Ranges and Lifetimes of Electrons in Irradiated Liquid Hydrocarbons. Application of the Modified Exponential Distribution Function

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A modified exponential function is developed for the description of the spatial distribution of electrons in irradiated liquid hydrocarbons. This distribution function is applied to calculations of ranges and lifetimes of electrons in a number of hydrocarbons. The temperature dependence of electron ranges is also investigated for some of the hydrocarbons. A calculation is made of electron scavenging in cyclohexane using this distribution function and the forced diffusion approximations.

Recently, there has been considerable interest in the behavior, properties and reactions of electrons in nonpolar liquids. Many studies have been made of spatial distributions[1-12] and lifetimes[13-18] of electrons in irradiated liquid hydrocarbons. It has been shown that the simple exponential distribution function can well account for some experimental results on electrons in liquid hydrocarbons.[6,10] However, the electron population probability derived from the simple exponential distribution function increases monotonously with decreasing ion-electron separation distance and becomes very large near or at zero distance. Such a behavior at very small distances seems unrealistic on general grounds.

In this work, we develop a modified exponential function for the spatial distribution of electrons, which removes the unrealistic behavior of the simple exponential distribution function at small distances and still retains the characteristics of the exponential distribution function at large distances, and apply it to calculations of ranges and lifetimes of electrons in a number of liquid hydrocarbons including alkanes, alkenes, dienes, alkynes and aromatics. We also investigate the temperature dependence of electron ranges in some of the hydrocarbons. Further, using this distribution function and the forced diffusion approximations, we attempt to calculate the dependence on the scavenger concentration of the yield of electrons scavenged in a cyclohexane solution, and compare these results with that obtained from Schuler's scavenging function.

Outline of Calculation

The Modified Exponential Distribution Function. The spatial distribution function for the thermalized electrons used in the present calculations is given by Eq. (1).

$$\phi(r) = (1/2)(\pi b_{ME} r)^{-3/2}\exp(-r/b_{ME}) \quad (1)$$

where r is the separation distance of an ion-electron pair, b_{ME} is the electron range parameter and determined from Eq. (6). $\phi(r)$ is a normalized function: $\int_0^\infty \phi(r)4\pi r^2 dr = 1$, and unlike the simple exponential distribution function, the function $\Phi(r)=4\pi r^2\phi(r)$ behaves in such a way that it changes smoothly with r, taking a maximum value at a finite value of r and becoming zero at $r=0$.

We define the average electron range by Eq. (2).

$$\bar{r}_{ME} = \int_0^\infty r\phi(r)4\pi r^2 dr = (3/2)b_{ME} \quad (2)$$

The Geminate Ion-Electron Recombination Time. Using the Nernst-Einstein relation, we can derive Eq. (3a) which gives the time-distance relationship for the geminate ion-electron pair.[13]

$$t = r^3/3Dr_c \quad (3a)$$

Here D is the sum of the diffusion constants of the ion and electron, and r_c is the Onsager distance, $r_c = e^2/\varepsilon kT$, where e is the electronic charge, ε is the dielectric constant of a liquid, k is Boltzmann's constant and T is the absolute temperature. If we make a correction for the effect of outward diffusive motion of electrons on the geminate recombination times in a similar manner as that used in Ref. 14, we obtain Eq. (3b) as the corrected time-distance relationship.

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

It is seen in Eq. (3b) that the greater is the ion-electron separation distance r, the greater is the correction term $[1+(4r/3r_c)]^{3/2}$. We define by Eq. (4a) or (4b) the average recombination time for the geminate ion-electron pairs, namely, the average lifetime of the geminate electrons.

$$\tau_g = \bar{r}_{ME}^3/3Dr_c, \quad (4a)$$

$$\tau_g' = (\bar{r}_{ME}^3/3Dr_c)[1+(4\bar{r}_{ME}/3r_c)]^{3/2} \quad (4b)$$

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 Free Ion Yield. The free ion yield G_{fi} is expressed by Eq. (5).

$$G_{fi} = G_t\int_0^\infty \phi(r)\exp(-r_c/r)4\pi r^2 dr \quad (5)$$

Substituting $\phi(r)$ given in Eq. (1) into Eq. (5) and integrating it, we get a simple equation in closed form (Eq. (6)).

$$G_{fi} = G_t[1+2(r_c/b_{ME})^{1/2}]\exp[-2(r_c/b_{ME})^{1/2}] \quad (6)$$

where G_t represents the total ion yield. In the present calculations G_t is assumed to be 4.3 for all the hydrocarbons. Equation (6) is used for determining b_{ME}.

The Yield of Electrons Scavenged by a Scavenger. The yield of electrons scavenged by a scavenger, $G(e_{sc}^-)$, is calculated using Eq. (7a) or (7b).

$$G(e_{sc}^-) = G_t\int_0^\infty \phi(r)[1-\exp(-kSt)]4\pi r^2 dr, \quad (7a)$$

$$G(e_{sc}^-) = G_t \int_0^\infty \phi(r)[1-\exp(-kSt')]4\pi r^2 dr \qquad (7b)$$

where k is the rate constant for reaction of electrons with the scavenger and S is the concentration of the scavenger. The time t or t' is given as a function of r by Eq. (3a) or (3b).

Results and Discussion

The results of the calculations are given in Tables 1—4 and Figs. 1 and 2.

Electron Ranges. In Tables 1, 2 and 3 are listed the ranges of electrons, b_{ME} and $\bar{r}_{ME}$, calculated from Eqs. (6) and (2) using experimental values of G_{fi} for alkanes; alkenes, dienes, and alkynes; and aromatics, respectively. For comparison the electron ranges, $\bar{r}_E$, obtained from the simple exponential distribution function, $\phi(r)=(4\pi b_E r^2)^{-1}\exp(-r/b_E)$, are also given for alkanes in Table 1. It should be noted that $\bar{r}_E$ is equal to b_E for the simple exponential distribution function. The value of $\bar{r}_{ME}$ or b_{ME} correlates with that of G_{fi}: the greater is the free ion yield, the greater is $\bar{r}_{ME}$ or b_{ME}. Such a correlation has been found with other spatial distribution functions for electron ranges.[12] It is seen in Table 1 that generally $\bar{r}_{ME}$ is somewhat greater than $\bar{r}_E$ for the same compound, although $\bar{r}_{ME}$ is equal to $\bar{r}_E$ for neopentane. Figure 1 illustrates a comparison between the modified and simple exponential distribution functions for electrons in cyclohexane at room temperature. In the calculations of these distribution curves, b_{ME}= 41.4 Å and b_E=57.5 Å were used, which were ob-

Table 1. Ranges and lifetimes of electrons in alkanes

Liquid	T (K)	G_{fi}	b_{ME} (Å)	$\bar{r}_{ME}$ (Å)	μ_e (cm²/V s)	τ_g (ps)	τ_g' (ps)	$\bar{r}_E$[k] (Å)
Methane	140	1.13[a]	448	672	430[f]	2.5	8.0	
Ethane	200	0.158[a]	72.2	108	0.97[f]	5.3	8.0	
Propane	238	0.166[a]	62.4	93.7	0.55[f]	6.1	9.1	
Cyclopropane	260	0.078[a]	39.7	59.5	0.011[f]	81	110	
n-Butane	296	0.19[b]	53.6	80.4				
	293	0.225[a]	56.4	84.5	0.27[f]	9.2	14	
Isobutane	294	0.31[c]	70.4	105.6				
n-Pentane	296	0.145[b]	45.0	67.4	0.14[g]	9.3	14	62.3
	293	0.12[d]	41.9	62.8				
Isopentane	296	0.17[b]	48.6	72.9				67.6
Neopentane	296	0.86[b]	142	212	70[h,i]	0.56	1.5	212
	294	1.09[e]	177	265	70[h,i]	1.1	3.4	
Cyclopentane	296	0.155[b]	43.6	65.4	1.1[j]	1.2	1.8	60.8
n-Hexane	296	0.131[b]	42.0	63.0	0.082[g]	14	20	57.9
	293	0.11[d]	39.3	59.0				
2-Methylpentane	296	0.148[b]	44.9	67.4				
3-Methylpentane	296	0.146[b]	43.8	65.7				60.6
2,3-Dimethylbutane	296	0.192[b]	48.6	72.8				68.0
2,2-Dimethylbutane	296	0.304[b]	62.8	94.2	12[h]	0.31	0.53	89.9
	293	0.40[d]	77.0	116				
Cyclohexane	296	0.148[b]	41.4	62.1	0.24[g]	4.7	6.9	57.5
					0.35[j]	3.2	4.7	
	293	0.11[d]	36.3	54.5	0.45[e]	1.7	2.4	
n-Heptane	296	0.131[b]	41.0	61.5				
2,4-Dimethylpentane	296	0.178[b]	48.2	72.2				
2,2,3-Trimethylbutane	296	0.290[b]	61.1	91.7				
n-Octane	296	0.124[b]	39.7	59.6				54.6
2,3,4-Trimethylpentane	296	0.174[b]	45.4	68.1				
2,2,4-Trimethylpentane	296	0.332[b]	65.6	98.4	7[j]	0.61	1.1	94.6
2,2,3,3-Tetramethylbutane	379	0.80[e]	101	151				
n-Nonane	296	0.117[b]	38.8	58.2				
2,2,4,4-Tetramethylpentane	295	0.83[e]	124	186	24[e]	1.2	3.1	
2,2,3,3-Tetramethylpentane	295	0.42[e]	71.9	108	5.2[e]	1.2	2.3	
n-Decane	296	0.117[b]	38.4	57.5				
2,2,5,5-Tetramethylhexane	293	0.67[e]	105	158	12[e]	1.5	3.4	
2,2,6,6-Tetramethylheptane	293	0.47[e]	81.3	122				
2,2,7,7-Tetramethyloctane	316	0.34[e]	56.7	85.0				
n-Tetradecane	296	0.120[b]	37.6	56.3				
Squalane	296	0.119[b]	36.7	55.1				

a) Ref. 4. b) Ref. 8. c) Ref. 5. d) Ref. 19. e) Ref. 2. f) Ref. 4. g) Ref. 20. h) Ref. 21. i) Ref. 22, Data at 300 K. j) Ref. 23. k) Ref. 22, values at 300 K.

Table 2. Ranges and lifetimes of electrons in alkenes, dienes, and alkynes

Liquid	T (K)	G_{fi}	b_{ME} (Å)	$\bar{r}_{ME}$ (Å)	μ_e (cm²/V s)	τ_g (ps)	τ_g' (ps)
Ethylene	170	0.010[a]	31.6	47.4	0.003[d]	150	180
Propylene	234	0.042[a]	32.9	49.3	0.008[d]	68	87
Butene-1	293	0.093[b]	36.8	55.3	0.064[e]	11	15
trans-Butene-2	293	0.080[b]	35.4	53.1	0.029[e]	22	30
cis-Butene-2	293	0.23[b]	52.5	78.7	2.2[e]	1.0	1.6
Isobutene	293	0.25[b]	52.7	79.0	1.44[e]	1.6	2.6
2-Methylbutene-2	292	0.26[b]	58.3	87.5	3.6[f]	0.83	1.4
2,3-Dimethylbutene-2	293	0.44[b]	76.9	115	5.8[e]	3.6	6.8
Hexene-1	293	0.10[b]	34.3	51.4			
	296	0.062[c]	28.6	42.8			
trans-Hexene-2	293	0.092[b]	34.7	52.0			
3,3-Dimethylbutene-1	296	0.17[c]	47.3	71.0			
trans-Hexene-3	293	0.10[b]	36.0	54.1			
cis-Hexene-3	293	0.13[b]	38.3	57.5			
Cyclohexene	293	0.20[b]	43.9	65.8	1.00[e]	1.5	2.3
	296	0.150[c]	37.9	56.9			
Propadiene	282	0.050[b]	28.8	43.2			
Butadiene-1,3	269	0.038[b]	26.3	39.5			
Pentadiene-1,4	293	0.067[b]	29.5	44.3			
Hexadiene-1,5	292	0.066[b]	28.5	42.7			
Heptadiene-1,6	292	0.067[b]	28.3	42.4			
Octadiene-1,7	292	0.065[b]	27.5	41.2			
Acetylene	198	0.020[b]	24.2	36.3			
Propyne	260	0.17[b]	32.8	49.1			
Butyne-2	293	0.32[b]	64.9	97.4			
Hexyne-1	253	0.10[b]	28.7	43.0			
Hexyne-2	293	0.19[b]	47.7	71.5			
Hexyne-3	293	0.212[b]	50.7	76.0			

a) Ref. 4. b) Ref. 3. c) Ref. 8. d) Ref. 4. e) Ref. 24. f) Ref. 25, data at 300 K.

Table 3. Ranges and lifetimes of electrons in aromatics

Liquid	T (°K)	G_{fi}	b_{ME} (Å)	$\bar{r}_{ME}$ (Å)	μ_e (cm²/V s)	τ_g (ps)	τ_g' (ps)
Benzene	292	0.081[a]	28.7	43.0	0.114[c]	3.7	5.0
	296	0.053[b]	28.4	42.6	0.6[d]	0.70	0.96
Toluene	292	0.093[a]	29.1	43.7	0.063[c]	7.3	10
t-Butylbenzene	296	0.09[b]	28.4	42.6			
1,2-Dimethylbenzene	292	0.094[a]	27.2	40.8	0.018[c]	22	31
1,3-Dimethylbenzene	292	0.082[a]	27.8	41.7	0.057[c]	7.0	9.6
1,4-Dimethylbenzene	292	0.073[a]	27.8	41.7	0.062[c]	6.1	8.2
1,2,3-Trimethylbenzene	292	0.12[a]	29.3	44.0	0.022[c]	24	34
1,2,4-Trimethylbenzene	292	0.083[a]	27.9	41.9	0.035[c]	12	16
1,3,5-Trimethylbenzene	293	0.087[a]	29.5	44.3	0.16[c]	2.9	4.0
1,2,3,4-Tetramethylbenzene	292	0.11[a]	29.3	43.9			
1,2,4,5-Tetramethylbenzene	353	0.15[a]	31.8	47.7			
Pentamethylbenzene	333	0.22[a]	38.3	57.5			
Hexamethylbenzene	448	0.6[a]	57.4	86.1			
Naphthalene	357	0.094[a]	22.4	33.7			
Anthracene	500	~0.1[a]	~16	~24			

a) Ref. 5. b) Ref. 8. c) Ref. 5. d) Ref. 25, data at 300 K.

TABLE 4. TEMPERATURE DEPENDENCE OF ELECTRON RANGES IN HYDROCARBONS

Liquid	T (K)	G_{fi}	b_{ME} (Å)	d (g/cm³)	$b_{ME}d$ (10^{-8} g/cm²)		Liquid	T (K)	G_{fi}	b_{ME} (Å)	d (g/cm³)	$b_{ME}d$ (10^{-8} g/cm²)	
n-Hexane[a]	296	0.131	42.1	0.656	28			383	0.22	42.3	0.577	24	
	297	0.138	43.0	0.656	28		Cyclohexene[b]	185	0.066	38.3	0.917	35	
	314	0.162	44.4	0.640	28			218	0.10	39.2	0.885	35	
	319	0.168	44.6	0.636	28			256	0.14	40.4	0.848	34	Av. 36
	328	0.183	45.6	0.627	29			293	0.20	43.9	0.813	36	
	333	0.195	46.5	0.621	29	Av. 29		331	0.27	47.9	0.776	37	
	348	0.217	47.7	0.609	29			358	0.33	51.7	0.750	39	
	352	0.226	48.4	0.604	29		Butadiene[b]	183	0.018	27.5	0.752	21	
	357	0.239	49.2	0.600	30			216	0.024	26.4	0.712	19	Av. 19
	363	0.248	49.8	0.594	30			240	0.030	26.2	0.684	18	
	371	0.256	50.0	0.586	29			269	0.038	26.3	0.650	17	
Cyclohexane[a]	296	0.149	41.5	0.776	32		Propyne[b]	183	0.090	27.5	0.760	21	
	305	0.169	43.1	0.767	33			210	0.12	29.9	0.725	22	Av. 22
	307	0.166	42.4	0.766	32			233	0.14	31.1	0.694	22	
	315	0.184	43.8	0.758	33			260	0.17	32.8	0.657	22	
	322	0.195	44.3	0.751	33		Benzene[c]	281	0.072	28.2	0.891	25	
	333	0.213	45.3	0.741	34	Av. 33		292	0.081	28.7	0.880	25	
	339	0.233	46.9	0.735	34			304	0.087	28.7	0.867	25	
	348	0.245	47.2	0.726	34			313	0.098	29.5	0.858	25	
	354	0.253	47.6	0.721	34			324	0.105	29.6	0.846	25	Av. 26
	357	0.263	48.2	0.718	35			333	0.12	30.7	0.837	26	
	368	0.279	48.8	0.707	34			345	0.13	31.0	0.823	26	
Hexene-1[b]	152	0.018	30.1	0.812	24			353	0.15	32.5	0.815	27	
	192	0.033	30.5	0.772	24			374	0.19	35.1	0.793	28	
	224	0.049	31.3	0.740	23		Toluene[c]	212	0.044	28.0	0.941	26	
	255	0.067	32.1	0.708	23			253	0.066	28.0	0.904	25	
	293	0.10	34.3	0.673	23	Av. 23.5		292	0.093	29.1	0.868	25	Av. 25
	323	0.13	36.2	0.640	23			322	0.12	30.3	0.840	25	
	354	0.18	39.9	0.607	24			354	0.15	31.3	0.811	25	

a) Ref. 7. b) Ref. 3. c) Ref. 5.

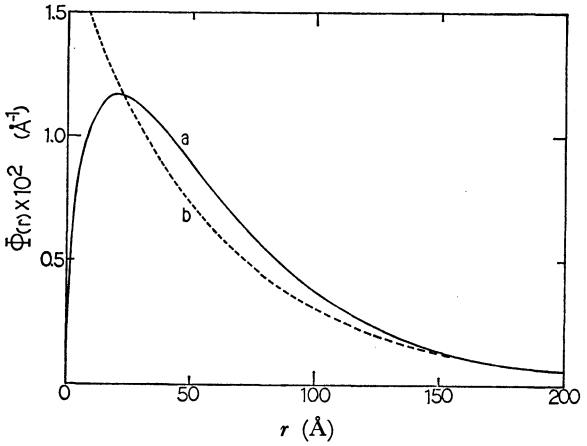

Fig. 1. Comparison between the spatial distribution functions for electrons in cyclohexane. a: modified exponential function, b: simple exponential function. See the text for the parameters used in the calculations.

tained using $G_{fi}=0.148$ and $G_t=4.3$. Table 4 shows the calculated temperature dependence of electron ranges b_{ME} for some of the hydrocarbons. It can be seen from Table 4 that b_{ME} increases with increasing temperature for these hydrocarbons except for butadiene where b_{ME} is nearly constant over the temperature range studied. Values of the parameter $b_{ME}d$ are also given in Table 4, where d is the liquid density. The value of $b_{ME}d$ is nearly constant for each of the hydrocarbons, although it decreases with increasing temperature for butadiene and tends to increase with increasing temperature for cyclohexene at higher temperatures. Thus, it appears that the electron range in liquid hydrocarbons is, approximately, inversely proportional to the medium density.

Geminate Recombination Times. The geminate ion-electron recombination times or the lifetimes of geminate electrons, τ_g and τ_g', are given for alkanes, alkenes and aromatics in Tables 1, 2 and 3, respectively. It can be seen from these tables that the values of τ_g or τ_g' are in the time range of 1—10 ps for most of the hydrocarbons and in the time range of 10—100 ps for some of the hydrocarbons. It is also seen that the geminate recombination time correlates with the electron mobility: the greater is the electron mobility, the shorter is the geminate recombination time. The geminate recombination times for electrons in liquid methane and neopentane are longer than expected from the electron mobilities in these liquids. This is due to the fact that the electron ranges are very large in methane and neopentane. It is interesting to note that the electrons in methane and neopentane are quasi-free electrons. The corrected

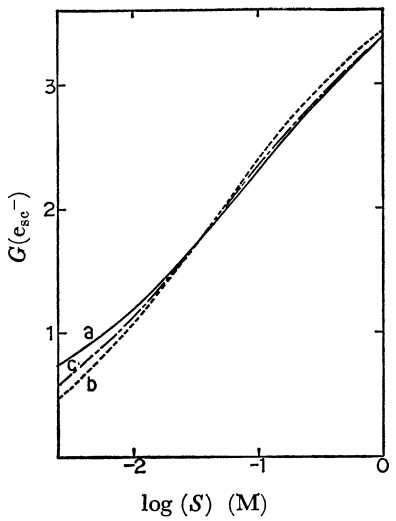

Fig. 2. Concentration dependence of the yield of electrons scavenged in a cyclohexane solution. a: calculated from Schuler's scavenging function, b: calculated from Eq. (7a), c: calculated from Eq. (7b). See the text for the parameters used in the calculations.

geminate recombination time, τ_g', is greater than the geminate recombination time, τ_g, derived directly from the Nernst-Einstein relation. The ratio of τ_g' to τ_g is different for individual compounds and depends on the value of $\bar{r}_{ME}/r_c$ as seen from Eqs. (4a) and (4b). For instance, the values of τ_g'/τ_g are large for methane and neopentane for which the values of $\bar{r}_{ME}/r_c$ are large.

Electron Scavenging in Cyclohexane. Figure 2 shows the yields of electrons scavenged, $G(e_{sc}^-)$, by a scavenger (carbontetrachloride) in cyclohexane, which were calculated as a function of the scavenger concentration. In Fig. 2, curve a was calculated using Schuler's scavenging function with $G_{fi}=0.12$, $G_t=4.2$ and $\alpha=12\ M^{-1}$.[26] It is well known that Schuler's scavenging function can satisfactorily reproduce the observed dependence on the scavenger concentration of the yield of electrons scavenged in irradiated liquid hydrocarbons. Curves b and c were calculated using Eqs. (7a) and (7b), respectively. The value of the parameter, k/D, involved in Eq. (7a) or (7b) was chosen so that the calculated curve fits reasonably curve a. The value of k/D thus chosen is 8.5×10^{14} $M^{-1}\,cm^{-2}$ in Eq. (7a) and $5.9\times10^{14}\ M^{-1}\,cm^{-2}$ in Eq. (7b). It is seen in Fig. 2 that curve a is closer to curve c than curve b and that curve c is very close to curve a at the scavenger concentrations higher than 10^{-2} M. However, curve c deviates from curve a at the scavenger concentrations lower than 10^{-2} M, and the deviation tends to increase with decreasing scavenger concentration. The value of k can be obtained from k/D making use of μ_e. Taking $\mu_e=0.24\ cm^2\,V^{-1}\,s^{-1}$,[20] k is calculated to be 5.2×10^{12} $M^{-1}\,s^{-1}$ from $k/D=8.5\times10^{14}\ M^{-1}\,cm^{-2}$ and $3.6\times10^{12}\ M^{-1}\,s^{-1}$ from $k/D=5.9\times10^{14}\ M^{-1}\,cm^{-2}$. The expermental values of k have been reported to be 4.3×10^{12},[27] 2.7×10^{12},[28] and $1.8\times10^{12}\ M^{-1}\,s^{-1}$ [20] for the reaction of electrons with carbon tetrachloride in cyclohexane. The values of k derived in the present work are reasonably compared with the experimental values, in particular, the value of $3.6\times10^{12}\ M^{-1}\,sec^{-1}$ is in good agreement with the experimental values. Thus, it appears that the present treatment can well account for the concentration dependence of electron scavenging in cyclohexane except for the low concentration region. Since the electrons scavengeable at low scavenger concentrations are mostly far away from their parent ions, Brownian motion of these electrons is as much effective as their drift motion in the Coulomb field and the use of the Nernst-Einstein relation is not appropriate for the description of the behavior of such electrons. The Smoluchowski equation must be properly solved for electrons in such a situation.[29]

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