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Field-dependent electron attachment in liquid tetramethylsilane[a]

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Field-dependent attachment of quasifree electrons to carbon tetrachloride, CCl_4, and ethyl bromide, EtBr, was observed in liquid tetramethylsilane (TMS) at 21 °C using a picosecond-pulse-conductivity technique. The field dependences of the electron-attachment rate constants, k_e's, of the two solutes, were measured at electric fields between 15 and 200 kV/cm and were found to parallel the energy dependences of the electron-attachment rates of the two scavengers in the gas phase; i.e., electron attachment to CCl_4 decreases with increasing field (energy) whereas electron attachment to EtBr increases with increasing field (energy). The observed field dependence of the k_e's is interpreted as being consistent with electron heating by the field, and we estimate that a field of 150 kV/cm increases the energy of an electron in TMS at 21 °C to ~0.1 eV. The effects of thermalizing third bodies on the field dependences of the k_e's are also discussed.

INTRODUCTION

Excess electrons have been successfully exploited over the last 15 years to probe electron transport and attachment processes in a wide variety of nonpolar fluids and thereby have contributed significantly to a better understanding of radiation chemistry and physics[1] and of other areas in which electrons play prominent roles, which include liquid-filled particle detectors,[2] dielectric breakdown,[3] artificial photosynthesis,[4] and a myriad of biological processes.[5] One of the fundamental electron-related problems of radiation chemical physics is the post-ionization competition between escape of an electron from its parent ion and recombination of the electron–ion pair. Onsager's treatment of this problem in gases[6] provided the basis for numerous studies of electron–ion escape vs recombination during the past two decades which followed the "rediscovery"[7] of the effect of an external field E on the enhancement of the escape of electrons from recombination in the steady-state conductivity studies of nonpolar liquids by Freeman[8] and Hummel and Allen.[9] In subsequent conductivity studies that were designed to provide a more direct measure of the free-ion yield, G_{fi}, of nonpolar liquids, Schmidt and Allen[10] and Schmidt[11] noted a marked decrease in the G_{fi} of liquid neopentane affected by efficient electron scavengers such as CCl_4 and SF_6. Similar observations were also reported by Freeman and coworkers,[12] and Mozumder and Tachiya demonstrated that the observed effects were consistent with scavenging of epithermal electrons.[13] Thus, these conductivity studies provided indirect evidence that epithermal electron attachment occurs in polyatomic liquids. (For a recent example of a conductivity study of the effect of E on G_{fi}, see Ref. 14.)

Another source of evidence which indicated that hot-electron effects occur in liquids is the work of Miller et al.[15]

who found that the dependence of the electron drift velocity v_d on the external field E in liquid argon, krypton, and xenon was analogous to the $v_d - E$ dependence observed in solid-state semiconductors in which hot-electron effects were well established.[16] In the rare-gas liquids three distinct regions of the dependence of v_d on E were observed, viz. (I, low E), $v_d \propto E$ (II, intermediate E), $v_d \propto E^{1/2}$, and (III, high E), saturation of v_d. With the development of faster pulse-conductivity techniques, regions I and II were also observed in the polyatomic liquids CH_4,[17] neopentane,[18] and tetramethylsilane, or TMS.[19] Further, by deconvoluting nanosecond pulse-conductivity measurements of v_d, Döldissen and Schmidt succeeded in observing region III in TMS.[20] Mozumder[21(a)] and Mozumder and Carmichael[21(b)] drew attention toward the implications of the field-dependent v_d's or electron mobilities, μ_e's, to the electron-escape/recombination problem, and Baird et al. further noted that field-dependent diffusion should also be considered in calculations of electron-escape probabilities.[22]

A third type of study which yielded results that are both consistent with hot-electron effects in liquids and are also relevant to the electron escape vs recombination problem was the observation of field-dependent electron attachment to the electron scavengers SF_6, N_2O, and O_2 in liquid argon and xenon.[23] In that study the field dependences of the measured electron attachment rate constants, k_e's of these three solutes were found to be analogous to the dependences of the gas-phase electron-attachment cross sections, σ_a's, on the electron energy, ϵ_e, which are well characterized.[24] Recently, Christophorou has demonstrated that these liquid-phase $k_e - E$ results can be combined with the field dependence of electron attachment in the gas phase to establish a liquid-phase scale of ϵ_e vs E if the ratios of the transverse diffusion coefficient of the electron, D_t, and μ_e are known in both the gas and liquid phases.[25] The present study can be viewed as an extension of the earlier $k_e - E$ study in the monoatomic liquids[23] to a polyatomic liquid and, therefore, as a first step in establishing a scale of ϵ_e vs E in a polyatomic liquid.

Before concluding this summary of field-dependent

v_d's, μ_e's, and k_e's in liquids which we consider to be consistent with hot-electron effects, we note that an alternative explanation for these field dependences and for the effects of nonattaching solutes on the field dependences of v_d or μ_e in the liquid rare gases[26] has been offered by Ascarelli.[27] In this alternate model Ascarelli proposed that shallow traps in the conduction bands of the liquid rare gases are of sufficient depth to effect the observed field dependences of μ_e[27(a), 27(d)] and k_e.[27(b), 27(c)] Criticism of this shallow-trap model by several independent groups[28] and Ascarelli's rebuttal to this criticism[27(d), 29] have also been presented.

The field-dependent k_e's reported herein appear to be consistent with hot electrons affecting the observed changes in k_e, and provide additional results for testing Ascarelli's shallow-trap model. Further, by providing direct evidence that field-dependent electron attachment occurs in a polyatomic liquid, the present study draws attention to the need to consider such effects more generally in the post-ionization competition between electron scavenging and electron–ion recombination. Finally, the observed $k_e - E$ dependencies should permit a more rigorous theoretical treatment of this competition and also should serve as an initial step in establishing an $\epsilon_e - E$ energy scale in a polyatomic liquid.

EXPERIMENTAL

Previous attempts to measure field-dependent k_e's in polyatomic liquids using the same nanosecond pulse-conductivity system that had been used to measure field-dependent k_e's in liquid argon and xenon[23] failed because faster time resolution was required.[30] The need for subnanosecond time resolution for the $k_e - E$ study may be illustrated by considering the lifetime of electrons in a high-μ_e liquid at a field exceeding the onset of the $v_d \propto E^{1/2}$ dependence (region II, *vide supra*) and with sufficient scavenger present to reduce the electron half-life with respect to attachment, $t_{1/2}^a$, to a time significantly less than one-half of the electron drift time, t_d. For TMS in a parallel-plate ion chamber with an interelectrode distance, d, of 0.2 mm across which 1 kV is applied, $t_d = 5.6$ ns; consequently, addition of sufficient scavenger to reduce $t_{1/2}^a$ to approximately one-third of 2.8 ns indicates that subnanosecond time resolution is needed to observe field-dependent k_e's in TMS.

The picosecond-pulse-conductivity system developed at the Hahn–Meitner Institute has been described in detail.[31] Reiterating briefly, a Radiation Dynamics L-band linear accelerator was used to produce a train of several 16 MeV electron pulses (30 ps FWHM) that were separated by 770 ps. These fine-structure pulses were collimated to irradiate only the interelectrode volume of a parallel-plate conductivity cell that terminated a 50 Ω transmission line. The cell electrodes were machined from stainless steel and the surfaces were highly polished. For the present experiments, the inner cylindrical electrode with a diameter of 5 mm was separated 0.2 mm from the high-voltage electrode by an outer cylinder of FIOLAX glass having an inner diameter of 8.7 mm and a length of 2 cm. For the cell filled with a liquid having a relative dielectric constant of 2 an interelectrode

capacitance of 1.95 pF is calculated, which yields a time constant $\tau_c = 97$ ps. This corresponds to a rise time (10%–90%) $\tau_r = 213$ ps. Adding the signal formation time of 40 ps and the rise time of the sampling head yields an instrumental rise time of 218 ps, which corresponds to an instrumental half-life $\tau_{inst} = 68$ ps. This value, which has been confirmed by evaluating the rise time of actual signals, was used to correct the observed data.

The transmission line was connected to a Tektronix S-4 sampling head, and the signal was stored for handling and display in a Nicolet 1072 instrument computer. If necessary the signal quality could be enhanced by using the instrument computer to subtract two single sweeps with opposite field polarities. This effectively doubled the nonrandom conductivity signal while reducing random noise and spurious nonrandom distortions by the electron beam. For evaluation and permanent storage, the data were transferred to a central computer. A standard linear regression method was used to fit the experimental data with an exponential decay, giving the half-life of the observed signal $t_{1/2}^0$. Geometrical subtraction of τ_{inst} from the signal half-life yields the electron half-life $t_{1/2}^e$.

TMS was chosen as the solvent for this study since the high μ_e of 100 cm^2/Vs at 20 °C[19,32] and the low E of ~20 kV/cm at which μ_e becomes field dependent[19] implies that excess electrons in TMS are quasifree. Recent studies of the Hall mobility[33] and the pressure dependence of the μ_e of TMS[34] further corroborate the quasifree nature of electrons in this liquid. In addition, TMS is the only solvent with these electron-transport properties which can also be handled easily at room temperature. CCl$_4$ and EtBr were chosen as the electron scavengers since both display energy-dependent but opposite attachment dependencies on the electron energy in the gas phase[24] and both are easily handled liquids at room temperature.

TMS (Merck Uvasol or Sigma 99.9 + %) was cooled to ~10 °C and purified by passage over a 1 m column of a 50/50 mixture of freshly activated silica gel and Molecular Sieve 4A. The pure TMS was transferred by vacuum distillation in a grease-free vacuum line to a storage bulb at − 78 °C where the TMS was stored at room temperature. The conductivity cells were evacuated prior to being filled with TMS that had been freshly degassed by several minutes of pumping on a refluxing system in which the cold finger upon which TMS condensed was maintained at − 196 °C. Stock solutions of CCl$_4$ or EtBr (both Fluka purum, used as received) were prepared in unpurified TMS and appropriate aliquots of the solutions were injected via syringe into TMS in the conductivity cell to yield $t_{1/2}^0$'s between 100 and 200 ps. In all experiments electron loss via attachment to adventitious impurities, drift to the anode and electron–ion recombination was less than 25% of the observed attachment rate; corrections for these electron-decay modes to the measured k_e's are discussed in the following section.

RESULTS

The electron-current decay curves in Figs. 1 and 2 illustrate the quality and the goodness-of-fit to an exponential decay of the uncorrected data as well as the effect of E on the
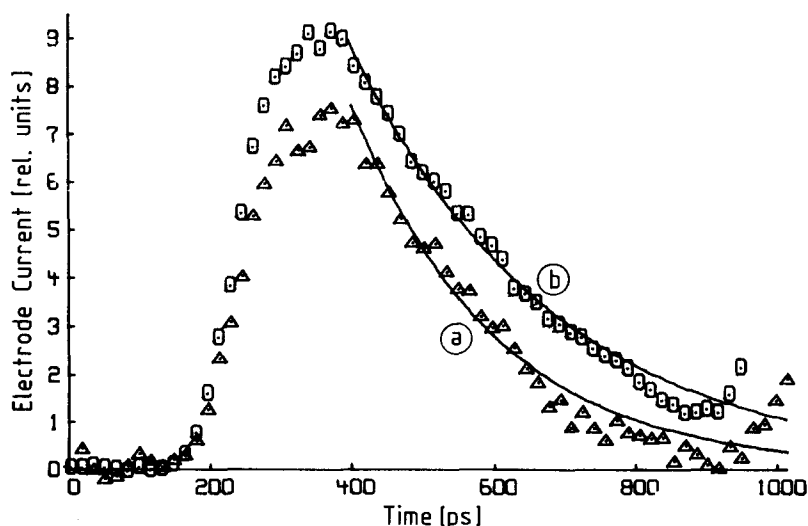
FIG. 1. Dependence of the observed electron decay on the external electric field E in a 96 μM solution of CCl_4 in TMS at 21 °C. (a) Decay at $E = 15$ kV/cm ($\triangle$); (b) decay at 175 kV/cm ($\square$). Computer fit (solid line) yields half-lives of 144 and 198 ps at 15 and 175 kV/cm, respectively.

rate of electron attachment to CCl_4 and EtBr. In Figs. 1(a) and 1(b), the observed signal half-life, $t_{1/2}^0$, increased from 144 ps at 15 kV/cm to 198 ps at 175 kV/cm in a 96 μM solution of CCl_4 in TMS in a conductivity cell having $d = 0.2$ mm. Concomitant with this increase in E, the electron drift time t_d, which was obtained from d/v_d using data of Ref. 20, decreased from 16.0 ns at 15 kV/cm to 2.70 ns at 175 kV/cm. To approximate the contribution of electron decay related to drift to the anode and other electron-loss processes, we assumed

$$1/t_{1/2}^0 = 1/t_{1/2}^a + 2/t_d + 1/t_{1/2}^s , \qquad (1)$$

where $t_{1/2}^0$ again is the observed signal half-life, $t_{1/2}^a$ is the electron half-life with respect to attachment to the scavenger, and $t_{1/2}^s$ is the electron half-life in the "pure" solvent at low field and is comprised of electron losses from attachment to impurities and recombination. Values of $t_{1/2}^s$ were obtained by measuring the electron half-life for each cell filling of TMS prior to the addition of the solute and making the appropriate correction for electron loss to drift. For the present example, $t_{1/2}^s$ was 1.6 ns which yields $t_{1/2}^a = 141$ and 248 ps at 15 and 175 kV/cm, respectively, when combined with the stated values of $t_{1/2}^0$ and t_d.

Figures 2(a) and 2(b) illustrate that an opposite field dependence was observed for electron attachment to EtBr. For a 40 mM solution of EtBr in the same conductivity cell as that used for the preceding measurement of attachment to CCl_4, the measured $t_{1/2}^0$ at 20 kV/cm was 260 ps whereas at 200 kV/cm $t_{1/2}^0$ decreased to 133 ps. Using Eq. (1) to correct these values with $t_d = 11.8$ and 2.56 ns at 20 and 200 kV/cm, respectively, and with $t_{1/2}^s = 4.0$ ns yields $t_{1/2}^a = 279$ ps at 20 kV/cm and 129 ps at 200 kV/cm.

The values of $t_{1/2}^0$ and $t_{1/2}^a$ obtained at several concentrations of CCl_4 and EtBr in TMS were converted to electron-attachment rate constants using

$$k_e = \frac{\ln 2}{t_{1/2}^a [S]}, \qquad (2)$$

where $[S]$ is the solute concentration. The rate constants determined from the uncorrected half-lives $t_{1/2}^0$'s are plotted in Fig. 3 as open circles vs the electric field. At a given E the $t_{1/2}^0$ measurement was repeated three to five times for each $[S]$, and $[S]$ was varied over the ranges stated in the figure legend. The variation of the results is indicated by error bars and the values of k_e obtained from the corrected $t_{1/2}^a$'s are indicated as filled circles. Comparison of the corrected and
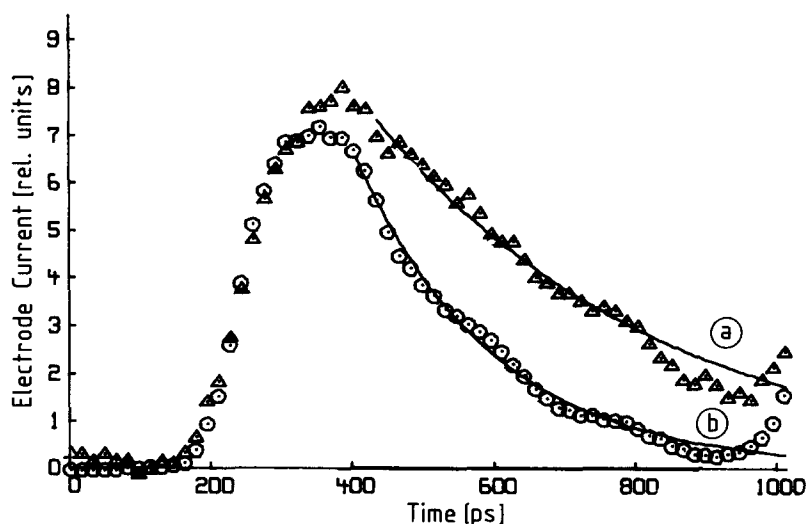

FIG. 2. Dependence of the observed electron decay on E in a 40 mM solution of EtBr in TMS at 21 °C. (a) Decay at $E = 20$ kV/cm ($\triangle$); (b) decay at 200 kV/cm ($\odot$). Computer fit (solid line) yields half-lives of 260 and 133 ps at 20 and 200 kV/cm, respectively.
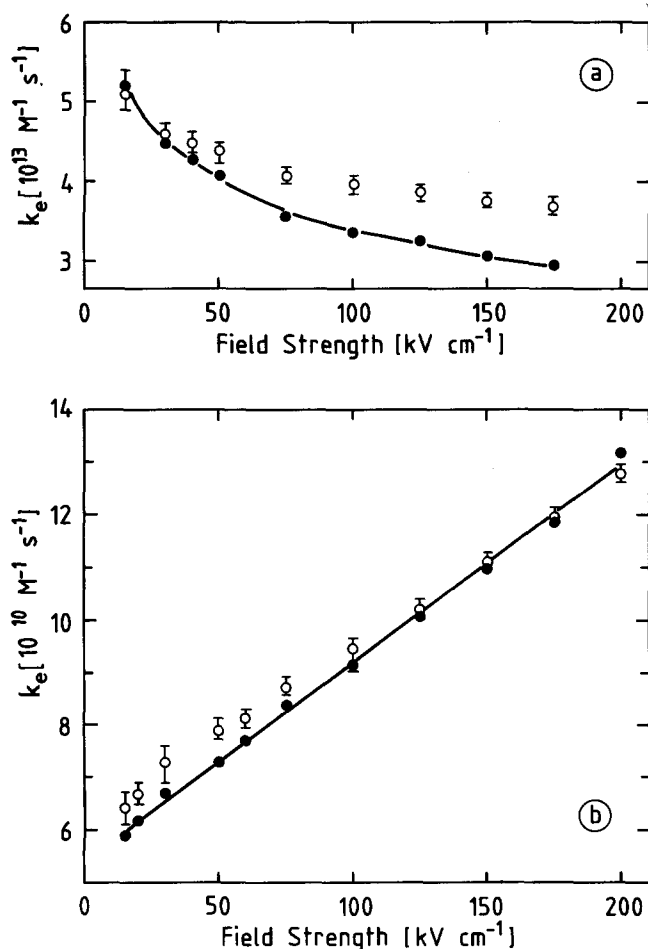
FIG. 3. Dependence of k_e on E in TMS at 21 °C for (a) [CCl$_4$] = 22 to 110 μM and (b) [EtBr] = 10 to 50 mM. Open circles with error bars are raw experimental data; filled circles are data corrected as described in the text.

TABLE I. Effect of nonattaching third bodies on μ_e and on the field dependence of the k_e's of CCl$_4$ and EtBr in TMS at 21 °C.

Scavenger	Third body	x_1[a]	μ_{mix} (cm^2/Vs)[a]	$k(20)/k(130)$[b]
CCl$_4$	None	0.00	100	1.50
	i-Octane	0.10	75	1.19
	c-Hexane	0.17	35	1.20
		0.37	10	1.09
EtBr	None	0.00	93	0.59
	c-Hexane	0.31	14	0.85

[a] The mole fraction of the low-mobility component x_1 was used in Eq. (4) to calculate μ_{mix}, the μ_e of the mixture; see the text.

[b] $k(20)/k(130)$ denotes ratio of k_e's at 20 and 130 kV/cm.

uncorrected k_e's demonstrates that the field dependence of k_e is an effect of the electric field and not a manifestation of the correction procedure.

In an attempt to ascertain the effect of a nonattaching third body on the field dependence of the k_e's of CCl$_4$ and EtBr, aliquots of cyclohexane or isooctane were added to the scavenger/TMS solutions. The effects of these solutes on k_e (E) are presented in Table I and discussed in the following section.

DISCUSSION

Before discussing field-dependent electron attachment, we note three diffusion-related factors that could have contributed to the observed effects under appropriate conditions but which appear to have made no significant contributions to k_e (E) in our picosecond measurements. The first of these involves the time-dependent nature of bimolecular reactions which has been shown to be of importance for fast reactions observed at a short time, t, if the condition $R/(\pi D_m t)^{1/2} \ll 1$ is not fulfilled[35]; here R is the effective encounter radius and D_m the mutual diffusion coefficient of the reactants. To make an order-of-magnitude approximation of the time-dependent factor at our earliest t which is ~50 ps after the observed maximum signal, we set $R = 10$ Å[36] and equate

D_m with the diffusion coefficient of the electron, D_e, which we estimate to be 2.5 cm^2/s at low fields at 294 K by applying the Nernst–Einstein equation to the low-field value of μ_e of 100 cm^2/Vs.[19,20] With these values of t, R, and D_e we infer that k_e is enhanced ~0.5% at low fields, and only a slightly greater enhancement is calculated at high fields where a value of $D_e = \sim 1$ cm^2/s is obtained with the Nernst–Einstein equation from Döldissen and Schmidt's value of $\mu_e = 40$ cm^2/Vs at 175 kV/cm.[20] Thus, time-dependent electron attachment was negligible in our picosecond measurements but could be significant for similar measurements made in low-mobility liquids.

The second diffusion-related factor that may have contributed to the observed field-dependent k_e's involves the relative values of the residence time of the electron in the vicinity of the scavenger, which is denoted τ_r, and the time required for the attachment process to occur, τ_a. Henglein[37] has proposed that the k_e of an efficient scavenger becomes less than diffusion controlled in high-mobility solvents when τ_r becomes a significant fraction of τ_a, which may be expressed via

$$k_e = 4\pi R\, D_e / (1 + \tau_a/\tau_r) . \qquad (3)$$

Henglein further noted that τ_r could be approximated by $R^2/2\, D_e$, which substituted in Eq. (3) yields

$$k_e = 4\pi R\, D_e / (1 + 2D_e \tau_a/R^2) . \qquad (3')$$

One readily sees from Eq. (3') that k_e in TMS could become field dependent at $E > E_c$ where μ_e and presumably D_e decrease with increasing E. If we again use the Nernst–Einstein derived values of D_e at 15 and 175 kV/cm of 2.5 and 1.0 cm^2/s, respectively (vide supra), and substitute these D_e's and the k_e's measured at the two E's into Eq. (3'), the resulting equations can be solved to yield τ_a, R, and, indirectly, τ_r. The values obtained for these parameters, however, are not reasonable; for example, the 50% decrease in the k_e of CCl$_4$ as E increases from 15 to 175 kV/cm requires that $\tau_a = 4.7 \times 10^{-18}$ s and $R = 0.52$ Å (and $\tau_r = 5.3 \times 10^{-18}$ s). Warman has noted that the lower limit to τ_a should be 3×10^{-14} s,[1(a)] and an R significantly less than the hard-sphere radius of CCl$_4$ is equally difficult to reconcile. Similarly, the doubling of the k_e of EtBr over the same range of fields requires that τ_a/R^2 be negative. We therefore conclude that the observed field dependencies of k_e are not related to diffusional effects through the τ_a/τ_r ratio. We add, however, that Eq. (3) may indeed be applicable to CCl$_4$ and

TABLE II. Values of k_e and of V_0 and P^- used to estimate E_T for solutions of CCl_4 in TMS and neopentane at 21 °C.

Solvent	k_e (M^{-1}s^{-1})[a]	V_0(eV)[b]	P^-(eV)[c]	χP^-(eV)[d]	E_T(eV)
TMS	5.4×10^{13}	−0.56	−0.97	−0.78	0.26
Neopentane	2.9×10^{13}	−0.45	−0.93	−0.74	0.33

[a] Reference 32(a).
[b] Reference 53(b).
[c] P^- was evaluated as described in Ref. 53(a) using an effective radius of CCl_4^- of 3.4 Å which was calculated as described in Ref. 37(b).
[d] $\chi = 0.8$ was assumed; see Refs. 37 and 53.

EtBr scavenging electrons in TMS provided that τ_a is field (energy) dependent, and we further propose that the τ_a of CCl_4 increases and that of EtBr decreases as electron heating by the field occurs.

The final point related to diffusion on which we comment pertains primarily to EtBr which was present at sufficient concentrations to significantly decrease μ_e and therefore D_e. For example, the 40 mM concentration of EtBr in the sample from which Fig. 2 was derived corresponds to 0.55 mol % which would reduce μ_e to 93 cm^2/Vs if we assume that the mobility equation for mixtures used by Wada et al.[38]; viz.

$$\mu_{mix} = \mu_h^{x_h} \mu_1^{x_1} \qquad (4)$$

is applicable to EtBr-TMS solutions. In Eq. (4), μ_{mix} is the μ_e of a mixture of high- and low-mobility components having respective μ_e's denoted by μ_h and μ_1 and present at respective mole fractions x_h and x_1. We also assume as a worst case a value of μ_1 of 5×10^{-4} cm^2/Vs, which is based on the mobility of the CH_3Br anion in c-hexane at 295 K.[39] Although alternative equations for the mobility of mixtures have also been presented from which a greater decrease of μ_e by EtBr would be estimated,[40] the only effect this decrease in μ_e would have on the field dependence of k_e would be a shift in the onset of the dependence to a higher field.[40(a)]

The effect of EtBr to decrease μ_e in TMS-EtBr mixtures is of minor significance compared to the effects of nonattaching "third bodies" such as c-hexane or i-octane which were added to TMS-scavenger solutions at x_1's exceeding 0.1 to determine if such third bodies inhibit electron heating by the external field. For the preliminary results listed in Table I, μ_{mix} was evaluated using Eq. (4) and μ_e's of c-hexane and i-octane of 0.22 and 5.5 cm^2/Vs, respectively, measured by Allen et al.[41] From the results in Table I it appears that k_e becomes field independent at a concentration of c-hexane > 30 mol % at which μ_{mix} is estimated to be < 15 cm^2/Vs. Further discussion of electron attachment to CCl_4 and EtBr in mixtures of c-hexane or i-octane in TMS will be deferred until a low-field study of electron attachment in such mixtures which is currently in progress is completed.[42]

The field dependences of the k_e's of CCl_4 and EtBr in TMS which are illustrated in Fig. 3 are analogous to the field dependences of the k_e's of SF_6, N_2O, and O_2 in liquid argon and xenon[23]; i.e., for both cases the $k_e - E$ dependencies mimic the gas-phase $\sigma_a - \epsilon_e$ dependencies.[24] This behavior is in marked contrast to the field dependence of the k_e of SF_6 in the "low-μ_e" liquids ethane and propane[43] in which the

electrons are highly localized.[18,19(b),44] In these low-μ_e liquids, the k_e of SF_6 increases with E at values of $E > E_c$, the critical field above which v_d increases approximately proportionally with E^2. The $v_d \propto E^2$ dependence was attributed to field-assisted detrapping of localized electrons in liquid C_2H_6[18,44(a)] and C_3H_8,[19(b)] and k_e was found to increase proportionally with the diffusion coefficient of the electron, D_e, which was obtained by applying the Nernst–Einstein equation to the measured μ_e's.[43] Thus, field-dependent electron attachment occurs in both mono- and polyatomic liquids with the attachment process being governed by the electron-transport mechanism of the medium. We shall now focus upon the implications of extended-state electron transport in TMS to the field-dependent k_e's observed in this study.

The Lekner theory of electron transport in liquid argon[45] which strongly influenced studies of μ_e in fluids for nearly a decade was modified[46] to accomodate the results from a number of studies in which a maximum in μ_e and a minimum in the conduction-band energy V_0 were found near the critical density.[47] In the theory that evolved, the mobility of electrons is considered to be mediated by deformation potentials in the conduction band which are induced by density fluctuations in the fluid, and the similarity of this theory to the deformation potential scattering theory developed by Shockley for the solid state[16] has been noted.[47] Studies in TMS of the density dependence of μ_e[32(b)] and V_0,[48] of the Hall mobility[33] and of the pressure dependence of V_0[34] indicate that the deformation potential scattering theory is also applicable to extended-state electron transport in TMS which implies that delocalized electrons in this liquid can also be heated by an electric field.

As noted in the Experimental section, CCl_4 and EtBr were chosen as the scavengers for this study since both exhibit strong but opposite $\sigma_a - \epsilon_e$ dependencies in the gas phase. Warman and Sauer have exploited the monotonic linear decrease observed for the gas-phase electron-attachment rate, αw, of CCl_4 as ϵ_e increases from thermal to 0.6 eV[24,49] to probe the electron temperature in irradiated gases,[50] which is similar to our use of CCl_4 in this work. In contrast to the energy dependence of the σ_a of CCl_4, thermal electron attachment to EtBr in the gas phase is several orders of magnitude less than that of CCl_4,[24,49] and αw increases with increasing ϵ_e to a maximum at 0.7 eV.[51]

The qualitative similarity between the liquid-phase field dependence of k_e and the gas-phase energy dependencies of σ_a or αw for CCl_4 and EtBr suggests that the observed

$k_e - E$ dependencies could be used to estimate the mean energy of electrons in TMS as a function of E. If we use the values of the k_e of CCl_4 at 15 and 150 kV/cm obtained from Fig. 3(a) as an example, k_e is seen to decrease by a factor of 1.7 over this range of fields. From the αw vs $\langle \epsilon \rangle$ plot of Christodoulides and Christophorou, i.e., Fig. 10(b) of Ref. 49(b), αw decreases by 1.7 from the $(3/2)\,kT$ value at $\langle \epsilon \rangle = 0.08$ eV. An analogous extrapolation for EtBr using the $k_e - E$ dependence in Fig. 3(b) and the αw vs $\langle \epsilon \rangle$ plot of Goans and Christophorou[51] is not possible since the lowest $\langle \epsilon \rangle$ at which αw was measured in the gas phase was ~ 0.2 eV.

We caution that this extrapolation of liquid-phase $k_e - E$ results to gas-phase $\alpha w - \langle \epsilon \rangle$ data is of questionable validity since the kinetics and thermodynamics of the electron attachment process differ markedly in the two phases.[1(a),24,37] An alternative approach to estimating the electron energy at high fields is to consider the liquid-phase energetics of the dependence of k_e on the electron energy; this has been done in several studies of the dependence of k_e on V_0 in various solvents.[24,37,52,53] Using the notation of Holroyd and Gangwer[53(b)] the total energy, E_T, available to an electron in solution that undergoes attachment is

$$E_T = V_0 - \chi P^- + \epsilon_k , \qquad (5)$$

where V_0 is again the conduction-band energy of the electron in the solvent, P^- is the polarization energy of the anion of which only a fraction χ (~ 0.8) is available to the electron at the moment of attachment,[37,53] and ϵ_k is the kinetic energy of the electron. We assume that the external field influences E_T only via ϵ_k (i.e., V_0, χ, and P^- are field independent) and use Holroyd's plot of k_e vs E_T for EtBr[53(b)] to estimate the increase of ϵ_k induced by the external field in this study. From Fig. 3(b) we note that the k_e increases by a factor of 1.9 as E increases from 15 to 150 kV/cm, and from Fig. 1 of Ref. 53(a) the k_e of EtBr increases by the same factor as E_T increases by 0.03 eV. Thus, a field of 150 kV/cm approximately doubles the kinetic energy of an electron in TMS-EtBr solutions.

A plot of k_e vs E_T for CCl_4 analogous to Holroyd's plot for EtBr is not available for estimating the field-induced enhancement of ϵ_k from the observed field dependence of the k_e of CCl_4 illustrated in Fig. 3(a). However, by combining the measured values of the k_e of CCl_4 in TMS and neopentane[32(a)] and the V_0's of these solvents[48,53(b)] with values of P^- and χP^- estimated as described in Ref. 53(a), the change in k_e with E_T for the CCl_4-TMS/neopentane system was derived (see Table II). The field-induced reduction of the k_e of CCl_4 in TMS by a factor of 1.7 as E increases from 15 to 150 kV/cm which is illustrated in Fig. 3(a) corresponds to a change of E_T of 0.06 eV obtained by interpolation of a log k_e vs E_T plot of the values of k_e and E_T listed in Table II. We again equate this change of E_T with an increase of ϵ_k and conclude that a field of 150 kV/cm increases the electron energy in TMS-CCl_4 solutions by approximately threefold.

At this time we cannot ascertain whether the agreement between $\epsilon_k \approx 0.06$ eV obtained from the liquid-phase dependence of the k_e of CCl_4 on E_T and $\langle \epsilon \rangle \approx 0.08$ obtained from gas-phase $\alpha w - \langle \epsilon \rangle$ results is of significance or merely for-

tuitous. It is also unclear if the difference in the values of ϵ_k derived from the $k_e - E$ dependencies of CCl_4 and EtBr is significant and related to less effective heating of electrons by the external field in the EtBr-TMS solutions than in CCl_4-TMS. The several hundredfold greater concentration of EtBr than CCl_4 indicates that numerous nonattaching electron-EtBr collisions occur which could inhibit electron heating by the field in the EtBr-TMS solutions. Observation of the field dependencies of k_e's of other solutes having well defined $\alpha w - \langle \epsilon \rangle$ dependencies in the gas phase and $k_e - E_T$ dependencies in the liquid phase should permit us to clarify these points.

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