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# A Comparative Study of Electron Capture by Solutes in $\gamma$-Irradiated 2-Methyltetrahydrofuran Glass at 77°K

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It is generally believed that the behavior of electrons produced by the $\gamma$-irradiation of molecular compounds depends upon the states of aggregation; the electrons in the liquid phase are solvated and their reactions are mostly diffusion-controlled,[1-3] while they are, of course, free in the gas phase. A study[4] made of the reaction of electrons with a number of organic halides in 2-methyltetrahydrofuran (MTHF) glass at 77°K has led to the conclusion that electrons behave as quasi-free electrons*[1] in the solid phase.

These studies of the behavior of electrons were, however, undertaken by different experimental techniques and the interrelation between electrons in the different phases is not clear at present.

1) F. Williams, *J. Am. Chem. Soc.*, **86**, 3954 (1964).

2) G. R. Freeman and J. M. Fayadh, *J. Chem. Phys.*, **43**, 86 (1965).

3) S. Sato, T. Terao, M. Kono and S. Shida, This Bulletin, **40**, 1818 (1967).

4) K. Fueki, N. Kato and Z. Kuri, presented at the 10th Symposium on Radiation Chemistry, Oct., 1967, Hiroshima, Japan.

*1 The term "quasi-free electron" in the solid phase was used for a nearly free electron, one whose interaction with a solvent is minor compared to that of a trapped or solvated electron.

It is widely accepted that nitrous oxide reacts with an electrons:

$$e^- + N_2O \longrightarrow N_2 + O^- \quad (1)$$

Recently it has been shown by kinetic studies involving the analysis of final products that Reaction (1) alone is not sufficient to explain the yield of nitrogen.[5-8]

In the present work, we have studied, by the spectrophotometric method, the reactivities of $N_2O$, $SF_6$, and $CO_2$ with electrons in MTHF glass at 77°K and compared the results with those in the liquid and gas phases.[3,9] We have also studied the reaction of nitrous oxide with electrons by analyzing the final products in connection with the measurements of the reaction intermediates.

When MTHF glasses containing biphenyl are irradiated with $\gamma$-rays at 77°K, a fraction of the

5) G. R. A. Johnson and J. M. Warman, *Nature*, **203**, 73 (1964).

6) W. J. Holtslander and G. R. Freeman, *Can. J. Chem.*, **45**, 1661 (1967).

7) R. A. Holroyd, *J. Phys. Chem.*, **72**, 759 (1968).

8) T. Kimura, T. Miyazaki, K. Fueki and Z. Kuri, This Bulletin, in press (1968).

9) W. J. Holtslander and G. R. Freeman, *J. Phys. Chem.*, **71**, 2562 (1967).

electrons produced are captured by biphenyl to form biphenyl anions. The anion gives a sharp absorption band with $\lambda_{max}=410$ m$\mu$ and a broad band with $\lambda_{max}=660$ m$\mu$. The absorption bands attributed to the biphenyl anion decrease in the presence of another electron scavenger (X) in the system. The relative electron attachment cross-section can be obtained from the following relation:[10)]

$$\frac{1}{G(C_{12}H_{10}^-)} = \frac{1}{G(C_{12}H_{10}^-)_0} + \frac{\sigma_X[X]}{G(C_{12}H_{10}^-)_0\sigma_{C_{12}H_{10}}[C_{12}H_{10}]}$$

where $G(C_{12}H_{10}^-)_0$ is the yield of the biphenyl anion in the absence of the second solute (X) and where $\sigma$ is the electron attachment cross-section. When the concentration of biphenyl is taken to be constant, $1/G(C_{12}H_{10}^-)$ is linearly related to the concentration of the second solute (Fig. 1). From the slopes and intercept of straight lines in Fig. 1 the relative electron-attachment cross-sections of $SF_6$, $N_2O$ and $CO_2$ in MTHF glass are obtained; they are listed in Table 1. The electron attachment

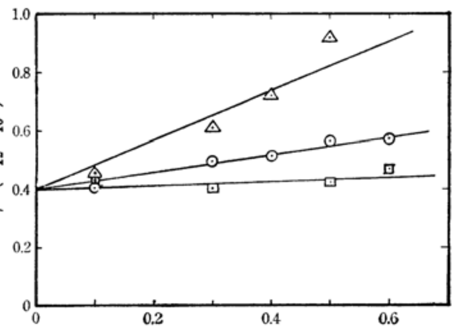


Fig. 1. $1/G(C_{12}H_{10}^-)$ *vs.* M% second solutes (X) in $\gamma$-irradiated MTHF solutions containing 0.2 M% biphenyl at 77°K.
△, $SF_6$; ⊙, $N_2O$; ⊡, $CO_2$

TABLE 1. RELATIVE ELECTRON-ATTACHMENT CORSS-SECTIONS OF $SF_6$, $N_2O$, AND $CO_2$

| | Solid | Gas[9)] | Liquid[3)] |
|---|---|---|---|
| $SF_6$ | 2.3 | 10 | 1.0 |
| $N_2O$ | 1.0 | 1.0 | 1.0 |
| $CO_2$ | 0.3 | 0 | 1.0 |

cross-sections of $SF_6$, $N_2O$ and $CO_2$ differ in the solid phase, while they are the same in the liquid phase. It has previously been proposed that the electron in the liquid phase is solvated and that its reactions with electron scavengers are diffusion-controlled.[1-3)] The electron-attachment cross-sections of $SF_6$, $N_2O$ and $CO_2$ in the solid phase are in the same order as those in the gas pahse. This implies that electrons are quasi-free electrons*[1] in the solid phase, as has been suggested in previous studies.[4,8)]

The reactions of nitrous oxide with biphenyl anions and with electrons in MTHF glass have been investigated by both the spectrophotometric measurement of biphenyl anions and the analysis of nitrogen. The absorption spectra of the biphenyl anion were measured after $\gamma$-irradiation to a dose of $8.49\times10^3$ rad, and nitrogen was measured at room temperature on the samples $\gamma$-irradiated at 7°K (dose: $3.91\times10^5$ rad) by a gas burette connected to a Toepler pump and a cupric oxide furnace kept at 240°C. The yield of biphenyl anions increases linearly with the dose, $8.49\times10^3$ to $3.91\times10^5$ rad. The effect of nitrous oxide on the yields of biphenyl anions and nitrogen is shown in Fig. 2. The yield of nitrogen increases rapidly

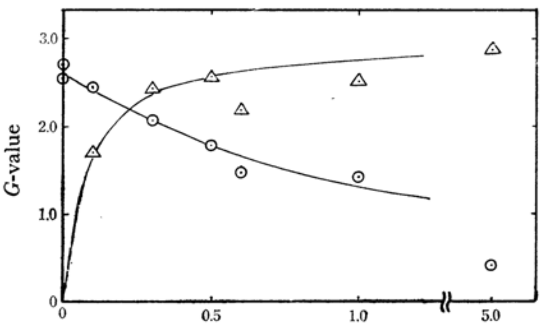


Fig. 2. Effect of nitrous oxide on the yields of biphenyl anion and nitrogen.
Concentration of biphenyl: 0.2 mol%
⊙—⊙, biphenyl anion
△—△, nitrogen

with an increase in the nitrous oxide and becomes constant at concentrations of nitrous oxide higher than 0.5 mol%, while the yield of biphenyl anions gradually decreases with an increase in the nitrous oxide. Though the decrease in biphenyl anions represents the amount of electrons captured by nitrous oxide, it does not correspond to the yield of nitrogen. The yield of nitrogen at high concentrations of nitrous oxide is about 2.6 (G unit), which is approximately equal to the yield of biphenyl anions in the absence of nitrous oxide. These results may be explained by the following scheme:

$$\text{MTHF} \rightsquigarrow \text{MTHF}^+ + e^- \quad (2)$$

$$e^- + C_{12}H_{10} \longrightarrow C_{12}H_{10}^- \quad (3)$$

$$e^- + N_2O \longrightarrow N_2 + O^- \quad (1)$$

$$C_{12}H_{10}^- + N_2O \longrightarrow N_2 + O^- + C_{12}H_{10} \quad (4)$$

Reaction (4) probably occurs while the sample is

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

being warmed to room temperature. Reaction (4) requires that the electron affinity of nitrous oxide is greater than that of biphenyl, 0.41 eV. It may be concluded that nitrous oxide reacts with an electron to form one nitrogen molecule in MTHF glass