# Extreme Solvent Effects on Reaction Rate Constants at Supercritical Fluid Conditions

The reaction rate constant was adjusted continuously over two orders of magnitude for the unimolecular decomposition of $\alpha$-chlorobenzyl methyl ether using the supercritical fluid solvent 1,1 difluoroethane. Activation volumes were observed as low as $-6{,}000\ cm^3/mol$, which is about an order of magnitude more negative than those reported previously in the literature for a homogeneous reaction. Spectral shift (solvatochromic) data were measured for phenol blue in the same fluid in order to interpret the rate data. A method is presented to predict solvent effects on rate constants at supercritical fluid conditions.

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## Introduction

In the highly compressible supercritical fluid state, density-dependent properties such as the solubility parameter and dielectric constant of a solvent, and the partial molar volume of a solute are extremely strong functions of temperature and pressure (Kim et al., 1985). This sensitivity of the "solvent strength" is a primary basis for supercritical fluid extraction (Paulaitis et al., 1983; Johnston, 1984; McHugh and Krukonis, 1986; Wong and Johnston, 1986) and chromatography (Randall, 1982), and could potentially be used to control certain chemical reactions, although few systems have been studied (Subramaniam and McHugh, 1986; Aida and Squires, 1986). A modest change in the temperature or pressure of a supercritical fluid solvent can strongly affect rates in reaction processes for two different thermodynamic reasons. Reaction rates can be altered significantly by adjusting the solubilities and thus the concentrations of reacting species over a wide range. The rate constant itself and thus the rates of certain reactions could potentially be adjusted over several orders of magnitude using a modest change in pressure to adjust the solvent strength. Whereas each of these effects on rates can be pronounced, very little information has been published concerning solvent effects on rate constants at supercritical conditions.

Our objective is to demonstrate experimentally the existence of an extremely large thermodynamic solvent effect on rate constants in the supercritical fluid state and to provide a theoretical explanation. A method is presented to predict this solvent effect over several orders of magnitude. Our criteria for choosing a model reaction are:

- The solvent effect should be large and well-characterized in liquids
- Side reactions should be minimal
- The reaction should be able to be monitored *in situ*
- The reaction should be simple in order to gain a fundamental understanding of the solvent effect

The thermal decomposition of $\alpha$-chlorobenzyl methyl ether fulfills all of the above criteria. For example, the rate changes by about five orders of magnitude as the solvent is changed from carbon tetrachloride to acetonitrile. Because this reaction is an ideal model for a wide class of polar reactions, the results should be applicable to many such reactions.

This work will test our previous predictions concerning solvent effects on rate constants at supercritical conditions (Kim and Johnston, 1986, 1987b). Previously, the solvent effect was predicted using solvatochromic data, that is, shifts in the absorption wavelength of an indicator dye caused by the solvent. Solvatochromic scales are used commonly to correlate solvent effects on reaction rate and equilibrium constants in the liquid state (Reichardt, 1979; Dack, 1976). This work will attempt to demonstrate that this technique is also applicable for the supercritical fluid state. The calculation of solvent effects on rate constants using solvatochromic parameters is extremely useful since the latter can be measured very rapidly.

There are potential advantages in using supercritical fluids solvents instead of liquid solvents for certain reactions, although they are poorly understood since only limited data are available.

1. The diffusion coefficient is about an order of magnitude larger (Paulaitis et al., 1983), so that overall rates may be larger, for example, for enzymatically catalyzed reactions (Hammond et al., 1985; Randolph et al., 1985).
2. The product of a reversible reaction or of an enzymatically catalyzed reaction could be removed continuously by a phase change using supercritical fluid extraction to improve the yield.
3. Additional types of reactions could be integrated with

supercritical fluid separation processes to achieve a large degree of control for producing a product of high purity (Subramaniam and McHugh, 1986).

4. The selectivity of a multiple-path reaction could be altered by adjusting concentrations and/or rate constants (Klein, 1986). For example, the selectivity of endo- to exo- product for parallel Diels-Alder reactions of methylacrylate and cyclopentadiene was adjusted in supercritical carbon dioxide (Kim and Johnston, 1987a).

5. Carbon dioxide, which is relatively inert, nontoxic, and nonflammable, is a desirable solvent for processing foods and pharmaceuticals. A fundamental understanding of the solvent effect on reaction rate constants in the supercritical region would be of great value for achieving many of these potential advantages.

## Experimental Method

The reactant $\alpha$-chlorobenzyl methyl ether was synthesized from benzaldehyde-dimethylacetal (Kwart and Silver, 1975). It was stored in dry ice under a nitrogen atmosphere. The initial concentrations of the reactant, $\alpha$-chlorobenzyl methyl ether, and a product, benzaldehyde, were calibrated using proton nuclear magnetic resonance (NMR). The solvent 1,1 difluoroethane (Linde, Halocarbon 152A, min. purity 98%) was used as received.

The experimental apparatus is shown in Figure 1. The 6.35 cm OD by 1.75 cm ID 316 stainless steel reactor contained two 2.5 cm dia. by 1 cm thick sapphire windows that were flat to within one wavelength of yellow light. A Teflon 0-ring was inserted between the window and a flat surface on the steel vessel. The pressure and temperature ranges were 0 to 400 bar and −30 to 250°C, respectively. The temperature was controlled to within ±0.3°C with a platinum resistance thermometer that extended 1 mm inside the inner surface of the cell, and two cartridge heaters. The reactor was insulated about the circumference and the temperature of the cell compartment of the spectrophotometer was maintained below 50°C using flowing air as a coolant. The pressure was adjusted using a 100 cm$^3$ syringe pump and was measured to within ±0.1% with a 710A Heise digital pressure gauge, which is traceable to an NBS standard. The pressure varied less than 0.5 bar during a run. Because the reactor and pump were separated using 3 m of 760 $\mu$m ID tubing, the amount of reactant and products that diffuses out of the reactor was determined to be negligible both experimentally and theoretically, for a time period of several hours. The concentration of products was measured using a Varian (Cary) 2290 UV-visible spectrophotometer.

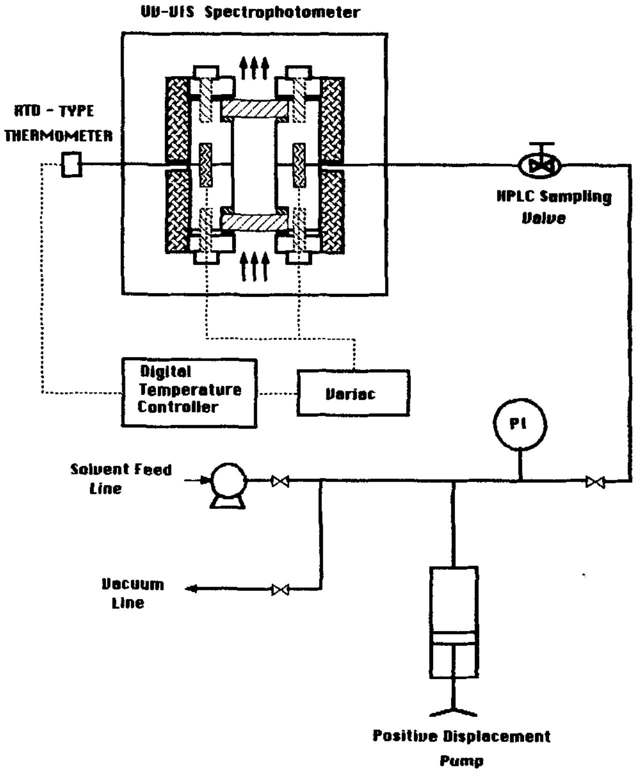

**Figure 1. Apparatus for measurement of reaction kinetics in supercritical fluids.**

To prepare for a run, the cell was evacuated and purged with nitrogen. This procedure was repeated three times. The temperature was equilibrated at the desired value and the sample loop was loaded at room temperature with oxygen-free ether. The ether was displaced into the cell by using the supercritical solvent to begin the reaction, and the pressure was adjusted immediately. The first-order kinetics was monitored *in situ* by measuring the benzaldehyde concentration. Each series of runs was performed in the order of increasing pressure to keep all of the reactants and products in the reaction cell. For rate constants on the order of $5 \times 10^{-7}$ and $1 \times 10^{-4}$, the uncertainties were approximately 50 and 5%, respectively. The rate constants in several experiments that were performed in liquid chloroform and carbon tetrachloride agreed with those of Kwart and Silver (1975) to within 10%.

## Thermodynamic Solvent Effect on Rate Constants

Thermodynamic solvent effects on reaction rate constants can be described using transition state theory. The reactants and transition state are assumed to be in equilibrium so that for the reaction

$$A + B \rightleftharpoons M^{\ddagger} \rightarrow \text{products} \tag{1}$$

the rate constant is

$$k = \kappa k_B T/h \cdot K^{\ddagger} \cdot \gamma_A \gamma_B / \gamma_M^{\ddagger} \tag{2}$$

and the equilibrium constant is

$$K^{\ddagger} = \gamma_M^{\ddagger} x_M^{\ddagger} / (\gamma_A x_A \gamma_B x_B) \tag{3}$$

The activation volume is defined by the pressure derivative of Eq. 2, where the rate constant must be expressed in pressure-independent units, for example, mole fraction units

$$\Delta v^{\ddagger} = -RT(\partial \ln k_x / \partial P)_T = \bar{v}_M^{\ddagger} - \bar{v}_A - \bar{v}_B \tag{4}$$

If the rate constant is expressed in concentration units, the isothermal compressibility is included in an alternative expression (Hamann, 1963)

$$RT(\partial \ln k_c / \partial P)_T = -\Delta v^{\ddagger} + (1 - n) RT k_T \tag{5}$$

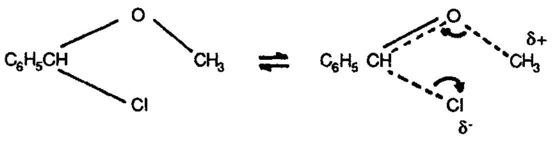

**Figure 2. Proposed polar transition state for thermal decomposition of $\alpha$-chlorobenzyl methyl ether (Kwart and Silver, 1975).**

where $n$ is defined by the sum of the stoichiometric coefficients of the reactants (when the coefficient is unity for the transition state). For a first-order reaction, $k_x = k_c$, and the units are $s^{-1}$. Here, $n = 1$, and the second term in Eq. 5 is zero. For a second-order reaction in a relatively incompressible liquid solvent, the second term in Eq. 5 is usually small compared to $\Delta v^{\ddagger}$ and is often neglected. In supercritical fluid solvents, it is important to include the compressibility term, except for the case of first-order reactions.

The standard state, which is present in both $K^{\ddagger}$ and in the activity coefficient, does not appear in Eq. 4 due to a cancellation that takes place upon differentiation of the logarithm of Eq. 2. There are two components of the activation volume: a repulsive or intrinsic part due to the change in occupied volume between the reactants and the transition state, and a part due to attractive solute-solvent forces. The repulsive part can be useful for investigating reaction mechanisms as it is a function of changes in molecular volume when bonds are broken or formed. The part due to attractive forces is significant particularly when there is a large change in the polarity between the reactants and the transition state. For a unimolecular decomposition reaction, the repulsive part of the activation volume is positive due to an increase in bond length as bonds are broken (Hamann, 1963). If the polarity of the transition state exceeds that of the reactants, the solvent-dependent part of the activation volume is negative due to electrostriction.

The thermal decomposition of $\alpha$-chlorobenzyl methyl ether

$$C_6H_5CHCl{-}O{-}CH_3 \rightarrow C_6H_5CHO + CH_3Cl \qquad (6)$$

was studied previously in a series of liquid solvents and determined to be first order (Kwart and Silver, 1975). A possible mechanism similar to an E1 mechanism was suggested and is shown in Figure 2. At 298 K, the activation energies are 122 and 26.4 kJ/mol in carbon tetrachloride and acetonitrile, respectively, while the activation entropies are −31.4 and −251 J/mol/K. The above mechanism is consistent with the observation that the solvation of the highly polar transition state increases with the polarity of the solvent. The solvent structure about the polar transition state is more ordered than about the reactant due to interactions of the large dipole with the dielectric solvent, that is, electrostriction. This effect is more pronounced for the more polar solvent. No side reactions were observed. Because of its simplicity, this reaction is a desirable candidate for gaining a fundamental understanding of the nature of solvent effects in the supercritical state.

**Table 1. Rate Constant for Unimolecular Decomposition of $\alpha$-Chlorobenzyl Methyl Ether in 1,1-Difluoroethane**

| Press. bar | Rate Constant, $k_x = k_c$, $10^6\ s^{-1}$ | | |
|---|---|---|---|
| | $T = 403$ K | $T = 423$ K | $T = 453$ K |
| 44.8 | 0.486 | 2.69 | 10.4 |
| 44.8 | 0.678 | 2.21 | — |
| 48.3 | 0.882 | 3.31 | 10.9 |
| 48.3 | 0.948 | 2.89 | — |
| 55.2 | 2.97 | 6.85 | 14.4 |
| 55.2 | 3.56 | 4.64 | — |
| 62.1 | 7.57 | 10.9 | 16.3 |
| 62.1 | 5.70 | 9.63 | — |
| 69.0 | 11.9 | 17.4 | 20.5 |
| 69.0 | 9.89 | 18.4 | — |
| 137.9 | 28.0 | 75.4 | 78.0 |
| 137.9 | — | 86.2 | — |
| 206.8 | — | 92.4 | — |
| 206.8 | — | 99.8 | — |
| 275.8 | 29.9 | 108.0 | 146.0 |
| 344.7 | 42.4 | — | — |

## Solvent Effect on Rate Constants at Supercritical Fluid Conditions

The measured first-order rate constants for the thermal decomposition of $\alpha$-chlorobenzyl methyl ether in 1,1-difluoroethane ($T_c = 386.6$ K, $P_c = 45.0$ bar) are listed in Table 1 for three isotherms. The 403 and 423 K isotherms are shown in Figure 3. At 300 bar and 403 K, the rate constant is nearly comparable to that in carbon tetrachloride at the same temperature. The rate constant is relatively insensitive with respect to pressure above 130 bar, where carbon dioxide is relatively incompressible. This result is similar to those of high-pressure kinetic studies in the liquid state in that a change in pressure of many hundreds of bars is required to achieve a significant change in the rate constant. For example, the rate constant for the Diels-Alder reaction of chloroprene and maleic anhydride changes only by a factor of 5.8 in acetone at 65°C for a change in pressure of 1,400 bar (McCabe and Eckert, 1974).

The data are striking in the highly compressible near-critical

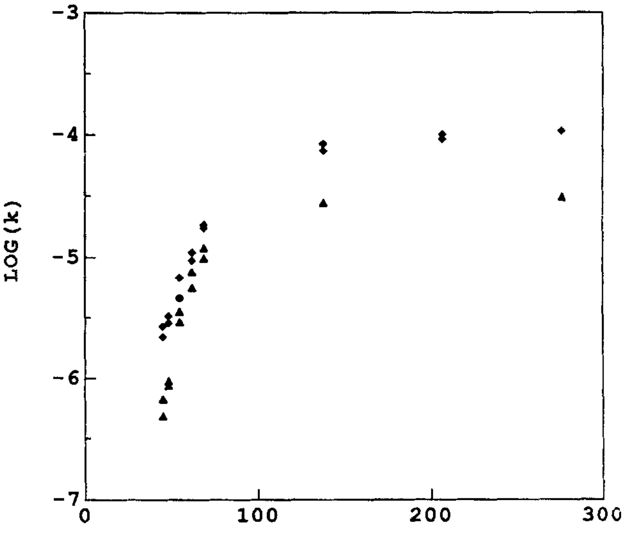

**Figure 3. Rate constant for unimolecular decomposition of $\alpha$-chlorobenzyl methyl ether in supercritical 1,1-difluoroethane.**

▲ 403 K; ◆ 423 K

region where the slope of the rate constant vs. pressure is extremely pronounced. At 403 K, the rate constant changes one order of magnitude as the pressure changes from 44.8 to 60 bar. It changes about two orders of magnitude between 44.8 and 340 bar. It would be possible experimentally to extend this range to about four orders of magnitude by lowering the pressure further, although it would extend the run time to about seven days. This isothermal change in a rate constant for a noncatalyzed homogeneous reaction in a single solvent is significantly greater than that of others reported in the literature (Reichardt, 1979; Subramanian and McHugh, 1986). This demonstrates a new principle in which the solvent effect on a rate constant can be adjusted with a single supercritical solvent instead of a variety of liquid solvents.

The 423 and 453 K isotherms are further removed from the critical point so that the density and thus the rate constant are somewhat less sensitive with respect to pressure, Figure 3, Table 1. The maximum slope for each isotherm is located at the same point as the maximum compressibility of the pure solvent for reasons that will become apparent upon examination of activation volumes.

## Activation Volumes in Supercritical Fluid Solvents

The activation volume, which is obtained from the slope of the logarithm of the rate constant vs. pressure, Eq. 4, is plotted vs. pressure in Figures 4 and 5 at 403 and 423 K, respectively. At 275 bar and 423 K, it is $-71.6$ cm$^3$/mol, which is a little more negative than values that are observed for liquid solvents. However, in the highly compressible region, the activation volume reaches $-6{,}000$ cm$^3$/mol at 403 K, and would approach even more extreme values at the pure solvent critical point for reasons discussed below. At the lowest pressures, the magnitude of the activation volume increases with pressure as does the isothermal compressibility. Beyond the point of maximum compressibility, the compressibility and thus the magnitude of the activation volume decrease sharply with pressure. This correspondence with the compressibility was also observed for partial molar volume data for naphthalene in carbon dioxide (Eckert et al., 1986).

The behavior of a solute near the critical point of an almost pure solvent has been studied using a lattice gas model (Wheeler, 1972; Gilbert and Eckert, 1985). It was shown that the activity coefficient of a solute at infinite dilution exhibits anomalous behavior near the critical point of the solvent. Activity coefficient vs. pressure isotherms resemble density vs. pressure isotherms for the pure fluid. At the critical point of the solvent where the isothermal compressibility is infinite, the slope of the infinite dilution activity coefficient vs. pressure isotherm is also infinite. As a result, the pressure derivative of the chemical potential, that is, the partial molar volume of the solute, also becomes infinite (Kim et al., 1985).

The pronounced values of the partial molar volume in the critical region may be understood by an examination of the triple product relationship

$$\bar{v}_i = v k_T n (\partial P/\partial n_i)_{T,V,nj} \tag{7}$$

At constant volume, the pressure decreases with the introduction of solute due to the attractive forces between the relatively polarizable solute and the much smaller solvent molecule (Eckert et al., 1986). In the highly compressible supercritical region, an extremely large volume contraction is required to return to the original pressure. As a result, the partial molar volume of the solute at infinite dilution becomes negative infinity as the compressibility of the solvent diverges.

For a large solute in a supercritical fluid, the minimum in the infinite dilution partial molar volume of a solute occurs at the maximum in the compressibility (Kim et al., 1985). We have also shown that a maximum in the slope of a solubility vs. pressure isotherm also occurs at this point. The data in Figures 4 and

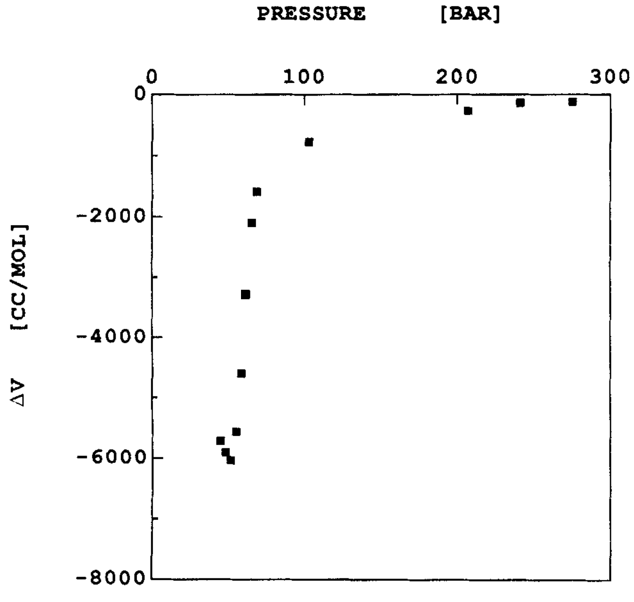

**Figure 4. Activation volume for unimolecular decomposition of $\alpha$-chlorobenzyl methyl ether in supercritical 1,1-difluoroethane at 403 K.**

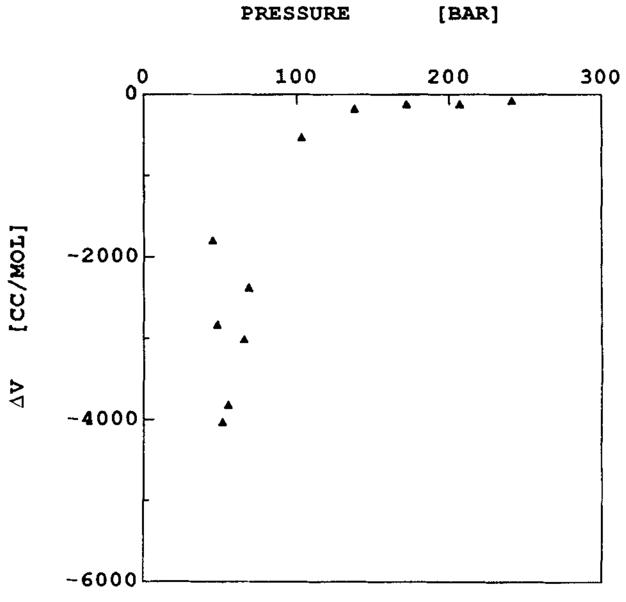

**Figure 5. Activation volume for unimolecular decomposition of $\alpha$-chlorobenzyl methyl ether in supercritical 1,1-difluoroethane at 423 K.**

5 indicate that the minimum in the activation volume or the point where the pressure effect on the rate constant is a maximum also occurs at this point where the compressibility is a maximum. All of these phenomena represent a strong divergence, as they are described by the derivative of a density variable with respect to a field variable (pressure) while holding a field variable (temperature) constant (Levelt-Sangers et al., 1983). At infinite dilution, the critical phenomena for the mixture become like those of the pure fluid so that these properties diverge at the critical point of the solvent.

The activation volume may be analyzed in terms of a repulsive part and an attractive part as described above. Using Eqs. 4 and 7, the activation volume may be expressed in terms of each of the above forces by

$$\Delta v^\ddagger = v k_T n[(\partial P/\partial n_M^\ddagger - \partial P/\partial n_A)^{rep} + (\partial P/\partial n_M^\ddagger - \partial P/\partial n_A)^{attr}] \quad (8)$$

The repulsive term, which is a function of the size of the reactants, transition state, and solvent, may be approximated at a given density using an equation of state for hard spheres. For reactions in the liquid state, the compressibility is small so that activation volumes are on the order of ±0 to 50 cm³/mol. Since the magnitudes of partial molar volumes are large in the highly compressible region, for example, −7,800 cm³/mol for naphthalene in carbon dioxide at 35°C and 79.7 bar (Eckert et al., 1986), the magnitude of activation volumes may also be large. Extremely pronounced activation volumes may be caused by a combination of the large compressibility along with (1) a repulsive contribution, or (2) an attractive contribution, or (3) both a repulsive and attractive contribution simultaneously. The first case has not been demonstrated experimentally. It is clear that the activation volume for the unimolecular decomposition of $\alpha$-chlorobenzyl methyl ether is dominated by the combination of the compressibility with the solute-solvent attractive forces. The repulsive term would give a positive activation volume due to bond breaking.

The effect of the compressibility on the activation volume may be treated separately from that of the solute-solvent forces using Eq. 8. A specific class of reactions will be considered in which the effect of attractive forces, for example, dipole-dipole and induction forces, is much greater than that of repulsive forces. For the van der Waals equation of state, the attractive part of the $\partial P/\partial n$ factor at infinite dilution is given by

$$n(\partial P/\partial n_2)^{attr} = -2a_{12}\rho^2 \quad (9)$$

For a given solvent at a given temperature and pressure, the magnitude of the activation volume increases in proportion to the difference in the solute-solvent attraction energies for the transition state and reactant. This difference in the $\partial P/\partial n$ factors may be expected to be larger for reactions with large changes in polarity during activation compared with isopolar reactions.

Solvent effects on reactions involving dipoles are often treated using Kirkwood's expression for the free energy of transferring a sphere, which contains a distribution of charges from a vacuum of unit dielectric constant to a medium of dielectric constant, $\epsilon$. The resulting expression for the rate constant is semiquantitative and is given by (Kirkwood, 1934; Laidler, 1965)

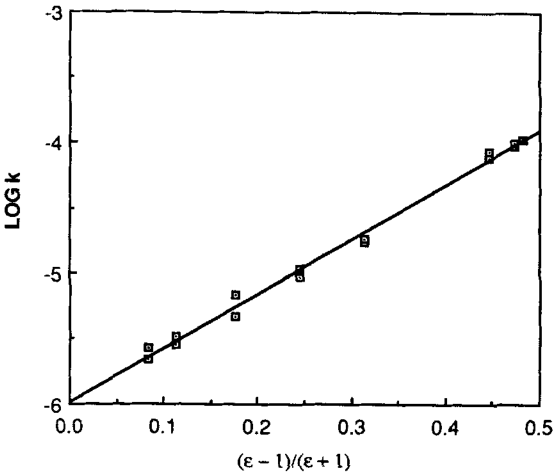

**Figure 6. Solvent effect on rate constant, $k_x - k_c$ (s$^{-1}$), for unimolecular decomposition of $\alpha$-chlorobenzyl methyl ether in supercritical 1,1-difluoroethane at 423 K using the Kirkwood expression, Eq. 10.**

$$\ln k = \ln k_g + \frac{e^2}{2k_BT}\left(\frac{1}{\epsilon} - 1\right)\left(\frac{z_A^2}{r_A} - \frac{z_A^2}{r_\ddagger}\right) + \frac{3}{8k_BT}\left(\frac{1-\epsilon}{\epsilon+1}\right)\left(\frac{\mu_A^2}{r_A^3} - \frac{\mu_\ddagger^2}{r_\ddagger^3}\right) \quad (10)$$

where $k_g$ is the rate constant in the gas phase. For the decomposition of $\alpha$-chlorobenzyl methyl ether, the second term is negligible since none of the species is ionic. The dielectric constants were calculated using the Onsager (1937) equation and densities that were calculated using the Peng-Robinson equation of state. The activation volume, which is obtained by differentiation of Eq. 10, is

$$\Delta v^\ddagger = \frac{3N_{avag}}{8}\left(\frac{\mu_A^2}{r_A^3} - \frac{\mu_\ddagger^2}{r_\ddagger^3}\right)\frac{\partial}{\partial P}\left(\frac{\epsilon-1}{\epsilon+1}\right) \quad (11)$$

For a given reaction, the pressure effect would increase as $\partial(\epsilon - 1)/(\epsilon + 1)/\partial P$ increases. Since the dielectric constant is a density-type variable, it is extremely sensitive with respect to pressure in the critical region. The derivative $\partial(\epsilon - 1)/(\epsilon + 1)/\partial P$ is related qualitatively to the compressibility so that there are some similarities between Eq. 8 and Eq. 11.

The application of the Kirkwood expression, Eq. 10, to the decomposition of $\alpha$-chlorobenzyl methyl ether in 1,1-difluoroethane is shown in Figure 6. Linear behavior would not be expected to be observed in general in the highly compressible near-critical region because of clustering, a phenomenon described below. The dipole moment change between the reactant and transition states is approximately 5 Debye according to this equation. This estimate is only approximate since it is based on the assumptions that there is no difference in the size of the reactants and transition state and that the effects of clustering are insignificant. The large increase in dipole moment upon activation is compelling evidence for a mechanism of the form given in Figure 2. It causes the solute-solvent attraction term in Eq. 8 to be quite large so that, for a solvent at a given temperature, pressure, and compressibility, the magnitude of the activation volume is larger than in previous studies (Simmons and Mason, 1972, Alexander and Paulaitis, 1987). For the decomposition of nitrogen pentoxide, the change in the dipole moment is extremely small so that the rate constant is similar in the gas phase and in solution (Laidler, 1965).

In a recent note (Dooley et al., 1987), it was claimed that there is an absence of unusual effects on $k_c$ near the mixture critical pressure based on data for three reactions taken from the literature: the dimerization of chlorotrifluorethane, hydrogen iodide decomposition, and the Menschutkin reaction of triethylamine and ethyl iodide. The third case is not relevant since the solvents were liquids and not supercritical fluids. The HI decomposition data in the literature are not well suited for the objective of showing large effects in the critical region for a number of reasons. The reduced temperature range was relatively far from unity compared to that in the present work, consequently the compressibility of the fluid mixture was smaller and was a weaker function of pressure. The pressure and the critical pressure of the mixture, which varied during the reaction as up to 20% of the HI decomposed, were not measured. In the third reaction, the dimerization of chlorotrifluorethane, the pressure effect was pronounced with an activation volume, which was calculated using the virial equation of state, of about 3,000 cm$^3$/mol at 120°C and 45 bar. In this bimolecular reaction, the pressure effect on $k_x$ was more pronounced than on $k_c$, Eqs. 4 and 5. In the unimolecular reaction of the ether in the present work, the two rate constants, $k_x$ and $k_c$, are identical. The large pressure effect for a unimolecular reaction was not anticipated by Simmons and Mason (1972) according to their Eq. 27, because it was assumed that the pressure dependencies on the fugacity coefficients of the reactant and the transition state would be similar. The pressure effect on the fugacity coefficient is a function of the partial molar volume. Our explanation is that although the pressure effect on the rate constant is a function of the difference between the partial molar volumes of the reactant and transition states, the difference of these large quantities may often be significant in the critical region even for a unimolecular reaction.

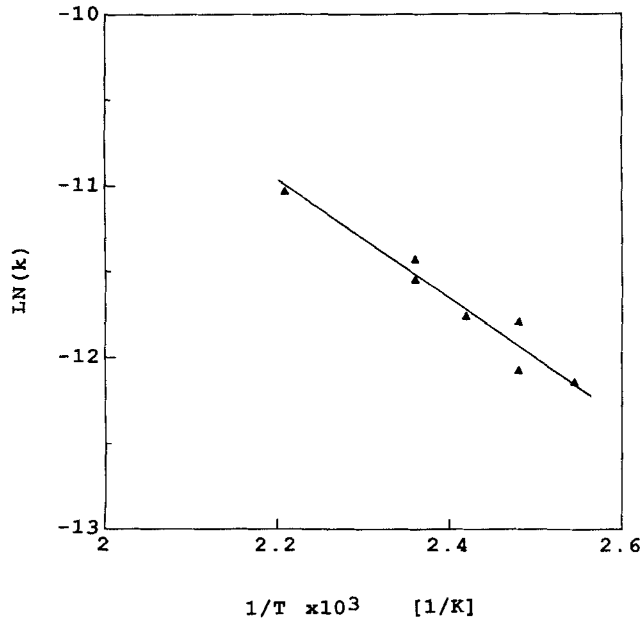

**Figure 7. Arrhenius activation energy plot for unimolecular decomposition of α-chlorobenzyl methyl ether in supercritical 1,1-difluoroethane at 6.2 MPa.**

**Table 2. Activation Enthalpies and Entropies for Thermal Decomposition of α-Chlorobenzyl Methyl Ether at 403 K**

| Solvent | $k$, 403 K s$^{-1}$ | $\Delta h\ddagger$ kJ/mol | $\Delta s\ddagger$ kJ/mol/K |
|---|---|---|---|
| Fluids | | | |
| $CF_2H_4$(6.2MPa) | $7.6 \times 10^{-6}$ | 24 | −285 |
| Liquids | | | |
| $CH_3CN$ | $4.6 \times 10^{-4}$ | 23 | −254 |
| $C_6H_5NO_2$ | $1.5 \times 10^{-2}$ | 75 | −96 |
| $CHCl_3$ | $7.2 \times 10^{-4}$ | 79 | −112 |
| $C_6H_5Cl$ | $1.9 \times 10^{-4}$ | 95 | −84 |
| $C_6H_5CH_3$ | $8.3 \times 10^{-5}$ | 105 | −66 |
| $CCl_4$ | $6.3 \times 10^{-5}$ | 118 | −34 |

In the compressible region, the range of the attractive forces is short compared to the distances between the molecules, so that the attractive forces influence the structure of the fluid (Alder et al., 1972). The highly compressible solvent is attracted preferentially around the large highly polarizable solute, as is evident from the large negative values of the partial molar volume. The local density and the local dielectric constant of the solvent exceed that of the bulk values, which increases solvation. This effect of clustering on the local dielectric constant and thus on the rate constant is described quantitatively in the last section.

The rate constant was measured for a series of temperatures at 62 bar (900 psia) in order to determine the activation energy, Figure 7. The activation energy, 27.6 kJ/mol, is much smaller for difluoroethane than for most of the liquid solvents studied by Kwart and Silver (1975), Table 2. The activation enthalpy, $\Delta h^\ddagger = \bar{h}^\ddagger - \bar{h}_A$, and activation entropy, $\Delta s^\ddagger = \bar{s}^\ddagger - \bar{s}_A$, were calculated using transition state theory, Eqs. 2–4. The activation enthalpy, which is given by

$$\Delta h^\ddagger / RT^2 = (\partial \ln k_x / \partial T)_{P,x} - 1/T \qquad (12)$$

does not depend upon the standard state. The activation entropy was obtained using Eq. 2 along with the $\Delta h^\ddagger$ from Eq. 12. For this definition of the activation entropy, the ratio of the activity coefficients in Eq. 2, $\gamma_A/\gamma_A^\ddagger$, is set equal to unity.

The activation enthalpy in supercritical difluoroethane is much smaller than in most of the liquid solvents in Table 2; for example, it is 55 kJ/mol less in difluroethane than in chloroform, which has a similar polarity. The results are interesting in that the activation enthalpy and entropy in supercritical difluoroethane are very different than in a liquid solvent of the same polarity. The activation energy includes an intrinsic ideal gas part, which would be greater than 118 kJ/mol (the value in the least polar of the solvents in Table 2), and a solvation part. This small activation enthalpy, which corresponds to a large negative solvation enthalpy of activation, suggests that there is a relatively strong interaction or electrostriction about the polar transition state relative to the less polar reactant state. The large negative activation entropy is consistent with the small activation enthalpy due to a highly ordered transition state. This relationship between the activation entropy and enthalpy was also observed for the liquid solvents. The activation enthalpy and entropy are similar for supercritical difluoroethane and for liquid $CH_3CN$ even though the latter is much more polar. The most likely explanation for these results is that the compressible fluid difluoroethane clusters about the reactant and transition state so that the local polarity exceeds the bulk polarity.

The magnitude of the partial molar enthalpy can also be extremely large in highly compressible fluids since it is directly related thermodynamically to the partial molar volume (Levelt-Sengers, 1986). For example the partial molar configurational enthalpy, $\bar{h}_2 - h^{ig}$, is about −500 kJ/mol for 2,3-dimethylnaphthalene in carbon dioxide at 35°C and 80 bar (Johnston et al., 1987). For the reaction of interest in supercritical 1,1-difluoroethane, the partial molar enthalpies for the reactant and transition state are large and negative so that the solvation enthalpy of activation is a relatively large negative value. It would be of interest in the future to examine the temperature effect even closer to the critical point, where the partial molar enthalpy of the solute is extremely pronounced, to determine the degree to which the activation enthalpy may be adjusted.

## Prediction of Rate Constant Using Solvatochromic Scales

The effect of the polarity of a solvent on reaction rate constants may be correlated more quantitatively with solvatochromic ($E_T$) scales than with the Kirkwood function (Reichardt, 1979). The transition energy, $E_T$, of phenol blue in a solvent is equal to $hcN_{Avag}/\lambda_{max}$ where $\lambda_{max}$ is the absorption wavelength at the maximum. The shift in $\lambda_{max}$ is a strong function of the polarity and/or the polarizability of the solvent since the dipole moment of the excited state is 2.5 Debye greater than that of the ground state (Reichardt, 1979). As a result, the energy of the excited state is stabilized more than that of the ground state by induction forces, dipole-dipole forces, and specific interactions such as hydrogen bonding. Therefore, the transition energy decreases as the "strength" of the solvent increases (red shift). Because of this large change in the dipole moment during electronic excitation, phenol blue is an extremely sensitive probe of the strength and structure of solute-solvent interactions. For example, the $E_T$ is 217 kJ/mol (51.96 kcal/mol) in *n*-hexane and 197 kJ/mol (47.03 kcal/mol) in methanol, a difference of 58 nm, while the experimental accuracy is ±0.2 nm (±0.08 kJ/mol).

In liquid solvents, the rate constant has been correlated with solvatochromic parameters for a number of reactions (Reichardt, 1979). For example, the rate constant of the unimolecular dissociation of *t*-butyl peroxyformate has been correlated accurately with the $E_T$ scale for phenol blue by (Kamlet et al., 1979)

$$\ln k_x = -aE_T + b. \tag{13}$$

In this work, the units of $k_x$ and $E_T$ are $s^{-1}$ and kJ/mol, respectively.

**Table 3. Transition Energies for Phenol Blue in 1,1-Difluoroethane**

| | $E_T$, kJ/mol | |
|---|---|---|
| Press. bar | $T = 403$ K | $T = 423$ K |
| 44.8 | 232.2 | 231.5 |
| 48.3 | 231.1 | 231.3 |
| 55.2 | 228.4 | 231.1 |
| 62.1 | 226.2 | 230.5 |
| 69.0 | 224.7 | 229.4 |
| 137.9 | 221.9 | 224.1 |
| 206.8 | 221.2 | 221.9 |
| 275.8 | 219.9 | 220.5 |
| 344.7 | 219.3 | — |

Spectroscopic $E_T$ data were measured in supercritical difluoroethane in order to correlate the rate constant data for the α-chlorobenzyl methyl ether decomposition reaction. The data are shown in Table 3, and the 423 K isotherm is shown as a function of density in Figure 8. As the density of the solvent about the dye increases, the red shift increases or $E_T$ shifts to lower energy. At a given density, the $E_T$ is relatively insensitive with respect to temperature over the small range studied. It is extremely sensitive with respect to pressure in the highly compressible critical region, as is the density.

The logarithm of the rate constant for the decomposition of α-chlorobenzyl methyl ether in supercritical 1,1 difluoroethane is correlated linearly vs. the $E_T$ of phenol blue in Figure 9 at a temperature of 403 K using Eq. 13. At 403 K, the slope, intercept, and correlation coefficient are 0.337 mol/kJ, 64.2, and 0.98, respectively. The units of $E_T$ are kJ/mol. At 423 K, the values are 0.337 mol/kJ, 65.1, and 0.95. The slope is nearly the same as the value of 0.342 that was obtained for a series of liquid solvents at 298 K (Kwart and Silver, 1975), although the intercept is different because of the activation energy. These results suggest that solvatochromic parameters are a useful tool for the prediction of pressure effects on rate constants in supercritical fluids.

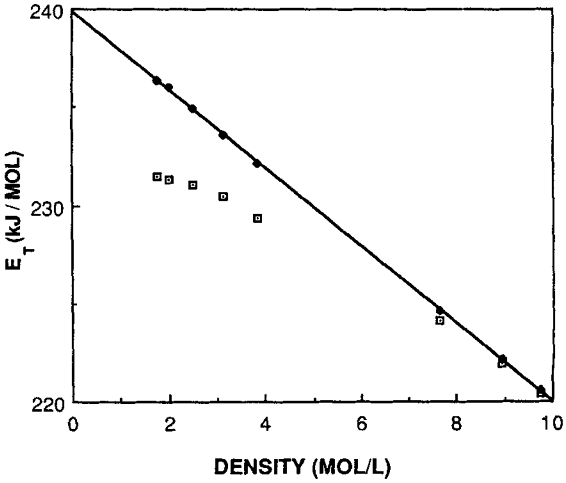

**Figure 8. Transition energy for phenol blue vs. density in supercritical 1,1-difluoroethane at 423 K.**

□ Observed values; Eq. 15

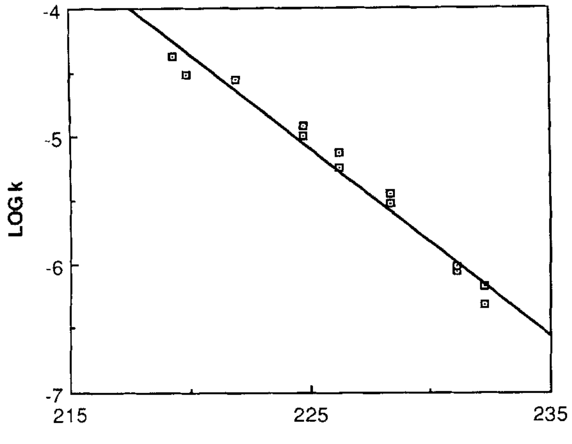

**Figure 9. Correlation of rate constant for unimolecular decomposition of $\alpha$-chlorobenzyl methyl ether with $E_T$ of phenol blue at 403 K.**

The observation that Eq. 13 is applicable for numerous reactions indicates that there is some similarity between the mechanisms of the two processes. In both cases, the solvent stabilizes a more polar excited state to a greater degree than a nonpolar ground of reactant state. The correlation of log $k$ vs. $E_T$ is linear even in the highly compressible region, a result that is not surprising since clustering occurs in both processes.

There are some differences in the two processes in that electronic excitation is much faster than the rate of generation of activated complexes of the ether. The solvent structure about phenol blue does not change during electronic excitation, which is much faster than molecular motion. Even so, phenol blue in the ground state must cause a substantial degree of clustering in the critical region, since it is known that clustering is substantial even in nonpolar systems, for example, for naphthalene in ethylene (Eckert et al., 1986). Another difference in the two processes is that repulsive forces affect some rate constants although they have little effect on the transition energy for electronic excitation. As a result, Eq. 13 is applicable only to reactions where the effect of the repulsive term is insignificant compared with the solute-solvent attraction term.

Solvent effects on several reactions at supercritical conditions were compared above in terms of either $\partial P/\partial n$ factors or dipole moments of reactants and transition states. A useful comparison may also be made using the solvatochromic $E_T$ parameter for phenol blue; however, it is limited to reactions where the solute-solvent attraction term is dominant compared with repulsion. Differentiation of Eq. 13 gives

$$\Delta v^{\ddagger} = +aRT(\partial E_T/\partial \rho)_T \rho k_T \qquad (14)$$

where the constant $a$ depends only on the nature of the reaction. At infinite dilution the properties $E_T$ and $k_T$ are a function only of the solvent. Even if the constant $a$ is small, for example, in an isopolar reaction, the magnitude of an activation volume can be extremely large if the compressibility is extremely large. The constant $a$ is a relative measure of solvent effects such as electrostriction on a rate constant vs. solvent effects on electronic excitation for phenol blue. For the Diels-Alder reaction of isoprene and maleic anhydride, there is only a modest change in polarity between the reactants and the transition state, so that the value of $a$ is only 0.251 mol/kJ (Kim and Johnston, 1986). For the Menschutkin reaction of tripropylamine and methyliodide where the transition state is much more polar than the reactants, $a$ is 0.674 (Kim and Johnston, 1987b). For the decomposition reaction of $\alpha$-chlorobenzyl methyl ether, $a$ is 0.337. For a given solvent at a given temperature and pressure, the ratio of activation volumes of two reactions is given approximately by the ratio of the $a$ constants. This approach is useful as it separates the activation volume into a reaction-dependent, solvent-independent part and a solvent-dependent, reaction-independent part. This separation can not be obtained using Eq. 8 since the $\partial P/\partial n$ factors are a function of the solvent as well as the reaction.

## Effects of Clustering on Rate Constant

Another major use for the $E_T$ data is to approximate the degree of clustering of a supercritical fluid about a large polar solute, in this case phenol blue or $\alpha$-chlorobenzyl methyl ether. Local densities of solvent about the solute will be determined in order to modify the Kirkwood expression to obtain a more meaningful correlation of the rate constant in the highly compressible region. Although the degree of clustering will be somewhat differing for phenol blue than for $\alpha$-chlorobenzyl methyl ether, it should not be grossly different since the polarizabilities of the molecules are similar.

The phenomenon of clustering has been explored previously for both nonpolar and polar supercritical mixtures. An Augmented van der Vaals equation was used successfully to include the effects of attractive forces on clustering for a variety of systems (Johnston et al., 1982). Clustering was described for water about an ion in the critical region using a modified Born equation (Wood et al., 1981). At 17.7 MPa ($P_r$ = 0.803) and 327°C ($T_r$ = 0.927) the local density of water about the ion was 0.9 g/cm$^3$ compared with a bulk density of 0.64 g/cm$^3$, which leads to a corresponding increase in the dielectric constant.

The degree of clustering will be approximated by comparing the spectroscopic data with the theory of McRae (1957). The McRae equation for the $E_T$ of a dye in a homogeneous polarizable dielectric solvent is

$$E_T = A\left(\frac{n^2-1}{2n^2+1}\right) + B\left(\frac{\epsilon-1}{\epsilon+2} - \frac{n^2-1}{n^2+2}\right) + C \qquad (15)$$

where $n$ is the refractive index. The constants $A$, $B$, and $C$ are functions of the properties of the dye such as the dipole moment and oscillator strength of the ground and excited states and the cavity radius. The calculated result for Eq. 15 is in agreement with the data at high density, yet it underpredicts the shift in the compressible region as it neglects the additional solvation from clustering that is due to attractive forces, Figure 8. Previously, it was shown that the local density of solvent about the dye may be estimated by a direct comparison of the data with the calculated result (Kim and Johnston, 1986, 1987b). For example, according to Figure 8, a homogeneous fluid with a density of 5 mol/L would give the same $E_T$, that is, 230 kJ/mol (55 kcal/mol), as the actual fluid at a bulk density of only 3.3 mol/L. This difference in densities diminishes to zero as the isothermal compressibility of the solvent becomes small.

Kirkwood-Buff solution theory was used previously to derive a relationship between the local density, $\rho^l$, the bulk density, and the compressibility (Kim and Johnston, 1986, 1987b)

$$(\rho^l - \rho)/\rho = a'k_T + b' \tag{16}$$

where $a'$ and $b'$ are functions of temperature. A similar relationship was derived independently (Debenedetti, 1987). The values of the local density, which were obtained from Figure 8, were correlated linearly using Eq. 16. This linear relationship was also observed for phenol blue in supercritical ethylene, carbon dioxide, and fluoroform and provides some justification for this technique for determining the local density (Kim and Johnston, 1986, 1987b).

The local densities obtained from the $E_T$ data will be used to include qualitatively the effects of clustering in the Kirkwood equation. Each local density was used to calculate a local dielectric constant using the Onsager equation. The local dielectric constant was used in the ordinary Kirkwood expression, Eq. 10. In the highly compressible near-critical region, the local dielectric constant exceeds the bulk value significantly due to the local solvent enrichment of the solute. As pressure increases, and the compressibility decreases, the local dielectric constant approaches the bulk value. As the result, the local dielectric constant changes less with pressure than the bulk value. According to the linear plot in Figure 10, the dipole moment change between the reactant and transition states in 8 Debye. Since the local dielectric constant is a weaker function of pressure than the bulk value over the range of interest, this value of 8 exceeds the value in Figure 6 by several Debye.

## Conclusions

A supercritical solvent can be used to bridge over a continuum the gap between gas phase and liquid phase kinetics. A rate constant was adjusted by an order of magnitude, using a pressure range of only 15 bar, to obtain an activation volume as low as $-6{,}000$ cm$^3$/mol, a result that is significantly greater than those reported in the literature. This suggests the possibility of a new design principle in which the solvent effect on a rate constant may be adjusted over a continuum with a single supercritical fluid instead of a series of liquid solvents.

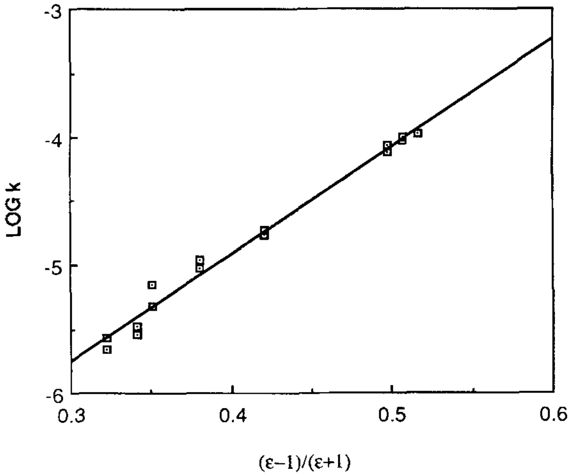

**Figure 10. Solvent effect on rate constant for unimolecular decomposition of $\alpha$-chlorobenzyl methyl ether in supercritical 1,1-difluoroethane using local values of dielectric constant in the Kirkwood expression, Eq. 10.**
$T$ = 423 K

There are two ways to interpret the extremely pronounced pressure effect on a rate constant in a highly compressible supercritical fluid. The first is based on the hypothesis that a given change in the solvent strength, for example, the solvatochromic transition energy $E_T$ or the local dielectric constant, causes the same change in the rate constant whether in a liquid or supercritical fluid state (Kim and Johnston, 1986, 1987b). The pressure effect is pronounced in supercritical solvents since a small change in pressure promotes a large change in the solvent strength. This work confirms the above hypothesis in that reaction rate constants in supercritical fluids can be correlated and in some cases predicted using solvatochromic parameters. The logarithm of the rate constant is linear with respect to $E_T$ since both the reaction and electronic excitation processes are influenced by a solvent effect on two states of differing polarity.

A second way to interpret the pressure effect is to examine the activation volume. This approach emphasizes the fact that partial molar volumes of solutes and therefore activation volumes can reach negative thousands of cm$^3$/mol in highly compressible near-critical fluids even though these values are small in liquid solvents. Activation volumes can be thousands of cm$^3$/mol even if the partial molar volumes of the reactants and transition state differ by only a small fraction.

The activation volume may be interpreted in terms of the property $\partial P/\partial n$, or $\partial E_T/\partial \rho$, or $\mu^2/r^3$; in each case it is a function of the compressibility as well. For the decomposition of $\alpha$-chlorobenzyl methyl ether, the large negative activation volume and entropy suggest that the clusters of solvent are more ordered about the transition state than the reactants. This pronounced thermodynamic solvent effect on a rate constant in a supercritical fluid can be explained by augmenting the Kirkwood expression to include clustering.

This description of the activation volume in terms of the density derivative of the solvatochromic parameter $E_T$ is useful for practical application as it separates the activation volume into a reaction-dependent, solvent-independent part and a solvent-dependent, reaction-independent part. In the future, a large amount of work is needed to explore the pressure effect for other types of reactions both at infinite dilution and finite concentration to continue to provide a fundamental understanding to aid the development of new processes.

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## Notation

$E_T$ = electronic transition energy for phenol blue
$k_x$ = rate constant based on mole fraction units
$k_T$ = isothermal compressibility, bar$^{-1}$
$n$ = refractive index
$\bar{v}_A$ = partial molar volume of $A$

### *Greek letters*

$\rho^l$ – local density
$\gamma$ – activity coefficient
$^\ddagger$ – transition state

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