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A Theoretical Consideration of the Electron-scavenging Process in Liquid Hydrocarbons. II. Pulse Irradiation

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A mathematical treatment of the electron recombination process is presented on the basis of the extended Smoluchowski equation, which includes the effects of several positive ions as ion cores in a spur and of a scavenger. The equation is reduced to the usual Smoluchowski equation for the geminate recombination in a special case. The time dependence of the electron concentration is obtained using a successive approximation. The results of numerical calculations for various reaction parameters are presented.

The geminate recombination of the electrons with the parent ions in the primary process in the radiolysis of the liquid phase has been discussed on the basis of a statistical treatment1–5) and of the basis of the Smoluchowski equation,6–11) using different approaches. The second method, used by Monchick,6) Mozumder,7) and Hummel8) is based on the approximation of the prescribed diffusion of the Smoluchowski equation. The presence of a singularity at the point of origin in this equation makes it difficult to solve analytically. Numerical calculations using an electronic computer were attempted by Ludwig.9) In spite of the difficulty of obtaining an accurate solution, the various experimental results, namely, the scavenging effect on the reaction products, the measurement of the electric conduction during irradiation, and the recent development of the spectroscopic tracing of the electron concestration after pulse irradiation, can be interpreted on this theoretical base. However, no unified theory based on a fundamental equation seems to have been proposed in explanation of the various experimental facts. In a previous paper the scavenger effect on the G value of electron recombination has been discussed.12)

In the present paper, the recombination of the electrons with parent ions after pulse irradiation will be treated by considering the character of a spur and the effect of the scavenger as an extended form of the Smoluchowski equation,12) which can be reduced to the usual Smoluchowski equation in the absence of a scavenger and in the presence of a single ion in the ion core. The successive approximation was applied to solve the extended form of the Smoluchowski equation, using two extreme cases, namely, the potential-control and diffusion-control cases. To solve the recombination relaxation of the electrons, the determination of the initial distribution of the electrons is important, so various initial distributions were tested in the numerical calculation. Inversely, the initial distribution can be obtained by the inverse Laplace transform from the analysis of the recombination process. In the ion-core model, an ion cluster at the center of the spur and the surrounding electrons are considered. The value of the central ion charge gradually decreases as the neutralization process progresses. The solution can be synthesized by the connection of the solutions for various effective charges in the ion core.

Theory

A) Fundamental Equation and Its Approximations. The fundamental equation for the electron recombination is based on the following form of the extended Smoluchowski equation, (I-12),13) in a spherical coordinate:

$$\frac{\partial c(r,t)}{\partial t} = D\frac{\partial^2 c(r,t)}{\partial r^2} + \left(\frac{2D}{r} + \frac{\alpha}{r^2}\right)\frac{\partial c(r,t)}{\partial r} - \beta c(r,t) \qquad (1)$$

where $C(r, t)$ is the concentration of electrons at a distance r from the center of the ion core and at a time t after the ionization of the central ions. D is the diffusion constant, α is determined by the Coulomb attraction, and β is the rate constant of the scavenger reaction. α decreases with an increase in t by the neutralization of the central ions, and also decreases with an increase in r by means of the screening effect of the electrons outside the ion core, as is shown by Eq. (2):

$$\alpha = N^+(t)eu/\varepsilon \qquad (2)$$

where $N^+(t)$ is the number of ions in the ion core, $\boldsymbol{e}$ is the electron charge, u is the mobility of the electrons, and ε is the dielectric constant. However, for the sake of simplicity, α is assumed to be a constant or a step function of time during the neutralization process.

A successive approximation has been used to solve the fundamental equation. An analytical expression of the solution can be obtained in the absence of either the diffusion term or the term of the Coulomb attraction. Therefore, the solutions in which these terms are absent can be used as the zero-th order approximation. For example, in the absence of diffusion term, Eq. (3) is given for the zero-th-order approximation of the potential-control case:

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1) G. R. Freeman, *J. Chem. Phys.*, **46**, 2822 (1967).
2) G. R. Freeman and J. M. Fayadh, *ibid.*, **43**, 86 (1965).
3) S. Sato, T. Terao, M. Kono, and S. Shida, This Bulletin, **40**, 1818 (1967).
4) S. Sato, *ibid.*, **41**, 304 (1968).
5) G. R. Freeman, *Adv. Chem. Ser.*. **82**, 339 (1968).
6) L. Monchick, *J. Chem. Phys.*, **24**, 381 (1956).
7) A. Mozumder, *ibid.*, **48**, 1659 (1968).
8) A. Hummel, *ibid.*, **48**, 3268 (1968).
9) P. K. Ludwig, *ibid.*, **50**, 1787 (1969).
10) A. Mozumder, *ibid.*, **50**, 3153 (1969).
11) A. Mozumder, *ibid.*, **50**, 3162 (1969).
12) H. Yamazaki and K. Shinsaka, This Bulletin, **43**, 2713 (1970).

$$\frac{\partial \chi_0(r,t)}{\partial t} = \frac{\alpha}{r^2}\frac{\partial \chi_0(r,t)}{\partial r} - \beta \chi_0(r,t) \qquad (3)$$

In the absence of the Coulomb interaction, Eq. (4) is obtained as a diffusion-control case:

$$\frac{\partial \omega_0(r,t)}{\partial t} = D\frac{\partial^2 \omega_0(r,t)}{\partial r^2} + \frac{2D}{r}\frac{\partial \omega_0(r,t)}{\partial r} - \beta\omega_0(r,t) \qquad (4)$$

or:

$$\frac{\partial r\omega_0(r,t)}{\partial t} = D\frac{\partial^2 r\omega_0(r,t)}{\partial r^2} - \beta r\omega_0(r,t) \qquad (4')$$

The solution for the s-th order approximation can be obtained by means of Eqs. (5) and (6) for the potential control and the diffusion control respectively:

$$\frac{\partial \chi_s(r,t)}{\partial t} = \frac{\alpha}{r^2}\frac{\partial \chi_s(r,t)}{\partial r} + D\frac{\partial^2 \chi_{s-1}(r,t)}{\partial r^2} + \frac{2D}{r}\frac{\partial \chi_{s-1}(r,t)}{\partial r} - \beta\chi_s(r,t) \qquad (5)$$

and·

$$\frac{\partial r\omega_s(r,t)}{\partial t} = D\frac{\partial^2 r\omega_s(r,t)}{\partial r^2} + \frac{\alpha}{r}\frac{\partial \omega_{s-1}(r,t)}{\partial r} - \beta r\omega_s(r,t) \qquad (6)$$

By the use of these recurrent equations, the higher-order solutions can be obtained.[14] The zero-th-order solutions are given by Eqs. (7), (8), and (9).[15]

$$\chi_0(r,t) = f(\alpha t + r^3/3)\exp(-\beta t) \qquad (7)$$

where f stands for an arbitrary function. Equation (7) is expressed by the integral representation:

$$\chi_0(r,t) = \int_0^\infty K_0(n)\exp(-\beta t - n\alpha t - nr^3/3)\mathrm{d}n \qquad (8)$$

where $K_0(n)$ is an arbitrary function of n, which is determined by the initial distribution of electrons. The zero-th-order solution in the diffusion-control case can be written by Eq. (9):

$$\omega_0(r,t) = \frac{\exp(-\beta t)}{2r\sqrt{\pi Dt}}\int_0^\infty \xi\varphi(\xi)\left[\exp\{-(r-\xi-R_0)^2/4Dt\} - \exp\{-(r+\xi-R_0)^2/4Dt\}\right]\mathrm{d}\xi \qquad (9)$$

where $\varphi(\xi)$ is the initial distribution of the electrons and where R_0 is the radius of the central-ion core. The first- and second-order approximations, χ_1 and χ_2, are given by Eq. (10) and Eq. (11) respectively:

$$\chi_1(r,t) = \int_0^\infty K_1(n)(1 + nDr^4/\alpha - n^2Dr^7/7\alpha) \times \exp\{-(\beta+n\alpha)t - nr^3/3\}\mathrm{d}n \qquad (10)$$

and

$$\chi_2(r,t) = \int_0^\infty K_2(n)(1 + nDr^4/\alpha - n^2Dr^7/7\alpha - 4nD^2r^5/\alpha^2 + 5n^2D^2r^8/2\alpha^2 - 24n^3D^2r^{11}/77\alpha^2 + n^4D^2r^{14}/98\alpha^2) \times \exp\{-(\beta+n\alpha)t - nr^3\}\mathrm{d}n \qquad (11)$$

Generally, the s-th order of approximation can be written by:

$$\chi_s(r,r) = \int_0^\infty K_s(n)H_s(n,\alpha,D,r)\exp(-\beta t - n\alpha t - nt^3/3)\mathrm{d}n \qquad (12)$$

where H_s is a function of n, α, D, and r. When an approximate electron concentration in the system is expressed as N_s, the approximate electron concentration as a function of the time is given by Eq. (13):

$$\begin{aligned} N_s(t) &= 4\pi\int_{R_0}^\infty r^2\chi_s(r,t)\mathrm{d}r \\ &= 4\pi\int_0^\infty K_s(n)\exp(-\beta t - n\alpha t) \times \left[\int_{R_0{}^3/3}^\infty H_s(n,\alpha,D,\xi)\exp(-n\xi)\mathrm{d}\xi\right]\mathrm{d}n \\ &= 4\pi\int_0^\infty K_s(n)\exp(-\beta t - n\alpha t)G_s(n,\alpha,D,R_0)\mathrm{d}n \qquad (13) \end{aligned}$$

where $G_s(n, \alpha, D, R_0)$ is the integral in the brackets, [ ] and is a function of n, α, D, and R_0. The approximate value of $N(t)$ and the time dependence of the electron concentration can be evaluated by using the approximate solutions of $C(r, t)$. Thus, the initial distribution of the electron and the time dependence of the electron concentration in the system are connected by the Smoluchowski equation. The initial distribution of electrons can be estimated from the time behavior of the electron concentration, which is itself determined by the pulse experiment. Therefore, the initial distribution can be expressed by the use of the inverse Laplace transforms[16] of the time dependence of the electron concentration in the system, as is shown in Eq. (14):

$$K_s(n)G_s(n,\alpha,D,R_0) = \frac{1}{8\pi^2 i}\int_{c-i\infty}^{c+i\infty} N_s(p/\alpha) \times \exp\{(\beta/\alpha + n)p\}\mathrm{d}p \qquad (14)$$

where the c in the integral is a constant. $G_0(n, R_0)$, $G_1(n, \alpha, D, R_0)$, and $G_2(n, \alpha, D, R_0)$, corresponding to these solutions χ_0, χ_1, and χ_2, are given by Eqs. (15),

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13) Ref. 12 will be referred to as I, while equations that appear in it will be referred to (I-—).

14) Equation (5) and (6) are solved by the following recurrent equations:

$$\chi_s(r,t) = \exp(-\beta t)\left[f(t + r^3/3\alpha D) - \frac{D}{\alpha}\int_0^r \exp(-\beta t)\left\{2r\frac{\partial \chi_{s-1}(r,t)}{\partial r} + r^2\frac{\partial^2 \chi_{s-1}(r,t)}{\partial r^2}\right\}\mathrm{d}r_{\,t=c_1-r^3/3\alpha}\right]$$

Where C_1 is a constant, where f is an arbitrary function, and where

$$\begin{aligned}\omega_s(r,t) &= \frac{\exp(-\beta t)}{2r\sqrt{\pi Dt}}\int_0^\infty \xi\varphi(\xi) \times \left[\exp\{-(r-\xi-R_0)^2/4Dt\} - \exp\{-(r+\xi-R_0)^2/4Dt\}\right]\mathrm{d}\xi \\ &+ \frac{\exp(-\beta t)}{2r\sqrt{\pi Dt}}\int_0^t \frac{\exp(\beta\tau)}{\sqrt{t-\tau}}\int_0^\infty \frac{\alpha}{\xi}\frac{\partial \omega_{s-1}(\xi,t)}{\partial \xi} \times \left[\exp\{-(r-\xi-R_0)^2/4D(t-\tau)\} - \exp\{-(r+\xi-R_0)^2/4D(t-\tau)\}\right]\mathrm{d}\xi\mathrm{d}\tau\end{aligned}$$

Where φ (ξ) is the initial distribution of the electrons and where R_0 means the radius of the central-ion core.

15) In the approximation by prescribed diffusion,[7] the product of ω_0 (r, t) and $N^+(t)$ is used for the $C(r, t)$ |solution.

16) for example, I. N. Sneddon, "Fourier Transforms," Mc-Grow-Hill Book Co, Inc., New York (1951), p. 30,

(16), and (17) respectively.

$$G_0(n, R_0) = \int_{R_0{}^3/3}^{\infty} \exp(-n\xi)\mathrm{d}\xi = \exp(-nR_0{}^3/3)/n \tag{15}$$

$$G_1(n, \alpha, D, R_0) = \int_{R_0{}^3/3}^{\infty} (1+nD(3\xi)^{4/3}/\alpha-n^2D(3\xi)^{7/3}/7\alpha)\exp(-n\xi)\mathrm{d}\xi \tag{16}$$

$$G_2(n, \alpha, D, R_0) = \int_{R_0{}^3/3}^{\infty} (1+nD(3\xi)^{4/3}/\alpha-n^2D(3\xi)^{7/3}/7\alpha -4nD^2(3\xi)^{5/3}/\alpha^2+5n^2D^2(3\xi)^{8/3}/2\alpha^2 -24n^3D^2(3\xi)^{11/3}/77\alpha+n^4D^2(3\xi)^{14/3}/98\alpha^2) \times\exp(-n\xi)\mathrm{d}\xi \tag{17}$$

B) Initial Conditions and Approximate Expressions of the Electron Concentration. From Eqs. (8)-(12) the various types of approximate solutions of electron concentrations can be obtained as a function of the time if the initial distribution of the electrons is given. One of the simplest examples of the initial distribution is the δ-function representation for the weight function, $K_s(n)$. When $K_0(n)$ is expressed by the δ-function in Eq. (8), $K_0(n)=\delta(n\text{-}n_0)$, where n_0 means a positive constant, the solution for the zero-th order approximation in the potential control case can be written as:

$$\chi_0(r, t) = \exp\{-(\beta+n_0\alpha)t-n_0r^3/3\} \tag{18}$$

n_0 can be represented by $2/r_{\max}^3$, where $r_{\max}$ is the distance at the maximum value of initial distribution.[12] Then, the electron concentration normalized by the initial value is given by Eq. (19):

$$N_0(t)/N_0(0) = \exp(-\beta t-n_0\alpha t) \tag{19}$$

Similarly, for the first-order approximation in the case of potential control, the distribution, $\chi_1(r, t)$, is:

$$\chi_1(r, t) = (1+n_0Dr^4/\alpha-n_0{}^2Dr^7/7\alpha) \times \exp\{-(\beta+n_0\alpha)t-n_0r^3/3\} \tag{20}$$

Then, $N_1(t)/N_1(0)$ is expressed by Eq. (21):

$$N_1(t)/N_1(0) = \exp(-\beta t-n_0\alpha t) \tag{21}$$

The same expression is obtained for the higher-order approximation for the distribution determined by $K_s(n)=\delta(n\text{-}n_0)$. The distribution determined by the superposition of the δ-function can also be considered:

$$K_0(n) = A\delta(n-n_1)+B\delta(n-n_2) \tag{22}$$

where n_1 and n_2 are positive constants and where A and B are constants for superposition. In this case, $N_0(t)/N_0(0)$ is given by Eq. (23):

$$\frac{N_0(t)}{N_0(0)} = \frac{\begin{pmatrix} An_2\exp(-\beta t-n_1\alpha t-n_1R_0{}^3/3)+ \\ Bn_1\exp(-\beta t-n_2\alpha t-n_2R_0{}^3/3) \end{pmatrix}}{An_2\exp(-n_1R_0{}^3/3)+Bn_1\exp(-n_2R_0{}^3/3)} \tag{23}$$

Similarly, $N(t)/N(0)$ is expressed by Eq. (24):

$$\frac{N_s(t)}{N_s(0)} = \frac{\begin{pmatrix} A\exp(-\beta t-n_1\alpha t)G_s(n_1, \alpha, D, R_0)+ \\ B\exp(-\beta t-n_2\alpha t)G_s(n_2, \alpha, D, R_0) \end{pmatrix}}{AG_s(n_1, \alpha, D, R_0)+BG_s(n_2, \alpha, D, R_0)} \tag{24}$$

The same quantities were evaluate for the diffusion-control equation. For the initial distribution, $\varphi(\xi)=\delta(\xi\text{-}r_{\max})/4\pi r_{\max}^2$, the zero-th order approximation solution is:

$$\omega_0(r, t) = \frac{\exp(-\beta t)}{8\pi r_{\max}r\sqrt{\pi Dt}}[\exp\{-(r-r_{\max}R_0)^2/4Dt\} -\exp\{-(r+r_{\max}-R_0)^2/4Dt\} \quad r>R_0 \tag{25}$$

where $r_{\max}$ is the distance between the electron and the ion for maximum distribution. $N_0(t)/N_0(0)$ is given by Eq. (26):[17]

$$N_0(t)/N_0(0) = \exp(-\beta t)\{1+(R_0/r_{\max})\mathrm{Erf}(r_{\max}/\sqrt{4Dt})\}/(1+R_0/r_{\max}) \tag{26}$$

Results and Discussion

The results of numerical calculation using various paremeters are shown in Figs. 1a and 1b and in Fig.

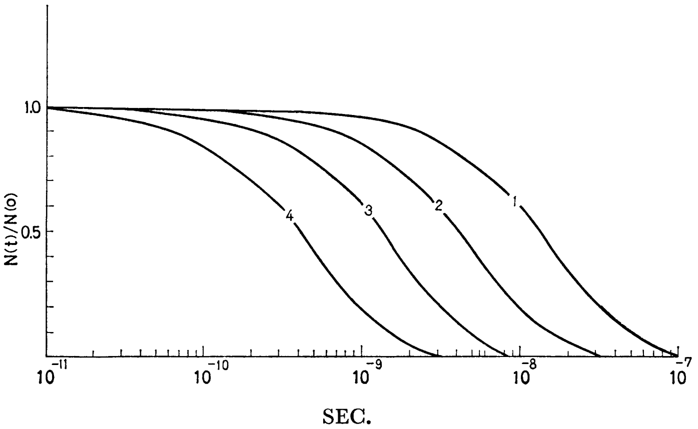

Fig. 1a. Number of electrons in a spur plotted as a function of time in the case of potential control, where the initial value was normalized to be unity. The numerical calculation was carried out using Eq. (23) and the following parameters in CGS unit without scavenger, $\beta=0$.

Curve 1: $A=0.0$, $B=1.0$, $n_1=3.9\times10^{18}$, $n_2=1.2\times10^{18}$, $\alpha=4.3\times10^{-11}$
Curve 2: $A=1.0$, $B=0.0$, $n_1=3.9\times10^{18}$, $n_2=1.2\times10^{18}$, $\alpha=4.3\times10^{-11}$
Curve 3: $A=0.0$, $B=1.0$, $n_1=3.9\times10^{18}$, $n_2=1.2\times10^{18}$, $\alpha=4.3\times10^{-10}$
Curve 4: $A=1.0$, $B=0.0$, $n_1=3.9\times10^{18}$, $n_2=1.2\times10^{18}$, $\alpha=4.3\times10^{-10}$

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[17] The error function, Erf(x), is defined by:

$$\mathrm{Erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x \exp(-z^2)\mathrm{d}z$$

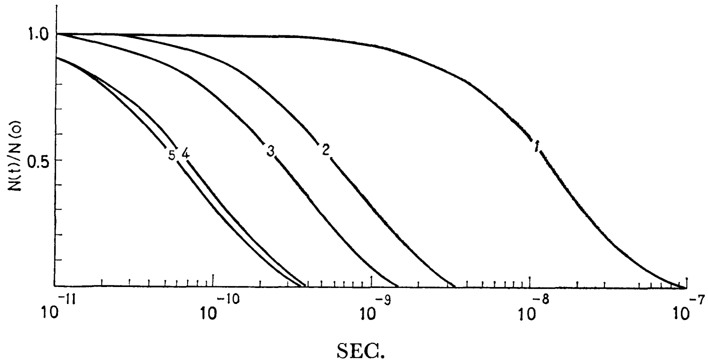

Fig. 1b. Number of electron in a spur plotted as a function of time in the case of potential control in the presence of electron scavenger except for curve 1.

Curve 1: $A=0.0$, $B=1.0$, $n_1=3.9\times10^{18}$, $n_2=1.2\times10^{18}$, $\alpha=4.3\times10^{-11}\sim4.3\times10^{-10}$, $\beta=0.0$, $R=2.0\times10^{-7}\sim1.0\times10^{-7}$
Curve 2: $A=1.0$, $B=0.0$, $n_1=3.9\times10^{18}$, $n_2=1.2\times10^{18}$, $\alpha=4.3\times10^{-11}$, $\beta=1.0\times10^{9}$, $R_0=2.0\times10^{-7}$
Curve 3: $A=1.0$, $B=0.0$, $n_1=3.9\times10^{18}$, $n_2=1.2\times10^{18}$, $\alpha=4.3\times10^{-10}$, $\beta=1.0\times10^{9}$, $R_0=2.0\times10^{-7}$
Curve 4: $A=1.0$, $B=0.0$, $n_1=3.9\times10^{18}$, $n_2=1.2\times10^{18}$, $\alpha=4.3\times10^{-11}$, $\beta=1.0\times10^{10}$, $R_0=2.0\times10^{-7}$
Curve 5: $A=1.0$, $B=0.0$, $n_1=3.9\times10^{18}$, $n_2=1.2\times10^{18}$, $\alpha=4.3\times10^{-10}$, $\beta=1.0\times10^{10}$, $R_0=2.0\times10^{-7}$

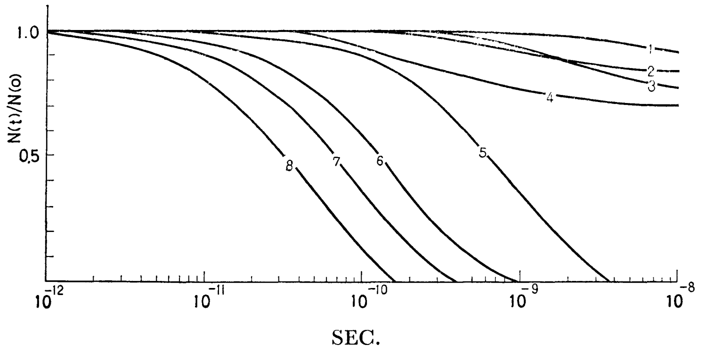

Fig. 2. Number of electrons in a spur plotted as a function of time in the case of diffusion control. The numerical calculation was carried out using Eq. (26) and the following parameters in CGS units.

Curve 1: $D=5\times10^{-5}$, $R_0=2\times10^{-7}$, $r_{\mathrm{max}}=8\times10^{-7}$
Curve 2: $D=5\times10^{-4}$, $R_0=2\times10^{-7}$, $r_{\mathrm{max}}=8\times10^{-7}$
Curve 3: $D=5\times10^{-5}$, $R_0=2\times10^{-7}$, $r_{\mathrm{max}}=4\times10^{-7}$
Curve 4: $D=5\times10^{-4}$, $R_0=2\times10^{-7}$, $r_{\mathrm{max}}=4\times10^{-7}$
Curve 5: $D=5\times10^{-5}$, $R_0=2\times10^{-7}$, $r_{\mathrm{max}}=4\times10^{-7}\sim8\times10^{-7}$, $\beta=1.0\times10^{9}$
Curve 6: $D=5\times10^{-5}$, $R_0=2\times10^{-7}$, $r_{\mathrm{max}}=4\times10^{-7}\sim8\times10^{-7}$, $\beta=5.0\times10^{9}$
Curve 7: $D=5\times10^{-5}$, $R_0=2\times10^{-7}$, $r_{\mathrm{max}}=4\times10^{-7}\sim8\times10^{-7}$, $\beta=1.0\times10^{10}$
Curve 8: $D=5\times10^{-5}$, $R_0=2\times10^{-7}$, $r_{\mathrm{max}}=4\times10^{-7}\sim8\times10^{-7}$, $\beta=2.0\times10^{10}$

2 for the potential-control process and the diffusion-control process respectively. In Fig. 1a, the time dependence of the electron concentration showed sigmoidal curves. The results of numerical calculation in the scavenger-free case are that the relaxation time of electron recombination is in the range of 10^{-10}—10^{-8} sec, depending mainly on the initial distribution of electron. If the scavenger is present in the system, the value of the relaxation time of the electron disappearance becomes much shorter, as is shown in Fig. 1b.

The case of diffusion control is shown in Fig. 2; here the geminate recombination partially took place, in contrast with the complete recombination in the case of potential control,(Fig. 1a). For the large value of scavenger concentration, the time dependence becomes almost equivalent in the diffusion-control and potential-control processes. Therefore, either method offers a reasonable approximation for the concentrated solution of the scavenger. In these calculations, the value of α was assumed to be constant. In the neutralization process, however, the value should be a step function. If $N^+(t)$ in Eq. (2) decreases from four to one by a step function during the successive neutralization, the time dependence of $N^+(t)/N(0)$ is shown in Fig. 3 with the curves for the fixed values of four and one in $N^+(t)$ in Eq. (2). The relaxation time decreased slightly with an increase in the effective charge of the ion core. The effect of the successive neutralization of the effective charge of the ion core from four to one decreases the rate of the electron recombination, (Fig. 3, Curve 4). The half-life of the electron recombination of the successive neutralization, (Curve 4) showed a intermediate value between that of the effective charge of one (Curve 3) and that of the effective charge of four, (Curve 5). Other calculations, *e.g.*, Mozumder's[7], Ludwig's[9],

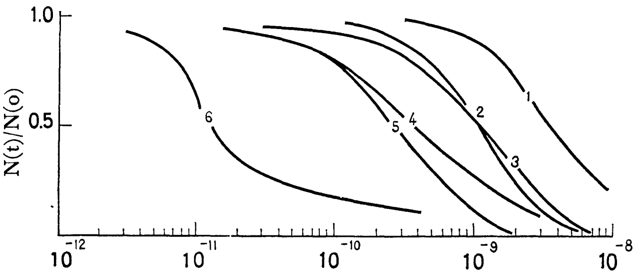

Fig. 3. The electron concentration as a function of time in the various methods of calculation without scavenger.
Curve 1: by Mozumder, (room temperature)
Curve 2: by Ludwig,
Curve 3: core charge to be constants, $N=1$, other parameters are corresponding to the case of curve 3 in Fig. 1a,
Curve 4: core charge to be changed, $N=4\sim1$,
Curve 5: core charge to be constant, $N=4$,
Curve 6: by Freeman

and Freeman's calculations,[5] are also quoted in Fig. 3. The relaxation times of electron recombination are 6×10^{-9}, 1×10^{-9}, 1×10^{-11}, and 4—10×10^{-10} sec for Mozumder, Ludwig, Freeman, and the present calculations respectively, while the corresponding values of $r_{\max}$ are 80, 80—112, 20, and 80—120 Å. Thus, the relaxation time of electron recombination largely depends on $r_{\max}$. The relaxation times evaluated by Ludwig, Mozumder, and the present methods are within the same order of magnitude. The slight difference in the relaxation time is due to the difference in the $r_{\max}$ and $N^+(t)$ values used in these calculations. The shorter relaxation time in the case of Freeman corresponds to the smaller value of $r_{\max}$. Some examples of these initial distributions were illustrated in a previous paper.[12] The real solution, $C(r, t)$, may be somewhere between the potential-control and diffusion-control cases, it is quite similar to $\chi_s(r, t)$ at the smaller distance of r and can be well approximated by $\omega_s(r, t)$ for a large r distance. Therefore, a linear combination of $\chi_s(r, t)$ and $\omega_s(r, t)$ by using a slowly-changing function of distance will provide a better approximation.

In the numerical calculation, the estimation of the various parameters involved in the theory is important in relative the theory to the experimental results. In this work, the main parameters are n, α, β, and R_0. The value of n is expressed in terms of the distance of the maximum distribution, namely, $n=2/r_{\max}^3$. The value of $r_{\max}$ can be determined by the thermalization length of the electron ejected from the parent ion by the primary act of radiation. According to Mozumder and Magee,[18] the value of the effective thermalization length is 80 Å. In this work, two values ($r_{\max}=80$ Å, 120 Å) are used.

The parameter, $\alpha(=N^+(t)eu/\varepsilon)$, of electron recombination can be estimated from the number of ions in the ion core in a spur, $N^+(t)$, and from the mobility of the electron, u. The fixed values of $N^+(t)(=4, 3, 2,1)$ and the variable value of $N^+(t)$ from four to one, decreasing with time as a step function, are considered in this work. The value of the mobility of the electron of $2\times10^{-3--4}$ cm^2 v^{-1} sec^{-1}[19] was used in estimating α. The β parameter is defined as the product of the rate constant and the concetration of the scavenger. The rate constants of most scavengers have an order of magnitude of 10^{10} M^{-1} sec^{-1}, and usually an appreciable effect of the scavenger is observed in the concentrations of the scavenger beginning from 10^{-1} M, so the value of β used in this calculation is in the range of $1.0\times10^{9-10}$ in terms of the scavenger effect. The reaction radius of the recombination of the electron and ions is in the range of 10 Å—20 Å, where the electron escape from the recombination seems to be negligible.

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[19] This value has been used in most calculations. Recently, quite a large value of u ($=2\times10^{-1}$ cm^2 V^{-1} sec^{-1}) was reported by Conrad and Silverman.[20] If this value had been used in the present calculation, Curves 3,4, and 5 in Fig. 3 would have shifted to shorter life times, thus coming to have the same order of magnitude as in Freeman's data, (Curve 6). On the contrary, a small value of u ($\approx1\times10^{-5}$ cm^2 V^{-1} sec^{-1}) can be expected from the experimental results of the pulse radiolysis of viscous squalane[21] at a low temperature and with a lifetime of over 10^{-6} sec, where bound and unbound states of electrons may be in equilibrium.

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