

A Theoretical Consideration of the Electron-scavenging Process In Liquid Hydrocarbons. III. Integral Transforms of the Distribution Functions

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The relations of integral transforms between various distribution functions are discussed using the potential control approximation ignoring the diffusion term in the Smoluchowski equation; the initial spatial distribution of the electron-ion pair or the initial distribution of electrons from the central ion core in a spur, $\chi(r, 0)$; the relative G -value of electron recombination, $G(k_s C_s)$, as a function of the concentration of the scavenger and the rate constant; the time dependence of the electron concentration, $N(t)$, after pulse irradiation; and the relaxation time spectrum, $K(n)$, of the decay of the electron concentration after pulse irradiation or of the weight function, $K(n)$, in the initial exponential distribution of thermalized electrons in a spur are shown to be connected by the square diagram of Laplace transforms:

$$\begin{array}{ccc} K(n) & \xrightarrow{\text{Laplace Transform}} & \chi(r, 0) \\ \downarrow \text{Laplace Transform} & & \downarrow \text{Laplace Transform} \\ N(t) & \xrightarrow{\text{Laplace Transform}} & G(k_s C_s) \end{array}$$

By the use of this relation, the various distribution functions are evaluated from the empirical formulas of $G(k_s C_s)$ proposed by Schuler *et al.* and by Hummel.

Recently many experimental results of various methods of the radiolysis of liquid hydrocarbons have been accumulated, and it has been shown that the quantities measured are connected by the functional relations. Schuler *et al.*¹⁾ proposed that the concentration dependence of the G -value of electron recombination and the change in ionic species after pulse radiolysis as a function of the time were related by the Laplace transform. Sato and Oka²⁾ and Tatsuya³⁾ found that the initial distribution of the electron-ion pair and the G -value of the electron recombination as a function of the scavenger concentration were interchangeable by the Laplace transform. In their studies, no information about the spatial distribution of electrons from the Smoluchowski equation is necessary in deriving these relations between functions. In a previous paper⁴⁾ the inverse Laplace transform was used by the present authors to obtain the lifetime spectrum in the decay function of the electron concentration, based on the Smoluchowski equation.

In this paper it is shown that, in addition to these rather phenomenological relations, the lifetime spectrum of the decay of the electron concentration is equivalent to the weight function of the superposition of the initial distribution. Four functions, $\chi(r, 0)$, $G(k_s C_s)$, $N(t)$, and $K(n)$, which indicate the initial distribution of electrons from the central ion core in a spur, the concentration dependence of the G -value of the electron recombination, the time dependence of the electron concentration, and the relaxation time spectrum respec-

tively, can be related by the Laplace transform by using the approximate solution ignoring the diffusion term of the Smoluchowski equation from the microscopic point of view. Thus, the experimental results are interconnected by these relations and depend on each other.

Theory

A. The Four Characteristic Functions and Their Transformations.

Phenomenological treatment is possible for the relation between the relative G -value of the electron recombination as a function of the scavenger concentration, $G(k_s C_s)$, and the electron concentration after pulse irradiation, $N(t)$, and for that between $G(k_s C_s)$ and the initial distribution of electrons, $\chi(r, 0)$. However, the introduction of the distribution functions of the electron concentration as spatial and time functions is necessary in order to describe these relations in detail and to extend them. An extended form of the Smoluchowski equation is used to obtain the approximate distribution function of electrons and to treat the effect of the spur.

The extended form of Smoluchowski equation for the spatial distribution of electrons in a spherical spur is expressed by Eq. (1)⁴⁾:

$$\frac{\partial C(r, t)}{\partial t} = D \frac{\partial^2 C(r, t)}{\partial r^2} + \left(\frac{2D}{r} + \frac{\alpha}{r_2} \right) \frac{\partial C(r, t)}{\partial r} - \beta C(r, t) \quad (1)$$

where r , t , D , and $C(r, t)$ refer to the radial distance, the time, the diffusion constant, and the distribution function of electrons, and where α and β are constants and are given by:

$$\alpha = N^+ eu/\epsilon \quad (2)$$

$$\beta = k_s C_s \quad (3)$$

where N^+ is the average number of ions in the core, e is the electron charge, u is the mobility of electrons, ϵ is

1) S. J. Rzed, P. P. Infelta, J. M. Warman, and R. H. Schuler, *J. Chem. Phys.*, **52**, 3971 (1970).

2) S. Sato and T. Oka, *This Bulletin*, **44**, 856 (1971).

3) M. Tatsuya, The 13th Conference of Radiation Chemistry, October (1970), Tokyo.

4) H. Yamazaki and K. Shinsaka, *This Bulletin*, **44**, 2611 (1971).

the dielectric constant, k_s is the rate constant of scavenging, and C_s is the concentration of the scavenger. The successive approximation of the potential control case is convenient in obtaining the solution.⁴⁾ The solution of the zeroth order equation,

$$\frac{\partial \chi_0(r, t)}{\partial t} = \frac{\alpha}{r^2} \frac{\partial \chi_0(r, t)}{\partial r} - \beta \chi_0(r, t) \quad (4)$$

is given by:

$$\chi_0(r, t) = \int_0^\infty K_0(n) \exp(-\beta t - n\alpha t - nr^3/3) dn \quad (5)$$

Thus, the approximate solution is given by the superposition of the exponential function with a weight function, $K_0(n)$. The initial distribution is expressed by:

$$\chi_0(\sqrt[3]{3\xi}, 0) = \int_0^\infty K_0(n) \exp(-n\xi) dn \quad (6)$$

by the substitution of the distance by $\xi = r^3/3$. In Eq. (6) the initial distribution is expressed by the Laplace transform of $K_0(n)$. Therefore, the weight function in the spur distribution, $K_0(n)$, is evaluated by the inverse Laplace transform of the initial distribution function and is given by:

$$K_0(n) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \chi_0(\sqrt[3]{3\xi}, 0) \exp(n\xi) d\xi \quad (7)$$

The total number, $N_0(t)$, of the electrons is obtained by the integration of the distribution function of electrons over a spur and is expressed by:

$$N_0(t) = 4\pi \int_{R_0}^\infty \chi_0(r, t) r^2 dr \quad (8)$$

where R_0 is the reaction radius of the recombination between an electron and an ion. Then, $N_0(t)$ is evaluated by Eqs. (5) and (8):

$$N_0(t) = 4\pi \int_0^\infty K_0(n) g_0(n, R_0) \exp(-n\alpha t) dn \quad (9)$$

where $g_0(n, R_0)$ is given by:

$$g_0(n, R_0) = \exp(-nR_0^3/3)/n \quad (10)$$

The lifetime spectrum of the electrons, $K_0(n)$, is evaluated by the inverse Laplace transform:⁴⁾

$$K_0(n) g_0(n, R_0) = \frac{1}{8\pi^2 i} \int_{c-i\infty}^{c+i\infty} N_0(p/\alpha) \exp(np) dp \quad (11)$$

The decay of the electron concentration after pulse irradiation was treated by Schuler *et al.*,¹⁾ and for an infinitesimal short duration of pulse irradiation the relation between $N_0(t)$ and $G(\beta)$ was given by:

$$G(\beta) = - \int_0^\infty \frac{d}{dt} \left(\frac{N_0(t)}{N_0(0)} \right) \exp(-\beta t) dt \quad (12)$$

where $G(\beta)$ is the portion of the G -value of electron recombination. Then, the inverse Laplace transform yields $N_0(t)$ by:

$$- \frac{d}{dt} \left(\frac{N_0(t)}{N_0(0)} \right) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} G(\beta) \exp(\beta t) d\beta \quad (13)$$

A similar relation was obtained between the initial distribution of electrons and the G -value of the electron recombination or the scavenging process, if the effect of the diffusion term of electron is ignored, where the position of the electron at time t after pulse irradiation is

determined by a time-distance relation.⁵⁾ $G(\beta)$ is expressed in terms of the Laplace transform of the initial distribution of electrons by:

$$G(\beta) = \frac{\int_0^\infty \chi_0(\sqrt[3]{3\xi} + R_0^3, 0) \exp(-\beta\xi/\alpha) d\xi}{\int_0^\infty \chi_0(\sqrt[3]{3\xi} + R_0^3, 0) d\xi} \quad (14)$$

where R_0 is the reaction radius. The inverse Laplace transform yields the initial distribution by:

$$\frac{\chi_0(\sqrt[3]{3\xi} + R_0^3, 0)}{\int_0^\infty \chi_0(\sqrt[3]{3\xi} + R_0^3, 0) d\xi} = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} G(\beta) \exp(\beta\xi/\alpha) d\beta \quad (15)$$

As a summary of these transforms of the four characteristic functions, the flow chart of the transformations is given in Fig. 1.

Therefore, $G(\beta)$ is expressed in terms of $K_0(n)$ by using the double Laplace transform via $\chi_0(\sqrt[3]{3\xi}, 0)$ or $N_0(t)$ in this flow chart:

$$G(\beta) = \frac{\int_0^\infty \int_0^\infty \exp\{-\beta\xi/\alpha - n(\xi + R_0^3/3)\} K_0(n) dn d\xi}{\int_0^\infty (K_0(n)/n) \exp(-nR_0^3/3) dn} \quad (16)$$

The transforms in the higher-order approximations, including the effect of diffusion, are given in Appendix A.

B. Example of Distribution Functions. As the first example of this scheme, the superpositions of the δ -functions as $K_0(n)$ in Eqs. (6) and (9) are considered in Eq. (17).

The operations⁶⁾ of the Laplace transforms on $K_0(n)$ yield $\chi_0(\sqrt[3]{3\xi}, 0)$ and $N_0(t)$, and the double Laplace transform either via $\chi_0(\sqrt[3]{3\xi}, 0)$ or $N_0(t)$ in Fig. 1 yields $G(\beta)$:

$$K_0(n) = \sum_i f_i \delta(n - n_i) \quad (17)$$

where f_i are constants:

$$\frac{N_0(t)}{N_0(0)} = \frac{\sum_i (f_i/n_i) \exp(-R_0^3 n_i/3 - \alpha n_i t)}{\sum_i (f_i/n_i) \exp(-R_0^3 n_i/3)} \quad (18)$$

$$G(\beta) = \frac{\sum_i (f_i/n_i) \exp(-R_0^3 n_i/3)}{1 + \beta/\alpha n_i} / \sum_i (f_i/n_i) \exp(-R_0^3 n_i/3) \quad (19)$$

$$\chi_0(r, 0) = \sum_i f_i \exp(-nr^3/3) \quad (20)$$

Equations (18) and (20) show that the decay function and the initial distribution can be expressed as a superposition of the exponential functions. Such a decay function of the electron concentration was observed by Yoshida⁷⁾ in hydrocarbon glass. In Eq. (19) the G -value of the recombination or the scavenging process is represented as a linear combination of functions of the Stern-Volmer or Langmuir type. Such a type of scavenger dependence was approximately verified in a previous paper.⁸⁾

5) F. Williams, *J. Amer. Chem. Soc.*, **86**, 3954 (1964).

6) For example, H. Bateman, "Tables of Integral Transforms. I," McGraw-Hill Book Co. Inc., New York (1954).

7) H. Yoshida, *Ann. Repts. Reactor Inst. Kyoto Univ.*, **3**, 153 (1970).

8) H. Yamazaki and K. Shinsaka, *This Bulletin*, **43**, 2713 (1970).

As the second example, $G(\beta)$ as a function of the square root of the concentration of the scavenger was proposed by Schuler *et al.*¹⁾ as in Eq. (21) for a wide range of scavenger concentrations:

$$G(\beta) = 1/(1 + \sqrt{A\beta}) \quad (21)$$

where A is a constant. A comparison between Schuler's expression and the present one for $G(\beta)$ is given in Appendix B. The operations⁹⁾ of the inverse Laplace and double inverse Laplace transforms of Eq. (21) yield $N_0(t)$, $\chi_0(\sqrt[3]{3\xi}, 0)$ and $K_0(n)$ for the case of the square-root dependence on the scavenger concentration:

$$\frac{N_0(t)}{N_0(0)} = 1 - 2\sqrt{\frac{\alpha t}{\pi}} + \frac{1}{\sqrt{\alpha}} \int_0^t \exp(t/\alpha) \operatorname{Erfc}(\sqrt{t/\alpha}) dt \quad (22)$$

$$\begin{aligned} \chi_0(\sqrt[3]{3\xi + R_0^3}, 0) / \int_0^\infty \chi_0(\sqrt[3]{3\xi + R_0^3}, 0) d\xi \\ = \left\{ \sqrt{\frac{1}{\pi\xi A\alpha}} - \frac{1}{A\alpha} \exp(\xi/A\alpha) \right\} \operatorname{Erfc}(\sqrt{\xi/A\alpha}) \end{aligned} \quad (23)$$

and

$$K_0(n) = \frac{\sqrt{nA\alpha}}{\pi(1+nA\alpha)} \exp(nR_0^3/3) \quad (0 < nR_0^3/3 < 1) \quad (24)$$

As the third example, Hummel's formula⁹⁾ for the G -value as the function of the concentration of the scavenger, corresponding to Eqs. (19) and (21), was expressed by:

$$G(\beta) = \exp(-\sqrt{A\beta}) \quad (25)$$

Similarly, $N_0(t)$, $\chi_0(\sqrt[3]{3\xi}, 0)$ and $K_0(n)$ can be obtained by using inverse Laplace transforms:⁶⁾

$$\frac{N_0(t)}{N_0(0)} = 1 - \frac{1}{2} \sqrt{\frac{A}{\pi}} \int_0^t t^{-3/2} \exp(-A/4t) dt \quad (26)$$

$$\frac{\chi_0(\sqrt[3]{3\xi + R_0^3}, 0)}{\int_0^\infty \chi_0(\sqrt[3]{3\xi + R_0^3}, 0) d\xi} = \frac{1}{2} \sqrt{\frac{A\alpha}{\pi\xi^3}} \exp(-\alpha A/4\xi) \quad (27)$$

and

$$K_0(n) = \frac{1}{\pi} \sin(\sqrt{nA\alpha}) \exp(nR_0^3/3) \quad (0 < nR_0^3/3 < 1) \quad (28)$$

Discussion

The various measurements for obtaining $N_0(t)$, $G(\beta)$, $\chi_0(r, 0)$ and $K_0(n)$ are interconnected. In view of this relation, the experiment of the pulse radiolysis, the scavenging method with product analysis, and the relaxation time measurement of the ESR spectrum to get information on the spatial distribution are all needed under the same conditions. As to $K_0(n)$, the first term in the expansion of $K_0(n)$ in Eq. (28) as a power series of n gives the same term as that of Eq. (24). The actual calculation to obtain the initial distribution from the results of the scavenging method was carried out by Sato and Oka⁹⁾ on the basis of Freeman's method of calculation.¹⁰⁾ They obtained equations corresponding to Eqs. (23) and (27). According to their calculation, the initial distributions due to Schuler's and Hummel's expressions of the G -value are almost the same for large values of r ; this corresponds to the fact that the weight

functions, $K_0(n)$, for Schuler's and Hummel's expressions are approximated by the same equation for the small values of n . Thus, $\chi_0(r, 0)$ can be estimated indirectly from $G(\beta)$, because $G(\beta)$ has been obtained experimentally in the presence of various scavengers. A few experiments have been made to obtain direct information about $\chi_0(r, 0)$, for example, by relaxation-time measurement in liquid hydrocarbons. In a preliminary result of the measurement of the relaxation-time of ESR, the distribution of electrons showed heterogeneity in the glass state.¹¹⁾

In the present pulse radiolysis for the determination of $N_0(t)$, the electron-ion recombination process can be detectable at low temperatures^{12,13)} where the lifetime of the recombination increases over μ sec. At low temperatures, however, the equilibrium between bound and unbound electrons, e_t^- and e_m^- , must be considered, and this factor has to be added to the fundamental equation. If the rate of equilibration between e_t^- and e_m^- is fast, Eq. (1) can be rewritten as:

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

$$(K = k_m/k_t = C_t/C_m) \quad (29)$$

where C_m and C_t are the distributions of unbound and bound electrons, k_m and k_t are the rate constants of equilibration between unbound and bound states, and K is an equilibrium constant between the bound and unbound states of electrons. The extremely small apparent values of the electron mobility, the diffusion constant, and the rate constant can be expected for a large values of K . Even when the coefficients in the equation are different, the equation remains in the same form in this approximation. In various types of distribution functions, the superposition of δ -functions for $K_0(n)$ and, therefore, the superposition of exponential functions for $N_0(t)$, are natural and reasonable, as is shown in the examples.

The square diagram of the Laplace transform in Fig. 1 was obtained by the zeroth order approximation, ignoring the diffusion term in the Smoluchowski equa-

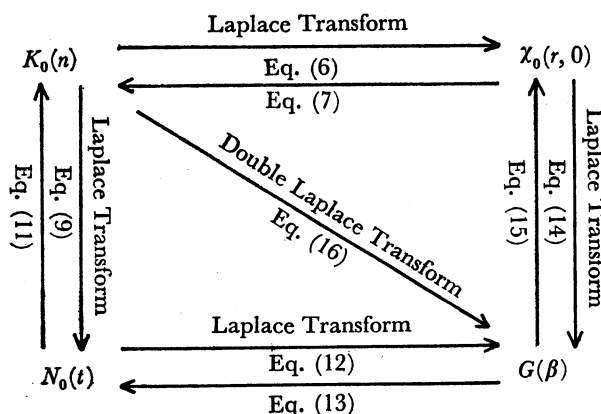


Fig. 1. Flow chart of the Laplace transforms of various distribution functions; $K_0(n)$, $\chi_0(r, 0)$, $N_0(t)$, and $G(\beta)$.

11) K. Oka, H. Yamazaki, and S. Shida, unpublished work.

12) I. A. Taub and H. A. Gillis, *J. Amer. Chem. Soc.*, **91**, 6507 (1969).

13) H. A. Gillis, N. V. Klassen, G. G. Teather, and K. H. Lokan, *Chem. Phys. Lett.*, **10**, 481 (1971).

9) A. Hummel, *J. Chem. Phys.*, **49**, 4840 (1968).

10) G. R. Freeman, *ibid.*, **46**, 2822 (1967).

tion. If the higher-order approximation including the diffusion term is used, the Laplace transform in the scheme should be replaced by a more complicated form of the integral transforms, as is shown in Appendix A. The validity of the potential control approximation can be discussed in the following two ways. In the first place, the Onsager radius has an order of magnitude of several hundreds Ångström in the liquid hydrocarbons, and most of the electrons ejected from the parent ions are within this region and are still localized in the range of the Coulomb field of the parent ions. Therefore, the potential term is more effective than the diffusion term for most of the electrons in the region inside of the Onsager radius. In the second place, it is most likely that the thermalized electrons do not show any sharp spatial distribution; this is because of diffused energy spectrum of the electrons ejected and because of the random collisions of thermalization. Moreover, the spatial distribution is broadened with time. The transport of the electrons by diffusional motion in one direction is quite small, because the second derivative of the electron distribution by the distance is negligibly small for the smoothed distribution.

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Appendix

A. *The Higher-order Approximation.* The s -th order equation is given by a recurrent equation:

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

The s -th order of approximation can be written by:

$$\chi_s(r, t) = \int_0^\infty K_s(n) H_s(n, \alpha, D, r) \exp(-\beta t - n\alpha t - nr^3/3) dn \quad (\text{A-2})$$

where H_s is a function of n , α , D , and r ; several examples of the explicit form are given by:

$$H_0(n, \alpha, D, r) = 1 \quad (\text{A-3})$$

$$H_1(n, \alpha, D, r) = 1 + nDr^4/\alpha - n^2Dr^7/7\alpha \quad (\text{A-4})$$

$$H_2(n, \alpha, D, r) = 1 + nDr^4/\alpha - n^2Dr^7/7\alpha - 4nD^2r^5/\alpha^2 + 5n^2D^2r^8/2\alpha^2 - 24n^3D^2r^{11}/77\alpha^2 + n^4D^2r^{14}/98\alpha^2 \quad (\text{A-5})$$

In the case of a pure recombination, ($\beta=0$), the initial dis-

tribution can be expressed by:

$$\chi_s(\sqrt[3]{3\xi}, 0) = \int_0^\infty K_s(n) H_s(n, \alpha, D, \sqrt[3]{3\xi}) \exp(-n\xi) dn, \quad (\text{A-6})$$

using the substitution, $r^3/3=\xi$, From Eqs. (8) and (A-2), $N_s(t)$ is given by:

$$N_s(t) = 4\pi \int_0^\infty K_s(n) g_s(n, \alpha, D, R_0) \exp(-n\alpha t) dn \quad (\text{A-7})$$

where $g_s(n, \alpha, D, R_0)$ is given by the integral of $H_s(n, \alpha, D, \sqrt[3]{3\xi})$:

$$g_s(n, \alpha, D, R_0) = \int_{R_0^{3/3}}^\infty H_s(n, \alpha, D, \sqrt[3]{3\xi}) \exp(-n\xi) d\xi \quad (\text{A-8})$$

The relaxation time spectrum, $K(n)$, can be expressed by the use of the inverse Laplace transform of the dependence of the electron concentration in the system:

$$K_s(n) g_s(n, \alpha, D, R_0) = \frac{1}{8\pi^2 i} \int_{C-i\infty}^{C+i\infty} N_s(p/\alpha) \exp(np) dp \quad (\text{A-9})$$

Equations (12) and (13) are valid for the relation between the functions of $N_s(t)$ and $G_s(t)$ in the presence of diffusion, because this relation is phenomenological and does not need the Smoluchowski equation as a basis for discussion. However, the $\chi_s(r, 0)$ and $G_s(\beta)$ functions are not directly connected by a Laplace transform, because the relation between t and r^3 can be held only by disregarding the diffusion term. A complicated relation can be obtained by the transforms via $K_s(n)$ and $N_s(t)$:

$$\begin{aligned} \chi_s(\sqrt[3]{3\xi}, 0) &= \int_0^\infty \frac{N_s(0) H_s(n, \alpha, D, \sqrt[3]{3\xi})}{8\pi^2 i g_s(n, \alpha, D, R_0)} \exp(-n\xi) \\ &\times \left[\int_{C-i\infty}^{C+i\infty} \left\{ \int_{p/\alpha}^\infty \frac{1}{2\pi i} \int_{C-i\infty}^{C+i\infty} G(\beta) \exp(\beta t) d\beta dt \right\} \right. \\ &\times \exp(np) dp \Big] dn \end{aligned} \quad (\text{A-10})$$

B. *The Expressions for $G(\beta)$.* This equation is expressed by $G(p) = G_{fi} + G_{gi}\sqrt{A\beta}/(1+\sqrt{A\beta})$, where $G(p)$, G_{fi} , and G_{gi} are the G -values of the yields of the secondary products from the ionic reaction and those of free and germinate electrons respectively. A fraction, $F(c)$, undergoing the reaction of germinate pairs with the scavenger solute is expressed by:

$$F(c) = [G(p) - G_{fi}]/G_{gi} \quad (\text{B-1})$$

where c is the concentration of the solute. $F(c)$ is represented using the Laplace transform of the life-time distribution, $f(t)$:

$$F(c) = 1 - \int_0^\infty \exp(-kct) f(t) dt \quad (\text{B-2})$$

where k is the rate constant with the solute. The life-time distribution is given by the differentiation of the fraction, $F(t)$, of the ion pair at time t , which is equal to the $N(t)/N(0)$ used in this paper:

$$f(t) = -dF(t)/dt \quad (\text{B-3})$$

The relative G -value or fraction of recombination, $G(\beta)$, considered in this paper is expressed by:

$$G(\beta) = \frac{G_{gi} - G_{gi}\sqrt{A\beta}/(1+\sqrt{A\beta})}{G_{gi}} = 1/(1+\sqrt{A\beta}) \quad (\text{B-4})$$