

Unique Pressure Effects on the Absolute Kinetics of Triplet Benzophenone Photoreduction in Supercritical CO₂

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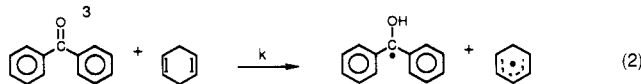
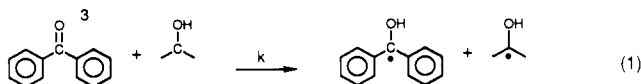
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Abstract: Laser flash photolysis studies of the hydrogen atom abstraction reaction of triplet benzophenone from 2-propanol and 1,4-cyclohexadiene in supercritical CO₂ reveal unusual pressure effects on absolute rate constants. Monitoring reactivity close to the critical temperature (*T_c*) revealed that bimolecular rate constants increase sharply with a decrease in pressure, approaching the critical point. Kinetic investigations along an isotherm further removed from *T_c* and predictive calculations on the pressure effect expected in supercritical CO₂ indicate that enhanced reactivity is due to local substrate clustering.

Introduction

The bulk properties of supercritical fluids (SCFs) have been extensively studied and in many cases are extremely well characterized. It is also well documented that dramatic changes in density-dependent bulk properties of SCFs (e.g., dielectric, solubility, diffusivity) may be achieved with small perturbations in temperature or pressure.¹⁻⁴ It would appear, then, to be a relatively simple matter to apply the well-known properties of SCFs to the control and manipulation of chemical reactivity. However, in the relatively few controlled investigations of chemical reactions in SCFs,⁵⁻¹⁹ it has been recognized that reactivity does not necessarily reflect the macroscopic properties of the fluid. In fact, reactivity is primarily controlled by molecular level interactions that are unique to SCFs. Therefore, a considerable amount of research activity has been devoted to understanding these molecular level interactions. Recently, investigations have focused on the application of steady-state²⁰⁻³⁶ and time-resolved³⁷⁻⁴² spectroscopies to elucidate the nature of solute/solvent and solute/substrate dynamics.

In a preliminary account of our laser flash photolysis (LFP) studies in supercritical (SC) CO₂, the reaction of benzophenone triplet (³BP) with 2-propanol (eq 1) was described.⁴¹ Reactivity



enhancements beyond those expected for both normal liquids and liquids under high pressure were observed when operations were carried out near the critical point of the solution. In this work the previous study has been extended to include probing of regions further removed from the critical point and ³BP reactivity toward a non-hydrogen-bonding substrate, 1,4-cyclohexadiene (eq 2). Analysis of these results is discussed in terms specific to factors that affect reactions in SCFs. Predictive calculations on the pressure effect expected in SC CO₂ are presented, as well as a discussion on the specific consideration of phase diagram perturbation.

Experimental Section

Materials. Benzophenone (Aldrich, Gold Label) was recrystallized from absolute ethanol. 2-Propanol (Fisher, ACS certified) was used as received. 1,4-Cyclohexadiene (Aldrich Chemical) was purified by bulb-to-bulb distillation prior to use. Carbon dioxide (Scott Specialty Gases, SFC grade, 2 ppm O₂) was used as received, unless otherwise specified.

Laser Flash Photolysis. The laser flash photolysis (LFP) apparatus has been described previously in detail.⁴³ Briefly, LFP experiments were

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carried out using perpendicular 355-nm laser excitation (~ 8 mJ, pulse width ~ 6 ns) from a Quanta Ray DCR-1 Nd:YAG laser system and a 1000-W pulsed xenon lamp as the monitoring source. 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 kinetic measurements at 580 nm and at appropriate wavelengths when absorption spectra were being measured.

General. Two different optical cells were used in these experiments. A previously described⁴⁴ optical cell of path length 1.3 cm was used with silicone o-rings for the alcohol reaction at 33.0 °C. The silicone o-rings were rinsed with cyclohexane repeatedly to remove contaminants. The remainder of the experiments were run with an improved o-ring-less optical cell, path length 1.7 cm, in which the windows have mechanical seals comprised of lead and graphite packing. Selected experiments were repeated with both cells yielding identical results.

Absolute rate constants were measured on two isotherms, 33.0 and 44.4 °C, for alcohol concentrations ranging from 5.7×10^{-3} to 6.01×10^{-2} mole fraction (0.03–0.9 M) and for 1,4-cyclohexadiene concentrations of 4.7×10^{-5} to 9.5×10^{-4} mole fraction (1×10^{-4} to 0.017 M). Benzophenone concentrations studied were in the range of 2.0 – 6.0×10^{-4} mole fraction (0.001–0.01 M). 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. Pressures studied ranged from 71 bar, which is slightly below the critical pressure, up to 110 bar for the experiments at 33.0 °C. For the 44.4 °C experiments, pressures were between 86 and 135 bar. A Model 901A Heise pressure gauge was used to monitor the pressure of the sample cell to ± 0.24 bar. The temperature of the cell, tightly fitted with insulation tape, was maintained at 33.0 °C ± 0.1 °C or 44.4 °C ± 0.1 °C via an Omega (Model CN-6070A) temperature controller equipped with a Watlow Firerod cartridge heater and a platinum resistance thermometer. The thermometer was fitted into the optical cell making direct contact with the fluid. The critical pressure and temperature of CO₂ are 73.98 bar and 31 °C, respectively. In all cases, care was taken to ensure that the samples were in the one-phase region (see discussion below).

Sample Preparation. The sample preparation apparatus consisted of the SFC grade CO₂ cylinder fitted with a dip tube in order to deliver liquid CO₂, an Isco high-pressure syringe pump (Model 1200, 266-mL capacity), and the 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. stainless steel high-pressure tubing and compartmentalized with high-pressure (HIP) line valves fitted with Teflon o-rings.

Prior to sample preparation the entire apparatus was extensively

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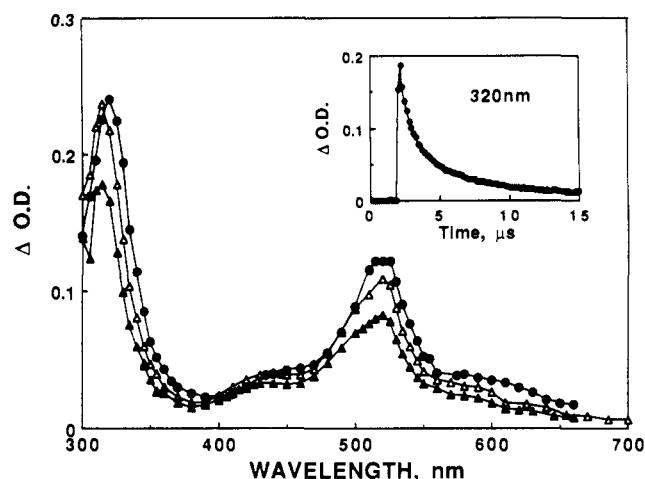


Figure 1. Transient absorption spectra observed 200 ns after 355-nm laser excitation of benzophenone in supercritical CO₂ (33.0 °C) at 140 (Δ) and 77 bar (▲) and in N₂-saturated liquid acetonitrile (●). Absolute values of ● have been divided by 3. Inset: ³BP decay observed at 320 nm in O₂-free CO₂ at 33.0 °C and 77 bar (see text).

purged with CO₂ at low pressures to minimize the presence of molecular oxygen. The 2-propanol was deaerated with high-purity N₂, and the alcohol reservoir was maintained under an atmosphere of N₂ during sample preparation. The amount of O₂ dissolved in the microliter portions of 1,4-cyclohexadiene used was considered to be insignificant.

For 2-propanol sample preparation, a desired amount of N₂-saturated alcohol was drawn into the syringe pump by applying a positive pressure of N₂ above the alcohol in the reservoir and lowering the piston in the syringe pump to the desired internal volume. The remaining volume of the pump was then filled at a constant flow rate with subcooled liquid CO₂ by surrounding the piston cylinder assembly of the syringe pump with an ice bath and submerging the 1/16-in. tubing between the cylinder and the pump in an ice bath. The 1,4-cyclohexadiene samples were prepared by injecting a known amount of diene into the injection valve in-line between the CO₂ cylinder and the syringe pump. The pump was then filled with subcooled liquid CO₂, as described, displacing the diene into the pump.

In all sample preparations sufficient time was allowed for thermal equilibrium to be achieved between the ice bath and the pump. Using the temperature of the ice bath (0 °C) and the pressure indicated on the Isco syringe pump, we determined the mole fractions of the samples using densities calculated from the analytic equation of state used by Angus et al.⁴⁵ in construction of the IUPAC CO₂ density data. These mole fractions can be readily verified by removing the ice bath and allowing the sample to reach thermal equilibrium with the environment, thus increasing the pressure. Under these conditions the CO₂ was still a subcooled liquid. Again, using the pressure indicated on the pump and the temperature of the surroundings, we estimated the mole fraction. There was good agreement ($\pm 2\%$) between the mole fractions calculated at this temperature and at $T = 0$ °C. To facilitate mixing, we heated the pump which increased the pressure such that the solution was one phase at all times.⁴⁶ Part of the contents of the Isco pump was then loaded into the sample cell, which contained an appropriate amount of crystalline benzophenone. The cell was then heated to facilitate mixing and raise the contents above the critical point. Benzophenone concentrations were determined with a Cary 1 UV-vis 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 equilibration at the individual pressures, as indicated by a stabilization in temperature and pressure.

Results

Prior to the LFP experiments, an examination of the ground-state absorption spectroscopy of benzophenone both in pure SC CO₂ and with added 2-propanol cosolvent was conducted to ensure complete solubility of the benzophenone under the LFP experimental conditions, as well as to explore the possibility of aggre-

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gation of benzophenone. Monitoring benzophenone absorption at 340 nm, we observed nearly identical linear Beer's law relationships (1–15 mM) for SC CO₂ and for liquid cyclohexane as solvents. This indicated that benzophenone was fully dissolved and in a nonassociated form under the LFP conditions (~10 mM). The total solubility of benzophenone was corroborated by solubility-limit measurements made in our laboratory for benzophenone in SC CO₂, which indicated that the LFP experiments were performed at least 25-fold below the solubility limit.⁴⁷ The absorption spectrum of ground-state benzophenone in SC CO₂ with and without cosolvent over the LFP experimental pressure range gave π - π^* and n - π^* absorption bands nearly identical to those observed in liquid cyclohexane. Addition of up to 3.5 mol % 2-propanol cosolvent to the SC CO₂ mixture resulted in only slight (± 2 nm) displacement of the benzophenone spectral bands.

Since ketone triplet lifetimes had not previously been explicitly measured in SCFs, initial LFP experiments were conducted with benzophenone in pure SC CO₂ to examine any unique factors that may control the natural nonradiative decay of triplet benzophenone (³BP). In contrast to the diffusion-controlled reactivity of ³BP toward molecular oxygen, ³BP shows no measurable reactivity toward CO₂. This was readily demonstrated by the observation of nearly identical ³BP lifetimes in N₂-saturated and CO₂-saturated liquid acetonitrile. In fact, LFP results in high-pressure CO₂ are remarkably similar to those in deaerated acetonitrile. As expected in a nonreactive solvent, LFP of benzophenone in SC CO₂ resulted in detection of ³BP within the ~8-ns laser pulse, and decay of the transient absorption signal occurred by second-order kinetics in the microsecond regime (see Figure 1, insert). LFP experiments in SC CO₂ conducted at 33.0 °C over the entire pressure range of 110–71 bar indicated no change in the mechanism of ³BP decay (i.e., triplet-triplet annihilation) with changing pressure. A small increase in the second-order rate constant was observed, however, with a decrease in pressure which is attributed to the increase in diffusivity expected as the density of the SCF is decreased from high to low pressure. This study was repeated with SFC grade CO₂ which was subjected to three freeze-pump-thaw cycles, in an attempt to further reduce the amount of molecular oxygen in the stock CO₂. No detectable difference was found between the two studies, demonstrating that the SFC grade stock CO₂ could be used safely in these investigations without concern of significant O₂ quenching of the triplet even at extremely low density. It should be noted that this is not the case when lower grades of CO₂ have been used, in which significant triplet quenching has been observed.

Nearly identical transient absorption spectra were also observed upon LFP of benzophenone in SC CO₂ and in liquid acetonitrile (Figure 1). The absorption maxima observed at 320 and 525 nm also remained unaltered in SC CO₂ at 33.0 °C when the pressure was reduced from 140 to 77 bar.

Absolute kinetics for the reaction of ³BP with 2-propanol and 1,4-cyclohexadiene (eqs 1 and 2) were obtained by measuring the change in the rate of decay of the triplet absorption signal with added quenching substrate. By substrate we are referring to the second reactant, in this reaction 2-propanol or 1,4-cyclohexadiene. The ³BP decay rapidly becomes pseudo-first-order in the presence of alcohol or diene. Therefore, fitting the time-resolved absorption trace with a single exponential yields the observed pseudo-first-order rate constant, k_{obs} , for the reaction of ³BP with alcohol or diene. Concurrent with the decay of ³BP, growth of the absorption signal of ketyl radical was observed, as predicted by eqs 1 and 2. Unfortunately, the UV-vis absorption spectrum of ketyl radical severely overlaps that of ³BP. Therefore, throughout these experiments, the absolute kinetics of ³BP were monitored at 580 nm, where ketyl radical absorption is negligible.

The reactivity of ³BP toward 2-propanol and 1,4-cyclohexadiene in SC CO₂ was investigated from high to low pressure, typically from 130 to 70 bar, along two isotherms, 33.0 and 44.4 °C. Individual experiments were performed for each concentration of quenching substrate. The mole fractions of alcohol and diene

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

2-propanol		1,4-cyclohexadiene
x ($T = 33$ °C)	x ($T = 44.4$ °C)	x ($T = 33$ °C, 44.4 °C)
6.18×10^{-3}	5.66×10^{-3}	4.72×10^{-5}
7.23×10^{-3}	7.12×10^{-3}	9.46×10^{-5}
9.76×10^{-3}	9.73×10^{-3}	1.42×10^{-4}
1.71×10^{-2}	1.70×10^{-2}	1.89×10^{-4}
3.03×10^{-2}	3.03×10^{-2}	2.84×10^{-4}
4.28×10^{-2}	4.27×10^{-2}	3.79×10^{-4}
6.01×10^{-2}	6.01×10^{-2}	9.47×10^{-4}

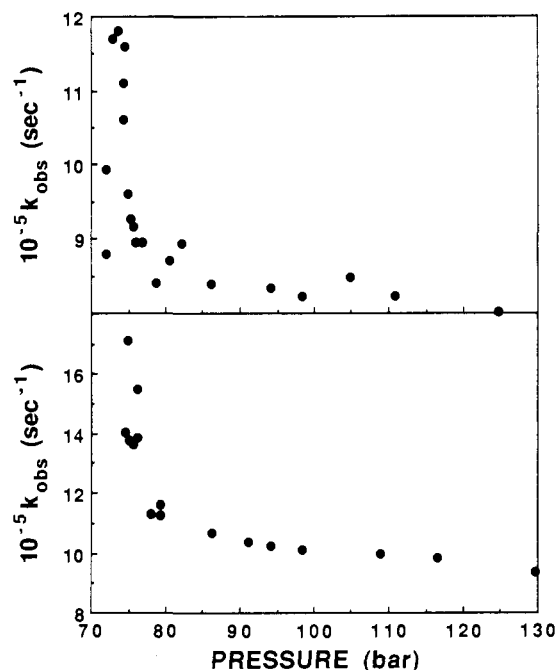


Figure 2. Pressure dependence of the pseudo-first-order rate constant for decay of ³BP at 33.0 °C in the presence of 0.25 mol % 2-propanol (top) and 4.7×10^{-3} mol % 1,4-cyclohexadiene (bottom).

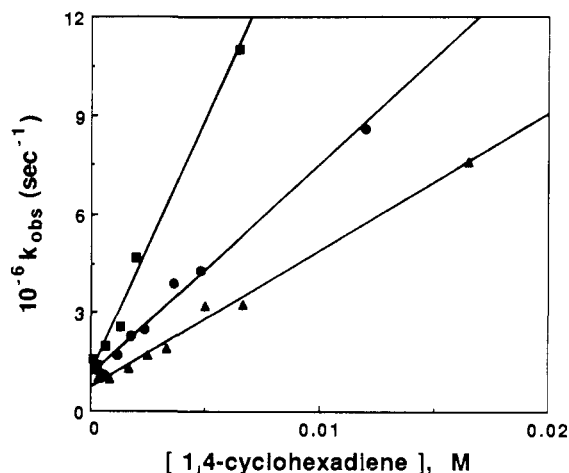


Figure 3. Bimolecular quenching plots for the reaction of ³BP with 1,4-cyclohexadiene in SC CO₂ at 110 (▲), 78 (●), and 75 (■) bar and 33.0 °C.

used are presented in Table I. The effects of pressure on k_{obs} for ³BP with 2.5×10^{-3} mole fraction 2-propanol and 4.7×10^{-5} mole fraction 1,4-cyclohexadiene at 33.0 °C are presented in Figure 2, top and bottom, respectively. Typically, the reactions of ³BP with both alcohol and diene demonstrated dramatic increases in k_{obs} as the critical point was approached. Bimolecular rate constants (k_{bi}), $\text{M}^{-1} \text{s}^{-1}$, for ³BP reactivity could be obtained at individual (constant) pressures from construction of bimolecular quenching plots of k_{obs} versus concentration of quenching substrate (S), according to $k_{\text{obs}} = k_0 + k_{\text{bi}}[\text{S}]$, where k_0 represents all modes

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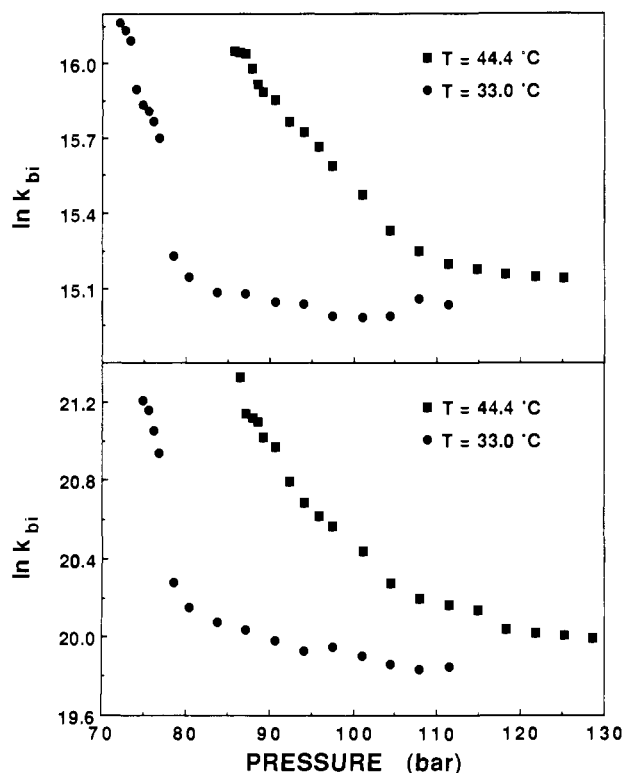


Figure 4. Pressure dependence on the bimolecular rate constant, k_{bi} ($M^{-1} s^{-1}$), at 33.0 °C (●) and 44.4 °C (■) for the reaction of ³BP with 2-propanol (top) and 1,4-cyclohexadiene (bottom).

of decay of ³BP in the absence of S. As in the examples presented in Figure 3 for the reaction of ³BP with 1,4-cyclohexadiene at 110, 78, and 75 bar and 33.0 °C, linear quenching plots were obtained for both substrates and at all pressures investigated.

Sharp increases in k_{bi} are also observed with a decrease in pressure, approaching the critical pressure, for the reaction of ³BP with both 2-propanol and 1,4-cyclohexadiene at 33.0 °C, Figure 4, top and bottom, respectively. It should be noted that the data presented here for 2-propanol at 33.0 °C are improvements on values presented in our preliminary study due to better estimates of the alcohol mole fractions based on subcooled liquid densities. k_{bi} increased from ca. 3.4 to $9.7 \times 10^6 M^{-1} s^{-1}$ for 2-propanol at 33.0 °C and from ca. $4.2 \times 10^8 M^{-1} s^{-1}$ to $1.54 \times 10^9 M^{-1} s^{-1}$ for 1,4-cyclohexadiene at the same temperature.

Investigations at 44.4 °C resulted in similar behavior for both reactions studied. In each case, modest increases in k_{bi} compared to the values at 33.0 °C were observed at high pressures due to thermal activation. Interestingly, increases in k_{bi} of magnitude similar to those seen at 33.0 °C, 2.6 for alcohol and 3.7 for diene, were observed at 44.4 °C (Figure 4) with a decrease in pressure, although with a more subtle slope. k_{bi} at 44.4 °C increased from ca. 3.7 to $9.3 \times 10^6 M^{-1} s^{-1}$ for 2-propanol and from $4.8 \times 10^8 M^{-1} s^{-1}$ to $1.8 \times 10^9 M^{-1} s^{-1}$ for 1,4-cyclohexadiene.

Discussion

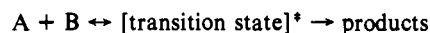
In our preliminary investigation of the reaction of ³BP with 2-propanol in SC CO₂ at 33.0 °C, we reported a pressure effect on the reaction that was both contradictory to that predicted by transition-state theory and opposite to that observed in normal liquid solutions.⁴¹ The possibility that this observation was anomalous, a ramification of the alcohol substrate, was of great concern to us. To determine the merit of this possibility required a nonhydroxylic hydrogen atom donating substrate that would not introduce further mechanistic complications. 1,4-Cyclohexadiene was chosen as that substrate since the reaction of ³BP with both alcohol and diene should proceed through similar diradicaloid transition states. Expansion of this study to include 1,4-cyclohexadiene and to investigate temperatures both near and significantly above the critical temperature of the solution has

resulted in new insights into the factors controlling the unique pressure effects observed for the reaction of ³BP in SC CO₂. It should be emphasized that great care must be taken in the interpretation of kinetic results obtained in SCFs. Below we will discuss those effects of the SCF solvent on the bimolecular reaction rate that are necessary to understand our interpretation of the kinetics results. Moreover, it is important to examine the phase behavior encountered when cosolvents are added to the SCF solvent, which should clarify the significant benefits of working with the more dilute 1,4-cyclohexadiene systems presented in this paper. Then we will review the laser flash photolysis results and provide an interpretation of the results.

Possible Ways To Affect Reactions in Supercritical Fluids.

While SCF solvents can act in a variety of ways to affect reaction rates, those necessary to understand the reaction of ³BP are the thermodynamic pressure effect on the rate constant, the effect of local densities, and the effect of local compositions. Other effects not pertinent to this reaction are discussed in greater detail elsewhere.⁴⁸

(a) **Pressure Effect on the Rate Constant.** The most pronounced effect of pressure on reactions in the supercritical region has been attributed to the thermodynamic pressure effect on the reaction rate constant. In terms of transition-state theory,⁴⁹ the reactants are in thermodynamic equilibrium with a transition state. Once the transition-state complex is formed it proceeds directly to products. With this analysis the pressure effect on the reaction rate constant for a bimolecular reaction can be given as follows:



$$RT \frac{\partial \ln k_{bi}}{\partial P} = -\Delta v^* - RTk_T \quad (3)$$

where

k_{bi} = bimolecular rate constant ($M^{-1} s^{-1}$)

$$\Delta v^* = \bar{v}_s - \bar{v}_A - \bar{v}_B$$

\bar{v}_i = partial molar volume of component i

k_T = isothermal compressibility

R = gas constant

T = absolute temperature

The last term in the equation is a result of the reactant concentrations changing with pressure. If the rate expressions are written in pressure-independent units (i.e., mole fraction), that last term drops out of the equation. Partial molar volumes in SCFs can be very dramatic, with values as large as $-15\,000 \text{ cm}^3/(\text{g mol})$ being reported in the literature.⁵⁰ As a result, the pressure effect on the reaction rate constant can be very significant. In contrast, partial molar volumes in liquids are on the order of $5\text{--}10 \text{ cm}^3/(\text{g mol})$ and activation volumes mostly reflect size changes in going from reactants to transition state. For a discussion of how both the repulsive size effects and the attractive interactions between a solute and the solvent influence partial molar volumes in SCFs, see Johnston and Haynes.⁹

(b) **Effects of Local Densities or Cage Effects.** A number of spectroscopic^{25,27,30–32,34,36} and theoretical^{51,52} studies show that the local density of SCF solvent around a dilute solute molecule can be significantly greater than the bulk density. This is especially true in the compressible region near the critical point. It is then conceivable that the locally higher density or the formation of a solvent "cage" could act to enhance or inhibit chemical reactions. It cannot be overemphasized that, in discussing the local density

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enhancement or solvent clustering, we are referring to experimental results and molecular dynamics simulations that suggest that, averaged over time, the density of SCF solvent molecules in the first few shells around a solute is higher than the bulk density. However, as discussed below, this "cluster" is very dynamic, exchanging molecules with the bulk within the picosecond time regime.

The experimental evidence for increased local densities includes both UV-vis absorption and fluorescence spectroscopies. In a number of studies using a variety of solvatochromic probes in CO₂, fluorofrom, ethylene, and ethane,^{25,27,32,34,36} investigators have observed shifts of the absorption or fluorescence maxima greater than those expected on the basis of the Onsager field strength obtained from bulk densities. In all cases, this was explained as the local density of the solvent around the solute being greater than the bulk density. Also, Brennecke et al.^{30,31} found that the change in the ratio of the intensity of two peaks in the steady-state fluorescence spectrum of pyrene, which is sensitive to the immediate solvent environment, corroborated the idea of local densities being greater than the bulk densities. While these probes measure the influence of the solvent at varying distances from the solute, they are all relatively short range and consistent in the observation of increased local densities around the solute.

In addition, there are several theoretical studies to support the idea of local densities being greater than the bulk densities around a solute in a SCF solution. Among these are the molecular dynamics (MD) studies of Petsche and Debenedetti,⁵² which clearly demonstrate that in an attractive mixture modeled with a simple Lennard-Jones potential the environment around a solute molecule is continuously enriched with solvent relative to bulk conditions. Very importantly, they point out the dynamic nature of the cluster, which loses its identity in a few picoseconds. Also important is the work of Lee and Cochran,⁵¹ who use integral equation theory to calculate radial distribution functions of the SCF solvent around a solute. They find that the first peak in the radial distribution function for the solute/solvent is significantly higher, suggesting a higher density of solvents within the first coordination sphere, and the tail of the solute/solvent distribution function remains above 1 for a much greater distance than in the solvent/solvent case. This long tail on the radial distribution function can, in itself, account for the large negative partial molar volumes of solutes in SCFs.⁵³ However, the large body of experimental and theoretical results summarized above suggests that there is also an enrichment in the local density immediately around the solute.

The question remains as to whether density enhancements can influence reaction rates. Clearly, clustering in general, which includes the long-range correlations which result in large negative partial molar volumes, influences the reaction rate through the pressure effect on the rate constant, as described in section a above. However, there is some evidence to suggest that the local density enhancement or formation of a solvent cage around the solutes can influence reactions. In the Heisenberg spin exchange reaction between nitroxide free radicals in near-critical and SC ethane, Randolph and Carlier⁵⁴ find rate constants greater than predicted by Stokes-Einstein for a diffusion-controlled reaction and explain the results as the solvent cage increasing the probability of reaction per collision. In the photoisomerization of diphenylbutadiene, Troe and co-workers³⁷ concluded that the reactant-solvent cluster interactions modified the barrier height for the reaction, thus facilitating its rate. Conversely, in the photolysis of dibenzyl ketones, absolutely no influence of solvent cage effects could be detected.¹⁵ We believe that there are two ways the local density enhancement might influence a reaction. First, if the reaction is sensitive to any density-dependent property, such as dielectric constant, the time-averaged locally dense medium, which would have a higher dielectric constant than the bulk, might influence that reaction. Second, the solvents around a solute might be seen as a cage, which could prevent entrance or escape of a species, such as hypothesized

in the photolysis of the dibenzyl ketones.¹⁵ In this case, we believe that an important consideration is the time scale of the reaction relative to the lifetime of the cage. The reaction must take place within the time that the cage has integrity for the local dense solvent cage to affect that reaction. According to the MD calculations, this time is on the order of picoseconds. Therefore, it is not surprising that reactions that occur on a longer time scale might not experience any cage effects. The reactions presented in the present study of the reaction of ³BP with 2-propanol or 1,4-cyclohexadiene are very slow in comparison, with characteristic time scales of ca. 10⁴ times longer than the believed persistence time for a solvent cage.

(c) Effects of Local Compositions. Another possible effect on the reaction rate in a SCF is change in local concentrations of reactants. Kim and Johnston²⁵ showed, using a solvatochromic probe in mixtures of CO₂ and cosolvents, that near the critical point the local concentration of a cosolvent around a solute molecule was a sensitive function of pressure and could be as high as 7 times that in the bulk. The question posed by these studies is whether the reaction rate between a solute and a cosolvent can be enhanced because the equilibrium local composition of one of the reactants is increased. The reactions presented here were chosen explicitly to mimic this situation, and the preliminary results of this study⁴¹ are the first to address this issue. Solute/solute interactions constitute the limiting case of cosolvent clustering in which the concentration of the cosolvent becomes very dilute and the cosolvent is chosen to be the same species as the solute. At present, the results of dimerization reactions suggest conflicting conclusions. In the photodimerization of cyclohexenone¹⁸ the authors attribute changes in the regioselectivity of the product to solute clusters that increase the local dielectric constant when operating near the critical point of the solution. Using time-resolved fluorescence spectroscopy, Bright and co-workers⁴² examined the rate of formation of pyrene excimers. The rate exactly followed that predicted by diffusion control, assuming a uniform initial distribution of solute molecules. This leads to the conclusion that solute aggregates either do not exist or do not influence the pyrene excimer formation reaction. All three of these influences, the pressure effect on the rate constant, local densities, and local composition changes, will be examined in analyzing the results of the hydrogen abstraction reaction between ³BP and 2-propanol or 1,4-cyclohexadiene below.

Phase Diagrams. In this paper we present results of the reaction of ³BP with 2-propanol or 1,4-cyclohexadiene in CO₂ at temperatures above and pressures both above and slightly below the critical temperature and pressure of pure CO₂. The addition of the benzophenone solute and the cosolvent (alcohol or diene) seriously influences the phase behavior of the mixture, especially when the concentrations are high, above 1 mol % or so. The purpose of this section is to describe the CO₂/2-propanol phase behavior to aid in the interpretation of those results and point out the prevalence of alcohol self-association and alcohol/CO₂ complexation. This should emphasize the improved reliability and ease of interpretation of the 1,4-cyclohexadiene results, which are taken at much lower concentrations and reduce the possibility of complexation with the solvent.

The total phase diagram for mixtures of CO₂ and cosolvents can be very complicated, and the different types of behavior have been discussed in detail elsewhere.^{55,56} Here we are interested only in the region where a few percent of the cosolvent has been added and at pressures and temperatures near the critical point of pure CO₂. When a cosolvent like 2-propanol is added to pure CO₂, it shifts the critical temperature and pressure of the mixture higher. While the estimation of the critical properties of mixtures is possible,⁵⁷ it is not particularly reliable, especially for mixtures

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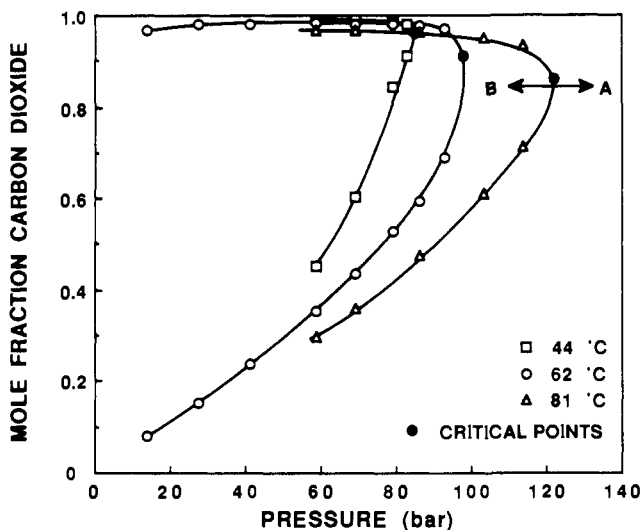


Figure 5. Phase diagram for CO₂/2-propanol mixtures. Data of Radosz, 1986.⁴⁶

that can form hydrogen bonds. Fortunately, several experimental studies^{46,58,59} have looked at the CO₂/2-propanol system, and some of the data are shown in Figure 5, which plots composition as a function of pressure for various isotherms. The areas inside the envelopes are the two-phase regions. Any mixture at a condition inside the envelope will split at constant pressure into two phases, a gas phase rich in CO₂ and a liquid phase that is mostly alcohol. Only at higher pressures, outside the phase envelope, will there be only a single phase. We hope to conduct all of our experiments in this one-phase region. The critical point is the intersection of the liquid equilibrium line (lower curve) and the vapor equilibrium line (upper curve), where the compositions of both phases become identical. Critical points extrapolated from the available data are shown as solid circles in the diagram. The solid lines are hand-drawn estimates of the phase envelopes based on the data available, for the purpose of illustration. Actual measured critical points for the alcohol concentration range used in the ³BP experiments (0.0025–0.0601 mole fraction) can be found in ref 59. They are consistent with the data shown in Figure 5, but including them on the graph further complicates the low alcohol concentration area. One should note that as the concentration at the critical point increases (lower mole fraction of CO₂), the critical temperature and pressure are increased. While it is not as clear for the lower concentrations where fewer phase envelope data are available, from the higher temperature curves one can see that it is possible to have just one phase at a pressure well below the critical pressure of the solution if one is operating at a temperature below the critical temperature. At a mixture mole fraction of alcohol of ca. 0.15, the critical temperature and pressure are about 81 °C and 120 bar. However, when operating at 62 °C, one can reduce the pressure all the way to ca. 98 bar before hitting the two-phase region (moving from point A to point B on Figure 5). It is for this reason that many of our reaction rate measurements are below the critical temperature and pressure of the solution yet still in the one-phase region. This is also consistent with the fact that at the higher temperature investigated in these reactions the phase split occurs at higher pressures.

This brings up another important point. The solution is most compressible (large change in properties like density, dielectric constant, etc. with very small changes in temperature or pressure) in the region nearest the critical point of the solution. The 15 mol % mixture in Figure 5 would be most compressible at 81 °C

and about 120 bar. At higher pressures it would be less compressible, and at lower pressures it would phase split. However, since in the example the operating temperature is only 62 °C, the region of highest compressibility is not necessarily the lowest pressure before it phase splits. This complicates the analysis of the reaction rate results significantly since the lowest pressure studied is not necessarily the nearest to the critical point of the solution. Moreover, to obtain bimolecular rate constants it is necessary to draw rate information from a variety of alcohol concentrations, all with different critical points. Clearly, it is highly preferable to conduct experiments with very dilute concentrations of the cosolvent. Such is the case with 1,4-cyclohexadiene, where the highest concentration is 9.5×10^{-4} mole fraction. At these low concentrations the critical point of the mixture is not significantly removed from the critical point of CO₂, so the lowest pressures should consistently correspond to the highest compressibility region nearest the critical point of the solution.

One additional advantage of using 1,4-cyclohexadiene is that it does not self-associate through hydrogen bonding. It is well-known that alcohols form dimers, trimers, and higher order oligomers in liquid solutions. This is also true, although apparently to a somewhat lesser extent, in SCFs, and the prevalence of hydrogen bonding is a function of pressure.⁶⁰ Moreover, there is evidence^{60–62} of the formation of a complex between a monomeric alcohol and the CO₂. This potential complexation would decrease the number of monomeric alcohol molecules available for reaction with the ³BP, thus further complicating the analysis. All these problems are eliminated in the reaction with 1,4-cyclohexadiene.

In summary, the addition of cosolvent and the solute itself can significantly move the critical point of the solution. For the purpose of understanding the solvent effect on the reaction, the most desirable situation is one in which both the solute and cosolvent are present in low concentrations. This is the case for the reaction of ³BP with 1,4-cyclohexadiene. To obtain reasonable reaction rates with the alcohol, the concentrations were as high as 6.01 mol %. Therefore, care will be taken in the interpretation of those data and more emphasis placed on the 1,4-cyclohexadiene results.

Laser Flash Photolysis Results. The first important observations from the LFP experiments are that the reaction mechanism in SC CO₂ appears to be the same as in liquids and the rates obtained are on the same order of magnitude as those in liquids. As in liquids, the reaction rates are approximately 3 orders of magnitude below diffusion control. Since the absorption spectrum of benzophenone in pure CO₂ over the pressure range of interest is essentially the same as that in liquids, the measured influence of pressure is its effect on the reaction of ³BP with the substrate, rather than its influence on benzophenone absorption.

Next, the results for the reaction of ³BP with both 2-propanol and 1,4-cyclohexadiene indicate that, on the basis of bulk compositions, both k_{obsd} and k_{bi} increase as the pressure is lowered, approaching the critical point of the solution, as shown in Figures 2 and 4. The increases are almost 4-fold, and the bimolecular rate constant for the 2-propanol/³BP reaction is greater than can be obtained at any pressure in neat 2-propanol liquid.^{63,64} The increases in k_{obsd} and k_{bi} persist even at 44.4 °C, which is further removed from the critical point of the solution, especially for the 1,4-cyclohexadiene reaction, as described above. Remarkably, the increases in the bimolecular rate constants (2.6 times for 2-propanol and 3.7 times for 1,4-cyclohexadiene) are essentially the same at 44.4 °C as they are at 33.0 °C. The rate constants are higher at the higher temperature, as expected. The higher temperature points cut off at a higher pressure than the lower temperature points because, with the cosolvent mixture, one crosses

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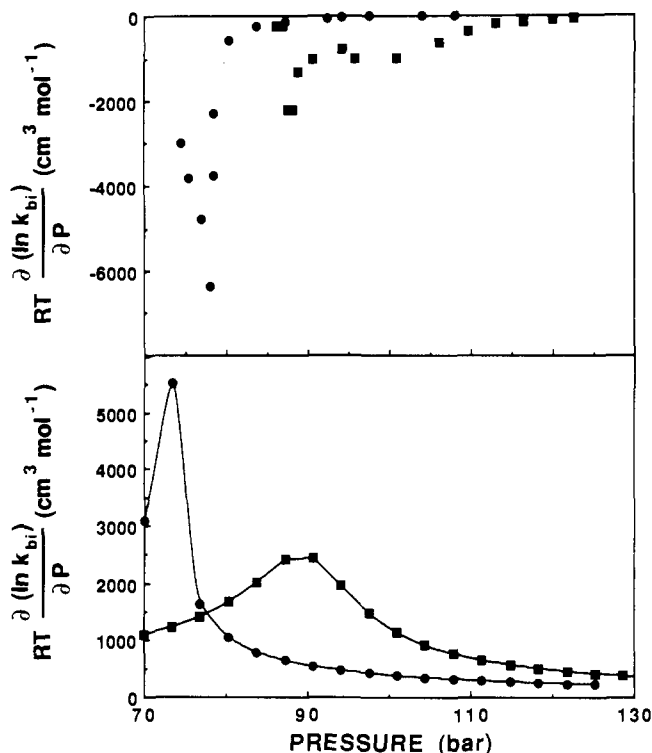


Figure 6. Top: Plot of the pressure effect (see text) on k_{bi} for ${}^3\text{BP} + 2\text{-propanol}$ at $33.0\text{ }^\circ\text{C}$ (●) and $44.4\text{ }^\circ\text{C}$ (■). Bottom: Plot of the pressure effect estimated from the Peng–Robinson equation of state (see text) for k_{bi} of ${}^3\text{BP}$ with 1 mol % 2-propanol in SC CO_2 at $33.0\text{ }^\circ\text{C}$ (●) and $44.4\text{ }^\circ\text{C}$ (■).

into the two-phase region at higher pressures when operating at $44.4\text{ }^\circ\text{C}$ instead of $33.0\text{ }^\circ\text{C}$, as discussed above.

Analysis. These are among the first kinetically controlled reactions to be reported that exhibit an increase in the rate constant at low pressure near the critical point, thus demonstrating the possibility of enhanced reactivity by operation in SCFs. However, the more important consideration is which of the factors discussed above are important in determining the increased reaction rate constant of ${}^3\text{BP}$ with 2-propanol and 1,4-cyclohexadiene in SC CO_2 . Clearly, more than one factor can be influencing the reaction. The questions are, Which are the predominant factors? and What can be learned about the influence of the solvent on these reactions? We shall explore the various possibilities discussed above and find that both the thermodynamic pressure effect on the rate constant and increased local compositions are important for these reactions. Please note that all the rate constants reported are based on bulk compositions.

(a) Pressure Effect on the Rate Constant. According to transition-state theory, the thermodynamic pressure effect on the rate constant is given by the activation volume and the isothermal compressibility (vide supra). For the ${}^3\text{BP}$ reactions this is given by

$$RT \frac{\partial \ln k_{bi}}{\partial P} = -(\bar{v}_{is} - \bar{v}_{\text{benzophenone triplet}} - \bar{v}_{\text{substrate}}) - RTk_T \quad (4)$$

One can compare the experimentally observed pressure effect on the rate constant to the partial molar volumes and isothermal compressibilities calculated from an equation of state.

The experimental pressure effect on the bimolecular rate constant, $RT(\partial \ln k_{bi}/\partial P)$, is determined by calculating the slope of a smoothed curve fit through the $\ln k_{bi}$ versus pressure data at various pressures and multiplying by RT . In the upper curves of Figures 6 and 7 these experimental estimates of $RT(\partial \ln k_{bi}/\partial P)$ are plotted as a function of pressure for both reactions. This pressure effect on the bimolecular rate constant is negative for both reactions and shows a sharp dip near the critical pressure. This shows that the rate decreases with pressure and that the rate is higher near the critical point.

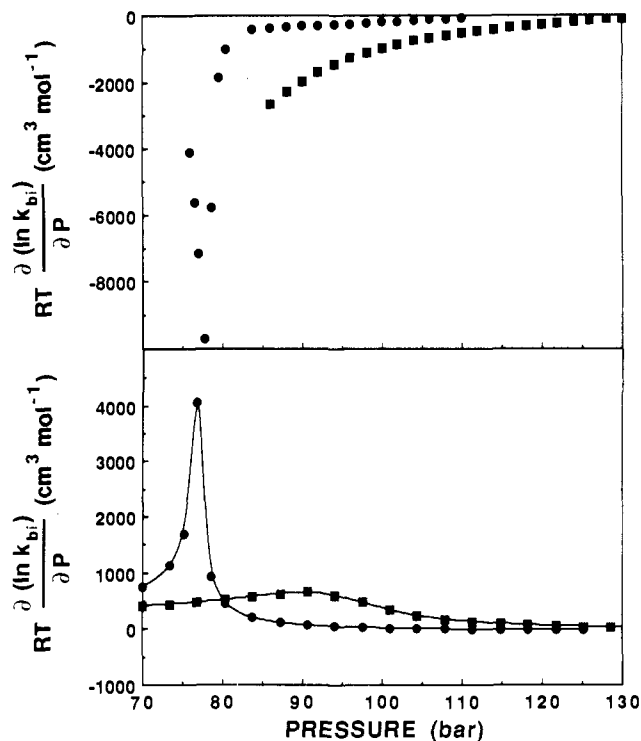


Figure 7. Top: Plot of the pressure effect on k_{bi} for ${}^3\text{BP} + 1,4\text{-cyclohexadiene}$ at $33.0\text{ }^\circ\text{C}$ (●) and $44.4\text{ }^\circ\text{C}$ (■). Bottom: Plot of estimated pressure effect (see text) on k_{bi} for ${}^3\text{BP}$ with 0.01 mol % 1,4-cyclohexadiene in SC CO_2 at $33.0\text{ }^\circ\text{C}$ (●) and $44.4\text{ }^\circ\text{C}$ (■).

The right side of eq 4 can be estimated with any appropriate equation of state. Obtaining quantitative estimates of partial molar volumes of dilute solutes in the supercritical region is very difficult since they can be large negative numbers [$>-10000\text{ cm}^3/(\text{g mol})$],⁵⁰ and the prediction of a derivative property is particularly demanding of any thermodynamic model of SCF phase behavior.⁴ For simplicity, we have chosen the Peng–Robinson equation of state⁶⁵ since it is known to yield reasonable values of thermodynamic properties for SCF mixtures,⁶⁶ 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 isothermal compressibility are given in the Appendix. The important point is that these equations require values for properties of the components, such as T_c , P_c , and the acentric factor (ω). These properties are not known for many of our compounds, including ${}^3\text{BP}$ and the transition state. While estimation techniques are available,⁵⁷ they do not provide very reliable values. Moreover, the calculated results are sensitive to the values chosen for the binary interaction parameters. In the absence of sufficient thermodynamic data to fit those parameters, we have set them at the default value of 0.0. Therefore, the calculated values of the activation volume and isothermal compressibility shown in the lower sections of Figures 6 and 7 (right side of eq 4) should be regarded as first approximations rather than absolute values. However, they should provide reasonable estimates of the trends expected. As seen in Figures 6 and 7, the estimated pressure effects on the rate constants for both reactions at both temperatures are positive; i.e., the rate constant should increase with increasing pressure and fall to lower values at the low pressures near the critical point. In other words, the estimated pressure effect on the rate constant is in the opposite direction of that observed.

There are several important features in the experimental and estimated pressure effects on the rate constants shown in Figures

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

component	T_c (K)	P_c (bar)	ω
carbon dioxide ^a	304.2	73.8	0.225
2-propanol ^b	508.3	47.6	0.248
1,4-cyclohexadiene ^c	582.5	22.8	0.216
triplet benzophenone ^c	821.0	33.0	0.557
2-propanol/ ³ BP transition state ^c	994.0	24.6	0.993
1,4-cyclohexadiene/ ³ BP transition state ^c	1037.3	22.8	0.63

^a Angus et al., 1976.⁴⁵ ^b Reid et al., 1978.⁵⁷ ^c Estimated; see text.

6 and 7. First, the pressure effect on the experimental rate constants at the higher temperatures is less than at lower temperatures, as expected, since the compressibility is lower further from the critical point. This can be seen from Figure 4, where the 33.0 °C isotherm becomes much steeper than the 44.4 °C isotherm at lower pressures. However, please note that the calculated values are still in the opposite direction; i.e., they predict a retarding of the rate near the critical point contrary to the experiments. Second, there is an apparent flattening of the experimental $RT(\partial \ln k_{bi}/\partial P)$ curve for 2-propanol (Figure 6) at 44.4 °C around a pressure of 95 bar. This comes from the relatively straight portion of the k_{bi} curve in Figure 4 at the same pressures. It is unclear if this apparent flattening of the slope is significant; however, there is no question that the slope continues to increase for 1,4-cyclohexadiene. If the flattening is real, it could be explained by the fact that for 2-propanol the lowest pressures are not necessarily those nearest the mixture critical points, also, the k_{bi} 's shown in Figure 4 are obtained from data with 2-propanol concentrations ranging from 0.25 to 6.01 mol %, which substantially moves the critical point of the mixture, as discussed under Phase Diagrams. This is a case in which we believe that the 1,4-cyclohexadiene data, which were obtained with more dilute cosolvent concentrations, are significantly more reliable and easier to interpret.

The conclusion from this analysis is that there does seem to be some thermodynamic pressure effect on the rate constant since the curves at 44.4 °C are not as steep as those at 33.0 °C. However, the estimates indicate that the rate constants should go down near the critical point, contrary to observation, so that the observed pressure effect on the reaction rate cannot be explained by the thermodynamic pressure effect on the rate constant.

(b) **Effects of Local Densities or Cage Effects.** The molecular dynamics results of Debenedetti and Petsche⁵² indicate persistence times for clusters of only a few picoseconds. Even assuming that for highly attractive mixtures the clusters could maintain their integrity for several hundred picoseconds, there is still no indication that the solvent shell should affect the reactions reported here since they take place on the order of hundreds of nanoseconds. Therefore, the body of available data and simulations suggest that there should not be any cluster or cage effects on these reactions.

(c) **Effects of Local Compositions.** The solvatochromic dye experiments of Kim and Johnston²⁵ suggest an increase in the local composition of the cosolvent around the solute. In the reactions reported here this would correspond to an increase in the local composition of the substrate (2-propanol or 1,4-cyclohexadiene) around the ³BP and could account for the increase in the rate constant, which is based on bulk concentrations. In actuality, the rate is given by $\text{rate} = k_{bi}[\text{³BP}][\text{substrate}]$, where [³BP] and [substrate] are the actual local concentrations of the components and k_{bi} is the actual bimolecular rate constant based on true concentrations (not bulk concentrations). However, per convention, we report the k_{bi} based on bulk concentrations. Therefore, an increase in the local concentration of the substrate could be parlayed into an apparent increase in k_{bi} if the local concentration increase more than compensates for the actual rate constant decrease due to the activation volume and isothermal compressibility, as discussed in section a above. It would be useful to measure the local composition of 2-propanol or 1,4-cyclohexadiene around the benzophenone directly by examining the solvatochromic shift when the substrate is added to the CO₂. Unfortunately, the measurable shift of the benzophenone absorption bands when

2-propanol or 1,4-cyclohexadiene is added to the SC CO₂ is very small, since the bands are broad and the $\pi-\pi^*$ and $n-\pi^*$ bands overlap. Therefore, the best estimates of local compositions in similar systems are the data of Kim and Johnston.²⁵

The solvatochromic dye measurements²⁵ indicate that the local composition of cosolvent increases to approximately 7 times the bulk concentration when the pressure is lowered from 300 bar down to 85 bar at 35 °C. The increase is most dramatic in the region between 100 and 85 bar. Unfortunately, Kim and Johnston do not report any values in the most compressible (approximately 73–80 bar) region near the critical point. Extrapolation of their curves would suggest even higher local compositions in this region, where many of our lower temperature rate data were taken. Moreover, the values reported²⁵ are increases in local mole fractions. The rate equations used here are based on concentrations. The possible local density increases discussed above would further increase the local concentration. For instance, a 5-fold increase in the local mole fraction coupled with a 2-fold increase in local density would result in a 10-fold increase in the local concentration. Therefore, it is reasonable that the increase in local concentration could more than compensate for the decrease in the actual rate constant estimated above.

Finally, there are no data available for the local compositions of cosolvents around dilute solutes as a function of pressure in supercritical fluids at temperatures significantly removed from the critical point. All of the Kim and Johnston cosolvent data²⁵ were taken at 35 °C. The higher temperature reaction rate data reported here suggest that local compositions should increase at lower pressures even at temperatures significantly above the critical point of the solution. Even though the experimental k_{bi} versus pressure curves for the 44.4 °C runs are not as steep as the lower temperature runs, the rate constant based on bulk concentrations still increases at the lower pressures. On the basis of these data, the local compositions should increase substantially at 44.4 °C as well.

Conclusions

Laser flash photolysis studies of the bimolecular reaction between benzophenone triplet and 2-propanol or 1,4-cyclohexadiene in supercritical CO₂ at both 33.0 °C and 44.4 °C indicate that the highest rate constants occur at lower pressures near the critical point of the solution. This occurs even though estimates of the activation volumes predict decreases in the rate constant as the pressure is lowered to the critical pressure. As a result, these studies are the first to show the beneficial influence of increasing the local concentration of substrate in the compressible region near the critical point.

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Appendix

Applying transition-state theory,⁴⁹ the thermodynamic pressure effect on the rate constant can be explained as

$$A + B \leftrightarrow [\text{TS}]^\ddagger \rightarrow \text{products}$$

$$RT \frac{\partial \ln k_{bi}}{\partial P} = -\Delta v^\ddagger - RTk_T \quad (\text{A1})$$

where

$$k_{bi} = \text{bimolecular rate constant (M}^{-1} \text{s}^{-1}\text{)}$$

$$\Delta v^\ddagger = \bar{v}_{is} - \bar{v}_A - \bar{v}_B$$

$$\bar{v}_i = \text{partial molar volume of component } i$$

$$k_T = \text{isothermal compressibility}$$

By definition the partial molar volume can be written as

$$\bar{v}_i = \left[\frac{\partial(nv)}{\partial n_i} \right]_{P,T,n_j}$$

where

n = total number of moles

v = molar volume of the mixture

In order to evaluate the right-hand side of eq A1, $-(\bar{v}_is - \bar{v}_A - \bar{v}_B) - RTk_T$, the partial molar volumes and k_T can be calculated from an equation of state. For simplicity, the Peng–Robinson equation of state⁶⁵ was used in calculating rough estimates of the partial molar volumes of ³BP, substrate, and the transition state, as well as k_T in the quaternary mixture (CO₂ being the fourth component).

The Peng–Robinson equation of state is given as

$$P = \frac{RT}{v - b_m} - \frac{a_m(T)}{v(v + b_m) + b_m(v - b_m)}$$

where

$$b_m = \sum_i z_i b_i$$

$$a_m(T) = \sum_i \sum_j z_i z_j \sqrt{a_i a_j} (1 - k_{ij})$$

k_{ij} = binary interaction parameter

z_i = component i mole fraction

$$b_i = 0.07780 \frac{RT_c}{P_c}$$

$$a_i(T) = a(T_c) \alpha(T_R, \omega)$$

$$T_R = \frac{T}{T_c}$$

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c}$$

$$\alpha = [1 + \beta(1 - T_R^{1/2})]^2$$

$$\beta = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

The Peng–Robinson equation of state requires the critical temperature, T_c , the critical pressure, P_c , and the acentric factor, ω , of the pure components. The properties that cannot be found in the literature, such as those for the ³BP, 1,4-cyclohexadiene, and the transition states for the alcohol and the diene reactions, were

roughly estimated using Joback's modification of Lyderson's method for T_c and P_c and Lee and Kesler's method for the acentric factor.⁵⁷ A structure similar to ground-state benzophenone was assumed for the ³BP in these calculations, and the transition states were assumed to be benzophenone/2-propanol and benzophenone/1,4-cyclohexadiene complexes for the alcohol and diene reactions, respectively. The values of the properties used in the Peng–Robinson equation of state for estimation of the partial molar volumes are given in Table II. Due to a lack of necessary information, the binary interaction parameters for all pair combinations were set to 0.

We now present a brief description of the method of calculation of the partial molar volumes using the Peng–Robinson equation of state. It is difficult to obtain

$$\left[\frac{\partial v}{\partial n_i} \right]_{P,T,v}$$

directly from the Peng–Robinson equation of state. From the triple product rule,

$$\bar{v}_i = \left(\frac{\partial v}{\partial n_i} \right)_{P,T,v_j} = - \frac{\left(\frac{\partial P}{\partial n_i} \right)_{T,v,n_j}}{\left(\frac{\partial P}{\partial v} \right)_{T,n}}$$

Taking the appropriate derivatives,

$$\left(\frac{\partial P}{\partial v} \right)_{T,n} \text{ and } \left(\frac{\partial P}{\partial n_i} \right)_{T,v,n}$$

can be obtained directly from the equation of state so that the partial molar volume of each component can be calculated from the triple product rule. The isothermal compressibility is simply

$$RT \frac{\partial \ln k_{bi}}{\partial P} = -\Delta v^\ddagger - RTk_T \quad (\text{A1})$$

The right-hand side of eq A1 can now be calculated by substituting in the appropriate partial molar volumes and k_T . A FORTRAN program was written to perform these calculations at various pressures on the two isotherms for both reactions. The predicted values of $RT(\partial \ln k_{bi}/\partial P)$ based on the Peng–Robinson equation of state are plotted against pressure in Figures 6 and 7 for both reactions.

Registry No. PhC(O)Ph, 119-61-9; CO₂, 124-38-9; CH₃CH(OH)CH₃, 67-63-0; 1,4-cyclohexadiene, 628-41-1.