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A Theoretical Consideration of the Electron-scavenging Process in Liquid Hydrocarbons

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The electron-scavenging process by a scavenger and the random recombination between ions and electrons in a spur in the radiolysis of nonpolar hydrocarbons have been investigated theoretically on the basis of the extended type of Smoluchowski equation. To obtain the approximate solutions, a model of the distribution of charged species in which a positive ion core is surrounded by electrons is assumed; several approximations are also made during the calculation. The reaction rate of the electron scavenging is expressed by the overlapping integral between the concentration of the electrons and that of the scavenger. The rate of the recombination reaction is approximately expressed as the total flux of the electrons flowing into the core of parent ions. The *G* value of electron scavenging shows a Langmuir-type dependence on the concentration of the electron scavenger. The values of the slope of the sigmoidal curve at the mid point and of the corresponding scavenger concentration almost agree with the experimental value.

In recent years a considerable number of experiments have been made on the ionic process in the radiation chemistry of liquid hydrocarbons; the quantitative interpretations of the experiments have become more important in ascertaining the various rates in the primary process. The theoretical treatments proposed hitherto for the reactions of the primary ionic process can be classified into the following four groups. The first method, utilized by Freeman[1,2] and by Sato *et al.*,[3,4] deals with the geminate recombination of ions, assuming an initial distribution of ion pairs. They evaluated the *G* value of free-electron formation as a function of the concentration of scavengers. The method seems to be successful in explaining the experimental results in nonpolar solvents. The second method, used by Monchick,[5] Mozumder,[6] and Hummel,[7] is based on the Smoluchowski equation of the distribution function of ion pairs in a static electric field. The third method, used by Schuler *et al.*,[8] investigates the reactions of ionic species by the scavenger technique and derives a simple formula from the nonhomogeneous kinetics of the recombination and scavenging processes. The last method, used by Schiller,[9,10] attempts to discuss the expansion and contraction of a spur or a track

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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] L. Monchick, *J. Chem. Phys.*, **24**, 381 (1956).

[6] A.Mozumder, *ibid.*, **48**, 1659 (1968).

[7] A. Hummel, *ibid.*, **48**, 3268 (1968).

[8] J. M. Warman, K. -D. Asmus and R. H. Schuler, *Advan. Chem. Ser.*, **82**, 25 (1968).

[9] R. Schiller, *J. Chem. Phys.*, **43**, 2760 (1965).

[10] R. Schiller, *ibid.*, **47**, 2278 (1967).

using a thermodynamic consideration with Debye's linear response between electric field and electric displacement, and to compare the theoretical values. These theories have been tested by the following experiments: (1) scavenger method,[3,8] (2) decay of the solvated electrons in pulse radiolysis,[11] (3) luminescence intensity due to the recombination after pulse radiolysis.[12,13]

Even in the detailed calculations of the first and second methods, the random recombinations between ions and electrons in a spur or a track have been ignored. This corresponds to the assumption of a simplified spur involving an electron and an ion. However, this effect of random recombination in a spur is important, especially for a spur or a track with a high ionization density. This paper will present a theory using a distribution function of ionic species and considering random recombination in a spur or a track, as in the diffusion theory of radicals.[14] Since the effect of dielectric relaxation in nonpolar solvents can be ignored, it is necessary only to consider the movements of ionic species under a static electric field.

Theory

A) Basic Equation and Its Approximation. The basic equation of distribution functions for positive and negative species may be represented in the following form of the extended Smoluchowski equations:

$$\frac{\partial C^-}{\partial t} = u \text{ grad } C^- \cdot \text{grad}\psi + uC^- \nabla^2 \psi + D_- \nabla^2 C^- - k_S{}^- S^- C^- - k_C C^+ C^- \tag{1}$$

$$\frac{\partial C^+}{\partial t} = -u \text{ grad } C^+ \cdot \text{grad}\psi - uC^+ \nabla^2 \psi + D_+ \nabla^2 C^+ - k_S{}^+ S^+ C^+ - k_C C^+ C^- \tag{2}$$

where the plus and minus signs of the superscripts and the subscripts denote the quantities for positive ions and electrons; C is the distribution function, D is the diffusion constant, u is the mobility, ψ is the static electric potential, S is the concentration of the scavenger, and k_S and k_C are the rate constants. ψ and C are connected by the Poisson equation (3):

$$\nabla^2 \psi = 4\pi \boldsymbol{e}(C^+ - C^-) \tag{3}$$

where $\boldsymbol{e}$ is the electron charge.

The G value of the recombination reaction can be expressed as the overlapping of the concentrations of the species, as shown in Eqs. (4), (5) and (6), if the original equations can be solved:

$$S_\beta^\pm = k_S^\pm S^\pm \iint C^\pm \mathrm{d}v\mathrm{d}t \tag{4}$$

$$S_n = k_C \iint C^+ C^- \mathrm{d}v\mathrm{d}t \tag{5}$$

$$(G_\pm / G_\pm^\circ) = 1 \Big/ \Big\{ 1 + (k_S^\pm S^\pm \iint C^\pm \mathrm{d}v\mathrm{d}t / k_C \times \iint C^+ C^- \mathrm{d}v\mathrm{d}t) \Big\} = 1/(1 + S_\beta / S_n) \tag{6}$$

where $G_\pm^0$ is the G value of total ionization and where $G_\pm$ is the G value of the recombination reaction of positive ions and electrons.

The last terms in Eqs. (1) and (2) are important, especially for the track with a high ionic density. However, in a track or in a spur ions and electrons seem to be separated from each other as a central ion core surrounded by the electron cloud, so that the overlap of these species can be neglected in the initial distribution. The term of overlapping can be approximated as the total flux of electrons flowing into the central ion core, where the overlap of the distribution of the ions and electrons is quite appreciable in the course of reaction. However, due to the non-linearity of the equations it is generally difficult to solve these equations. Therefore, appropriate approximations are required to obtain the distribution of electrons. Equations (1), (2), and (3) may be expressed as a function of r and t in the cylindrical or spherical coordinate by ignoring the last term of the second-order reaction:

$$\frac{\partial C^-}{\partial t} = u\left(\frac{\partial \psi}{\partial r}\right)\frac{\partial C^-}{\partial r} + C^- u(1/r^n)\frac{\partial}{\partial r}\left(r^n \frac{\partial \psi}{\partial r}\right) + D_-(1/r^n)\frac{\partial}{\partial r}\left(r^n \frac{\partial C^-}{\partial r}\right) - k_S^- S^- C^- \tag{7}$$

$$\frac{\partial C^+}{\partial t} = -u\left(\frac{\partial \psi}{\partial r}\right)\frac{\partial C^+}{\partial r} - C^+ u(1/r^n)\frac{\partial}{\partial r}\left(r^n \frac{\partial \varphi}{\partial r}\right) + D_+(1/r^n)\frac{\partial}{\partial r}\left(r^n \frac{\partial C^-}{\partial r}\right) - k_S^- S^- C^- \tag{8}$$

($n=1$, cylindrical coordinate; $n=2$, spherical coordinate)

The potential function in the equation is given by Eq. (9) for the spherical coordinate:

$$\psi(r,t) = \boldsymbol{e}(N^+)r,t(-N^-(r,t))/\varepsilon r \tag{9}$$

where ε is the dielectric constant and where

$$N^\pm(r,t) = \int_0^r C^\pm(r,t)\mathrm{d}v \tag{10}$$

One of the simplest models of the distribution of species is that the positive ion cluster is surrounded by the electrons ejected from the central ion cluster. If the ions are confined within the radius, r, the force from the central ion cluster is expressed by Eq. (11). In this approximation the motion of the electrons is much faster than that of ions, so that the spacial distribution of electrons is given by Eq. (12), which is reduced to the usual form of the Smoluchowski equation when $N^+(t)=1$ and $k_S^- S_S^- = 0$

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[11] J. P. Keene, E. J. Land and A. J. Swallow, *J. Amer. Chem. Soc.*, **87**, 5284 (1965).

[12] P. K. Ludwig and M. Burton, *Advan. Chem. Ser.*, **82**, 542 (1968).

[13] P. K. Ludwig, *J. Chem. Phys.*, **50**, 1787 (1969).

[14] A. H. Samuel and J. L. Magee, *ibid.*, **21**, 1080 (1953).

$$\nabla^2\phi = 0 \quad r>R_0,$$

$$\mathrm{grad}\phi\cdot\mathrm{grad}\ C^- = \left(\frac{\partial C^-}{\partial r}\right)\left(\frac{N^+(t)e}{\varepsilon r^2}\right) \tag{11}$$

$$\frac{\partial C^-}{\partial t} = \left\{\frac{uN^+(t)e}{\varepsilon r^2}\right\}\frac{\partial C^-}{\partial r} + \frac{D_-}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C^-}{\partial r}\right) - k_S^- S^- C^- \tag{12}$$

where R_0 means the radius of the central ion core. In the following discussion, the plus and minus signs of the superscripts and the subscripts are omitted for the sake of simplicity, because only the distribution of electrons is going to be discussed. The total amount of the recombination reaction can be approximated by the total flux of the electrons flowing into the core of the parent ions in place of Eq. (5). The flux consists of the terms of the diffusion and the electric potential:

$$S_n = u \iint_{R_0} \left(C\ \mathrm{grad}\phi + \frac{D}{u}\mathrm{grad}C\right)\mathrm{d}s\mathrm{d}t \tag{13}$$

When G_- and $G_-{}^0$ are expressed by G_e and $G_e{}^0$ respectively, Eq. (6) gives Eq. (14). The two terms in Eq. (13) are going to equilibrate at the r_c distance.

$$(G_e/G_e{}^0) = 1/(1+S_\beta/S_n) \tag{14}$$

$$[u\ C\ \mathrm{grad}\phi + D\ \mathrm{grad}C]_{r_c} = 0 \tag{15}$$

The electrons separated by a longer distance than r_c become free electrons. In the case of a pair consisting of an ion and an electron, the scavenging probability is expressed by the function of r/r_c, and r_c is a constant. However, in the ion-cluster system it varies with the time. The next step is the actual calculation of the concentration distribution. Several models may be proposed for evaluating the distribution function.

B) Model I. The first model is derived by ignoring the diffusion term and by using $\bar{N}$, the mean number of ions for $N^+(t)$ in Eq. (11):

$$\frac{\partial C}{\partial t} = \frac{\alpha}{r^2}\frac{\partial C}{\partial r} - \beta C \tag{16)*1}$$

where $\alpha = \bar{N}eu/\varepsilon$ and $\beta = k_s S$. When $C(r,t)$ is factorized by $T(t)\cdot R(r)$, the factorized functions are given by the following equations:

$$T(t) = c\ \exp\{(-\beta + m\alpha)t\},\ R(r) = c\ \exp(mr^3/3) \tag{17}$$

where c and m are constants. The solution is obtained by the superposition of these solutions. One of the boundary condition is $C(\infty,\infty)=0$, so m should be negative.

By substituting n for $|m|$, the solution is given by Eq. (18):

$$C(r,t) = \sum_n c_n\ \exp\{-(\beta+n\alpha)t\}\cdot\exp(-nr^3/3) \tag{18}$$

where c_n are constants determined by the initial distribution. The distribution of electrons can be approximated by considering only one term in the summation of Eq. (18). The probability of the initial distribution, $\phi(r,0) = (1/N^-)C(r,0)\cdot$

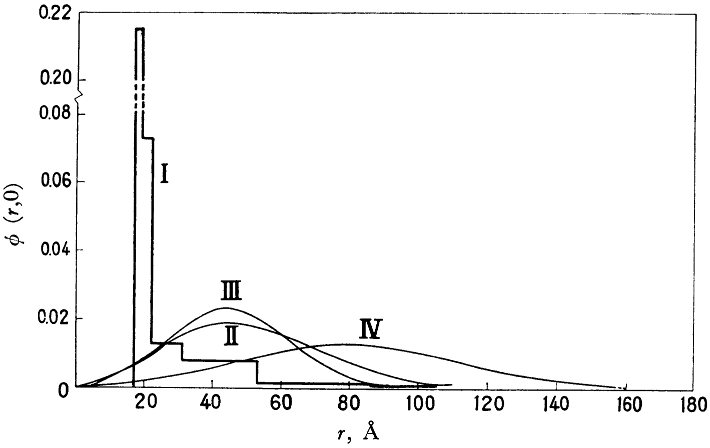

Fig. 1. The initial distribution of the separation distance between the positive-ion core and the surrounding negative electron cloud along with those estimated by Freeman and by Sato for ion pairs.

ϕ (r, 0): the probability of initial distribution of the separation distance between the ion pairs in the cases of I and II and between the potitive-ion core and the surrounding negative electron cloud in the cases of III and IV; I: by Freeman, see Ref. 1 and Ref. 4; II: by Sato, see Ref. 4; III: this work, assuming that the distance, r_{max}, at a maximum initial distribution coincides with the distance where curve II reaches its maximum ($r_{max} \cong 45$ Å); IV: this work, assuming that $r_{max} = 80$ Å.

[*1] The general solution of Eq. (16) can be expressed by:

$$C(r,t) = \exp(-\beta t)\cdot f(t+r^3/3\alpha) \tag{18'}$$

where f is an arbitrary function.

$4\pi r^2$, obtained by means of Eq. (18) is shown in Fig. 1, along with the results of Freeman and of Sato. The value of r_{max} was chosen as 80 Å in the tentative calculations in view of the previous values,*2 but the curve corresponding to 45 Å is also shown in Fig. 1. The overlap between the electron and scavenger distribution may be evaluated as follows:

$$S_\beta = k_S S\int_{R_0}^{\infty} C(r,t)\ 4\pi r^2 \mathrm{d}r\mathrm{d}t$$

$$= \frac{4\pi C k_S S\ \exp(-nR_0^3/3)}{n(\beta+n\alpha)} \tag{19}$$

In the vicinity of the ion cluster, the total current of electrons can be approximated by the electric potential term. The flux of electrons flowing into the central ion cluster is, then, obtained by means of Eq. (20):

$$S_n = \frac{4\pi\bar{N}euC}{\varepsilon(\beta+n\alpha)}\exp(-nR_0^3/3) \tag{20}$$

The ratio of the G values, G_e/G_e^0, of the electron formation is given by Eq. (21). The G_e/G_e^0 is expressed as a sigmoidal curve of the first order of the concentration of the electron scavenger:

$$(G_e/G_e^0) = 1/(1+k_S S\varepsilon/\bar{N}eun) \tag{21}^{*3}$$

C) Model II. In the second model the diffusion term is ignored. However, the change in the number of ions in the central cluster is considered to be a function of the time. The basic equation is, then, given by Eq. (22):

$$\frac{\partial C}{\partial t} = \frac{N(t)eu}{\varepsilon r^2}\frac{\partial C}{\partial r} - k_S SC \tag{22}$$

As in the previous model, the use of factorization, $C(r,t) = T(t)\cdot R(r)$, yields the following equation:

$$\frac{1}{\alpha(t)T(t)}\frac{\partial T(t)}{\partial t} + \frac{\beta}{\alpha(t)} = m \tag{23}$$

$$\frac{1}{r^2R(r)}\frac{\partial R(r)}{\partial r} = m$$

where $\alpha(t)$ and β are given by $\alpha(t)=N(t)eu/\varepsilon$ and $\beta = k_S S$. By the integration of these equations, $T(t)$ and $R(r)$ are obtained:

$$T(t) = c\ \exp(-\beta t)\cdot\exp\left\{m\int^t \alpha(t)\mathrm{d}t\right\} \tag{24}$$

$$R(r) = c\ \exp(mr^3/3)$$

Therefore, the general solution of Eq. (22) is given by the superposition of the product of $T(t)$ and $R(r)$ and by the substitution of n for $|m|$, since m should be negative.

$$C(r,t) = \sum_n c_n\ \exp(-\beta t)$$

$$\times \exp\left\{-n\int^t \alpha(t)\mathrm{d}t\right\}\exp(-nr^3/3) \tag{25}$$

The overlapping, S_β, and the flux, S_n, can be evaluated as in the case of the first model.

$$S_\beta = 4\pi k_S S\sum_n c_n\int_0^\infty \exp\left\{-\beta t - n\int^t \alpha(t)\mathrm{d}t\right\}$$

$$\times\frac{1}{n}\exp(-nR_0^3/3)\mathrm{d}t \tag{26}$$

$$S_n = 4\pi\sum_n c_n\int_0^\infty \alpha(t)$$

$$\times \exp\left\{-\beta t - n\int^t \alpha(t)\mathrm{d}t\right\}\exp(-nR_0^3/3)\mathrm{d}t \tag{27}$$

Therefore, the S_β/S_n ratio is given by Eq. (28):

$$S_\beta/S_n = k_S S\varepsilon/eu\langle N(t)\cdot n\rangle \tag{28}$$

where $N(t)\cdot n$ is given by Eq. (29):

$$\langle N(t)\cdot n\rangle =$$

$$\frac{\int\sum_n N(t)\cdot n\cdot\frac{c_n}{n}\exp\left\{-\beta t - n\int^t\alpha(t)\mathrm{d}t\right\}\exp(-nR_0^3/3)\mathrm{d}t}{\int\sum_n\frac{c_n}{n}\exp\left\{-\beta t - n\int^t\alpha(t)\mathrm{d}t\right\}\exp(-nR_0^3/3)\mathrm{d}t} \tag{29}$$

The final expression of the G value as a function of the scavenger concentration is given by Eq. (30):

$$(G_e/G_e^0) = 1/\{1+k_S S\varepsilon/eu\langle N(t)\cdot n\rangle\} \tag{30}$$

where the brackets express the average of the quantities. The average value can be written by the one-term approximation:

$$\langle N(t)\cdot n\rangle = \frac{n\int_0^\infty N(t)\exp\left\{-n\int_0^t\alpha(t)\mathrm{d}t-\beta t\right\}\mathrm{d}t}{\int_0^\infty\exp\left\{-n\int^t\alpha(t)\mathrm{d}t-\beta t\right\}\mathrm{d}t} \tag{31}$$

If $\alpha(t)$ is assumed to be a decreasing function expressed by a second-order reaction, $\alpha(t)=1/(1/\alpha(0)+bt)$, Eq. (31) is reduced to Eq. (32):

$$\langle N(t)\cdot n\rangle = \frac{n\varepsilon}{eu}\frac{\int_0^\infty(1/\alpha(0)+bt)^{-n/b-1}\exp(-\beta t)\mathrm{d}t}{\int_0^\infty(1/\alpha(0)+bt)^{-n/b}\exp(-\beta t)\mathrm{d}t} \tag{32}$$

where $\alpha(0)$ and b denote the initial value of $\alpha(t)$ at $t=0$ and a positive constant respectively. Therefore, after the integration of Eq. (32), and assuming $n/b\approx 1$ and $\alpha(0)/\alpha\approx 2$, (G_e/G_e^0) can be expressed as in Eq. (33):

$$(G_e/G_e^0) = 1/\{1+k_S S\varepsilon/1.4eu\bar{N}n\} \tag{33}$$

D) Model III. In the third model the effect of diffusion is taken into account, so that the

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*2 For example, Sato,[4] r_{max} ($\cong$45 Å); Ludwig,[13] r_{max} (=80 Å, 112 Å).

*3 By using the general solution (18″),

$$C(r,t) = \exp(-\beta t)\int_0^\infty F(n)\exp\{-n(\alpha t+r^3/3)\}\mathrm{d}n \tag{18''}$$

where $F(n)$ is an arbitrary function of n, the G value is evaluated as a function of the scavenger concentration.

$$(G_e/G_e^0) = 1/\left\{1+\left(\beta\int_0^\infty F(n)e^{-nR_0^3/3}\frac{1}{n(\beta+n\alpha)}\mathrm{d}n\right.\right.$$

$$\left.\left./\alpha\int_0^\infty F(n)e^{-nR_0^3/3}\frac{1}{(\beta+n\alpha)}\mathrm{d}n\right)\right\} \tag{21'}$$

basic equation of the distribution is as given by Eq. (34):

$$\frac{\partial C}{\partial t}=\left(\frac{uNe}{\varepsilon r^2}\right)\frac{\partial C}{\partial r}+\frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right)-k_S SC \tag{34}$$

The following two equations are obtained by factorizing $C(r,t)$:

$$\frac{1}{T(t)}\frac{\mathrm{d}T(t)}{\mathrm{d}t}+\beta=-n\alpha$$

$$\frac{\mathrm{d}^2R(r)}{\mathrm{d}r^2}+\left(\frac{2}{r}+\frac{\alpha}{Dr^2}\right)\frac{\mathrm{d}R(r)}{\mathrm{d}r}+\frac{n\alpha}{D}R(r)=0 \tag{35}$$

By multiplying the appropriate coefficient M_n, the solution is expressed by an integral form:

$$C(r,t)=\sum_n M_n\cdot R_n(r)\cdot T_n(t) \tag{36}$$

S_β and S_n are then evaluated from $C(r,t)$ by:

$$S_\beta=k_S S\sum_n M_n\int R_n(r)\mathrm{d}v\cdot\int T_n(t)\mathrm{d}t \tag{37}$$

$$S_n=\frac{uNe}{\varepsilon R_0^2}\sum_n M_n\int R_n(R_0)\mathrm{d}s\int T_n(t)\mathrm{d}t \tag{38}$$

(G_e/G_e^0) can be expressed by a formula of the Langmuir type:

$$(G_e/G_e^0)=$$

$$1\Big/\left[1+\left(\frac{k_S S\varepsilon R_0^2}{u\overline{N}e}\right)\frac{\sum_n M_n\left\{\int R_n(r)\mathrm{d}v\right\}\cdot\left\{\int T_n(t)\mathrm{d}t\right\}}{\sum_n M_n\left\{\int R_n(R_0)\mathrm{d}s\right\}\cdot\left\{\int T_n(t)\mathrm{d}t\right\}}\right] \tag{39}$$

Since S is involved in the integrals of $R_n(r)$ and $T_n(t)$, the actual result is generally quite a complicated function of S. However, a simplified approximation of the integrals gives a Langmuir formula of the first order of S:

$$(G_e/G_e^0)=\left\{1+\frac{k_S S\varepsilon}{ue\overline{N}}\cdot K\cdot\frac{1}{n}\right\} \tag{40}$$

and:

$$K=$$

$$\frac{1+\{\Gamma(7/3)3^{4/3}-(1/7)\Gamma(10/3)3^{7/3}\}(D/\alpha n^{1/3})\exp(nR_0^3/3)}{[1+DnR_0^4/\alpha-Dn^2R_0^7/7\alpha]}$$

where n is a constant.

E) Results and Discussion. The result of the scavenger reaction is usually expressed by a plot of G_e/G_e^0 against the logarithm of the scavenger concentration, which shows a sigmoidal which is characterized by the concentration of the midpoint of the curve and the value of the slope at that point.

As the first step in comparing theory and experiment, let us examine the slope of the sigmoidal curve. In this theory the slope at the middle of the sigmoidal curve is given by Eq. (41):

$$\left(\frac{\mathrm{d}(G_e/G_e^0)}{\mathrm{d}\ \log[S]}\right)_{1/2}=-\frac{1}{4\log \mathrm{e}}[S]_{1/2}\left(\frac{\mathrm{d}(S_\beta/S_n)}{\mathrm{d}[S]}\right)_{1/2} \tag{41}$$

where the 1/2 suffix indicates the values corresponding to $G_e/G_e^0=1/2$.

TABLE 1. COMPARISON OF THEORY AND EXPERIMENT OF THE SLOPE AT $G_e/G_e^0=1/2$

Theoretical	Experimental
First model: $-\frac{1}{4\log \mathrm{e}}=-0.58^{(a)}$	$-0.50^{(e)}$
	$-0.47^{(f)}$
Second model: $-\frac{1}{4\log \mathrm{e}}=-0.58^{(b)}$	$-0.49^{(g)}$
	$-0.57^{(h)}$
Third model: $-\frac{1}{4\log \mathrm{e}}=-0.58^{(c)}$	$-0.40^{(i)}$

(a), (b) and (c) are calculated according to Eqs. (21), (33) and (40), respectively.

(d) All the experimental values in Table 1 are obtained by assuming that $G_e^0=3.0$.

(e) Obtained from the curve of cyclohexane-N_2O system in Ref. 4.

(f) Obtained from the curve of cyclohexane-C_2H_5OD system in Ref. 4.

(g) Obtained from the curve of cyclohexane-N_2O system in Ref. 1.

(h) Obtained from the curve of cyclohexane-D_2S system in Ref. 1.

(i) Obtained from the curve of cyclohexane-CH_3Cl system in Ref. 8.

TABLE 2. COMPARISON OF THEORY AND EXPERIMENT OF THE SCAVENGER CONCENTRATION AT $G_e/G_e^0=1/2$

Theoretical (mol/l)	Experimental (mol/l)
First model: $\frac{u\overline{N}en^{(a)}}{k_S\varepsilon}=0.17—0.017$	$0.020^{(e)}$
	$0.131^{(f)}$
Second model: $\frac{1.4\,u\overline{N}en^{(b)}}{k_S\varepsilon}=0.24—0.024$	$0.019^{(g)}$
	$0.131^{(h)}$
Third model: $\frac{u\overline{N}en^{(c)}}{k_S\varepsilon K}=0.17—0.017$	$0.056^{(i)}$

* The superscripts in this table, (a)—(i), are the same with those in Table 1.

** In the calculation the following values are used: ε; the dielectric constant, 2, u; the mobility of electron for unit force, $6.0\times 10^{-1\sim-2}$ esu cm sec^{-1} dyn^{-1} $(=2\times10^{-3\sim-4}$ cm^2 v^{-1} sec$^{-1})$, r_{max}; the radius where the distribution probability, $\frac{4\pi}{N^-}r^2C(r,t)\mathrm{d}r$ becomes maximum, 80 Å, $\overline{N}$; the average number of positive ions in cluster, 3, k_S; the reaction constant of electron with scavenger, 10^{10} M^{-1} sec^{-1}, e; the electron charge, 4.8×10^{-10} esu.

*** The following points are also taken into consideration. n can be replaced by $2/r_{max}^3$. D is the diffusion constant of electron calculated from the relation, $D=ukT/e$ where k is Boltzmann's constant, 1.38×10^{-16} erg·deg^{-1} and T is the absolute temperature taken as 300°K in this calculation and the evaluated value of D is $5.1\times10^{-5\sim-6}$ cm^2 sec^{-1}. K is the correction factor for diffusion process and the evaluated value of K is 1.

The values evaluated from the various models are shown in Table 1 along with the experimental values.

As the second measure, the value of the concentration at the mid-point of the sigmoidal curve is shown in Table 2. As is shown in Table 1 and Table 2, the theoretical values agree almost entirely with the experimental values. An even more plausible result can be obtained by changing N, *e.g.*, from four to zero, and by combining solutions with various values of N. The theory can be extended for the analysis of the effect of LET and the dependence of the density of the reactant on the electron-scavenging process.

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