

Thermodynamics of Electron Attachment to Pyrimidine and Styrene in Supercritical Ethane

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The reaction of excess electrons with pyrimidine and styrene was studied in supercritical ethane. The equilibrium constant for attachment was large when the solute was pyrimidine and small for styrene, although their electron affinities are comparable. At pressures above 100 bar, the rate constant for electron attachment to pyrimidine (k_a) was time resolved using the short pulse of the laser-electron accelerator facility (LEAF). The rate constant, k_a , is large and nearly independent of pressure and temperature; thus, the volume of activation is close to zero. At lower pressures, the equilibrium constants for this reaction were derived from the changes in the mobility of excess electrons. The free energy is a function of the polarization energy, which was evaluated with a compressible continuum model. The small equilibrium constant in the case of styrene is attributed to a smaller polarization energy. Values of ΔV_r , obtained from changes of ΔG_r with pressure, range from -9.0 to -0.4 L/mol. The observed volume changes are compared to electrostriction volumes calculated by the model. Electron attachment occurs with a large decrease in entropy associated with clustering of ethane molecules around the ion formed. Observed values of ΔS_r are comparable to expected values calculated from $\Delta S_r = (\alpha/\chi_T)\Delta V_r$.

Introduction

Solvated electrons in aqueous solution readily react with aromatic hydrocarbons such as styrene and substituted pyrimidines, like uracil and thymine.¹ Electrons in alkane solvents also react fast with these solutes. The rate constant for attachment to pyrimidine in 2,2,4-trimethylpentane is $3 \times 10^{13} \text{ m}^{-1} \text{ s}^{-1}$ at 293 K,² and that for attachment to styrene in the same solvent is $8.3 \times 10^{12} \text{ m}^{-1} \text{ s}^{-1}$ at 298 K.³ Furthermore, electron attachment is reversible in both cases; that is, the anion formed readily gives the electron back to the hydrocarbon solvent. The equilibrium constants have been measured in 2,2,4-trimethylpentane, and ΔG_r is -0.70 eV for attachment to pyrimidine at 298 K and -0.48 eV for attachment to styrene. These reactions occur with a large decrease in entropy that is associated with the change in solvent density around the ions.

Here, we report the first study of the reactivity of aromatic compounds, styrene and pyrimidine, with excess electrons in supercritical ethane. For pyrimidine, the reaction is



From equilibrium measurements, we obtain not only the free energy of reaction but also the volume change, ΔV_r , from changes in ΔG_r with pressure. As was shown in a study of electron attachment to CO_2 ,⁴ the change in volume is largely due to the large negative partial molar volume of ions in supercritical fluids because of extensive clustering of solvent molecules around the anion. Because pyrimidine is larger than

CO_2 , the present results provide a test of the effect of ion radius. Earlier it was predicted that the partial molar volume of ions in supercritical fluids is largely independent of ion radius.⁴ Because styrene has an electron affinity of -0.25 eV,⁵ which is comparable to that for pyrimidine,⁶ -0.33 eV, we had expected it to react similarly.

Experimental Section

Samples of ethane (MG Industries, scientific grade) were purified by passage through a Pall filter (GLPV2C2H6VMM4). The quantity of ethane needed was then measured, by liquid volume at 195 K, and condensed into the pressure cell, which is described elsewhere.⁴ The lifetime and mobility of excess electrons in the purified ethane was first checked under the various experimental conditions. Generally, the electron lifetime was on the order of $10 \mu\text{s}$. The pyrimidine (Aldrich 99%) and styrene (Aldrich 99+%) were degassed at 195 K several times prior to use. GC/MS analysis showed the pyrimidine to be free of electron-attaching impurities, and no impurities were found in the styrene. Solutions of these solutes in ethane were prepared by measuring a known pressure of the vapor in a calibrated volume, maintained at 306 K, and then condensing the sample into the conductivity cell, cooled to 77 K.

The results reported here were obtained by pulse conductivity in one of two ways. Individual rate constants for electron attachment (k_a) and detachment (k_d) were determined using the fast X-ray pulse of the LEAF facility. The currents from the

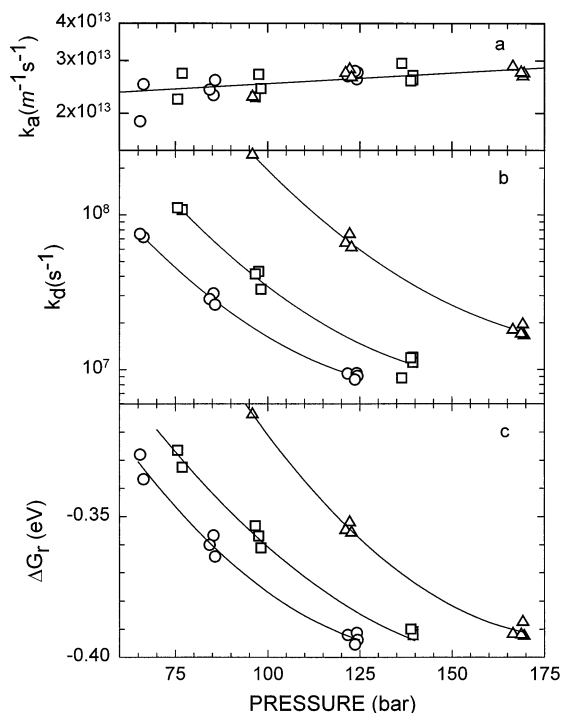


Figure 1. Data obtained at LEAF for reaction 1 in supercritical ethane. (a) Rate constant for electron attachment to pyrimidine versus pressure at (○) 33, (□) 37, and (△) 45 °C. (b) Rate constant for electron detachment from pyrimidine⁻ versus pressure and temperature. Symbols as in part a. (c) Free energy for reaction 1 versus pressure and temperature. Symbols as in part a. Solid lines are quadratic fits.

cell were amplified using an EG&G preamplifier (model 5185) and recorded using a 1.5 GHz LeCroy 9362 oscilloscope. Electron mobilities, which lead to equilibrium constants for electron attachment, were determined with the X-ray pulse of the 2 MeV van de Graaff. During measurements, the sample temperature was controlled to 0.05 K using an Omega (CN77530-C2) temperature controller.

Density and compressibility values for ethane ($T_c = 32.3$ °C and $P_c = 48.84$ bar) were calculated using an equation of state developed by Younglove.⁷ Volumes of electrostriction and energies of polarization in SC ethane were calculated according to a compressible continuum model described elsewhere.⁴

Results

Pyrimidine. Rate constants for electron attachment and detachment were determined using the short pulse of LEAF. Typical current traces exhibited a fast decay followed by an equilibrium current, the height of which depended on conditions. Analysis of such decays, by the method outlined earlier,⁴ led to values of k_a and k_d for reaction 1. The rate constants are independent of the concentration of pyrimidine, which was varied from 0.15 to 1 μM . As shown in Figure 1a, the attachment rate constant, k_a , is large and is nearly constant, changing little with pressure and temperature. In contrast, the detachment rate constant, k_d (Figure 1b), increases with increasing temperature and decreases with increasing pressure. Values of the free energy for attachment to pyrimidine, obtained using the equation

$$\Delta G_r = -RT \ln(k_a/k_d) \quad (2)$$

are shown in Figure 1c as a function of pressure at three temperatures, 306, 310, and 318 K.

At lower pressures, the detachment rate becomes too fast, precluding analysis in terms of individual rate constants. Here,

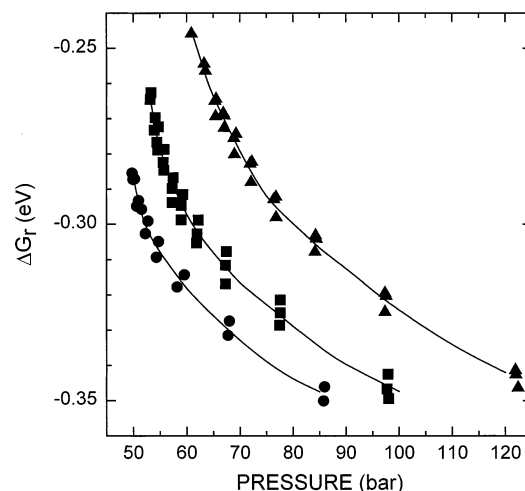


Figure 2. Free energy of reaction for attachment to pyrimidine versus pressure at (●) 33, (■) 37, and (▲) 45 °C. Data are from mobility measurements. Solid lines are polynomial fits.

TABLE 1

T (K)	P (bar)	K_4 (m^{-1})	ΔG_r (eV)
306	82.5	2600	-0.21 ± 0.02
310	94.5	2000	-0.20 ± 0.02

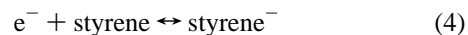
the equilibrium was studied by measuring changes in the mobility of excess electrons. The mobility decreased in proportion to the concentration (between 6 and 17 μM) of pyrimidine present. The electron mobility in supercritical ethane is high, generally between 20 and 70 $\text{cm}^2/(\text{V s})$ under these conditions. The effect on the mobility depends on pressure. At 310 K, the presence of 17 μM pyrimidine reduces the mobility from 24.3 to 3.4 $\text{cm}^2/(\text{V s})$ at 98 bar. The same concentration reduces the mobility from 67.9 to 46.9 $\text{cm}^2/(\text{V s})$ at 52 bar.

The pyrimidine acts as a temporary trap for electrons. Values of the equilibrium constant, K_1 , were derived from the observed mobilities using eq 3, where μ_0 is the electron mobility in pure ethane under the same conditions.

$$\mu = \mu_0(1 + K_1[\text{Pyr}])^{-1} \quad (3)$$

In this way, values of the free energy of reaction were obtained, and they are shown in Figure 2. At all three temperatures, ΔG_r decreases sharply as the pressure increases.

Styrene. Styrene was found to be much less reactive toward electrons than pyrimidine. Consequently large concentrations (from 8 to 73 μM) of styrene were used. At the highest concentration, reductions in mobility of 10–20% were obtained from which values of the equilibrium constant for reaction 4 were estimated. The use of large quantities of styrene caused a



reduction in the lifetime of the electron to as low as 2 μs due to the presence of an unidentified impurity. This required drift time measurements at higher voltages, and since the mobility is slightly field dependent in ethane, the results shown in Table 1 are upper limits for the values of K_4 and the free energies have a large uncertainty.

An attempt made to detect this reaction at LEAF gave negative results. However, if the rate constant for attachment is $\sim 10^{13} \text{ m}^{-1} \text{ s}^{-1}$ like pyrimidine, then based on the results in Table 1 the lifetime of the styrene anion would be of the order of nanoseconds, making observation impossible this way.

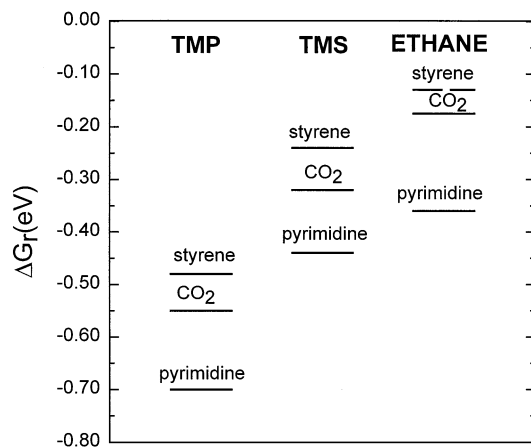


Figure 3. Diagram of the free energy (indicated by horizontal lines) for electron attachment to various solute molecules in TMP and TMS at 298 K and 1 bar and in supercritical ethane at 310 K and 100 bar. Data are from this work and refs 2, 3, and 8.

Discussion

Energetics. In supercritical ethane, electron reaction with pyrimidine is much more favorable than reaction with CO₂. This is in part due to the large value of k_a that is 2 orders of magnitude larger than k_a for CO₂. The rate constants for electron detachment from the corresponding anions are comparable. Thus, the free energies for reaction 1 are lower than the free energies for the corresponding reaction with CO₂ in ethane. This is illustrated for a pressure of 100 bar and a temperature of 310 K in Figure 3. This figure also shows values of the free energies of electron attachment reactions to pyrimidine and styrene as well as CO₂ in two nonpolar liquids, tetramethylsilane (TMS) and 2,2,4-trimethylpentane (TMP). The reactions are most favorable in TMP; the free energy of reaction is shifted higher in TMS, and the shift is a nearly constant value of 0.24 eV for each of these reactions. The free energies shift even higher in supercritical ethane. The shifts from TMP to ethane, for the conditions stated, are 0.34 eV for pyrimidine and 0.38 eV for CO₂. It would be reasonable, based on this correlation, to expect a similar shift for styrene, which leads to a predicted free energy of -0.12 eV at 100 bar and 310 K for reaction 4, in fair agreement with the approximate value found. Thus, despite the similar electron affinities of styrene and pyrimidine, the free energies for attachment in solution are quite different. This difference is ascribed to the magnitude of the polarization energy of the negative ion in solution (see below).

As shown in the earlier study of electron attachment to CO₂, evaluation of the polarization energy of ions in supercritical ethane must take into account the extensive clustering around ions. To do this, we utilize a compressible continuum model.^{4,9} In this model, the electric field, $E(r)$, at a distance r from the ion gives rise to a pressure P .

$$P = P_{\infty} + (\epsilon(r) - 1)\epsilon_0[E(r)]^2/2 - \int_{\infty}^r \epsilon_0[E(r)]^2/2 \left(\frac{d\epsilon(r)}{dr} \right) dr \quad (5)$$

Where $\epsilon(r)$ is the dielectric constant as a function of r , P_{∞} is the background pressure, and ϵ_0 is the permittivity of a vacuum. The third term gives a negligibly small contribution and was ignored previously. Although it was checked that the calculations made earlier^{4,9} agree within 1% with those obtained by taking this third term into account, we used the analytically accurate

TABLE 2: Free Energy Changes for $e^- + \text{Pyrimidine} \leftrightarrow \text{Pyrimidine}^-$

P (bar)	ΔG_r (eV)	V_0 (eV)	$E(P_{cc}^-)$ (eV)	$\Delta G_r(\text{gas}) - E_t$ (eV)
$T = 306 \text{ K}$				
50	-0.287	-0.174	-0.932	0.47
60	-0.318	-0.176	-0.968	0.47
70	-0.333	-0.172	-0.982	0.48
85	-0.359	-0.164	-0.997	0.47
130	-0.399	-0.151	-1.025	0.47
$T = 310 \text{ K}$				
55	-0.278	-0.172	-0.919	0.47
60	-0.297	-0.179	-0.944	0.47
70	-0.317	-0.176	-0.965	0.47
85	-0.344	-0.17	-0.983	0.47
130	-0.386	-0.156	-1.015	0.47
$T = 318 \text{ K}$				
70	-0.279	-0.178	-0.922	0.46
85	-0.307	-0.177	-0.953	0.47
100	-0.324	-0.174	-0.971	0.47
130	-0.364	-0.165	-0.994	0.46
160	-0.387	-0.156	-1.010	0.47

form here. The density $\rho(r)$ at each point is calculated from P using the equation of state (EOS).⁷ Several iterations are required to obtain a constant $\rho(r)$.

In the compressible continuum model proposed by Luo and Tucker,¹⁰ the local density profile $\rho(r)$ is calculated in a similar but slightly different way. We determined $\rho(r)$ so that $E(r)$, $P(r)$, and $\epsilon(r)$ all become consistent. They used an equation thermodynamically derived by Frank,¹¹ which relates $\rho(r)$ and $E(r)$ (their eq 4) and made $\rho(r)$, $E(r)$, and $\epsilon(r)$ consistent without referring to $P(r)$ explicitly. However, both methods are equivalent. In fact, Frank's eq 13, on which their eq 4 is based together with other thermodynamical relations, is equivalent to our (A-1). Their eq 4 corresponds to our eq 5 and the equation of state.

The polarization energy is then calculated from

$$E(P^-) = 2\pi \int_{r_{\text{ion}}}^{\infty} \epsilon_0 \epsilon(r) [E(r)]^2 r^2 dr - e^2/8\pi\epsilon_0 r_{\text{ion}} \quad (6)$$

where r_{ion} is the radius of the ion. For pyrimidine, r_{ion} is estimated to be 0.257 nm from Bondi's volume increments.¹² A small energy of compression is added to $E(P^-)$ to give the total polarization energy in this model, $E(P_{cc}^-)$.

Values of the polarization energy calculated this way are shown in Table 2 as a function of pressure at each of the three temperatures studied. The stability of the ion increases with pressure. This change in $E(P_{cc}^-)$ accounts for most of the change in the free energy of reaction, ΔG_r , which changes from about -0.28 eV at the lowest pressures studied to about -0.4 eV at the highest.

The free energy of reaction depends as well on the energy of the electron in the fluid, $V_0 + E_t$, according to the equation

$$\Delta G_r = \Delta G_g + E(P_{cc}^-) - (V_0 + E_t) \quad (7)$$

The free energy of electron attachment to pyrimidine in the gas phase, ΔG_g , can be calculated from the data using eq 7. Values of V_0 for ethane have been measured as a function of density,¹³ and E_t is assumed, as before,⁴ to be small. Values of $\Delta G_g - E_t$ were calculated and, as shown in the final column of Table 2, are quite constant, the average value being 0.47 ± 0.01 eV. This value corresponds to an electron affinity of pyrimidine of -0.52 eV, which differs from the reported value of -0.33 eV. A similar difference was found for the reaction of electrons with CO₂ in supercritical ethane.⁴

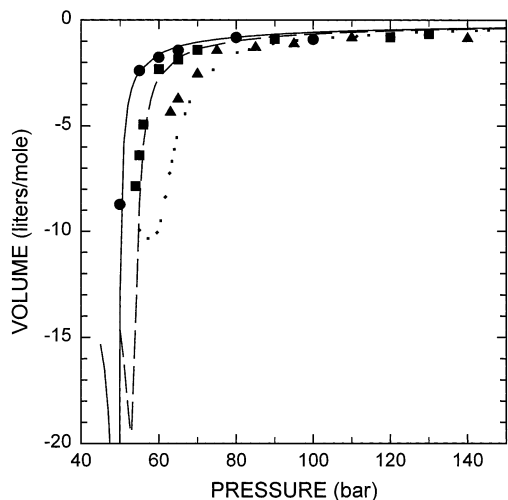


Figure 4. Volume changes for electron attachment to pyrimidine in SC ethane. Points are experimental values of ΔV_r at (●) 33, (■) 37, and (▲) 45 °C. Lines calculated by compressible continuum model: (solid line) 33 °C; (dashed line) 37 °C; (dotted line) 45 °C.

Calculations for styrene ($r_{\text{ion}} = 0.296 \text{ nm}$)¹² indicate the magnitude of the polarization term is 0.12 eV less than that for pyrimidine. This term accounts in large part for the smaller equilibrium constant for eq 4.

Volume Changes. There is essentially no change in the rate of attachment of electrons to pyrimidine, k_a , either with temperature or pressure, indicating the activation energy as well as the activation volume, ΔV_a^\ddagger , are both close to zero. The latter is evaluated from

$$\Delta V_a^\ddagger = -RT \ln k_a/dP \quad (8)$$

The activation volumes for detachment, ΔV_d^\ddagger , evaluated by an equation analogous to eq 8, are equal in magnitude, but opposite in sign, to the reaction volumes discussed below. The values of ΔV_d^\ddagger decrease with increasing pressure. These results contrast with those found for electron attachment to CO_2 in ethane where ΔV_a^\ddagger is approximately 50% of ΔV_r . However, the results are similar to those obtained for attachment to pyrimidine in liquid TMS^2 in that ΔV_a^\ddagger is near zero. It may be concluded that for electron attachment to pyrimidine the activated state is close to the reactants.

The overall volume changes in reaction 1 are evaluated from the slopes of the lines in Figures 1c and 2 using the equation

$$\Delta V_r = d\Delta G_r/dP \quad (9)$$

The points in Figure 4 show the values of ΔV_r obtained this way. The values decrease with decreasing pressure and the minimum values observed are -8.7, -6.4, and -4.4 L/mol at 33, 37, and 45 °C, respectively. Even lower values are expected at lower pressures, but this could not be verified because reaction 1 is too unfavorable there.

The observed volume changes are associated with electrostriction (clustering) of ethane molecules around pyrimidine anions. Actually ΔV_r is the difference between the partial molar volume of products and reactants,

$$\Delta V_r = \bar{V}(\text{pyr}^-) - \bar{V}(\text{pyr}) - \bar{V}(\text{e}^-) \quad (10a)$$

but $\bar{V}(\text{e}^-)$ is presumed to be small because the electron is quasi-free, as evidenced by the high mobility.⁴ Thus, the volume

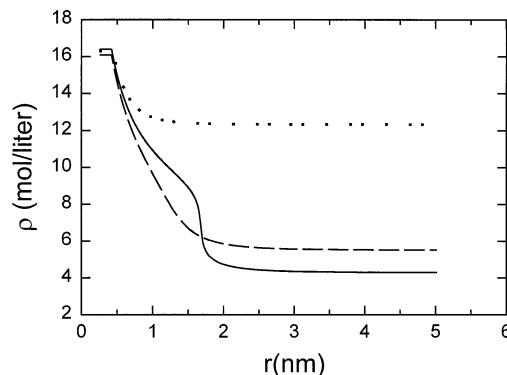


Figure 5. Density distribution around a pyrimidine⁻ ion as a function of distance: solid line at 306 K and 48 bar; dashed line at 318 K and 59 bar; dotted line at 310 K and 120 bar.

changes are given by the difference

$$\Delta \bar{V}_r = \bar{V}(\text{pyr}^-) - \bar{V}(\text{pyr}) \quad (10b)$$

The partial molar volumes of neutral aromatic compounds in supercritical fluids are small and positive at high pressures but large and negative at pressures where the compressibility (χ_T) is a maximum.¹⁴ Data specifically for pyrimidine in ethane are not available. Some generalizations are possible based on earlier studies. The partial molar volume of a solute, $\bar{V}(s)$, in a supercritical fluid can be represented by an equation of the type¹⁵

$$\bar{V}(s) = a\chi_T + b \quad (11)$$

When b is taken as the molar volume of the solute and a is a negative term dependent on temperature, experimental data on partial molar volumes for various solutes can be represented qualitatively with eq 11.¹⁶ Thus, in general, $\bar{V}(s)$ is expected to be slightly positive at high pressures, where χ_T is small, and large and negative at pressures near the compressibility maximum.

The first and most important volume term in eq 10b is that due to electrostriction by the ion which was calculated using the compressible continuum model outlined above. This involves integrating the density of the ethane clustered around the ion,

$$V_{\text{el}} = 4\pi \int_{r_{\text{ion}}}^{\infty} [\rho(r) \int_{V_{\infty}}^{V(r)} dV] r^2 dr \quad (12)$$

The calculated density as a function of distance from the ion is shown for some conditions of pressure and temperature in Figure 5. A common feature of all these curves is the gradual decrease in density with distance. The curves indicate that there must be a full first shell of ethane molecules around the ion, while subsequent shells have vacancies, the number of which increase with distance from the ion. The enhanced density around the ion extends as far out as 1.7 nm. Calculated volumes of electrostriction, from eq 12, are shown by the lines in Figure 4 and are in fair agreement with observed values of ΔV_r , but at high pressure the points fall consistently below the calculated values. While at low pressures the points are above the calculated lines.

These deviations can be attributed to the $\bar{V}(\text{pyr})$ term in eq 10b. At high-pressure $\bar{V}(\text{pyr})$ is expected to be approximately equal to the molar volume of pyrimidine, which is 0.079 L/mol (see eq 11). This positive value of $\bar{V}(\text{pyr})$ contributes to the negative deviations observed at high pressure (Figure 4). At low pressures, the term containing the compressibility dominates, making $\bar{V}(\text{pyr})$ negative. A recent IR study confirmed

TABLE 3: Volume Changes (in L/mol) for $e^- + S \leftrightarrow S^-$

<i>P</i> (bar)	<i>S</i> = pyrimidine (<i>r</i> _{ion} = 0.257 nm)		<i>S</i> = CO ₂ (<i>r</i> _{ion} = 0.23 nm)	
	$\Delta V_r(\text{exptl})$	<i>V</i> _{el}	$\Delta V_r(\text{exptl})$	<i>V</i> _{el}
<i>T</i> = 306 K				
110	−0.70	−0.51	−0.88	−0.52
80	−0.82	−0.80	−1.06	−0.82
70	−1.29	−1.04	−1.12	−1.06
60	−1.76	−1.6	−2.24	−1.62
50	−8.71	−13.0	−9.4	−13.1
<i>T</i> = 310 K				
120	−0.80	−0.50	−0.87	−0.51
90	−0.90	−0.77	−1.07	−0.79
80	−1.19	−0.97	−1.26	−0.99
70	−1.41	−1.36	−1.95	−1.38
60	−2.31	−2.72	−3.03	−2.76
55	−6.4	−8.71	−9.7	−8.86

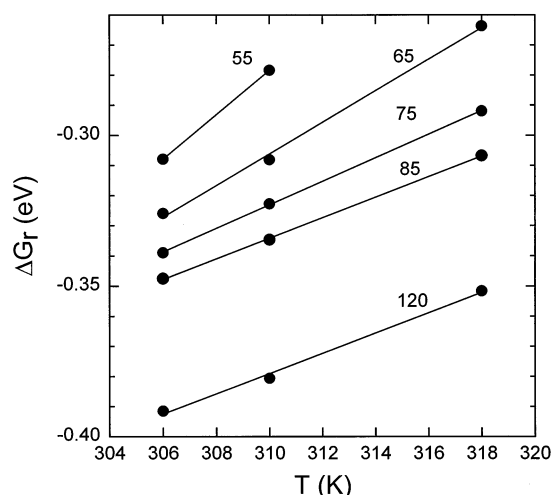
the existence of enhanced local density around aromatic compounds in a supercritical solvent (CO₂).¹⁷ Thus, experimental values of ΔV_r are expected to be above the predicted values of *V*_{el} at low pressures, as we observe at the lowest pressures studied (Figure 4). At even lower pressures, larger deviations are possible. The predicted minimum values of *V*_{el} are −60.4, −19.5, and −10.4 L/mol at 33, 37, and 45 °C, respectively. Experimental values are not available for comparison.

It was predicted in an earlier paper⁴ that the increase in density around an ion due to electrostriction should not be very sensitive to ion radius. We show in Table 3, a comparison of experimental reaction volumes for electron attachment to pyrimidine and to CO₂ under various conditions. Calculated values of electrostriction are shown for the same conditions. There is little effect of ion radius on the calculated values of *V*_{el}. The calculated values of *V*_{el} and the experimental values of ΔV_r show the same trend for both molecules, indicating that electrostriction by the ions is the principal source of volume change. However, as discussed above, the partial molar volume of the neutrals must be considered. This can be seen by comparing the difference between the reaction volumes for electron attachment to CO₂ and pyrimidine. That difference is in reality the volume change for the reaction



An earlier paper⁴ showed no evidence for clustering around neutral CO₂, and since the calculated electrostriction volumes of the two ions are similar, any volume change is attributed to $\bar{V}(\text{pyr})$. The values of ΔV_r for pyrimidine (col 2) are generally less than ΔV_r for CO₂ (col 4), indicating $\bar{V}(\text{pyr})$ is negative. Above 60 bar, this difference is small, amounting to a few tenths of a liter per mole. This is also reflected in the free energy of reaction 13, which (by difference) is about 0.18 eV, changing only slightly with pressure above 60 bar. However, at lower pressures, there are significant differences and the volume change for reaction 13, ascribed to $\bar{V}(\text{pyr})$, is as much as −3 L/mol at 55 bar and 310 K.

Entropy Changes. The large volume changes due to electrostriction are necessarily accompanied by large entropy changes. Entropy decreases occur when electrons attach to molecules in the liquid phase,^{2,3,8} and the effect is expected to be magnified in supercritical fluids. In Figure 6, values of ΔG_r are plotted versus temperature. The slopes of the lines, equal to $-\Delta S_r$, increase as the pressure decreases. Entropy and enthalpy changes are shown in Table 4. The value of ΔS_r

**Figure 6.** Free energy for electron attachment to pyrimidine versus temperature at various pressures (in bar) as indicated on the graph.**TABLE 4: Entropy and Enthalpy Changes for $e^- + \text{Pyrimidine} \rightleftharpoons \text{Pyrimidine}^-$**

<i>P</i> (bar)	ΔH_r (kcal/mol)	ΔS_r (cal/(K mol))	ΔV_r^a (L/mol)	α_T/χ (cal/(L K))	ΔS_{el} (cal/(K mol))
55	−60 ^b	−173 ^b	−6.39	32.0	−204.6
65	−44.5	−120.8	−1.86	50.1	−93.2
75	−35.3	−90.0	−1.33	59.2	−78.7
85	−32.0	−78.5	−1.04	66.0	−68.6
120	−32.8	−77.6	−0.80	82.9	−66.3

^a Experimental volume changes observed at 310 K ^b These values are based on data at only two temperatures

changes from ~ -173 cal/(K mol) at 55 bar to -78 cal/(K mol) at 120 bar. There is a corresponding large change in ΔH_r .

The large entropy changes are associated with the large density increases (clustering) around the ions. It was shown in studies of electron attachment in liquids that the entropy of electrostriction, ΔS_{el} , is related to the volume change by

$$\Delta S_{el} = (\alpha_T/\chi_T)\Delta V_r \quad (14)$$

where $\alpha_T = (1/V) dV/dT$. The ratio α_T/χ_T depends on *P*, *T*, and ρ and will thus have various values depending on distance from the ion. However, to evaluate the validity of eq 14 in supercritical fluids, the values of α_T and χ_T were computed here from the EOS. Values of ΔS_{el} were then calculated using eq 14 and the corresponding experimental values of ΔV_r and are shown in the last column of Table 4. The calculated values show the same trend with pressure as shown by the experimental values and account for most of the entropy change. Thus eq 14 appears to be valid in supercritical fluids and provides a way to estimate the entropy change.

Summary. This and the previous paper on CO₂⁴ have provided both experimental and theoretical information about the thermodynamics of electron capture reactions in supercritical ethane. The results are consistent with calculations of a compressible continuum model. Sharp minima in ΔV_r are predicted to occur near the compressibility maxima at each temperature. To obtain data at the minima, attachment reactions more exoergic than that for pyrimidine will have to be studied.

Appendix A

Equation 5 was derived by considering the force balance exerted on a small volume element $dx dy dz$, whose center is placed at (*x*,*y*,*z*).

This volume element takes the force from the pressure P

$$\begin{aligned}
 & \left(P\left(x - \frac{dx}{2}\right) - P\left(x + \frac{dx}{2}\right) \right) dy dz, \\
 & \left(P\left(y - \frac{dy}{2}\right) - P\left(y + \frac{dy}{2}\right) \right) dz dx, \\
 & \left(P\left(z - \frac{dz}{2}\right) - P\left(z + \frac{dz}{2}\right) \right) dx dy \\
 & = -\left(\frac{\partial P}{\partial x} dx dy dz, \frac{\partial P}{\partial y} dy dz dx, \frac{\partial P}{\partial z} dz dx dy \right) \\
 & = -\left(\frac{\partial P}{\partial x}, \frac{\partial P}{\partial y}, \frac{\partial P}{\partial z} \right) dx dy dz \\
 & = -(\text{grad}P) dx dy dz
 \end{aligned}$$

On the other hand, this volume element also takes the force from the electric field \mathbf{E} , as it is polarized and has a dipole moment of $\epsilon_0(\epsilon_r - 1)E dx dy dz$.

$$\begin{aligned}
 & \epsilon_0(\epsilon_r - 1) dx dy dz \left(E_x \frac{\partial E_x}{\partial x} + E_y \frac{\partial E_y}{\partial x} + E_z \frac{\partial E_z}{\partial x}, E_x \frac{\partial E_x}{\partial y} + \right. \\
 & \quad \left. E_y \frac{\partial E_y}{\partial y} + E_z \frac{\partial E_z}{\partial y}, E_x \frac{\partial E_x}{\partial z} + E_y \frac{\partial E_y}{\partial z} + E_z \frac{\partial E_z}{\partial z} \right) \\
 & = \epsilon_0(\epsilon_r - 1) dx dy dz \frac{\text{grad}(E^2)}{2}
 \end{aligned}$$

Because the sum of these two forces must be zero, the relation

$$\text{grad}P = \epsilon_0(\epsilon_r - 1) \frac{\text{grad}(E^2)}{2} \quad (\text{A-1})$$

is obtained. Equation 5 was derived by integrating this equation for the special case of spherical symmetry.

$$\frac{\partial P}{\partial r} = \frac{\epsilon_0(\epsilon_r - 1)}{2} \frac{\partial E^2}{\partial r}$$

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