Behavior of Positive Hole in a γ-Irradiated 3-Methylpentane Glass at 77°K

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In order to elucidate the behavior of a positive hole in irradiated alkane glasses, the effect of solutes having ionization potential lower than that of a glass matrix molecule upon the decay of a trapped electron was examined in a 3-methylpentane glass at 77°K by means of electron spin resonance. The decay was found to be explained in terms of the superposition of two exponentially decaying processes, as in the absence of a solute. Although the fast process was not affected by a solute, the slow process was further slowed by the addition of a solute. The effect of a solute is described by the empirical relation, $k/k_0=1/(1+fN)$, where k and k_0 are the rate constants of the slow decay in the presence and in the absence of a solute, respectively. N is the mole fraction of a solute. The observed values of the slowing-down efficiency, f, increase in parallel with the decreasing values of ionization potential of solutes: 2-methyltetrahydrofuran, diethylether, methylvinylether, 2-methylpentene-1 and *n*-butylvinylether. The results are interpreted in terms of trapping of a positive hole by a solute molecule and positive hole tunneling from a hole trap to a trapped electron.

Several investigations have been reported on the trapping process of an electron and its reactions in saturated hydrocarbon glasses irradiated by ionizing radiations at 77°K.[1] Little consideration, however, has been given to the behavior of a positive hole in the glasses. Louwrier and Hamill reported the absorption spectra attributable to the positive hole trapped by higher alkane solutes, a radical cation of higher alkanes, in a 3-methylpentane glass at 77°K, the behavior of which suggested that the charge recombination process involved hole migration by fast resonant charge transfer in a neat glass and by slow electron tunneling in a doped glass.[2,3] The hole migration was elucidated also by an electron spin resonance (ESR) study of the radical cation of tetramethylethylene in a 3-methylpentane glass by Ichikawa and Ludwig.[4]

The present authors studied the behavior of a trapped electron in an irradiated 3-methylpentane glass at 77°K and found that its decay was expressed by the superposition of fast and slow exponential decays.[5] The slow decay was found to be dependent on the 2-methylpentene-1 added to the glass, which suggests that it is due to the migration of positive charge. On the other hand, the fast decay was thought to be due to the migration of an electron. Recently, they have observed the ESR spectra attributable to a trapped positive hole in irradiated 3-methylpentane and 3-methylhexane glasses at 77°K.[6] The spectra were replaced by that of a solute cation when vinylethers were added to the glasses.[7] These facts also imply that migration and trapping of the positive hole are involved in ionic processes in an irradiated 3-methylpentane glass.

In the present investigation, the effect of several solutes on the slow decay of a trapped electron in a 3-methylpentane glass is studied in order to elucidate the behavior of a positive hole in detail. The results obtained confirm the previous interpretation that the slow decay of a trapped electron is caused by the migration of the positive hole in the glass.

Experimental

3-Methylpentane, 2-methylpentene-1, and *n*-butylvinylether were purified by the same treatment as described previously.[7] Ethylether and 2-methyltetrahydrofuran were fractionally distilled three times over sodium and distilled *in vacuo* into a sodium-potassium mirrored vessel repeatedly until the mirror was no longer damaged. Methylvinylether was passed through a column of potassium hydroxide, dried with calcium hydride and distilled into a sodium-potassium mirrored vessel five times *in vacuo*.

The samples were distilled into ESR sample tubes of pure quartz and sealed under the pressure less than 10^{-4} mmHg. The amount of a solute was estimated from the volume and gas pressure.

Irradiation was carried out at 77°K in the dark to a dose of 5.2×10^{18} eV/g. ESR measurements were carried out with the aid of a conventional X-band spectrometer with 100 kHz magnetic field modulation and at the low microwave power of 0.3 milliwatts, at 77°K in the dark.

Ionization potentials were measured by means of a conventional mass spectrometer, by determining the threshold of appearance potentials with a linear extraporation method.

Results

The ESR signal of a neat 3-methylpentane glass irradiated at 77°K is composed of three spectra: a sextet spectrum due to a 3-methylpentyl radical, a broad unresolved spectrum due to a trapped positive hole (the cation radical of 3-methylpentane) and a sharp singlet spectrum due to a trapped electron, as reported previously.[5,6] The trapped electron decays rapidly at 77°K in the dark. The decay includes two exponentially decaying processes; the rate constants are 0.2 and 0.04 min^{-1} for the fast decay and the slow

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[1] See for example, W. H. Hamill, "Radical Ions," ed. Keiser and Kevan, Intersci. Publ., New York, (1968), p. 321; J. E. Willard, "Fundamental Processes in Radiation Chemistry," ed. Ausloos, Intersci. Publ., New York, (1968), p. 599.

[2] P. W. F. Louwrier and W. H. Hamill, *J. Phys. Chem.* **72**, 3878 (1968).

[3] P. W. F. Louwrier and W. H. Hamill, *ibid.*, **74**, 1418 (1970).

[4] T. Ichikawa and P. K. Ludwig, *J. Amer. Chem. Soc.* **91**, 1023 (1969).

[5] M. Irie, K. Hayashi, S. Okamura. and H. Yoshida, *J. Chem. Phys.* **48**, 922 (1968).

[6] H. Yoshida, T. Shiga, and M. Irie, *ibid.*, **52**, 4906 (1970).

[7] M. Irie, K. Hayashi, S. Okamura, and H. Yoshida, *Intern. J. Radiat. Phys. Chem.* **1**, 297 (1969).

[8] K. Watanabe, T. Nakamura, and J. Mottl, *J. Quant. Spectrosc.* **2**, 369 (1962).

one, respectively.[5]

Even if a small amount of a hole scavenger is added, the decay of the trapped electron is still caused by the two processes, as shown in Fig. 2 of Ref. 5. However, the rate constant of the slow decay decreases with the increasing concentration of the added solute. Fig. 1 shows the effect of an added solute, representatively of *n*-butylvinylether. The yield of a slowly decaying electron increases very slightly with the addition of a solute. These facts imply that a small amount of a solute (less than 10^{-1} mol%) provides few additional physical trapping sites for an electron but interrupts the charge neutralization process. It should be noted that the fast decay of a trapped electron is not affected by the addition of a small amount of a solute.

As to the dependence of the rate constant of the slow decay of a trapped electron upon the concentration of a solute, representative results are shown in Fig. 2. Changes in the rate constant follow the empirical relation,

$$k/k_0 = 1/(1+fN) \qquad (1)$$

where k_0 and k are the rate constants in the absence and in the presence of a solute, respectively. N and f are the mole fraction of a solute and the slowing-down efficiency proper to each solute, respectively.

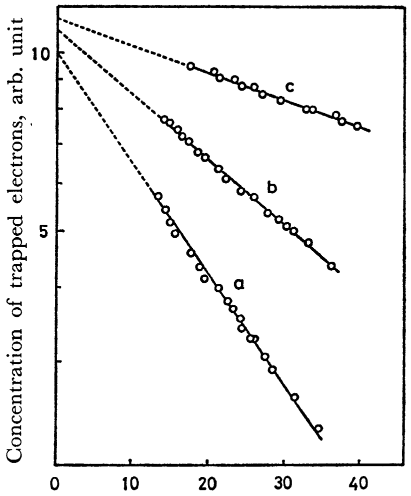

Fig. 1. Decay of trapped electrons in 3-methylpentane glass at 77°K in the presence and in the absence of *n*-butylvinylether. Radiation dose: 5.2×10^{18} eV/g. Concentration of *n*-butylvinylether: (a) 0, (b) 6.6×10^{-3} mol% and (c) 3.2×10^{-2} mol%.

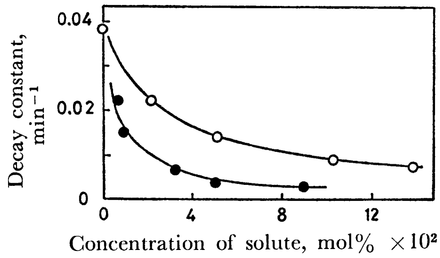

Fig. 2. Relation between the first order rate constant of the slow decay of trapped electrons at 77°K in 3-methylpentane glass irradiated to a dose of 5.2×10^{18} eV/g and the concentration of added solutes, (○) methylvinylether and (●) *n*-butylvinylether. Curves are derived from the relation (1). See text.

The slowing-down efficiency of several solutes thus determined and their values of ionization potential are listed in Table 1. All the solutes have ionization potential lower than that of 3-methylpentane. The slowing down efficiency increases with the increasing difference of ionization potential between a solvent molecule and a solute. This is illustrated in Fig. 3.

TABLE 1. RELATION BETWEEN THE SLOWING-DOWN EFFICIENCY AND THE IONIZATION POTENTIAL OF SOLUTES ADDED TO THE IRRADIATED 3-METHYLPENTANE GLASS

Solute	Slowing-down efficiency f	Ionization potential (eV)	
		This work	Reported value[a)]
n-Butylvinylether	1.4×10^4	8.44	——
2-Methylpentene-1	5.4×10^3	8.94	——
Methylvinylether	3.4×10^3	9.14	8.93
Diethylether	3.2×10^3	9.43	9.53
2-Methyltetrahydrofuran	2.7×10^3	——	9.54[b)]
3-Methylpentane	——	10.20	10.08

a) See Ref. 8. b) Ionization potential of tetrahydrofuran.

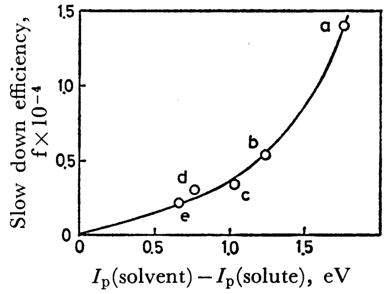

Fig. 3. Relation between the slowing-down efficiency and the difference of ionization potential between the glass matrix molecule and the added solutes, (a) *n*-butylvinylether, (b) 2-methylpentene-1, (c) methylvinylether, (d) diethylether, and (e) 2-methyltetrahydrofuran.

The ionization potential has not yet been reported for some of the solutes. Therefore, it was determined by the conventional mass spectrometric method, being shown in the third column of Table 1. Although the method seems unfortunately not to give the absolute values of significance, the difference between them may be enough significant to be related with the slowing-down efficiency. The ionization potential previously reported for some solutes is cited in the fourth column for comparison.

Discussion

The solutes examined have ionization potential lower than that of 3-methylpentane and negative electron affinity. Therefore, they are able to stabilize the positive hole in the glass forming a radical cation, whereas they do not capture electrons chemically. The results shown in Fig. 3 provide the evidence that the slow decay of a trapped electron is caused by the migration of a positive hole to the immobile deeply trapped electron. If the decay resulted from the migration of an electron itself, the slowing-down efficiency might depend on the nature of a solute molecule such as dipole moment (dielectric constant) and electron affinity, rather than on ionization potential. However, this is not the case. For example, the slowing-down efficiency of 2-methylpentene-1 is found to be larger than that of methylvinylether, though the dipole moment of the former is evidently smaller than that of the latter.

The above argument leads also to the conclusion that the fast decay of a trapped electron is thought to be caused independently of a solute by the migration of an electron, as suggested previously.[5] This necessarily requires electron population in two kinds of traps, a shallow trap and a deep trap. The shallow trap is intrinsic to non-polar hydrocarbon glasses formed by preferably oriented C–H bond dipoles,[9] while the deep trap involves a solute molecule or an impurity molecule which can not be removed by the purification of 3-methylpentane.

What is to be considered is why the positive hole trapped by the solute still moves, bringing about the slow decay of a trapped electron. In order to account for the slow dark decay of a trapped hole in a 3-methylpentane glass containing a higher alkane solute, Louwrier and Hamill postulated hole migration involving electron tunneling from a solute molecule to a solute radical cation.[2,3] In their case where the concentration of a solute was rather high ($\sim$1 mol %), the tunneling occurred more readily with the increasing concentration of a solute. In the present experiment for low concentration of a solute (less than 10^{-1} mol %), the slow decay of a trapped electron may be interpreted in terms of hole tunneling from a trapped positive hole to the trapped electron, rather than that between solute molecules.

A rough estimation of the rate of tunneling can be made by assuming a one-dimensional potential barrier as shown in Fig. 4, where the region A is the potential well formed by a solute molecule which traps a positive hole. In the region C, there is a trapped electron which the hole tunnels to and recombines with. If one takes the potential in this region as zero, U_0 and V_0 are approximated by the values of ionization potential of solute and glass matrix molecules, respectively. If one assumes that the trapped positive hole has the same energy eigenvalue as that in the potential well of infinite height and length of a, the flow of probability at the region C is expressed by the following relation,

$$\lambda = \frac{2(E-U_0)\sqrt{2mE}}{maV_0} \exp\left(-2\hbar^{-1}l\sqrt{2m(V_0-E)}\right) \qquad (2)$$

which is identical with the rate of charge neutralization.[10] The mass of a hole is taken to be the same as that of an electron, m. $E-U_0$ is the kinetic energy of a positive hole in the ground state, being estimated to be 0.1 eV. V_0-E can be approximated with the difference of ionization potential between glass matrix and solute molecules, $\sim$1 eV. The widths of a well, and of a barrier l, are taken to be 5×10^{-8} (molecular dimension) and 4×10^{-7} cm (charge separation distance), respectively. These numerical estimates lead to $\lambda\sim10^{-4}$ sec^{-1}, which is consistent with the observed rate constant of the slow decay of a trapped electron in the presence of a solute.

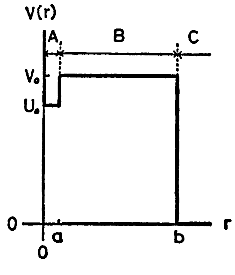

Fig. 4. A simplified one-dimensional trapping potential of positive hole. Region A is the potential well formed by a solute molecule which traps a positive hole. An electron is trapped in region C. V_0 and U_0 are ionization potential of solvent molecule and solute molecule, respectively.

The absolute value obtained above is somewhat arbitrary, because it is rather sensitive to the estimated values, especially those of V_0 and l. However, equation (2) accounts for the experimental results well at least qualitatively. If the ionization potential of a solute is lower and therefore V_0-E is larger, the trapped electron decays more slowly. Consequently, the slowing-down efficiency is expected to be larger. This agrees qualitatively to what was observed.

With the increasing concentration of a solute, the positive hole is more readily trapped, on the way back to the electron in a deep trap, by a solute molecule. This results in a trend that the average distance between a trapped positive hole and an electron (the average value of l in Eq. (2)) is lengthened by an increase of concentration, as far as the tunneling occurs between a solute molecule and a trapped electron. The above argument accounts for qualitatively the observed dependence of the rate constant of the slow decay of a trapped electron upon the concentration of a solute as shown in Fig. 2. The reason why the effect of a solute follows the empirical relation (1) still remains unknown, because of lack of knowledge on the distribution of distance l.

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[9] H. Yoshida and T. Higashimura, *Can. J. Chem*, **48**, 504 (1970).

[10] According to the potential shown in Fig. 4, the wave function in the region C is easily obtained by a usual treatment, as

$$\Psi_{\mathrm{C}} = \frac{k_1\cos k_1a-\kappa\sin k_1a}{\sqrt{2\pi a}\,(ik_3-\kappa)} \exp(-\kappa l)\ \exp\{ik_3(r-b)\},$$

where

$$k_1=\sqrt{\frac{2m}{\hbar^2}\ (E-U_0)},\ k_3=\sqrt{\frac{2m}{\hbar^2}E},\ i\kappa=\sqrt{\frac{2m}{\hbar^2}\ (E-V_0)},$$

and

$$l=b-a\,.$$

Using the approximation $k_1a=\pi$, the wave function is reduced to

$$\Psi_{\mathrm{C}} = \frac{k_1}{\sqrt{2\pi a}\,(\kappa-ik_3)} \exp(-\kappa l)\ \exp\{ik_3(r-b)\}\,.$$

Therefore, the flow of probability is obtained as Eq. (2). See for example, G. Araki, "Quantum Chemistry," Baifukan, Tokyo, (1961), p. 505.