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Laser Flash Photolysis and Integral Equation Theory To Investigate Reactions of Dilute Solutes with Oxygen in Supercritical Fluids

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Abstract: The absolute reactivity of triplet benzophenone (^{3}BP) and benzyl free radical ($Ph\dot{C}H_2$) toward molecular oxygen (O_2) in supercritical CO_2 and CHF_3 has been measured by laser flash photolysis (LFP). The transient reactants may be considered to be infinitely dilute solutes reacting with a gaseous cosolvent in a supercritical fluid mixture. Both reactants were found to undergo kinetically controlled reactivity with O_2 and the measured bimolecular rate constants (k_{bi}) were found to decrease with a decrease in solvent density at reduced pressures between 1.0 and 2.5. These results are consistent with solute reactivity with a "nonattractive" cosolvent. The results are compared with those previously obtained for the reaction of ^{3}BP with an "attractive" cosolvent, 1,4-cyclohexadiene, in supercritical CO_2 and CHF_3, in which enhanced ^{3}BP reactivity was observed due to preferential cosolvent/solute solvation. Integral equation theory has also been applied to model these ternary systems, and the results indicate how the strengths of local solvation forces can influence kinetically controlled reactions in supercritical fluids. These results represent the first corroborative analysis using absolute reaction kinetics and integral equation theory to probe preferential cosolvent solvation in ternary supercritical fluid mixtures.

Introduction

Experimental,[1] theoretical,[2] and simulation[1e,3] investigations have now clearly documented that the local solvent density of a supercritical fluid (SCF) about a dilute solute may be significantly greater than the bulk density of the fluid. The addition of an "attractive" cosolvent to a dilute solute supercritical mixture may also result in enhanced local cosolvent compositions about the dilute solute.[2c,4] Although "attractive, non-attractive, and repulsive" have been used previously to characterize SC solvents in binary systems,[2a,3a,3b] here we use "attractive" to refer to a cosolvent whose local composition around the solute is greater than the bulk value. Conversely, a "non-attractive" cosolvent is one whose local composition around the solute would be expected to be less than the bulk. As observed in solvatochromic measurements,[1a–f] the local composition reflects the time-averaged equilibrium structure around a dissolved solute since solvation in liquids and SCFs[3a] occurs very rapidly, i.e., on the picosecond time scale. Both local effects, local density enhancement (solvent clustering) and preferential cosolvent solvation, have the potential to enhance reactivity of a chemically reactive system beyond that expected for bulk conditions. In our efforts to further identify and characterize specific factors that control various types of chemical reactivity in SCFs, we were interested in the investigation of kinetically controlled reactions of dilute solutes with potentially "non-attractive" cosolvents. The reactions investigated here occur on the nanosecond to microsecond time scale, well after the equilibrium solvation structure around the solute has been established. In the present study we have investigated the reactions of triplet benzophenone (^{3}BP) and benzyl free radical ($Ph\dot{C}H_2$) with a gaseous cosolvent, oxygen, in supercritical carbon dioxide (CO_2) and fluoroform (CHF_3), eqs 1 and 2, respectively.

$$^3BP + {}^3O_2 \rightarrow BP + {}^1O_2 \tag{1}$$

$$Ph\dot{C}H_2 + O_2 \rightarrow PhCH_2O_2^{\bullet} \tag{2}$$

Oxygen was chosen as a reactive cosolvent since, in general, based on the strength of interactions between each of the species, one would not anticipate that ^{3}BP or $Ph\dot{C}H_2$ would demonstrate any preference for solvation with O_2 over the SCF solvents, CO_2 and CHF_3. Experimentally, a lack of preferential cosolvent solvation was, indeed, observed for the O_2 cosolvent system. These results are compared to the results of a previous study for the reaction of ^{3}BP with an "attractive" cosolvent, 1,4-cyclohexadiene, in which preferential cosolvent solvation was observed.[5,6] Integral equation theory has also been applied to model these ternary systems and fully corroborates the experimental results.

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Integral Equation Calculations

We will compare the experimental results presented here to previous investigations of the reaction of ^{3}BP with 1,4-cyclohexadiene in supercritical fluids.[5,6] We will show the qualitative differences in the two studies can be explained in terms of differences in the strength of the local interactions between the molecules and the resulting differences in preferential solvation. To support this explanation, we will present the results of integral equation calculations that model the mixtures used in the two studies. Integral equation theories for the molecular correlation functions yield the local microstructures of supercritical fluid mixtures,[7] showing the relationship between differences in molecular interaction forces and the degree of preferential solvation. The solvent–solute and cosolvent–solute correlation functions can be used to obtain the local mole fractions of solvent and cosolvent molecules around a solute molecule. We have previously presented the first calculations of this type for ternary supercritical mixture over a wide range of densities for the pyrene/CO_2/CHF_3 system, in order to explain some interesting spectroscopic results.[8]

The integral equation is based on the Ornstein–Zernike (OZ) relation[9] between the total correlation function, $h_{ij}(r)$, and the direct correlation function, $c_{ij}(r)$, for mixture components i, j. For ternary mixtures $i, j = 1, 2$, and 3.

$$r\gamma_{ij}(r) = 2\pi\sum_k \varrho_k \int_0^\infty \mathrm{d}s\, s\, c_{ik}(s) \int_{|r-s|}^{r+s} \mathrm{d}t\, t\, h_{kj}(t) \qquad (3)$$

where $\gamma_{ij}(r) = h_{ij}(r) - c_{ij}(r)$ is the indirect correlation function. The Percus–Yevick closure is

$$c_{ij}(r) = [1 + \gamma_{ij}(r)](\exp[-\beta u_{ij}(r)] - 1) \qquad (4)$$

where $\beta = 1/kT$. This equation can be solved by (i) direct iterations (Picard's method), (ii) the Newton–Raphson method with a coarse graining basis function, i.e., Labik–Gillan[10] prescription, or (iii) Baxter's Wiener–Hopf factorization[11] of the OZ equation. To solve eq 4, Cummings and Monson[12] have applied Baxter's method. The same method has been used by Wu et al.[2a] for binary supercritical solute–solvent mixtures. The Labik–Gillan method has been explored by Cochran, Johnson, and Lee[13] and Pfund and Cochran[14] for ternary mixtures. Here we applied the highly efficient Labik–Gillan numerical technique[13] which combines Newton–Raphson (NR) and direct iteration (DI) methods. The details of the Labik–Gillan method were described elsewhere.[2a]

Table 1. Lennard-Jones Parameters Used in the Integral Equation Calculations

component	ϵ/k (K)	σ (Å)
carbon dioxide	232.2	3.643
oxygen	118.0	3.355
1,4-cyclohexadiene	436.7	5.227
benzophenone	625.7	6.580

For this first study, we have used Lennard-Jones (spherical) potentials, $u_{ij}(r)$, for the solute benzophenone (**2**), the solvent CO_2 (**1**), and the cosolvent O_2 or 1,4-cyclohexadiene (**3**) with different size (σ_{ij}) and energy (ϵ) parameters. (See Table 1.)

$$u_{ij}(r) = 4\epsilon\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] \qquad (5)$$

This is a drastic simplification of the real molecular interactions between benzophenone, CO_2, O_2, and 1,4-cyclohexadiene, which involve directional polar and multipolar forces. Moreover, the Lennard-Jones parameters for benzophenone do not account for its being in the triplet electronic state. However, we are interested in the etiological roles that size and energy play in the determination of solvation structures that are inherent already in a simple potential such as the Lennard-Jones potential. In the future, additional features due to orientational ordering could be unequivocally and separately determined.

Experimental Section

Materials. Benzophenone (Aldrich, Gold Label) was used as received. 1,3-Diphenylacetone (dibenzyl ketone) (Aldrich, 99%) was further purified by multiple chromatographies (silica gel column; 50% CH_2Cl_2/hexanes). Oxygen (Mittler Supply, 98% purity) and carbon dioxide (Scott Specialty Gases, SFC grade) were used as received. Fluoroform (DuPont Freon-23, 98% purity) was sequentially passed through multiple high-pressure oxy-traps (Alltech) and multiple high-pressure charcoal traps (Alltech). All liquid solvents were Fisher, ACS certified and used as received.

Method. The high-pressure apparatus, sample preparation, and application of LFP to SCF samples have recently been described in detail.[5] Briefly, LFP experiments were performed using laser excitation perpendicular to a pulsed 1000-W xenon lamp monitoring source. Transient absorption signals were digitized with a Tektronix 7912 AD digitizer and a VAX-11/780 was used for experimental control and computer analysis. Laser excitation was provided from either a Quanta Ray DCR-1 Nd:YAG (266 or 355 nm; ~10 mJ; pulse width ~6 ns) laser system or a Lambda Physik EMG 101 MCS excimer laser operated at 308 nm (XeCl) (4–100 mJ; pulse width 10 ns). The choice of laser excitation and excitation conditions depended on the individual experiment (vide infra). Ground state absorption spectra were measured using a SLM-Aminco Spectronic 3000 Array spectrophotometer fitted with a custom sample holder for the high-pressure optical cells.

Sample Preparation. The apparatus used to prepare gaseous cosolvent/SCF solvent samples consisted of the solvent gas cylinder (CO_2 or CHF_3), an O_2 gas cylinder, an Isco high-pressure syringe pump (Model 260D) thermostated with a water jacket and recirculation bath (Brinkmann Instruments, Model Lauda K-2/R or GCA Precision R12B), and the high-pressure optical cell. The high-pressure stainless steel optical 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 packing. The design and construction of the cells have been described in detail elsewhere.[15] Each of the components of the sample preparation apparatus were connected with $^1/_{16}$ in. stainless steel high-pressure tubing and high-pressure (HIP) valves fitted with Teflon O-rings.

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The sample apparatus was evacuated prior to sample preparation. Gaseous oxygen was purged through the system at low pressure for 15–20 min with the internal volume of the syringe pump set at a desired value. A known volume of low-pressure (typically around 20 psig) oxygen was then enclosed in the syringe pump and brought to a constant desired temperature, typically 25 °C. The system was allowed to equilibrate for ~1 h. The amount of oxygen in the pump could then be determined from the ideal gas law $PV = nRT$, using the temperature, the total volume, and the pressure of the system, as indicated by the pressure transducer in the Isco pump and verified with a Heise pressure gauge. These values were further checked against the Pitzer compressibility-factor correlations and the generalized virial-coefficient correlations.[16] All methods of calculation agreed within 5%.

With a desired known amount of oxygen housed in the syringe pump the contents of the pump were cooled to 0 °C and then filled with subcooled liquid solvent (CO_2 or CHF_3). By using the temperature and pressures of the Isco syringe pump the amount of solvent added could be determined using measured density data[17] for pure CO_2 or using densities calculated from an empirical equation of state[18] for pure fluoroform. The oxygen cosolvent mole fractions were then determined knowing the amount of oxygen initially added and the number of moles of solvent added. Pure solvent densities could be used due to the small concentrations of O_2 required for quenching in the kinetic experiments. These mole fractions were verified by raising the temperature of the recirculating water to ambient, thus increasing the pressure. At these conditions the solvent was still subcooled liquid. The pressure and temperature in the high-pressure syringe pump were again used to estimate the mole fraction. Agreement between the mole fractions calculated at this temperature and at $T = 0$ °C was ±2%. The pump was then heated to above the critical temperature, raising the pressure well above the critical pressure such that the solution became one phase. The O_2 mixtures were sufficiently dilute that the addition of these low concentrations of O_2 were not expected to significantly change the critical point from that of the pure solvent. The critical pressure and temperature of CO_2 are 73.8 bar and 31 °C, respectively. The critical pressure and temperature of fluoroform are 48.2 bar and 25.9 °C, respectively. For all experiments, the supercritical mixture was allowed to thoroughly equilibrate (1–2 h) at the desired elevated temperature and pressure prior to loading of the LFP cells.

Typically, a LFP SCF sample was prepared by evacuation of the optical cell followed by loading of the cell with a portion of the contents of the Isco pump (O_2/solvent mixture), which contained an appropriate amount of crystalline benzophenone or dibenzyl ketone. The cell was heated to facilitate mixing and raise the contents above the critical point. Benzophenone or dibenzyl ketone concentrations were adjusted to ca. 0.8 absorbance units at the laser excitation wavelength. The solute concentrations have previously been determined to be well below (up to 25-fold) the solubility limit.

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 the desired 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. The thermometer was fitted into the optical cell making direct contact with the fluid.

Results

Laser Flash Photolysis. Experiments were performed on two isotherms of equivalent reduced temperature (T_R), at T_R = 1.013 and 1.062, in CO_2 (T = 35, 50 °C) and fluoroform (T = 29.8, 44.5 °C). Additional higher temperature experiments were performed in CO_2 at T = 70 and 90 °C. Depending on the specific experiment (vide infra), investigations were carried out by two independent methods, by varying O_2 concentrations at constant mole fraction conditions (from high to low pressure by release of homogeneous solution) or at constant molarity (from low to high pressure by addition of pure solvent). In the constant mole fraction method, absolute rate constants were measured for the reactions of ^3BP or $Ph\dot{C}H_2$ with O_2 in CO_2 at O_2 concentrations of 4.26×10^{-5} to 8.01×10^{-4} mole fraction (1.7×10^{-4} to 1.6×10^{-2} M) and in CHF_3 for an O_2 mole fraction range of 6.57×10^{-5} to 5.85×10^{-4} (2.9×10^{-4} to 8.3×10^{-3} M). The cosolvent compositions are given in Table 2.

Table 2. O_2 Mole Fractions, x, in Supercritical CO_2 and Supercritical CHF_3 Cosolvent Mixtures

CO_2(solvent) 35 °C; 50 °C	CO_2(solvent) 70 °C; 90 °C	CHF_3(solvent) 29.8 °C; 44.5 °C
4.35×10^{-5}	4.26×10^{-5}	6.57×10^{-5}
1.33×10^{-4}	1.10×10^{-4}	1.45×10^{-4}
4.28×10^{-4}	3.57×10^{-4}	3.07×10^{-4}
6.34×10^{-4}	5.00×10^{-4}	5.42×10^{-4}
8.01×10^{-4}	6.49×10^{-4}	5.85×10^{-4}

We have previously investigated the spectroscopic characteristics of both ^3BP and $Ph\dot{C}H_2$ in pure supercritical CO_2[19] and CHF_3.[20] The characteristic absorption bands[21a] of ^3BP (320 and 525 nm) are readily observed following 355-nm laser excitation of benzophenone in CO_2 and CHF_3 and are nearly identical to those observed in liquid CH_3CN.[5] The absorption bands did not shift significantly from the liquid to the supercritical solvents. Alternatively, the sharp absorption band of $Ph\dot{C}H_2$ observed at 317 nm following 308-nm LFP and Type 1 homolytic fragmentation of dibenzyl ketone in normal liquids[21b] is significantly shifted to 310 nm in supercritical CO_2 and CHF_3. The spectroscopic displacement is actually a bathochromic shift from the 305.3-nm gas-phase value[21c] and is primarily due to London dispersion forces. The $Ph\dot{C}H_2$ band also demonstrates only a slight (0.5–1 nm) shift with variation in supercritical solvent density.[19,20]

The kinetic behavior of both ^3BP and $Ph\dot{C}H_2$ has also been investigated[20] in pure supercritical CO_2[19] and CHF_3 and the intermediates were found to decay with pure second order kinetics by triplet–triplet annihilation and radical–radical termination reactions, respectively. Absolute rate constants for the reactions of ^3BP and $Ph\dot{C}H_2$ with O_2 were obtained by measuring the change in the rate of decay of the triplet or radical absorption signal with added quenching O_2. The decays are pseudo first order in the presence of O_2. Therefore, fitting the time-resolved absorption trace with a single exponential yields the observed pseudo-first-order rate constant, k_{obs}. Individual experiments were performed for each concentration of O_2 at various pressures along each isotherm (through either the constant mole fraction or constant molarity method). Typically, the reactions with O_2 demonstrated gradual increases in k_{obs} with an increase in pressure. As an example, Figure 1 presents the effects of pressure on k_{obs} for ^3BP with 1.33×10^{-4} mole fraction of O_2 at 35 °C in CO_2 and for $Ph\dot{C}H_2$ with 6.6×10^{-5} mole fraction of O_2 at 29.8 °C in CHF_3.

It should be noted that there was initial concern of running these experiments under static conditions. This was due to the report of a dependence of $Ph\dot{C}H_2$ decay kinetics on laser shot

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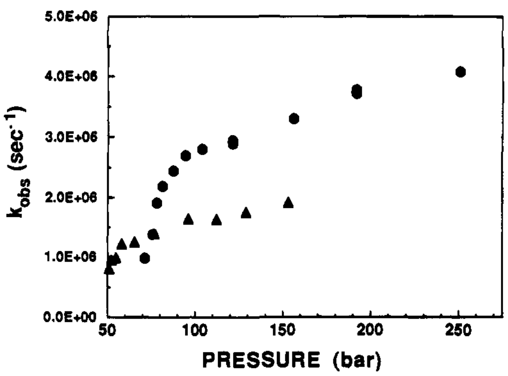

Figure 1. Pressure dependence of the pseudo-first-order rate constant for the decay of ^{3}BP in the presence of 1.33 × 10^{-4} mole fraction of oxygen in CO_2 at 35 °C (●), and for $Ph\dot{C}H_2$ in the presence of 6.6 × 10^{-5} mole fraction of oxygen in CHF_3 at 29.8 °C (▲).

number and shot frequency in the investigation of measuring absolute rate constants for the reaction of $Ph\dot{C}H_2$ with O_2 in organic liquid solvents.[21b] The unusual kinetic behavior was attributed to partial O_2 depletion in the region of the solution being examined due to poor gas–liquid equilibration. Therefore, a laser shot and frequency investigation was performed for the reactions of both ^{3}BP and $Ph\dot{C}H_2$ with O_2 in supercritical CO_2 and CHF_3. No variation in decay rate constants was observed, demonstrating that O_2 depletion is not influencing our kinetic results.

Bimolecular rate constants (k_{bi}), M^{-1} s^{-1}, for ^{3}BP and $Ph\dot{C}H_2$ reactivity could be obtained at individual (constant) pressures from construction of bimolecular quenching plots of k_{obs} versus concentration of O_2, $[O_2]$, according to $k_{obs} = k_0 + k_{bi}[O_2]$, where k_0 represents all modes of decay of reactant (^{3}BP or $Ph\dot{C}H_2$) in the absence of O_2. Linear quenching plots were obtained for both reactions with O_2 at all pressures and temperatures studied. Examples of k_{obs} versus $[O_2]$ concentration at constant pressures for both ^{3}BP and $Ph\dot{C}H_2$ in CO_2 at 35 °C are presented in Figure 2.

Pressure Effect on k_{bi} at T_R = 1.013 in CO_2. Figure 3 presents k_{bi} for the reaction of both ^{3}BP and $Ph\dot{C}H_2$ with O_2 in SC CO_2 at T_R = 1.013 (35 °C). Modest increases in k_{bi} from 7.4 × 10^8 (M^{-1} s^{-1}) at 82 bar to 1.05 × 10^9 (M^{-1} s^{-1}) at 208 bar were observed over the pressure range studied for the ^{3}BP reaction while similar increases (9.7 × 10^8 (M^{-1} s^{-1}) at 79 bar to 1.43 × 10^9 (M^{-1} s^{-1}) at 208 bar) were observed for the $Ph\dot{C}H_2$ reaction with slightly greater absolute values. The lines in the figure are predicted values, which will be explained later. The pressure effects on k_{bi} for both reactions were essentially identical with the exception of absolute value. Initially, we were concerned whether homogeneous solution was indeed being released in the constant mole fraction method and these results were, therefore, verified by repeating both reactions at 35 °C in CO_2 with the constant molarity method. The constant molarity results are also shown in Figure 3. The two methods yielded nearly identical results for each reactant. Thus, we concluded that the constant mole fraction method was providing accurate results and was used for the remainder of the studies.

Pressure Effect on k_{bi} at T_R = 1.013 in CHF_3. The influence of changing solvent polarity was investigated by studying both reactions with O_2 in the polar solvent CHF_3. Figure 4 presents k_{bi} for the reaction of both ^{3}BP and $Ph\dot{C}H_2$ with O_2 in SC CHF_3 at T_R = 1.013 (29.8 °C). Modest increases in k_{bi} from 8.70 × 10^8 (M^{-1} s^{-1}) at 53 bar to 1.09 × 10^9 (M^{-1} s^{-1}) at 132 bar were observed over the pressure range studied for the ^{3}BP reaction while similar increases (7.18 × 10^8 (M^{-1} s^{-1}) at 53 bar to 1.17 × 10^9 (M^{-1} s^{-1}) at 132 bar) were observed for the $Ph\dot{C}H_2$ reaction. The pressure effects on k_{bi} for both reactions were essentially identical. The lines in the figure are predicted values, which will be explained later.

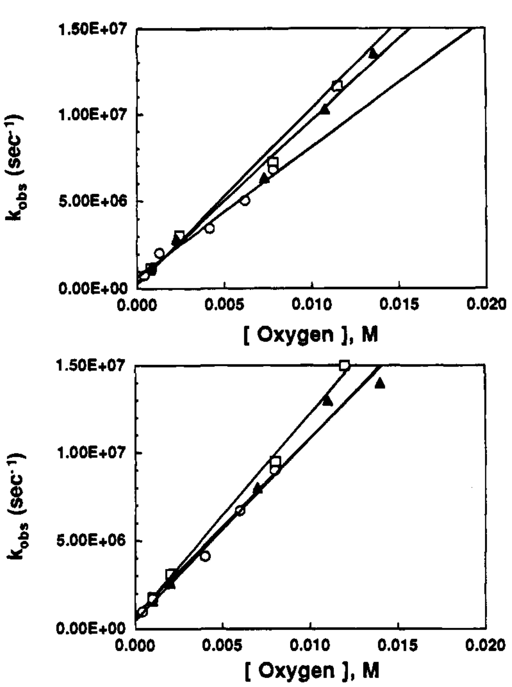

Figure 2. Determination of the bimolecular rate constants from the pseudo-first-order rate constants at various pressures (80 (○), 111 (▲), and 138 bar (□)) for the reactions of oxygen with ^{3}BP (top) and $Ph\dot{C}H_2$ (bottom) in CO_2 at 35 °C.

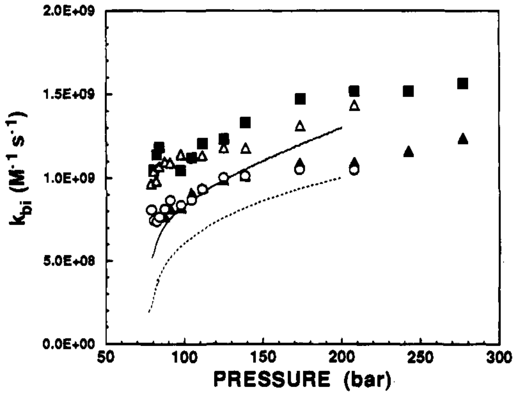

Figure 3. Pressure dependence of the experimental bimolecular rate constants for the reaction of oxygen with ^{3}BP (constant mole fraction method (○) and constant molarity method (▲)) and the reaction of oxygen with $Ph\dot{C}H_2$ (constant mole fraction method (Δ) and constant molarity method (■)). All reactions are in CO_2 at 35 °C. The pressure effects predicted from transition state theory for ^{3}BP (- - -) and $Ph\dot{C}H_2$ (—) are also included (see text).

Pressure Effect on k_{bi} at T_R = 1.062 in CHF_3 and CO_2. Similar results were obtained for the reaction of both ^{3}BP and $Ph\dot{C}H_2$ with O_2 in SC CHF_3 and CO_2 at T_R = 1.062 (44.5 and 50 °C, respectively). Increases in k_{bi} from 9.97 × 10^8 (M^{-1} s^{-1}) at 63 bar to 1.13 × 10^9 (M^{-1} s^{-1}) at 173 bar were observed over the pressure range studied for the ^{3}BP reaction while similar increases (8.20 × 10^8 (M^{-1} s^{-1}) at 63 bar to 1.00 × 10^9 (M^{-1} s^{-1}) at 153 bar) were observed for the $Ph\dot{C}H_2$ reaction in CHF_3 at 44.5 °C. Increases in k_{bi} from 8.49 × 10^8 (M^{-1} s^{-1}) at 84 bar to 1.11 × 10^9 (M^{-1} s^{-1}) at 208 bar were observed over the pressure range studied for the ^{3}BP reaction while similar increases (8.98 × 10^8 (M^{-1} s^{-1}) at 84 bar to 1.09 × 10^9 (M^{-1} s^{-1}) at 208 bar) were observed for the $Ph\dot{C}H_2$ reaction in CO_2 at 50 °C.

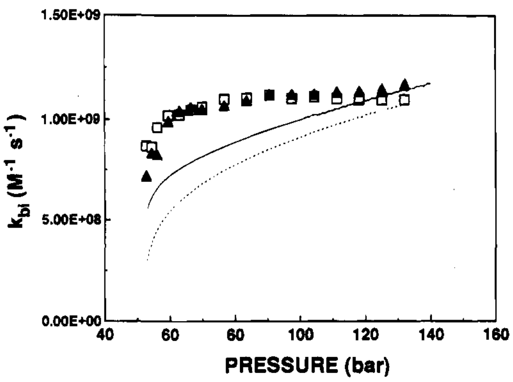

Figure 4. Pressure dependence of the experimental bimolecular rate constants for the reaction of oxygen with ^3BP (□) and $Ph\dot{C}H_2$ (▲) in CHF_3 at 29.8 °C. The pressure effects predicted from transition state theory for ^3BP (- - -) and $Ph\dot{C}H_2$ (—) are also included (see text).

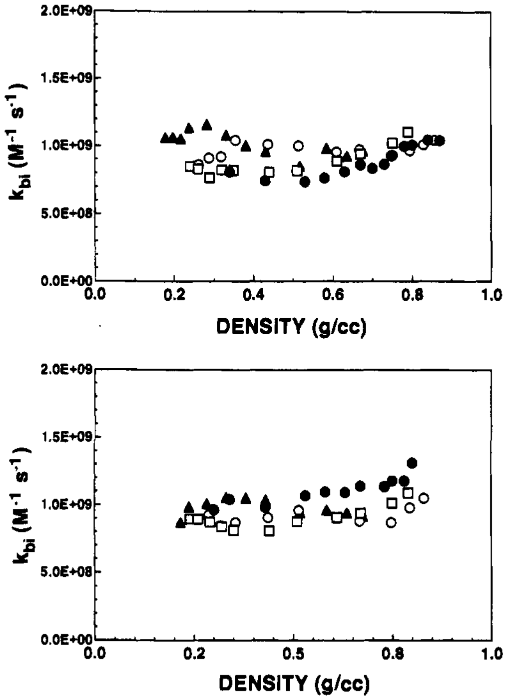

Figure 5. Bimolecular rate constants for the reaction of ^3BP with oxygen in CO_2 (top) and for the reaction of $Ph\dot{C}H_2$ with oxygen in CO_2 (bottom) at 35 (●), 50 (□), 70 (○), and 90 °C (▲).

Temperature Effect. The effect of temperature on the reactivity of ^3BP and $Ph\dot{C}H_2$ with O_2 in SC CO_2 was investigated in an attempt to determine Arrhenius parameters for these reactions under supercritical conditions. We note, however, that the temperature range for this study was limited at low temperature by maintaining SC conditions and at high temperature by operation under the safety constraints of our current equipment. The dependence of k_{bi} on solvent density at 35, 50, 70, and 90 °C for the reaction of ^3BP with O_2 in SC CO_2 and for $Ph\dot{C}H_2$ with O_2 in CO_2 is presented in Figure 5.

Integral Equation Results. The unique pressure effect observed for the quenching reaction of ^3BP with 1,4-cyclohexadiene and 2-propanol in supercritical fluids has been attributed to the local concentration enhancement of the quencher (cosolvent) around the solute (^3BP) molecules.[5,6] However, the pronounced pressure effect was not observed for the oxygen quenching reactions of ^3BP and $Ph\dot{C}H_2$ in SCFs. In order to explore these two different reactions theoretically and investigate the degree of preferential solvation at supercritical conditions, we have used integral equation calculations to model the two ternary systems: CO_2/1,4-cyclohexadiene/BP and CO_2/O_2/BP.

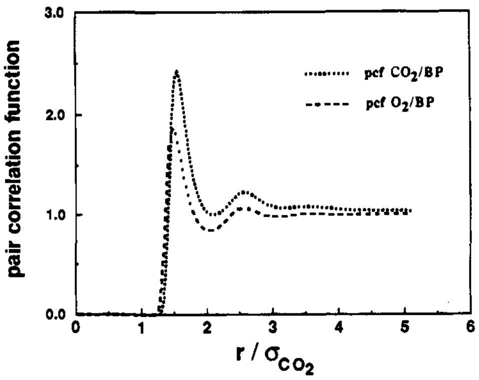

Figure 6. Pair correlation functions (g_{ij}) for BP$-CO_2$ and BP$-$oxygen in a mixture of 1 × 10^{-4} mol % benzophenone/99.99 mol % CO_2/0.01 mol % oxygen at a reduced density of 0.39 and 42 °C.

As discussed above, we used the Percus$-$Yevick closure and Lennard-Jones potentials to obtain the pair correlation functions. The L-J size and energy parameters of each component were calculated from its critical density and critical temperature according to $\varrho_c\sigma^3 = 0.31$ and $kT_c/\epsilon = 1.31$, respectively, as determined by the best estimate of the critical point for a Lennard-Jones fluid via direct simulation of phase coexistance,[22] and are listed in Table 1. The L-J parameters between unlike molecules were calculated according to the formulas $\epsilon_{ij} = (\epsilon_i\epsilon_j)^{1/2}$ and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. The critical properties for 1,4-cyclohexadiene and benzophenone were estimated by Joback's modification of Lydersen's method[23] while the experimental values of critical properties were available for CO_2[17b] and oxygen.[23]

To simulate the quenching experiments discussed above, we performed the integral equation calculations of ternary mixtures of 1.0 x10^{-4} mol % benzophenone/99.99 mol % CO_2/0.01 mol % oxygen and 1.0 × 10^{-4} mol % benzophenone/99.99 mol % CO_2/0.01 mol % 1,4-cyclohexadiene at 42 °C (a temperature intermediate between the T_R = 1.013 and 1.062 investigated experimentally), with all molecules approximated as L-J spheres. As an example, the CO_2/benzophenone and O_2/benzophenone pair correlation function plots are given in Figure 6 at a reduced density of 0.39 and 42 °C. A cut-off distance was chosen arbitrarily as $3.6\sigma_{CO_2}$ for the local concentration calculations, which roughly corresponds to 2.5 solvent shells. The calculated local mole fraction of 1,4-cyclohexadiene around benzophenone in CO_2 is shown in Figure 7. While the magnitude of the local compositions changes somewhat if the cut-off distance is changed, the qualitative features of Figure 7 remain the same. The local mole fraction of 1,4-cyclohexadiene is about two times as large as the bulk mole fraction at lower densities and it decreases to about the bulk value with an increase in density. However, the local concentration of oxygen around benzophenone in CO_2 (also shown in Figure 7) exhibited an opposite trend: the local mole fraction of oxygen is slightly lower than the bulk and it increases with an increase in density, approaching the bulk value at high pressures. It is clear that the different solvation behaviors observed are driven primarily by the relative strength of different molecular interactions in near-critical conditions. If the molecular interaction between solute molecule and cosolvent molecule is stronger than that between solute molecule and solvent molecule, the solute molecules will be preferentially solvated by cosolvent molecules, as is the case for CO_2/1,4-cyclohexadiene/BP. On the other hand, if the molecular interaction between the solute molecule and solvent

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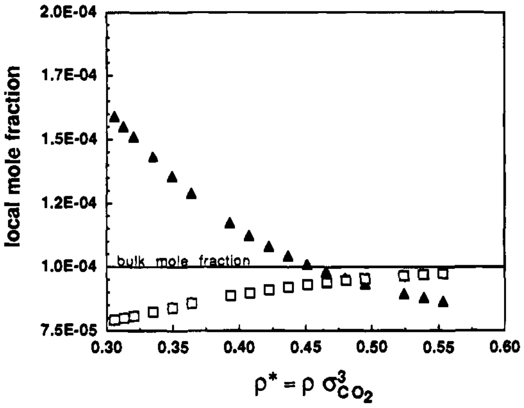

Figure 7. Local mole fractions of cosolvent (oxygen (□) or 1,4-cyclohexadiene (▲)) around benzophenone in a mixture with bulk composition of 1×10^{-4} mol % benzophenone/99.99 mol % CO_2/0.01 mol % cosolvent at 42 °C. The density is reduced with the L-J size parameter of CO_2, $\sigma^3_{CO_2}$ (see text). The critical density corresponds to approximately $\varrho^* = 0.31$.

molecule is stronger than that between the solute molecule and the cosolvent molecule, a depletion of cosolvent around the solute molecules would be observed, as is the case for CO_2/oxygen/BP.

Discussion

Even though SCFs demonstrate great potential as reaction media due to the ability to produce dramatic changes in bulk physical properties (e.g., density, diffusivity, and dielectric constant) with small perturbations in temperature or pressure, there are other factors that may also influence chemical reactivity in SCFs, such as, the thermodynamic pressure effect on reaction rate constants or SCF solvation dynamics. Therefore, a major challenge in understanding chemical reactivity and, hopefully, developing the ability to predict the behavior of potentially important chemical reactions in SCFs is the identification and characterization of the individual factors that control and drive chemical reactivity in SCFs.

Previously, in our efforts to address this challenge, we have investigated the potential influence of solvent density and cosolvent composition enhancements (clustering or cage effects) on diffusion-controlled reactions.[19,20] The triplet–triplet annihilation reaction of ^{3}BP and the free radical termination reaction of $Ph\dot{C}H_2$ were investigated in supercritical CO_2, CHF_3, C_2H_6, and modified CO_2 (1 mol % CH_3CN). Both reactions were found to occur at the diffusion-controlled limit (when appropriate spin statistical factors were taken into account) in each of the SCF mixtures studied and under all conditions, which were typically above reduced densities of 1. These results demonstrated that the locally higher density of solvent or cosolvent around the reactive solutes in no way enhanced or slowed the bimolecular annihilation or termination reaction. Therefore, we demonstrated that, in general (in the absence of other specific interactions), diffusion-controlled reactions in SCFs are controlled by the bulk physical property of diffusivity. It should be noted that there appeared to be some controversy in the literature concerning diffusion-controlled reactions, in that pyrene excimer formation had been reported to be either diffusion controlled or up to an order of magnitude below diffusion controlled, dependent on the specific SCF or SC mixture investigated.[24] However, in subsequent experiments and analysis, those researchers have found that pyrene excimer formation occurs at the diffusion-controlled limit under all conditions reported previously.[25] Thus, there is currently general agreement that for reactions that are diffusion controlled in normal liquids, one should also observe diffusion-controlled reactivity under SC conditions.

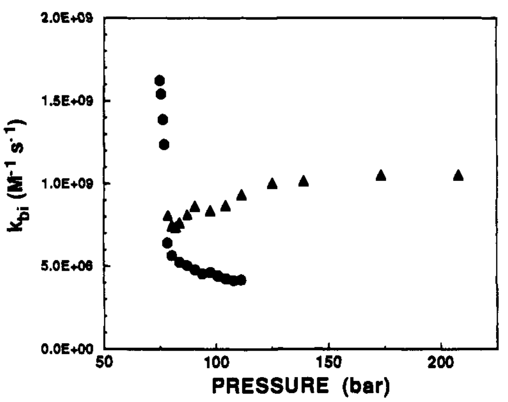

Figure 8. Comparison of the pressure dependence of the bimolecular rate constants for the reaction of ^{3}BP with 1,4-cyclohexadiene (●) and oxygen (▲) at 35 °C in CO_2.

As previously mentioned, for kinetically-controlled reactions the phenomenon of local solvent density and cosolvent enhancements about a reactive dilute solute have the potential to influence observed reactivity. Solvatochromic probes have been extremely successful in the identification of enhanced solvent–solute and cosolvent–solute interactions by the detection of spectral shifts of absorption or fluorescence maxima greater than those expected based on the Onsager field strength obtained from bulk densities. Such solvatochromic measurements have indicated that the enhanced local densities and local compositions occur most dramatically in the low-density subcritical region and in the highly compressible region of the SCF.[1,26] We have previously investigated[6] the kinetically-controlled hydrogen-abstraction reaction of ^{3}BP with 1,4-cyclohexadiene and 2-propanol and have used solvatochromic measurements and transition state theory analysis to demonstrate that enhancements in reactivity could be obtained by local cosolvent enrichment in these mixtures with "attractive" cosolvents. Therefore, solvation primarily controlled the observed reactivity in these reactions. In the case of "non-attractive" cosolvents one would not expect solvatochromic probes to exhibit spectral shifts so they are not a particularly useful tool for these mixtures. Therefore, our kinetic measurements in the present investigation will be analyzed in terms of the thermodynamic pressure effect on reaction rate constants and the use of integral equation theory.

Pressure Effect. The bimolecular rate constants (k_{bi}) for the reactions of ^{3}BP and $Ph\dot{C}H_2$ with oxygen increase very slightly with increasing pressure. This is true in both supercritical CO_2 and CHF_3 and for the entire range of pressures investigated (P_R = 1 to 2.5). This is in striking contrast to the trends reported for the reaction of ^{3}BP with 1,4-cyclohexadiene or 2-propanol in supercritical CO_2, CHF_3, or C_2H_6.[5,6] This dramatic difference can be seen in Figure 8, which shows the influence of pressure on k_{bi} for the reaction of both ^{3}BP + O_2 and ^{3}BP + 1,4-cyclohexadiene in CO_2 at 35 °C.

In the previous study, the apparent increase in k_{bi} for ^{3}BP + 1,4-cyclohexadiene was attributed to the increased concentration of 1,4-cyclohexadiene around the ^{3}BP solute at lower pressures.

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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
fluoroform	299.1[a]	48.2[a]	0.260[a]
carbon dioxide	304.2[b]	73.8[b]	0.225[b]
oxygen	154.6[c]	50.4[c]	0.025[c]
1,4-cyclohexadiene	582.5[d]	22.8[d]	0.216[e]
benzyl radical	597.8[d]	42.9[d]	0.27[e]
triplet benzophenone	821.0[d]	33.0[d]	0.557[e]
oxygen/benzyl radical transition state	640.7[d]	41.0[d]	0.417[e]
oxygen/^{3}BP transition state	893.1[d]	28.4[d]	0.649[e]
1,4-cyclohexadiene/^{3}BP transition state	1037.3[d]	22.8[d]	0.630[e]

[a] Reference 18. [b] Reference 17b. [c] Reference 23. [d] Estimated, Joback's modification of Lyderson's method, ref 23, p 14. [e] Estimated, standard method, ref 23, p 23.

This was rationalized in terms of the stronger intermolecular forces between ^{3}BP and 1,4-cyclohexadiene than between ^{3}BP and the solvent (e.g., CO_2). This conclusion was further supported by the predicted values of the pressure effect on the rate constants, derived from transition state theory.[27] According to this model, the reactants and transition state are in thermodynamic equilibrium

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

so that the thermodynamic pressure effect on a bimolecular rate constant[28] is given by

$$RT\left(\frac{\partial \ln k_{\mathrm{bi}}}{\partial P}\right)_T = -\Delta v^{\ddagger} - RT\,k_{\mathrm{T}} \qquad (6)$$

where k_{bi} = bimolecular rate constant ($\mathrm{M^{-1}\,s^{-1}}$), $\Delta v^{\ddagger} = \bar{v}_{\mathrm{TS}} - \bar{v}_{\mathrm{A}} - \bar{v}_{\mathrm{B}}$ = reaction activation volume, $\bar{v}_i$ = partial molar volume, k_{T} = isothermal compressibility, R = gas constant, and T = absolute temperature.

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. The pressure effect can be significant since partial molar volumes of solutes in SCFs as large as $-15\,000$ $\mathrm{cm^3/mol}$ have been reported in the literature.[29] In the previous study[6] we used the Peng–Robinson equation of state to estimate the pressure effect on the rate constants and found that they should actually increase with increasing pressure. Thus, it was concluded that the apparent increase in k_{bi} for ^{3}BP + 1,4-cyclohexadiene was actually due to the increased local composition of the diene around the ^{3}BP at lower pressures.

Using the same method employed previously, we calculated the expected pressure effect on the reaction of $^3\mathrm{BP} + O_2$ and $\mathrm{Ph\dot{C}H_2} + O_2$ in both SC CO_2 and CHF_3. These calculations require the critical properties (T_c, P_c) and acentric factor (ω) of the components which are not known for many of our components and have, therefore, been estimated by appropriate group contribution methods.[23] The Joback's modification of Lyderson's method[23] was used to estimate both T_c and P_c and the standard method[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.

Under all conditions the predictions from transition state theory show that the rate constants for both reactions should increase slightly with pressure for all temperatures studied, in agreement with experimental observations. As an example, the experimental and predicted pressure effect on the rate constants are shown for both $^3\mathrm{BP} + O_2$ and $\mathrm{Ph\dot{C}H_2} + O_2$ in Figure 3 (CO_2 as the solvent) and Figure 4 (CHF_3 as the solvent). The predictions suggest that the bimolecular rate constants should increase very modestly (by no more than a factor of 2) with increasing pressure over the range of pressures investigated. Thus, one is led to conclude that increased local concentrations of the diene exist around the ^{3}BP in a $^3\mathrm{BP/diene/CO_2}$ or $^3\mathrm{BP/diene/CHF_3}$ mixture and serve to enhance the ^{3}BP + 1,4-cyclohexadiene reaction rate. However, the local concentration of oxygen around ^{3}BP in a $^3\mathrm{BP/O_2/CO_2}$ or $^3\mathrm{BP/O_2/CHF_3}$ mixture and of oxygen around $\mathrm{Ph\dot{C}H_2}$ in a $\mathrm{Ph\dot{C}H_2/O_2/CO_2}$ or $\mathrm{Ph\dot{C}H_2/O_2/CHF_3}$ mixture is not greater than the bulk value and does not result in an enhanced reaction rate.

To summarize, the calculated trends from transition state theory for the pressure effect on the rate constants for all the reactions of ^{3}BP and $\mathrm{Ph\dot{C}H_2}$ presented in this and a previous[6] study predict that the rate constants should be increasing slightly with increasing pressure. $^3\mathrm{BP} + O_2$ and $\mathrm{Ph\dot{C}H_2} + O_2$ follow this trend but ^{3}BP + 1,4-cyclohexadiene and ^{3}BP + 2-propanol do not. Although the reactions are very different, transition state theory suggests that they should all be influenced only modestly by pressure, increasing slightly with increasing pressure. We are attributing the dramatic differences in the experimentally measured pressure effect on the various reactions to differences in the local concentration of the cosolvent (O_2, diene, or 2-propanol) around the solute (^{3}BP or $\mathrm{Ph\dot{C}H_2}$). To further support these conclusions, we have performed integral equation calculations as a means of determining the relative trends of the local compositions of 1,4-cyclohexadiene versus oxygen around ^{3}BP in a particular SC solvent with changing pressure.

The local compositions determined from the integral equation calculations and shown in Figure 7 demonstrate the trends distinctly. At high pressures, where the densities are more liquid-like, the local mole fractions are close to the bulk values for both cosolvents. However, at lower pressures ^{3}BP is preferentially solvated by 1,4-cyclohexadiene in a $^3\mathrm{BP/diene/CO_2}$ model mixture. Conversely, at lower pressures ^{3}BP shows a slight preference for CO_2 in a $^3\mathrm{BP/O_2/CO_2}$ mixture. Thus, the local mole fraction of O_2 is actually slightly *below* the bulk value. These calculations are in excellent agreement with the experimental measurements of the reaction rates. The rate of the reaction of ^{3}BP with diene is enhanced by the increased local concentration of the diene around the ^{3}BP at lower pressure (as shown in Figure 7), resulting in apparently increased k_{bi} (as shown in Figure 8). Conversely, the local environment around ^{3}BP is not enhanced in O_2 (as shown in Figure 7); thus, k_{bi} changes very little with pressure (as shown in Figure 8). The remarkable agreement between the integral equation and experimental results indicates that the seemingly different pressure effect on the quenching reactions of ^{3}BP with oxygen and 1,4-cyclohexadiene in supercritical fluids is mainly a manifestation of different preferential solvation behavior.

Temperature Effects. We measured the reaction rates for $^3\mathrm{BP} + O_2$ and $\mathrm{Ph\dot{C}H_2} + O_2$ in CO_2 at temperatures from 35 to 90 °C, as shown in Figure 5, in an attempt to determine Arrhenius activation parameters for the two reactions. However, the bimolecular rate constants at a given density do not vary significantly with temperature for either of the reactions, indicating essentially no measurable activation energy over the temperature range studied. While both reactions are well below

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the diffusion-controlled limit, the negligible dependence on temperature is consistent with the literature for both reactions (vide infra).

Benzophenone is an important photochemical species due to its extensive use as a triplet photosensitizer. The relatively high triplet energy, $E_T = 69$ kcal/mol,[30] of ^{3}BP allows for extremely efficient (typically 100%) energy transfer to occur between ^{3}BP and compounds of lower E_T. For the reaction of ^{3}BP with ground-state triplet O_2 (eq 1) the quantum yield of singlet O_2 production is only 0.3,[31] even though the reaction occurs with a bimolecular rate constant of $\sim 2 \times 10^9$ M^{-1} s^{-1} in room temperature liquid.[31a,32] Recently, this discrepancy has been addressed in the investigation of the temperature dependence for the reaction of ^{3}BP and other aromatic ketones with O_2.[33] Strong non-Arrhenius behavior was observed. This was especially true for the reaction of ^{3}BP above 20 °C where a negligible temperature dependence and a negative temperature dependence (at higher temperatures) were observed. The results clearly indicated a temperature-dependent change in the reaction mechanism that is believed to involve the participation of a reversible exciplex.[31a,33] However, at a particular temperature the rate constant for the reaction of ^{3}BP with O_2 does not appear to be density dependent.[33] Therefore, when comparing the reaction rates along any given isotherm we anticipate that the disappearance of ^{3}BP could show indications of preferential solvation.

The reaction of free radicals with oxygen is an important elementary step in the oxidation of hydrocarbons in both the liquid and gas phase (e.g., liquid-autooxidations and combustion, respectively). The absolute reactivity for the reaction of $Ph\dot{C}H_2$ + O_2 has been measured in both solution and the gas phase. Rate constants in ambient organic liquids of $k_{bi} = 1-3 \times 10^9$ M^{-1} s^{-1} have been reported[21b] and are somewhat below that expected for diffusion control. It was also noted that k_{bi} values tend to become lower in solvents of lower viscosity. However, unlike some other resonance stabilized free radicals the reverse reaction of eq 2, the β-scission of the benzylperoxy radical, was determined[21b] to be unimportant on the time scale of the measurement of k_{bi}. Rate constants in the range of $k_{bi} = 6 \times 10^8$ to 1×10^9 M^{-1} s^{-1} have been reported for the reaction of $Ph\dot{C}H_2 + O_2$ in the gas phase.[34] Interestingly, this reaction is believed to be essentially an irreversible kinetically-controlled reaction at lower temperatures (~22−100 °C); however, the reaction demonstrates no measurable temperature dependence in this temperature range.[34a] This behavior is not unique to benzyl free radical and may be a consequence of a temperature-dependent pre-exponential factor.[35] Although there is essentially no activation barrier to this reaction, in the temperature range of our study, we anticipate that local solvation could influence the reaction because it does not occur immediately upon collision. The rate of back dissociation for $Ph\dot{C}H_2 + O_2$ is significant, however, at elevated temperatures (>125 °C). The gas-phase kinetics, thermochemistry, and equilibrium constants for the reaction of $Ph\dot{C}H_2 + O_2$ have recently been reported by two independent groups.[36]

In summary, the reactions of both ^{3}BP + O_2 and $Ph\dot{C}H_2$ + O_2 in CO_2 exhibit negligible temperature dependence, consistent with the studies of these reactions in the liquid and gas phases.

Conclusions

In this paper we have presented bimolecular rate constants for the reactions of ^{3}BP and $Ph\dot{C}H_2$ with O_2 (a "non-attractive" cosolvent) in SC CO_2 and CHF_3, as measured by laser flash photolysis. The rate constants increase only slightly with increasing pressure and are consistent with the lack of preferential solvation of the solute by the oxygen cosolvent. This is in striking contrast to the results obtained for the reaction of ^{3}BP with 1,4-cyclohexadiene (an "attractive" cosolvent), which increase dramatically at lower pressures, and have been explained by the increased local concentration of the diene around the ^{3}BP solute. We have presented integral equation calculations modeling both ternary systems (^{3}BP/1,4-cyclohexadiene/CO_2 and ^{3}BP/O_2/CO_2) that fully corroborate the experimental observations. Thus, by the use of both experimental measurements of absolute reaction kinetics and theoretical integral equation calculations, we have shown how the degree of preferential solvation can influence the rates of kinetically controlled reactions in supercritical fluids and developed a method to predict the influence of solvation on reactivity in mixtures with both "attractive" and "nonattractive" cosolvents. In addition, these particular reactions are important in understanding hydrothermal reactivity in the presence of oxygen, which has applications in supercritical water oxidation.

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