BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 856—857 (1971)

The Spatial Distribution of Secondary Electrons Produced in the γ-Radiolysis of Cyclohexane

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(Received October 13, 1970)

In order to analyze the reactions of charged species produced in liquid-phase radiolysis, it is important to know the spatial distribution of secondary electrons, even if it is qualitative. Recently, Warman, Asmus, and Schuler proposed an empirical equation for the charge scavenging[1] from which they derived a distribution function for the lifetime of the charged species produced in the radiolysis of hydrocarbon solutions.[2] On the other hand, we ourselves have previously discussed the kinetics of the electron scavenging of nitrous oxide in the radiolysis of several hydrocarbons by assuming a Gauss function as the spatial distribution of secondary electrons.[3] By combining these two procedures, we have realized that it is possible to derive a spatial distribution of secondary electrons in the γ-radiolysis of cyclohexane. The present note will report the procedure of deriving the distribution function and will discuss the implications of this function.

Procedure[4]

The G-value of the electrons scavenged by an electron scavenger is expressed by the following equation, based on an appropriate assumption:[3]

$$G_s = G_{fi} + G_{gi}\left\{1-\int_0^\infty \phi(r)\ (1-N_s)^{nz}\ 4\pi r^2\ \mathrm{d}r\right\}. \qquad (1)$$

Here, G_{fi} and G_{gi} are the G-values of free and geminate electrons respectively. $\phi(r)$ is the distribution function of the distance between a thermalized electron and its parent positive ion. N_s is the mole fraction of the electron scavenger, n is the number of jumps which an electron makes before neutralization, and z is the number of new neighboring molecules when an electron makes a jump. As has been established by Williams,[5] the following relation exists between n and r: $n=r^3/3\sigma^2 r_c$. Here, r_c is the Onsager length and σ is the mean distance of a jump made by the electron.

When the concentration of the electron scavenger is not large, $(1-N_s)^{nz}$ may be replaced by $\exp(-nz\,N_s)$. Then, by changing a variable from r to x ($x=r^3$), we can obtain the following equation:

$$G_s = G_{fi} + G_{gi}\left\{1-\frac{4\pi}{3}\int_0^\infty \phi(x^{1/3})\ \exp(-kSx)\mathrm{d}x\right\}. \qquad (2)$$

Here, S is the concentration of the scavenger in mol l^{-1}, k is a constant $(2z/\sigma^2 r_c)(M/10^3\rho)$, M is the molecular weight of cyclohexane, and ρ is the density.

So far, two empirical equations have been proposed for expressing the relation between the G-value of scavenged electrons and the concentration of the electron scavenger. One of them has been proposed by

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

[2] S. J. Rzad, P. P. Infelta, J. M. Warman, and R. H. Schuler, *J. Chem. Phys.*, **52**, 3971 (1970).

[3] S. Sato, T. Terao, M. Kono, and S. Shida, This Bulletin, **40**, 1818 (1967); S. Sato, *ibid.*, **41**, 304 (1968).

[4] A similar treatment was proposed by M. Tatsuya at the 13th Conference of Radiation Chemistry at Tokyo, Oct., 1970, though there are small differences in details.

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

Warman, Asmus, and Schuler:[1]

$$G_s = G_{fi} + G_{gi}\frac{\sqrt{\alpha S}}{1+\sqrt{\alpha S}}\,. \qquad (3)$$

The other has been proposed by Hummel:[6]

$$G_s = G_{fi} + G_{gi}\{1-\exp(-\sqrt{\alpha S})\}\,. \qquad (4)$$

Here, α is a parameter which can be determined experimentally. According to Warman *et al.*, the value of α is 16 l mol^{-1} for most of the effective electron scavengers. Now, utilizing the table of the Laplace transformation, we can derive the following two spatial distribution functions by combining Eqs. (2) and (3), and Eqs. (2) and (4):

$$\phi(r) = \frac{3k}{4\pi\alpha}\left\{\left(\frac{\alpha}{\pi k r^3}\right)^{1/2} - e^{kr^3/\alpha}\,\mathrm{erfc}\left(\frac{kr^3}{\alpha}\right)^{1/2}\right\} \qquad (5)^{7)}$$

and

$$\phi(r) = \frac{3}{8\pi}\left(\frac{\alpha}{\pi k}\right)^{1/2} r^{-9/2}\exp\left(-\frac{\alpha}{4kr^3}\right). \qquad (6)$$

Numerical calculations can easily be made by substituting the following values: r_c=280 Å (Onsager length in cyclohexane at 25°C), σ=5.4 Å (diameter of a cyclohexane molecule), and z=6. The results are shown in Fig. 1. A Gauss function used for our calculations in previous papers is also plotted.

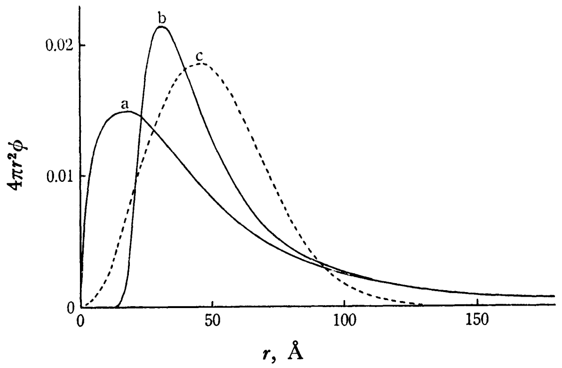

Fig. 1. Spatial distributions of secondary electron. a, Eq. (5); b, Eq. (6); c, the Gauss function (r_{av}=50 Å).

Discussion

A few years ago, Freeman and Fayadh estimated the spatial distribution of the secondary electrons produced in the γ-radiolysis of liquids[8] by using the tables proposed by Lea for the range of high-energy electron.[9] The distribution function, which is expressed by a step function, is quite similar in its form to curve b in Fig. 1. Judging from the many successful calculations made by Freeman and his collaborators,[10] the function (6) may be useful for the approximate calculation of the kinetics of the reactions of the charged species produced in the liquid-phase radiolysis because of its rather simple form.

According to Warman *et al.*, Eq. (3) is better than (4) for expressing the concentration dependence of G_s observed in the radiolysis of cyclohexane. They plotted $1/(G_s-G_{fi})$ as a function of $1/\sqrt{\alpha S}$ and estimated the value of G_{gi} by extrapolating the linear relationship to $S\to\infty$.[1] However, judging from the form of the distribution function (5), this procedure is questionable. As is shown in Fig. 1, the curve a has a large contribution at smaller values of r. Such a state, for example, at r=3 Å, would not be an ionized state, but a highly excited state, because of the strong interaction with the parent positive ion. Therefore, their procedure may include such a contribution of the reaction as the following:

$$\text{cyclo-}C_6H_{12}^* + S \rightarrow C_6H_{12}^+ + S^-$$

In other words, the value of G_{gi} estimated by their procedure may be a little larger than that of the so-called geminate ions.

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[6] A. Hummel, *J. Chem. Phys.*, **49**, 4840 (1968).

[7] $\mathrm{erfc}(y) = 1 - \frac{2}{\sqrt{\pi}}\int_0^y e^{-t^2}dt$

[8] G. R. Freeman and J. M. Fayadh, *ibid.*, **43**, 86 (1965).

[9] D. E. Lea, "Actions of Radiations on Living Cells," Cambridge University Press, New York (1955), 2nd, ed., p. 29.

[10] G. R. Freeman, *Radiat. Res. Rev.*. **1**, 1 (1968).