mechanism applies here, then the mobility should be given by

$$\mu = (e/6kT)\Lambda^2 \nu_0 \exp(-E_a/kT)$$
(12)

In Figure 3 the high-pressure mobility data are plotted according to eq 12. Comparison of eqs 5 and 12 shows that the preexponential constant C is equal to $e\Lambda^2 v_0/6k$. If one assumes values of the jump distance equal to the molecular diameters (6.6 Å for benzene and 7.0 Å for toluene), then, from the derived values of C, ν_0 turns out to be 2.6 × 10¹⁴ s⁻¹ for benzene and 3.1 × 10¹⁴ s⁻¹ for toluene. These frequency factors are quite comparable to values obtained when this model was applied to electron transport in solid and liquid alkanes.23,24

The observed activation energies for hopping are 0.12 and 0.13 eV for benzene and toluene, respectively. These values are quite comparable to the activation energy (0.11 eV) reported for the negative ion mobility in C_6F_6 . The activation energy of selfdiffusion of benzene at 1 kbar, as measured by the viscosity,²⁵ is 0.12 eV. Thus, as in the case of C_6F_6 the hopping process appears to involve some kind of molecular reorientation. Not only are the

London, 1949; Chapter 12.

activation energies similar, but also the mobility in C_6F_6 is 0.018 $cm^2/(V s)$, which is quite comparable to the value observed here for toluene at high pressure of 0.057 $\text{cm}^2/(\text{V s})$. The electron must be more deeply trapped in C_6F_6 because its electron affinity is more than 2 eV higher than that of either benzene or toluene. Yet this large difference in energetics appears to be irrelevant to the hopping rate.

In conclusion, the results of this study have given considerable insight into the mechanism of electron transport in these liquids. At room temperature and 1 bar there are about equal numbers of electrons and anions in benzene. The free energy of reaction is positive at 1 bar but decreases with increasing pressure. This is due in part to the polarization energy which becomes 10% greater because the dielectric constant is greater (for toluene ϵ = 2.510 at 1 kbar). Also contributing is an increase in the energy level of the electron in the solvent. At high pressure mainly anions are present, and the drift mobility is explained by electron hopping.

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Registry No. Benzene, 71-43-2; toluene, 108-88-3.

Electron Attachment to Benzene and Toluene in Nonpolar Solvents at High Pressure

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The effect of dilute concentrations of the aromatic hydrocarbons benzene and toluene on the electron mobility in some nonpolar liquids was studied as a function of pressure from 1 bar to 3 kbar and as a function of temperature from 20 to 100 °C. These aromatics have no effect on the electron mobility in n-pentane at low pressure and no effect on the mobility in tetramethylsilane at any pressure or temperature studied. However, above 1 kbar the mobility in n-pentane is reduced by the presence of these aromatics, an effect which increases with pressure. This effect is attributed to reversible electron attachment: e_s^- + aromatic \Rightarrow aromatic⁻. This equilibrium is shifted to favor the anions at high pressure both because the electron in the solvent becomes destabilized and because the volume change is large and negative, of the order of $-100 \text{ cm}^3/\text{mol}$. The results indicate that the benzene anion is more stable than the toluene anion in solution.

Introduction

The purpose of this study is to investigate how pressure, temperature, and solvent affect the reversible electron attachment equilibria

$$e_{c}^{-}$$
 + benzene \Rightarrow benzene⁻ (1a)

$$e_{c}^{-}$$
 + toluene \rightleftharpoons toluene⁻ (1b)

where e_s^{-} designates the electron in the solvent, *n*-pentane. The influence of solvent on such equilibria is a function of the ground-state energy of the electron, which is different in each solvent. If this energy is low, for example, these reactions are less likely to occur. A determination of the equilibrium constants K_{1a} and K_{1b} provides a measure of the ground-state energy of the electron for the solvent. Also, a pressure study can show how this energy varies with density.

High-pressure studies are also useful to measure the volume changes for such reactions. Similar reactions have been shown to have very large volume changes, of the order of -100 to -300 cm³/mol,^{1,2a} which have been attributed primarily to electrostriction of the solvent around the product anion.

Equilibria of this type have been observed at 1-bar pressure with benzene derivatives that are more electrophilic than benzene itself. For example, excess electrons in *n*-hexane react reversibly with styrene, with an electron affinity of -0.01 eV, and the equilibrium constant is 3×10^9 M⁻¹ (or 2×10^9 kg/mol)^{2b} at 25 °C.³ Similarly, electrons react with *p*-difluorobenzene, electron affinity of -0.35 eV, for which the equilibrium constant is 4 \times 10^5 M^{-1} (or 2.6 × 10^5 kg/mol)^{2b} in hexane at 25 °C.⁴ A linear relationship between free energy of reaction, ΔG_r , and electron affinity has been suggested.⁴ From this it is estimated that ΔG_r for reactions 1a and 1b in hexane would be about +0.2 eV since the electron affinities of benzene and toluene are -1.15 and -1.11 eV, respectively.⁵ This ΔG_r corresponds to an equilibrium constant of approximately 10^{-3} kg/mol. The value for *n*-pentane as a solvent is not expected to be very different from this.

In a related study of the effect of pressure on the electron mobility in pure benzene and toluene,² the results were interpreted

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Figure 1. Current trace observed for a 1.3% solution of benzene in *n*-pentane at 23 °C and 1750 bar. Voltage applied is 1997 V.

TABLE I: Effect of Benzene on Electron Mobility in Tetramethylsilane

	Т.	P, bar					
liquid	°Ċ	250	500	1000	1500	2000	2500
TMS ^e	18	93.4	89.9	87.7	87.5	86.0	85.7
TMS + 1% benzene	23	92.4	90.1	88.3	88.0	87.4	87.0
TMS ^a	60	92.9	86.5	80.0	78.0	76.0	75.8
TMS + 1% benzene	60	94.3	86.9	82.7	79.6	78.1	77.9

^a Mobilities from ref 8.

in terms of the equilibria given by eq 1. The analysis indicated values of K = 1 kg/mol around 500-bar applied pressure. For dilute solutions like those used in this study ($\approx 1\%$) the equilibrium would be shifted in favor of the electron in the solvent. However, the pure solvent results² also showed that K increased 1 order of magnitude for an increase in pressure of 350 bar. Thus, observation of these equilibria at higher pressures was anticipated for 1% solutions.

In this study electron mobilities are reported as a function of temperature and pressure for dilute solutions of benzene and toluene in two solvents: n-pentane and tetramethylsilane. The results show that electron attachment and detachment (reaction 1) occur at high pressure in n-pentane. Our results are not in accord with an earlier report⁶ that toluene traps electrons irreversibly in tetramethylsilane at 1 bar.

Experimental Section

The benzene (Mallinckrodt, AR grade) and toluene (Wiley, 99%) were purified as described.² The n-pentane (Fisher, HPLC grade 99.5%) was purified by first washing with H₂SO₄ and H₂O followed by degassing and subsequent treatment with silica gel and NaK. The tetramethylsilane (Wacker, calorimetry grade) was purified similarly, except the acid wash was omitted.

Densities and compressibilities of *n*-pentane were estimated by means of the Tait equation as described earlier.⁷ Dielectric constants were calculated from densities, using the Clausius-Mosotti equation.

Mobilities (μ) were determined by the time-of-flight method. With *n*-pentane, electrical fields of 10^4 to 2.6×10^4 V/cm were employed; with TMS, the fields were less than 300 V/cm. For drift times in the millisecond range transient currents were recorded in a LeCroy 6810 waveform recorder. For shorter drift times an 8828B digitizer was utilized. Figure 1 shows a typical conductivity trace for benzene at 23 °C and 1750 bar. The observed drift time (173 μ s) at 1997 V corresponds to a mobility of 0.0165 cm²/(V s), since the electrode separation is 0.0756 cm. The mobility is significantly reduced here from that in pure npentane by the small amount of benzene added.

Results

Table I shows the mobility of excess electrons in a solution containing 1% benzene in tetramethylsilane. Also shown are values of the mobility for the pure solvent.⁸ The mobility is essentially



Figure 2. Effect of pressure on the mobility of electrons in n-pentane containing benzene (open points for 1.3%, filled points for 2.5%). Dashed lines are mobilities in pure *n*-pentane, ref 7; temperatures are in $^{\circ}C$ as indicated.



Figure 3. Effect of pressure on the mobility of electrons in n-pentane containing 0.6% toluene. Dashed lines are for the pure solvent (ref 7). Temperatures are in °C as indicated.

unaffected by benzene to pressures of 2.5 kbar. The presence of benzene in the sample was verified by GC/MS analysis.

The mobility of electrons in *n*-pentane is also unaffected by the presence of 1.3% benzene to 1 kbar at 23 °C, as is shown in Figure 2. (The mobility in the pure solvent⁷ is indicated by the dashed lines.) Above this pressure the mobility drops off abruptly. The overall decrease observed is nearly 2 orders of magnitude. As the temperature increases the drop-off moves to higher pressures. At high pressure log μ decreases in a nearly linear manner with pressure. The presence of 2.5% benzene in pentane (results shown by the filled points in Figure 2) has an even greater effect in reducing the mobility.

Figure 3 shows the data for a 0.6% solution of toluene in n-pentane. The results are very similar to those for benzene solutions. In this case there is no effect of the toluene at 23 °C until the pressure exceeds 1.25 kbar. The measurements extend to 3 kbar. Again log μ decreases linearly with pressure at high pressure. A higher concentration of toluene has a greater effect in reducing the mobility as was found for benzene. As is shown below the effect is proportional to concentration.

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Figure 4. Dependence of K_{eq} for electron reaction with benzene on pressure and temperature (in °C as indicated): open points, 1.3% benzene; filled points, 2.5%.

Discussion

Analysis. The lack of an effect of benzene on the mobility of electrons in tetramethylsilane and n-pentane at low pressures shows that no irreversible attachment occurs under these conditions. The decrease in mobility observed in n-pentane at high pressure, on the other hand, is attributed to the reversible attachment (reaction 1).

As the pressure increases the equilibrium shifts to the right because of the expected negative ΔV for this reaction. When the electron is on the aromatic, a significant fraction of the time the mobility is reduced because ions have a lower mobility. The aromatic is an "extrinsic trap", but its behavior is analogous to an intrinsic trap. The effect on the mobility is the same as for solvent traps⁹

$$\mu_{\rm obs} = \mu_{\rm s} / (1 + K[{\rm A}]) + \mu_{\rm A} K[{\rm A}] / (1 + K[{\rm A}])$$
(2)

where K is the equilibrium constant for reaction 1 and [A] stands for the concentration of benzene or toluene. For most of the results the second term has been neglected. It is only important when μ_{obs} is comparable to $\mu_{A^{-}}$. The mobility of anions in *n*-pentane is expected to decrease with increasing pressure due to the viscosity increase. At 2 kbar the anion mobility should be about 2×10^{-4} cm²/(V s), which is an order of magnitude less than the mobility measured here at the highest pressure at 23 °C. If the second term is neglected, the observed mobility, μ_{obs} , is the mobility of the electron in *n*-pentane, μ_s , times the fraction of the time the electron is not attached to A.

Values of the equilibrium constant are derived from the observed mobilities, the known values of μ_s ,⁷ and the concentration of aromatic, using eq 2. The values of μ_s above 2.5 bar were extrapolated from existing data. The resulting values of K, shown in Figures 4 and 5, increase rapidly with pressure (by about 1 order of magnitude in 700 bar) and decrease with increasing temperature. As shown in Figure 4, the two different benzene concentrations give approximately the same values of K. Similar results were obtained for solutions of toluene in *n*-pentane, shown in Figure 5. Only the low-concentration results were used in each case for derivation of the volume and energy changes below.

Volume Changes. From the slopes of plots in $\ln K$ vs pressure, such as Figures 4 and 5, one obtains the volume change for the reaction given by

$$\Delta V_{\rm r} = -RT \, \mathrm{d} \, \ln \, K / \mathrm{d}P \tag{3}$$

The volume changes, calculated by least-squares fitting of five



Figure 5. Dependence of K_{eq} for electron reaction with toluene on pressure and temperature (in °C as indicated): open points, 0.6% toluene; filled points, 1.2%.

TABLE II:^{*a-c*} Volume Changes (cm³/mol) for $e_s^- + C_6H_6 \rightleftharpoons C_6H_6^-$

press.		temp, °C					
bar		23	33	41	60	80	100
1750	ΔV ϵ χ_{T}	-106 2.036 0.516	-114 2.023 0.519				
2000	Δ <i>ν</i> ε Χτ	-89 2.054 0.469	-93 2.040 0.471	-104 2.036 0.483	-108 2.020 0.511		
2250	Δν ϵ Χτ	(-87)	-90.5 2.055 0.431	-84 2.051 0.442	-93 2.037 0.466	-103 2.019 0.485	
2500	ΔV ϵ χ_{T}	(-81)				-88 2.035 0.446	-92 2.018 0. 46 7
2750	ΔV ϵ χ_{T}						-80 2.034 0.432

 ${}^{a}\chi_{T}$ values multiplied by 10⁴ (units are bar⁻¹). b Values in parentheses are from Figure 5. c Estimated error in ΔV is 3 cm³/mol.

TABLE III:^{*a,b*} Volume Changes (cm³/mol) for e_s^- + Toluene = Toluene⁻

press.		temp, °C					
bar		23	40	60	80		
2000	ΔV	-103	-104				
	e	2.054	2.036				
	Χт	0.469	0.481				
2250	$\widetilde{\Delta V}$	-90	-96	-104			
	e	2.070	2.051	2.037			
	χт	0.430	0.440	0.466			
2500	$\widetilde{\Delta}V$	-71.5	-80	-90	-96		
	e	2.085	2.067	2.053	2.035		
	Хт	0.397	0.406	0.428	0.446		
2750	$\widetilde{\Delta V}$			-79	-83		

 $^{a}X_{T}$ values multiplied by 10⁴ (bar⁻¹). ^{b}The estimated error in $\Delta \mathcal{V}$ is 3 cm³/mol.

points of each ΔV_r , are given in Tables II and III. The volume changes are negative and of the order of $-100 \text{ cm}^3/\text{mol}$. As the pressure increases, at any temperature the absolute volume change becomes smaller. The absolute value of ΔV_r increases as the temperature increases at any pressure. These volume changes scale roughly with the compressibility of the solvent and are therefore attributed to electrostriction of the solvent by the two charged species in reaction 1.

$$\Delta V_{\rm r} = \Delta V_{\rm es}({\rm A}^{-}) - \Delta V_{\rm es}({\rm e}_{\rm t}^{-}) \tag{4}$$

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Figure 6. Plot of experimental values of $-\Delta V_r$ vs $\epsilon^{-2} d\epsilon/dP$.

The volume change due to electrostriction of pentane by trapped electrons has been estimated⁷ and is approximately $-5 \text{ cm}^3/\text{mol}$ for the pressures and temperatures employed in this work. The volume change for electrostriction is given by classical theory¹⁰ as

$$\Delta V_{\rm es} = -N(e^2/2R\epsilon^2) \,\,\mathrm{d}\epsilon/\mathrm{d}P \tag{5}$$

where N is Avogadro's number. Values of the terms $\epsilon^{-2} d\epsilon/dP$ were calculated from its equivalent, $(\chi_T/3\epsilon^2)(\epsilon - 1)(\epsilon + 2)$. Thus, a plot of $-\Delta V_r$ vs $\epsilon^{-2} d\epsilon/dP$ should have a slope of $Ne^2/2R(A^-)$ $-Ne^2/2R(e_t^-)$. Such a plot is shown in Figure 6, which includes the data for both benzene and toluene. The slope of the line is 6.05×10^6 cm³ bar/mol, and since $Ne^2/2R(e_t^-)$ was found to be 4.3×10^5 cm³ bar/mol for *n*-pentane,⁷ this result corresponds to an anion radius of 1.1 Å, which is considerably less than the radii of 3.3 and 3.5 Å deduced from the molecular volumes of benzene and toluene, respectively. However, this value of *R* is comparable to the value of 1.4 Å deduced from a similar study of mobility in pure benzene and toluene.²

The magnitudes of the observed volume changes are clearly much larger than predicted by electrostriction theory when an anion radius derived from the molecular volume is used. Other effects that might contribute to the volume change were considered. Dimer anion formation is expected to be unimportant in these dilute solutions. The volume change observed for reaction of electrons with benzene in a methylamine-ammonia solvent $(-71 \text{ cm}^3/\text{mol})^{11}$ was attributed to a large positive molar volume of the electron in the amine solvent. This is not the case in *n*-pentane; there is a small negative volume change associated with trapping in *n*-pentane.⁷

Energy Changes. In order to evaluate the other thermodynamic quantities, the values of the equilibrium constants were plotted vs 1/T at several pressures according to the equation

$$\ln K = -\Delta H_r / RT + \Delta S_r / R \tag{6}$$

Such plots are straight lines, and ΔH_r is obtained from the slope and ΔS_r from the intercept. The value of ΔG_r at 25 °C is obtained from $\Delta G_r^{298} = -298R$ ln K^{298} . The results are shown in Table IV. The free energy change is slightly negative for both reactions and decreases with increasing pressure. The entropy change is large and negative and increases with increasing pressure. The enthalpy change remains roughly constant at -11 kcal/mol.

At any one pressure the benzene anion is slightly more stable than the toluene anion as reflected in the values of ΔG_r in Table IV. Taking the differences, one finds that for the reaction

$$toluene^- + benzene \rightarrow toluene + benzene^-$$
 (7)

in *n*-pentanc at high pressure ΔG_r is -0.014 eV. This reaction has been studied in an ether solvent at -100 °C where ΔG_r is

TABLE IV: 7	Thermodynamic	Data for e, +	$A \rightleftharpoons$	A ⁻ at	25 °	°C
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 				_
P, bar	$\Delta H_{\rm r},$ kcal/mol	$\Delta G_r^{298}, a$ kcal/mol	$\Delta S_{\rm r},$ cal/(K mol)	
	A =	Benzene		
1750	-11.0	-1.58	-31.6	
2000	-10.7	-2.15	-28.8	
2250	-10.5	-2.67	-26.4	
2500	-10.6	-3.15	-25.0	
	A =	= Toluene		
2000	-11.0	-1.78	-30.8	
2250	-10.9	-2.37	-28.5	
2500	-10.6	-2.88	-25.9	
2750	-10.2	-3.24	-23.3	

^a The estimated error in ΔG_r is 0.05 kcal/mol.

-0.022 eV.¹² The free energy changes are comparable in the two solvents even though the conditions are very different. In both solutions the benzene anion is more stable than the toluene anion. The reverse is true in the gas phase based on the reported electron affinities.⁵

The free energy change observed for reaction 1 will be dependent on the particular solvent chosen because the ground-state energy of the electron is different in each solvent. For n-pentane the energy level of the electron is expected to be close to that for *n*-hexane, which is -0.2 to -0.3 eV at 1 bar.³ Pressure is expected to raise this level to about 0 eV at 2.5 kbar based on theoretical predictions for other hydrocarbons.¹³ It is this increase as well as the enhanced stabilization energy of the anion at high pressure that makes ΔG_r negative. A similar line of reasoning can explain the lack of reaction in TMS. In this solvent the ground state of the electron is at -0.65 eV,³ considerably lower than in *n*-pentane. The ground state is the conducting state in this solvent, and work function measurements indicate this state moves up to -0.42 eV^{14} at 2.5 kbar. Since the free energy change for reaction 1 is a measure of the ground-state energy of the electron, by comparison to the *n*-pentane results it is clear that ΔG_r for reaction 1 in TMS must be large and positive; that is, the equilibrium constant is expected to be very small in agreement with observation.

Summary

As surmised in the Introduction, the equilibria given in eq 1 are far to the left at atmospheric pressure. In dilute (1%) solutions of benzene and toluene in either tetramethylsilane or *n*-pentane the electron is not on the aromatic long enough to affect the mobility. Electrons may react with benzene at 1 bar. The rate constant would be at most equal to the rate for attachment to *p*-difluorobenzene, which is $1.1 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ in *n*-hexane.⁴ However, the anion formed would be very short-lived, of the order of 10^{-15} s , since $K \approx 10^{-3} \text{ kg/mol}$.

The anions of benzene and toluene become more stable at high pressure, and this stability is due both to a destabilization of the electron in the solvent and to an enhancement of the polarization energy by the anion. The volume changes for these reactions are large and negative and attributed to electrostriction. The magnitude of the observed volume changes are larger than predicted by classical theory. The reason for this discrepancy is unknown. Further study is needed to understand these volume changes and the role of electrostriction in these electron attachment reactions.

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Registry No. Benzene, 71-43-2; toluene, 108-88-3; *n*-pentane, 109-66-0; tetramethylsilane, 75-76-3.

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