J. Phys. Chem. A **1999,** *103,* 550−556

Electron Attachment to CO_2 in Supercritical Ethane

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Received: October 1, 1998

Thermal electrons attach reversibly to CO_2 in supercritical ethane. The equilibrium constants range from 40 to 2×10^4 m^{-1} for pressures from 50 to 220 bar at 33 and 37 °C. The attachment rate increases and the detachment rate decreases as the pressure increases. The lifetime of CO_2^- is between 20 and 100 ns in the high-pressure range. The reaction volume changes more than an order of magnitude, from −20.0 to −0.5 L/mol over the pressure and temperature ranges studied. The activation volume is approximately 50% of the reaction volume. Electrostriction volumes of the CO_2^- ion, calculated by a compressible continuum model, account for the main part of the observed reaction volumes. The calculation shows that the high-density region around each CO_2^- extends to 1 nm.

Introduction

For ionic reactions taking place in supercritical fluids, the partial molar volume of the ions can have a significant effect on rates. Further, the partial molar volumes should change with pressure, dramatically near the critical pressure, because of sharp changes in compressibility. Pulse radiolysis studies have already shown the possibility of studying cation reactions[1] and electron transfer[2] in supercritical fluids. Such studies provide data on the activation volumes. In this study of the equilibrium reaction

$$e^- + CO_2 \underset{k_d}{\overset{k_a}{\rightleftharpoons}} CO_2^- \qquad (1)$$

we obtain values for the partial molar volume of the CO_2^- anion from the measured reaction volume as a function of pressure. It is hoped that the information on volumes from this and similar studies will be useful in predicting the pressure dependence of ionic reactions, such as electron transfer, in nonpolar supercritical fluids.

The electrons are produced by a pulse of X-rays that cause ionization in the ethane. Only the fraction of the electrons that escape geminate combination to become free ions are available for reaction. The yield of free ions for supercritical ethane is expected to be between 5 and 30% of the initially formed ions, since this yield depends primarily on density and has been measured for comparable densities.[3]

Reaction 1 is already known to occur in nonpolar liquids,[4] where equilibrium constants range from 10^5 to 10^9 M^{-1}, depending on the liquid and on the temperature. This equilibrium depends strongly on pressure in liquids, shifting to the right with increasing pressure.[5,6] The derived reaction volumes range from −130 to −300 cm^3/mol. These volumes are associated with electrostriction of the solvent around CO_2^-, which includes a glasslike first layer of solvent molecules.[7] The activation volume for electron attachment to CO_2 in liquids is also negative and ranges from 30 to 40% of the overall reaction volume.

Two methods are used here to determine the equilibrium constant, K_1, of reaction 1. Both utilize measurements of the conductivity following the X-ray pulse. In one, K_1 is derived from the change in mobility of the electrons[6] as a result of temporary attachment to CO_2. This method is useful when K_1 is small. In the second method the actual electron attachment rate constant, k_a, and the detachment rate, k_d, are determined and K_1 equated to k_a/k_d. This latter method requires the short pulse available at the new 10 MeV laser electron accelerator facility.

Here, we report how the equilibrium constant, and thus the free energy, for reaction 1 changes with pressure and temperature in supercritical ethane. The reaction volumes are evaluated at various pressures and temperatures and compared to values calculated from a semicompressible continuum model. From the change of the individual rates with pressure, we obtain activation volumes. The attachment rate decreases linearly as the free energy of reaction increases. A similar dependence was reported for liquids.[8]

Experimental Section

The ethane, MG Industries-Scientific Grade, was purified by degassing at 77 K and passage through a Gaskleen Purifier (Pall Corp.). The quantity of ethane required in each experiment was measured out in vacuo, by its volume at 195 K, and then condensed into the conductivity cell, which was cooled to 77 K. The CO_2 (Matheson 99.99%) was degassed at 77 K and dried by passage through a trap at 195 K. Aliquots of CO_2 were measured out in a vacuum and condensed into the conductivity cell after the electron mobility and lifetime in the ethane had been measured.

The conductivity cell, fabricated from 304 stainless stell, is a 4 in. long tube with $^1/_4$ in. walls, which is closed at the bottom

10.1021/jp983931u CCC: $18.00

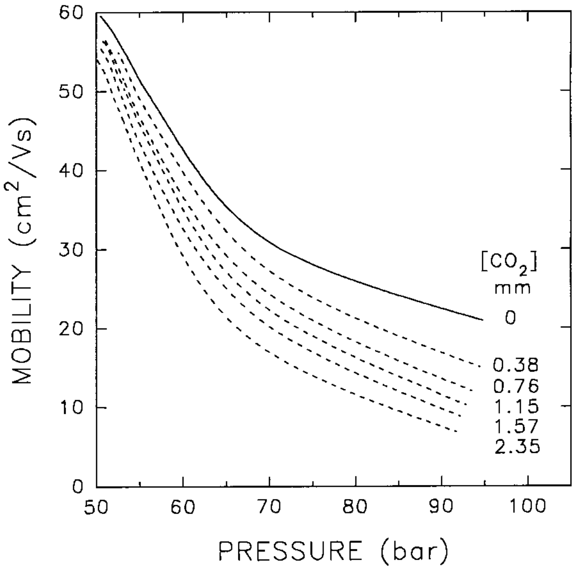

Figure 1. Electron mobility vs pressure at 33 °C. Solid line is for pure ethane. Dotted lines are for solutions containing indicated concentrations of CO_2 in mmolal.

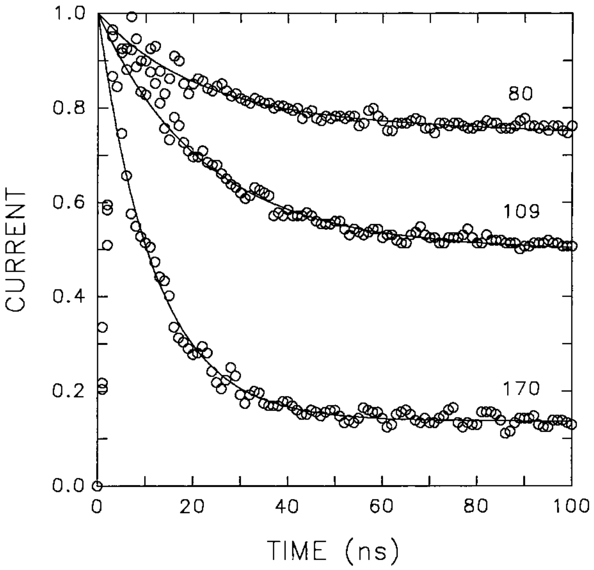

Figure 2. Conductivity traces for 0.77 mm CO_2 in ethane at 33 °C. Upper trace for 80 bar, middle trace 109 bar, and lower trace 170 bar. Solid lines are calculated fits to the data (see text).

and has a flange at the top for electrical feedthroughs. The electrodes consist of aluminum films evaporated onto quartz plates. The separation between plates is $d = 0.299$ cm. Pressure measurements utilize a pressure transducer (Setra, model 212) accurate to 0.45 bar. The temperature of the cell and connecting tubing is controlled to 0.05 °C during experiments. Temperature is measured with a Pt thermometer, calibrated to 0.1 °C. Resistance of the Pt is read with a Data Precision ohmmeter.

Densities and dielectric constants of ethane are calculated at the temperature and pressure used in each experiment from an equation of state (EOS).[9] Compressibilities (χ) are determined from the derivative of the EOS. It was assumed that this EOS applied as well for solutions containing CO_2 at concentrations up to 2.4 m*m*.

For electron mobility and lifetime measurements, samples were irradiated with 60 ns X-ray pulses, obtained by impinging electron pulses from the 2 MeV Van de Graaff accelerator on a lead target. The mobility (μ) was derived from the current signal by measuring the drift time, t_D, as a function of applied field E and the equation

$$\mu = d/(t_D E) \tag{2}$$

The electron mobility in supercritical ethane measured at 33 °C is shown in Figure 1 by the solid line. The electron lifetime, or rate of reaction with residual impurities (k_{imp}), was determined by a fit of the current signal to the equation

$$i = i_o(1 - t/t_D)\exp(-k_{imp}t)$$

For rate constant measurements, the new laser electron accelerator (LEAF) was used to provide 30 ps pulses of 8 MeV electrons.[11] The electron pulse was again stopped in a lead target, giving Bremstrahlung pulses, which irradiated the samples. The electron current was detected with an EG&G preamplifier (model 5185), rise time of 2 ns, operated on ×100 using the 50 Ω input. The amplified waveform was captured in a LeCroy 9362 1.5 GHz oscilloscope. To minimize noise, the signals from several pulses were averaged together. Typical conductivity traces obtained for solutions of CO_2 in ethane at various pressures are shown in Figure 2. The currents reach plateaus because of an equilibrium concentration of electrons in the sample. The electron concentration (n) is described by two coupled partial differential equations:

$$dn/dt = -v_D\, dn/dx - k_a n[CO_2] + k_d[CO_2^-] - k_{imp}n[S] \tag{3}$$

$$d[CO_2^-]/dt = k_a n[CO_2] - k_d[CO_2^-] \tag{4}$$

where v_D is the drift velocity given by μE. An analytic solution of these equations, obtained by Tachiya,[10] was used to analyze the current traces by trying different values of the two unknown parameters k_a and k_d until the best fit was obtained. The smooth lines in Figure 2 are examples of the fits obtained.

Results

Mobility Data. The addition of CO_2 to ethane causes a decrease in the measured mobility of electrons. This is shown in Figure 1; the solid line is the mobility in pure ethane, and the dashed lines are for CO_2 present. The effect is proportional to the concentration of CO_2. The largest effect is observed at high pressure. This reduction is attributed to the temporary attachment of electrons to CO_2, which increases the drift time and decreases the mobility. The observed mobility (μ) is given by[12]

$$\mu = \mu_o(1 + K_1[CO_2])^{-1} \tag{5}$$

where μ_o is the mobility of the quasi-free electrons in pure ethane. Measurements of the mobility with and without CO_2 present provide, with eq 5, values of K_1, the equilibrium constant of reaction 1. Here, it is assumed that the mobility of the CO_2^- ion is small by comparison to that of the electron and therefore makes a negligible contribution to the current. The mobility of positive ions in supercritical ethane is 0.002−0.004 $cm^2\ V^{-1}\ s^{-1}$ in the range studied.[13] Negative ions would have similar mobilities, which justifies our assumption.

Values of K_1 determined this way are shown as a function of pressure for two temperatures in Figure 3. Data obtained at five different concentrations of CO_2, from 0.38 to 2.35 m*m*, resulted in very similar values of K_1, indicating reaction 1 is bimolecular; that is, 1 mol of electrons reacts with 1 mol of CO_2. The solid lines are calculated by least-squares quadratic fits over segments

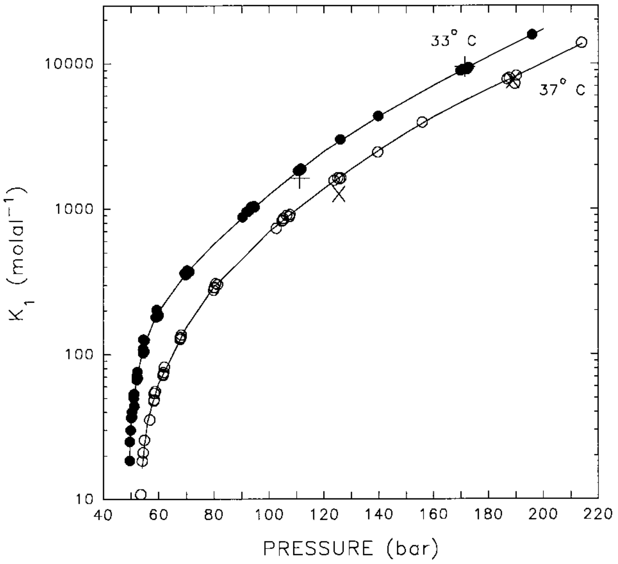

Figure 3. Equilibrium constants for reaction 1 as a function of pressure: filled circles, 33 °C; open circles, 37 °C. Solid lines are obtained from second-order polynomial fits (see text). Values of K_{eq} obtained from k_a/k_d are indicated by + for 33 °C and × for 37 °C.

of the pressure range at a time. Some measurements were made using concentrations of CO_2 between 5 and 10 m*m*; the results were in agreement with the low-concentration data and led to the points at the lowest pressures shown in Figure 3.

Rate Constants. At pressures above 80 bar it was possible to time-resolve the rates of electron attachment to CO_2 and detachment from CO_2^-. This necessitated using the short pulse available at LEAF because, as is shown in Figure 2, the observed currents decay rapidly in the first 60 ns for concentrations of CO_2 in the mmolal range. The height of the equilibrium current, or "plateau", depends on pressure, decreasing as the pressure is increased. The "plateau" current is a measure of the rate of electron detachment from CO_2^-, which decreases with increasing pressure.

Analysis of such curves, by the method indicated under Experimental Section, led to values of k_a and k_d shown in Figure 4. With increasing pressure k_a increases and k_d decreases at both temperatures studied. Measurements were made at concentrations of CO_2 between 0.18 and 0.77 m*m*, and the rate of attachment was independent of concentration in this range. This is shown by the clustering of points at particular pressures in Figure 4, indicating again that electrons attach to one molecule of CO_2.

The equilibrium constant for reaction 1, K_1, can be calculated from the ratio k_a/k_d. Average values of K_1, obtained this way at high pressure, are plotted in Figure 3 and are in good agreement with values of K_1 obtained from mobility.

Discussion

The electron attachment equilibrium, represented by reaction 1, is very sensitive to pressure in supercritical ethane. K_1 increases most rapidly at temperatures and pressures closest to the critical point, but K_1 is still increasing rapidly at the highest pressures studied. The rate constant for the attachment reaction also increases with pressure. The magnitude of the rate constant is well below that expected for a diffusion-controlled reaction of an electron, which has been estimated to be 6 × 10^{13} m^{-1} s^{-1} in SC ethane.[14]

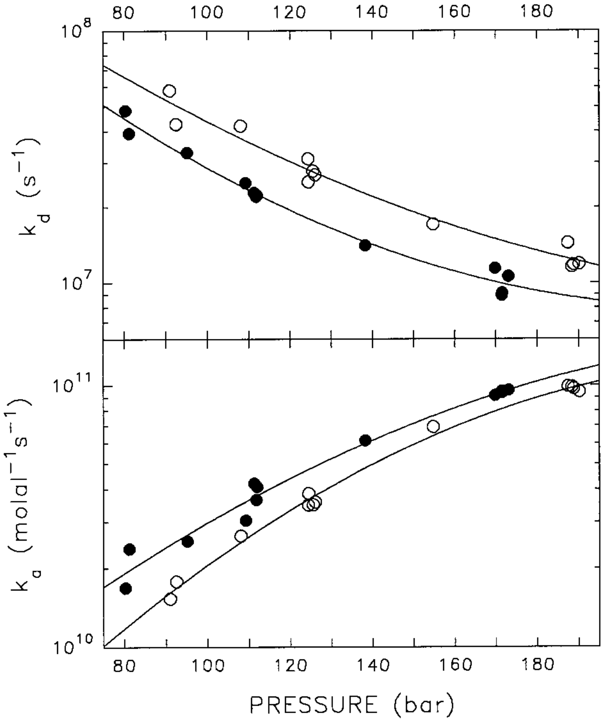

Figure 4. Effect of pressure on the detachment rate (top) and attachment rate (bottom) at (●) 33 and (○) 37 °C. Solid lines are second-order fits to the data.

Volume Changes. Experimental values of the volume changes in reaction 1 are calculated from the derivative of the fitted curves in Figure 3 and the relationship

$$\Delta V_r = -RT\, d(\ln K_1)/dP \qquad (6)$$

The results are shown by the points in Figure 5. The minimum values, −20 L mol^{-1} at 33 °C and −12 L mol^{-1} at 37 °C, are observed at the lowest pressures that could be studied. At even lower pressures this reaction becomes unfavorable (see Energy Changes below) and could not be observed. At the highest pressures studied, where the ethane is most dense, ΔV_r is −0.54 and −0.55 L s mol^{-1}, respectively at 33 and 37 °C, values approaching those reported in liquid alkanes (−0.13 to −0.30 L/mol).[5,6]

The volume change in a reaction is the difference in partial molar volumes of reactants and products, which in this case is

$$\Delta V_r = \bar{V}(CO_2^-) - \bar{V}(CO_2) - \bar{V}(e^-) \qquad (7)$$

The latter term is the partial molar volume of the electron, which is presumed to be small relative to the observed volume changes. This term depends, among other factors, on whether the electron is trapped in ethane. The high mobility at low pressures implies the electron is largely quasi-free, in which case the interaction with solvent molecules is weak. However, at densities greater than 14 mol/L, theory predicts that the electron is trapped at 340 K.[15] The partial molar volume of the electron in nonpolar liquids depends on the difference of two terms: the cavity volume and the electrostriction volume.[16] The latter depends on the magnitude of the compressibility. Applying this model to ethane and using the cavity radius of 0.51 nm predicted by theory,[15] we estimate that the partial molar volume of the trapped electron in ethane is less than 0.1 L/mol at a density of 14 mol/L. At lower densities localization is less important and $\bar{V}$(e) is presumed to be less. Thus, to a good approximation, we can say the observed volume changes are given by

$$\Delta V_r = \bar{V}(CO_2^-) - \bar{V}(CO_2) \tag{8}$$

Experimental data on the partial molar volume of CO_2 in ethane were not found. Ab initio calculations indicate the interaction between CO_2 and ethane molecules is minimal (−0.3 kcal/mol).[17] However, a higher level calculation, using MP2 perturbation theory, shows the interaction is somewhat stronger (−1.2 kcal/mol).[18] Nonetheless, these values are small relative to that produced by the electric field around the CO_2^- ion. An IR study[19] showed that the frequency of the ν_2 bending mode of CO_2 in ethane shifted with the dielectric constant, from which it may be concluded that there is no significant enhancement of dielectric constant or density around CO_2 in ethane. Clustering of ethane molecules around neutral CO_2 is not likely. It is expected therefore that the dominant term in ΔV_r is $\bar{V}(CO_2^-)$, which is essentially the electrostriction around the ion (see below).

Values of the activation volume for the attachment and detachment reactions, calculated from the slopes of the smooth curves through the rate constant data in Figure 4, are shown in Table 1. Similar to the reaction volumes, the magnitudes of the activation volumes decrease with increasing pressure. For this reaction the magnitudes of ΔV_a and ΔV_d are comparable, indicating that at the activated state the volume change is approximately one-half that for the overall reaction. The results for ΔV_a can be compared to a study of electron attachment to NO in supercritical ethane.[14] For that reaction ΔV_a was reported to be −0.17 L/mol at 33 °C and 71 bar and −0.11 L/mol at 37 °C and 82 bar; higher pressures were not studied. At 80 bar the activation volumes for attachment to CO_2 are −0.60 and −0.76 L/mol at 33 and 37 °C, respectively, much larger in magnitude than observed for NO. The reason is not entirely clear.

The present results can also be compared to data on this reaction in liquid alkanes, where values of ΔV_r range from −0.13 to −0.30 L/mol, depending on conditions. Activation volumes for attachment are typically one-third of ΔV_r in liquids.[5,6] That is, the activated state is closer to the reactants in liquids, meaning that less electrostriction of the solvent has occurred at this state.

As is shown by the above discussion, ΔV_r for reaction 1 varies over a wide range from −20 to −0.5 L/mol, depending on temperature and pressure. Electrostriction by CO_2^- is believed to be the dominant effect. The results are compared here with calculated values of electrostriction given by two models: the classical continuum model[20] and a compressible continuum model.

The classical formulation of electrostriction has been shown[5] to lead to the formula

$$V_{el} = -(e^2/(6r_{ion}\epsilon^2))\chi_T(\epsilon + 2)(\epsilon - 1)/\epsilon^2 \tag{9}$$

where a constant value for the dielectric constant, ϵ, is assumed. The radius of the CO_2^- ion is taken to be 0.23 nm, the same as used for studies of this reaction in liquids.[5,6] Values of ϵ and χ_T for each pressure and temperature are derived from the EOS. The predicted values of V_{el} for this model are shown by the dotted lines in Figure 5.

TABLE 1: Activation Volumes for k_a and k_d

temp (°C)	pressure (bar)	ΔV_a (L/mol)	ΔV_d (L/mol)	ΔV_r (L/mol)
33	80	−0.60	+0.62	−1.12
	100	−0.53	+0.53	−1.06
	150	−0.36	+0.31	−0.67
	200	−0.19	+0.10	−0.29
37	80	−0.76	+0.56	−1.32
	100	−0.67	+0.50	−1.17
	150	−0.43	+0.35	−0.78
	200	−0.18	+0.20	−0.38

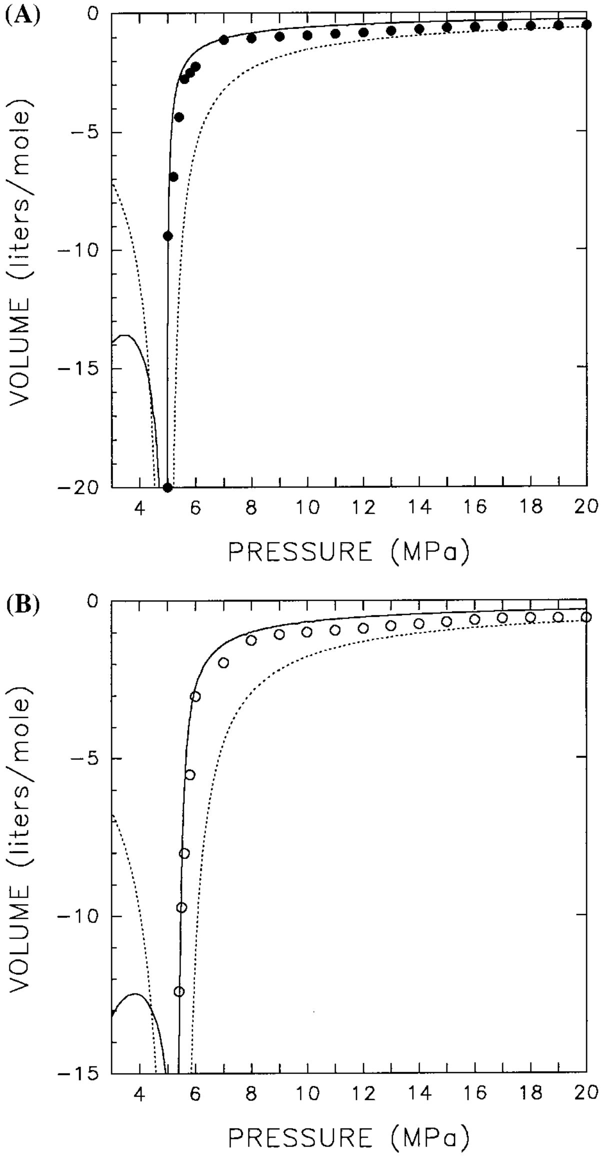

Figure 5. (A) Reaction volumes for electron attachment to CO_2: (●) 33 °C. Solid line is the electrostriction volume around CO_2^- calculated by the compressible continuum model. Dotted line is from eq 9. (B) Reaction volumes for electron attachment to CO_2: (○) 37 °C. Solid line is the electrostriction volume around CO_2^- calculated by the compressible continuum model. Dotted line is from eq 9.

Because clustering of ethane around ions is expected to have a significant effect in supercritical fluids, the classical continuum model is not expected to be a good approximation of electrostriction volume. In the compressible continuum model we take this clustering into account as an increase in density and dielectric constant around the ion. Our formulation of this model, presented earlier,[14] utilizes eq 10 to calculate the pressure (P) at each point

$$P = P_\infty + (\epsilon(r) - 1)\epsilon_o E(r)^2/2 \tag{10}$$

around the ion, where P_∞ is the pressure expected in the absence of the ion, $\epsilon(r)$ is the distance-dependent dielectric constant, and $E(r)$ is the electric field at a distance r due to the charge on the ion and is given by $e/(4\pi\epsilon_r\epsilon_o r^2)$, where ϵ_o is 8.85 × 10^{-12}

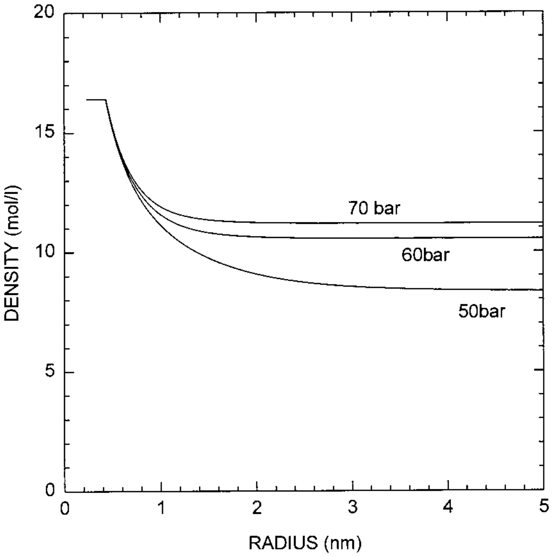

Figure 6. Density distribution around a CO_2^- ion as a function of distance in SC ethane at 33 °C at indicated pressures.

TABLE 2: Electrostriction Volumes (V_{el}) at 310 K

	ion radius (nm)		
pressure (bar)	0.2	0.3	0.4
54	−14.5	−14.4	−14.3
75	−1.15	−1.13	−1.08
100	−0.67	−0.65	−0.61
125	−0.49	−0.48	−0.45
150	−0.40	−0.38	−0.36
200	−0.29	−0.28	−0.26

C V^{-1} m^{-1}. The density, $\rho(r)$, at each point is deduced from the pressure using the EOS; $\epsilon(r)$ is obtained from $\rho(r)$ and the Clausius−Mosotti equation. The calculation is iterated, reevaluating $E(r)$ each time, until a constant $\rho(r)$ is obtained.

The calculated density around a CO_2^- ion as a function of r in supercritical ethane is shown for several pressures at 33 °C in Figure 6. The density drops off gradually with distance; there are no sharp breaks in the curves. The radius at which the density becomes the same as the background density, ρ_∞, is pressure-dependent. This distance is large at low pressures but becomes shorter at high pressures. Consequently, the volume changes, which involve the integral of the density, are pressure-dependent.

The volume change of electrostriction is obtained by eq 11,

$$V_{el} = 4\pi\int_{r_{ion}}^{\infty}[1/V(r)\int_{V_\infty}^{V(r)} dV]r^2\,dr \qquad (11)$$

where $V(r)$ is ρ^{-1}. Values of V_{el} were evaluated with eq 11 for a series of pressures at 33 and 37 °C and are shown by the solid lines in Figure 5. This model gives excellent agreement with observed reaction volumes, especially in the low-pressure region. The calculations predict that the minimum values of the electrostriction volume are −60.3 L/mol at 49.5 bar and 33 °C and −20.1 L/mol at 52.7 bar and 37 °C. The classical model (eq 9) predicts corresponding minimum values of −501 and −95 L/mol. The equilibrium with CO_2 (eq 1) is too unfavorable to obtain experimental data at the minima.

Calculations were made for different ion radii to see how changes in this parameter affect the predicted electrostriction volume. This is of interest in reactions such as charge transfer where one would like to know if there is a volume change expected when the charge moves from one ion to a molecule of different size. The results at 310 K are shown in Table 2 for three radii: 0.2, 0.3, and 0.4 nm. At any one pressure there is very little difference in the calculated volumes for this range of ion radii, even in the region of high compressibility. It should also be noted that classically the electrostriction volume (eq 9) is proportional to the radius^{-1}. These results indicate that the large partial molar volumes of ions in supercritical fluids are associated with the clustering of solvent molecules around the ions, an effect that is largely independent of the ion radius. Data on other equilibria, similar to reaction 1, are needed to verify this interesting prediction.

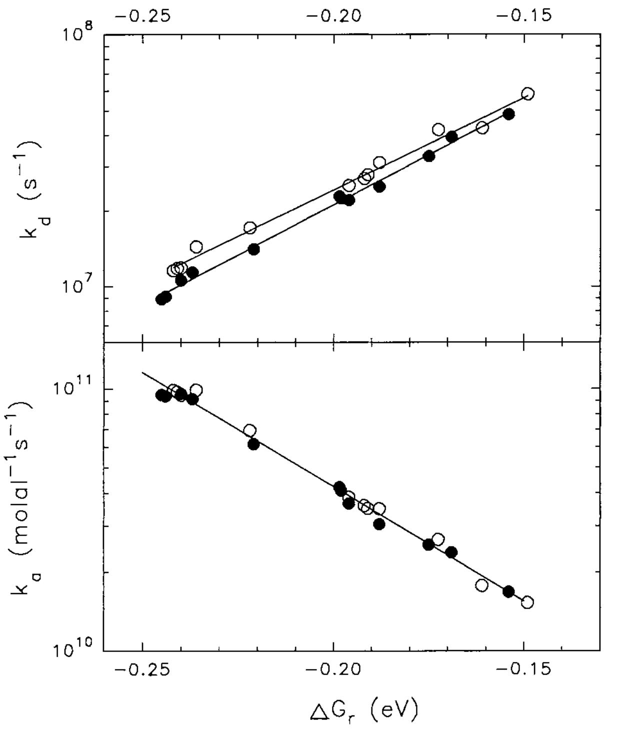

Figure 7. Dependence of detachment rate (top) and attachment rate (bottom) on ΔG_r: (●) 33 °C; (○) 37 °C.

Energy Changes. The free energy of reaction 1 changes with pressure from values near −0.09 eV at low pressure to around −0.25 eV at high pressure. This shift is associated with the polarization energy of the CO_2^- ion and the energy of the electron. In liquid hydrocarbons the polarization energy is about −1.5 eV and leads to values of ΔG_r for eq 1 between −0.3 and −0.6 eV.[6] This reaction is less favorable in supercritical ethane where $\Delta G_r \geq -0.25$ eV. However, as in the liquid, $\ln k_a$ decreases linearly with ΔG_r, as shown in Figure 7. The slope of the solid line is −20 eV^{-1}, quite similar to that found for liquids.[8] Thus, such plots not only are of predictive utility for liquids but also extend to supercritical fluids as well. The dependence of k_d on ΔG_r is also linear as shown by the upper plot in Figure 7.

To evaluate the polarization energy in supercritical ethane, we used the compressible continuum model. The energy of an ion in a nonpolar supercritical fluid is given by the difference:

$$E(P^-) = 4\pi\int_{r_{ion}}^{\infty}(1/2)\epsilon_0\epsilon(r)[E(r)]^2r^2\,dr - 4\pi\int_{r_{ion}}^{\infty}(1/2)\epsilon_0[E_0(r)]^2r^2\,dr \quad (12)$$

The second term refers to the ion in a vacuum and becomes

$$-e^2/(8\pi\epsilon_0 r_{ion})$$

The first term refers to the ion in a SCF and was evaluated for

TABLE 3: Energy Changes Associated with Reaction 1: $e^- + CO_2 \rightleftharpoons CO_2^-$

pressure (bar)	density (mol/L)	ΔG_r (eV)	V_o (eV)	E(Born) (eV)	E_C (eV)	$E(P_{CC}^-)^a$ (eV)	$\Delta G_r(\text{gas}) - E_t$ (eV)
Temperature = 33 °C							
50	8.30	−0.094	−0.174	−0.74	0.045	−1.06	0.79
52	9.39	−0.111	−0.178	−0.82	0.041	−1.08	0.79
54	9.83	−0.122	−0.179	−0.85	0.039	−1.08	0.78
60	10.5	−0.139	−0.176	−0.90	0.036	−1.10	0.78
70	11.2	−0.156	−0.172	−0.94	0.032	−1.11	0.78
80	11.6	−0.168	−0.169	−0.97	0.030	−1.12	0.78
100	12.2	−0.188	−0.16	−1.01	0.026	−1.14	0.79
125	12.7	−0.210	−0.153	−1.04	0.022	−1.154	0.79
150	13.1	−0.227	−0.14	−1.066	0.020	−1.165	0.80
175	13.4	−0.243	−0.135	−1.086	0.018	−1.175	0.80
200	13.7	−0.257	−0.13	−1.103	0.016	−1.183	0.80
Temperature = 37 °C							
56	8.6	−0.089	−0.176	−0.761	0.045	−1.06	0.795
58	9.22	−0.103	−0.178	−0.806	0.042	−1.07	0.79
60	9.6	−0.111	−0.179	−0.834	0.04	−1.08	0.79
70	10.6	−0.135	−0.176	−0.904	0.035	−1.10	0.79
80	11.2	−0.154	−0.172	−0.941	0.032	−1.11	0.78
100	11.9	−0.175	−0.167	−0.987	0.028	−1.127	0.785
125	12.4	−0.197	−0.158	−1.024	0.024	−1.143	0.79
150	12.9	−0.217	−0.149	−1.051	0.021	−1.155	0.79
175	13.2	−0.232	−0.14	−1.073	0.018	−1.166	0.79
200	13.5	−0.246	−0.135	−1.091	0.016	−1.174	0.79

[a] $E(P_{CC}^-)$ are values of the polarization energy calculated with a compressible continuum model as described in text.

various conditions utilizing the distance-dependent dielectric constant, ϵ(r), evaluated above.

An additional term was added to take into account the compression of ethane from the volume it occupies without an ion, V_∞, to the volume it occupies in the presence of an ion, V_r. This energy E_C is given by

$$E_c = -4\pi \int_{r_{\text{ion}}}^{\infty} [1/V(r) \int_{V_\infty}^{V(r)} P \, dV] r^2 \, dr \tag{13}$$

Then the total polarization energy, $E(P_{CC}^-)$, equals $E(P^-) + E_C$. The values of these terms as a function of pressure and temperature are shown in Table 3. The contribution of compression is small and decreases in magnitude with increasing pressure.

The value of the polarization energy, $E(P_{CC}^-)$, changes only slightly as the pressure increases; the change from 50 to 200 bar at 33 °C is 0.12 eV (see Table 3). Calculations using the Born equation give values of the polarization energy that are not as low as those given by the compressible continuum model. The change in E(Born) from 50 to 200 bar at 33 °C is 0.36 eV because of changes in the dielectric constant. As the pressure increases, the value calculated by the Born equation approaches that calculated by the compressible continuum model. Thus, although the Born equation is considered to be reasonably accurate at high densities and in liquids, in supercritical fluids the clustering of solvent molecules around the ion must be taken into account specifically. The fact that $E(P_{CC}^-)$ changes little with pressure is consistent with calculations, indicating the cluster size is largely independent of pressure (see Figure 6).

The free energy of reaction 1 is related to the free energy in the gas phase, ΔG_r(gas), according to[21]

$$\Delta G_r = \Delta G_r(\text{gas}) + E(P_{CC}^-) - V_o - E_t \tag{14}$$

where V_o is the conduction band energy and E_t the trap energy in the fluid. The last term is presumed to be small, since over the pressure range studied the electron in ethane is mostly quasi-free, as discussed above. Values of V_o shown in Table 3 were taken from a study[22] of liquid ethane at comparable densities to those of SC ethane. As the pressure increases, V_o tends to increase; the change from 52 to 200 bar is 0.05 eV. Thus, the electron is destabilized and the ion is stabilized with increasing pressure, and the free energy, which changes in this pressure range by 0.17 eV, reflects both terms.

We have used eq 14 along with measured values of ΔG_r, V_o, and calculated values of $E(P_{CC}^-)$ to determine $\Delta G_r(\text{gas}) - E_t$. The results, shown in the last column of Table 2, indicate this quantity remains constant regardless of the temperature or pressure of the SCF. The value obtained (−0.79 eV) corresponds to an electron affintiy of CO_2 of −0.84 eV if we take $T\Delta S_r$(gas) = 0.05 eV[6] and ignore electron trapping ($E_t = 0$) at the temperatures studied. This value is slightly lower than theoretical values, which range from −0.62 to −0.81.[23] It is also lower than an experimental result from a gas-phase study of −0.6 ± 0.2 eV.[24] A liquid-phase study, similar to the present one, led to −0.61 eV.[21] If we take a small negative value of E_t (−0.1 eV), then our calculated electron affinity is in agreement with both the theoretical estimates and the gas-phase value to within the stated experimental uncertainties.

Conclusion

The present results provide quantitative information on the extent of clustering of solvent around CO_2^- ions in supercritical ethane. Our results indicate there is clustering of ethane around CO_2^- to distances from 0.7 to 1.0 nm. Similar values were obtained for the radii of the positive ions in supercritical ethane from a mobility study.[13] The partial molar volume of ions in ethane are found to be insensitive to the ion radius. At the concentrations of CO_2 used, there is no evidence of reaction of $CO_2^-$with CO_2.

Acknowledgment. The authors thank James Wishart and Steven Howell for the operation of LEAF and thank Harold Schwarz for help in implementing data acquisition. This research was carried out at Brookhaven National Laboratory and supported under Contract DE-AC02-98-CH10886 with U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. K.I. and M.N. are supported by a Grant in Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

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