Solvation Effects on Reactions of Triplet Benzophenone in Supercritical Fluids

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Laser flash photolysis of the hydrogen abstraction reaction of triplet benzophenone (^3BP) from 2-propanol and 1,4-cyclohexadiene in supercritical ethane and fluoroform was investigated. Bimolecular rate constants based on bulk concentrations decrease with an increase in pressure along both isotherms studied. These results corroborate our previous studies in CO_2 that show increased reaction rates due to enhanced local compositions of cosolvent around the ^3BP solute. Analysis of the results includes prediction of the thermodynamic pressure effect on the rate constant, which suggests an increase in the rate constant with pressure, as well as the effects of increased local cosolvent concentrations about ^3BP. Spectroscopic measurements of the local composition of 2-propanol about a solute in supercritical CO_2 are used to explain the apparent discrepancy between experiment and prediction, providing reasonable evidence that the local environment can influence kinetically controlled reactions in supercritical fluids.

Introduction

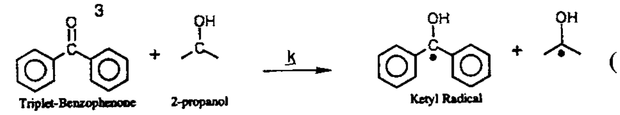
A significant number of experimental, theoretical, and simulation works have established that the local environment about a dilute solute in a supercritical fluid (SCF) or SCF/cosolvent mixture can be significantly different than the bulk. As in liquid solutions, solvation of a solute influences the nature of the local environment around that solute. We are interested in investigating how this solvation influences reactions in SCF mixtures. It has been shown that the local density of solvent around a dilute solute can be enhanced by as much as twice the bulk density in regions near and significantly below the critical point (Kim and Johnston, 1987a; Petsche and Debenedetti, 1989; Wu et al., 1990; Brennecke et al., 1990; Eckert and Knutson, 1993). Other studies have suggested that the local density augmentation exhibits a maximum between 0.4 and 0.8 of the critical density (Knutson et al., 1992; Sun et al., 1992; Carlier and Randolf, 1993). In addition, there is evidence that the local composition of cosolvent in the cybotactic sphere about a solute can be substantially greater than the bulk in SCF/cosolvent mixtures (Kim and Johnston, 1987b; Yonker and Smith, 1988; Ellington et al., 1994). These unique molecular-level environments in SCFs provide the capability of influencing and manipulating reactivity in SCFs with simple adjustments in temperature and pressure. Most of these measurements of the local environment were made using absorption and fluorescence probes of which the spectral characteristics are influenced by van der Waals, dipole/dipole, and dipole/induced dipole forces whose potential energies decay as $1/r^6$. Therefore, most of the contribution to the spectral features are from the first shell or two of solvent around the solute.

Some investigations have specifically focused on the potential impact that these local environments have on reactions in SCFs (Schroeder et al., 1990; Gehrke et al., 1990; Wu et al., 1991; Randolf and Carlier, 1992; Zagrobelny et al., 1992; Zagrobelny and Bright, 1992; Zagrobelny and Bright, 1993; Chateauneuf et al., 1992; Roberts et al., 1992, 1993a, 1993b; Ellington et al., 1994).

In a preliminary account we reported on effects of enhanced local cosolvent concentrations on kinetically controlled bimolecular reactions between a dilute solute and added cosolvent in SC CO_2. Laser flash photolysis (LFP) was used to examine the hydrogen abstraction reaction of benzophenone triplet (^3BP) with 2-propanol (Eq. 1) or cyclohexadiene (Eq. 2) in supercritical CO_2. Dramatic decreases in the bimolecular rate constant were observed with an increase in pressure throughout the intermediate density range (0.25 g/cm^3 < ρ < 0.6 g/cm^3). The experimental pressure effect on the rate constants (decreasing rate constant with an increase in pressure) was in contrast to that predicted from the thermodynamic pressure effect from transition state theory (Hamann and Bradley, 1963; Evans and Polanyi, 1935), which suggests that the rate constant should increase with an increase in pressure. This difference was credited to increased local concentrations of the cosolvent (2-propanol or 1,4-cyclohexadiene) about the ^{3}BP as the pressure was reduced.

In this article we further investigate the influence of solvation effects on bimolecular reactions of ^{3}BP with cosolvents in SCFs. The objectives of this article are (1) to study the ^{3}BP reaction with cosolvents in polar and nonpolar SCFs in order to verify the reaction mechanism and to investigate the importance of differing partial molar volumes in the various solvents; (2) to improve previous kinetic results based on recently available mixture density data and to present an empirical means of estimating the mixture densities of our systems; (3) to provide predictions of the thermodynamic pressure effect on the biomolecular rate constants and to make comparisons with experimental results; (4) to measure local compositions of cosolvent about a solute probe under conditions that mimic our reaction conditions; and (5) to provide analysis of the kinetic results of the reactions based on the local environment. This analysis will further confirm the significant influence that the local environment has on these kinetically controlled bimolecular reactions.

Specifically, here we extend the LFP investigations of the hydrogen abstraction reaction of ^{3}BP with two cosolvents, 2-propanol (Eq. 1) and 1,4-cyclohexadiene (Eq. 2), to supercritical ethane (C_2H_6) and fluoroform (CHF_3).



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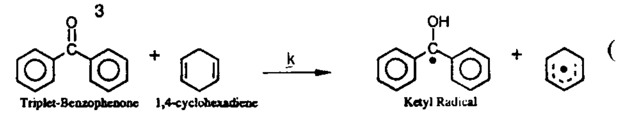

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When benzophenone is irradiated with laser light the molecules are excited to their first excited singlet state and quickly experience intersystem crossing to the ground triplet state (^{3}BP). This ground triplet state is very reactive toward hydrogen atom donors, such as 2-propanol or 1,4-cyclohexadiene. The triplet and the alcohol or diene react to form a ketyl radical. The triplet has an absorption spectrum in the ultraviolet–visible (UV–vis) range, so reaction kinetics can be determined with time-resolved absorption spectroscopy by monitoring the depletion of the triplet as it reacts. This reaction serves as a sensitive probe of the effect that enhanced local cosolvent concentrations can have on a reaction in a SCF, since it is the situation in which a dilute solute (^{3}BP) is reacting with a cosolvent (2-propanol or 1,4-cyclohexadiene). We report the results of the ^{3}BP reaction with 1,4-cyclohexadiene in SC ethane and fluoroform, as well as the results of the abstraction from 2-propanol in SC fluoroform. These results are discussed in terms specific to factors that affect reactions in SCFs, namely, the thermodynamic pressure effect on the rate constant, local density augmentations, and local composition effects. The purpose of this work is to examine the influence of local concentrations on reactions in detail and to study the influence of changing solvent polarity. New solvatochromic measurements of the local compositions of 2-propanol in SC CO_2, using the method of Kim and Johnston (1987b), are presented and will be used to provide semiquantitative analysis of the local composition effect on the reaction of ^{3}BP and 2-propanol in SC CO_2.

Experimental Studies

Materials

Benzophenone (Aldrich, Gold Label) and 2-propanol (Fisher, ACS certified) were used as received. 1, 4-Cyclohexadiene (Aldrich Chemical) was purified by bulb-to-bulb distillation prior to use. Fluoroform (Dupont Freon-23, 98% purity) and ethane (Scott Specialty Gases, Ultra High Purity grade, 99.9% or Linde, CP grade) were passed sequentially through multiple high-pressure oxy-traps (Alltech) and multiple high-pressure charcoal traps (Alltech). Carbon dioxide (Scott Specialty Gases, SFC Grade, 2 ppm O_2) and phenol blue (*N,N*-dimethylindoaniline, Aldrich > 97%) were used as received.

Procedure

The high-pressure apparatus, the sample preparation, and the application of LFP to SCF samples were described in detail by Roberts et al. (1992) and Chateauneuf et al. (1992). LFP experiments were conducted using laser excitation (~ 8 mJ, pulse width, ~ 6 ns) from a Quanta Ray DCR-1 Nd:YAG laser system perpendicular to a pulsed 1000-W xenon lamp monitoring source. Transient absorption signals were digitized with a Tektronix 7912 AD, and a VAX-11/780 was used for experimental control and computer analysis. A 420-nm cutoff filter was used during the kinetic measurements at 580 nm and when absorption spectra were being measured at wavelengths greater than 420 nm.

General

The high-pressure cells used in these experiments had a 3-mL capacity (1.7-cm path length) and were fitted with Suprasil quartz windows having mechanical seals composed of lead and graphite packing (Roberts et al., 1992).

Experiments were performed on two isotherms, at $T_R = 1.007$ and $T_R = 1.044$, in fluoroform ($T = 28°C$, $T = 38.8°C$) and ethane ($T = 34.2°C$, $T = 45.6°C$). These reduced temperatures correspond to the same reduced temperatures studied previously in CO_2 (Roberts et al., 1992) ($T = 33°C$, $T = 44.4°C$). Absolute rate constants were measured for the reaction of ^{3}BP with 1,4-cyclohexadiene in ethane at 1,4-cyclohexadiene concentrations of 4.7×10^{-5} to 9.5×10^{-4} mole fraction (4.0×10^{-4} to 1.7×10^{-2} M) and in fluoroform for a 1,4-cyclohexadiene mole fraction range of 7.6×10^{-5} to 1.4×10^{-3} (4.0×10^{-4} to 2.0×10^{-2} M). Rate constants for the reaction of ^{3}BP with 2-propanol were measured in fluo-

Table 1. 1,4-Cyclohexadiene and 2-Propanol Mole Fractions, x

1,4-Cyclohexadiene		2-Propanol	
CHF_3	C_2H_6	CHF_3	CO_2
7.61×10^{-5}	8.65×10^{-5}	7.13×10^{-3}	5.66×10^{-3}
1.52×10^{-4}	1.74×10^{-4}	1.40×10^{-2}	7.12×10^{-3}
3.61×10^{-4}	3.83×10^{-4}	3.72×10^{-2}	9.73×10^{-3}
7.58×10^{-4}	6.93×10^{-4}	5.03×10^{-2}	1.70×10^{-2}
1.45×10^{-3}	1.44×10^{-3}	7.02×10^{-2}	3.03×10^{-2}
			4.27×10^{-2}
			6.01×10^{-2}

roform at 2-propanol concentrations of 5.7×10^{-3} to 5.0×10^{-2} mole fraction (0.03 to 0.75 M). These cosolvent compositions are given in Table 1. Concentrations of benzophenone were approximately millimolar (on the order of 10^{-4} mole fraction); however, only a small fraction of the benzophenone was excited to the triplet state so that the concentration of the reactive species was much lower, approximately on the order of micromolar. In other words, the systems studied can be considered solvent/cosolvent/solute systems, where the SCF is the solvent, the 2-propanol or the 1,4-cyclohexadiene is the cosolvent, and the ^3BP is an infinitely dilute solute.

Pressures studied in ethane ranged from 51.3 bar, slightly above the critical pressure, up to 91 bar for the experiments at 34.2°C. For the 45.6°C experiments in ethane, pressures studied were between 63 and 105 bar. In fluoroform, experiments were performed between 49 and 125 bar at 28°C and between 60 and 125 bar at 38.8°C.

A model 901A Heise pressure gauge was used to monitor the pressure of the sample cell to ±0.24 bar. The samples were brought to temperature and maintained at ±0.1°C with an Omega (model CN-6070A) temperature controller equipped with a Watlow Firerod cartridge heater and a platinum resistance thermometer making direct contact with the fluid. The critical pressure and temperature of ethane and fluoroform are 48.7 bar and 32.2°C, and 48.2 bar and 25.9°C, respectively.

LFP sample preparation

The sample preparation apparatus consisted of the solvent gas cylinder (ethane or fluoroform), an Isco high pressure syringe pump (model 260D), and a high pressure optical cell. Also included was either a reservoir containing 2-propanol or an in-line Reodyne HPLC injection valve for 1,4-cyclohexadiene sample preparation. Each component was connected with 1/16-in. (1.6-mm) stainless steel high pressure tubing and compartmentalized with high pressure (HIP) line valves fitted with Teflon O-rings.

The entire system was evacuated prior to sample preparation to minimize the presence of molecular oxygen. The 2-propanol was deaerated with high-purity N_2, and the alcohol reservoir was maintained under an atmosphere of N_2 during sample preparation. The amount of O_2 dissolved in the μL portions of 1,4-cyclohexadiene was considered to be insignificant.

For 2-propanol sample preparation, a desired amount of N_2-saturated alcohol was drawn into the syringe pump by applying a positive pressure of N_2 above the alcohol in the reservoir and by lowering the piston in the syringe pump to the desired internal volume. Cooling water (0°C) was then circulated through a jacket that surrounds the piston and cylinder assembly of the syringe pump, and the 1/16-in. (1.6-mm) tubing between the gas cylinder and the syringe pump was submerged in an ice bath. The remaining volume of the pump was subsequently filled with subcooled liquid solvent.

The 1,4-cyclohexadiene samples were prepared by injecting a known amount of 1,4-cyclohexadiene into the injection valve in-line between the solvent cylinder and the syringe pump. The pump was then filled with subcooled liquid solvent, as described, displacing the 1,4-cyclohexadiene into the pump.

In all sample preparations sufficient time was allowed for thermal equilibrium to be achieved between the temperature jacket and the pump. Using the temperature of the cooling water (0°C) and the pressures indicated on the Isco syringe pump, the mole fraction of the 1,4-cyclohexadiene samples was determined using densities calculated from the equation of state developed by Hori et al. (1982), for pure fluoroform, and the 32 parameter Benedict-Webb-Ruben equation of state for pure ethane (Younglove and Ely, 1988). Pure solvent densities could be used due to the small concentrations of 1,4-cyclohexadiene in the kinetic experiments. Verification of this method of mole fraction determination was presented previously (Roberts et al., 1992). The mole fractions of the 2-propanol samples were determined using mixture densities calculated by the method presented later in the experimental section. The average estimated uncertainty in the mole fractions is 2%. The pump was heated to above the critical temperature, raising the pressure well above the critical pressure such that the solution should be one phase at all times. The 1,4-cyclohexadiene mixtures were sufficiently dilute that the addition of these low concentrations of 1,4-cyclohexadiene should not significantly change the critical point from that of the pure solvent. Conversely, the 2-propanol was present in concentrations of up to 5 mol %. Unfortunately, we are not aware of any high pressure phase data for CHF_3/2-propanol mixtures. However, we maintained the system well above the equivalent reduced conditions of CO_2/2-propanol mixtures of the same concentrations (Radosz, 1986; Gurdial et al., 1993). The sample was allowed to mix and equilibrate for at least 12 hours. Part of the contents of the Isco pump was then loaded into the high pressure optical cell, which contained an appropriate amount of crystalline benzophenone. The cell was heated to facilitate mixing and raise the contents above the critical point. Benzophenone concentrations were determined with a Cary 1 UV–vis spectrophotometer or an SLM-Aminco Spectronic 3000 Array spectrophotometer and were typically 0.8 absorbance units at the laser excitation wavelength. Laser experiments were run from high to low pressures by allowing the homogeneous solution to escape via an external valve. Ample time was allotted for equilibrium at the individual pressures, as indicated by a stabilization in temperature and pressure.

Local composition sample preparation

Local compositions of 2-propanol were determined using the solvatochromatic probe phenol blue, following the method developed by Kim and Johnston (1987b).

UV–vis absorption spectra of 2.0×10^{-6} mol fraction phenol blue (near infinite dilution) in SC CO_2, in a CO_2/2-propanol mixture, and in pure 2-propanol were measured at 45°C at various pressures over the range of 80 bar to 250 bar.

SC Samples. A magnetic stirring bar was placed into a 250-mL vessel along with 2.3×10^{-3} g of phenol blue. The vessel was then submerged in an ice bath and allowed to come to thermal equilibrium. The vessel was evacuated and then either pressurized with CO_2 or the CO_2/2-propanol mixture. The mixture was then heated and mixed for at least 12 hours.

Part of the contents of the vessel was then transferred to a high pressure optical cell. The optical cell was maintained at 45°C and the pressure was monitored as described earlier. After equilibration, experiments were run by measuring three absorption spectra of the sample at a desired pressure. The maximum wavelengths, λ_{max}, were determined by smoothing the absorption spectra and subsequently determining where the first derivative was zero. The three values obtained for the three spectra were then averaged. Successive experiments were run from high to low pressure by allowing the homogeneous solution to be vented, and sufficient time was allowed for equilibration at the various pressures. The uncertainty in λ_{max} was ± 0.2 nm. These experiments were repeated several times to ensure reproducibility.

Liquid Samples. Absorption spectra of phenol blue in pure 2-propanol were measured in the following manner: 1.0×10^{-3} g of phenol blue was dissolved in 200 mL of 2-propanol. The high pressure optical cell was filled with this binary solution. The temperature was controlled at 45°C. An HIP model 50-6-16 hand-pressure generator was connected to the optical cell, and additional 2-propanol was added to increase the pressure. The λ_{max} was determined as described earlier.

SCF/2-propanol mixture density calculations

Kinetic experiments were performed using mixtures of known mole fraction. Data were acquired at a number of pressures for that given mole fraction sample. Since kinetic analysis requires the reactant concentrations in molarity, the mixture density is required at a variety of pressures along each isotherm. In an earlier study (Roberts et al., 1992) we presented results of the reaction of ^{3}BP with 2-propanol in SC CO_2 in which the biomolecular rate constants were calculated using cosolvent molar concentrations at the various pressures estimated from the mole fraction of the sample and the density of pure CO_2. Due to a lack of 2-propanol/CO_2 mixture density data, the mixture density was assumed to be equivalent to pure CO_2 densities as a first approximation. Subsequently, Tilly et al. (1994) measured mixture densities of 2-propanol/CO_2 mixtures, which we have used to improve our calculation of the previously reported bimolecular rate constants. Tilly et al. (1994) measured mixture densities at 45 and 55°C, and the results of their study are presented in Figure 1. We have used an empirical means of estimating mixture densities of cosolvent systems of this type and make comparison to the data of Tilly et al. (1994). Then this method is extended for use in the 2-propanol/CHF_3 system.

The mixture density can be estimated satisfactorily by multiplying the pure SCF density by a ratio of mixture density to pure density calculated from an equation of state (Tomasko, 1992; Ellington et al., 1994). In this case we have selected the Peng-Robinson (PR) equation of state (Peng and Robinson, 1976), as in Eq. 3.

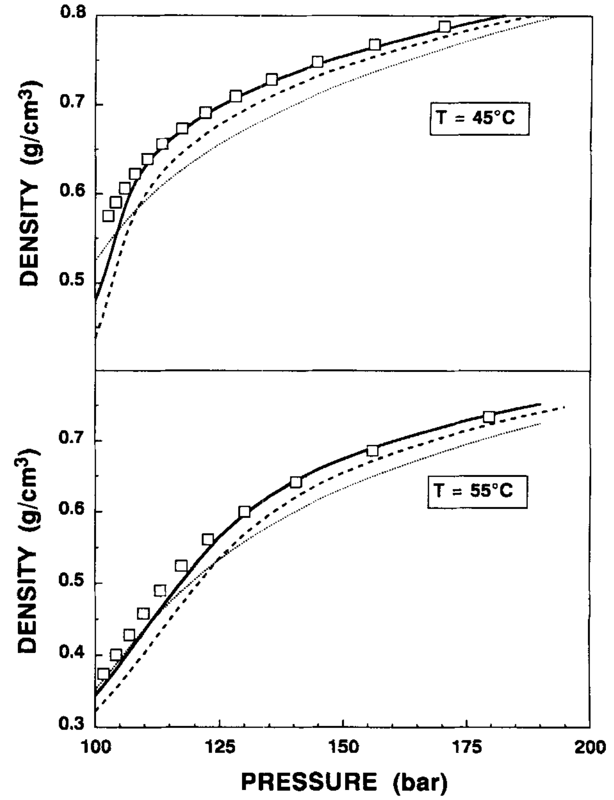

Figure 1. Densities of a 1 mol % 2-propanol/CO_2 mixture at 45° C (top) and 55° C (bottom).

Calculated by Eq. (3) (——) (see text) and the Peng-Robinson equation of state (······) compared to the experimental data (□) of Tilly et al. (1994) and pure CO_2 densities (- - -) (Angus et al., 1976).

$$\rho_{\text{mixture}} = \rho_{\text{pure solvent}} * [\,\rho_{\text{PRmixture}}/\rho_{\text{PRpure solvent}}\,]. \tag{3}$$

Pure CO_2 densities were calculated from the analytic equation of state developed by Angus et al. (1976) used in compilation of the IUPAC CO_2 density data. The mixture/pure density ratio was calculated from the Peng-Robinson equation of state with the binary interaction parameter (k_{ij}) in the Peng-Robinson equation set to give the best fit to the density data of Tilly et al. (1994). A comparison of the 1 mol % 2-propanol/CO_2 density data of Tilly et al. (1994) at 45°C and the densities calculated from this method are shown in Figure 1 (top). A k_{ij} of 0.15 was determined to give the best fit. For comparison, the pure CO_2 densities calculated from the equation of Angus et al. (1976) and the mixture densities calculated strictly from the Peng-Robinson equation with a k_{ij} of -5.0×10^{-3}, suggested by Tilly et al. (1994), are plotted as well. Clearly, the empirical method successfully reproduces the experimental data.

Figure 1 (bottom) compares experimental and estimated 1 mol % 2-propanol/CO_2 densities at 55°C. The experimental data are from Tilly et al. (1994), and the estimated values are calculated by multiplying the pure CO_2 density by the ratio of mixture to pure density calculated from the Peng-Robinson equation of state (optimum $k_{ij} = 0.1$). The pure IUPAC CO_2 densities and the mixture densities calculated from the Peng-Robinson equation of state alone are presented in the figure at both temperatures, as well. The empirical method of calculating the mixture densities satisfactorily reproduced the data of Tilly et al. (1994), and we have used this empirical technique to estimate the mixture density at our reaction conditions.

We have used the empirical method of calculating mixture densities given by Eq. 3 to correct our previously reported bimolecular rate constants for the reaction of ^{3}BP with 2-propanol at 44.4°C in SC CO_2. The kinetic measurements of the ^{3}BP reaction with 2-propanol in CO_2 at 44.4°C extended to lower densities than those studied in the experimental measurements of Tilly et al. (1994) at 45°C. We therefore expand our use of the model with best fit k_{ij} to the lower pressures in the kinetic experiments. As shown previously, the optimum values of k_{ij} used in this empirical method showed some temperature dependence from 45 to 55°C. Therefore, we will only use this method of mixture density estimation to reanalyze our previous results at 44.4°C ($T_R = 1.044$), where we feel confident in the appropriate value of k_{ij} and the estimates of mixture densities. We will not extrapolate this method to the lower temperature studied, $T = 33°C$ ($T_R = 1.007$), where there are no experimental mixture densities available to use to determine an appropriate k_{ij}. Moreover, we expect the estimates of mixture densities to be very sensitive to the value of k_{ij} at those conditions.

We used the method described earlier to determine the density of 2-propanol/CHF_3 mixtures as well. The pure CHF_3 density, determined from the equation of state developed by Hori et al. (1982), was multiplied by the ratio of mixture to pure density calculated from the Peng-Robinson equation of state. Since we are not aware of any 2-propanol/CHF3 mixture density data, the k_{ij} value used was 0.15, the optimum value for the 2-propanol/CO_2 system.

Results

We present the results of the hydrogen abstraction reaction of ^{3}BP with either 1,4-cyclohexadiene or 2-propanol in SC CHF_3 and ethane. ^{3}BP was formed and monitored by LFP of benzophenone, as described earlier. LFP of benzophenone in pure SC CHF_3 resulted in the characteristic absorption spectrum of ^{3}BP. Figure 2 contains the absorption spectrum of ^{3}BP in pure SC CHF_3 measured 250 ns after the laser pulse. The absorption spectrum in CHF_3 is identical to the spectra obtained in pure CO_2 and liquid acetonitrile (Figure 2). Very little pressure effect was observed on the ^{3}BP absorption maximum measured over the pressure range of interest in SC CHF_3. In the absence of a hydrogen donor (cosolvent), ^{3}BP will react with itself in a diffusion-controlled triplet-triplet annihilation reaction. Insert A of Figure 2 shows a typical plot of ^{3}BP absorbance measured at a particular wavelength as a function of time in pure CHF_3. These absorbance signals decay by second-order kinetics over the entire pressure range studied, suggesting no change in the mechanism of ^{3}BP's natural decay (triplet-triplet annihilation), which we have studied in detail and have reported elsewhere (Roberts et al., 1993a). In that study, the decay process in pure CHF_3 was shown to follow simple diffusion-controlled behavior over the entire pressure range studied. In contrast, ^{3}BP shows some reactivity toward ethane (Roberts et al., 1993a), so we do not present the absorption spectrum of ^{3}BP in pure ethane. However, the reaction of the 1,4-cyclohexadiene with the ^{3}BP can still be studied under the proper concentration conditions where the contribution from the reaction with the 1,4-cyclohexadiene is sufficient to be distinguished from the reaction with the ethane solvent.

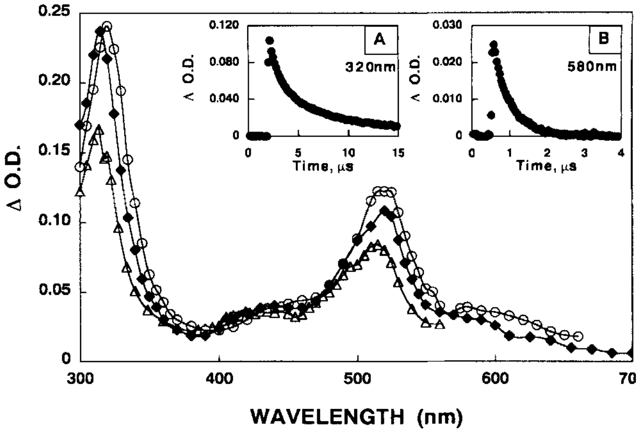

Figure 2. Transient absorption spectra observed 250 ns after 355-nm laser excitation of benzophenone in supercritical CHF_3 (Δ) (28.0°C, $T_R = 1.007$) at 120 bar, supercritical CO_2 (♦) (33.0°C, $T_R = 1.007$) at 140 bar, and in N_2-saturated liquid acetonitrile (○).

Absolute values (○) have been divided by 3. Insert A: ^{3}BP decay observed at 320 nm in pure CHF_3 at 28.0°C and 100 bar (see text). Insert B: ^{3}BP decay observed at 580 nm in a 1.5×10^{-4} mol % 1,4-cyclohexadiene/CHF_3 mixture at 28.0°C and 125 bar (see text).

The absolute kinetics for the reaction between the ^{3}BP and the cosolvent were obtained by monitoring the change in the rate of decay of the ^{3}BP absorption with added cosolvent (2-propanol or 1,4-cyclohexadiene). In these experiments, a vast excess of cosolvent is present compared to the concentration of ^{3}BP; therefore, the kinetics are pseudo-first order. Fitting the ^{3}BP decay with a single exponential (Figure 2, insert B) gives an observed pseudo-first-order rate constant, k_{obsd}. The disappearance of ^{3}BP was monitored at 580 nm in order to eliminate interference from the product, ketyl radical (see Eqs. 1 and 2), which has an absorption band similar to ^{3}BP but with negligible intensity at 580 nm. Reactions were studied from high to low pressure along two isotherms, $T_R = 1.007$ and $T_R = 1.044$, at several compositions of cosolvent that are presented in Table 1. In all cases, the observed rate constants were found to decrease with an increase in pressure above the critical pressure.

The rate of ^{3}BP decay with added cosolvent is a combination of its bimolecular reaction with cosolvent, and its first-order contribution from its unimolecular deactivation and any pseudo-first-order reaction with impurities:

$$\text{RATE} = -\frac{d[^3\text{BP}]}{dt} = k_{\text{obsd}}[^3\text{BP}]$$
$$= k_0[^3\text{BP}] + k_{bi}^{\text{bulk}}[^3\text{BP}][\text{cosolvent}]_{\text{bulk}} \quad (4)$$

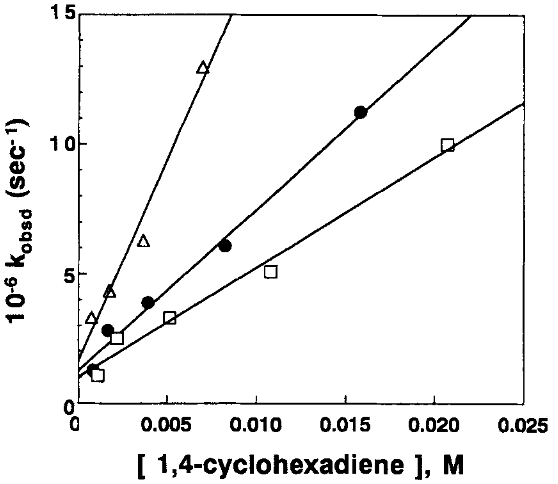

Figure 3. Bimolecular quenching plots for the reaction of ^{3}BP with 1,4-cyclohexadiene in supercritical CHF_3 at 125 (□), 56 (●), and 49 (△) bar and 28.0°C.

where

k_{obsd} = observed pseudo-first-order rate constant [s^{-1}]
k_o = first-order rate constant in absence of cosolvent [s^{-1}]
k_{bi}^{bulk} = bimolecular rate constant [$M^{-1}s^{-1}$] based on bulk cosolvent concentrations
[^{3}BP] = triplet benzophenone concentration [M]
$[\text{cosolvent}]_{bulk}$ = bulk cosolvent concentration [M]

Therefore, solving for k_{obsd},

$$k_{obsd} = k_0 + k_{bi}^{bulk}[\text{cosolvent}]_{bulk}. \quad (5)$$

According to Eq. 5, the bimolecular rate constant based on bulk conditions can be obtained by plotting the observed rate constants at any given (constant) pressure vs. the corresponding bulk concentrations of cosolvent, which will be detailed in the analysis section. The slope of this linear plot yields the bimolecular rate constant based on bulk concentrations of the reactants, k_{bi}^{bulk}. Note that k_{bi}^{bulk} determined in this manner are based on bulk concentrations of cosolvent. Figure 3 displays representative plots to determine the bimolecular rate constants for the reaction of ^{3}BP with 1,4-cyclohexadiene in CHF_3 at various pressures. The bimolecular rate constants for the reaction of ^{3}BP with 1,4-cyclohexadiene and 2-propanol are presented and discussed in the following sections. As we demonstrate below, these bimolecular rate constants yield information on the interaction between the cosolvent and the solute and are therefore excellent probes of the microenvironment in SCF systems. To demonstrate the significant influence of preferential solvation of cosolvent on these reactions, the bimolecular rate constants for the reaction of ^{3}BP with 2-propanol will be reanalyzed based on measurements of local concentrations of cosolvent around ^{3}BP.

1,4-Cyclohexadiene reaction

In a previous study (Roberts et al., 1992) we presented results of the reaction of ^{3}BP with 1,4-cyclohexadiene in SC CO_2. In that study we reported bimolecular rate constants that showed dramatic 4-fold decreases as the pressure was increased from 75 bar to 110 bar. This pressure effect is in contradiction to that predicted from the thermodynamic pressure effect on the rate constant that suggested that the rate constants should experience an increase over the same pressure change. The behavior was observed at both T = 33°C (T_R = 1.007) and T = 44.4°C (T_R = 1.044). The explanation presented was that preferential solvation of cosolvent around ^{3}BP in SC CO_2 was responsible for the apparent increase in the bimolecular rate constant.

The reaction with 1,4-cyclohexadiene was chosen for investigation in the previous study and in the present study because 1,4-cyclohexadiene does not have the possibility of self-association and its reaction with ^{3}BP has been studied extensively in liquids. Also, it is attractive because the reaction can be studied with low concentrations of 1,4-cyclohexadiene cosolvent. At these concentrations the phase behavior of the system should not be significantly different from that of the pure solvent.

To examine whether the solvation effects observed in our previous report are specific to the CO_2 solvent system, here we have expanded the investigations to include studies in both a polar (CHF_3) and a nonpolar (ethane) solvent. The studies were conducted at the same reduced temperatures (T_R = 1.007 and T_R = 1.044) and over a similar reduced pressure range.

As in the study with CO_2 as the solvent, the bimolecular rate constants based on bulk concentrations for the reaction of ^{3}BP with 1,4-cyclohexadiene exhibit a dramatic decrease as the pressure is increased in SC CHF_3 at both temperatures studied. The new results are shown in Figure 4 and demonstrate that k_{bi}^{bulk} ranged from 1.6×10^9 $M^{-1} \cdot s^{-1}$ to 4.3×10^8 $M^{-1} \cdot s^{-1}$ at 28°C and from 1.1×10^9 $M^{-1} \cdot s^{-1}$ to 4.4×10^8 $M^{-1} \cdot s^{-1}$ at 38.8°C in SC CHF_3. The average estimated

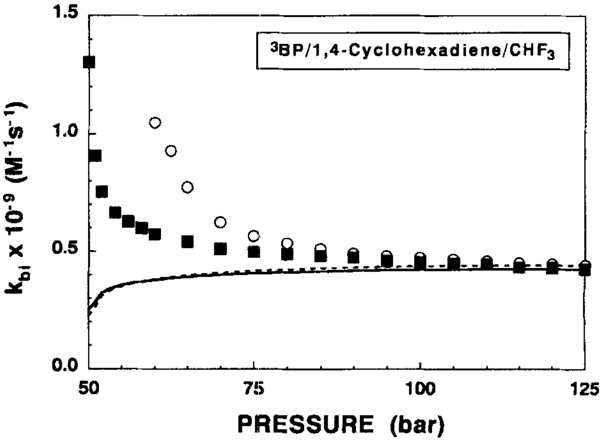

Figure 4. Pressure dependence of experimental bimolecular rate constants for reaction of ^{3}BP with 1,4-cyclohexadiene in supercritical CHF_3.

Based on bulk 1,4-cyclohexadiene concentrations at 28.0°C (■) and 38.8°C (○). (——) and (– – –) represent predictions of the thermodynamic pressure effect on the rate constants using the Peng-Robinson equation (see text) at 28.0°C and 38.8°C, respectively.

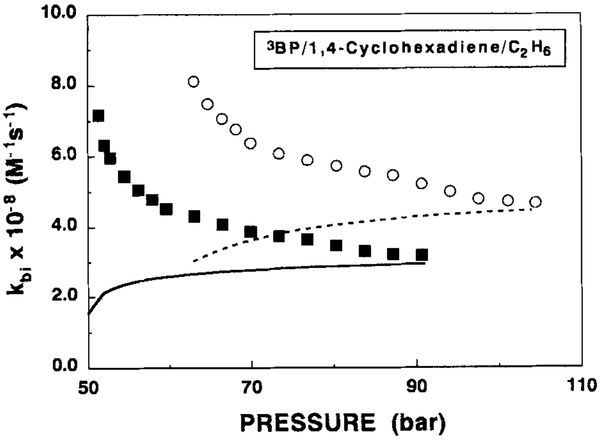

Figure 5. Pressure dependence of the experimental bimolecular rate constants for the reaction of ^{3}BP with 1,4-cyclohexadiene in supercritical ethane.

Based on bulk 1,4-cyclohexadiene concentrations at 34.2°C (■) and 45.6°C (○). (——) and (– – –) represent predictions of the thermodynamic pressure effect on the rate constants using the Peng-Robinson equation (see text) at 34.2°C and 45.6°C, respectively.

uncertainty in the k_{bi}^{bulk} is $\pm 9\%$ at 28°C and $\pm 8\%$ at 38.8°C. The lines in Figures 4 through 7 are calculated values of the pressure effect on the reactions and are explained later.

Unlike CO_2 and CHF_3, which behave as inert solvents, ^{3}BP reacts with ethane to form ketyl radical (Roberts et al., 1993a) as mentioned earlier. Fortunately, the rate of the reaction of ^{3}BP with ethane is small, so the reaction of ^{3}BP with 1,4-cyclohexadiene can still be studied in ethane as long as the concentrations of 1,4-cyclohexadiene are such that the reaction with 1,4-cyclohexadiene dominates. It was determined that the mole fractions of 1,4-cyclohexadiene in ethane studied here satisfied this criterion.

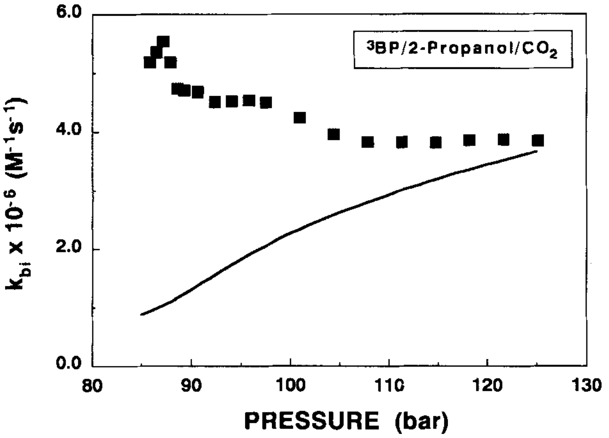

Figure 6. Experimental bimolecular rate constants (■) for the reaction of ^{3}BP with 2-propanol in supercritical CO_2.

Based on bulk 2-propanol concentrations vs. pressure, compared to predictions (——) of the thermodynamic pressure effect on the rate constants using the Peng-Robinson equation (see text) at 44.4°C.

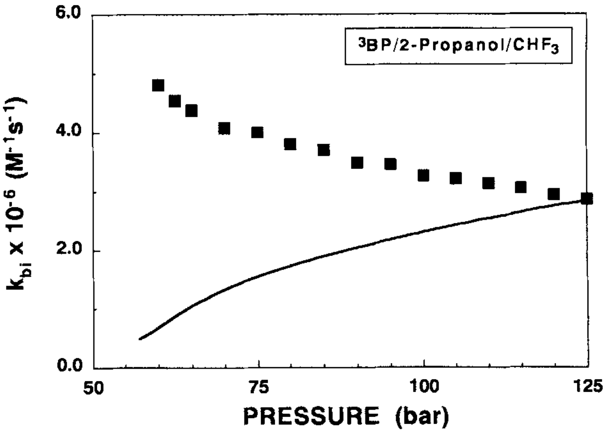

Figure 7. Experimental bimolecular rate constants (■) for the reaction of ^{3}BP with 2-propanol in SC CHF_3.

Based on bulk 2-propanol concentrations vs. pressure, compared to predictions (——) of the thermodynamic pressure effect on the rate constants using the Peng-Robinson equation (see text) at 38.8°C.

As in SC CO_2 and CHF_3, k_{bi}^{bulk} for the reaction of ^{3}BP with 1,4-cyclohexadiene in ethane demonstrate dramatic decreases as the pressure is increased on both isotherms studied, as shown in Figure 5. Values of k_{bi}^{bulk} in ethane ranged from 7.2×10^8 $M^{-1} \cdot s^{-1}$ to 3.2×10^8 $M^{-1} \cdot s^{-1}$ at 34.2°C and 8.1×10^8 $M^{-1} \cdot s^{-1}$ to 4.7×10^8 $M^{-1} \cdot s^{-1}$ at 45.6°C. The average estimated uncertainty in the k_{bi} is $\pm 9\%$ at 34.2°C and $\pm 8\%$ at 45.6°C.

Interestingly, decreases in k_{bi}^{bulk} of similar magnitude were observed on both reduced isotherms in both solvents, although the pressure effect is more subtle at the higher temperatures. The rate constants, k_{bi}^{bulk}, at $T_R = 1.044$ were slightly higher than at $T_R = 1.007$ in both CHF_3 and ethane due to thermal activation. Note that these bimolecular rate constants are based on bulk concentrations of cosolvent.

2-Propanol reaction

The reactivity of ^{3}BP toward 2-propanol is significantly lower than its reactivity toward 1,4-cyclohexadiene. Investigation of the ^{3}BP reaction with 2-propanol presented challenges in that higher concentrations of 2-propanol compared to 1,4-cyclohexadiene are required. Higher cosolvent concentrations (> 1%) can have significant influence on the phase behavior and, unfortunately, only limited data are available for the mixture densities of such systems. However, the alcohol cosolvent system served as a good probe since it allowed further analysis of the pressure effect on the rate constant based on the local environment. This effect was achieved by using measured local compositions of 2-propanol around a solute in SC CO_2, which is presented in a later section.

Previously we reported on the reaction of ^{3}BP with 2-propanol in SC CO_2. Due to a lack of mixture-density data for this system, rate constants were initially determined using cosolvent concentrations estimated from pure CO_2 densities, as a first approximation. Tilly et al. (1994) have since measured mixture densities of 2-propanol/CO_2 mixtures close to our reaction conditions, allowing implementation of an empirical means of mixture density estimation (see "Experimental" section). We have used this method of estimating mixture densities to obtain more accurate values of the cosolvent concentration and, subsequently, to improve our calculation of the kinetics of the ^{3}BP reaction with 2-propanol at 44.4°C, in SC CO_2. The results of this are presented in Figure 6. The k_{bi}^{bulk} obtained still exhibit a decrease with an increase in pressure. At 44.4°C, k_{bi}^{bulk} ranged from 5.2×10^6 $M^{-1}\cdot s^{-1}$ at 85.8 bar to 3.8×10^6 $M^{-1}\cdot s^{-1}$ at 125 bar. The average estimated uncertainty in the k_{bi} is $\pm9\%$ at 44.4°C. The k_{bi}^{bulk} results presented in Figure 6 are based on the bulk concentrations of 2-propanol.

The new data presented here are for the reaction of ^{3}BP with 2-propanol in SC CHF_3 at the same reduced temperature as studied in SC CO_2, $T = 38.8°C$, $T_R = 1.044$. Despite the large difference in the polarity of the solvent, the bimolecular rate constants obtained in CHF_3 (Figure 7) illustrate the same behavior as in CO_2. Values of k_{bi}^{bulk} decrease from 4.8×10^6 $M^{-1}\cdot s^{-1}$ at 60 bar to 2.9×10^6 $M^{-1}\cdot s^{-1}$ at 125 bar on the 38.8°C isotherm. The mixture densities used in the calculation of the 2-propanol concentrations in CHF_3 were determined by using the method described earlier (see "Experimental" section). The average estimated uncertainty in the k_{bi} is $\pm8\%$ at 38.8°C.

Local composition measurements

The local concentration of a cosolvent around a dilute solute in an SCF can be greater than the bulk (Kim and Johnston, 1987b; Yonker and Smith, 1988; Ellington et al., 1994). Solvatochromic probes have been used to estimate the local composition enhancements by monitoring changes in the wavelength of maximum absorption of the probe. Kim and Johnston (1987b) have used the solvatochromic scales of phenol blue to measure the local composition of several cosolvents around the probe in SC CO_2 at 35°C. In their report, Kim and Johnston (1987b) developed a model for estimating the local composition based on solvatochromic measurements and coordination number considerations (as discussed below). Yonker and Smith (1988) used a linear contribution of solvatochromic shifts method to estimate the local composition of 2-propanol in CO_2 about the probe 2-nitroanisole at several temperatures. Unfortunately, the bulk compositions in that study greatly exceeded those of interest here. However, they serve as a source of qualitative comparison. Ellington et al. (1994) used the linear method to measure the local compositions of methanol about phenol blue in SC CO_2 and used the measured local composition enhancements to analyze the kinetics of the reaction of phthalic anhydride with methanol in SC CO_2 at 40 and 50°C. They determined that the measured local compositions could account for increased reaction rate constants at lower pressures.

We have measured the local compositions of our reaction systems in order to further determine the influence of the local environment on reactivity. Ideally, the local composition of 2-propanol or 1,4-cyclohexadiene about benzophenone in the SCFs should be measured; however, the wavelength shifts of benzophenone were not enough to serve as a sufficient solvatochromic probe of the local environment in these SCFs. Thus, we have chosen to use the solvatochromic probe phenol blue as a model solute. Attempts to measure the local composition of 1,4-cyclohexadiene around phenol blue proved unsuccessful because the addition of the small amount of 1,4-cyclohexadiene used in these kinetic experiments did not sufficiently shift the maximum absorption. However, the addition of 2-propanol in the bulk composition range of interest did result in a sufficient shift in $\lambda_{\max}$ to allow measurement of the local composition about phenol blue. We have applied the solvatochromic method developed by Kim and Johnston (1987b) to estimate the local composition of 2-propanol in SC CO_2 at 45°C, and these local composition values were then used to further analyze the kinetic results presented in the previous section. The 2-propanol/CO_2 mixture was then used as a representative system for more detailed analysis of the kinetics data, as discussed below.

The more polar excited state of phenol blue is stabilized to a greater extent than the ground state as the solvent strength is increased (Kim and Johnston, 1987b). Therefore, as solvent strength is increased the transition energy, $E_T = hc/\lambda_{\max}$, decreases and $\lambda_{\max}$ shifts to longer wavelengths. In a mixed solvent, the solvatochromic shift is due to interaction of one or both solvent components with the probe molecule and the relative strength of these interactions. According to the solvatochromic model of Kim and Johnston (1987b), the mixture residual transition energy can be expressed as a sum of contributions of both solvent components as:

$$\Delta E_{Tm} = X_{12} Z_m (\Delta E_{T1}/Z_{12}) + X_{32} Z_m (\Delta E_{T3}/Z_{32}), \quad (6)$$

where ΔE_{Ti} is the residual energy of transition of phenol blue in a selected solvent i, and X_{12} and X_{32} are local mole fractions of CO_2 (1) and 2-propanol (3) about the probe phenol blue (2). The residual energy of transition is defined by

$$\Delta E_{Ti} = E_{Ti} - E_T^{\text{ideal gas}} \quad (7)$$

at constant temperature and pressure, where Z_{i2} is the coordination number for a pure solvent i about the probe (2) and Z_m is the coordination number for the solvent mixture about the probe (2). Local compositions of 2-propanol can therefore be estimated from measured wavelength shifts in the mixture and in both pure solvents.

Measurements of $\lambda_{\max}$ in pure CO_2, pure 2-propanol, and a 1 mol % 2-propanol/CO_2 mixture were made at 45°C over the pressure ranges of interest and are presented in Table 2. The $\lambda_{\max}$ data in the pure solvents were fit with smooth curves. Local compositions of 2-propanol were then estimated from Eq. 6 using the measured $\lambda_{\max}$ values in the mixed solvent and the corresponding $\lambda_{\max}$ values of the pure solvents determined from the fit curves. The method of Kim and Johnston (1987b) requires densities for each solvent and solvent mixture at the mixture conditions for determination of the coordination numbers. Densities of the pure CO_2 and the mixed solvent were determined as described in the experimental section. The density of the pure 2-propanol at various conditions was calculated by appropriate methods (Reid et al., 1987). The local composition results at 45°C are given in Figure 8. The local compositions of 2-propanol are greater

Table 2. λ_{max} for Phenol Blue in SCF CO_2, SCF CO_2/2-Propanol Mixture (1 mol %), and 2-Propanol at 45°C

SCF CO_2		SCF CO_2/2-Propanol Mixture (1 mol %)		2-Propanol	
P (bar)	λ_{max}	P (bar)	λ_{max}	P (bar)	λ_{max}
81.9	514.6	85.2	521.8	74.1	597.6
85.6	516.7	87.2	522.6	85.3	597.6
86.0	516	90.6	524.2	95.6	597.7
88.6	516.7	101.6	527.7	106.8	597.7
91.0	517.8	114.8	529.0	150.0	598.0
101.8	521.7	132.3	530.7	199.3	599.2
151.1	527.8	168.9	532.8		
201.0	530.6	199.9	533.0		
250.0	531.7	250.0	533.5		

than the bulk 1 mol % at all conditions studied, indicating that local composition enhancements are significant at these conditions. The local compositions at 45°C increased from 1.4 mol % at 250 bar to 9.0 mol % at 90 bar and then decreased to 8.5 mol % at 85 bar. If the linear model of Yonker and Smith is used (in which the ratios of the coordination numbers (Z_m/Z_{12} and Z_m/Z_{32}) are assumed equal to 1.0), similar results are obtained, yielding a local composition of as much as 8 mol % at the lower pressures. An experimental uncertainty of ±1 mol % was estimated based on variation in repetitive scans of the absorption spectrum of phenol blue in both pure CO_2 and the 2-propanol/CO_2 mixture. The magnitude of these 2-propanol local composition enhancements agree well with values reported by Kim and Johnston (1987b) for similar alcohols, such as methanol and ethanol, at 35°C and Yonker and Smith (1988) for 2-propanol at 44°C. For instance, Yonker and Smith (1988) reported a local composition nearly four times that of the bulk at 110 bar and 44°C for a bulk 5.1 mol % 2-propanol solution. This corresponds reasonably well with our local composition enhancement of 6 ± 1 times at 100 bar and 45°C for a bulk 1 mol % 2-propanol solution. Since the local compositions are significantly greater than the bulk at temperatures well removed from the critical temperature, this suggests that changes in the local environment are not direct functions of proximity to the critical point, but are controlled by short-range solvation interactions, which are important over a wide range of temperatures and pressures. While the observation of a slight maximum in the local compositions is interesting, it is hard to draw any conclusions about that feature due to the relatively large experimental uncertainty in these data (±1 mol %).

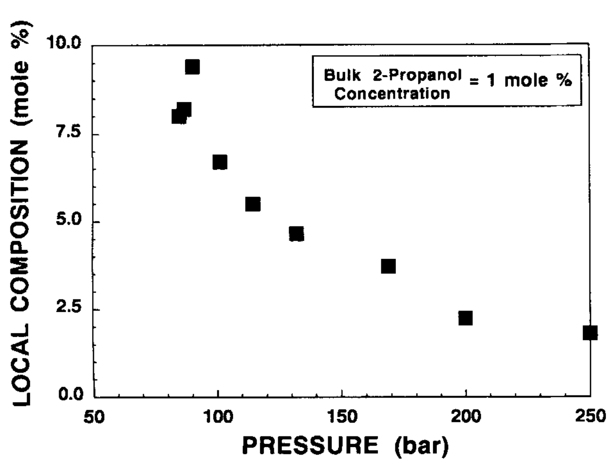

Figure 8. Local compositions of 2-propanol about phenol blue in 1 mol % 2-propanol/supercritical CO_2 at 45°C vs. pressure.

Overall, the local composition enhancements reported here are large enough to have a significant effect on reactivity and therefore on the experimentally determined rate constants of the hydrogen abstraction reactions of ^{3}BP.

Discussion

SCFs can have a variety of effects on reactions (Brennecke, 1993), and those pertinent to the ^{3}BP reaction are the thermodynamic pressure effect, the effect of local density augmentations, and the effects of increased local compositions of cosolvent (for more discussion of SC solvent effects on reactions see Brennecke, 1993; Roberts et al., 1992). The influence of each of these effects in regards to the H-abstraction reactions of this study are discussed below.

Thermodynamic pressure effect

Transition state theory (Evans and Polanyi, 1935) assumes a reaction model in which there is a thermodynamic equilibrium between the reactants and a transition state:

$$A + B \leftrightarrow [\text{transition state}]^{\neq} \rightarrow \text{products}.$$

From this the thermodynamic pressure effect on a bimolecular rate constant (Hamann and Bradley, 1963) can be obtained as

$$RT\left(\frac{\partial \ln k_{bi}}{\partial P}\right)_T = -\Delta v^{\neq} - RTk_T, \qquad (8)$$

where

k_{bi} = biomolecular rate constant ($M^{-1} \cdot s^{-1}$)
$\Delta v^{\neq} = \bar{v}_{TS} - \bar{v}_A - \bar{v}_B$ = reaction activation volume
$\bar{v}_i$ = partial molar volume
k_T = isothermal compressibility
R = gas constant
T = absolute temperature

Application to the H-abstraction reactions:

$$RT\left(\frac{\partial \ln k_{bi}}{\partial P}\right)_T + -(\bar{v}_{TS} - \bar{v}^3_{\text{BP}} - \bar{v}_{\text{cosolvent}})^{\neq} - RTk_T. \qquad (9)$$

The thermodynamic pressure effect is simply the difference in the partial molar volumes of the transition state and the two reactants minus a compressibility term as in Eq. 9. The thermodynamic pressure effect on reactions can be significant, with values of partial molar volumes in SCFs being reported in the literature (Eckert et al., 1986) as large as $-15{,}000$ cm^3/mol.

An equation of state can be used to calculate both the partial molar volumes and the isothermal compressibility. One can then compare the predicted pressure effect on the rate

Table 3. Critical Properties Used in Estimation of Partial Molar Volumes from the Peng-Robinson Equation of State

Component	T_c (K)	P_c (bar)	ω
Ethane	305.4*	48.7*	0.099‡
Fluoroform	299.1**	48.2**	0.260‡
Carbon dioxide	304.2†	73.8†	0.225†
2-Propanol	508.3‡	47.6‡	0.665‡
1,4-Cyclohexadiene	582.5§	45.4§	0.216§§
Triplet benzophenone	821.0§	33.0§	0.557§§
2-Propanol/^{3}BP transition state	994.0§	24.6§	0.993§§
1,4-Cyclohexadiene/ ^{3}BP transition state	1037.3§	22.8§	0.630§§

*Younglove and Ely (1988).
**Hori et al. (1982).
†Angus et al. (1976).
‡Reid et al. (1987).
§Reid et al. (1987); estimated-Joback's modification of Lydersons method (p. 14).
§§Reid et al. (1987); estimated-standard methods (p. 23).

constant from an equation of state to that obtained experimentally. For simplicity, we have chosen the Peng-Robinson equation of state since it is known to yield reasonable values of thermodynamic properties for SCF mixtures (Ellison, 1986), although, as with any cubic equation, it is expected to experience difficulties near the critical point. The details of the calculation of the partial molar volumes and k_T can be found elsewhere (Ellington et al., 1994). These calculations require the critical properties (T_c, P_c) and acentric factor (ω) of the components that are not known for many of our components and have therefore been estimated by appropriate group contribution methods (Reid et al., 1987). The Joback's modification of Lyderson's method (Reid et al., 1987, p. 14) was used to estimate both T_c and P_c, and the standard method (Reid et al., 1987, p. 23) was used to estimate the acentric factor. Table 3 contains the critical properties and acentric factors used in the calculations. The binary interaction parameters have been set to the default value of zero due to a lack of thermodynamic data for our system of components.

The results of the predicted pressure effect on the rate constant, $(\partial \ln k_{bi}/\partial P)_T$, were numerically integrated to predict trends in k_{bi} with pressure for direct comparison with experimental bimolecular rate constants. This comparison will be made in order to demonstrate the rate of change in the rate constants with pressure on an isotherm. The predicted k_{bi} at high pressure is assigned the value of the experimental k_{bi} at the same high pressure. In other words, the experimental and predicted bimolecular rate constants are forced to match at high pressure. Please note that the purpose of these calculations is to predict the change in k_{bi} with changing pressure and not the absolute value of k_{bi}.

1,4-Cyclohexadiene Reaction. Results of the calculations for the reaction between ^{3}BP and 1,4-cyclohexadiene are shown in Figures 4 (CHF_3) and 5 (ethane) at both reduced temperatures. Comparison of the experimental and predicted rate constants show opposite trends in the pressure effect on the rate constants. The predictions suggest that the rate should increase with an increase in pressure on both isotherms, while experiments show a dramatic decrease in the rate constant with increasing pressure. These results suggest that there does seem to be some thermodynamic pressure effect on k_{bi}, but that the observed effect of pressure cannot be explained solely by the thermodynamic pressure effect on the rate constant. Similar results were obtained in our previous study of the ^{3}BP reaction with 1,4-cyclohexadiene in SC CO_2, where opposite trends were observed between the predicted and experimental pressure effects on k_{bi}. Thus we conclude that there are other influences on the reactivity, namely, enhanced local concentration effects.

2-Propanol Reaction. A comparison of the experimental and predicted rate constants for the reaction of 2-propanol in CO_2 at 44.4°C and CHF_3 at 38.8°C are given in Figures 6 and 7, respectively. Predictions suggest that the rate constants should increase with pressure where the experimental rate constants based on bulk concentrations demonstrate a decrease with increasing pressure. Therefore, as in the case of the reaction with the more dilute cosolvent 1,4-cyclohexadiene, the reaction of ^{3}BP with 2-propanol demonstrates an experimental pressure effect on the rate constant opposite to that predicted from transition state theory using the Peng-Robinson equation. These opposite trends between prediction and experiment suggest that there are influences on reactivity other than the thermodynamic pressure effect on these reactions in SCFs.

Peng-Robinson k_{ij} Dependence. The calculated results are very sensitive to the values of the binary interaction parameters used. The binary interaction parameters between the species are not known and have been set to the default value of zero in the preceding calculations. For all systems, a slight increase in k_{bi} is calculated with an increase in pressure. We have varied the values of k_{ij} over a reasonable range in order to estimate the uncertainty in these calculations. Increasing all binary interaction parameters from 0.0 to 0.2 had essentially no effect on the calculations for all reactions. Increasing the strength of the interaction between one or two pairs of molecules will give an indication of the influence the individual k_{ij} have on the calculations. Selectively changing the k_{ij} of the ^{3}BP/cosolvent, or the transition state/solvent, or the ^{3}BP/transition state interactions, while leaving all other parameters at the default value of zero, had little or no influence on the predictions. Increasing the cosolvent/solvent k_{ij} to 0.2, and leaving all others set at 0.0, had a small effect on the calculations, exhibiting a slightly greater increase in the predicted k_{bi} with pressure than when all k_{ij} are set to 0.0. The only combinations of k_{ij} that demonstrate dramatic influence on the calculations are the situations in which there is a large disparity between the strength of the ^{3}BP/solvent interaction compared to the transition state/solvent interaction. If we set the k_{ij} for the ^{3}BP/solvent interaction to a value of 0.2 and leave the transition state/solvent interaction set at 0.0, the calculations suggest a much more dramatic increase in the predicted rate constant compared to the case where all k_{ij} are set to 0.0. Conversely, changing the transition state/solvent k_{ij} to 0.2 and leaving the ^{3}BP/solvent k_{ij} set at 0.0 yielded predicted rate constants that actually *decrease* with an increase in pressure. These latter two situations are, however, physically unrealistic cases since the transition state and ^{3}BP are of similar size and polarity and should have similar interactions with the solvent. The k_{ij} for the ^{3}BP/solvent interaction should be similar to that of the transition state/solvent. To demonstrate this, we have performed calculations in which the transition state/solvent $k_{ij} = 0.2$ and the ^{3}BP/solvent $k_{ij} = 0.15$, and vice versa, and found very similar predictions compared to situations where both the transition state/solvent and the ^{3}BP/solvent k_{ij} were set to 0.0 or 0.2. In all cases an increase in the predicted rate constant was observed with an increase in pressure. Hence, we believe that the calculated values of the activation volume and k_T should be regarded as first approximations rather than absolute values, but that they should give reasonable estimates of the trends expected.

The sensitivity of the predicted pressure effect to the estimates of the critical constants and acentric factors obtained from the group contribution methods was also investigated. Varying the critical temperatures of the ^{3}BP and the transition state for the 1,4-cyclohexadiene and 2-propanol reactions by more than ±30°C demonstrated an increase in the predicted rate constant with pressure in all cases. The variation of ±30°C was chosen because it represents changing an entire functional group in the molecule (Reid et al., 1987, p. 14). Varying the critical pressures and acentric factors of the ^{3}BP and the transition state for the 1,4-cyclohexadiene and 2-propanol reactions by more than ±15% also demonstrated an increase in the predicted rate constant with pressure in all cases. Again, the variation of ±15% was chosen since it represents changing an entire functional group. These results demonstrate that the prediction of an increase in rate constant with pressure is reasonably insensitive to different estimates of the critical constants and acentric factor.

In summary, the thermodynamic pressure effect from the Peng-Robinson equation predicts an increase in the rate constant with an increase in pressure for the ^{3}BP reaction with both 1,4-cyclohexadiene and 2-propanol at all conditions studied. In contrast, the experimental rate constants based on bulk concentrations of cosolvent k_{bi}^{bulk} decrease with pressure for both reactions. Clearly, the experimental rate constants based on bulk concentration cannot be explained solely by the thermodynamic pressure effect. This suggests that other effects, namely local composition enhancements and local density augmentations, have significant influence on these H-abstraction reactions.

Local concentration effects

It has been shown that the local environment about a dilute solute in an SCF or an SCF mixture can significantly differ from the bulk. There are two potential local effects that could influence these types of reactions in SCF systems. First, the local density of an SCF solvent about a dilute solute has been shown to be enhanced by as much as twice the bulk density in regions near and significantly below the critical point (Kim and Johnston, 1987a; Petsche and Debenedetti, 1989; Wu et al., 1990; Brennecke et al., 1990; Eckert and Knutson, 1993; Knutson et al., 1992; Sun et al., 1992; Carlier and Randolf, 1993). Second, there is evidence of enhanced local compositions of cosolvent about a dilute solute in SCF mixtures (Kim and Johnston, 1987b; Yonker and Smith, 1988; Ellington et al., 1994), with possibility of affecting reactivity in SCFs by changing the equilibrium reactant concentrations. The reactions in this study specifically mimic this situation, as discussed below. The influence of these local effects on reactions in SCFs have been discussed in detail elsewhere (Roberts et al., 1992; Brennecke et al., 1993; Ellington et al., 1994).

In our previous account of the ^{3}BP reaction with 1,4-cyclohexadiene and 2-propanol in CO_2 it was concluded that increased local concentrations of cosolvent around ^{3}BP could explain the apparent discrepancy between experiment and prediction. Here we measure a similar decrease in k_{bi}^{bulk} in CHF_3 and ethane. Because the thermodynamic pressure effect indicates an increase in the rate constant with pressure, we conclude that enhanced local concentrations of 1,4-cyclohexadiene or 2-propanol around ^{3}BP have significant influence on these reactions.

To further investigate this we measured local compositions of one of the cosolvents around a dilute solute mimicking the experimental conditions presented in the results section. In the following section we use these measured local composition enhancements along with estimates of overall local density augmentations to recalculate bimolecular rate constants based on this local environment for the reaction of 2-propanol with ^{3}BP in CO_2, as an example. These local concentration-based rate constants, k_{bi}^{local}, are compared with predictions of the thermodynamic pressure effect to determine if the local concentration enhancement can account for the apparent discrepancy between the predictions and experimental values of the rate constant based on bulk concentrations.

Local concentration analysis of 2-propanol reaction in CO_2

If the increased local cosolvent concentration around ^{3}BP is sufficient to influence the hydrogen-abstraction reactions presented here, it would be useful to base the calculation of the bimolecular rate constant on the local concentration of the cosolvent, k_{bi}^{local}. Accounting for the local concentration, Eq. 5 for the ^{3}BP reaction with 2-propanol can be written as

$$k_{\text{obsd}} = k_0 + k_{bi}^{\text{bulk}}[\text{2-propanol}]_{\text{bulk}}$$
$$= k_0 + k_{bi}^{\text{local}}[\text{2-propanol}]_{\text{local}},$$

where

k_{bi}^{bulk} = bimolecular rate constants based on bulk concentrations [$M^{-1}\cdot s^{-1}$]
k_{bi}^{local} = bimolecular rate constants based on local concentrations [$M^{-1}\cdot s^{-1}$]
$[\text{2-propanol}]_{\text{bulk}}$ = bulk 2-propanol concentrations [M]
$[\text{2-propanol}]_{\text{local}}$ = local 2-propanol concentrations [M]

Solving for k_{bi}^{local}, one obtains the following relationship between k_{bi}^{local}, k_{bi}^{bulk}, and the ratio of the local to bulk concentration:

$$k_{bi}^{\text{local}} = k_{bi}^{\text{bulk}} \frac{[\text{2-propanol}]_{\text{bulk}}}{[\text{2-propanol}]_{\text{local}}}. \tag{10}$$

There are two factors that contribute to the increase in local cosolvent concentration, the local composition enhancement and the overall density enrichment of the mixed solvent about the solute. It was shown in the previous local composition section that the local mole fraction of 2-propanol exceeds the bulk by as much as 8 times. The local composition studies of Kim and Johnston (1987b) for similar alcohols show that the ratios of local to bulk composition are reasonably insensitive to the bulk composition within the 1 to 5% bulk composition range. Therefore, the ratios of local to bulk composition at

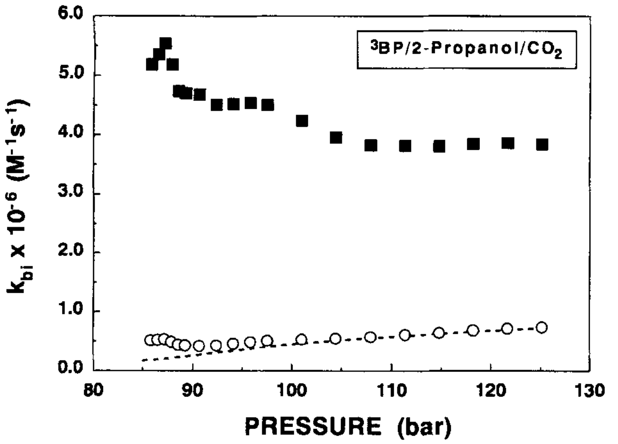

Figure 9. Experimental bimolecular rate constants for the reaction of ^{3}BP with 2-propanol in supercritical CO_2.

Based on bulk 2-propanol concentrations, k_{bi}^{bulk} (■), and based on local 2-propanol concentrations, k_{bi}^{local} (○), vs. pressure at 44.4°C. (– – –) represents predictions of the thermodynamic pressure effect on the rate constants using the Peng-Robinson equation (see text) at 44.4°C.

45°C were determined by fitting a smooth curve to the data in Figure 8 for the 1 mol % 2-propanol solution at a given pressure, where 1 mol % is an intermediate composition used in the kinetic experiments. Secondly, we must take into account increased local densities of the mixed solvent around the solute. As an approximation, we have used the ratio of local density to bulk density reported by Knutson et al. (1992) for pure CO_2 at the same conditions. These values are more conservative estimates than those others have reported, and at our conditions (temperature and pressure) never exceed a ratio greater than 1.25. Including both the local composition and local density effects, the local concentration of 2-propanol was determined by

$$\frac{[\text{2-propanol}]_{\text{local}}}{[\text{2-propanol}]_{\text{bulk}}}=\frac{[\text{local density}][\text{local composition}]}{[\text{bulk density}][\text{bulk composition}]}, \quad (11)$$

where values of [local density/bulk density] were estimated from the data of Knutson et al. (1992) for pure CO_2 at the same temperature and pressure. Values of [local composition/bulk composition] were determined from a smoothed curve through the new data we presented in Figure 8.

Equations 10 and 11 were used to calculate k_{bi}^{local}, and the results are plotted in Figure 9 along with the corresponding values of k_{bi}^{bulk}. From comparison of these rate constants it is evident that the local concentrations of 2-propanol have a dramatic effect on the bimolecular rate constants. The bulk-based bimolecular rate constants, k_{bi}^{bulk}, decrease with increasing pressure, whereas the local concentration-based rate constants, k_{bi}^{local}, increase slightly with pressure, thus changing the trend in the pressure effect. Also shown in Figure 9 are the predictions of the thermodynamic pressure effect calculated from the Peng-Robinson equation. This predicts the rate of change of k_{bi} with pressure and not the absolute values. Here the high pressure value has been set to the k_{bi}^{local} high pressure value for comparison of the trends. Remarkable agreement is obtained by comparing k_{bi}^{local} and the predictions. Both k_{bi}^{local} and the predicted rate constants exhibit an increase with an increase in pressure. The apparent discrepancy between the experimental rate constants and prediction has been explained by taking into account the local concentrations of the cosolvent. Therefore, we believe we have shown reasonable evidence that reactivity in SCFs can be greatly affected by the local microstructure.

These results corroborate the recent findings of Ellington et al. (1994) in which they investigated the effects of local cosolvent concentration enhancements on the esterification of phthalic anhydride with methanol in SC CO_2. They reported dramatic decreases in the apparent bimolecular rate as the pressure was increased over an intermediate density range, and showed that these changes in rate constant could not be explained by the thermodynamic pressure effect on the rate constant. Rather, they attributed the apparently large values of the rate constants at lower pressures to an actual increase in the local concentration of methanol around the phthalic anhydride solute.

Conclusion

We present new experimental bimolecular rate constants for the reactions of ^{3}BP with 2-propanol and ^{3}BP with 1,4-cyclohexadiene in supercritical CHF_3 and C_2H_6 obtained by laser flash photolysis on two isotherms. The greatest experimental rate constants occur at the lowest pressure studied and decrease with increasing pressure when based on bulk concentrations. The trends here are identical to previous results for these H-abstraction reactions in supercritical CO_2. Predictions of the thermodynamic pressure effect on the rate constants indicate an increase in the rate constant with pressure for both reactions at all conditions. The apparent discrepancy between the pressure effect on the experimental rate constants and prediction can be explained by enhanced local compositions of cosolvent about the ^{3}BP in the SCFs. Solvatochromic measurements were made to experimentally estimate the local compositions of 2-propanol about a solute in supercritical CO_2. These estimated local compositions of 2-propanol were used to correct the experimental rate constants to reflect the local cosolvent concentration. These local composition-based rate constants exhibit an increase with pressure and show strong agreement with the trends predicted from the thermodynamic pressure effect. Therefore, the opposite pressure effects between the raw experimental rate constants and prediction has been explained by accounting for the enhanced local concentrations of cosolvent about the ^{3}BP, demonstrating the impact that the local environment has on kinetically controlled reactions in SCFs. We believe the results observed in this work will also be observed in similar kinetically controlled reactions between dilute solutes and cosolvent with nonpolar transition states and relatively nonpolar reactants. Therefore, the potential effects of local composition on kinetically controlled solute/cosolvent reactions should be considered.

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Notation

c = speed of light
$E_T^{\text{ideal gas}}$ = transition energy of dye in vapor phase
ΔE_{T_m} = residual transition energy in ternary mixture
h = Planck's constant
P = pressure
X = bulk composition
X_{ij} = local composition of component i about molecule j

Subscript

TS = transition state

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