Effect of an Electric Field on Electron Attachment to SF_6 in Liquid Ethane and Propane

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The effect of an external electric field, E, on the electron attachment rate constant, k_e, of SF_6 was studied by a pulsed-conductivity technique in liquid ethane and propane at temperatures ranging from 133–176 K and 156–216 K, respectively. At constant temperature, k_e was independent of E at fields less than E_c, the critical field above which the mobility becomes field-dependent, but at $E > E_c$, k_e increased proportionally with D_e, the diffusion coefficient of the electron. Application of diffusion-controlled reaction theory to the $k_e - D_e$ dependence yielded an effective encounter radius of 14.5 Å for the e^--SF_6 reaction pair in both liquids. This encounter radius is discussed in terms of the electron-SF_6 interaction energy and models of electron transport and attachment in low-mobility liquids.

I. Introduction

The ubiquitous role that electrons play in processes ranging from dielectric breakdown [1] to photosynthesis [2] and biological redox reactions [3] accounts for the current intense interest in the physico-chemical properties of excess electrons in disordered systems. Quasifree electrons in nonpolar molecular liquids are especially amenable to study due to the ease with which electrons can be generated by pulse radiolysis or flash photolysis and monitored by conductivity or optical techniques [4]. Studies of this type have provided information on electron transport processes in which the electron mobility, μ_e, varies over more than a millionfold range and on electron reaction processes such as recombination, attachment and detachment.

Studies of the field dependence of μ_e have been particularly useful in elucidating the detailed mechanism of electron transport in a number of liquids [5], and studies of the field dependence of electron attachment in liquid argon and xenon complemented the field-dependent mobility studies of these liquids in demonstrating that electrons in these liquids are indeed heated by the external field [6]. We undertook the present study of field-dependent k_e's in liquid ethane and propane to determine if such a study would analogously complement our field-dependent mobility studies of these liquids and thereby provide a clearer understanding of the electron transport mechanism in low-mobility liquids.

II. Experimental

The pulsed-irradiation and electron current monitoring system were as described earlier [7] with the exception that a 2 ns irradiating pulse was used for electron half-lives in the 20 – 40 ns time region. Parallel-plate sample cells having interelectrode distances of 0.3 – 0.9 mm were used with the larger distances being used for measurements at the higher temperatures to minimize electron loss to the electrodes. We were restricted from measuring field-dependent k_e's at temperatures higher than those reported due to limitations imposed by a combination of the time resolution of the detection system, electron loss to the electrodes and the voltage that could be applied without causing dielectric breakdown.

Sample preparation was as described earlier [7] except that the pre-irradiation step used in the solvent purification procedure was eliminated when we found that impurities which had been removed by pre-irradiation were re-introduced in subsequent vacuum distillations that were required in adding SF_6 to the samples. As a result of excluding pre-irradiation, we were unable to obtain sufficiently

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pure solvents for measurements at temperatures lower than those reported.

The concentration of SF_6 was varied from 0.6 – 7 μM and was chosen to optimize attachment to SF_6 at each temperature studied with the inter-electrode distance that was used. This concentration range was sufficient to provide more than an hundredfold excess concentration of SF_6 compared to the concentration of electrons and with this excess of scavenger, pseudo-first-order kinetics applied to the attachment reactions [6, 7].

The observed electron half-life, T_0, was read directly from the oscillogram and was corrected by T_b for electron losses arising from drift to the electrodes and/or attachment to residual impurities in the pure solvents. Values of T_b were determined immediately prior to adding SF_6 to the sample by measuring electron lifetimes in the "pure" solvent over the entire range of electric fields and under the same conditions of temperature and dose/pulse as those that were employed in the subsequent SF_6-scavenging experiment. The corrected electron half-life T_c was obtained from the expression $T_c^{-1} = T_0^{-1} - T_b^{-1}$ and was combined with [S] the SF_6 concentration [5] to yield the electron attachment rate constant $k_e = \ln 2/T_c[S]$. Measurements of k_e made under conditions where T_b^{-1} was more than 30 per cent of T_0^{-1} were rejected to minimize errors introduced by this correction procedure. We estimate that the total error in the reported values of k_e is ± 25 per cent.

III. Results

Several typical examples of the effect of an electric field on electron attachment to SF_6 are presented in Figure 1. At fields ranging from 50 – ~90 kV/cm, k_e is independent of E whereas at higher fields an increase of k_e with increasing field was observed. The onset of the field-enhanced attachment coincides with the onset of the supralinear field dependence of the electron mobility which we had reported earlier [5]. This field-enhanced attachment of electrons to SF_6 in liquid ethane and propane contrasts with the marked decrease in the k_e of SF_6 at $E > E_c$ in liquid argon and xenon [6].

The dependence of k_e on the electron diffusion coefficient, D_e, is shown for ethane and propane in Figs. 2 and 3, respectively. Values of D_e in these plots were obtained by using our earlier measurements of μ_e [5] in the Nernst-Einstein equation, $D_e = \mu_e k_B T/e$, where k_B is the Boltzman constant, T is the absolute temperature and e is the elementary electron charge. At temperatures for which no mobility data were available, values of μ_e were interpolated from our earlier results.

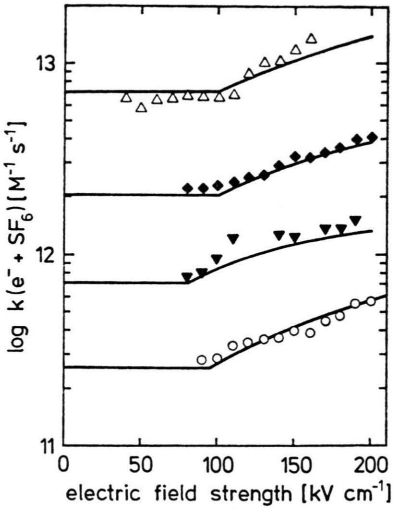

Fig. 1. Effect of electric field on electron attachment rate constant of SF_6 in liquid ethane at 133 (○) and 173 K (△) and in liquid propane at 177 K (▼) and at 195 K (◆). Solid lines were calculated using (3′) with $R = 14.5$ Å and D_e evaluated with Nernst-Einstein equation and published values of μ_e [5].

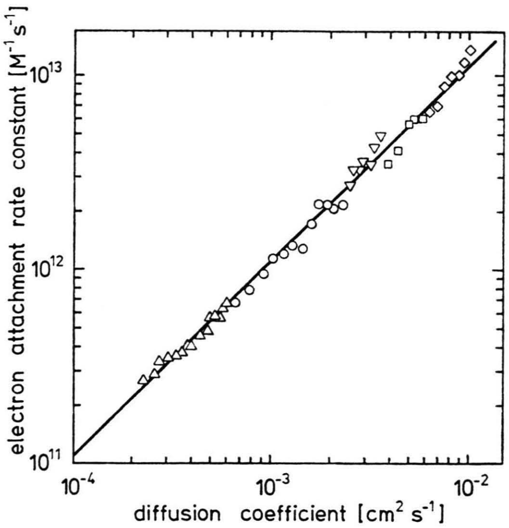

Fig. 2. Dependence of electron attachment rate constant on the electron diffusion coefficient in liquid ethane at 133 (△), 141 (○), 153 (▽), 165 (□) and 173 K (◇).

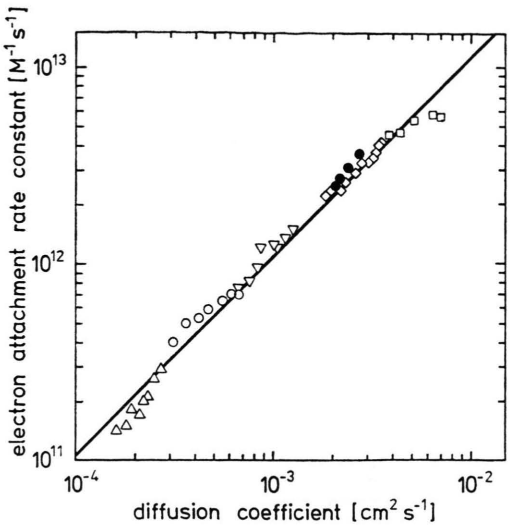

Fig. 3. Dependence of electron attachment rate constant on the electron diffusion coefficient in liquid propane at 156 (△), 165 (○), 177 (▽), 195 (◇), 197 (●), and 216 K (□).

Comparison of the low-field scavenging data in Figs. 1 – 3 with our earlier SF_6-attachment results reveals that the k_e's in this paper are generally ~20 per cent less than those reported previously, which is within the experimental error.

IV. Discussion

A) Diffusion – vs. Attachment-Controlled Reactions

The most general form of expressing the rate constants of reactants in a condensed phase is Noyes' [8] modification of the Smoluchowski equation

$$k_0^{-1} = k_d^{-1} + k_c^{-1}, \tag{1}$$

where k_0 is the observed second-order rate constant which is composed of two components that reflect the rate, k_d, at which reactants diffuse together and the rate, k_c, at which the chemical reaction occurs. For further refinements to (1) and a recent detailed discussion of the boundary conditions that apply, the reader is referred to Logan [9] and Naqvi et al. [10], respectively.

The time-dependent diffusional component of k_0 is given by

$$k_d(t) = 4\pi R D \left[1 + \frac{R}{(\pi D t)^{1/2}}\right], \tag{2}$$

where R is the encounter radius which is the sum of the effective radii of the electron, R_e, and the SF_6 molecule, R_{SF6}. D is the sum of the diffusion coefficients, which for this study of the electron and SF_6 are D_e and D_s, respectively. For electron attachment to SF_6, $D_e \gg D_s$ and D_e can be equated with D in (2). Also, under the conditions of our experiment the minimum value of $(\pi D_e t)^{1/2}$ is ~300 Å which is $\gg R$ (*vide infra*); consequently, k_d is time-independent in our experiments and (2) reduces to:

$$k_d = 4\pi R D_e. \tag{2'}$$

Substituting (2′) in (1) and rearranging yields

$$k_0' = 4\pi R D_e \bigg/ \left(1 + \frac{4\pi R D_e}{k_c}\right). \tag{3}$$

Schiller and Nyikos [11] have discussed the applicability of (3) to the reactions of electrons with several solutes in a variety of solvents in which D_e ranges from 0.002 – 2 cm^2/s. For electron attachment to most solutes in these solvents, they applied partial electron localization theory [12] and assumed different reactivities, k_l, and k_f, of localized and quasifree electrons, respectively [11]. For an electron acceptor such as SF_6, however, which has no onset energy of electron attachment in the gas phase [6], k_l was assumed equal to k_f and both were equated with k_c. With these assumptions and values of $k_l = k_f = k_c = 2.1 \times 10^{14}\ M^{-1}\ s^{-1}$ and $R =$ 8.9 Å, Schiller and Nyikos obtained a good fit of k_0 for electron attachment to SF_6 with available experimental data [11]. A detailed treatment of k_c was presented by Funabashi and Magee and by Henglein [13].

The fraction $4\pi R D_e / k_c$ in the denominator of (3) approached unity at the highest values of D_e that Schiller and Nyikos studied, viz. $D_e \cong 2\ cm^2/s$, whereas at the lowest D_e value of 0.002 cm^2/s, $4\pi R D_e / k_c < 0.01$ [11]. Our study is restricted to conditions at which $D_e < 0.01\ cm^2/s$, $4\pi R D_e / k_c \ll 1$ and (3) reduces to

$$k_0 = 4\pi R D_e. \tag{3'}$$

The proportionality between k_0, which we equate with k_e, and D_e predicted with (3′) is observed experimentally as Figs. 2 and 3 demonstrate. The value of R obtained from a least-sequares fit of the C_2H_6 and C_3H_8 data is 14.5 Å which is significantly greater than the R of 8.9 Å found by Schiller and Nyikos for electron attachment to SF_6 in n-hexane, isooctane and neopentane [11].

B) Dynamics of Electron Attachment to SF_6

Baird has discussed electron attachment to SF_6 in non-polar liquids in terms of the electron-SF_6 interaction energy, $U(r)$ which is given by

$$U(r) = -\frac{\alpha e^2}{2\varepsilon r^4} f, \tag{4}$$

where e is the charge of the electron, α is the SF_6 polarizability, ε is the dielectric constant of the solvent, and f is a screening function that accounts for the reduction of $U(r)$ due to solvent molecules between the electron and SF_6 [14]. Electron-hexadecapole interaction, which depends on r^{-5} [15], was ignored. Baird considered a Lekner [16] and a continuous [17] screening function and found for both cases that R calculated from $U(r)$ was significantly less than that derived from the observed rate constant. This can be demonstrated by calculating the distance, r_a, at which $U(r)$ balances the thermal energy, $\frac{3}{2} k_B T$:

$$r_a = \left(\frac{\alpha e^2}{3\varepsilon k_B T}\right)^{1/4}. \tag{4'}$$

At 195 K where $\varepsilon \approx 1.8$ [14] and $\alpha(SF_6) = 6.5$ Å^3 [18], a value of $r_a = \sim 7$ Å is found. Although r_a is significantly greater than the hard core radius of SF_6 of 2.9 Å [14], it is only about one-half the empirical value of R. Thus, it appears that the observed k_e values cannot be explained by electron-solute interactions alone. Baird has suggested that the discrepancy between r_a and R may be due to a breakdown of (4) at distances approaching R and/or electron tunneling to SF_6 at R [14]. Although these explanations are plausible, consideration of the electron transport mechanism provides an alternative interpretation.

C) Effect of Electron Transport Mechanisms on R

We have studied the high-field dependence of the electron mobility in liquid ethane and propane [5] and found that the observed dependence of u_e on E and T is consistent with either Bagley's phenomenological model of electrons jumping over multiple barriers [19] or the small polaron model of electron transport described by Holstein [20] and Efros [21]. Under the field and temperature conditions that we investigated in this and earlier studies, the equation describing small polaron transport reduces to Bagley's equation for u_e (E, T), which is

$$\mu_e(E,T) = \mu_e(0,T)\frac{\sinh(e\lambda E/2 k_B T)}{e\lambda E/2 k_B T}, \tag{5}$$

where λ is the distance between barriers.

Funabashi and Rao modified (5) to include fluctuating heights of the electron barriers and derived a value of $\lambda = 7.5$ Å for electrons in propane [22]. More recently, Rao et al. [23] considered our high field methane-ethane studies [24] and by introducing disorder into the electron-hopping mechanism found a value of $\lambda = 10$ Å. Electron transport over multiple barriers was also considered by Tachiya who found that transport over barriers of fluctuating heights exhibited the same field-dependent mobility as given by (5) if the number of electrons at available jumping sites is statistically averaged [25].

From our studies and those of Rao et al. and Tachiya, it is apparent that quantitatively deriving a value of λ for electron transport in ethane and propane is complex. Further, all of these studies are merely one-dimensional treatments of a three-dimensional problem and therefore, as Rao et al. have pointed out, caution must be observed in utilizing electron transport parameters extracted from such treatments. Thus, we conclude only that a value of λ the order of 10 Å is consistent with the best theoretical models of electron transport in liquid ethane and propane that are currently available.

The empirical encounter radius of $R = 14.5$ Å derived from the slopes of Figs. 2 and 3 suggests that R exceeds r_a because electrons "instantaneously" hop to the electron-induced dipole capture radius of SF_6 from a distribution of distances of which λ is a mean value. If we identify the electronic reaction radius R_e with λ and as an upper bound take r_a for R_{SF6}, then $R = 17$ Å is obtained which compares favourably with the experimental value.

A similar conclusion was reached by Yakovlev et al. [26] who found a value of $R = 17$ Å for electron attachment to pyrene in normal and cyclohexane and a localized electron radius of 13 Å, which was assumed to be the electron state from which reaction occurs in these "low mobility" liquids. In the hexanes under the experimental conditions of Yakovlev et al. [26], $r_a \cong 7$ Å, and we propose that the λ of $7 - 10$ Å in ethane and propane is analogous to $R - r_a = 17$ Å $- 7$ Å $= 10$ Å in the hexanes. Testing this hypothesis must await measurements of the field dependence of μ_e in normal and cyclohexane.

D) Implications to Electron-Ion Lifetime Distributions

The observed field-enhanced electron attachment rates in liquid ethane and propane reported in this study contrast with the field-dependent k_e's in liquid xenon and argon that we reported earlier [6]. In the solvents of the latter study, the attachment rate is dependent upon the electron energy which exceeds $k_B T$ beyond a critical field at which the onset of a sub-linear dependence of the electron mobility on the field occurs. In the present study, however, k_e increased proportionally with the field-enhanced electron diffusion coefficient while the electrons remained at thermal energy. Both of these studies illustrate that the k_e of a scavenger can become spatially dependent when the scavenger concentration is sufficiently large so that attachment occurs in the field of the parent ion. These field-dependent attachment studies and studies of the effect of field-dependent mobility on the electron escape probability [27] appear to have important implications to electron-ion lifetime distributions calculated from the concentration dependence of electron scavenging in steady-state radiolysis experiments [28].

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