Electron Scavenging by Bromobenzene in the Radiolysis of Heptane, 1-Hexene and Their Mixtures

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(Received April 28, 1975)

A quantitative study has been made of electron scavenging by bromobenzene in the radiolysis of heptane, 1-hexene and their mixtures. Experimental data were analyzed using Schuler's scavenging function. It has been found that the total ion yields are 4—5 G units in these liquids and the value of the reactivity parameter decreases with increasing fraction of 1-hexene. Further analysis of the data was made in terms of the exponential spatial distribution function for the electrons. A discussion is given to physical parameters derived from such analysis.

In recent years considerable efforts have been focussed on reactions of electrons in irradiated liquid hydrocarbons. Chemical and physical methods have both been applied to elucidation of quantitative aspects of electron reactions in liquid hydrocarbons. Most previous studies of electron reactions were concerned with electrons in alkanes.

In the present work we have made a quantitative study of electron scavenging by bromobenzene in the radiolysis of heptane, 1-hexene and their mixtures. We have determined the total ion yields and values of the reactivity parameter from the Schuler plot of experimental data. We have further analyzed the experimental data in terms of the exponential spatial distribution function for the electrons and derived from such analysis some physical parameters that are related to the behavior of electrons in these liquid hydrocarbons. We also include in this paper a comparative study of electron distributions in irradiated cyclohexane and 2,2,4-trimethylpentane.

Experimental

Bromobenzene (Nakarai Kagaku research grade) was distilled and passed through a column of activated alumina. Heptane (Merck spectrograde) was passed through a column of activated silica gel. The purity of heptane was 99.9% and a major impurity was hexane. 1-Hexene (Tokyo Kagaku Seiki standard material, >99% stated purity) was used as received. Impurities in 1-hexene were not identified.

Samples containing the desired amount of bromobenzene were degassed by freeze-pump-thaw cycles and sealed off the vacuum line. The samples were irradiated at 23 °C with ^{60}Co γ-rays for one hour at a dose rate of 3.19×10^{19} eV g^{-1}·hr^{-1}. The dose absorbed in the samples was determined by correction for the appropriate electron density differences. The benzene produced from bromobenzene was measured by a Hitachi K53 gas chromatograph with a flame ionization detector. The column used in the gas chromatograph was 30% hexatriacontane on Celite 545.

Results and Discussion

Yield of Electrons Scavenged by Bromobenzene in Heptane–1-Hexene Solutions. Figure 1 shows plots of the yield of benzene produced *vs.* the concentration of 1-hexene for heptane–1-hexene solutions. In Fig. 1, curves a and b show such plots for the solutions containing 0.238 and 0.0143 M bromobenzene, respectively. It is seen in Fig. 1 that the yield of benzene decreases gradually with increasing 1-hexene concentration. It appears that significant decreases in benzene yield are observed around 2 and 7 mol% 1-hexene. The decrease of the benzene yield at 10.5 mol% 1-hexene amounts to 0.6 and 0.5 G units for the solutions containing 0.238 and 0.0143 M bromobenzene, respectively. Further, we have measured the yield of benzene as a function of the bromobenzene concentration for (a) heptane solutions, (b) heptane–1-hexene solutions (5.54 mol% 1-hexene), (c) heptane–1-hexene solutions (10.5 mol% 1-hexene) and (d) 1-hexene solutions. The concentration of bromobenzene was varied from 1.4×10^{-2} to 3.2×10^{-1} M. The data have been treated by assuming the reaction mechanism presented in the previous paper[1] and applying the scavenging function (Eq. (1)) developed by Schuler and his coworkers.[2]

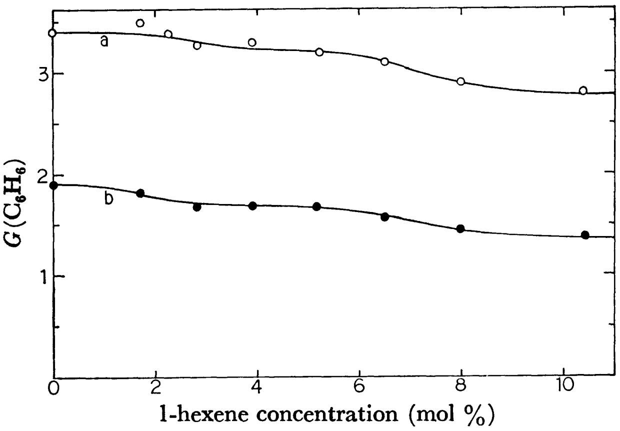

Fig. 1. The yield of benzene *vs.* concentration of 1-hexene in heptane–1-hexene solutions containing (a) 0.238 M and (b) 0.0143 M bromobenzene.

$$\frac{1}{G(C_6H_6)-G_{fi}}=\frac{1}{G_{gi}}+\frac{1}{G_{gi}\alpha^{1/2}S^{1/2}} \tag{1}$$

where G_{fi} and G_{gi} represent the yields of free and geminate ions, respectively, S is the concentration of bromobenzene, and α is a parameter which represents the reactivity of the electron toward the solute relative to the recombination processes. Figure 2 shows plots of Eq. (1) for four sets of experimental data. These results indicate that the data correspond to the predicted concentration dependence. Since it was difficult to measure the free ion yield by our analytical technique, values of G_{fi} for pure heptane and 1-hexene were taken from Ref.

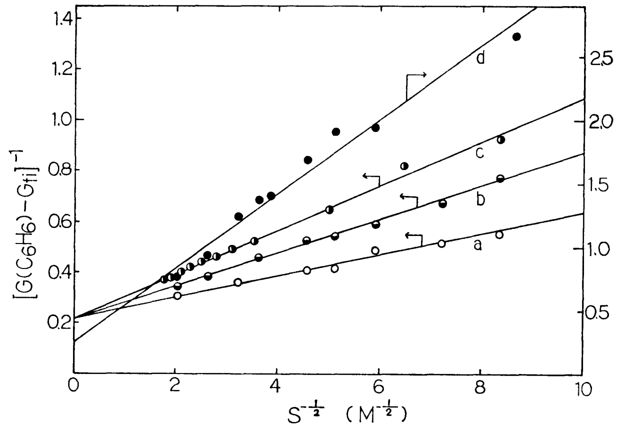

Fig. 2. Plots of $[G(C_6H_6)-G_{fi}]^{-1}$ *vs.* $[\text{bromobenzene}]^{-1/2}$ for heptane–1-hexene solutions. a: heptane, b: heptane-5.54 mol% 1-hexene, c: heptane–10.5 mol% 1-hexene, d: 1-hexene.

3, and those for the heptane–1-hexene mixtures were estimated in a manner that will be described later. The geminate ion yield and the total ion yield, G_t, determined from Eq. (1) are given in Table 1 together with the free ion yield used. The values of G_t thus obtained are 4.7—4.8 for pure heptane and heptane–1-hexene mixtures, and 4.0 for pure 1-hexene. The G_t values of 4.7—4.8 are somewhat higher than those obtained for alkanes in the previous work.[1] The G_t value of 4.0 for 1-hexene is based on the data points more scattered than those for the other solvents, and this value of G_t is perhaps a lower limit for the total ion yield in 1-hexene. Values of the reactivity parameter α are also given in Table 1. It is seen in Table 1 that the value of α decreases with increasing fraction of 1-hexene and the α value in 1-hexene is about 1/36 of that in heptane. The significance of this trend in α will be discussed later.

Prior to a further analysis of the present experimental data, we will make a comparative study of spatial distribution functions and scavenging functions for electrons in cyclohexane and 2,2,4-trimethylpentane because such a study should provide a basis for further analyzing our data on the heptane–1-hexene systems.

TABLE 1. VALUES OF THE PARAMETERS DERIVED FROM SCHULER'S SCAVENGING FUNCTION

Fraction of 1-hexene (mol %)	G_{fi}	G_{gi}	G_t	α (M^{-1})
0	0.13[a]	4.5_5	4.7	27
5.54	0.12[b]	4.7	4.8	10
10.5	0.12[b]	4.6	4.7	6.3
100	0.062[a]	3.9_5	4.0	0.75

a) Ref. 3. b) See text.

Spatial Distribution and Scavenging Functions for Electrons in Cyclohexane and 2,2,4-Trimethylpentane. Spatial Distributions: First, we attempt to compare the exponential spatial distribution function (Eq. (2))[4] for electrons in cyclohexane and 2,2,4-trimethylpentane with the corresponding spatial distribution function (Eq. (4))[5,6] derived from Schuler's lifetime distribution function[7] by assuming the time-distance relation given by Eq. (3).[8]

$$\left.\begin{aligned} \phi(r) &= 0 && \text{for } r \leq r_0 \\ \phi(r) &= (4\pi br^2)^{-1}\exp\left[(r_0-r)/b\right] && \text{for } r \geq r_0 \end{aligned}\right\} \tag{2}$$

where b is the electron range parameter, r_0 is the reaction radius and r is the ion-electron separation distance.

$$t = r^3/(3Dr_c) \tag{3}$$

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.

$$\phi_g(r) = \frac{\lambda}{4\pi Dr_c}\left[\left(\frac{3Dr_c}{\pi\lambda r^3}\right)^{1/2} - \exp\left(\frac{\lambda r^3}{3Dr_c}\right)\operatorname{erfc}\left(\frac{\lambda r^3}{3Dr_c}\right)^{1/2}\right] \tag{4}$$

where $\lambda=k/\alpha$ and k is the rate constant for reaction of the electron with a scavenger. Since Eq. (4) is applicable to geminate electrons, it is required for a quantitative comparison between the two distribution functions that the exponential distribution function also be normalized with respect to the geminate electron distribution. Therefore, we have actually used Eq. (5) for comparison instead of Eq. (2).

$$\phi_g(r) = (G_t/G_{gi})[1-\exp(-r_c/r)]\phi(r) \tag{5}$$

The probability of finding the geminate electrons between r and $r+dr$ is given by Eq. (6).

$$\Phi(r)dr = 4\pi r^2\phi_g(r)dr \tag{6}$$

Values of physical parameters used in the calculations are listed in Table 2. 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 $D_e=kT\mu_e/e$.

Figures 3 and 4 show the spatial distribution $\Phi(r)$ for the geminate electrons in cyclohexane and 2,2,4-trimethylpentane, respectively. In these figures, curve a represents the exponential distribution function and curve b shows Schuler's distribution function. It is seen in Figs. 3 and 4 that curve a is very close to curve b down to the ion-electron separation distance $r\sim35$ Å for cyclo-

TABLE 2. PHYSICAL PARAMETERS USED IN THE CALCULATION OF SPATIAL DISTRIBUTIONS OF ELECTRONS IN CYCLOHEXANE AND 2,2,4-TRIMETHYLPENTANE

Solvent	r_c (Å)	b (Å)	μ_e $(cm^2\ V^{-1}\ s^{-1})$	Solute	α (M^{-1})	k $(M^{-1}\ s^{-1})$
Cyclohexane	279[a]	57.5[b]	0.24[c]	CCl_4	12[e]	2.7×10^{12} [g]
2,2,4-Trimethyl-pentane	291[a]	96.1[b]	7[d]	C_2H_5Br	5[f]	6.3×10^{12} [c]

a) Ref. 3. b) Ref. 1. c) Ref. 14. d) Ref. 16. e) Ref. 17. f) Ref. 18. g) Ref. 19.

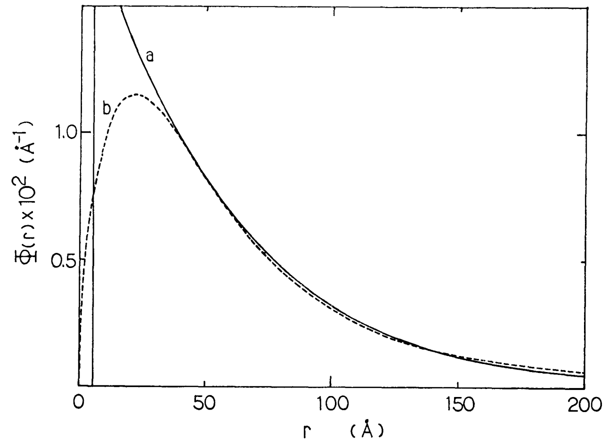

Fig. 3. Spatial distributions of electrons in cyclohexane. a: exponential function (r_0=5 Å), b: Schuler's function. See Table 2 for parameters used in the calculations.

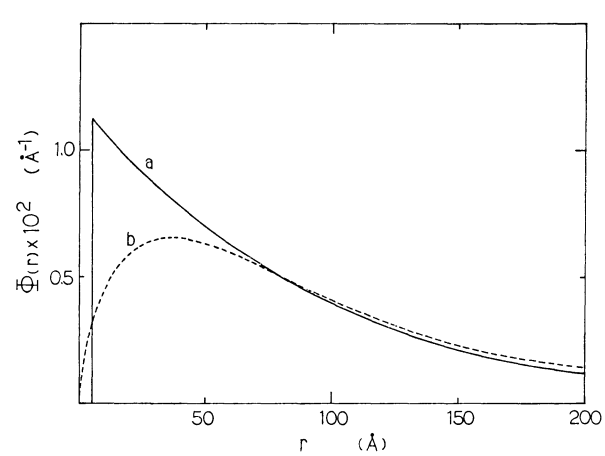

Fig. 4. Spatial distributions of electrons in 2,2,4-trimethylpentane. a: exponential function (r_0=5 Å), b: Schuler's function. See Table 2 for parameters used in the calculations.

hexane and $r \sim 60$ Å for 2,2,4-trimethylpentane. Experimentally, quantitative kinetic studies of electron scavenging in liquid hydrocarbons are usually made at solute concentrations less than 0.5 M. It can be shown that most of the electrons scavengeable in scavenging experiments are distant from their parent ions farther than the distances mentioned above.[9] Thus, it is expected that the exponential distribution function would be able to account for experimental results on electron scavenging in liquid hydrocarbons. This also implies that the choice of the reaction radius is practically a trivial problem. It should be stressed that the exponential distribution function has the advantage that the range parameter b can be readily determined from the free ion yield by Eq. (7).

$$\int_0^\infty \phi(r) \exp(-r_c/r) 4\pi r^2 dr = G_{fi}/G_t \tag{7}$$

A calculation is described below on the concentration dependence of electron scavenging in cyclohexane and 2,2,4-trimethylpentane.

Scavenging Functions: It has been shown by Hummel[10] that the recombination probability $P_{q,r}$ of an ion-electron pair separated by r in the presence of scavenger is given by Eq. (8).

$$P_{q,r} = \frac{2\exp(-qr)[1-\exp(-r_c/r)]}{1+\exp(-2qr)+2qr^2 r_c^{-1}[1-\exp(-r_c/r)]} \tag{8}$$

where $q=(kS/D)^{1/2}$ and S is the concentration of scavenger. The yield of electrons scavenged, $G(e_{sc}^-)$, in the presence of scavenger is given by Eq. (9).

$$G(e_{sc}^-) = G_t \int_0^\infty \phi(r)(1-P_{q,r}) 4\pi r^2 dr \tag{9}$$

Empirically, the concentration dependence of the yield of electrons scavenged by a scavenger in liquid hydrocarbons can be well described by Schuler's scavenging function (Eq. (10)).[2]

$$G(e_{sc}^-) = G_{fi} + G_{gi}\{(\alpha S)^{1/2}/[1+(\alpha S)^{1/2}]\} \tag{10}$$

Figures 5 and 6 show the concentration dependence of the yields of electrons scavenged by carbon tetrachloride in cyclohexane and by ethyl bromide in 2,2,4-trimethyl-

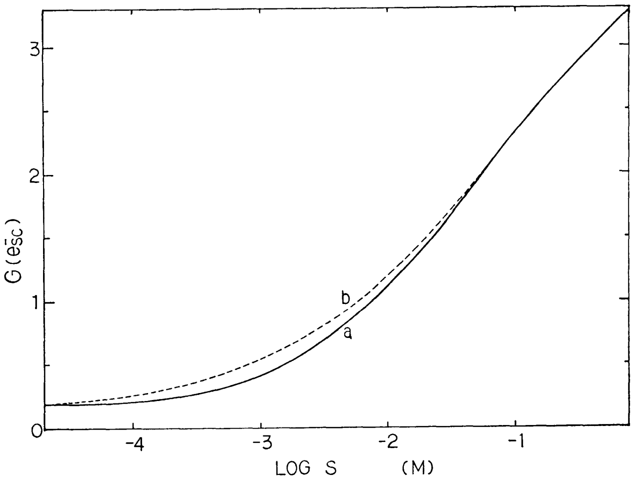

Fig. 5. The calculated concentration dependence of the yield of electrons scavenged by carbon tetrachloride in cyclohexane. a: calculated from Eq. (9) using the exponential distribution function, b: calculated from Schuler's scavenging function (Eq. (10)).

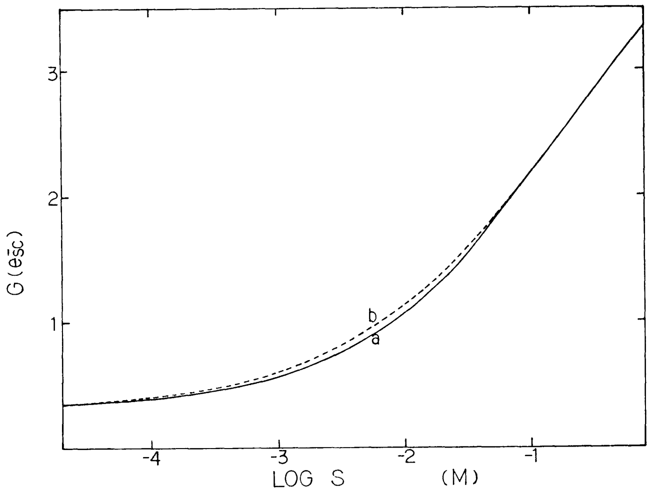

Fig. 6. The calculated concentration dependence of the yield of electrons scavenged by ethyl bromide in 2,2,4-trimethylpentane. a: calculated from Eq. (9) using the exponential distribution function, b: calculated from Schuler's scavenging function (Eq. (10)).

pentane, respectively. In these figures, curve a was calculated from Eq. (9) using the exponential distribution function for $\phi(r)$ and curve b was obtained from Eq. (10). It is seen in Figs. 5 and 6 that the shape of curve a is similar to that of curve b over the entire range of the scavenger concentration studied. Although there is some discrepancy between curves a and b around $S\sim10^{-3}$ M for cyclohexane, the experimental data points lie between the two curves in this concentration region.[7] Thus, we have been able to demonstrate that the exponential distribution function can well account for the concentration dependence of electron scavenging in liquid hydrocarbons and that this is due to the fact that the exponential distribution function is similar in its significant portion to Schuler's distribution function.

Analysis of Experimental Data on Electron Scavenging by Bromobenzene in Heptane, 1-Hexene and Their Mixtures. In this section, we will describe the procedure to evaluate physical parameters of the hydrocarbon mixtures, analyze using the exponential distribution function the concentration dependence of the yield of electrons scavenged by bromobenzene in heptane, 1-hexene and their mixtures, and discuss the significance of physical parameters derived from such analysis.

Physical Parameters of Heptane-1-Hexene Mixtures: The electron range b of a mixture is given by Eq. (11).[11]

$$(bd)^{-2} = x_1(b_1d_1)^{-2} + x_2(b_2d_2)^{-2} \qquad (11)$$

Here the density d of the mixture is obtained as $d=x_1d_1+x_2d_2$, where d_1 and d_2 are the densities of the mixture components, and x_1 and x_2 are their mole fractions. The free ion yield in a mixture can be determined from Eq. (7) using b in Eq. (11). The free ion yields thus obtained are given for the heptane–1-hexene mixtures in Table 1. The dielectric constant ε of a mixture can be calculated from the Clausius-Mosotti equation (Eq. (12)).

$$\varepsilon = [1+(8\pi\bar{\alpha}n/3)]/[1-(4\pi\bar{\alpha}n/3)] \qquad (12)$$

Here the isotropic polarizability $\bar{\alpha}$ of the mixture is given by $\bar{\alpha}=x_1\bar{\alpha}_1+x_2\bar{\alpha}_2$, where $\bar{\alpha}_1$ and $\bar{\alpha}_2$ are the isotropic polarizabilities of the mixture components, and the number density n of molecules in the mixture is given by $n^{-1}=x_1n_1^{-1}+x_2n_2^{-1}$.[12]

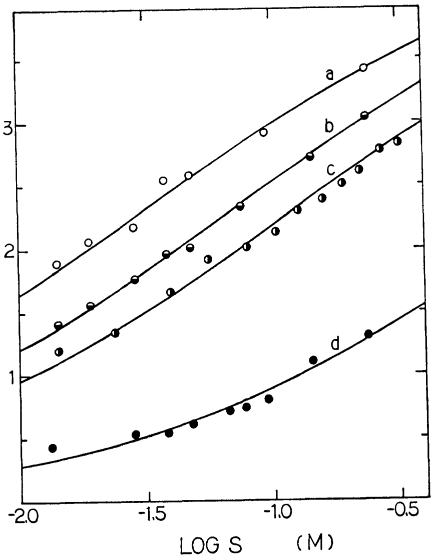

Fig. 7. The calculated and observed yields of electrons scavenged *vs.* concentration of bromobenzene in heptane-1-hexene solutions. a: heptane, b: heptane-5.54 mol% 1-hexene, c: heptane-10.5 mol% 1-hexene, d: 1-hexene. Curves show the calculated yields.

Comparison between the Calculated and Observed Yields of Electrons Scavenged: Using Eqs. (7), (8), and (9) we have calculated the yields of electrons scavenged by bromobenzene in heptane, 1-hexene and their mixtures. Figure 7 shows the calculated and observed yields of electrons scavenged plotted against the concentration of bromobenzene. It is seen in Fig. 7 that the calculated curves agree well with the experimental data within experimental error. The parameters used in the calculations are b, k, and D. The electron range b was obtained from the free ion yield as already mentioned. The rate constant k for reaction of the electron with a scavenger and the diffusion constant D appear only as the ratio of k/D in Eq. (8). Accordingly, k/D is the only adjustable parameter in the calculations. The curves shown in Fig. 7 were calculated with the properly chosen values of k/D by best fitting them to the experimental data. The values of k/D thus obtained are given in Table 3. Knowing the value of D or the electron mobility, we can get the value of k. Unfortunately, values of D are not known for electrons in our systems, so we are unable to determine values of k. The relative values of k/D are also given in Table 3 as $(k/D)_N/(k/D)_1$, where $(k/D)_1$ stands for heptane. It is seen in Table 3 that the relative value of k/D decreases with increasing fraction of 1-hexene. If the reaction of the electron with bromobenzene in these liquid hydrocarbons is diffusion-controlled, *i.e.*, k is directly proportional to D, the relative value of k/D should be unity for all the hydrocarbons studied. It is not the case for our systems. This result indicates that electron scavenging by bromobenzene in these hydrocarbons is not a diffusion-controlled reaction. For comparison we have also calculated the relative value of k/D using the time-distance relationship derived from the Nernst-Einstein relation. In this approximation, Eq. (13) holds.[13]

$$k/D = 3\alpha r_c/b^3 \qquad (13)$$

From Eq. (13) we can calculate k/D with known values of α, r_c and b. The relative values of k/D thus obtained are given in the last column of Table 3. It can be seen from Table 3 that these relative values of k/D are in good agreement with those derived from the theoretical scavenging function. Such an agreement implies that the effect of Brownian motion on the behavior of electrons in the Coulomb field is rather small for the electrons scavengeable at the scavenger concentrations studied.

It has recently been shown[14] that the rate constant k for reaction of the electron with a scavenger in different hydrocarbon solvents is, in some cases, proportional to the square root of the electron mobility μ_e in the corresponding solvents. If we assume that this relation between k and μ_e holds for our systems, we can calculate the relative value of μ_e from that of k/D. The relative values of μ_e thus calculated are given in Table 3 as μ_N/μ_1, where μ_1 stands for heptane. It is seen in Table 3 that

TABLE 3. SOME PHYSICAL PARAMETERS DERIVED FOR ELECTRONS IN HEPTANE, 1-HEXENE AND THEIR MIXTURES

Fraction of 1-hexene (mol %)	k/D[a] (10^{14} M^{-1} cm^{-2})	N	$\frac{(k/D)_N}{(k/D)_1}$[a]	μ_N/μ_1[b]	$\frac{(k/D)_N}{(k/D)_1}$[c]
0	2.3	1	1	1	1
5.54	1.1	2	0.47	4.5	0.41
10.5	0.67	3	0.29	12	0.27
100	0.20	4	0.087	130	0.082

a) Determined from the best fit of the calculated scavenging curve to the experimental data. b) Based on the assumption that k is proportional to $\mu_e^{1/2}$. c) Calculated using the Nernst-Einstein relation.

the value of μ_N/μ_1 increases with increasing fraction of 1-hexene, and the electron mobility in 1-hexene is two orders of magnitude greater than that in heptane. If we assume that the electron mobility in heptane is 0.06 cm^2 V^{-1} s^{-1} based on the electron mobility in hexane (0.09,[16] 0.07,[20] 0.08[14] cm^2 V^{-1} s^{-1}), we obtain μ_e= 7.8 cm^2 V^{-1} s^{-1} for electrons in 1-hexene, which is of the same order of magnitude as the electron mobilities in 2-methylpropene (1.44 cm^2 V^{-1} s^{-1}),[21] *cis*-2-butene (2.2 cm^2 V^{-1} s^{-1}),[21] 2-methyl-2-butene (3.6 cm^2 V^{-1} s^{-1})[20] and 2,3-dimethyl-2-butene (5.8 cm^2 V^{-1} s^{-1}).[21] It is possible, however, that the value of μ_e thus derived for electrons in 1-hexene is somewhat overestimated, since the reactivity parameter α is rather sensitive to the experimental data on electron scavenging.

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