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Isothermal Decay of Trapped Electron in Irradiated 2-Methyltetrahydrofuran Glass

Tsuneki ICHIKAWA, HIROSHI YOSHIDA, and Koichiro HAYASHI
Faculty of Engineering, Hokkaido Universtiy, Kita-ku, Sapporo
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The isothermal decay of the electron trapped in gamma-irradiated 2-methyltetrahydrofuran glass was studied by electron spin resonance measurements at 92—95 K. Shape of the decay curves was found to be independent not only of radiation dose but also of temperature if they were plotted on the time scale in unit of half-life at each temperature studied. Although the decay follows neither a first order nor a second order reaction, the activation energy is able to be determined uniquely to be 0.8 eV. These results indicate that the mobilization of trapped electron is caused by repeated sequences of detrap-retrap due to thermal distortion or destruction of traps and that the evolution of decay is determined by the initial distribution of the electron-cation separation. On the basis of Nernst-Einstein assumption, the normalized distribution of the separation distance is numerically obtained and found to be close to a Gaussian function, though the absolute value of distance is unable to be determined because of the lack of knowledge of diffusion coefficient for the migration of electron in the glass. The effect of partial photobleaching of the trapped electron on the isothermal decay for the rest of electron was also studied and found to be the same as that of partial thermal bleaching.

2-Methyltetrahydrofuran (MTHF) glass is one of the glassy matrices where the nature of radiation-formed trapped electron has been most extensively studied by a number of techniques such as electron spin resonance (ESR) and optical absorption measurements.[1-4] The radiation-formed intermediates observed in this glass are mostly trapped electron and free radical. The former is characterized by an ESR sharp single line spectrum and a broad optical absorption spectrum with the maximum at about 1200 nm. The latter shows a seven line ESR spectrum, which is interpretable as due to the free radical formed by the cleavage of a hydrogen atom attached to tertiary carbon atom of MTHF molecule[5] or alternatively due to radical cation formed by the intramolecular hydrogen transfer reaction in the primary cation.[6] Although further studies seem needed to distinguish between these two possible interpretations, the present authors suggested that the decay of the trapped electron (at least, a considerable part of it) is caused by the charge neutralization process between the electron and the radical

1) L. Kevan, "Actions Chimiques et Biologiques des Radiations, 15éme sèrie," ed. M. Haissinsky, Masson et Cie., Editeurs, Paris (1971), p. 81. Almost all papers published before 1969 are collected in this review paper.

2) (a) D. P. Lin and L. Kevan, *J. Chem. Phys.*, **55**, 2629 (1971); (b) D. P. Lin, P. Hamlet, and L. Kevan, *J. Phys. Chem.*, **75**, 1226 (1972); (c) D. P. Lin, and L. Kevan *ibid.*, **76**, 636 (1972); (d) T. Huang, I. Eisele, D. P. Lin, and L. Kevan, *J. Chem. Phys*,. **56**, 4702 (1972).

3) (a) K. F. Baverstock and P. J. Dyne, *Can. J. Chem.*, **48**, 2182 1970); (b) F. P. Sargent, *ibid.*, **48**, 3453 (1970); (c) C. Chachaty,, A. Forchioni, J. Désalos, and M. Aris, *Int. J. Radiat. Phys. Chem.* **2**, 69 (1970); (d) J. R. Moller, *J. Chem. Phys.*, **56**, 5173 (1972).

4) (a) H. Yoshida and T. Higashimura, *Can. J. Chem.*, **48**, 504 (1970). (b) T. Shiga, T. Warashina, H. Yoshida, and S. Okamura, *Ann. Repts. Res. Reactor Inst. Kyoto Univ.*, **3**, 19 (1970); (c) M. Irie, K. Hayashi, S. Okamura, and H. Yoshida, *J. Phys. Chem.*, **75**, 476 (1971); (d) H. Yoshida, M. Ogasawara, T. Warashina, and T. Higashimura, *J. Chem. Phys.*, **56**, 4234 (1972).

5) (a) F. S. Dainton and G. A. Salmon, *Proc. Roy. Soc. Ser. A*, 285, 319 (1965); (b) F. S. Dainton, G. A. Salmon, J. Tepley, and J. P. Keene, *Proc. Chem. Soc.*, London, **1964**, 265.

6) (a) D. R. Smith and J. J. Pieroni, *Can. J. Chem.*, **43**, 876 (1965); (b) D. R. Smith and J. J. Pieroni, *ibid.*, **43**, 2141 (1965).

cation, by measuring the recombination luminescence.[7]

The isothermal decay of the trapped electron in this glass was studied by optical absorption[5] and ESR measurements.[6] The decay is now known to be independent of radiation dose and to be a composite first order reaction, which suggests that electron is trapped in close proximity of its partner positive charge to recombine with. However, the decay at about 77K was too slow to determine the exact shape of the decay curve.[6] Recently, Ogasawara *et al.* studied the decay at temperatures higher than 95.6K.[8] They found also, that the decay was independent of the radiation dose. In this study it was difficult to observe the whole shape of decay curves because the decay was very rapid.

Photobleaching of the trapped electron and photo-induced conductivity were also studied by Baverstock and Dyne,[3a] and Huang *et al.*[2d] These investigations gave an insight into the nature of electron traps in the glass. The electron is released from its trap to the conduction level by the absorption of light and then migrate to cationic entities to recombine with. The low quantum efficiency for the photobleaching suggested that electron undergoes detrap-retrap sequences repeatedly until it disappears. However, the migration of electron has not been studied well when it is thermally mobilized.

Smith and Pieroni studied the paramagnetic relaxation of the trapped electron in this glass, and estimated the separation distance between paramagnetic species at 77K.[6a] This result gave an evidence of the non-uniform spatial distribution of the radiation-formed intermediates, though it was not known which is important between the distance between trapped electrons or the distance between trapped electron and other paramagnetic intermediates in determining the relaxation process studied. Kevan *et al.* presumed the relaxation depending upon the interdistance between the trapped electrons and estimated the radius of spur (probably assumed that a spur contains more than one electron) to be 63 Å.[2a] Recent study of electron-electron double resonance of the irradiated MTHF glass showed that the cross relaxation between the trapped electron and the entity giving the seven line ESR spectrum played an important role in the paramagnetic relaxation process in the glass.[9] This suggests that the trapped electron is closely correlated with the free radical (or the radical cation).

If one assumes that the composite first order decay of the trapped electron is dependent upon the time required for it to migrate to its partner cation, precise determination of the decay curve may give another approach to study the distribution of electron-cation separation. On the basis of differential equation of diffusion under the influence of Coulombic attraction between oppositely charged ions, Ludwig showed a mathematical way to correlate the evolution of decay with the distribution of separation distance of isolated ion pairs in liquids.[10] Hamill and his co-workers studied the recombination luminescence in viscous liquids after pulse irradiation and examined it in terms of the initial distribution of ion pair separations.[11] Such an approach seems essentially applicable to the thermal decay of the trapped electron in the glassy matrices.

With this respect, it will be worth determining the shape of the isothermal decay of trapped electron at the temperature where the decay is appropriately fast to be studied precisely and conveniently. In the present investigation, the MTHF glass was chosen, because the nature of trapped electron has been well elucidated and the trapped electron decays at temperatures controlled rather easily.

Experimental

MTHF was purified as described elsewhere.[7] It was dried with sodium-potassium alloy under vacuum and sealed in ESR sample tubes of pure quartz (inner diameter: 0.3 cm) also under vacuum. Irradiation was carried out with ^{60}Co gamma-rays at the dose rate of 7×10^{17} eV/g min at 77K in dark.

The irradiated sample was quickly transferred into a variable temperature Dewar insert attached to the ESR resonant cavity, of which temperature was adjusted beforehand by flowing cold nitrogen gas from liquid. The intensity of the trapped electron ESR spectra were repeatedly recorded at constant temperature with a conventional X-band ESR spectrometer (JEOL JES-ME-2X) using a modulation width of 0.8 G and a microwave power level of 0.1 mW. The temperature was monitorred with a thermocouple positioned at the bottom of the sample tube with the accuracy of ±0.1 K. The temperature monitor was calibrated by comparing with the temperature measured by another thermocouple burried in the sample.

Photobleaching of the trapped electron was carried out with light of an incandescent lamp through a cut-off filter ($\lambda>660$ nm). During the photobleaching, the sample was rotated to avoid a spatially inhomogeneous bleaching.

The absorption spectrum of the trapped electron was recorded with a conventional recording spectrophotometer (Hitachi, EPS-3) for the sample in a rectangular quartz cell of 1.0×1.0 cm^2 immersed in liquid nitrogen.

Results

ESR spectral shape observed from irradiated MTHF glass is composed of a sharp single line spectrum due to trapped electron and a seven line spectrum due to free radical superposing each other. Although both spectra are stable at 77K, the former spectrum decays rapidly at temperatures higher than 90K accompanying a partial decay of the latter.[3b,4c,6a,8] Isothermal decays of the trapped electron were obtained at several temperatures between 92.2 and 95.0K by observing the change in intensity of the single line spectrum (correction was made for the free radical spectrum superposing on the trapped electron spectrum.)

Dependence of the decay upon radiation dose was studied in the range of 0.7—2.0×10^{19} eV/g, as shown in Fig. 1. Immediately after warming the samples from 77K to a proper temperature, the intensity of the

7) T. Ichikawa, H. Yoshida, and K. Hayashi, *J. Nucl. Sci. Tech.*, in press.

8) M. Ogasawara, K. Ohno, K. Hayashi, and J. Sohma, *J. Phys. Chem.*, **74**, 3221 (1070).

9) H. Yoshida, D-F. Feng, and L. Kevan, *J. Chem. Phys.*, in press.

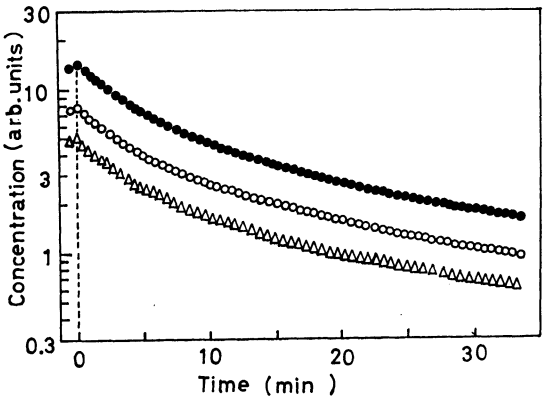

Fig. 1. Isothermal decay of trapped electron in MTHF glass irradiated to (●) 2×10^{19}, (○) 1×10^{19} and (△) 0.7×10^{19} eV/g at 77K and measured at 93.4K.

spectrum shows a slight increase. It may be caused by shorter paramagnetic relaxation times (especially spin-lattice relaxation time) at higher temperature. Under the present condition of ESR measurements, the microwave power level is a little too high to avoid a partial saturation of the trapped electron spectrum. Therefore, the intensity increases more or less when the relaxation times becomes shorter. It was assumed that the temperatures where the isothermal decay should be studied were reached when the observed decay curves reached the maximum. So the zero time for the isothermal bleaching was arbitrarily selected as shown in Fig. 1.

Depending on the radiation dose, the initial concentration of the trapped electron changes. However, the semilogarithmic plots of the decays can be completely superimposed if normalized at the initial concentration, which indicates that the rate of decay is independent of the radiation dose or the concentration of trapped electron. The decay does not follow an exponential curve nor is resolved into a few exponential curves.

Figure 2 shows the dependence of the isothermal decay upon temperature. The zero time was chosen as was done in Fig. 1. The scale of abscissas was chosen, so that the half-life ($t_{1/2}$, the time for the decay to 50% of the initial concentration), of the trapped electron has a fixed length for all temperatures examined.

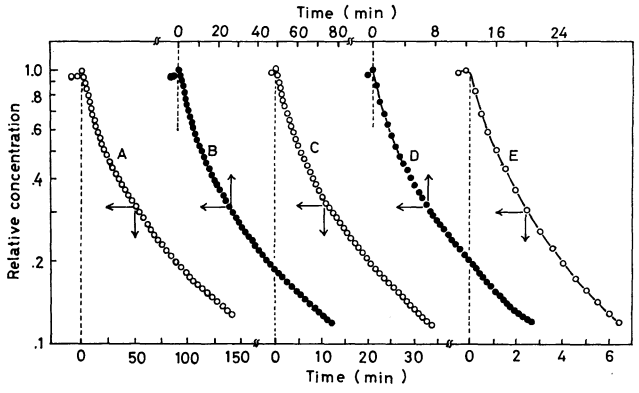

Fig. 2. Isothermal decay of trapped electron in MTHF glass irradiated to 1×10^{19} eV/g at 77K and measured at (A) 92.2, (B) 92.8, (C) 93.4, (D) 94.0, and (E) 95.0K.

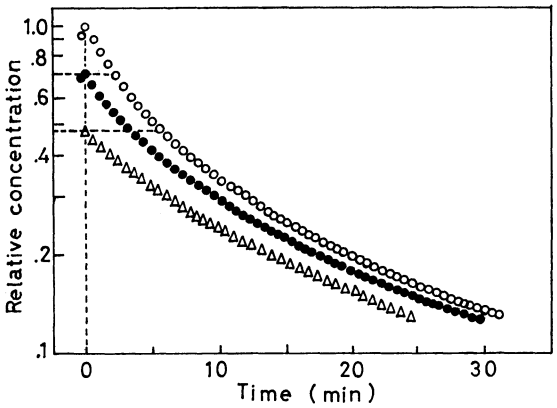

Fig. 3. Isothermal decay of trapped electron in MTFH glass irradiated to 1×10^{19} eV/g and measured at 93.4K after a partial photobleaching of trapped electron with light of $\lambda>660$ nm to (●) 70% and (△) 47% of its initial concentration. The decay without the photobleaching (○) is shown for comparison.

The concentration of trapped electron was also normalized to be unity at $t=0$. The decay becomes much faster with increasing temperature. However, the observed decay curves are again superimposed on each other, except a slight deviation observed for the curve at 95.0K, the highest temperature examined.

The decay curves were examined also after a partial photobleaching of the trapped electron with light of wavelength longer than 660 nm. They are shown in Fig. 3 as well as the decay curve obtained without the photobleaching. Evidently, the decay behavior after the partial photobleaching is the same as that after partial thermal bleaching. The curves A and B, obtained after the partial photobleaching, can be superposed on the curve C without photobleaching when they are horizontally shifted. Partial bleaching either thermally or by light affects equally on the decay behavior of the rest of trapped electron.

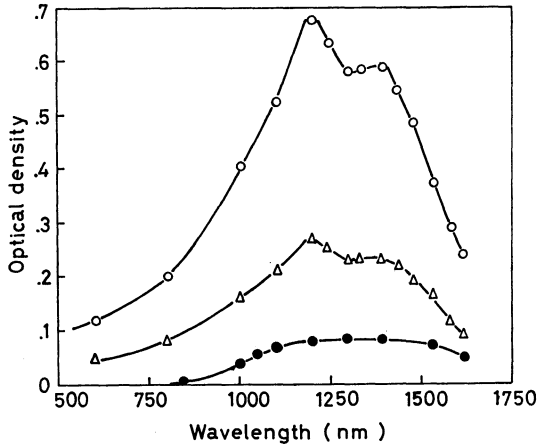

Fig. 4. Optical absorption spectra of trapped electron in MTHF glass irradiated to 7×10^{17} eV/g and measured at 77K (○) before and (△) after a partial photobleaching to 40% of its initial concentration. The spectra shown were obtained by subtracting the spectrum of the glass completely photobleached from those of the glasses containing the trapped electron. The residual spectrum (●) was determined as the difference in absorption between the glass irradiated and completely photobleached and the unirradiated glass.

Optical absorption spectrum of the trapped electron was studied immediately after the irradiation and after subsequent partial photobleaching of the trapped electron to 40% of its initial concentration both at 77 K. The results shown in Fig. 4 was obtained by subtracting the absorption of the sample irradiated and completely photobleached from that of the sample with trapped electron. It should be noted that a broad absorption was found at the wavelength region of 800—1600 nm, even after the complete photobleaching of trapped electron. This unidentified absorption disappeared when the irradiated glass was melted. The results clearly indicate that the absorption spectrum of trapped electron does not change in its shape during its decay.

Discussion

Activation Energy for the Decay of Trapped Electron. Since the decay curves show the same shape independent of the radiation dose and temperature, they can be characterized by a single parameter, for example, half-life. This implies that the apparent activation energy can be defined uniquely for the whole decay cruves. In other words, the activation energy remains unchanged during the decay.

The Arrhenius plot of the half-life is shown in Fig. 5, where the half-life appeared in the previous literatures are included for comparison. A good linear relationship is found in the temperature range studied in the present investigation. The present results seem consistent with the previous ones cited, though the activation energy tends to decrease with decreasing temperature.

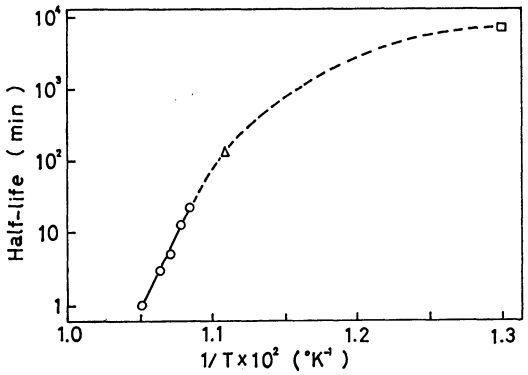

Fig. 5. Arrhenius plot of the half-life of trapped electron in irradiated MTHF glass when isothermally bleached. Half-lives estimated from the previous literatures (△) by Dainton and Salmon and (□) by Smith and Pieroni are also shown for comparison.

The activation energy is determined to be 0.8 eV (19 kcal/mol) from Fig. 5 in the temperature range of 92—95 K. The value is compared with the activation energy 14 kcal/mol determined in the same temperature range by Dainton *et al.* from the optical absorption measurements. They used the sample in a optical absorption cell of the cross section of 0.5×1.5 cm^2 and they mentioned that it took about 2.5 min to attain thermal equilibrium.[5a] In addition, the sample temperature is thought to have been inhomogeneous during rapid warming of a big sample. These factors may fortuitously cause a smaller activation energy. It should be noted also that the time 0.5 min of the transient rise of the sample temperature in the present investigation may have been a little too long to study the fast isothermal decay at 95 K and caused the slight distortion of the decay curve.

Ogasawara *et al.* studied previously the isothermal decay of the trapped electron in irradiated MTHF glass at temperatures higher than 95.6 K and obtained the activation energy of 6.1 kcal/mol.[8] The reason why the activation energy suddenly changes at around 95 K is not known well, though it may be attributed to the glass transition point of the MTHF glass.[12]

Decay Process of Trapped Electron. A unique value of activation energy for the whole decay process indicates that a single kind of migration process as well as a single kind of trap is responsible for the decay of trapped electron. In the MTHF glass, the primary cationic entity is believed to be stabilized by the intermolecular protonation or the intramolecular hydrogen transfer reaction.[5,6] The free radicals in this glass disappear in recombining with each other at about 100K somewhat higher than the temperature where the trapped electron decays very rapidly.[6a,8] This indicates that the stabilized cationic entity with the same size as MTHF molecule cannot migrate in the temperature range studied in the present investigation. Accordingly, the moving entity during the isothermal decay of trapped electron is the electron itself released from its trap.

The activation energy of 0.8 eV is considerably higher than that for the decay of trapped electron in irradiated 3-methylhexane glass caused by the migration of electron, 0.13 eV.[13] However, it is apparently less than the energies corresponding the absorption maximum of trapped electron and the threshold wavelength for its photobleaching.[2d,3a] Release of electron from its trap is very probably caused by the thermal distortion or destruction of the trap but not by the vertical transition up through the conduction level. Among the three possbile models for the mechanism of thermal mobilization of the trapped electron proposed by Kevan,[1] (1) diffusion of the matrix solvated electron as an entity, (2) tunneling between matrix traps due to matrix diploe reorientation, or (3) diffusion of a quasi-free electron, the present results support the second possibility. The strong temperature dependence does not indicate quantum tunneling of electron[3d,14] from electron trap to cation. With this respect, it may be interesting to compare the activation energy for the electron decay with that obtained from the temperature dependence of the viscosity of MTHF glass, 0.88 eV, in the temperature range of 92.0—101.5 K.[15]

10) P. K. Ludwig, *J. Chem. Phys.*, **50**, 1787 (1969).
11) (a) J. A. Leone and W. H. Hamill, *ibid.*, **49**, 5294, 5304 (1968). (b) T. Sawai and W. H. Hamill, *ibid.*, **56**, 5524 (1972).
12) M. Bodard and R. Marx, *J. Polymer Sci.*, **C16**, 4241 (1968).
13) H. Yoshida, *Ann. Repts. Res. Reactor. Inst. Kyoto Univ.*, **3**, 153 (1970).
14) M. Irie, H. Yoshida, K. Hayashi, and S. Okamura, This Bulletin, **45**, 2347 (1972).
15) A. G. Ling and J. E. Willard, *J. Chem. Phys.*, **72**, 1918 (1968).

Irrespective of the radiation dose and the temperature, all observed isothermal decay curves are superimposed on each other. A non-exponential decay indicates that the decay is not determined by a single thermally activated process of releasing electron from its original trap but by a sequence of detrap-retrap processes which the electron undergoes until it reaches at the predestined cation to recombine with. Therefore, the distribution of the life time of trapped electron is determined by the distribution of the number of detrap-retrap processes required for the electron to encounter the cation. An alternative interpretation may be that the decay was determined by the distribution of trap depth and the charge neutralization process involved a single thermally activated process of detrapping from the original trap. However, this is excluded by the observed constancy of the activation energy throughout the whole evolution of decay.

It was well established by the study of low temperature pulse radiolysis measurements[16] and by the study of irradiation at 4 K[4a,17] that the electorn formed in the MTHF glass is trapped primarily in a shallow trap and then the trap depth is deepened by the orientation of the matrix molecules at 77 K. However, the absorption spectrum of trapped electron stable at 77 K exhibits a structure attributable to two different depth of trap, and the shallow trap transforms to the deep one by warming the glass up to 85 K.[18] In the present measurements at higher temperature, the decay of deeply trapped electron may have been observed after the complete transformation of the shallow trap to the deep one, so that only one value of the activation energy may have been determined. After the partial photobleaching at 77 K, no change was found in the shape of the absorption spectrum. Therefore, the trapped electrons both in the shallow and deep traps are equally bleached by light of continuous spectrum ($\lambda>660$ nm). After that, the shallow trap may have been deepened by warming to the temperature of subsequent isothermal decay.

Electron-Cation Separation. On the basis of the assumption of isolated electron-cation pair and the neutralization time proportional to migration path length of electron or the number of detrap-retrap cycles before encountering with its partner cation, the evolution of electron decay can be correlated with the separation distance between the electron and the cation by the well known Smoluchowski equation.[10,19] However, if we assume that the migration of electron is to a large extent determined by the Coulombic interaction only, it is described simply by the Nernst-Einstein relationship,[20]

$$-\frac{dr}{dt}=\frac{Dr_c}{r^2} \tag{1}$$

where r is the distance between electron and cation, D is the diffusion coefficient of electron, and r_c is Onsager length defined as

$$r_c=\frac{e^2}{\varepsilon kT} \tag{2}$$

By integrating Eq. (1) under the initial condition $r=r_i$ at $t=0$, the following relationship is obtained between r and t:

$$r_i^3-r^3=3Dr_ct \tag{3}$$

This gives the recombination time t_r for the electorn initially at r_i as

$$t_r=\frac{r_i^3}{3Dr_c} \tag{4}$$

which turns out to be $dr_i/dt_r=Dr_c/r_i^2$. Consequently, the survival probability of electron, P, is defined by the probability density of finding electron at r_i at $t=0$, $W(r_i)$, which is the initial distribution of separation distance between trapped electron and cation:

$$-\frac{dP}{dt_r}=W(r_i)\cdot\frac{dr_i}{dt_r}=\frac{Dr_c}{r_i^2}\cdot W(r_i) \tag{5}$$

The left-hand side of the above equation is the decay rate obtained from the normalized decay curve of the trapped electron. If one transforms t_r and r_i to dimensionless parameters $\tau=t_r/t_{1/2}$ and $x_i=(Dt_{1/2}r_i)^{-1/3}\cdot r_i$, the following relation is obtained:

$$-x_i^2\cdot\frac{dP(\tau)}{d\tau}=W(x_i) \tag{6}$$

Equation (6) gives straightforwards the initial distribution of separation $W(x_i)$ from the observed decay curve by using the relationship $3\tau=x_i^3$. The distribution is temperature independent because not only the product $Dt_{1/2}$ but also r_c remains unchanged in a small range of temperature studied.

The initial distribution is numerically obtained from the whole evolution of the electron decay. In the same way, the probability of finding electron at reduced distance x at reduced time $\tau=\tau_1$ during the isothermal decay can be obtained from the evolution of decay in the region of τ larger than τ_1, using the relationship

$$-x^2\cdot\frac{dP(\tau+\tau_1)}{d\tau}=W(x,\tau_1) \tag{7}$$

Thus obtained distribution of the initial separation distance as well as those during the isothermal decay[21] is shown in Fig. 6.

The initial distribution qualitatively agrees with the Gaussian distribution, $W(x_i)=x_i^2\exp(-\alpha x_i^2)$, which was used to estimate the average separation between ion pair in irradiated liquid hydrocarbon.[22] The disagreement at large x_i values is much improved if the Smoluchowski equation is rigorously applied in the present analysis.[23] It should be noted that the maximum of distribution function and the average separation increase during the isothermal decay. This is

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17) H. Hase, M. Noda, and T. Higashimura, *ibid.*, **54**, 2975 (1971).
18) T. Sawai and W. H. Hamill, *J. Phys. Chem.*, **73**, 3452 (1969).
19) A. Mozumdar, *J. Chem. Phys.*, **48**, 1659 (1968).
20) F. Williams, *J. Amer. Chem. Soc.*, **86**, 3954 (1964).
21) Computations were carried out at the Computing Center of Hokkaido University.
22) S. Sato, This Bulletin, **41**, 304 (1968).
23) T. Ichikawa, H. Yoshida, and K. Hayashi, to be published.

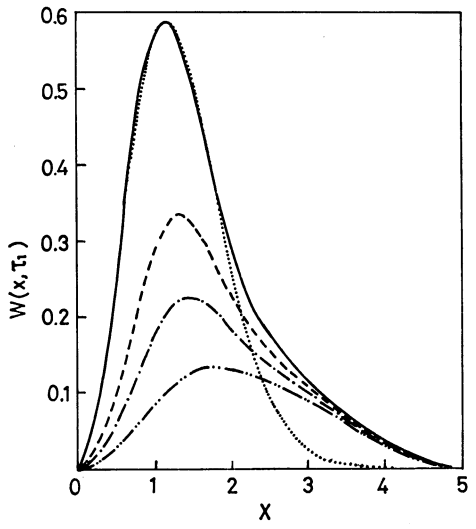

Fig. 6. Distribution of electron-cation separation distance in irradiated MTHF glass before and during the thermal decay of trapped electron determined from its isothermal decay curves. $W(x,\tau_1)$ is the probability density of finding electron at the reduced distance x at the reduced time τ_1. The distribution is shown for $\tau_1=0$ (——), 1/2 (– – –), 1 (–·–), and 2 (–··–). The definition of x and τ is given in the text. Gaussian distribution (·····) is also shown for comparison.

due to relatively short life time of electron at short distance from cation (see equation 3). This trend is more pronounced when the diffusion term in the Smoluchowski equation is taken into account in deriving the distribution.[23]

The quantum efficiency for the photobleaching of trapped electron in the MTHF glass was found to be much smaller than unity.[2d,3a,24] This implies that the electron undergoes several detrap-retrap cycles until it recombines with cation when photobleached. The present results of the effect of partial photobleaching on the subsequent isothermal decay (see Fig. 3) gives another evidence of the detrap-retrap cycles under the bleaching light. It indicates that the change in $W(x, \tau_1)$ during the photobleaching is the same as that during the isothermal decay of electron which is characterized by the migration of electron described by equation (1) but not by the single thermal activation process of detrapping from the original trap.

The decrease in the quantum efficiency of photobleaching with bleaching time was attributed to two class of trapped electron: one is electron trapped in proximity with cation and another is that trapped homogeneously in the glass.[24] However, such a classification of trapped electron seems unnecessary. The average distance between unbleached electron and cation increases longer and longer during the photobleaching, so that the number of detrap-retrap cycles required for the electron to recombine with the cation increases with photobleaching time, which results in a smaller quantum efficiency.

Lin and Kevan observed the increase in the paramagnetic relaxation times of trapped electron in the MTHF glass by a partial photobleaching, if the glass was irradiated to the dose at which the spurs did not overlap with each other.[2c] They thought that this result gave an evidence that a spur contains more than one trapped electron. However, if one presumes that the stabilized cationic entity is still paramagnetic (radical cation),[6,7] the observed change in the paramagnetic relaxation times during the photobleaching is interpreted by the increase in average distance between electron and the cation as shown in Fig. 6. Although the change in the separation distance seems to be slight, the spin-spin dipolar interaction depends on the inverse cube of the distance and very sensitive to the change in the distance.

24) P. J. Dyne and O. A. Miller, *Can. J. Chem.*, **43**, 2696 (1965).