

gates. Conversely, preliminary findings suggest that effects of the presence of ethanol on the behavior of solvated electrons in amine-rich solutions is much less definitive. It has been observed<sup>21</sup> that ethylenediamine is an extremely effective inhibitor of the decay of aromatic radical anions ( $\text{Ar}^- + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{ArH} + \text{C}_2\text{H}_5\text{O}^-$ ) in ethanol below ca. 68 mol % of ethanol, suggesting<sup>21</sup> existence of a distinctive (2:1) hydrogen bonded ethanol-ethylenediamine complex. This and the present work suggest that the electron solvating mechanism in ethylenediamine is, relative to that in ethanol, quite insensitive to the presence of ethanol-ethylenediamine complexes. This may be an indication that nonspecific long-range electron-solvent interactions predominate in ethylenediamine and in ethylenediamine-rich solutions.

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## Chemical Reaction Rates of Quasi Free Electrons in Nonpolar Liquids

Augustine O. Allen\* and Richard A. Holroyd

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973 (Received September 9, 1973)

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A method is described for determining reaction rates of molecules dissolved in nonpolar liquids with electrons produced by ionization of the solvent. It is based on modification by the added substance of the current-growth curve which is seen when the liquid, in an electric field, is suddenly exposed to X-rays, and which is used for mobility determination by the Hudson method. The rate constants for recombination of electrons with positive ions, determined by the Langevin method in *n*-pentane, *n*-hexane, and tetramethylsilane, are diffusion controlled and hence proportional to the electron mobilities; this rate constant in tetramethylsilane is  $5 \times 10^{16} \text{ M}^{-1} \text{ sec}^{-1}$ . The electron reactions with  $\text{CCl}_4$ ,  $\text{CH}_3\text{I}$ , and  $\text{O}_2$  are not diffusion controlled; the rates are generally higher in solvents which show higher electron mobilities, but the increase is less than proportional. Different behavior is shown with  $\text{C}_2\text{H}_5\text{Br}$ ; the electron reaction rate is lower in the high-electron-mobility solvents neopentane and tetramethylsilane than in hexane or 2,2,4-trimethylpentane, and its temperature coefficient, which is positive in hexane, becomes unexpectedly negative in the former solvents, and amounts to  $-1.7\%$  per degree in neopentane. New electron mobility determinations are reported for methylcyclohexane, *n*-hexane, *n*-pentane, cyclohexane, neopentane, and tetramethylsilane.

### Introduction

The mobility of electrons in liquid hydrocarbons has been widely studied recently,<sup>1-5</sup> and varies greatly from one hydrocarbon to another; the mobility in neopentane is several hundred times greater than in normal pentane. The temperature coefficient of the mobility is positive and is larger in the lower mobility liquids, which suggests<sup>6</sup>

that the electrons are thermally activated from a trapped or solvated state, where their mobility may be no greater than that of ordinary ions, into a quasi-free state resembling the high-mobility condition seen in liquid argon. In pulse radiolysis of several hydrocarbons,<sup>7,8</sup> absorptions in the infrared are seen which are attributed to these trapped or solvated electrons.

The question of the chemical reactivity of excess electrons in hydrocarbons arose in the experiments of Schuler and coworkers<sup>9</sup> on the dependence of the yield on concentration of electron scavengers. Absolute rate constants for the reaction of free electrons with added solutes have been determined by measurements on the nanosecond time scale of the rate of decay of conductivity following an extremely short pulse of electron radiation,<sup>10,11</sup> and by optical methods.<sup>8</sup> Determination of these reaction rates provides an important method of learning about the nature of the excess electron in the liquid environment. We have developed different methods of determining these rate constants and have obtained some interesting results. We measure in separate experiments (a) the reaction rate of electrons with added molecules and (b) the rate of recombination of electrons with positive ions.

### Experimental Methods

*Reaction of Electrons with Added Molecules.* We use an adaptation of the Hudson method<sup>12</sup> of measuring electron mobilities used by Schmidt in our laboratory.<sup>1</sup> In this method a field is applied between parallel metal plates immersed in the liquid and X-rays are suddenly turned on to fill the space between the plates with radiation of uniform intensity. The time required for the electron current to reach a steady state is determined by the mobility.

To describe our adaptation to rate constant determinations, let us first review the theory of Hudson's mobility measurement. The current induced in the external circuit by motion of one electron in the space between the plates is given by

$$i = ev_e/d \quad (1)$$

where  $e$  is the charge on the electron,  $d$  is the distance between the plates, and  $v_e$ , the velocity of drift of the electron in the field, equals  $\mu\mathcal{E}$ , where  $\mu$  is the mobility and  $\mathcal{E} = V/d$  is the applied field. If the electron density is  $n_e(x,t)$ , the observed current per unit electrode area due to electrons is

$$I_e(t) = (v_e e/d) \int_0^d n_e dx \quad (2)$$

X-Rays are turned on at  $t = 0$  and generate electrons at a rate  $a \text{ sec}^{-1} \text{ cm}^{-3}$ . Then, by continuity, if diffusion is negligible

$$\partial n_e / \partial t = a - v_e (\partial n_e / \partial x) \quad (3)$$

Boundary conditions:  $t = 0$ ,  $n_e = 0$  (for all  $x$ );  $t \geq d/v_e$ ,  $\partial n_e / \partial t = 0$ ,  $n_e = ax/v_e$ . If  $y = x/v_e$  and  $z = n_e - at$ , (3) becomes

$$\partial z / \partial t + \partial z / \partial y = 0 \quad (4)$$

with boundary conditions  $t = 0$ ,  $z = 0$ ;  $t \geq d/v_e$ ,  $z = a(y - t)$ .

Any function of  $(t - y)$  satisfies (4); the general solution is  $z = \psi(t - y)$ . The solution consistent with the boundary conditions is  $z = 0$  when  $t - y \leq 0$ ;  $z = a(y - t)$  when  $t - y \geq d/v_e$ . Thus the solution of (3) is  $n_e = at$  for  $v_e t \leq x$ ;  $n_e = ax/v_e$  for  $v_e t \geq x$ . Thus  $n_e$  increases linearly with  $x$  up to  $x = v_e t$ , beyond which  $n_e$  is constant. The same result is obtained by the method of Laplace transforms.

The electron current per unit area is

$$I_e = (v_e e/d) \left( \int_0^{v_e t} axv_e^{-1} dx + \int_{v_e t}^d at dx \right) = ae v_e [t - (v_e/2d)t^2] \quad (5)$$

The steady-state value of the electron current is attained when  $t = d/v_e$  and is given by

$$I_e(\text{max}) = aed/2 \quad (6)$$

The total steady-state current due to carriers of both signs is by definition  $aed$  and eq 6 merely says that half of the current is, on the present assumptions, carried by electrons.

Thus the electron component of the current rises parabolically to a maximum value where it stays. Superimposed on this is a positive ion current which likewise rises parabolically to a maximum. The current-time curves observed in this work and earlier<sup>1</sup> show that, in the microsecond time scale, the electron mobility is hundreds of times greater than that of the positive ions so that the concentration of positive ions has only begun to increase when that of the electrons has attained its maximum. The positive component is hence rising essentially linearly and the rise of the electron current is attained by subtracting from the total current the linearly rising current due to the positive ions. Any mobile positive hole must become localized within a fraction of a microsecond, and contributes negligibly to the observed current.

To determine the effect of additives we note that if a substance is present in concentration (S) which reacts with electrons with rate constant  $k_s$ , and if  $k = k_s(S)$ , then (3) becomes

$$\partial n_e / \partial t = a - kn_e - v_e (\partial n_e / \partial x) \quad (7)$$

Boundary conditions:  $t = 0$ ,  $n = 0$ ;  $t \geq d/v_e$ ,  $dn_e/dt = 0$ ,  $n_e = (a/k)[1 - \exp(-ky)]$ . To solve, let  $z' = [n_e - (a/k)] \exp(kt)$  or  $n_e = z'[\exp(-kt)] + a/k$ ; then

$$\partial z' / \partial t + \partial z' / \partial y = 0 \quad (8)$$

which is identical in form with (4). The solution is now  $t - y \leq 0$ ,  $z' = -a/k$ ;  $(t - y) \geq 0$ ,  $z' = -(a/k) \exp[k(t - y)]$ . Thus for  $x/v_e \geq t$ ,  $n_e = (a/k)[1 - \exp(-kt)]$ ; for  $x/v_e \leq t$ ,  $n_e = (a/k)[1 - \exp(-kx/v_e)]$ . Integration gives

$$I_e = \frac{eav_e}{dk} \left\{ \left( d - \frac{v_e}{k} \right) [1 - \exp(-kt)] + v_e t \exp(-kt) \right\} \quad (9)$$

$$I_e(\text{max}) = ead(v_e/dk) \{ 1 - (v_e/dk)[1 - \exp(-dk/v_e)] \} \quad (10)$$

The maximum current (eq 10) is seen to depend only on the parameter  $p = dk/v_e$ , the ratio of the time required for the electrons to drift across the cell to the mean time for reaction with the scavenger. Since the total current is  $ead$ , we have for the ratio  $R$  of the steady-state electron current to the total steady-state current

$$R = [\exp(-p) + p - 1]p^{-2} \quad (11)$$

We generated X-rays from 1.9-MeV electrons impinging on a gold target in a Van de Graaff generator. The hydrocarbons (Phillips Research grade) and tetramethylsilane (NMR grade) were purified by passage through activated silica gel, followed by stirring over liquid NaK alloy, and finally by several passages of the vapor bubbling through NaK which was heated to sufficiently high temperatures ( $\sim 200^\circ$ ) to form mirrors on the walls of the glass tubing, so that the hydrocarbon vapors mixed with potassium vapors in the course of their passage. The liquid was distilled under vacuum into a cell such as those previously described.<sup>1</sup>

The cell was closed with a metal valve. Directly beyond

this valve, and separated by a calibrated volume of only about 1 cc, was a second valve which was used when it was decided to make small additions of a second component. In that case the assembly was connected to the vacuum line. The line was filled with vapor of the second material to a desired pressure, usually of the order of 0.1–1 Torr; this vapor was allowed to fill the small space between the two valves; the outer valve was then closed and the inner valve opened. The cell was removed from the line, inverted, and the cooled solution was thoroughly mixed by bubbling which resulted from the contact of the cool liquid with the metal inlet tube. The vapor volume in the cell was always small compared to the liquid volume so that a negligible fraction of the added material remained in the vapor phase.

During irradiation, to prevent stray currents arising from X-rays or other sources outside the cell, the cell was enclosed in a metal box which was fitted with connections for shielded cables leading from the high voltage power supply and to the measuring equipment. The box was insulated with styrofoam and the temperature of the cell could be controlled by passing a current of heated or cooled air through the box. A grounded metal plate was placed across the box to prevent passage of current through the ionized air in the box from the input to the output lead. Even with this plate present the current curves were found to be distorted if nitrogen rather than air, or even nitrogen–air mixtures, were used to cool the cell.

The amplifier to measure the electron current utilized two field effect transistor differential fast amplifiers (Analog Devices 46J). The high input impedance ( $10^{11} \Omega$ ) of these amplifiers provided a match to that of the cell. The first stage provided a current-to-voltage conversion of  $1 \text{ V}/10^{-5} \text{ A}$  and this was followed by a second stage times 100 amplification. Thus overall the response was  $1 \text{ V}/10^{-7} \text{ A}$ . The response time of the amplifier was  $1 \mu\text{sec}$ . The signal was fed into a Biomation 802 transient recorder which digitized the signal with a precision of 1 part in 256 and stored 1024 data points with time resolution capability of  $0.5 \mu\text{sec}$ . The stored signal could be displayed and photographed, transferred to magnetic tape, or fed to an x-y recorder.

In agreement with previous workers it was found that the purity of the samples was greatly improved by irradiation with about 1 krad of X-rays. Figure 1 shows a typical trace of current vs. time obtained with a relatively pure sample of hydrocarbon.

To determine the effective impurity level in a given liquid preparation, we determine first the steady-state electron current per unit radiation intensity from data such as that shown in Figure 1. In a second run done at much lower radiation intensity, the charge collected from the cell over an irradiation period of at least 20 sec is fed directly into an electrometer (Keithley 610 BR) to determine total steady-state current (which is proportional to the free ion yield  $G_{fi}$  and therefore depends on the applied field). In both cases the unit of radiation intensity is the electron beam current incident on the gold target at 1.9 MeV. The total charge incident on the gold target is read by a current integrator. Comparison of the runs yields the ratio  $R$ , from which we determine  $p$  from eq 11. Since  $p = d^2 k_S(S)/\mu V$  and we know  $d$ ,  $\mu$ , the applied voltage  $V$ , and the concentration ( $S$ ), the difference in  $p$  before and after addition of a metered amount of scavenging material gives us the rate constant  $k_S$  for reaction of the electrons with



Figure 1. Electron current vs. time observed in pure neopentane at  $E = 198 \text{ V/cm}$ ; vertical scale, 1 major division =  $2 \times 10^{-8} \text{ A}$ ; horizontal scale, 1 major division =  $50 \mu\text{sec}$ .  $T = 23^\circ$ .

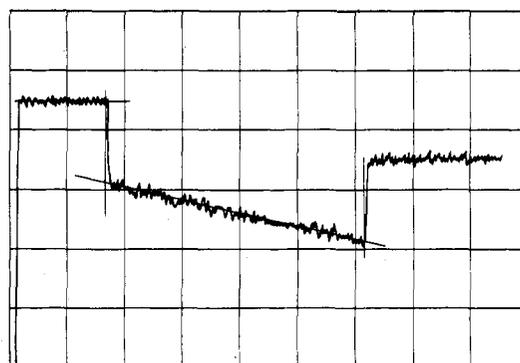


Figure 2. Electron current vs. time observed in neopentane containing  $45 \mu\text{M}$  EtBr and  $6.9 \mu\text{M}$   $\text{CCl}_4$ ;  $E = 5250 \text{ V/cm}$ ; vertical scale, 1 major division =  $1 \times 10^{-8} \text{ A}$ ; horizontal scale, 1 major division =  $50 \mu\text{sec}$ .  $T = -13^\circ$ .

the added material. In practice, two to four successive additions were made, with the rate constant determined after each addition. For each determination, three current–time curves were taken at each of three or more values of the field, the results being averaged to obtain the rate constant. Figure 2 shows a typical current–time trace taken with added solutes.

Having determined the value of  $p$ , the electron mobility in any given preparation was determined by computer fitting the data on the rise of the electron current vs. time to the appropriate form of eq 9, by an iterative least-squares program. This procedure should result in more accurate determination of  $\mu$  than possible by the uncorrected Hudson method.

**Ion Mobilities.** The linear rate of current rise after the electron current has reached its maximum can be used to estimate the mobilities of the positive ions and of the negative ions formed by addition of electron scavengers. The initial rate of rise of the positive ion current, obtained from an equation analogous to (5) is

$$(dI_+/dt)_0 = ae v_+ = ae \mu_+ V/d \quad (12)$$

When reactive solutes are present, negative ions are generated at a rate  $kn_e$ . The ion mobilities  $\mu_+$  and  $\mu_-$  are so much smaller than  $\mu_e$  that when  $n_e$  has attained its steady-state value,  $(n_e)_{\text{max}} = (a/k)[1 - \exp(-kx/v_e)]$ , the ion concentrations  $n_+$  and  $n_-$  are very small and are growing essentially at their initial rates. Hence in considering the growth of  $n_-$ , we make a negligible error in assuming that at  $t = 0$ ,  $n_e = (n_e)_{\text{max}}$ . The continuity equation for  $n_-$  is

$$\partial n_- / \partial t = k(n_e)_{\max} - v_-(\partial n_- / \partial x) = a[1 - \exp(-ky'v_-/v_e)] - \partial n_- / \partial y' \quad (13)$$

where  $y' = x/v_-$ . Boundary conditions:  $t = 0, n_- = 0$ ;  $t \geq d/v_-, \partial n_- / \partial t = 0$ , hence  $n_- = ay' - (a/k)(v_e/v_-)[1 - \exp(-ky'v_-/v_e)]$ .

To solve, let  $z'' = n_- - ay' + (av_e/kv_-) \exp(-ky'v_-/v_e)$ . Equation 4 or 8 now holds for  $z''$ . The solution, under the given boundary conditions, is

$$x \leq v_-t, n_- = ax/v_- - (a/k)(v_e/v_-)[1 - \exp(-kx/v_e)] \quad (14)$$

$$x \leq v_-t, n_- = at + (a/k)(v_e/v_-) \exp(-kx/v_e)[1 - \exp(ktv_-/v_e)]$$

To find the initial rate of growth of the negative ion current, (14) is integrated over  $x$  to find  $I_-$ , the result is differentiated with respect to  $t$ , and at  $t = 0$  becomes

$$(dI_-/dt)_0 = av_-e[p - 1 + \exp(-p)]p^{-1} = av_-eRp \quad (15)$$

where  $p = dk/v_e$ , as before. The total ion current, given by the slope of the final current growth curve seen in runs such as those of Figure 2, is

$$[d(I_+ + I_-)/dt]_0 = (aeV/d)(\mu_+ + \mu_-Rp) \quad (16)$$

Therefore, in a series of runs in which  $R$  and therefore  $p$  is varied by addition of scavenger, if the observed slopes divided by  $aeV/d$  are plotted against  $Rp$ , the intercept of the resulting line will be  $\mu_+$  and the slope  $\mu_-$ . Ion mobility values so obtained will be presented in a later paper.

The recombination coefficient of electrons with positive ions in our cells was obtained by a method similar to that used by Langevin<sup>13</sup> in 1902 for studying recombination of ions in gases. When a very short pulse of X-rays is applied to a fluid, Langevin showed that the fraction  $f$  of the ions which avoids recombination and is collected by parallel plate electrodes increases with the applied field and decreases with the radiation intensity according to the formula

$$f = (1/u) \ln(1 + u) \quad u = \alpha n_0 d^2 / (\mu_+ + \mu_-) V \quad (17)$$

where  $\alpha$  is the recombination rate constant (or "recombination coefficient"). Langevin's derivation neglected the effect of space charge, which necessarily results in a distortion of the field as the voltage or intensity is varied to obtain lower values of  $f$ . The correction for space charge was considered by Boag<sup>14</sup> and was found to be rather surprisingly small, and could be approximated closely over the whole range of  $f$  from 100 to 5% by dividing  $u$  by a constant factor, which we denote by  $\beta$ , and which should lie between 0.8 and 0.9.

The pulses were obtained from a Febetron Model 705 with 2-MeV electrons incident on a tungsten target. With this machine the large majority of the X-rays are obtained within  $10^{-8}$  sec, with a small tail extending to somewhat longer times. The X-ray intensities were kept low enough so that a negligible amount of recombination occurred during the pulse, as required by the Langevin derivation. Radiation intensities were varied by changing the position of the cell with respect to the X-ray target, and the amount of charge collected was measured for several different fields applied at each position. The relative intensities at the different positions used were monitored with thermoluminescent dosimeters. Successive pulses given by the machine were ordinarily reproducible within a few per

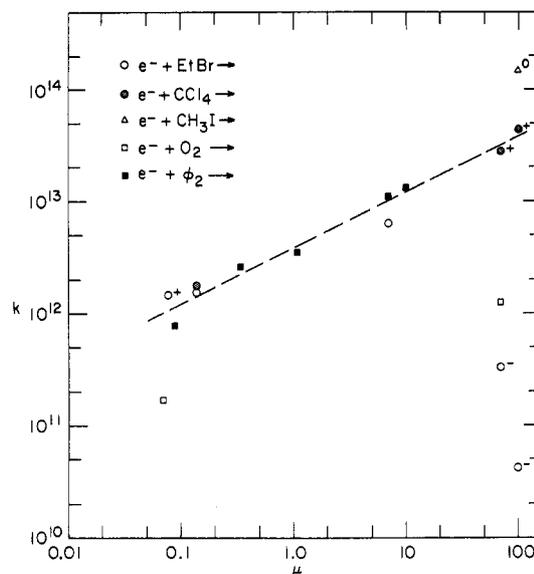


Figure 3. Rate constants  $k_S$  in units of  $M^{-1} \text{ sec}^{-1}$  for reaction of electrons with various solutes at  $23^\circ$ , plotted as a function of electron mobility. Dotted line is drawn with slope one-half.

cent; in some cases the individual pulses used were monitored for relative intensity by an ionization chamber. Relative values of  $n_0$  at the different applied fields were thought of in terms of the free ion yield  $G = G_0(1 + \phi(V/d))$ , where for low mobility hydrocarbons  $\phi$  is a constant (the Onsager slope-to-intercept ratio) given by  $300 e^3 / 2\epsilon k^2 T^2 V \text{ cm}$ , where  $\epsilon$  is the dielectric constant and  $e$  and  $k$  are the electronic charge and Boltzmann constant in electrostatic units. For high-mobility materials  $\phi$  is an empirical function taken from our measurements of steady-state current as a function of field, as described above for the determination of  $p$ . If  $D$  is the dose in rads in any particular pulse,  $n_0 = 6.24 \times 10^{13} cDG \times 10^{-2} \rho$ , where  $\rho$  is density of the liquid and  $c$  is an unknown correction factor introduced by shielding effects in the apparatus and possible errors in the values chosen for  $G_0$ . Since the total charge  $Q_0$  produced by the radiation is equal to  $n_0 Ad / 6.24 \times 10^{18} \text{ C}$ , where  $A$  is the electrode area, and since the observed charge collected  $Q = fQ_0$ , it follows that  $10^7 Q = fcDGApd$ . Since  $u = (\alpha/\beta\mu)6.24 \times 10^{11} cDG\rho d^2 V^{-1}$ , substitution into eq 17 gives

$$10^7 Q = \frac{AV}{(\alpha/\beta\mu)6.24 \times 10^{11} d} \ln(1 + (DG/V) \times (\alpha/\beta\mu)6.24 \times 10^{11} c\rho d^2) \quad (18)$$

The quantities in this equation which are experimentally varied are  $V$  and  $D$ .  $G$  is assumed to be a known function of  $V$  and other quantities are known constants of the apparatus or material. The data were fit to the above equation by a least-squares computer program to give values for the unknowns  $\alpha/\beta\mu$  and  $c$ .

## Results

Reproducibility of  $\mu$  was sometimes disappointing, basically because of the noise in the traces inherent in the requirement that the intensity be kept low to prevent ion recombination. When the liquid is noticeably impure the fit of the observed current-time curve to eq 9 depends critically upon the slope of the first portion of the rising current curve and on the exact time of the start of the pulse, and also upon the very small differences in slope of

TABLE I: Electron Mobilities

Liquid	Temp, °C	Mobility, cm <sup>2</sup> V <sup>-1</sup> sec <sup>-1</sup>	
		Present work	Lit.
Methylcyclohexane	23	0.068	
	-12	0.023	
	51	0.129	
<i>n</i> -Hexane	23	0.082	0.09, <sup>a</sup> 0.08 <sup>b</sup>
	-18	0.015	0.027 <sup>b</sup>
	-44	0.005	0.009 <sup>b</sup>
<i>n</i> -Pentane	23	0.14	0.075, <sup>c</sup> 0.16 <sup>a</sup>
Cyclohexane	23	0.24	0.35, <sup>a</sup> 0.45 <sup>d</sup>
Neopentane	23	54	55, <sup>a</sup> 70, <sup>b</sup> 50, <sup>d</sup> 70 <sup>e</sup>
	-15	44	
Tetramethylsilane	23	100	90 <sup>a</sup>
	-9	88	
	-35	87	
	-78	65	

<sup>a</sup> Reference 1. <sup>b</sup> Reference 4. <sup>c</sup> Reference 2. <sup>d</sup> Reference 3. <sup>e</sup> G. Bakale and W. F. Schmidt, *Chem. Phys. Lett.*, submitted for publication.

the curve toward the end, all of which are greatly obscured by the noise. We believe our results (except for neopentane) are good to  $\pm 10\%$ . In general the best values of  $\mu$  that we have obtained are in agreement with those already reported. Table I shows the values of  $\mu$  that we have found together with those given in the literature. We prefer our value for cyclohexane to the higher values reported in the literature, but we intend to continue to study this material. The positive temperature coefficient found for  $\mu$  in tetramethylsilane is small but probably significant.

The ratio of the rate constant to the mobility for electrons reacting with positive ions was determined for pure pentane, hexane, and tetramethylsilane. The purity determinations on these preparations showed that under the conditions of the recombination coefficient measurements, over 95% of the recombination reactions involved electrons. The same determination was also made for solutions of ethyl bromide in pentane and of methyl iodide in tetramethylsilane at concentrations such that over 95% of the recombination reactions involved negative ions rather than electrons. The results in tetramethylsilane are less accurate than the others because the very high mobility of the electron required working at low doses per pulse (of the order of a few millirads). Table II shows that when account is taken of the Boag factor of 0.85 the ratio of the recombination coefficient to the mobilities for both electrons and negative ions is equal to the theoretical diffusion-controlled value,  $4\pi e/\epsilon$ . The slight negative deviation found for pure tetramethylsilane may be real but is probably within experimental error. The reported<sup>8</sup> value for  $\alpha$  of  $2 \times 10^{14} M^{-1} \text{sec}^{-1}$  in *n*-hexane is too high to be reconcilable with the theory<sup>15</sup> of diffusion-controlled reaction rates, in view of the now well-attested value of the electron mobility.

Thus when the reaction radius is sufficiently large ( $\sim 300 \text{ \AA}$ ) as it is in recombination of ions in media of low dielectric constant, the reaction of electrons remains diffusion controlled and the rate constant increases proportionally to the mobility. The recombination constant for electrons in tetramethylsilane is probably the largest bimolecular rate constant ever observed for any process in either gas or liquid phase.

Rate constants obtained for reactions of the electrons with ethyl bromide, carbon tetrachloride, methyl iodide,

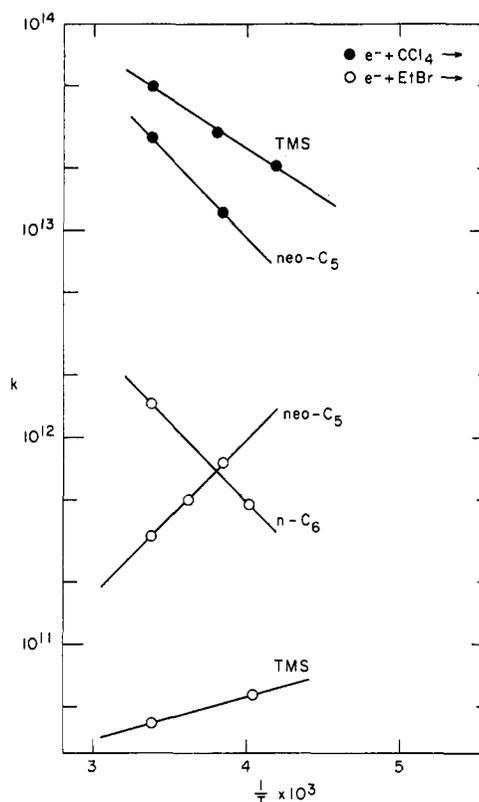


Figure 4. Rate constants  $k_S$  ( $M^{-1} \text{sec}^{-1}$ ) as a function of  $1/T$ .

and oxygen in various solvents are listed in Table III. We judge these values are accurate to about  $\pm 20\%$ . In addition it was shown that adding a concentration of  $3.7 \times 10^{-5} M$  of methanol to tetramethylsilane had no appreciable effect on the electron current. The data at  $23^\circ$  are plotted against the mobility of the solvents in Figure 3, together with data of Beck and Thomas<sup>11</sup> on reactions of biphenyl with electrons in various solvents. In no case does the rate constant for any given solute increase proportionally to the mobility. Rather there is an increase which appears to go roughly with the square root of the mobility for biphenyl, oxygen, and carbon tetrachloride; but in the case of ethyl bromide the rate constant reaches a maximum and sharply declines when we reach the high mobility solvents neopentane and tetramethylsilane.

Figure 4 gives plots of the rate constant data against temperature for those cases where determinations were made at more than one temperature. In accordance with the usual procedure the plots are made as the logarithm of  $k_S$  against the reciprocal absolute temperature. Carbon tetrachloride showed as expected a positive temperature coefficient, but for ethyl bromide in the high-mobility solvents the temperature coefficient is negative, while methyl iodide in tetramethylsilane gives a zero temperature coefficient within the experimental error.

## Discussion

The liquids used here show an astonishing range of electron mobilities ranging at room temperature from 0.07 in methylcyclohexane to 100 in tetramethylsilane. The lower mobilities show a larger temperature coefficient than the higher, and the motion of the excess electron is generally agreed to be an activated process, with the electron being promoted to states of higher energy and higher mobility by thermal agitation of the molecules in its neighborhood,

TABLE II: Electron-Ion Recombination Rates

Compound	$\alpha/\beta\mu$ $\times 10^6$	$\mu$	$\alpha^a$		$\alpha/\beta\mu \times 10^6$ (theor) <sup>b</sup>
			$\text{cm}^3 \text{sec}^{-1}$	$M^{-1} \text{sec}^{-1}$	
<i>n</i> -Pentane	1.11	0.14	$1.32 \times 10^{-7}$	$7.9 \times 10^{13}$	1.16
<i>n</i> -Pentane + EtBr	1.17				1.16
<i>n</i> -Hexane	1.15	0.08	$7.8 \times 10^{-8}$	$4.7 \times 10^{13}$	1.13
TMS (1) <sup>c</sup>	0.94	100	$8.0 \times 10^{-5}$	$4.8 \times 10^{16}$	1.16
TMS (2) <sup>c</sup>	1.08	100	$9.1 \times 10^{-5}$	$5.5 \times 10^{16}$	1.16
TMS + MeI (1)	1.14				1.16
TMS + MeI (2)	1.18				1.16

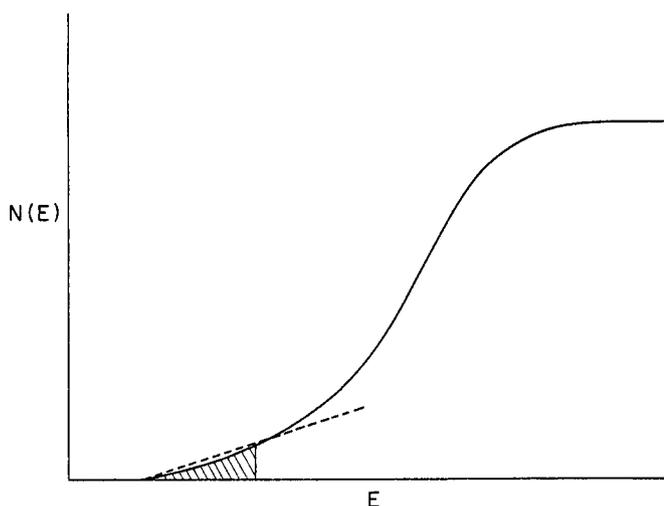
<sup>a</sup> Assuming  $\beta = 0.85$ . <sup>b</sup>  $4\pi e/0.85\epsilon$ . <sup>c</sup> Two different preparations of tetramethylsilane.

TABLE III: Rate Constants of Electron Reactions

Solvent, S	Reactant	Temp, °C	Assumed $\mu$ , $\text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$	[S] $\times 10^6$ , M	$k \times 10^{-12}, M^{-1} \text{sec}^{-1}$	
					Obsd	Av
Methylcyclohexane	O <sub>2</sub>	23	0.068	0.55	0.19	0.17
		23	0.068	0.85	0.17	
		23	0.068	1.44	0.16	
<i>n</i> -Hexane	C <sub>2</sub> H <sub>5</sub> Br	20	0.078	0.37	1.46	1.5
		-24	0.019	0.39	0.47	0.47
		23	0.08	0.063	0.67	0.85
<i>n</i> -Pentane	C <sub>2</sub> H <sub>5</sub> Br	23	0.14	0.57	1.03	1.6
				0.10	1.6	
				0.20	1.5	
Cyclohexane	CCl <sub>4</sub>	23	0.14	0.29	1.5	1.8
				0.083	1.9	
				0.16	1.8	
Cyclohexane	CCl <sub>4</sub>	23	0.24	0.106	1.77	1.8
				0.235	1.75	
				0.49	1.98	
Cyclohexane	CH <sub>3</sub> I	23	0.24	0.069	1.94	2.0
				0.103	1.97	
				0.201	1.97	
2,2,4-Trimethylpentane	C <sub>2</sub> H <sub>5</sub> Br	23	7.0	0.408	2.28	6.3
				0.31	6.5	
				0.62	6.5	
Neopentane	C <sub>2</sub> H <sub>5</sub> Br	24	68	1.25	6.0	0.34
				2.5	0.32	
				16.9	0.36	
				44.7	0.34	
				17.7	0.48	
				46.7	0.52	
				18	0.63	
				47.5	0.89	
				6.5	28.6	
				6.9	12.4	
Tetramethylsilane	C <sub>2</sub> H <sub>5</sub> Br	23	101	0.56	1.34	0.042
				1.45	1.13	
				9.75	0.037	
				78.8	0.043	
Tetramethylsilane	CCl <sub>4</sub>	23	101	216	0.046	0.059
				231	0.059	
				1.39	41	
				4.52	61	
				7.77	59	
				1.45	30	
				1.50	21	
				0.324	162	
				0.361	152	
				Tetramethylsilane	CH <sub>3</sub> I	
0.361	152					
90	30					
82	21					
Tetramethylsilane	CH <sub>3</sub> I	-34	82	1.50	21	21
				23	101	
Tetramethylsilane	CH <sub>3</sub> I	-46	78	0.361	152	152
				0.361	152	

while spending most of its time in states of much lower mobility and lower energy. These states are apparently similar to the solvated electrons seen in polar liquids, since several irradiated hydrocarbons have been shown<sup>7,8</sup> to exhibit an infrared spectrum similar to that attributed to solvated electrons in other liquids. The observed mobility is thus equal to the mobility actually characteristic of the upper or mobile states, multiplied by the fraction of the time that the electron spends in these states.

The ion recombination coefficient formula of Langevin is based on the assumption that the motion of ions is essentially diffusive in character. Debye<sup>15</sup> showed that the formula did indeed correspond to a diffusion-controlled reaction, in which singly charged ions of opposite sign would react with one another whenever they attained a distance apart or "reaction radius" of  $e^2/\epsilon kT$ , which in the liquids studied is close to 300 Å. We have seen that the electron-ion recombination rate accurately follows the



**Figure 5.** Hypothetical density of states  $N(E)$  vs.  $E$  for the excess electron bound in nonpolar liquid. States in the shaded area are localized.

formula, and we conclude that the motion of the excess electron in the mobile state is governed by random diffusion and that the effective mean free path for this motion must be less than 300 Å. This behavior is quite different from that of the electron in the conduction band of a semiconductor such as crystalline germanium, in which the bulk recombination coefficient is many orders of magnitude smaller than given by the Langevin formula.<sup>16</sup>

When we turn to the reaction rate of the electron with neutral molecules, the situation is altogether different. As we pass from one liquid to another the rate is no longer proportional to the mobility of the electron, but appears to be roughly proportional to  $\mu_e^{1/2}$ . As far as the present data go, carbon tetrachloride and methyl iodide seem to behave in this respect quite similarly to the results reported for biphenyl by Beck and Thomas.<sup>11</sup> Oxygen also appears to behave similarly, although the rates of reaction with this solute are considerably lower (see also ref 7b). Although the data are as yet too sparse to draw any firm conclusions, we may suggest that the similar behavior of these dissimilar solutes shows that we are dealing with a property of the electron in the solvent.

Although the electron-molecule rate constants in hexane are large, their failure to keep pace with the mobility in higher-mobility solvents strongly suggests that they are not diffusion limited. The rates for hexane, if diffusion limited, would correspond to reaction radii of 10 Å at 297°K, and 16 Å at 245°K. The diffusion-limited rate must be at least as great as any observed rate; so the effective reaction radius of the electron in the mobile state of hexane must be 15 Å or more.

It seems reasonable to suppose that these rates are limited by the same factor responsible for the low rates of bulk electron-ion recombination in semiconductors (namely, the fact that the wave function of the electron is so extended that its overlap with any particular reactive solute molecule is relatively small). This of course refers to the state of the electron in its upper mobile energy level, not in any trapped or solvated lower energy state. The suggestion is that in the liquids composed of more symmetrical molecules the wave function of the electron approaches more closely to the plane wave approximation which was found to explain the mobility data quantitatively for liquid argon, whereas in normal pentane or hex-

ane where the potential fields are irregular the wave function in the mobile state is less extended. This conclusion is not in accord with the view<sup>6,17</sup> that the upper mobile states of the electron in hexane and neopentane are very similar:

The observed mobility  $\mu_e$  is

$$\mu_e = \mu_0 P_m \quad (19)$$

where  $\mu_0$  is the mean electron mobility in the mobile states and  $P_m$  is the probability of finding the electron in a mobile state at any time. Since empirically  $\mu_e = A_0 \exp(-E/kT)$ , it has been assumed that  $\mu_0 = A_0$  and  $P_m = \exp(-E/kT)$ . Alternative explanations however are possible. Mott and Davis<sup>18</sup> point out that the localized lower states lie in a tail at the lower end of the excess electron band, as shown schematically in Figure 5, where the density of states,  $N(E)$ , is plotted vs. electron energy  $E$ . The lower part of the curve, containing all the states occupied at ordinary temperatures, can be approximated by the straight line  $N(E) = mE$ , if the zero of  $E$  is taken as the energy in the lowest available level. Since the probability of finding an electron with energy between  $E$  and  $E + dE$  is  $N(E) \exp(-E/kT)$

$$P_m = \int_{\Delta E}^{\infty} mE \exp(-E/kT) dE / \int_0^{\infty} mE \times \exp(-E/kT) dE \quad (20)$$

where  $\Delta E$  is the energy difference between the lowest localized state and lowest mobile state. On evaluating the integrals, we find

$$\mu_e = \mu_0 (1 + \Delta E/kT) \exp(-E/kT) \quad (21)$$

For *n*-hexane,  $\mu_e = 0.08$ ,  $\Delta E/kT$  is about 8 and we find  $\mu_0 = 27$ . For tetramethylsilane  $\mu_e = 100$ ,  $\Delta E/kT$  is about 0.4 and  $\mu_0 = 107$ . Whether this difference in  $\mu_0$  implies as large an effect as we see on the rate constants remains to be determined by further analysis.

Ethyl bromide differs from the other solutes in that its rate of reaction with electrons decreases sharply as we go to liquids of high electron mobility. In the gas phase, ethyl bromide shows a maximum rate for reaction with electrons at an electron energy of about 0.7 eV, while such rates for the other compounds studied here continually increase with decreasing electron energy.<sup>19</sup>

It has been shown by studies of metallic work functions and photoionization in liquids<sup>20</sup> that the energy  $V_0$  of the excess electron in various liquids at room temperature (relative to the vacuum) is lower the higher the electron mobility. If we plot our room temperature rate constants against  $V_0$ , the points for ethyl bromide and for the others fall on curves which are reminiscent of the respective curves found for carbon tetrachloride and for ethyl bromide in the gas phase. Data on other compounds will be obtained to test this parallelism further.

Ethyl bromide is unusual in another way in showing a negative temperature coefficient in neopentane and tetramethylsilane, while for carbon tetrachloride the coefficient is positive, and for methyl iodide about zero. In *n*-hexane the ethyl bromide apparent activation energy, 3.5 kcal, though positive, is smaller than that of the mobility, about 5 kcal; and we conclude that for the electrons in the upper mobile state the reaction with ethyl bromide has a negative temperature coefficient in this solvent also. Although free electrons react more rapidly with this molecule as the electron's kinetic energy increases from thermal, the lower vibronic states of the molecule seem to be

more reactive toward quasi free electrons than the higher. It would be interesting to study this reaction in the gas phase as a function of temperature.

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## Gauche-Trans Rotational Isomerism in Ethylamine. The Far-Infrared Spectra of $\text{CH}_3\text{CH}_2\text{ND}_2$ and $\text{CH}_3\text{CD}_2\text{ND}_2$ <sup>1</sup>

A. S. Manocha, E. C. Tuazon,\*

Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

and W. G. Fateley

Department of Chemistry, Kansas State University, Manhattan, Kansas 66502 (Received November 26, 1973)

The gauche-trans rotational isomerism of ethylamine in the vapor phase has been studied by an analysis of the far-infrared spectra of  $\text{CH}_3\text{CH}_2\text{ND}_2$  and  $\text{CH}_3\text{CD}_2\text{ND}_2$ . The potential function for internal rotation about the C-N bond, derived through a one-dimensional approximation, is  $2V(\alpha) = -303.2(1 - \cos \alpha) + 184.4(1 - \cos 2\alpha) + 734.7(1 - \cos 3\alpha) - 19.3(1 - \cos 6\alpha) \text{ cm}^{-1}$ . The difference between the potential energy minima of the gauche and trans conformations is  $104 \text{ cm}^{-1}$ , the gauche being the more stable form.

### Introduction

Internal rotation about the C-N bond in ethylamine gives rise to two distinct stable isomers, the trans and gauche forms. The rotation of the amino group about the C-N axis is geometrically asymmetric. The asymmetry will be reflected in the form of the potential function governing the motion. It has been pointed out by Lowe<sup>2a</sup> that the study of molecules with asymmetric internal rotors will provide more information concerning the origins of barrier to internal rotation than those obtainable from molecules with highly symmetric rotors (e.g.,  $\text{CH}_3$  group). Recently, Radom, Hehre, and Pople<sup>2b</sup> predicted rotational barriers and conformational energy differences in several molecules, including ethylamine, from *ab initio* molecular orbital theory. They related physical effects such as staggered arrangements of bonds, stabilization due to electron donation and electron withdrawal in bonds and

orbitals, and relative directions of dipole moment components to components of the potential function expressed as a Fourier series in the internal angle.

In this work, the gauche-trans isomerism of ethylamine is studied by an analysis of the observed frequencies belonging to the torsional motion of the amino group. The simpler vapor-phase far-infrared spectra of the deuterated species  $\text{CH}_3\text{CH}_2\text{ND}_2$  and  $\text{CH}_3\text{CD}_2\text{ND}_2$ , as compared to that of the light molecule  $\text{CH}_3\text{CH}_2\text{NH}_2$ , enabled a good approximate potential function to be derived through a one-dimensional model.

### Experimental Section

$\text{CH}_3\text{CH}_2\text{ND}_2$  was generated from a sample of  $\text{CH}_3\text{CH}_2\text{ND}_2 \cdot \text{DCl}$  (obtained by direct exchange of  $\text{CH}_3\text{CH}_2\text{NH}_2 \cdot \text{HCl}$  with  $\text{D}_2\text{O}$ ) by treatment with a freshly ignited sample of  $\text{CaO}$ .  $\text{CH}_3\text{CD}_2\text{ND}_2$  was prepared