The e⁻ + 1,3-Butadiene ⇌ 1,3-Butadiene⁻ Equilibrium in *n*-Hexane

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The rate constants for attachment of excess electrons to 1,3-butadiene (k_a) and detachment from the butadiene anion (k_d) in *n*-hexane are reported. The equilibrium constant, $K_{eq} = k_a/k_d$, increases rapidly with pressure and decreases as the temperature increases. At -7 °C attachment is observed at 1 bar. At high pressures the attachment rate is diffusion controlled. The activation energy for detachment is about 21 kcal/mol; detachment is facilitated by the large entropy of activation. The reaction volumes for attachment range from -181 cm³/mol at 400 bar to -122 cm³/mol at 1500 bar and are largely attributed to the electrostriction volume of the butadiene anion ($\Delta \bar{V}_{el}$). Values of $\Delta \bar{V}_{el}$ calculated by a model, which includes a glassy shell of solvent molecules around the ion, are in agreement with experimental reaction volumes. The analysis indicates the partial molar volume of the electron in hexane is small and probably negative. It is shown that the entropies of reaction are closely related to the partial molar volumes of reaction.

Introduction

Previous studies[1,2] have established that some molecules with large negative electron affinities, which do not attach electrons at 1 bar in nonpolar liquids, do attach electrons when the pressure is increased. Attachment was even observed to toluene, which has an electron affinity of -1.1 eV. Study of such reactions as a function of temperature and pressure allows determination of the thermodynamic changes and the volume change on reaction. Such studies provide the opportunity to assess the shift occurring on a change of phase from gas to liquid. The magnitude of the volume change in these reactions is large, typically -100 to -300 cm³/mol, larger than that expected for electrostriction of the solvent by the product ion from classical theory. In a recent paper on electron attachment to CO_2 in nonpolar liquids,[3] it was suggested that the theory should take into account the fact that the solvent is highly compressed (more dense) around the ion, which compromises the assumption of a constant dielectric constant in the classical theory. More recently Schwarz[4] calculated the volume changes for the CO_2 reaction, taking the density increase around the ion specifically into account. The resulting electrostriction volumes are in even worse agreement with experiment than the classical model predictions. However, when a frozen first shell of solvent molecules around the ion is included, the calculated values agree with the experimental reaction volumes. The present results provide more volume information on a different reactant and solvent and the opportunity to test this theory further.

The adiabatic electron affinity of 1,3-butadiene is -0.62 eV,[5] which is much less negative than that of toluene, suggesting the equilibrium

$$e^- + \text{1,3-butadiene} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \text{1,3-butadiene}^- \qquad (1)$$
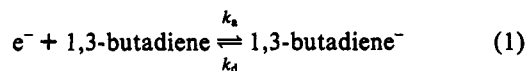
may be observed in hexane at lower pressures than was the attachment to toluene. Although there were no prior rate data for reaction 1 in hydrocarbon solvents, the rate constant for electron attachment to 1,3-butadiene in water is 8×10^9 M⁻¹ s⁻¹.[6] In a less polar matrix, methyltetrahydrofuran, at 77 K butadiene

attaches electrons and the spectrum of the anion has been reported.[7] Indirect evidence of attachment of electrons to conjugated diolefins comes from studies of the free ion yields for these neat hydrocarbons. The free ion yields for 1,3-cyclohexadiene and 1,4-cyclohexadiene are 0.075 and 0.23 ion pairs/100 eV, respectively.[8] The lower yield in the conjugated diolefin was attributed by the authors to anion formation. Even less direct evidence for reaction 1 is provided by mobility data. While electrons are quite mobile in liquid 1,4-cyclohexadiene ($\mu = 5.8$ cm²/(V s)), an electronic signal was not seen in 1,3-cyclohexadiene,[8] which is negative evidence consistent with anion formation in the latter.

Finally, information on reaction 1 is of interest because diolefins are minor products of the radiolysis of hydrocarbons.[9] Thus, it is important to have rate data on these reactions in order to know if such products can interfere with other reactions of the electron.

Experimental Section

The *n*-hexane (Wiley, 99.8%) was washed first with sulfuric acid followed by several washes with deionized water. After drying, the hexane was degassed, passed through molecular sieves and silica gel, and stored several months over NaK alloy. The 1,3-butadiene (Matheson Instrument grade) was degassed prior to use. Small amounts of butadiene, measured by pressure in a calibrated volume on a vacuum line, were frozen into the conductivity cell containing the *n*-hexane at 77 K. Mixing was accomplished by establishing a thermal gradient after warming the sample to room temperature. The cell was placed inside a thermostated pressure vessel and exposed to 0.8-μs X-ray pulses generated with a 2-MeV van de Graaff accelerator.

The electron current produced by the X-ray pulse showed a fast decay followed by a long "equilibrium current", as in Figure 1. These traces were analyzed to obtain the rate constant for attachment to butadiene (k_a) and the detachment rate constant (k_d), as described earlier.[10] The analysis included a correction for the small buildup of butadiene anion during the pulse.[3] Some current traces showed a linear decay; these were used to determine the electron mobility from the observed drift time.

Calculation of the electrostriction volume of butadiene⁻ according to the method of Schwarz[4] requires data on the density (d) of hexane as a function of temperature and pressure. We fit density data[11,12] as a function of pressure to a Tait equation:
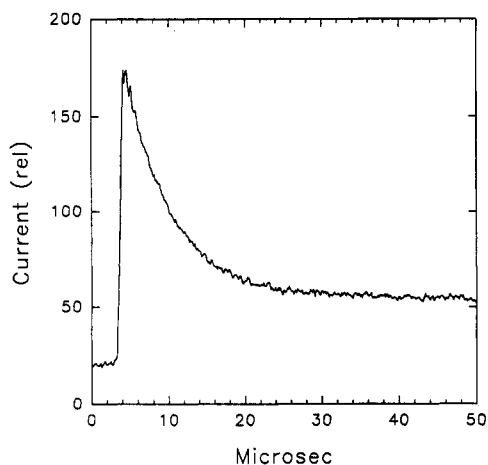
Figure 1. Trace showing equilibrium current. Sample is 0.53 μm butadiene in n-hexane at 300 bar and –7 °C.

$$d_0/d = 1 - A \ln(1 + P/B) \qquad (2)$$

Values of A and B for each temperature are given in Table 1. The calculations were made with a value of the hard core radius (r) of 2.44 Å for the butadiene anion. This radius was obtained from the hard core volumes.[13]

Results

In purified samples of n-hexane, prior to the addition of butadiene, the lifetime of the electron due to trapping by impurities was approximately 1 ms. This lifetime increased at higher pressures and decreased with increasing temperature. In these samples the electron current decayed linearly to base line at applied voltages (V) over 300 V. The point at which the current returns to the base line defines the drift time (t_D). The electron mobility (μ) is calculated from $\mu = l^2/(Vt_D)$, where l is the effective plate separation. The mobility of electrons in hexane μ(hx) was measured at several temperatures; the results for 0.5 °C are shown in Table 2. The results obtained at other temperatures are in agreement with earlier data.[14]

At 1 bar and temperatures of 12 °C and above, 1,3-butadiene, at concentrations below 1 μM, had no effect on the electron current traces. The decay was linear and the mobility the same as in the purified samples. Thus, there was no evidence for attachment under these conditions. As the pressure is increased, or the temperature lowered, the existence of equilibrium is first detected as a decrease in mobility (μ). The mobility is proportional to the fraction of electrons not attached to butadiene which is [e⁻]/([e⁻] + [butadiene⁻]) (the mobility of butadiene⁻ is negligible); thus,

$$\mu = \mu(hx)/(1 + K_{eq}[\text{butadiene}]) \qquad (3)$$

and K_{eq}, the equilibrium constant of reaction 1, if significantly large, can be determined from mobilities for the solution, the mobilities in pure hexane, μ(hx), and eq 3. Such results are shown in Figure 2 by the dark points. For some temperatures where μ(hx) was not measured it was obtained by interpolation using, in part, earlier data[14] and assuming the temperature dependence was of the form $\ln \mu = \Delta G/RT + \ln \mu_0$ (see eq 7 below).

As the pressure is increased further, the conductivity traces are of the type shown in Figure 1. The attachment and detachment rate constants can be determined and the equilibrium constant evaluated as $K_{eq} = k_a/k_d$. Values of K_{eq} obtained this way are shown by the lighter points in Figure 2. Where there is overlap with values of K_{eq} determined by mobility measurements, there is reasonable agreement. The concentrations of butadiene used were from 0.18 to 0.71 μm; K_{eq} is independent of concentration in this range. The effect of pressure is large; at low temperatures K_{eq} increases by a factor of about 50 in 500 bar. There is an
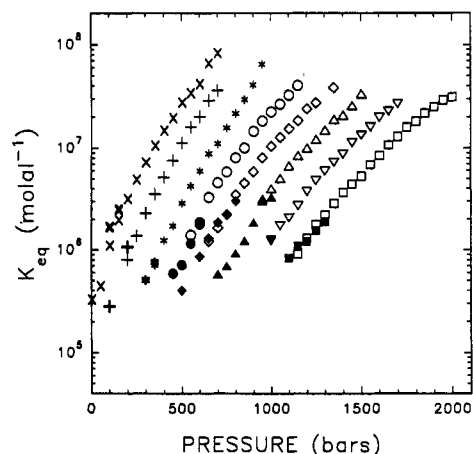

Figure 2. K_{eq} for electron attachment to butadiene versus pressure at various temperatures (°C): X, –7; +, 2, *, 12; O, 23; ◇, 30; △, 41; ▽, 50; □, 60.

TABLE 1: Tait Parameters

$T/°C$	density/(g/cm³)	Tait parameter	
		A	B/bar
–7	0.683	0.0894	698
2	0.675	0.0904	657
12	0.666	0.0914	613
23	0.657	0.0923	565
30	0.650	0.0928	536
41	0.640	0.0934	492
50	0.631	0.0938	456
60	0.622	0.0942	419

TABLE 2: Electron Drift Mobilities in Hexane at 0.5 °C

pressure/ bar	mobility/ (cm²/(V s))	$V_{tr}{}^a$/ (cm³/mol)	pressure/ bar	mobility/ (cm²/(V s))	$V_{tr}{}^a$/ (cm³/mol)
1	0.0387		1750	0.0200	–5.9
250	0.0338	–11.0	2000	0.0189	–5.0
500	0.0304	–10.0	2250	0.0179	–5.4
750	0.0271	–8.9	2500	0.0168	–5.4
1000	0.0250	–7.7	2750	0.0159	–4.6
1250	0.0229	–6.9	3000	0.0152	
1500	0.0215	–6.2			

^{a} Volume change on trapping of the electron.

upper pressure above which the detachment rate is too small; in other words the "equilibrium current" is too close to the base line to measure.

At high pressures attachment rates can still be measured. Rate constants for attachment to butadiene throughout the temperature and pressure range are shown in Figure 3. Only at –7 °C could a value of k_a be obtained at 1 bar. At low temperatures k_a goes through a maximum with increasing pressure; above a certain pressure k_a decreases with increasing pressure at each temperature studied.

Individual rate constants for autodetachment, k_d, are available only over a finite pressure range at each temperature. These rates are shown in Figure 4. At 1 bar and –7 °C $k_d = 5 \times 10^5$ s⁻¹.

Attachment Rate Constants. The rate constant of electron attachment to 1,3-butadiene in n-hexane increases with increasing temperature and decreases with increasing pressure at higher pressures. The rate constant is about 50% of that observed for electron attachment to other small molecules like CCl_4 and N_2O in this solvent.[15] The temperature and pressure dependences of the rate are similar to the behavior of the rate of attachment of electrons to CO_2 in 2-methylbutane.[3] The electron mobility in hexane also decreases with pressure (see Table 2 and ref 14) and increases with temperature, suggesting the rate of attachment to butadiene may be diffusion limited. To test this hypothesis, values of k_a/μ(hx), where k_a is in molar units here, were calculated
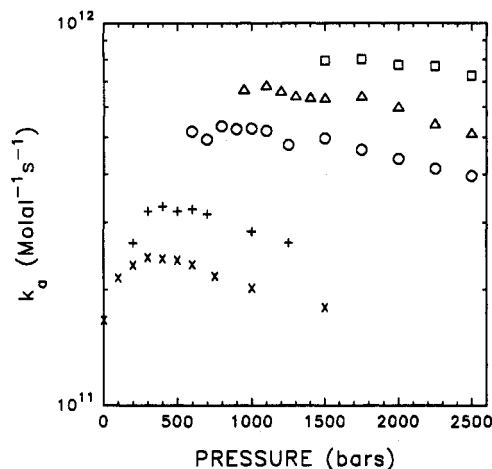
Figure 3. Rate constant for attachment to 1,3-butadiene versus pressure at various temperatures. Points as denoted in Figure 2.
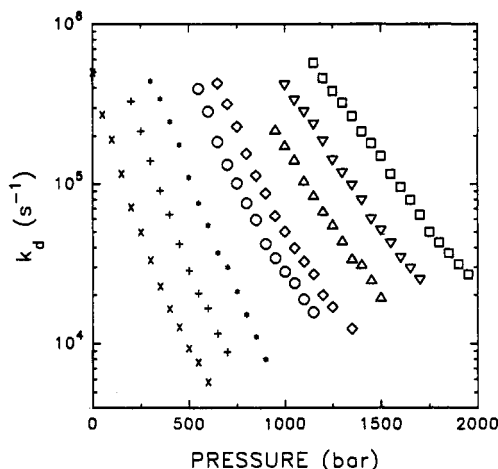

Figure 4. Rate constant for detachment from butadiene anion versus pressure at various temperatures. Points as denoted in Figure 2.

TABLE 3: Detachment Rates

pressure/ bar	ΔH^*/ (kcal/mol)	k_d(298 K)/s^{-1}	ΔS^*/ (cal/(K mol))	ΔV_d^*/ (cm^3/mol)
300	20.0	2.3×10^6	37.6	165
400	21.0	1.3×10^6	40.0	182
750	22.3	1.25×10^5	39.7	157
1000	20.0	2.9×10^4	29.1	126
1250	20.3	9.3×10^3	27.7	112
1500	21.8	2.8×10^3	30.5	111

under various conditions. At 23 °C this ratio is constant at 1.6 $\times 10^{13}$ V M^{-1} cm^{-2} above 700 bar. This corresponds to a radius $R_a = 8.3$ Å in the equation k_a/μ(hx) $= 4\pi R_a k_B T N_a/1000e$. Values for this ratio at other temperatures were similar: for example at -7 and $+60$ °C k_a/μ(hx) $= 1.32 \times 10^{13}$ and 1.40×10^{13} V M^{-1} cm^{-2}, respectively. The average radius derived from the attachment rate constants is 7.6 ± 0.7 Å.

Detachment Rate Constants. The data for detachment from the butadiene anion were analyzed to obtain activation volumes for detachment ($\Delta \bar{V}_d^*$) by fitting rate constant data (Figure 4) to a linear regression on pressure. The activation volumes are shown in the last column of Table 3. These values are comparable in magnitude, but opposite in sign, to the overall reaction volumes (see below). By extrapolation of the 23 °C data it can be inferred that $k_d \geq 1.0 \times 10^7$ s^{-1} at 1 bar. At higher temperatures the extrapolated values are even larger. Even if attachment occurs at 1 bar, because of rapid detachment the reaction is not observed.

To obtain activation energies and entropies for detachment, the rate was assumed to follow a transition-state equation of the form

$$k_d = (k_B T/h) \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \quad (4)$$

The parameters were evaluated from plots of $\ln(k_d/T)$ versus $1/T$. The enthalpies of activation (see Table 3) are large; nevertheless the electron overcomes this barrier, which is on average 20.9 kcal/mol. The driving force for detachment is the large increase in entropy associated with detachment, as was also noted for detachment from aromatic anions.[16] The activation entropies are given in Table 3.

Reaction Volumes. Reaction volumes for electron attachment to 1,3-butadiene were calculated from the data in Figure 2; that is, using the relation,

$$\Delta \bar{V}(1) = -RT \, \partial(\ln K_{eq})/\partial P \quad (5)$$

The middle ranges of each data set were used which gives an average volume at each temperature at the pressure indicated since $\ln K_{eq}$ plots are slightly curved. Points at the high and low end of each pressure range have larger experimental errors and were not used. The resulting volumes are given in Table 4, column 6. The volumes range from -181 cm^3/mol at 400 bar to -122 cm^3/mol at 1500 bar; the statistical errors in these values are ±6 cm^3.

The change in the partial molar volume in reaction 1 is given by $\bar{V}(B^-) - \bar{V}(B) - \bar{V}(e^-_s)$. $\bar{V}(B^-) - \bar{V}(B)$ is the volume of electrostriction around the ion assuming no intrinsic volume change. The last term is very nearly equal to the volume change on going from a quasi-free electron to a solvated electron, as the quasi-free electron can have little effect on the solvent and still have such a large mobility. Therefore,

$$\Delta \bar{V}(1) = \Delta \bar{V}_{el} - \Delta \bar{V}(e^-_s) \quad (6)$$

The volume of the electron in hexane was determined earlier[17] from a study of the effect of pressure on the electron mobility (μ). The two state model was assumed; that is, the free energy for the reaction: $e^-_{qf} \rightleftharpoons e^-_s$ is

$$\Delta G° = -RT \ln(\mu_{qf}/\mu) \quad (7)$$

The volume change associated with trapping of the electron, V_{tr}, was calculated from $\partial(\Delta G°)/\partial P$. The quasi-free mobility (μ_{qf})

TABLE 4: Reaction Volumes[a]

temperature/°C	pressure/bar	d_0/(g/cm^3)	ϵ_0	χ_0/(10^5 bar^{-1})	$\Delta V(1)$/(cm^3/mol) exptl	ΔV(el)/(cm^3/mol) eq 8	ΔV(el)/(cm^3/mol) glass	$\Delta V(1)$/(cm^2/mol) calc
-7	300	0.705	1.972	9.3	-170	-88	-209	-198
2	400	0.705	1.972	8.9	-181	-85	-203	-193
12	600	0.711	1.982	8.1	-170	-76	-188	-178
23	750	0.712	1.985	7.6	-154	-72	-179	-170
30	750	0.708	1.976	7.8	-166	-74	-179	-168
41	1000	0.713	1.987	6.9	-159	-65	-165	-156
50	1250	0.720	2.001	6.2	-128	-59	-152	-144
60	1500	0.725	2.009		-122		-141	-134

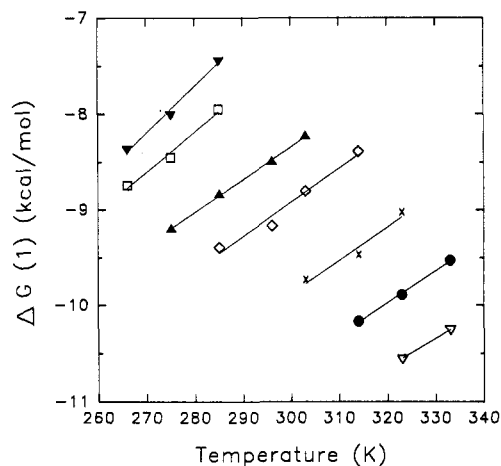[a] $r = 2.44$ Å assumed; molar polarization $= 29.9$ cm^3.

Figure 5. Free energy for reaction 1 plotted versus temperature (K) at various pressures (bar): ▼, 300; □, 400; ▲, 600; ◊, 750; X, 1000 bar; ●, 1250; ▽, 1500.

was assumed to be independent of pressure. A similar analysis of the mobility data in Table 2 leads to the values of $V(e^-_s)$ shown for 0.5 °C. The values decrease in magnitude with increasing pressure and as shown earlier[18] increase with temperature. For the conditions of T and P given in Table 4 the volumes range from −11 to −7 cm³/mol.

The Drude–Nernst equation for the volume of electrostriction of the solvent around an ion, V_{el}, can be written as[4,18]

$$\Delta \bar{V}_{el} = -(e^2 d\chi/2r\epsilon^2)\, \partial\epsilon/\partial d \quad (8)$$

where χ and ϵ refer to the compressibility and dielectric constant of hexane at T and P. This model assumes a sphere with unit charge immersed in a continuum with constant dielectric constant. To calculate ΔV_{el}, the parameters were evaluated using the Tait equation (eq 2); the derivative of ϵ was obtained from the Clausius–Mosotti equation and a molar polarization of 29.9 cm³ for n-hexane. The resulting volumes of electrostriction for the corresponding temperatures and pressures, given in Table 4 in the seventh column, are about half of the experimental values.

Electrostriction volumes for butadiene⁻ were also calculated as in ref 4, which gave good agreement for electrostriction volumes around CO_2^-. Nine hexane molecules will fit around this ion, one more than around CO_2. The electrostriction volumes for butadiene⁻ are given in Table 4 in the column labeled glass. The calculated volume changes for (1), final column, are about 11 ± 9 cm³/mol more negative than the observed values, but overall the agreement is very good and certainly within the error of the calculation.

Other Thermodynamic Parameters. The equilibrium constant for the attachment of electrons to butadiene decreases rapidly with increasing temperature. Thus the free energy of reaction increases rapidly with temperature (see Figure 5), and since $\Delta G°(1) = \Delta H°(1) - T\Delta S°(1)$, the entropy of reaction must be large and negative. Values of the enthalpy and entropy of this reaction, shown in Table 5, were evaluated at several pressures from plots of $\Delta G°(1)$ vs T. The enthalpy of reaction is fairly independent of pressure, as was found for electron attachment to CO_2.[3]

Free Energy. The free energies of reaction at 298 K, calculated at each pressure, were plotted versus density of n-hexane and extrapolated to the density at 1 bar. Such plots are linear, as was shown for the reaction of electrons with CO_2.[3] The extrapolated value of $\Delta G°_{298}$ at 1 bar is −4.84 kcal/mol. The free energy of reaction decreases with increasing pressure to −10.7 kcal/mol at 1250 bar. The value of $\Delta G°_{298}(1)$ at 1 bar corresponds to an equilibrium constant of $3.5 \times 10^3\ m^{-1}$ for reaction 1. This value, combined with the earlier estimate of k_d, indicates the attachment rate, k_a, is $\geq 3.5 \times 10^{10}\ m^{-1}\ s^{-1}$ at 1 bar.

The free energy change of reaction 1 can be related to the gas-phase value by

$$\Delta G°(1)_{(s)} = \Delta G°(1)_{(g)} + \Delta G_{sol}(B^-) - \Delta G_{sol}(B) - \Delta G_{sol}(e^-) \quad (9)$$

where $\Delta G°_{sol}(B^-) - \Delta G°_{sol}(B)$ is the free energy of polarization, ΔG_{el}. The electron affinity of butadiene is negative but has been estimated to be −14.3 kcal/mol from the position of an electron scattering resonance.[5] The entropy difference between the butadiene negative ion and butadiene is assumed to be just that due to the multiplicity, $R \ln 2$, and the entropy of the electron is 5 cal/(mol·deg), so $\Delta G°(1)_{(g)}$ is $14.3 + 0.0036T$, which is 15.3 kcal/mol at 2 °C. Since the energy required to transfer an electron from the gas to the quasi-free state in liquid hexane is 0.0 eV,[20] $\Delta G°_{sol}(e^-)$ could be estimated from the electron mobility by eq 7 if the quasi-free mobility were known. It is reasonable to assume that it is 30 cm²/(V s) within a factor of about 3, so at 2 °C and 500 bar, $\Delta G°_{sol}(e^-)$ is about −3.8 ± 0.6 kcal/mol. Thus, an experimental free energy of polarization can be estimated as $\Delta G°(1)_{(s)} - 19.1$. Since $\Delta G°(1) = -8.88$ kcal/mol at 2 °C and 500 bar, $\Delta G_{el} = -28$ kcal/mol kcal/mol.

At 2 °C and 500 bar the free energy of polarization calculated for the model with a glass phase (corrected for the free energy required to form the glass) is −33.8 kcal/mol. The free energy calculated by the simple Born equation is −33.7 kcal/mol. It is evident that the calculated free energies are nearly independent of the model used to calculate them but that the calculated value is about 6 kcal/mol more negative than the experimental value. A similar result is obtained at other temperatures and pressures (±1 kcal/mol). There are two obvious reasons for the 6 kcal/mol difference. First, the calculated value is unlikely to be more accurate. The ion radius was taken as a hard core radius, 2.44 Å, which is appropriate for volume calculations because all volume outside that radius is compressible. It is commonly assumed that for free energy calculations the radius should be larger than this, to take into account the finite size of the induced dipoles. If r_0 is taken as 3.0 instead of 2.44 Å, then almost complete agreement is found. On the other hand, the reported electron affinity of butadiene may not refer to the same structure as is assumed for the liquid. It is assumed that in the liquid phase the ion radius is the same as the butadiene radius, but the gas-phase electron scattering resonance may refer to some larger radius.

Entropy. The entropy change for electron attachment to butadiene (slopes of lines in Figure 5) is large and approximately the same in magnitude as the entropy of activation for detachment (see above) but opposite in sign. The entropies are comparable to values reported for electron attachment to styrene, −44.5 cal/(deg mol),[16] and difluorobenzene, −30.9 cal/(deg mol),[19] in

TABLE 5: Thermodynamic Parameters

pressure/bar	temperature/°C	$\Delta G°(1)$/(kcal/mol) exptl	$\Delta H(1)$/(kcal/mol)	$\Delta S(1)$/(cal/(K mol))	$\Delta S°$ calcd	α_T/χ/(cal/(deg cm³))
300	2	−8.00	−21.4	−48.8	−48.6	0.262
400	2	−8.45	−19.9	−42.0	−47.5	0.271
600	12	−8.84	−18.6	−34.1	−46.6	0.274
750	23	−9.16	−19.6	−35.5	−45.8	0.279
1000	41	−9.47	−20.3	−34.9	−44.2	0.289
1250	50	−9.89	−20.8	−33.9	−41.0	0.304

hexane. Earlier it was concluded[16] that the magnitude of the entropy change decreases as the size of the anion increases. For comparison it should be noted that the entropy for attachment to molecules in the gas phase is small, less than 3 cal/(deg mol) in absolute value.[21]

The entropy of solvation of ions in hydrocarbons is closely related to the volume of electrostriction. This is most easily seen by consideration of the entropy expression which can be derived from the Born equation

$$\Delta S_{el} = -(e^2 d\alpha_T/2r\epsilon^2)\ \partial\epsilon/\partial d$$

and the Drude–Nernst equation, eq 8. These lead to

$$\Delta S_{el}/\Delta \bar{V} = \alpha_T/\chi \tag{10}$$

which is a particular application of the more general equation $(\partial S/\partial V)_T = \alpha_T/\chi$.[22] This equation is particularly useful when there is no source of order other than a density variation.

The ratio α_T/χ varies with temperature and pressure (or density) and so will vary with the distance from the ion. The magnitude of this variation can be estimated by computing the entropy and volume of electrostriction for models which specifically include the effect of density variation on the free energy of electrostriction. The entropy of electrostriction was computed from the slopes of calculated free energies vs temperature, $\Delta S^\circ = (\Delta G^\circ/\Delta T)_P$. The calculation for the case in which no glass phase was considered led to $\Delta S^\circ/\Delta \bar{V} = 1.1\alpha_T/\chi$. The model with the glass phase gave $\Delta S^\circ/\Delta \bar{V} = 1.2\alpha_T/\chi$, but this large value arises from one of the simplifying assumptions made in the development: that the density of the glass phase at low pressure would be 1.2 times that of the liquid at all temperatures, while the compressibility of the glass is one-third as large as that for the liquid. This means that α_T/χ is assumed to be three times larger in the glass phase than in the liquid phase, whereas near a phase transition the ratio should be nearly the same in the two phases. If the assumption is made that α_T/χ is the same in both phases, *i.e.* each is one-third as large in the glass as in the solid, then it is found that $\Delta S^\circ/\Delta \bar{V}$ is about 5% smaller than α_T/χ. It is clear that the exact value depends on knowledge of the glassy state, which is not available.

A simple, less model-dependent approach will be used here. The portion of the entropy change of reaction 1 which is due to electrostriction will be computed from eq 10 using experimental values of the partial molar volume change (smoothed to allow interpolation) and values of α_T/χ computed for the bulk liquid from the Tait equation. The total entropy change of reaction 1 is

$$\Delta S^\circ(1) = S^\circ(B^-) - S^\circ(B) - S^\circ(e^-_s) \tag{11}$$

If it is assumed that there is little change in B itself upon adding an electron other than the change in multiplicity, then

$$S^\circ(B^-) - S^\circ(B) = \Delta S_{el}(B^-) + R \ln 2$$

and for the electron,

$$S^\circ(e^-_s) = \Delta S_{el}(e^-_s) + S^\circ(e^-_{qf})$$

and since the net electrostriction entropy is $\Delta S^\circ_{el}(B^-) - \Delta S^\circ_{el}(e^-_s)$, eq 11 becomes

$$\Delta S^\circ(1) = (\alpha_T/\chi)\Delta\bar{V}(1) + R \ln 2 - S^\circ(e^-_{qf}) \tag{12}$$

The results are given in Table 5. It may be seen that the observed entropy change is 7 ± 4 cal/(deg mol) more positive than $(\alpha_T/\chi)\Delta\bar{V}$. If eq 12 is taken literally, then $S^\circ(e^-_{qf}) = -5 \pm 4$ cal/(deg mol), which is about that expected from the gas-phase value (+5 cal/(deg mol)) when the changes in standard state to 1 m (-5.5 cal/(deg mol)) and the free volume available to the electron (about 30% or -2.4 cal/(deg mol)) are considered. On the other hand, while this consistency is gratifying, it relies heavily on the accuracy of eq 10. It is perhaps better to turn the conclusion around and say that the correlation between the entropy change and the volume change of reaction 1 indicates that the presence of the ion in the hydrocarbon solvent produces no significant change in organization of the liquid other than that due to density changes.

Conclusions

The electrostatic model of ions in nonpolar liquids which includes one molecular layer of glass explains the large volume changes observed for reaction 1. Because it explains the volume changes, it also explains the entropy change, but it is far simpler and just as accurate to derive the entropy of electrostriction from the volume change through the factor α_T/χ. The free energy calculated for ion solvation is almost the same whether a model involving a glass layer is used or not. In fact the simple Born expression is as accurate as any other method for calculating free energies.

References and Notes

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