BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(8), 2236—2239 (1975)

Lifetimes of Electrons in Irradiated Liquid Alkanes

Kenji FUEKI

Department of Synthetic Chemistry, Nagoya University Chikusa-ku, Nagoya 464

(Received March 26, 1975)

A calculation has been made of lifetimes of electrons in irradiated liquid alkanes on the basis of the lifetime distribution function for the geminate electrons derived from the exponential distribution function for electron ranges. The results show that the intrinsic electron lifetimes correlate with the electron mobilities and most of the geminate electrons recombine within 1 ns in the alkanes at room temperature. A consideration is given to the effect of pulse duration time on the apparent electron lifetime and the observable yield of electrons in *n*-hexane.

In recent years there has been much interest in the behavior and properties of electrons in nonpolar liquids in some branches of chemistry and physics. In radiation chemistry considerable efforts have been paid to this research field both theoretically and experimentally. As such an effort, a number of studies have been made of ranges of electrons in irradiated liquid hydrocarbons, in which various spatial distribution functions for the thermalized electrons have been used and tested by comparison with experiment. At present it appears that a Gaussian-power function[1)] and an exponential function[2-4)] are the best among the prescribed forms of electron distribution functions for liquid alkanes. As an alternative approach to an understanding of the behavior of electrons in irradiated liquid hydrocarbons, we may discuss the lifetime distribution of the thermalized electrons. Most of previous studies on this subject have dealt with only very limited hydrocarbons such as cyclohexane and *n*-hexane.[5-8)] Also, values of the diffusion constant of the electron used in earlier studies are inappropriate in the light of recent electron mobility data. The diffusion constant of the electron is a crucial factor in determining electron lifetimes. More recent studies have used the appropriate values of the diffusion constant of the electron.[9,10)] Schuler and his coworkers[11)] have developed a phenomenological model for the description of electron lifetimes in irradiated liquid hydrocarbons which is based on their scavenging function.

In this work, we attempt to calculate the lifetime distribution of electrons in irradiated liquid alkanes on the basis of the exponential distribution function for electron ranges and recent experimental data on electron mobilities. Here we deal with seven alkanes (*n*-pentane, cyclopentane, neopentane, *n*-hexane, cyclohexane, 2,2-dimethylbutane and 2,2,4-trimethylpentane) for which the electron mobilities vary over three orders of magnitude.

Model and Lifetime Distribution Function

First, we assume a model in which an instantaneous pulse of radiation is given to dielectric liquids and ranges of electrons produced are expressed by the exponential distribution function as given by Eq. (1).

$$\left.\begin{array}{ll} \phi(r) = 0, & r \leq r_0 \\ \phi(r) = (1/4\pi b r^2)\exp[(r_0 - r)/b], & r \geq r_0 \end{array}\right\} \quad (1)$$

where b is the range parameter and r_0 is the reaction radius. Using the time-distance relationship, $t = r^3/3Dr_c$, derived from the Nernst-Einstein relation[5)] and $4\pi r^2\phi(r)dr = f(t)dt$, we get Eq. (2) for the lifetime distribution function or the existence function for geminate ion-electron pairs.

$$F(t) = \int_t^{\infty} f(t)dt = \exp\{(3Dr_c)^{1/3}[t_0^{1/3} - (t+t_0)^{1/3}]/b\}, \quad 0 \leq t \leq t_f$$

$$t_0 = r_0^3/3Dr_c, \quad r_c = e^2/\varepsilon kT \quad (2)$$

where D is the sum of the diffusion constants of the ion and electron, e is the electronic charge, ε is the dielectric constant of a liquid, k is Boltzmann's constant and T is the absolute temperature. Equation (2) represents the fraction of electrons present at time t after an instantaneous pulse of radiation. t_f is a characteristic time dfined as $F(t_f) = G_{fi}/G_t$, where G_{fi} and G_t are the free ion yield and the total ion yield, respectively. t_f means the time at which the geminate recombination of ion-electron pairs practically completes.

We may define another characteristic time $t_{1/e}$ for the geminate recombination. $t_{1/e}$ is the time at which the value of $F(t)$ falls to 1/e of its value at $t=0$. Since t_0 is very small, $t_{1/e}$ is given, to a very good approximation, by Eq. (3).

$$t_{1/e} = b^3/3Dr_c \quad (3)$$

$t_{1/e}$ is exactly given by Eq. (3) for $r_0 = 0$.

Since the Nernst-Einstein relation neglects the effect of outward diffusive motion of electrons on the geminate recombination times, the use of this relation tends to underestimate the geminate recombination times. In the calculations of electron lifetimes, therefore, we have also attempted to correct for this effect in a similar manner to that used in Ref. 12. Such a corrected time t' is given by Eq. (4)

$$t' = t[1 + (4/3r_c)(3Dr_c)^{1/3}t^{1/3}]^{3/2} \quad (4)$$

We now consider a square pulse of duration τ. In this case the existence function is expressed by Eq. (5), assuming $r_0 = 0$.

$$F(t) = (1/\tau)\int_0^{\tau} \exp[a(t^* - t)^{1/3}]dt^* \quad (5)$$

where $a = (3Dr_c)^{1/3}/b$ and time is measured from the onset of the pulse. Performing the integration in Eq. (5) leads to Eq. (6).

$$\begin{aligned} F(t) &= (3/\tau a)\{(2/a^2) - [t^{2/3} + (2/a)t^{1/3} + (2/a^2)] \\ &\quad \times \exp(-at^{1/3})\}, \quad t \leq \tau \\ F(t) &= (3/\tau a)\{[(t-\tau)^{2/3} + (2/a)(t-\tau)^{1/3} + (2/a^2)] \\ &\quad \times \exp[-a(t-\tau)^{1/3}] - [t^{2/3} + (2/a)t^{1/3} + (2/a)^2] \\ &\quad \times \exp(-at^{1/3})\}, \quad t \geq \tau \end{aligned} \quad (6)$$

It can be shown that $F(t)$ in Eq. (6) for $\tau=0$ reduces $F(t)$ in Eq. (2) with $r_0=0$.

Values of physical parameters used in the calculations are listed in Table I. Since the diffusion constant of the electron is usually much greater than that of the ion, the diffusion, constant D may be approximated by the diffusion constant of the electron, D_e, which is related to the electron mobility μ_e by $D_e=kT\mu_e/e$. The electron mobility in *n*-hexane at -80 °C was calculated from a mobility equation $\mu_e=\mu_0\exp(-E/RT)$ where $\mu_0=120\ \mathrm{cm^2V^{-1}\,s^{-1}}$ and $E=4.3$ kcal mole^{-1}.[16,22] The results of the calculations are given in Tables 2 and 3, and Figs. 1—3. The results in Table 2 and Fig. 1 were obtained using $r_0=5$ Å, and those in Table 3 and Figs. 2 and 3 were calculated with $r_0=0$.

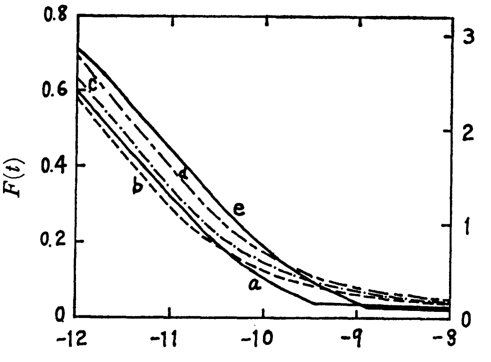

Fig. 1. Decay of electron population in cyclohexane and *n*-hexane at 23 °C. Time is measured from the input of an instantaneous pulse of radiation. a: cyclohexane, exponential function; b: cyclohexane, Schuler's function ($\alpha=12\ \mathrm{M^{-1}}$, $k=4.3\times10^{12}\ \mathrm{M^{-1}\,s^{-1}}$); c: cyclohexane, Schuler's function ($\alpha=12\ \mathrm{M^{-1}}$, $k=2.7\times10^{12}\ \mathrm{M^{-1}\,s^{-1}}$); d:cyclohexane, Schuler's function ($\alpha=12\ \mathrm{M^{-1}}$, $k=1.8\times10^{12}\ \mathrm{M^{-1}\,s^{-1}}$); e: *n*-hexane, exponential function.

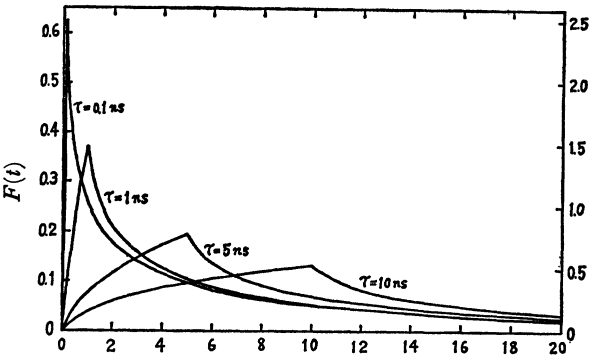

Fig. 2. Growth and decay of electron population in pulse-irradiated *n*-hexane at -80 °C. Time is measured from the onset of the pulse.

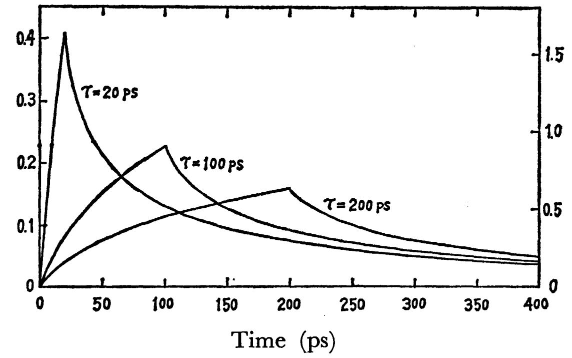

Fig. 3. Growth and decay of electron population in pulse-irradiated *n*-hexane at 23 °C. Time is measured from the onset of the pulse.

Results and Discussion

Lifetimes of Electrons in Liquid Alkanes. In Table 2 are presented the calculated characteristic times for the geminate recombination of ion–electron pairs in seven alkanes at 23 °C. In the calculations two approximations were used for the time-distance relation: one is the forced diffusion approximation (FD), in which the Nernst-Einstein relation is used; the other is the forced diffusion approximation with a random diffusion correction (FRD), in which Eq. (4) is used for the corrected time t'. It is seen in Table 2 that the FRD approximation yields the characteristic recombination times greater than does the FD approximation. The differences between values obtained with these two approximations are greater for t_f and t_f' than for $t_{1/e}$ and $t_{1/e}'$. This is understandable noting that $t_{1/e}$ or $t_{1/e}'$ represents the geminate recombination time for the electrons not very far away from their parent ions and on which the strong Coulomb field acts, while t_f or t_f' represents the recombination time for the electrons distant from their parent ions and being subjected to the thermal force almost as strong as the Coulomb force. It can be seen from Tables 1 and 2 that the greater is the electron mobility, the greater is the ratio of $t_{1/e}'$ to $t_{1/e}$, for instance, this ratio is the greatest for neopentane and the smallest for *n*-hexane, while the ratio of t_f' to t_f is about the same (~3) for all the hydrocarbons studied. The magnitude of t_f or t_f' decreases with increasing electron mobility. Similarly, the value of $t_{1/e}$ or $t_{1/e}'$ decreases with increasing electron mobility with one exception of neopentane for which $t_{1/e}$ or $t_{1/e}'$ is somewhat greater than expected from the electron mobility in neopentane. Such an exception is due to the fact that the electron range b in neopentane is much greater than those in the other hydrocarbons as shown in Table 1 and that $t_{1/e}$ is proportional to b^3 (see Eq. (3)). The use of $G_{fi}=0.86$ and $G_t=3.7$ for neopentane yields $b=250$ Å[2] which is close to the b value given in Table 1.

Figure 1 shows the calculated time dependence of electron population in cyclohexane and in *n*-hexane after an instantaneous pulse of radiation. In Fig. 1 $G_e(t)$ represents the yield of electrons present at time t, calculated setting $G_e(t)=G_t$. Curve a was calculated using the exponential distribution function and the FRD approximation for electrons in cyclohexane. Curves b, c and d for cyclohexane were calculated using Schuler's distribution function for electron life times[11] with the reactivity parameter, $\alpha=12\ \mathrm{M^{-1}}$,[23] and the absolute rate constant, $k=4.3\times10^{12}$,[24] 2.7×10^{12},[25] and $1.8\times10^{12}\ \mathrm{M^{-1}\,sec^{-1}}$,[18] respectively, for the reaction of electrons with carbon tetrachloride. It is seen in

TABLE 1. PHYSICAL PARAMETERS USED IN THE CALCULATIONS AT 23 °C

Liquid	r_c[a] (Å)	b[b] (Å)	μ_e (cm^2/V·s)	G_{fi}[a]	G_t
n-pentane	306	65.3	0.16[d]	0.145	4.0[b]
Cyclopentane	288	62.2	1.1[d]	0.155	4.0[b]
Neopentane	318	232[c]	70[e,f]	1.2[c]	5.5[c]
n-Hexane	299	58.1	0.08[e,g]	0.131	4.0[b,h]
Cyclohexane	279	57.5	0.24[g]	0.148	4.0[b,i]
2,2-Dimethylbutane	293	92.8	12[f]	0.304	4.3[b]
2,2,4-Trimethylpentane	291	96.1	7[d]	0.332	4.8[j]

a) Ref. 13. b) Ref. 14. c) Ref. 3. d) Ref. 15. e) Ref. 16. f) Ref. 17. g) Ref. 18. h) Ref. 19. i) Ref. 20. j) Ref. 21.

TABLE 2. CHARACTERISTIC TIMES FOR GEMINATE ION-ELECTRON RECOMBINATION IN LIQUID ALKANES AT 23 °C

Liquid	FD		FRD	
	$t_{1/e}$ (ps)	t_f (ps)	$t'_{1/e}$ (ps)	t_f' (ps)
n-Pentane	7.4	290	11	800
Cyclopentane	0.99	37	1.4	100
Neopentane	0.73	2.7	2.0	11
n-Hexane	11	460	15	1200
Cyclohexane	3.7	140	5.3	390
2,2-Dimethylbutane	0.30	5.9	0.50	18
2,2,4-Trimethylpentane	0.57	12	0.98	38

TABLE 3. CALCULATED HALF-LIFE TIMES AND YIELDS OF ELECTRONS IN PULSE-IRRADIATED *n*-HEXANE

t (°C)	τ	$t_{1/2}$	G (e$^-$)
−80	ns	ns	
	10	13.5	0.52
	5	7.8	0.77
	1	2.4	1.5
	0.1	0.64	2.5
	0	0.13	4.0
23	ps	ps	
	200	290	0.63
	100	170	0.90
	20	53	1.6
	0	3.5	4.0

Fig. 1 that curves b and c are very close to curve a and that curve d gives somewhat higher values of $F(t)$ or $G_e(t)$ than does curve a, but curve d is also comparable to curve a on the time scale. It should be noted, however, that curve a underestimates considerably electron lifetimes in the long-time limit for the geminate ion–electron recombination. Schuler's lifetime distribution function predicts the time dependence of $t^{-1/2}$ in the long-time limit,[11] while Eq. (2) does not predict the $t^{-1/2}$ dependence. This discrepancy arises from the fact that the use of the Nernst-Einstein relation is not appropriate for the description of motion of electrons distant from their parent ions since Brownian motion of electrons is as important as the electron drift in the Coulomb field for such electrons. Curve e shows $F(t)$ or $G_e(t)$ calculated using the exponential distribution function and the FRD approximation for electrons in *n*-hexane. The shape of the curve is similar to that for cyclohexane, but the geminate recombination time in *n*-hexane is longer than that in cyclohexane. It is noted that in the calculations, an extremely low dose rate is assumed, resulting in an indefinitely long lifetime of the free electrons.

Lifetimes of Electrons in Pulse-Irradiated n*-Hexane.* Figures 2 and 3 show the growth and decay of electron population in *n*-hexane at −80 °C and 23 °C, respectively, calculated using Eq. (6) for a square pulse of duration τ. The duration time τ is taken as 0.1, 1, 5 and 10 ns at −80 °C and 20, 100 and 200 ps at 23 °C. It can be seen from Figs. 2 and 3 that the electron population increases with time, reaches a maximum at $t=\tau$ and then decreases with increasing time. It is also seen that the shorter is the duration time of the pulse, the higher is the maximum of electron population and the greater is the apparent decay rate of electrons. Table 3 summarizes the half-life time, $t_{1/2}$, for the decay of electrons and the yield of electrons, G(e$^-$), at the maximum of electron population. The half-life time for $\tau=0$ is the shortest at each temperature and indicates the intrinsic lifetime of the geminate electrons at that temperature. The lifetimes of electrons at −80 °C are much longer than those at 23 °C. This difference arises from the fact that the electron mobility at −80 °C is much lower than that at 23 °C as shown by the temperature dependence of the mobility equation.

Comments on Pulse Radiolysis Observations of Electrons in Liquid Hydrocarbons. Optical absorption spectra of trapped electrons were observed by the pulse radiolysis technique in liquid hydrocarbons: *n*-hexane, cyclohexane, methylcyclohexane and isopentane at 20 °C;[26] *n*-hexane and 3-methylhexane at −80 °C;[27] methylcyclohexane at −113 °C;[28] squalane at −165∼−70 °C;[29] propane at −185 and −165°C.[30] The decay of electrons observed at room temperature obeys the second-order kinetic law and these electrons are regarded as the free electrons.[26] Studies of the decay of electrons at low temperatures suggest that the initial decay of electrons observed is due to the geminate recombination with their parent ions.[27–30] However, there are only very limited experimental data available for a quantitative comparison between theoretical calculations and the observed characteristics of decay of electrons. Such a comparison has recently been made successfully for electrons in pulse-irradiated liquid propane.[31] It is hoped that a more detailed experimental study will be undertaken on the decay of the geminate electrons in *n*-hexane to test the applicability of the present model.

References

1) J.-P. Dodelet, K. Shinsaka, U. Kortsch, and G. R. Freeman, *J. Chem. Phys.*, **59**, 2376 (1973).

2) G. C. Abell and K. Funabashi, *ibid.*, **58**, 1079 (1973).

3) J.-P. Dodelet and G. R. Freeman, *ibid.*, **60**, 4657 (1974).

4) A. Mozumder, *ibid.*, **60**, 4305 (1974).

5) F. Williams, *J. Amer. Chem. Soc.*, **86**, 3954 (1964).
6) G. R. Freeman, *Adv. Chem. Ser.*, **82**, 339 (1968).
7) A. Hummel, *J. Chem Phys.*, **49**, 4840 (1968).
8) A. Mozmuder, *ibid.*, **48**, 1659 (1968).
9) A. Mozumder, *ibid.*, **55**, 3026 (1971).
10) J.-P. Dodelet and G. R. Freeman, *Can. J. Chem.*, **50**, 2729 (1972).
11) R. H. Schuler and P. P. Infelta, *J. Phys. Chem.*, **76**, 3812 (1972).
12) F. Williams, *J. Chem. Phys.*, **48**, 4077 (1968).
13) W. F. Schmidt and A. O. Allen, *J. Phys. Chem.*, **72**, 3730 (1968).
14) M. Tanaka and K. Fueki, *ibid.*, **77**, 2524 (1973).
15) W. F. Schmidt and A. O. Allen, *J. Chem. Phys.*, **52**, 4788 (1970).
16) R. M. Minday, L. D. Schmidt, and H. T. Davis, *J. Phys. Chem.*, **76**, 442 (1972).
17) G. Bakale and W. F. Schmidt, *Chem. Phys. Lett.*, **22**, 164 (1973).
18) A. O. Allen and R. A. Holroyd, *J. Phys. Chem.*, **78**, 796 (1974).
19) J. M. Warman and S. J. Rzad, *J. Chem. Phys.*, **52**, 485 (1970).
20) J. M. Warman, K.-D. Asmus, and R. H. Schuler, *J. Phys. Chem.*, **73**, 931 (1969).
21) S. J. Rzad and K. M. Bansal, *ibid.*, **76**, 2374 (1972).
22) R. M. Minday, L. D. Schmidt, and H. T. Davis, *J. Chem. Phys.*, **54**, 3112 (1971).
23) G. W. Klein and R. H. Schuler, *J. Phys. Chem.*, **77**, 978 (1973).
24) J. H. Baxendale, J. P. Keene, and E. J. Rasburn, *J. Chem. Soc. Faraday I*, **70**, 718 (1974).
25) A. O. Allen, T. E. Gangwer, and R. A. Holroyd, *J. Phys. Chem.*, **79**, 25 (1975).
26) J. H. Baxendale, C. Bell, and P. Wardman, *J. Chem. Soc. Faraday I*, **69**, 776 (1973).
27) J. T. Richards and J. K. Thomas, *Chem. Phys. Lett.*, **10**, 317 (1971).
28) J. H. Baxendale, C. Bell, and P. Wardman, *ibid.*, 12, 347 (1971).
29) I. A. Taub and H. A. Gillis, *J. Amer. Chem. Soc.*, **91**, 6507 (1969).
30) H. A. Gillis, N. V. Klassen, G. G. Teather, and K. H. Lokan, *Chem. Phys. Lett.*, **10**, 481 (1971).
31) K. Fueki, to be published.