Electron Attachment to NO in Supercritical Ethane

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Electron attachment to NO was studied in supercritical ethane at 33, 37, and 47 °C as a function of pressure (35−110 bar). The rate constant for electron attachment increases with increasing pressure at all temperatures studied. The most dramatic increases are observed near the critical pressure. The activation volume for this reaction is negative and quite large in magnitude, especially in this region. The activation volume depends on the isothermal compressibility. The results are compared to volume changes predicted by a compressible continuum model.

Introduction

Supercritical fluids (SCFs) have been used in industry for extraction processes for many years. A key advantage of such fluids is that they are often environmentally benign. Future development of SCFs in applications to processes involving charged species requires knowledge about the physical properties of ions. In particular, little is known about the partial molar volumes of ions in nonpolar SCFs. In the method used here, anions are made by attachment of electrons to a solute in SC ethane. The electrons are produced by exposure of the fluid to a pulse of X-rays.

Many of the reactions that have already been studied in supercritical ethane are diffusion-controlled. The rate constant for spin exchange between neutral free radicals, for example, decreases with increasing pressure and is inversely dependent on the fluid viscosity.[1] Similar results were obtained for benzyl radical recombination in supercritical ethane.[2] The rate constant for an electron-transfer reaction in supercritical ethane was recently found to be independent of pressure over a wide pressure range.[3]

Liquid-phase studies of electron attachment to various solutes, including CO_2,[4−6] butadiene,[7−9] and pyrimidine,[10] have shown that the overall volume changes (V_r) for these reactions are, without exception, negative. For reaction with CO_2 the volume changes are between −130 and −290 cm³/mol, depending on the liquid. Thus, the attachment equilibria shift to favor the anion with increasing pressure. The shift is due to the negative reaction volumes, which are largely determined by the negative partial molar volume of the product anion. It has been shown that, in the case of electron reaction with CO_2[11] and butadiene,[7] the volume changes are due entirely to electrostriction of the solvent, which is proportional to the isothermal compressibility (χ_T) of the liquid. Since the compressibility is much larger in supercritical fluids than in liquids and goes through a maximum

in the critical region, our curiosity was aroused as to how this would affect electron reactions. Our studies aim to see how the reaction rate is influenced by this sharp change in χ_T and to measure reaction volumes in SCFs. This information can then be used to evaluate the partial molar volumes of ions in nonpolar supercritical fluids.

Here we report on the electron attachment to NO in supercritical ethane. Although the electron affinity of NO is rather low, 0.026 eV, and NO⁻ can readily detach an electron in ethane at low pressure,[12] detachment was not observed in this work. This is due to the polarization energy, which in denser media stabilizes NO⁻.

$$e^- + NO \rightarrow NO^- \tag{1}$$

Consequently, only the activation volume can be evaluated but not the reaction volume. The volumes of activation for electron attachment to N_2O and CO_2 in liquid tetramethylsilane are about −60 cm³/mol,[1,13] which are only a fraction of the overall reaction volumes. Electron attachment reactions in liquids are usually accelerated by pressure, except in circumstances where they are diffusion-controlled.

The volume change in this reaction is the difference

$$V_a^* = \bar{v}_{NO^-*} - \bar{v}_{NO} - \bar{v}_{e^-} \tag{2}$$

The partial molar volume of NO in ethane is not known but is presumably small as is indicated by values reported for methane in ethane, also a small but nonpolar molecule.[14]

Experimental Section

The high-pressure conductivity cell used resembles the one described earlier.[15] Gases are condensed into the cell by cooling it to −196 °C. The electrodes and guard ring consist of thin aluminum films evaporated onto quartz plates. A pressure transducer (Setra, model 212) is attached to the cell, the rated accuracy of which is 0.45 bar. The cell was placed in a
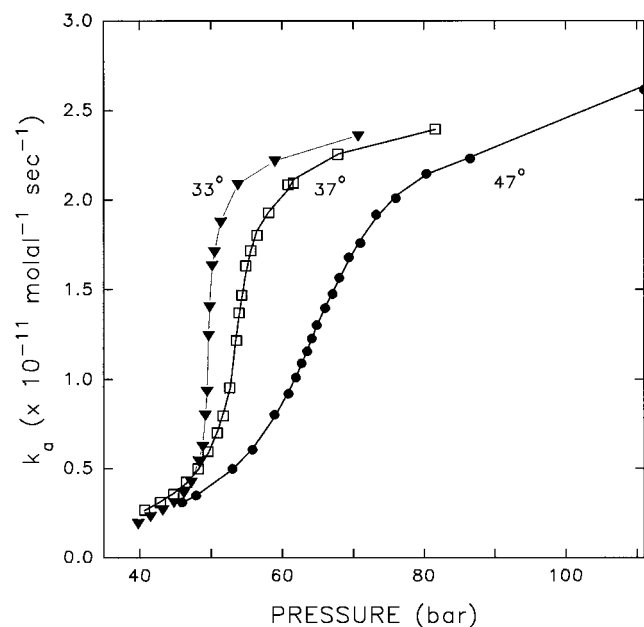
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Figure 1. Rate constant, k_a, for electron attachment to NO in supercritical ethane as a function of pressure at (▼) 33.0 °C, (□) 37.0 °C, and (●) 47.0 °C.

temperature-regulated box and the temperature controlled to 0.05 °C. The temperature was measured by a Pt thermometer, mounted inside the cell, which was calibrated to 0.1 °C by a precalibrated Omega thermometer. Resistance was read with a Data Precision ohmmeter.

Ethane, MG Industries, Scientific Grade, is purified by degassing and passage through an ethane Gaskleen purifier (Pall Corp.). The lifetime of electrons in the purified supercritical ethane is >10 μs at ≈180 bar. Matheson C.P. Grade NO is used as received.

Samples are irradiated with X-ray pulses obtained by impinging 1.9 MeV electron beam pulses from a Van de Graaff accelerator on a lead target. The current signals from the cell containing purified ethane are analyzed both for mobility, by a time-of-flight method, and for the rate of reaction of electrons with impurities. A measured amount of NO is then added and the current signal again analyzed for the reaction rate with NO. The concentrations of NO used were in the 10−20 μm range.

The densities and dielectric constants of ethane are calculated from the temperature and pressure using an equation-of-state given by Younglove.[16] The compressibility is also calculated from the derivative of the EOS.

Rate measurements are made at constant molality and constant temperature beginning at the highest pressure. The molality of the solution is determined by the number of moles of NO added to the ethane, the weight of which is known from the pressure−density equation.[16] Then, aliquots of the gases are released through the valve, and a new rate measurement is made after each release. It is assumed that proportionate amounts of each gas are let out so that the molality of the sample remains the same.

Results

Rate measurements were made at 33.0, 37.0, and 47.0 °C (T_c for ethane is 32.23 °C) and over the pressure range 35−180 bar. Figure 1 shows the rate constant of reaction 1 versus pressure at three temperatures. The rate constant is about 4×10^{10} m^{-1} s^{-1} at low pressure and increases more than an order of magnitude over the pressure range studied. The increase is

most rapid at pressures in the region just above the critical pressure of ethane.

The activation volume of reaction 1 was calculated at each temperature using the relation

$$V_a^* = -RT \, d(\ln k_a)/dP \qquad (3)$$

The slope, $d(\ln k_a)/dP$, was evaluated by fitting the data, over a limited pressure range, to a third-order polynomial:

$$\ln k_a = A + BP + CP^2 + DP^3$$

The results are shown in Figure 2. The activation volumes are quite large and negative; at the minima the values of V_a^* are −27, −9.2, and −2.3 L/mol at 33.0, 37.0, and 47.0 °C, respectively.

The pressures at which the minima occur and the pressures where the rate of attachment increases most rapidly (Figure 1) are near the pressures where the compressibility of ethane reaches a maximum at that temperature. The compressibility, as shown in Figure 3, exceeds that for liquids by orders of magnitude under certain conditions.

Discussion

The rate of electron attachment to NO in SC ethane is not diffusion controlled since the rate constant increases with pressure and is much less than that expected for diffusion control. A diffusion-controlled reaction rate should decrease with increasing pressure since the viscosity of ethane increases with pressure. The results contrast with what has been observed in supercritical ethane for radicals where, typically, the rate decreases with increasing pressure (see Introduction). The rate of a diffusion-controlled electron reaction in ethane can be estimated from the mobility. This rate constant is given by

$$k_D = 4\pi r \mu k_B T$$

where r is the reaction radius and μ the electron mobility. The electron mobility decreases with increasing pressure in ethane[17] and is in the range between 10 and 100 cm²/(V s) for most of the experimental conditions. Thus, k_D would be about 6×10^{13} m^{-1} s^{-1} if r is taken as 0.5 nm. Our observed rate constants
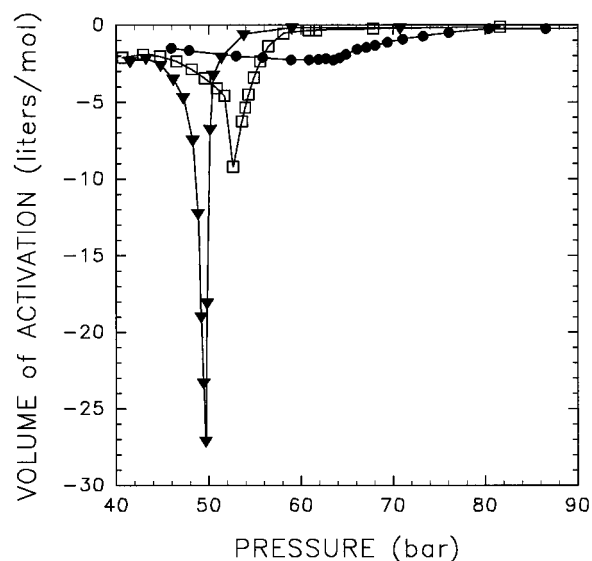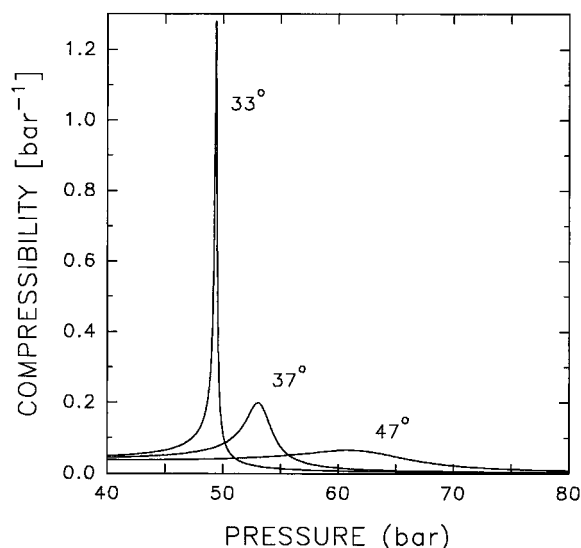

Figure 2. Volumes of activation, V_a^*, for electron attachment to NO in supercritical ethane at (▼) 33.0 °C, (□) 37.0 °C, and (●) 47.0 °C.

Electron Attachment to NO in Supercritical Ethane

J. Phys. Chem. B, Vol. 102, No. 21, 1998 **4191**

Figure 3. Compressibility of supercritical ethane versus pressure at the temperatures (in °C) indicated.

Figure 4. Calculated density of ethane as a function of distance from NO$^-$ at 33.0 °C and pressures indicated.

are more than 2 orders of magnitude less than this; thus, the estimation of the activation volume using eq 3 is justified.

In general, the partial molar volume of a neutral solute, $\bar{v}_2$, in a supercritical fluid may be positive or negative depending on whether the solute fluid interaction potential is repulsive or attractive. The magnitude of $\bar{v}_2$ is often large near the critical point. For a gas (vinyl chloride) in ethene, $\bar{v}_2$ is also reported to be negative near the critical density.[18] No specific information about $\bar{v}_2$ for NO in ethane was found. Models for the estimation of $\bar{v}_2$ that have been considered show that $\bar{v}_2$ in supercritical fluids depends strongly on the compressibility of the fluid.[19]

Whatever the value of $\bar{v}_{\text{NO}}$, there will be a volume change on attachment of an electron to NO and the difference $\bar{v}_{\text{NO}^-*} - \bar{v}_{\text{NO}}$ is the volume change due to electrostriction of the fluid by the ion, V_{el}. Thus, eq 2 becomes

$$V_a^* = V_{\text{el}} \qquad (2')$$

The partial molar volume of the electron is assumed to be zero. That it is quite small is justified by the following argument. The mobility of the electron in supercritical ethane is high,[17] ranging from 20 to 100 cm^2/(V s) for the conditions studied. This high mobility infers that the electron is practically quasi-free; that is, electrons are traveling as nearly plane waves, and there are very small interactions with the medium. For comparison, these mobilities correspond to electron diffusion coefficients of 0.5−3 cm^2/s, calculated from $D = \mu kT/e$. The diffusion coefficient of ethane molecules, calculated from the Stokes−Einstein relation, $D = kT/6\pi(\eta)R$, is in the range (2−4) × 10^{-4} cm^2/s in the same supercritical region. Ions in supercritical ethane have even lower diffusion coefficients, between 5 × 10^{-5} and 8 × 10^{-5} cm^2/s, based on our positive ion mobility measurements.[20] Thus, the results provide a measure of electrostriction in SC ethane. In liquids, according to the classical model,[21] the electrostriction volume of an ion is proportional to dϵ/dP, where ϵ is the dielectric constant. If the Clausius−Mosotti equation is assumed, then V_{el} becomes[7,11]

$$V_{\text{el}} = -(e^2/6r_{\text{ion}}\epsilon^2)\chi_{\text{T}}(\epsilon + 2)(\epsilon - 1)/\epsilon^2 \qquad (4)$$

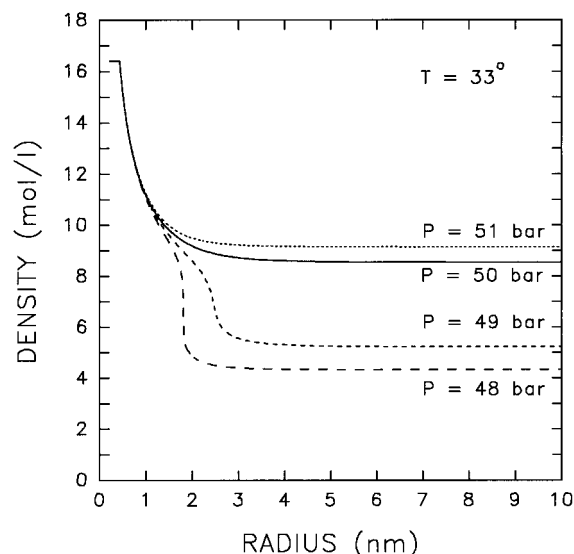where r_{ion} is taken as 0.21 nm as derived from the liquid density

by the method of Henglein.[22] Thus, volume changes will be dependent on χ_{T}.

The continuum model, as expressed by eq 4, is an approximation even for liquids[11] and is unlikely to be applicable to a supercritical gas because of clustering around ions. Rather, electrostriction is expected to increase the density and dielectric constant and decrease the compressibility of ethane in the vicinity of the NO$^-$ ion. Theory should take these effects into account. Our approach considers the effect of the electric field (E_r) around an ion as an induced pressure. The field (in MKS units) is[23]

$$E_r = e/(4\pi\epsilon_r\epsilon_o r^2) \qquad (5)$$

and the pressure (P) is given by[24]

$$P = P_\infty + (\epsilon_r - 1)\epsilon_o E_r^2/2 \qquad (6)$$

where P_∞ is the pressure of the gas at a long distance from the ion or the pressure expected in the absence of an ion; ϵ_r is the dielectric constant, which is a function of distance, r, from the ion. With the pressure defined at each point, the distance-dependent density, ρ_r, can be calculated at each point from the Younglove EOS.[16]

$$P = f(\rho) \qquad (7)$$

From the density, the value of ϵ_r is deduced from eq 8 using the Clausius−Mosotti equation and C_m defined by Younglove.

$$\epsilon_r = (1 + 2\rho_r C_m)/(1 - \rho_r C_m) \qquad (8)$$

The new values of ϵ_r are then used to reevaluate E_r in eq 5, and the cycle, consisting of eqs 5−8, is repeated until no further change in ρ_r is observed. The results of this calculation show that a region of high density extends outward about 1.5 nm from the NO$^-$ ion. Typical examples of the density as a function of distance are shown in Figure 4 for 33 °C. An approximation made here was to assume that the density could not exceed the limiting high-pressure density given by the EOS, even in the high-pressure region close to the ion; for example, the high-pressure density of ethane is 16.4 mol/L at 33 °C. At distances beyond 3 nm the densities return to that given by the EOS for this temperature and pressure. There are sharp breaks in density
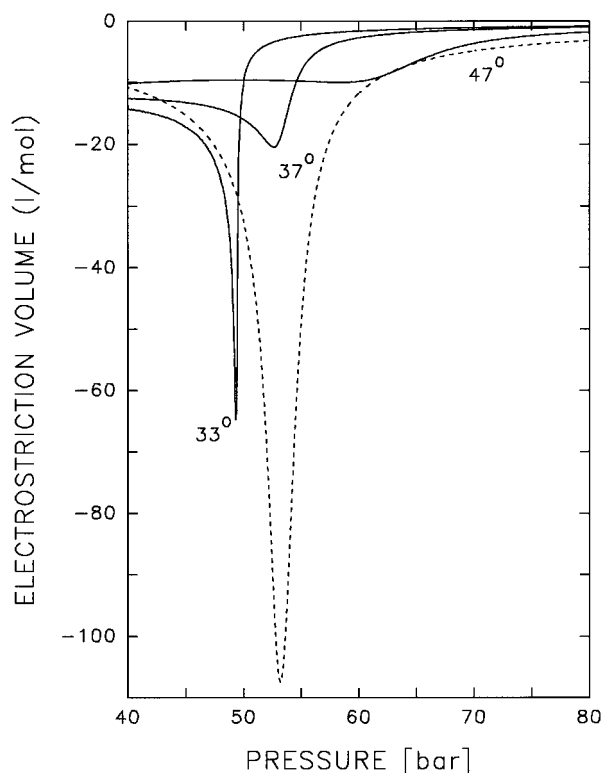
Figure 5. Volumes of electrostriction around NO$^-$ calculated by the compressible continuum model are given by the solid lines; temperatures in °C as indicated. Dashed line is a classical calculation (eq 4) for 37 °C.

at certain radii for some of the curves. The breaks occur only for pressures that are less than the pressure where the compressibility is a maximum. For 33 °C this is 49.4 bar. For low pressures the local pressure is less than 49.4 bar at radii beyond the break, and the ethane is much less compressible. Consequently, the clusters have sharp edges in the dense gas below this pressure. For clusters in the supercritical region, above this pressure of 49.4 bar, there are no breaks because the local pressure is always greater than 49.4 bar.

The volume change due to the presence of the ion is obtained from the density by integrating over space.

$$V_{el} = 4\pi \int_{r_{ion}}^{\infty} (1 - \rho_r/\rho_\infty) r^2 \, dr \qquad (9)$$

This calculation was carried out for a series of pressures and at three temperatures. The results are shown by the solid lines in Figure 5.

There is a remarkable similarity between the calculated V_{el} and the observed V_a^*. The asymmetry of the peaks is reproduced: at high pressure the curves approach zero, whereas at low pressure the curves are well below zero. The sharp minima occur near the pressures where the compressibilities are the largest at each temperature. The positions and relative magnitudes of these minima correspond approximately with the positions and relative magnitudes of the minima in the activation volumes in Figure 2. Calculated values of V_{el}, given by the classical model, eq 4, are shown for 37 °C by the dashed line in Figure 5. The minimum is much deeper and the curve is more symmetrical than that given by the compressible continuum model. The asymmetry is to be expected given the existence of clusters or regions of high density around ions. At high pressure the background density of the fluid is more comparable to the density in the cluster so the volume change

is small. At low density the fluid density is low, and the volume change for creation of the cluster is larger.

The experimental magnitudes of the V_a^* values are less than the calculated values of V_{el}. As noted in the Introduction, activation volumes for electron attachment reactions in liquids are often less than reactions volumes. This could be due to the fact that the activated complex, NO$^-$*, will be a Rydberg-like state (large r), and the surrounding ethane molecules will not be in their fully relaxed arrangement.

In conclusion, we observe sharp increases in electron attachment rates in supercritical ethane. These increases occur at pressures where the compressibility values are maximal. In addition, large negative activation volumes are observed for electron attachment. The activation volume is due to electrostriction of the ethane by NO$^-$*. The dependence of V_a^* on pressure and temperature is very similar to that expected from theory.

References and Notes

(1) Randolph, T. W.; Carlier, C. *J. Phys. Chem.* **1992**, *96*, 5146.

(2) Roberts, C. B.; Zhang, J.; Brennecke, J. F.; Chateauneuf, J. E. *J. Phys. Chem.* **1993**, *97*, 5618.

(3) Takahashi, K.; Jonah, C. D. *Chem. Phys. Lett.* **1997**, *264*, 297.

(4) Nishikawa, M.; Itoh, K.; Holroyd, R. *J. Phys. Chem.* **1988,** *92*, 5262.

(5) Ninomiya, S.; Itoh, K.; Nishikawa, M.; Holroyd, R. *J. Phys. Chem.* **1993**, *97*, 9488.

(6) Holroyd, R. A.; Itoh, K.; Nishikawa, M. *Chem. Phys. Lett.* **1997**, *266* 227.

(7) Holroyd, R. A.; Schwarz, H. A.; Stradowska, E.; Ninomiya, S.; Itoh, K.; Nishikawa, M. *J. Phys. Chem.* **1993**, *98,* 7142.

(8) Holroyd, R. A.; Stradowska, E.; Itoh, K.; Nishikawa, M. *Radiat. Phys. Chem.* **1996**, *47*, 39.

(9) Chen, P.; Holroyd, R. A. *J. Phys. Chem.* **1995**, *99*, 14528.

(10) Chen, P.; Holroyd, R. A. *J. Phys. Chem.* **1996**, *100*, 4491.

(11) Schwarz, H. A. *J. Phys. Chem.* **1993**, *97*, 12954.

(12) Viggiano, A. A.; Morris, R. A.; Paulson, J. F. *J. Phys. Chem.* **1990**, *94*, 3286.

(13) Holroyd, R. A. In *Linking the Gaseous and Condensed Phases of Matter;* Christophorou, L. G., Illenberger, E., Schmidt, W. F., Eds.; NATO ASI B326; Plenum Press: New York, 1994.

(14) Sage, B. H.; Lacey, W. N. *Ind. Eng. Chem.* **1939**, *31*, 1497.

(15) Cipollini, N. E.; Holroyd, R. A.; Nishikawa, M. *J. Chem. Phys.* **1977**, *67*, 4636.

(16) Younglove, B. A.; Ely, J. F. *J. Phys. Chem. Ref. Data* **1987**, *16*, 577.

(17) Nishikawa, M.; Holroyd, R. A.; Sowada, U. *J. Chem. Phys.* **1980**, *72*, 3081.

(18) Ehrlich, P.; Fariss, R. H. *J. Phys. Chem.* **1969**, *73*, 1164.

(19) Liu, H.; Macedo, E. A. *Ind. Eng. Chem. Res.* **1995**, *34*, 2029.

(20) Holroyd, R. A.; Nishikawa, M.; Itoh, K., unpublished results.

(21) Drude, P.; Nernst, W. Z. *Phys. Chem.* **1894**, *15*, 79.

(22) Henglein, A. *Can. J. Chem.* **1977**, *55*, 2112.

(23) Wood, R. H.; Quint, J. R.; Groller, J.-P. E. *J. Phys. Chem.* **1981**, *85*, 3944.

(24) Whalley, E. *J. Chem. Phys.* **1963**, *38*, 1400.