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THE POLARITY EFFECTS ON THE YIELD OF THE TRAPPED ELECTRON PRODUCED IN GLASSY ALCOHOLS

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The yields of the trapped electron produced in alkyl alcohol and ethylene glycol at 77 °K glasses were determined. For all alcohol glasses, the yields declined in the high dose irradiation of gamma rays. It has been shown that the maximum concentration of the trapped electron increases with dielectric constant of the alcohol.

The effects of the polarity of the medium on the yields of the ionic species have been the subject of several studies[1-4], and it has been shown that the G value for the solvated electron produced in alkyl alcohols and organic amines at room temperature increases with dielectric constant of the medium[2,3]. Recently, for some glassy alcohols at 77°K, the G values for the trapped electron were determined by Teplý et al[5]. Although their results were somewhat conflicting in the case of n-pentanol and n-hexanol glasses, the same trend as in the case of the liquid phase was also observed.

In the present work, the trapped electron yield at 77°K was determined for several glassy alcohols up to a dose of 15 x 10^{20} eV/g, and it was shown that not only the G value but also the maximum concentration increases with the polarity of the alcohol. In the high dose irradiation, the decrease in the trapped electron yield was observed for all glassy alcohols, and was attributed to a participation of the trapped electron in a hole scavenging reaction.

Experimental

The alcohols were distilled from 2,4-dinitrophenylhydrazine sulfuric acid solution to eliminate the ketonic impurities. Further, the fractional distillation was carried out and only the middle fraction was supplied to the sample preparation.

The samples were prepared by the same procedures as reported before[6]. All the alcohols, except for methanol, were made into glassy states by rapid freezing to 77°K, while the latter remained nearly polycrystalline. Gamma irradiations were carried out with a Co-60 source at a dose rate of 0.14 x 10^{20} eV $g^{-1}hr^{-1}$.

The ESR measurements were made in the absence of power saturation as previously described[6]. After the photobleaching of the irradiated samples with a light of wavelengths longer than 390 nm, the central parts of the ESR spectra decreased and the increases in the alcohol radicals were observed. The relative yields of the trapped electron were measured from the changes in the signal intensity of the central parts of the normalized spectra. Absolute yields were determined from the comparison with a signal intensity of calibrated amount of DPPH radical in THF glass.

Results and Discussion

In the low dose irradiation, all the samples developed deep blue and the color easily decayed by the photobleaching. On the other hand, the high dose irradiation brought about decline of the color, and especially the n-pentanol glass became transparent after the gamma irradiation over 15×10^{20} eV/g. The ESR spectra of the irradiated samples before and after the photobleaching were essentially similar to those of the previous work by Kroh et al.[7], and the signal intensity of the alcohol radical was increased by the photobleaching.

For all of the alcohol glasses, the dose-yield curves are analogous to those obtained for ethylene glycol-water glass[6] and ethanol glass[8]. Figure 1 shows a typical pattern of dose dependencies for the yields of the trapped electron, trapped hydrogen atom and the $CH_3CH_2\dot{C}HOH$ radical which were produced in n-pentanol glass at 77°K. While the yields of the latter two continue to increase over the entire dose range, the trapped electron yield saturates at ca. 4×10^{20} eV/g, and it decreases with the absorbed dose above 5×10^{20} eV/g. The decrease in the trapped electron yield has been also observed for 10M NaOH glass irradiated above 5×10^{20} eV/g at 77°K[9]. Based on the observation that both the ESR line and the optical density due to the trapped electron in the specimen, which had been irradiated up to 9×10^{20} eV/g, were increased by the elevation of temperature from

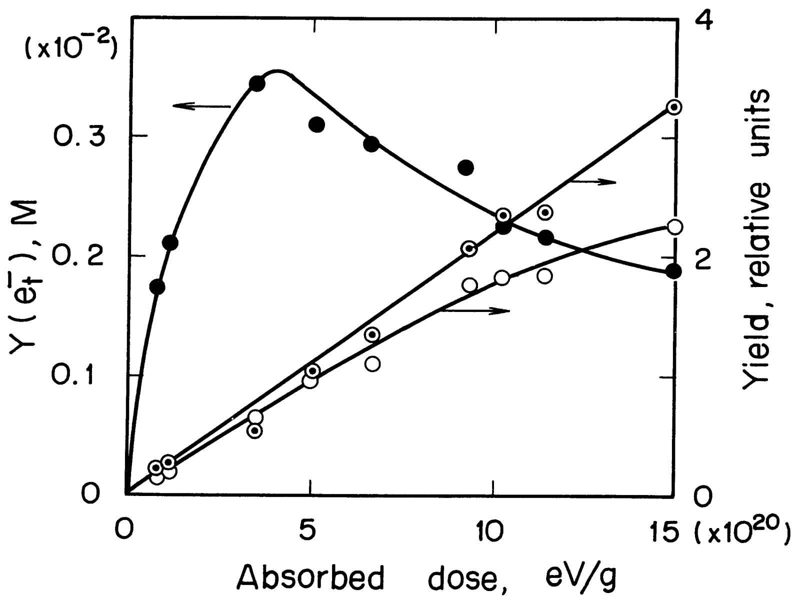

Fig.1 Dose dependencies for the yields of trapped electron, trapped hydrogen atom and $CH_3CH_2\dot{C}HOH$ radical produced in n-propanol glasses at 77°K.
●: trapped electron, ⊙: trapped hydrogen atom
○: $CH_3CH_2\dot{C}HOH$ radical

TABLE 1. THE G VALUES AND THE MAXIMUM CONCENTRATIONS OF THE TRAPPED ELECTRON IN VARIOUS GLASSY ALCOHOLS AT 77°K.

Alcohol	G value	C_M, M	Absorbed dose, eV/g
Methanol*	2.3	1.2×10^{-2}	6.0×10^{20}
Ethanol	2.3	0.73	6.8
n-Propanol	1.5	0.36	4.0
i-Propanol	1.1	0.52	4.8
n-Butanol	0.68	0.32	2.9
i-Butanol	0.58	0.22	3.0
n-Pentanol	0.60	0.22	3.1
Ethylene glycol	1.8	1.4	6.5

* : The samples were nearly polycrystalline.

77°K to 120°K, Kevan et al. attributed the decrease in the higher dose region to a formation of dielectron center. However, this was not the case in the glassy alcohols. The dielectron center would be produced only in the most polar media such as the concentrated alkaline glasses. In the case of alcohol glasses, a plausible explanation for the decrease in the higher dose region may be due to a participation of the trapped electron in a hole scavenging reaction. The positive species and $RCH_2\dot{O}$ radical which are stabilized in the matrix at 77°K can scavenge a mobile electron:

$$RCH_2OH \rightsquigarrow RCH_2OH^+ + e_m^-$$
$$\rightsquigarrow R\dot{C}HOH + H$$
$$RCH_2OH^+ + RCH_2OH \longrightarrow RCH_2OH_2^+ + R\dot{C}HOH \text{ (or } RCH_2\dot{O})$$
$$RCH_2OH_2^+ + e_m^- \longrightarrow R\dot{C}HOH + H_2$$

and

$$RCH_2\dot{O} + e_m^- \longrightarrow RCH_2O^-$$

On the other hand, the trapped electron may act as a hole scavenger as follows:

$$e_t^- + RCH_2OH^+\text{(hole)} \longrightarrow RCH_2OH$$

The last process would lead the decreases in the yields of the trapped electron and alcohol radical. These reaction schemes are supported by the observation that the dose-yield curve of the propanol radical became convex at the dose where the trapped electron yield declined, as seen in Fig.1.

The G value and the maximum concentrations of the trapped electron, C_M, for the various glassy alcohols are summarized in Table 1. In the case of alkyl alcohols, they diminish with the increase in the carbon chain of the alcohol. The findings agree with a trend of the solvated electron yield observed for alcohol solution at room temperature[2)], though the G values for the trapped electron are about twice of those for the solvated electron. In Fig.2, the value of C_M is plotted against dielectric constant, D_s, at 25°C. Although dielectric constant of glass phase is different from that of liquid phase, the sequence of the

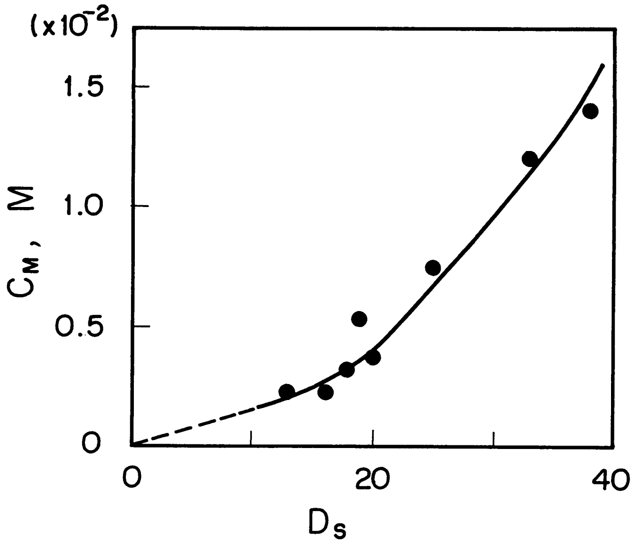

Fig.2 The relationship between C_M and D_s

magnitude is the same in both phases. Therefore, the present results indicate that the density of trapping site for the electron decreases with the polarity of the medium. As seen in the figure, the curve extrapolates to the origin. This is consistent with the fact that the trapped electron yields in the non-polar media are very low. Because Coulomb interaction is long range in the medium of low dielectric constant, the electron which is able to escape from geminate recombination may be captured by a positive species. This would lead to a lower yield of the trapped electron.

More detail on the observations and the interpretations for the dose dependencies of the trapped electron yields will be reported later.

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