The Trapping Efficiency for Electrons in Polar Glasses at 77°K

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The trapped electron yields in alcohols and methanol-water mixtures at 77°K as a function of the electron scavenger concentration have been measured. The reciprocal of the trapped electron yield increased linearly with the concentrations of phenol, acetone, and acrylamide. The relative trapping efficiency for electrons was found to increase with an increase in the dielectric constant of the matrix at room temperature. The relative travelling distance of electrons in these matrices was also estimated.

Extensive studies have been made of the formation of the trapped electrons in irradiated glasses of polar or non-polar substances.[1] The presence of electron scavengers,[1d,2,3] such as acrylamide, nitrate ions, nitrite ions, monochloroacetate, and acetone, decreases the yield of the trapped electrons, and these scavenging experiments showed that the mobile electron was the precursor of the trapped electron. Electrons produced by γ-irradiation or photoionization are trapped efficiently in polar glassy states at 77°K, and the absorption spectra of the trapped electrons are characterized by a very broad band in the visible or near-infrared spectral region.

Ekstrom and Willard[4] measured the optical absorption and ESR spectrum of the trapped electrons in γ-irradiated organic glasses covering a range in polarity, from 3-methylpentane to glycerol. They showed that the absorption maximum was shifted towards shorter wavelengths with an increase in the polarity of the matrix molecules, and the ESR line width increased. These results were explained by using a model in which the electrons are trapped in pre-existing cavities in the matrix.

Recent experiments, such as the pulse radiolysis of polar glasses at 77°K[5] and studies of water-ethylene glycol glass irradiated at 4°K,[6] have suggested that the mobile electrons were trapped in deeper traps at 77°K than at 4°K, indicating an orientational relaxation of the molecules at 77°K, and that the electrons trapped in the deeper traps had an absorption similar to that of the trapped electron irradiated with ^{60}Co γ-rays at 77°K. If the polarity of the solvent correlates with the formation processes of the trapped electrons, one can expect that the travelling distance of electrons prior to trapping in other words, the trapping efficiency of the matrix molecules for the mobile electrons, will depend on the polarity. The present investigation will show that the trapping efficiency depends on the polarity of the matrix molecules. The experiments were performed using glasses of alcohols and methanol-water mixtures containing phenol, acetone, or acrylamide at 77°K.

Experimental

The alcohols (isopropanol, ethanol, and methanol) were purified by distilling them twice after they had been refluxed for 24 hr with 2,4-dinitrophenyl hydrazine-sulfuric acid. The water was triply distilled. The solutions were purged with bubbling nitrogen prior to ^{60}Co γ-ray irradiation at 77°K. Methanol (5 mol% H_2O) and ethanol (5 mol% H_2O) formed clear glasses, and the other solutions were glassy with a few small cracks. Pyrex cells ($\sim$2 mm thick) were mainly used for the irradiation and for the optical measurements of trapped electrons. Metal cells ($\sim$3 mm thick) with high-purity silica windows were used for the measurement of the optical absorption below 400 nm in phenol solutions. The absorption spectra were measured at 77°K with a Cary Model 14R spectrophotometer. The optical densities of the trapped electrons (OD(e_t^-)) in various matrices were obtained by subtracting the OD after bleaching by light transmitting at $\lambda > 540$ nm (using a Toshiba V-054 glass filter) from the OD after γ-irradiation. Since the Pyrex cell absorbs from the visible to the UV region after γ-irradiation at 77°K, and since the intensity decreases upon optical bleaching, a correction was made for the OD (e_t^-). Irradiation was carried out at 77°K using a 5K Ci ^{60}Co source at a dose rate of 4×10^{19} eV/g hr, as determined by ferrous sulfate dosimetry.

Results and Discussion

The absorption spectra of the trapped electrons were observed in alcohols and methanol-water mixtures.[9] The results are summarized in Table 1. The presence of an electron scavenger decreases the trapped electron yield, but the position of the absorption maximum is not affected. Figure 1 shows the trapped electron yield *vs.* the irradiation dose at

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2) W. A. Seddon and R. D. Smith, *Can. J. Chem.*, **45**, 3083 (1967).

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4) A. Ekstrom and J. E. Willard, *J. Phys. Chem.*, **72**, 4599 (1968).

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6) T. Higashimura, M. Noda, T. Warashina, and H. Yoshida, *ibid.*, **53**, 1152 (1970).

7) T. Sawai and W. H. Hamill, *J. Phys. Chem.*, **73**, 2570. (1969)

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9) The composition of the methanol-water mixture is given in a mole percentage.

Table 1. Absorption maximum of trapped electrons in glassy alcohols and methanol-water mixtures at 77°K

Matrix	λ_{max} nm
isopropanol	640 (613)
ethanol	530 (530)
methanol	520 (514)
75%methanol-25%water	530 (526)[a]
40%methanol-60%water	555 (550)[b]

( ): λ_{max} measured by G. Ershov and A. K. Pikaev, ref. (1e),
a: 70%methanol-30%water, b: 50%methanol-50%water

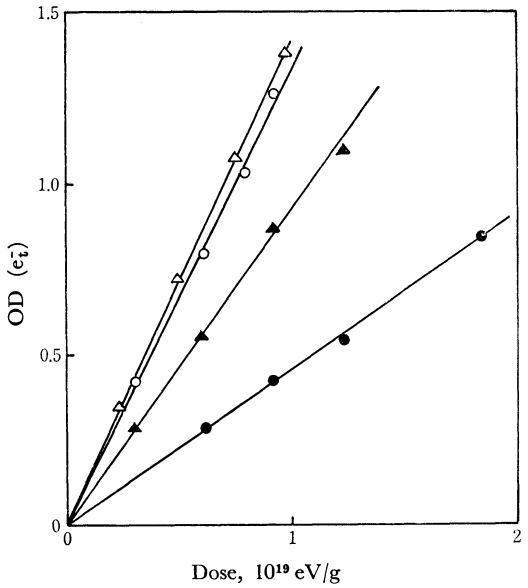

Fig. 1. Trapped electron yield as a function of dose in ethanol and methanol-water at 77°K.
○: ethanol, △: 40% methanol-60% water
●: 1.2 mol% phenol in ethanol
▲: 1.0 mol% phenol in 40% methanol-60% water

77°K obtained from 1.2 mol% phenol in ethanol and 1.0 mol% phenol in a 40% methanol - 60% H_2O mixture, and from the same solutions without any solute. The trapped electron yield is linear in dose in all the systems; the yields from systems without a solute seem to be almost the same, but the effect of phenol on the yield is quite different in different mixtures. This seems to be the effect of the electron-trapping efficiency of the matrices, which is correlated with the polarity. In the presence of phenol, the absorption maximum which is attributed to the C_6H_6OH radical appears at 345 nm in addition to the trapped electron band. It has been shown that phenol scavenges an electron to form the C_6H_6OH radical.[7] The radical yield increases with an increase in the concentration of phenol, and the radiation dose, $OD(C_6H_6OH)$ is larger in methanol than in the 40% methanol - 60% H_2O mixture at the same phenol concentration. The spectra of irradiated phenol in methanol and in 40% methanol - 60% H_2O at 77°K are shown in Fig. 2. Figure 2 suggests that the trapping efficiency by the matrix for the mobile electron is much smaller in methanol than in

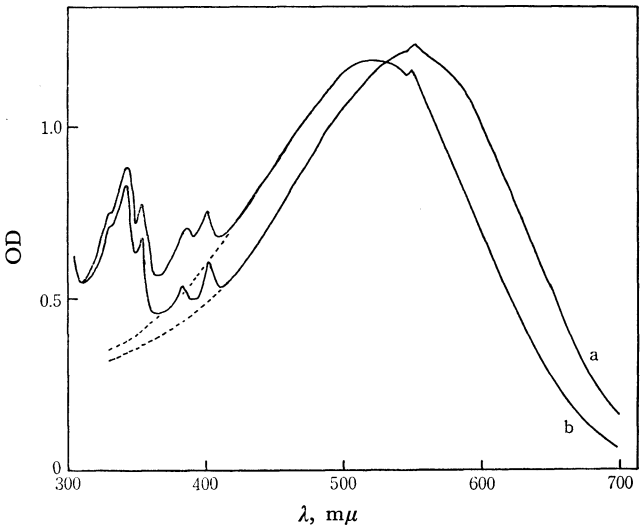

Fig. 2. Spectrum of irradiated phenol in methanol and in 40% methanol-60% water at 77°K.
a : 1.6 mol% phenol in 40% methanol-60% water
b : 0.8 mol% phenol in methanol
Dose: 1×10^{19} eV/g

the methanol-water mixture, since the $OD(C_6H_6OH)$ and $OD(e_t^-)$ in methanol are almost equal to those in the latter matrix, even though the phenol concentration is quite different. The trapping efficiency seems to correlate with the dielectric constant of the matrices; that is, the matrix with higher dielectric constant has the higher trapping efficiency.

It has been considered that the trapped electrons are produced by the reaction of mobile electrons with trapping sites in the solid state, and that the depth of the trapping sites is correlated with the dielectric constant of the matrix. The mechanisms for electron trapping are not very clear, but mobile electrons (e_m^-) may either recombine with positive holes to form excited molecules or react with traps (T) or scavengers (S) as is described in the following scheme:

$$M \rightsquigarrow M^+ + e_m^- \quad (1)$$

$$e_m^- + M^+ \rightarrow M^* \quad (2)$$

$$e_m^- + T \rightarrow e_t^- \quad (3)$$

$$e_m^- + S \rightarrow S^- \quad (4)$$

The linearity of the e_t^- yield with the dose, however, shows that reaction (2) can be neglected. From these simple competition reactions, it follows that:

$$G(e_t^-) = G_0(e_t^-)k_3[T]/(k_3[T]+k_4[S]) \quad (I)$$

where $G(e_t^-)$ and $G_0(e_t^-)$ are the trapped electron yields with and without a solute respectively. Since $G(e_t^-)$ can be replaced by the optical density:

$$1/OD(e_t^-) = 1/OD_0(e_t^-)(1+k_4[S]/k_3[T]) \quad (II)$$

The plot of $1/OD(e_t^-)$ *vs.* [S] at a constant dose should be linear for each matrix. $1/OD(e_t^-)$ plotted as a function of the concentrations of phenol, acetone, and acrylamide in isopropanol, ethanol, methanol, and methanol-water mixtures at 77°K is shown in Figs. 3, 4, and 5. $1/OD(e_t^-)$ is a linear function of

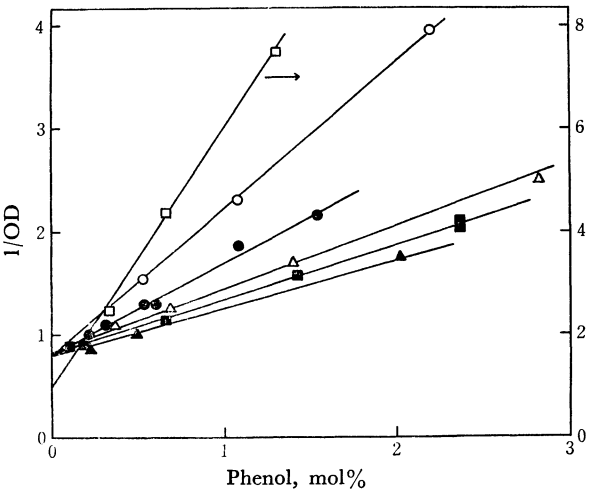

Fig. 3. Trapped electron yield as a function of phenol concentration in various matrices.
□: isopropanol, ○: ethanol, ●: methanol
△: 75% methanol-25% water, ■: 60% methanol-40% water, ▲: 40% methanol-60% water

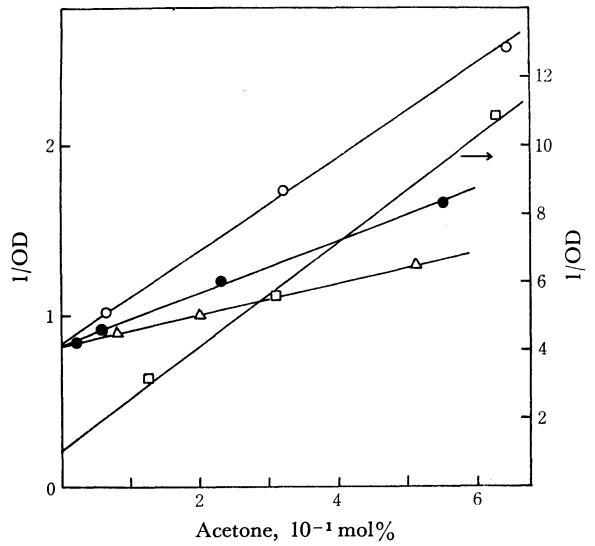

Fig. 4. Trapped electron yield as a function of acetone concentration.
□: isopropanol, ○: ethanol, ●: methanol
△: 75% methanol-25% water

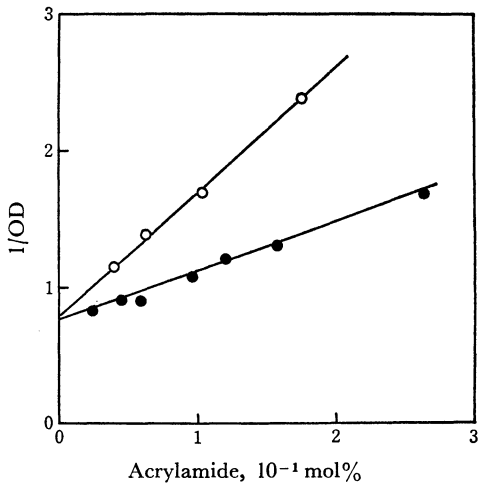

Fig. 5. Trapped electron yield as a function of acrylamide concentration.
○: ethanol, ●: methanol

the solute concentration in all cases. The fact that $1/OD(e_t^-)$ in Fig. 3 is linear with the concentration of phenol to 2 mol% suggests that the trapping sites for e_m^- are unlikely to be destroyed even at a relatively high concentrations of the solute. From the slopes Figs. 3, 4, and 5, the relative trapping efficiencies

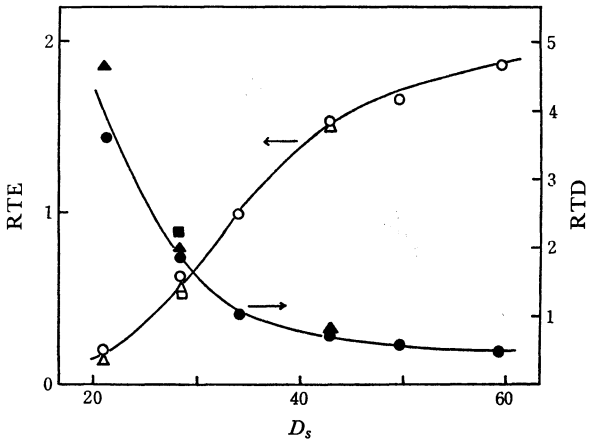

Fig. 6. Relative trapping efficiency (RTE) and relative travelling distance (RTD) for electrons in various matrices at 77°K as a function of dielectric constant of the matrix.
○●: phenol, △▲: acetone, □■: acrylamide

Table 2. Relative trapping efficincy for mobile electron and solute concentration required to reduce OD to 1/2 OD_0 in alcohols and methanol-water mixtures

		isopropanol	ethanol	methanol	75%methanol 25%water	60%methanol 40%water	40%methanol 60%water
Phenol	RTE	0.20	0.63	1.0	1.6	1.7	1.9
	[S]	0.22	0.54	0.86	1.26	1.44	1.66
Acetone	RTE	0.12	0.56	1.0	1.6		
	[S]	0.080	0.29	0.53	0.82		
Acryl amide	RTE		0.47	1.0			
	[S]		0.090	0.22			
Dielectric constant*		21	26.8	34.2	43.2	50.0	58.8

*: Dielectric constant at room temperature RTE: Relative trapping efficiency
S: Solute concentration required to reduce OD to 1/2 OD_0, mol%.

$(K_3[T]/k_4)$ in different matrices can be obtained. These results, which are normalized to the methanol matrix, are summarized in Table 2. The relative values of k_3 [T] as a function of the static dielectric constant (D_s) of the matrix at room temperature are plotted in Fig. 6. The trapping efficiency increases with the increase in D_s in the matrices. The intercepts in Figs. 3, 4, and 5 give $1/G_0(e_t^-)\varepsilon$, since OD is related to $G\varepsilon$; these figures show that the $G_0(e_t^-)\varepsilon$ values are almost the same in alcohols and in methanol-water mixtures except for the case of isopropanol.

The relative trapping efficiencies in various matrices should correlate with the travelling distance for mobile electrons prior to trapping. Dyne and Miller[8] and Seddon and Smith[2] have calculated the travelling distance on the bases of experiments with biphenyl in organic glass and acrylamide in alkaline glass respectively. Adopting the mathematical procedure described by Dyne and Miller[8] the root mean-square distance which electrons move prior to trapping, $(\bar{r}^2)^{1/2}$, can be estimated from the concentration of the solutes required to reduce the electron yield to one half its initial value. These concentrations ([S]) in various matrices are listed in Table 2. The relative travelling distances for mobile electrons in alcohols and methanol-water mixtures at 77°K are plotted in Fig. 6. In contrast with the relative trapping efficiency, the distance decreases with the increase in the dielectric constant at room temperature. However, further investigation seems to be necessary, especially concerning the temperature dependence of D_s and various phenomena occuring in the glassy state irradiated at 77°K, in order to correlate these facts with the phenomena in various matrices at 77°K.

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