process unitl the concentration of 3MP radicals in this solution becomes equal to that produced in pure 3MP under the same irradiation condition, and the residual 3MP radicals disappear very slowly as those in pure 3 MP. The 3MP radicals which disappear rapidly may combine with some intermediates formed in close proximity to those 3MP radicals. Aggregation of phenyl halides in 3MP glass may be responsible for this phenomenon, because such a rapid decay of solvent radicals as that in 3MP glass is not observed in MTHF glass. Aggregation of alkyl iodides in 3MP glass at 77°K has previously been suggested by Claridge and Willard[10] and Mittal and Hamill.[11] The detailed mechanism for the rapid decay of 3MP radicals has not yet been established.

The narrow ESR singlet and the broad singlet observed in a γ-irradiated aqueous alkali-metal hydroxide glass containing phenyl iodide are apparently the same as those in an aqueous alkali-metal hydroxide glass without the solute. These singlets are attributed to trapped electrons and the O^- radical ions respectively.[12-18] The ESR spectrum obtained after photobleaching of the trapped electron signal is identified with that of the phenyl radical.[19] The low yield of phenyl radicals observed is probably due to the low solubility of phenyl iodide in aqueous solution at 77°K.

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5) D. R. Smith and J. J. Pieroni, *Can. J. Chem.*, **43**, 876 (1965).

6) F. S. Dainton and G. A. Salmon, *Proc. Roy. Soc.*, **A285**, 319 (1965).

7) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 4372 (1966).

8) J. P. Guarino, M. R. Ronayne and W. H. Hamill, *Radiation Res.*, **17**, 379 (1962).

[*1] H-abstraction by phenyl radicals from alkanes at 77°K has previously been shown by Bennett *et al.* (Ref. 19).

9) T. Kimura, T. Miyazaki, K. Fueki and Z. Kuri, unpublished results.

10) R. F. C. Claridge and J. E. Willard, *J. Am. Chem. Soc.*, **89**, 510 (1967).

11) J. P. Mittal and W. H. Hamill, *ibid.*, **89**, 5749 (1967).

12) D. Schulte-Frohlinde and K. Eiben, *Z. Naturforsch.*, **17a**, 445 (1962); *ibid.*, **18a**, 199 (1963).

13) M. J. Blandamer, L. Shields and M. C. R. Symons, *Nature*, **200**, 902 (1963); *J. Chem. Soc.*, **1964**, 4352.

14) T. Henriksen, *Radiation Res.*, **23**, 63 (1964).

15) P. N. Moorthy and J. J. Weiss, *Phil. Mag.*, **10**, 659 (1964).

16) P. B. Ayscough, R. G. Collins and F. S. Dainton, *Nature*, **205**, 965 (1965).

17) L. Kevan, *J. Am. Chem. Soc.*, **87**, 1481 (1965).

18) J. Zimbrick and L. Kevan, *J. Chem. Phys.*, **47**, 2364 (1967).

19) J. E. Bennett, B. Mile and A. Thomas, *Proc. Roy. Soc.*, **293**, 346 (1966).

It is understandable in view of the difference in bond dissociation energy between C-H and O-H that the phenyl radical can abstract an H-atom from the solvents in MTHF and 3MP glasses, but not in aqueous alkali-metal hydroxide glass at 77°K.

The 300 or 290 mμ band in the optical absorption spectrum of γ-irradiated 3MP glass containing phenyl iodide or bromide is attributed to H-atom addition to the benzene ring.[20] The 710, 620 and 580 mμ bands observed in 3MP containing phenyl iodide, bromide and chloride are attributed to the respective halide cations, because the same absorption bands are observed in *n*-BuCl glass, in which positive holes migrate to the solutes and electrons are trapped in the matrix.[7] Recently, Baker *et al.* have measured various ionization potentials of phenyl halides by photoelectron spectroscopy.[21] According to their results, the difference in energy between the lowest and second ionization energy bands is ~2 eV, which is in general agreement with the transition energies of the cation bands observed in the present study. The lowest ionization energy bands are attributed to the removal of an electron from the orbitals corresponding to the highest occupied π orbitals in benzene and the second ionization energy bands to the removal of an electron from halogen lone pairs. Thus the observed cation bands are attributed to the $n \rightarrow \pi$ transition of an electron in the phenyl halide cations. The assignment of the 560 mμ band observed in γ-irradiated phenyl iodide in 3MP glass is not established at present.

Since the 410 and 520 mμ bands observed in γ-irradiated 3MP glass containing phenyl iodide increase in intensity with time after termination of the γ-irradiation, these bands must be attributed to secondary intermediates produced by the reaction between primary intermediates. These bands are tentatively assigned to a complex, $C_6H_5I\cdot I$, which may be produced by ion recombination between $C_6H_5I^+$ and I^-. Such an assignment is consistent with the result that the cation band decreases in intensity with time. The 390 and 480 mμ bands produced by γ-irradiation of alkyl iodides (RI) in alkane matrices at 77°K have previously been assigned to $RI\cdot I$.[11] However, the possibility of I_2^- [10] for the 410 mμ band cannot be excluded at present. The 330 mμ band observed in 3MP containing phenyl bromide may be attributed to $C_6H_5Br\cdot Br$, although the possibility of Br_2^- cannot be excluded. Further study is required to establish the assignment of the secondary reaction intermediates.

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20) B. Chutny, *Nature,* **213**, 593 (1967).

21) A. D. Baker, D. P. May and D. W. Turner, *J. Chem. Soc., (B)*, **1968**, 22.