Distribution of Trapped Electron-Cation Distance in γ-Irradiated 2-Methyltetrahydrofuran Glassy Matrix

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An approach was presented to elucidate the distribution of trapped electron-cation distance from isothermal decay of the trapped electron by numerically solving the Smoluchowski equation and was applied to the observed isothermal decay of trapped electron at 92.2—95.0 K in 2-methyltetrahydrofuran glass irradiated by γ-rays at 77 K. The distribution curve (the probability density of finding initially the electron at the distance r) thus obtained was close to a Gaussian function.

One of the important features of radiation chemistry in condensed media is in spatial inhomogeneity of the formation of primary active entities such as electrons, ions and free radicals. It is generally accepted that the distance of an electron from its counterpart cation is smaller than average distance between pairs of the electron and the cation, and that the charge recombination process occurs mostly as an isolated event (spur reaction in liquid media). The electron-cation distance when the electron is trapped or solvated is dependent upon the kinetic energy of the secondary electron, the energy loss process and trapping or solvation process in condensed media. Distribution of the electron-cation distance was studied in liquid media by means of electron scavenge method[1-3] and electrical conductivity measurements,[4-6] and some analytical expressions were given for it. However, it is difficult to study the distribution in glassy matrices. Only average distance between the trapped electron and its counterpart cation has been estimated from the effect of electron scavenger upon the yield of the trapped electron[7-9] and also from paramagnetic relaxation measurements of the trapped electron.[10-13]

Recently we studied the isothermal decay of the trapped electron in 2-methyltetrahydrofuran (MTHF) glassy matrix irradiated by γ-rays at 77 K and found that the time profile of the decay at several temperatures above 92 K was independent of either radiation dose or temperature, if the time scale was corrected with an Arrhenius factor.[14] The results indicate that the electron is trapped close to its counterpart cation and suggest that its decay is determined solely by the electron-cation distance. This leads to the point that the time profile of the decay is correlated to the distribution of the distance and, therefore, the analysis of the decay curve may give a new approach to elucidate the distribution of the distance in glassy matrices.

The principal aim of the present paper is in reexamining the time profile of the isothermal decay of the trapped electron in MTHF glassy matrix previously reported[14] in order to show the possibility of elucidating the distribution of the distance on the basis of the Smoluchowski equation which describes the migration of electron in the matrix.

Theoretical Background

Assuming that (1) the electron migrates in the matrix as a classical particle, (2) it is formed in pairing with a cation, and (3) the mean free path of the electron is much smaller than the migration path traveled before charge recombination, the migration of the electron is regarded as the diffusion under the spherical Coulombic field due to the cation. In such circumstances, the time profile of the electron decay can be correlated with the distribution of the distance between the electron and the cation by the well known Smoluchowski equation,[15]

$$\frac{1}{D}\frac{\partial W(r,t)}{\partial t}=\frac{\partial^2 W(r,t)}{\partial r^2}+\left(\frac{2}{r}+\frac{r_C}{r^2}\right)\frac{\partial W(r,t)}{\partial t}, \tag{1}$$

where r is the distance, t time, D diffusion coefficient, $W(r,t)$ the probability density of finding the electron at r and at t, and $r_C(=e^2/\varepsilon kT)$ the Onsager length. Since the electron is presumed to disappear only in recombining with the cation, a boundary condition of the differential equation is given as

$$[W(r,t)]_{r=r_0}=0 \tag{2}$$

where r_0 is so-called recombination radius. The initial distribution is given by $W(r,0)$. On the other hand, the time profile of the electron decay, $P(t)$, is given by the spatial integration of $W(r,t)$ as

$$P(t)=\int_{r_0}^{\infty} W(r,t)4\pi r^2 dr \tag{3}$$

and $dP(t)/dt$ is given by the rate of electron flow across the spherical surface of reaction radius,

$$\frac{dP(t)}{dt}=-4\pi r_0^2 D\left[\frac{\partial W(r,t)}{\partial r}\right]_{r=r_0}. \tag{4}$$

The aim of the present study is in the derivation of $W(r,t)$ from the given $P(t)$ corresponding to the observed time profile of the electron decay. This turns out to solve Eq. (1) under the boundary conditions (2) and (4), but Eq. (1) is generally unable to be solved analytically. Several approximation methods have been invented and used, which encompass the prescribed diffusion method,[16,17] the Laplace transformation method[18] and perturbation methods.[19,20] These methods, however, are not useful for the present aim, because they derive $W(r,t)$ from a given $W(r,0)$ but not from a given $P(t)$.

One of modifications of the Smoluchowski equation is the Nernst-Einstein relationship, where the diffusion term in Eq. (1) is completely neglected.[21] On this basis, one can readily derive the initial distribution from the time profile of the electron decay:

$$W(r,0)=-\left[\frac{dP(t)}{dt}\right]_{t=t'} \tag{5}$$

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where

$$t' = \frac{r^3 - r_0^3}{3Dr_C}.$$

In this case however, the calculated distribution is not very accurate because of the neglect of the diffusion term.[22]

More accurate distribution is expected to be derived by taking the diffusion term into account. This can be achieved by expanding the time profile of the observed electron decay into the Dirichlet series,

$$P(t) = \sum a_i \exp(-k_i t), \tag{6}$$

and by transforming the probability density as

$$W(r, t) = \sum R_i(r) \exp(-k_i t). \tag{7}$$

Thus the Smoluchowski equation can be transformed into ordinary differential equation:

$$\frac{d^2R_i(r)}{dr^2} + \left(\frac{2}{r} + \frac{r_C}{r^2}\right)\frac{dR_i(r)}{dr} + \frac{k_i}{D}R_i(r) = 0. \tag{8}$$

The boundary conditions of the above equation,

$$[R_i(r)]_{r=r_0} = 0 \tag{9}$$

and

$$\left[\frac{dR_i(r)}{dr}\right]_{r=r_0} = \frac{k_i a_i}{4\pi r_0^3 D} \tag{10}$$

are obtained also by transforming Eqs. (2) and (4). Equation (8) is solved, for example, by Runge-Kutta-Gill method and the initial distribution of the distance between the trapped electron and the cation is to be obtained numerically.

Observed Isothermal Decay

According to our recent study,[14] the electron trapped in the γ-irradiated MTHF glassy matrix decay rapidly in following a pseudo-first order reaction (independent of the radiation dose and the initial concentration of the electrons), when the glassy matrix is warmed to temperature higher than 92 K. This strongly suggests that an electron is trapped close to its counterpart cation and that no spatial overlapping occurs between the electron-cation pairs.

The time profile of the electron decay in the temperature range 92.2—95.0 K was observed by electron spin resonance method, and found to be superimposable on each other if the time scale was corrected by the half-life of the electrons at each temperature (the corrected time is real time devided by the half-life, $\tau = t/t_{1/2}$). The dependence of $t_{1/2}$ upon temperature followed the Arrhenius relation, which gave an activation energy of 0.8 eV in the temperature range examined. This large activation energy indicates that the charge recombination results from the migration of electron in the matrix at temperatures close to its liquifying temperature. On the other hand, the activation energy becomes smaller and approaches to zero by lowering temperature, which is consistent with the view that the charge recombination is caused essentially by quantum mechanical tunnelling of electron from its trap to the cation at low temperature.[23,24]

Quantum efficiency of photobleaching trapped electron was examined for γ-irradiated MTHF matrix at 77 K and found to be much smaller than unity.[7] This indicates that the electron photoliberated from its trap does not recombine at once with the cation, but undergoes several detrap-retrap cycles before the charge recombination. This retrapping efficiency is most probably higher at higher temperature because of the ease of reorientation of the matrix molecules to solvate the electron.

These two facts, the large activation energy and the small quantum efficiency, indicate that the lifetime of electron at elevated temperature is determined by the migration path length travelled by the electron before charge recombination and, therefore, by the number of thermal activation process (trap-detrap process). It turns out that the temperature independent time profile of the electron decay is directly correlated to the distribution of the electron-cation distance before the glassy matrix is warmed. The observed time profile of the decay to be analyzed in the following chapter is taken from the previous paper[14] and shown in Fig. 1 with open circles.

Calculation and Results

Because the diffusion coefficient D is temperature dependent, the time profile of the electron decay to be obtained from a given distribution of the electron-cation distance based on Eq. (1) is necessarily temperature dependent. However, the fundamental Smoluchowski equation is readily transformed by using the corrected diffusion coefficient

$$D_0 = Dt_{1/2} \tag{11}$$

into

$$\frac{1}{D_0}\frac{\partial W(r, \tau)}{\partial \tau} = \frac{\partial^2 W(r, \tau)}{\partial r^2} + \left(\frac{2}{r} + \frac{r_C}{r^2}\right)\frac{\partial W(r, \tau)}{\partial r}. \tag{12}$$

This differential equation gives temperature independent correlation between the distribution of the distance and the time profile of the electron decay, if the latter is plotted in the corrected time scale ($\tau = t/t_{1/2}$) and if D_0 is temperature independent. This is really the case as observed previously.[14] The temperature independent corrected diffusion coefficient implies that the migration of the electron is thermal activation process and it is controlled by thermal detrapping of electron (or thermal collapse of electron trap). The value of r_C is regarded as constant in a narrow range of temperature.

Starting from Eq. (12), Eqs. (6), (7), (8) and (10) are rewritten as follows:

$$P(\tau) = \sum a_i \exp(-k_i \tau), \tag{13}$$

$$W(r, \tau) = \sum R_i(r) \exp(-k_i \tau), \tag{14}$$

$$\frac{d^2R_i(r)}{dr^2} + \left(\frac{2}{r} + \frac{r_C}{r^2}\right)\frac{dR_i(r)}{dr} + \frac{k_i}{D_0}R_i(r) = 0 \tag{15}$$

and

$$\left[\frac{dR_i(r)}{dr}\right]_{r=r_0} = \frac{k_i a_i}{4\pi r_0^3 D_0}. \tag{16}$$

The observed time profile of the electron decay (shown in Fig. 1) was graphically analyzed and expanded

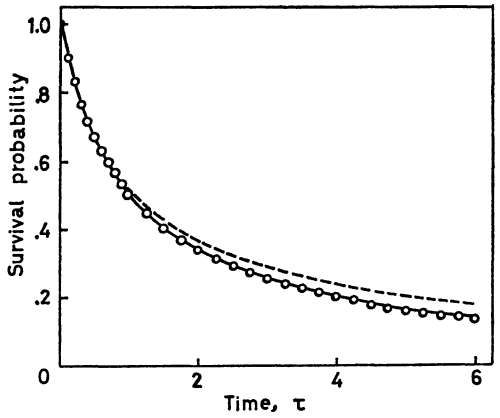

Fig. 1. Time profile of the decay of trapped electron in γ-irradiated MTHF glassy matrix (○) observed at about 93 K, (solid line) computed from the initial distribution of electron-cation distance given by open (for $r \leq 40$ Å) and filled circles (for $r \geq 40$ Å) in Fig. 2, and (dashed curve) computed from the initial distribution of the distance given by the dashed curve in Fig. 2 based on Eq. (15).

by the Dirichlet series

$$P(\tau) = 0.34 \exp(-0.15\tau) + 0.46 \exp(-0.90\tau) + 0.20 \exp(-2.85\tau). \quad (17)$$

In order to calculate numerically the initial distribution $W(r,\tau)$ from the observed $P(\tau)$ based on the differential equation (15) and the boundary conditions (9) and (16), the numerical values of r_0, r_c and D_0 should be known. The Onsager length r_c at 93 K was estimated to be 624 Å from the dielectric constant of the glassy matrix, 2.88.[25] The reaction radius r_0 was taken to be 10 Å rather arbitrarily, but the ambiguity in r_0 affects little the calculated initial distribution, because the migration of electron toward the cation is fast in its vicinity. Although there is no means to estimate the diffusion coefficient D and, therefore, the corrected diffusion coefficient D_0, the latter was arbitrarily taken to be 66 Å^2. This value gave the average initial distance between the trapped electron and the cation of about 50 Å, which seems plausible for accounting for the previous results of paramagnetic relaxation of the trapped electron in the MTHF glassy matrix.[10]

The calculated initial distribution of the distance is shown by the solid curve in Fig. 2. The oscillatory feature at large r resulted from the essential fact that the boundary value problem is not well-posed for the parabolic partial differential equation such as Eq. (12). It turns out that small errors inevitably included in the observed boundary condition (the decay curve, especially at large τ) deteriorate the calculated initial distribution of the distance at large r. If one ignores the unrealistic oscillation, the distribution curve is approximated, as shown by open and filled circles in Fig. 2, by

$$W(r, 0) = 2.5 \times 10^{-6} \exp(-r^2/1600) \quad \text{for } r_0 < r \leq 40\text{Å} \quad (18)$$

and

$$W(r, 0) = 11.5 \times 10^{-6} \exp(-r/16) \quad \text{for } r \geq 40\text{Å} \quad (19)$$

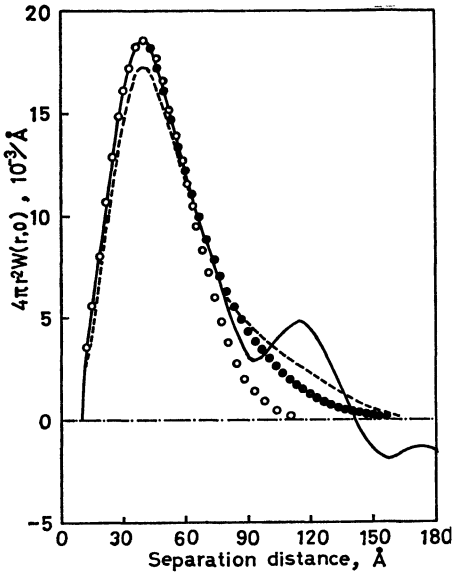

Fig. 2. Initial distribution of electron-cation distance in γ-irradiated MTHF glassy matrix derived from the time profile of electron decay shown by open circles in Fig. 1, (solid curve) on the basis of the Smoluchowski equation (15) and (dashed curve) on the basis of the Nernst-Einstein approximation (Eq. (5)). Open circles and filled ones show the smoothed distribution curve given by Eqs. (18) and (19), respectively. For $r > 40$ Å, the filled circles express the distribution better.

where r is measured in Å unit. Although the curve is not expressed by a single function, its whole shape is rather close to the Gaussian function. In order to check the validity of smoothing the oscillatory feature and that of the relationships (18) and (19), the time profile of the electron decay was reconstructed from them by using the finite difference approximation based on the Smoluchowski equation (12) (see Appendix). The result is shown by the solid curve in Fig. 1. It agrees very well with the observed time profile from which the initial distribution of the distance was derived.

Discussion

It has been shown above that the initial distribution of the distance of the trapped electron from its counterpart cation in the glassy matrix can be derived, on the basis of the Smoluchowski equation describing the behavior of electron under the spherical Coulombic field, by observing the isothermal decay of the trapped electron. The same approach may be applicable also to study the distance between solvated electron and its counterpart cation in liquid media, if the complete time profile of the prompt decay of the solvated electron becomes available by the pulse radiolysis experiments with time resolution high enough.

From mathematical point of view, the present procedure of deriving the initial distribution of the distance from the time profile of the electron decay is the translation of a boundary condition of the

Smoluchowski equation into its initial condition. The scavenger method for studying the distribution[3] is essentially one of the modification of the present method: in the scavenger method the time profile of the electron decay was obtained indirectly from the Laplace transformation of the scavenging curve.[26] However, this method presumes that electron can react with scavenger only after the thermalization (or solvation). The initial distribution of the distance was also derived from the field dependence of electric conductivity during irradiation. In this case, the probability of escaping geminate recombination and of contributing to the conductivity decreases with decreasing electron-cation distance. Therefore, this method is suitable to study the distribution only at large r. Contrary, the present method gives reliable information for small r but not for large r, because the later part of the electron decay is experimentally less accurate, which is translated into the distribution at large r.

The most direct correlation between the electron decay and the distribution of the distance is given by the Nernst-Einstein approximation (relationships (5) and (6), where t, t' and D should be replaced by τ, τ' and D_0 to analyze the decay data in Fig. 1). According to this approximation, the observed electron decay shown in Fig. 1 gave straightforwards the distribution curve shown by the dashed line in Fig. 2. The neglect of the diffusion term in the Smoluchowski equation caused a small but apparent depression of the curve for small r. Such tendency should become enhanced and the diffusion term cannot be ignored, if the distribution is very sharp and if the initial distance is as large as the Onsager length. The dashed line in Fig. 1 shows the time profile of the electron decay reconstructed from the distribution given by the dashed curve in Fig. 2 by means of the finite difference approximation based on the Smoluchowski equation (12). Here also, the contribution of the diffusion term is apparently seen from the deviation of the dashed line from the solid line.

The half-life, $t_{1/2}$, of the trapped electron was found to be temperature dependent with an activation energy of 0.8 eV (19 kcal/mol) and a pre-exponential factor of 1×10^{-42} s in the temperature range 92.2—95.0 K.[14] Based on Eq. (11) and the presumed value of 66 Å^2 for D_0 (see the preceding section), the diffusion coefficient, D, is calculated to be 10^{-7} cm^2 s^{-1} in this temperature range within the framework of the present procedure. On the other hand, Huang and Kevan measured the drift mobility of 0.055 cm^2 V^{-1} s^{-1} at 77 K for electrons photoliberated from their trap in γ-irradiated MTHF glassy matrix.[27] Assuming that the well known relationship, $\mu/D=e/kT$, between the mobility and the diffusion coefficient is valid for these electrons, we can obtain the diffusion coefficient of 3.6×10^{-4} cm^2 s^{-1}.

A big difference in the diffusion coefficient may be attributed to the difference in the mechanism of electron transport. The measurement of the drift mobility dealt with the electrons photoliberated into conduction state, which seem to have reached the collecting electrode without suffering retrapping in the matrix.[27] The electrons in the present investigation are mobilized by thermal detrapping probably due to thermal collapse of the trapping site and they seem to be more or less solvated during their migration. Therefore, it is reasonable that their diffusion coefficient is much smaller than that for the electrons in conduction state. If the big diffusion coefficient, 3.6×10^{-4} cm^2 s^{-1}, is used in deriving D_0 on trial, the observed isothermal decay of Eq. (17) gives an initial average distance between the trapped electron and its counterpart cation of more than 10^6 Å, which is unrealistically too big.

A drawback in the present approach is in the lack of the available numerical data on the diffusion coefficient D, measurements of which are highly desirable.

All numerical computations in this investigation were made by using facilities of the Computing Center of Hokkaido University.

Appendix

The Smoluchowski equation (12) is solved straightforward to give the solution $W(r,\tau)$, if the initial condition $W(r,0)$ as well as the bounday condition is given. The finite difference approximation is one of the most appropriate method to solve the equation numerically. The difference equation corresponding to the differential equation (12) is

$$W_{m,n+1} = W_{m,n} + \frac{D_0K}{H^2}(W_{m+1,n}-2W_{m,n}+W_{m-1,n}) + \frac{D_0K}{2H}\left\{\frac{2}{r_0+mH}+\frac{r_C}{(r_0+mH)^2}\right\}(W_{m+1,n}-W_{m-1,n}) \quad \text{(A1)}$$

where $W_{m,n}=W(r,\tau)$, $r=r_0+mH$ and $\tau=nK$. The time profile of the electron decay $P(\tau)=P_n$ is given as

$$P_n = \sum_{i=0}^{M} 4\pi(r_0+iH)^2HW_{i,n}. \quad \text{(A2)}$$

The upper limit of summation, M, should be so large that $4\pi(r_0+MH)^2W_{M,n}$ is vanishingly small. P_n was computed consecutively under the given initial condition $W_{m,0}$ and the boundary condition $W_{0,n}$, $W_{M,n}=0$. In the calculation, the parameters were taken as small as $H=0.6$ Å and $K=0.002$ and as large as $M=500$, which were tested to be small or large enough for the good approximate solution to be obtained.

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