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Diffusion-Controlled Reactions in Supercritical CHF_3 and CO_2/Acetonitrile Mixtures

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Abstract: We present results of the triplet–triplet annihilation (TTA) process of benzophenone ($Ph_2C{=}O$) and the self-termination reaction of benzyl radical ($Ph\dot{C}H_2$) to investigate the possibility of diffusion-controlled processes being hindered or enhanced in supercritical fluids (SCFs) or fluid mixtures. However, both reactions occur essentially at the diffusion-control limit in supercritical fluoroform (CHF_3) and carbon dioxide (CO_2) doped with 1 mol % acetonitrile (CH_3CN) when spin statistical factors are taken into account. The reaction kinetics were measured by laser flash photolysis at various pressures above the critical pressure along three isotherms. This study corroborates our earlier report of these reactions in supercritical CO_2 and ethane (C_2H_6). In all of the fluids and fluid mixture, the locally higher density of the solvent around the solutes in no way enhances or slows the bimolecular annihilation or termination reaction. In addition, there is no evidence of enhanced solute–solute interaction. Finally, we studied the photocleavage of dibenzyl ketone (DBK) and the subsequent decarbonylation of the phenylacetyl radical ($PhCH_2\dot{C}O$) and did not observe any enhanced cage effects or anomalous behavior due to the increased local density.

Introduction

There is a growing body of experimental,[1-5] theoretical,[6,7] and simulation[8] evidence that the local density of solvent around a solute in a supercritical fluid (SCF) is greater than the bulk density. The local density augmentation (solvent clustering) is most pronounced in the compressible region near the critical point and the low-density subcritical regions of the fluid.[9] In addition, there is evidence that when a cosolvent such as acetone or methanol is added to a SCF, the local composition of the cosolvent is significantly greater than the bulk value.[10-12] This has resulted in speculation about the possibility of the increased local density affecting reaction rates and whether one might expect cage effects in SCFs that are enhanced beyond those experienced in normal liquids. Recently, there have been two cases of unusual reactivity in SCFs that have been attributed to the local density enhancement. Randolph and Carlier[13] measured the bimolecular rate constants for the Heisenberg spin exchange reaction between nitroxide free radicals in supercritical ethane. They found rate constants greater than normal diffusion control and attributed this to an increase in the collision times due to local density augmentation around the encounter pair. Zagrobelny and Bright studied pyrene excimer kinetics in SC CO_2[14] and C_2H_4[15] and found that the pyrene excimer formation occurred at diffusion control but that the lifetime of the excimer fluorescence was greatly lengthened over solution behavior due to a protective sequestering of the excimer by the solvent clusters. Conversely, in SC CHF_3[15] the pyrene excimer formation in the compressible region was approximately ten times below diffusion control. It was argued that the fluoroform cluster interacts much more strongly with the pyrene molecules than the CO_2 or C_2H_4 clusters and is sufficient to impede the excimer formation. In an extremely intriguing follow-up report[16] they found that the addition of less than 1 mol % acetonitrile or methanol to SC CO_2 could slow the pyrene excimer formation by as much as a factor of 6. In addition, 1% of methanol *increased* the lifetime of the excimer by three orders of magnitude from that expected in either liquid solutions or pure CO_2[14] and 1% of acetonitrile *decreased* the lifetime of the excimer by three orders of magnitude over pure CO_2. No explanation was given for this dramatic change in the emissive rate of decay of the pyrene excimer.

In order to test the generality of this evidence of increased local solvent and cosolvent density in supercritical fluids both enhancing and retarding reactions, we have used laser flash photolysis (LFP) and time-resolved absorption to study two reactions that follow simple diffusion-controlled bimolecular reactivity in liquids. In our first report,[17] we found that the triplet–triplet annihilation (TTA) process of triplet benzophenone (^{3}BP) and the free radical termination reaction of benzyl radical occur at diffusion control in SC CO_2 and C_2H_6 when the appropriate spin statistical factors are taken into account. We did not see any anomalous behavior due to local density augmentation or solute/solute interactions. Moreover, in forming the benzyl radicals from the photocleavage of dibenzyl ketone and the decarbonylation of phenylacetyl radical we did not see any evidence of SCF cage effects. In this paper we extend our investigations of diffusion-controlled reactions to a polar SC solvent and cosolvent to test the generality of the previously reported hindrance of diffusion-controlled reactions in SC CHF_3

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and cosolvent mixtures.[15,16] We present new results of the TTA process of benzophenone triplet and the free radical termination reaction of benzyl radical in SC CHF_3 and SC CO_2 with 1 mol % acetonitrile.

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). Fluoroform (Dupont Freon-23, 98% purity) was sequentially passed through multiple high-pressure oxy-traps (Alltech) and multiple high-pressure charcoal traps (Alltech). Carbon dioxide (Scott Specialty Gases, SFC grade) was used as received. Acetonitrile (Fisher, HPLC grade, UV cutoff 190 nm) was used without further purification.

Method. The high-pressure apparatus, sample preparation, and application of LFP to SCF samples have recently been described in detail.[17,18] Briefly, LFP experiments were performed by 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). Cutoff filters were used at all wavelengths greater than 420 nm in both spectral and kinetic measurements to eliminate overtones.

High-pressure optical cells of 3 mL capacity were used in these experiments and are as described previously.[17] In all experiments the laser excitation beam was focused to completely fill the 7 mm diameter window. An effective path length of 7 mm has been verified.[17]

Sample preparation involved placing an appropriate amount of crystalline precursor into the optical cell which was then evacuated and filled with either CHF_3 or CH_3CN/CO_2 mixture. The solvent was added to the cell with an Isco Model 260D high-pressure syringe pump or an HIP Model 50–6–16 hand-operated pressure generator. Precursor concentrations were determined with a Cary 1 UV–vis spectrophotometer or a SLM-Aminco Spectronic 3000 array spectrophotometer and were typically 0.2 to 0.8 absorbance units at the laser excitation wavelength, which corresponds to approximately millimolar concentrations of precursor (on the order of 10^{-4} mol fraction).

The 1.0 mol % CH_3CN/CO_2 cosolvent mixtures were prepared by drawing an appropriate amount of N_2-saturated CH_3CN into the Isco syringe pump. Cooling water (0 °C) was then circulated through a jacket that surrounds the piston and cylinder assembly of the syringe pump and the remaining volume of the pump was subsequently filled with subcooled liquid CO_2. Using the temperature of the ice bath and the pressure indicated on the syringe pump, the mole fraction of the CH_3CN/CO_2 was determined with densities calculated from the analytic equation of state used by Angus et al.[19] in construction of the IUPAC CO_2 density data. This assumes that the mixture was sufficiently dilute to be adequately described by the pure CO_2 density equation. We anticipate the error in the CH_3CN concentration due to this assumption to be less than 5%. To facilitate mixing, we heated the pump which increased the pressure such that we believe the solution was one phase at all times. To our knowledge there are no published high-pressure phase equilibrium data for the CH_3CN/CO_2 mixture. However, we maintained the solution at conditions well above the two phase region for other commonly used cosolvents.[20] Further details of cosolvent sample preparation can be found elsewhere.[18]

Pressure in the cell was monitored to ±0.24 bar with a Heise (Model 901A) pressure gauge. The required temperature was maintained to ±0.1 °C with an Omega (Model CN-6070 A) temperature controller equipped with a Watlow Firerod cartridge heater and a platinum resistance thermometer which made direct contact with the fluid.

The reactions in CHF_3 were examined on the 28, 35, and 50 °C isotherms while CH_3CN/CO_2 experiments were performed at 35 °C. Depending on the specific experiment (vide infra), investigations were carried out under either constant mole fraction conditions, from high to low pressure by release of homogeneous solution, or constant molarity conditions, from low to high pressure by addition of solvent. The critical pressures and temperatures are 73.8 bar and 31.0 °C for CO_2 and 48.4 bar and 25.9 °C for CHF_3.

Results and Discussion

The triplet–triplet annihilation of ^{3}BP and the benzyl radical recombination are both bimolecular reactions that occur by diffusion control when spin statistical factors are taken into account (vide infra) in liquids,[21–25] which means that the rate of formation of the product from the encounter complex (AA) is very fast compared to the rate of formation of the diffusive encounter complex itself. In such a fully diffusion controlled reaction the observed rate constant is related to diffusion-controlled rate constant by $2k^{AA}{}_{obs} = k_{diff}$. However, it has long been recognized that diffusion-controlled reactions must obey conservation of spin multiplicity so that a spin statistical factor (σ) must be taken into account according to eq 1.

$$2k^{AA}_{obs} = \sigma k_{diff} \qquad (1)$$

Most ground-state reactions occur on the ground-state singlet surface throughout the reaction and are multiplicity-allowed processes with a spin statistical factor of 1. However, in the interaction of two triplets the encounter complexes formed have nine possible spin states, and for the interaction of two doublet free radicals there are four. Taking the stoichiometry of the reactions into account, the spin-statistical factor is 5/9 for the disappearance of ^{3}BP and 1/4 for the termination of $Ph\dot{C}H_2$.[21] Diffusion-controlled reactions and spin statistical factors for the triplet–triplet annihilation of ^{3}BP and benzyl radical recombination are discussed in more detail in our previous report.[17]

1. Triplet–Triplet Annihilation of ^{3}BP. We have shown that the TTA of ^{3}BP in SC CO_2 along two isotherms occurs with clean second-order decay kinetics, which are attributed to the annihilation process. The bimolecular rate constants ($2k_{TTA}$) correlated very well with $^5/_9k_{diff}$ over the entire pressure range studied in agreement with spin statistical arguments.[17] No evidence of enhanced cage effects due to increased local solvent density about diffusive encounter pairs nor enhanced solute/solute interactions were observed in those experiments.

Here we present results of the TTA process of ^{3}BP in both SC fluoroform and CH_3CN modified CO_2. As in the pure CO_2 studies, ^{3}BP generated from 355-nm LFP decays with clean second-order decay kinetics in CHF_3 with no indication of abnormal reactivity, complexation, or deactivation of the ^{3}BP with CHF_3. Also, there was no indication of quenching of ^{3}BP by molecular oxygen or other impurities. However, experiments run in CHF_3 prior to the application of the oxygen and charcoal traps resulted in short-lived, first-order decays. This quenching was attributed to molecular oxygen and other contaminants in the stock CHF_3. Therefore, care was taken to remove these impurities so only clean second order decay traces remained, which were attributed to the TTA process. An iterative technique[17,26] was applied to determine the amount of first order competition, and in these experiments no significant first-order contribution could be detected. Similarly, decay kinetics in the

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CH_3CN/CO_2 cosolvent mixture were found to be purely second order and contained no first order contributions.

The extinction coefficient (ϵ) of ^3BP is required to obtain the actual bimolecular rate constant. This relationship is defined by

$$\Delta\left(\frac{1}{[A]}\right) = \frac{2k_{TTA}}{\epsilon l}t \qquad (2)$$

where $\Delta(1/[A])$ is the change in the ΔOD of ^3BP and l is the effective excitation path length. We have determined that the ϵ of ^3BP in CO_2 is within 10% of the literature value of ϵ of ^3BP in CH_3CN at 320 nm, which is 11 500 (M^{-1} cm^{-1}).[27] To obtain ϵ of ^3BP in SC CHF_3, LFP experiments were performed in which laser conditions and the ground-state absorption of BP were carefully matched in SC CHF_3 and CO_2. Comparisons of the ^3BP OD in these experiments were made and it was found that the ϵ for the laser generated triplets in CHF_3 were equivalent to those in CO_2 at 320 nm within 5%. Also, there is a <2% variance in ϵ over the entire pressure range studied. Due to the small variation of ϵ with solvent and solvent density, kinetics were measured at 320 nm and $2k_{TTA}$ was calculated with use of the literature value of 11 500 M^{-1} cm^{-1}. We found no significant difference between the ϵ in pure CO_2 and CO_2 with 1 mol % CH_3CN. Therefore, our measurements show that the extinction coefficient is essentially identical and equal to 11 500 M^{-1} cm^{-1} in pure SC CO_2, SC CO_2 with 1% CH_3CN, SC C_2H_6, SC CHF_3, and liquid CH_3CN.

(a) $2k_{TTA}$ in SC CHF_3. The TTA process of ^3BP was studied in SC CHF_3 along three isotherms (28, 35, 50 °C) covering temperatures near and far removed from the critical temperature of CHF_3 (T_c = 25.9 °C). Values of $2k_{TTA}$ ranged from 4.2×10^{10} M^{-1} s^{-1} to 1.4×10^{11} M^{-1} s^{-1} when measured at constant ^3BP mole fraction along the 28 °C isotherm from pressures of 111 to 49 bar (Figure 1, top). The values of $2k_{TTA}$ increase slightly with a decrease in pressure at pressures far removed from the critical point and then sharply increase below 55 bar in the compressible region approaching the critical point. Investigations at 35 and 50 °C (Figure 1, middle and bottom) resulted in similar behavior although the increases in $2k_{TTA}$ are less dramatic. At 35 °C, $2k_{TTA}$ increased from 4.9×10^{10} M^{-1} s^{-1} at 121 bar to 1.2×10^{11} M^{-1} s^{-1} at 53 bar. $2k_{TTA}$ values increased from 5.5×10^{10} to 1.8×10^{11} M^{-1} s^{-1} when the pressure was decreased from 171 to 67 bar at 50 °C.

The error in $2k_{TTA}$ from the standard deviation of kinetic fits is less than ca. 2%. The error associated with reproducibility ranged from ca. 5% in the high-density region to 10% in the low-density highly compressible region near the critical pressure. These density-dependent errors were typical of all LFP experiments performed in this work and do not include errors in extinction coefficients.[17]

In Figure 1 the experimental values of $2k_{TTA}$ are compared with k_{diff} and $^5/_9k_{diff}$. Values of k_{diff} were estimated by application of the Stokes–Einstein based standard Debye equation (SE/D), $k_{diff} = 8RT/3\eta$, and viscosities of CHF_3 calculated by the Reichenberg method.[28] In our prior publication[17] we compared three methods of obtaining k_{diff} in CO_2: (1) from previously measured viscosity data[29] and application of the (SE/D) equation; (2) from viscosities calculated by the method of Thodos et al.,[30] which correlates dense gas viscosity to fluid density, and the SE/D equation; and (3) from measured diffusion coefficients[31] (D) for naphthalene as a model aromatic and the Smoluchowski equation, $k_{diff} = 4\pi N\rho D10^{-3}$, where N is Avogadro's number and ρ is the reaction distance. The values of k_{diff} determined by all three methods were in excellent agreement. Due to this excellent agreement and the lack of experimental data that is needed in methods (1) and (3), only the SE/D method with estimated viscosities (using the Reichenberg method for CHF_3 and the method of Thodos et al. for CO_2) was used in the present studies. It should be noted that use of the SE/D relationships is known to consistently result in slight overestimations of the diffusion coefficient and, subsequently, k_{diff} in supercritical fluids.[32]

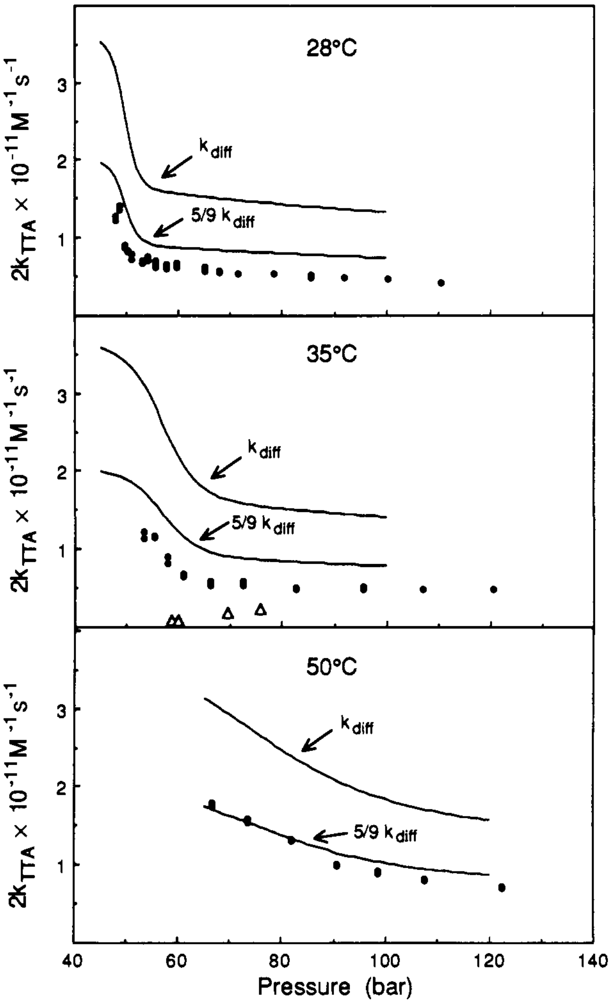

Figure 1. Plot of the pressure dependence of the TTA rate constant (●) of ^3BP in SC CHF_3 at 28 (top), 35 (middle), and 50 °C (bottom) compared to respective k_{diff} values (see text). Also included at 35 °C (middle) are rate constants for pyrene excimer formation at 35 °C (△) reported by Zagrobelny and Bright[15] (see Conclusions).

In Figure 1, $2k_{TTA}$ values along each isotherm follow the shape of the k_{diff} curve very well, indicating no change in the mechanism of the reaction. They fall significantly below the diffusion limit in SC CHF_3 but match $^5/_9k_{diff}$ very well over the entire pressure range studied. The experimental values fall slightly below the calculated $^5/_9k_{diff}$ curve, but this is expected since it is common for the SE/D equation to slightly overpredict k_{diff} in SCFs . Therefore, it is clear that the TTA of ^3BP proceeds essentially at diffusion control in SC CHF_3 at all temperatures and pressures measured, when spin statistical factors are taken into account. As in SC CO_2 and C_2H_6, the CHF_3 cluster does not in any way impede the annihilation reaction.

(b) $2k_{TTA}$ in SC CO_2/Acetonitrile. In order to investigate the effects of cosolvent on this TTA process, we report results of investigations in SC CO_2 with CH_3CN as a cosolvent. The TTA process of dilute ^3BP was studied in a 1.0 mol % CH_3CN/CO_2 mixture at 35 °C at constant mole fraction of cosolvent, which

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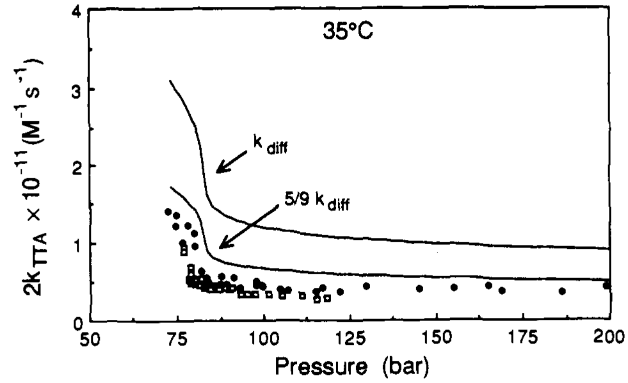

Figure 2. Plot of the pressure dependence of the TTA rate constant of ^3BP in a 1 mol % CH_3CN/CO_2 mixture (□) and in pure SC CO_2 (●) at 35 °C compared to k_{diff} values calculated by method 2 (see text).

corresponds to a 0.18 M concentration of CH_3CN at the highest pressure of 118 bar and a 7.7×10^{-2} M mixture at the lowest pressure of 76 bar. $2k_{TTA}$ values increased from 2.8×10^{10} M^{-1} s^{-1} at 118 bar to 9.3×10^{10} M^{-1} s^{-1} at 76 bar, as shown in Figure 2. Also in Figure 2 are the results of $2k_{TTA}$ in pure SC CO_2, as well as the k_{diff} and $^5/_9k_{diff}$ curves. k_{diff} was estimated by method (2) given in the previous section. The values of $2k_{TTA}$ in the CH_3CN/CO_2 mixture are almost identical with those in pure SC CO_2 and follow the $^5/_9k_{diff}$ curve very well, demonstrating a dramatic increase as the critical pressure is approached. Over the entire pressure range the values of $2k_{TTA}$ in the CH_3CN/CO_2 mixture are *slightly* lower than those in pure CO_2; however, it should be noted that cosolvents can slow diffusion in a SCF up to 10–20%,[33] mostly due to the slight increase in bulk density that occurs when a cosolvent is added to the solution at a given temperature and pressure.

The experiments were repeated at a constant CH_3CN molarity of 7.7×10^{-2} M, which is the same concentration that Zagrobelny and Bright[16] found to significantly hinder the formation of pyrene excimers in a CH_3CN/CO_2 mixture. The constant molarity experiments were conducted by starting at low pressure and adding pure CO_2 to the sample cell, thus increasing the pressure and keeping the molar concentration constant. The results obtained for $2k_{TTA}$ for the annihilation reaction of ^3BP from both the constant mole fraction and the constant molarity experiments were identical within experimental error, following the $^5/_9k_{diff}$ curve as shown in Figure 2. Therefore, from the results of the TTA of ^3BP, there is no indication that the addition of a cosolvent to the SCF significantly slows or impedes diffusion controlled reactions.

2. Benzyl Radical Termination Reaction. We have shown that the benzyl radical termination reaction occurred with clean second-order kinetics in SC CO_2 and C_2H_6 with values of $2k_T$ near the diffusion-controlled limit when the appropriate spin statistical factor (1/4) was taken into account.[17] Here we extend the previous studies to include SC CHF_3 and a SC CO_2/CH_3CN cosolvent mixture. Special attention is given to spectral shifts in the benzyl radical absorption spectrum and changes in the benzyl radical absorption extinction coefficients, which exhibited interesting behavior in SC CO_2 and C_2H_6.

(a) Benzyl Radical Absorption Spectrum. Benzyl radical ($Ph\dot{C}H_2$) was generated by the photodecomposition of dibenzyl ketone (DBK).[34-36] The mechanism of DBK decomposition is presented in the following section. The ground-state absorption spectrum of DBK demonstrated no spectral shifts in SCFs compared to cyclohexane. However, shifts are observed for the primary absorption band of ($Ph\dot{C}H_2$) in SCFs. For example, λ_{max} of ($Ph\dot{C}H_2$) shifted from about 317 nm in liquid cyclohexane and acetonitrile[37-39] to about 310 nm in SC CO_2 and C_2H_6.[17] This was attributed to the difference in dispersion forces in the different solvents rather than to a pressure-induced mechanistic change, based on the fact that no spectral shift is observed in cyclohexane over the pressure range of 1–141.4 bar. The absorption maximum of benzyl radical in SC CHF_3 is at approximately 309 nm and there is no significant shift in the primary absorption band when the solvent density is varied from high pressure(145 bar) to low pressure (59 bar) at 35 °C, as shown in Figure 3, top. The absorption spectra of ($Ph\dot{C}H_2$) in a mixture of CO_2 and 1 mol % CH_3CN taken at 35 °C and two pressures are compared to that in pure CO_2 in Figure 3, bottom. No significant spectral shift due to the addition of a small amount of cosolvent is observed and the absorption spectrum does not shift significantly with a change in the density of the mixture.

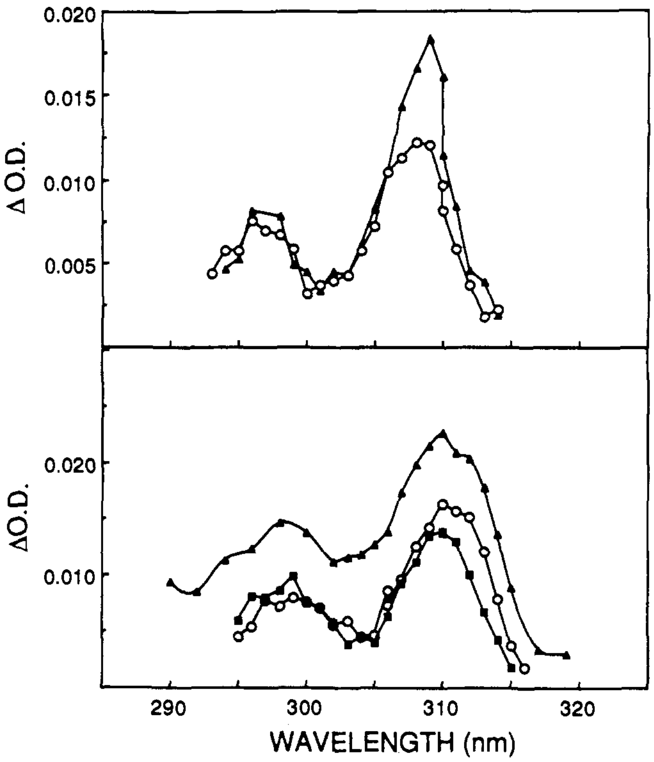

Figure 3. Top: Benzyl radical absorption spectra obtained at 35 °C in SC CHF_3 at 146.4 (▲) and 59.6 bar (○). Bottom: Benzyl radical absorption spectra obtained at 35 °C in SC CO_2 at 130.8 (▲) and in a 1 mol % CH_3CN/CO_2 mixture at 178.2 (○) and 81.3 bar (■).

Solvatochromic probes have been used to measure local density increases[1,2] and local composition increases[11,12] in SCFs and SCF/cosolvent mixtures. The general conclusion is that both local densities and local compositions can be significantly greater than the bulk values in low density SCFs. Although the absorption maximum of ($Ph\dot{C}H_2$) is different in the SCFs than in liquids, it is not a good probe of local density or local composition because the shifts are so small. Nonetheless, the absence of a bathochromic shift with pressure in SC CHF_3 is in accordance with the idea of density enhancement in the low-density region nearer the critical point of the solvent. It is well-known that the bathochromic shift for a solute in solution compared to the isolated molecule is proportional to a function f of the refractive index ($f = n^2 - 1/2n^2$

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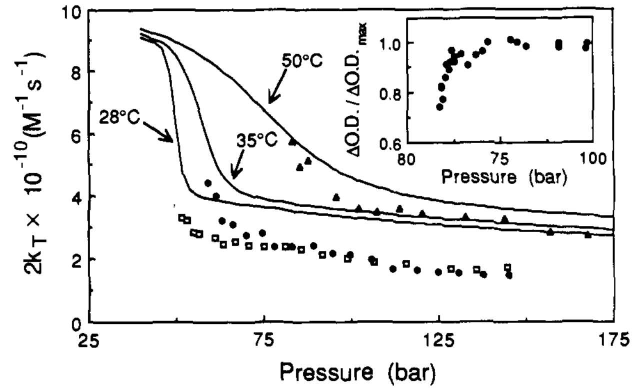

Figure 4. Plot of the pressure dependence of the $2k_T$ of benzyl radical in SC CHF_3 at 28 (□), 35 (●), and 50°C (▲) compared to respective $^1/_4k_{diff}$ values (see text). Insert: Benzyl radical ϵ pressure dependence in SC CHF_3 at 35 °C.

+ 1). Since the refractive indices of SCFs change significantly with pressure, on the basis of bulk solvent properties one would expect a small solvatochromic shift over the pressure range investigated. Therefore, the absence of any shift with pressure may be an indication of enhanced local densities, as has been reported previously.[1-5] Overall, $(Ph\dot{C}H_2)$ demonstrates no significant solvatochromic behavior in CHF_3 or in a 1 mol % CH_3CN/CO_2 mixture, as was the case with pure CO_2 and C_2H_6.[17]

(b) Benzyl radical ϵ and Self-Termination Reaction in SC CHF_3. LFP (308 nm, 100 mJ) of DBK in thoroughly deoxygenated cyclohexane resulted in a clean second-order decay kinetics of $(Ph\dot{C}H_2)$ at 317 nm,[17] and the absolute rate constant for $(Ph\dot{C}H_2)$ termination ($2k_T$) of 4.75×10^9 $M^{-1} s^{-1}$ was in excellent agreement with literature values,[40] when the published value of 8800 $M^{-1} cm^{-1}$ was used for the extinction coefficient.[40] The measurement of $2k_T$ in SCFs requires determination of the extinction coefficient ϵ as a function of pressure. Unlike the ϵ of benzophenone triplet, which remained essentially constant in all the SCFs, in SC CO_2 and C_2H_6 the ϵ of $(Ph\dot{C}H_2)$ changed by as much as 35%.[17]

Matched LFP experiments, similar to those described for benzophenone, were performed with DBK in SC CHF_3 and cyclohexane. The extinction coefficients of benzyl radical in CHF_3 demonstrate similar dependence on pressure for all three temperatures (28, 35, and 50 °C). The relative extinction coefficient versus pressure at 35 °C is presented as an insert in Figure 4. At sufficiently high pressure, the extinction coefficient is the same as in cyclohexane within reasonable experimental error (5%) but decreases dramatically at lower pressures, as is the case for pure CO_2 and C_2H_6.[17]

The bimolecular rate constants for the radical termination were determined in CHF_3 with use of the corrected extinction coefficients as a function of pressure. These values of $2k_T$ in CHF_3 at three temperatures are shown in Figure 4, compared with the $^1/_4k_{diff}$ predicted by using method (2) described above. The values of $2k_T$ range from about 1.6×10^{10} $M^{-1} s^{-1}$ at 144 bar and 28 °C to 5.7×10^{10} $M^{-1} s^{-1}$ at 83 bar and 50 °C. It is clear that the radical termination process at all three temperatures follows the diffusion-controlled curve when the appropriate spin statistical factor is taken into account even near the critical point. While the experimental values consistently fall slightly below the $^1/_4k_{diff}$ curve, we do not think the difference is significant based on the uncertainty in the measurements (which can be as large as +20% at low pressures) and the fact that the Stokes Einstein/Debye equation is known to overpredict the diffusion coefficient somewhat in SCFs.

(c) Benzyl radical ϵ and Self-Termination Reaction in a 1 mol % CH_3CN/SC CO_2 Mixture. As in the TTA reaction of benzophenone triplet, we are interested in the effect of a small amount of cosolvent on the rate of the recombination reaction of benzyl radical. Surprisingly, when we performed the matched experiments described above to determine the extinction coefficient of $(Ph\dot{C}H_2)$ as a function of pressure, we did not observe any significant change in the extinction coefficient in the 1 mol % CH_3CN/CO_2 mixture over the pressure range of 75 to 166 bar. This is particularly interesting because the ϵ dropped by as much as 35% at low pressures in pure CO_2. The reason for the dramatic influence of a small amount of cosolvent on the ϵ is not clear: the effect of solvent density and increased local concentration of cosolvent on extinction coefficients is currently under investigation in our laboratory.

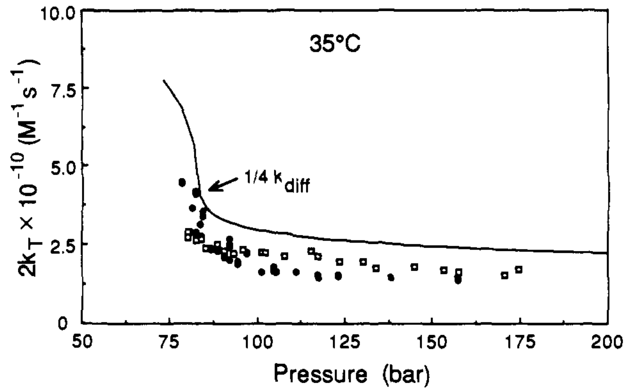

Figure 5. Plot of the pressure dependence of the $2k_T$ of benzyl radical in a 1 mol % CH_3CN/CO_2 mixture (□) and in pure CO_2 (●) at 35 °C compared to $^1/_4k_{diff}$ values calculated by method 2 (see text).

With use of the measured extinction coefficients, the rate constants for the benzyl radical termination in a 1 mol % CH_3CN/CO_2 are shown in comparison to the results in pure CO_2 and the calculated $^1/_4k_{diff}$ curve in Figure 5. The rate constants with the added cosolvent are essentially identical with those in pure CO_2, which followed the $^1/_4k_{diff}$ curve remarkably well. Therefore, a small amount of cosolvent added to SC CO_2 does not slow or impede the benzyl radical recombination reaction in any way.

3. DBK Photodecomposition and Decarbonylation of $(PhCH_2\dot{C}O)$. The photodecomposition of DBK and the subsequent decarbonylation of $(PhCH_2\dot{C}O)$ did not show any evidence of cage effects in SC CO_2 or C_2H_6.[17] This corroborated the product studies of Fox and co-workers,[41] who found no change in the quantum yield of photodecomposition of nonsymmetrical substituted DBKs in SC CO_2 or C_2H_6 with change in solvent density. Since the attractive forces between DBK and CHF_3 or a 1 mol % CH_3CN/CO_2 mixture are stronger than with either of the two nonpolar fluids studied previously, we were interested in determining if there is any effect of increased local density or solvent cages in these polar fluids.

The decomposition of DBK in normal liquids is well-established[34-36] and occurs according to Scheme I.

The intersystem crossing to triplet and type I homolytic cleavage to form benzyl and phenylacetyl radical (steps 1–3) occurs on the subnanosecond time scale.[39] We anticipate that steps 3–5 have the most potential for being influenced by the solvent. We have shown in the previous section that the benzyl radical recombination occurs near diffusion control and is not influenced by the local solvent or cosolvent concentration in either CHF_3 or a CH_3CN/CO_2 mixture. This leaves the cleavage (step 3) and the decarbonylation of phenylacetyl radical (step 4) for examination.

The formation of benzyl radical in both CHF_3 and the CH_3CN/CO_2 mixture occurs in a two-step mechanism. Monitoring the $(Ph\dot{C}H_2)$ absorption signal, there is an instantaneous "jump" corresponding to step 3 and a first-order growth corresponding to step 4, as shown in Figure 6, insert. As in pure CO_2 and C_2H_6, the ratio of "jump" to growth in CHF_3 and the CH_3CN/CO_2 mixture did not change with pressure, indicating no change in the

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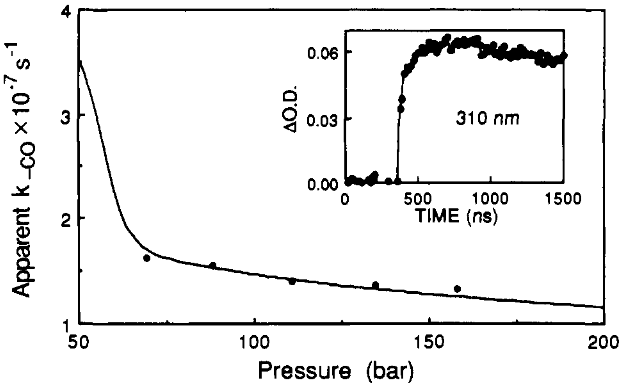

Figure 6. Plot of the apparent pressure dependence of k_{-CO} for ($PhCH_2\dot{C}O$) in SC CHF_3 at 35 °C. Insert: Typical absorption trace observed at 310 nm, following LFP of DBK in SC CHF_3 at 35 °C.

Scheme I (step)

$$(PhCH_2)_2C{=}O \xrightarrow{h\nu} (PhCH_2)_2C{=}O^{1*} \qquad (1)$$

$$(PhCH_2)_2C{=}O^{1*} \xrightarrow{ISC} (PhCH_2)_2C{=}O^{3*} \qquad (2)$$

$$(PhCH_2)_2C{=}O^{3*} \rightarrow Ph\dot{C}H_2 + PhCH_2\dot{C}{=}O \qquad (3)$$

$$PhCH_2\dot{C}{=}O \xrightarrow{k_{-CO}} Ph\dot{C}H_2 + CO \qquad (4)$$

$$2Ph\dot{C}H_2 \xrightarrow{2k_T} PhCH_2CH_2Ph \qquad (5)$$

mechanism; i.e., there is no cage effect on the geminate radical pair that would force in-cage radical–radical recombination. The rate of decarbonylation of ($PhCH_2\dot{C}O$) in CHF_3 is shown in Figure 6. As in SC CO_2 and C_2H_6,[17] the rate of decarbonylation is essentially constant but increases slightly at lower pressures. This can be explained as an artifact of the competing decay $2k_T$ process which overlaps the absorption growth. The $2k_T$ process, as shown in the previous section, follows the $^1/_4k_{diff}$ curve and is faster in the compressible low-pressure region. The solid line shown in Figure 6 is the k_{diff} curve (scale not included) and its purpose is to emphasize that the apparent increase in the decarbonylation rate is actually due to the competing $2k_T$ process. For more detailed discussion see Roberts et al.[17] Therefore, we conclude that there are no cage effects or influence of increased local solvent or cosolvent density on the decomposition of DBK and the subsequent decarbonylation of ($PhCH_2\dot{C}O$) even in SC CHF_3 or a CH_3CN/CO_2 mixture. As with SC CO_2 and C_2H_6, we believe this is reasonable since, according to molecular dynamics simulations,[8] the "solvent cage" around the solute maintains its integrity for only a few nanoseconds, significantly shorter than the time required for decarbonylation (step 4).

Conclusions

The rate constants for the TTA of ^3BP and benzyl radical recombination in SC CHF_3 and a 1 mol % CH_3CN/CO_2 mixture occur at the diffusion controlled limit when spin statistical factors are taken into account. There is no evidence of enhanced solute/solute interactions and the higher local density of solvent and cosolvent around the solute does not in any way enhance or impede the diffusion and reaction process. Enhanced solute/solute interactions might result in an apparent enhancement in the reaction rate and increased solvent local density might act to slow a reaction. However, we believe it is highly unrealistic to suggest that the compromising effect of enhanced solute/solute interactions and cage effects would exactly cancel, resulting in apparent diffusion control. Therefore, we conclude that both reactions follow diffusion control (with spin factors) and that there is no evidence of solute/solute, solute/solvent, or solute/cosolvent interactions in SCFs affecting simple diffusion controlled reactions. We believe this is reasonable because although there is ample evidence[1-12] of enhanced local densities and local compositions of cosolvent around a solute in SCFs and SCF mixtures, molecular dynamics simulations[8] indicate that the local solvent environment maintains its integrity for only a few nanoseconds, which is much shorter than the time scale of the diffusion process. Enhanced solute/solute (or solute/cosolvent) effects, which have been suggested by both experimental[18,42-45] and theoretical[6,12,46] evidence, may be absent in this study due to the extreme dilution of the ^3BP or benzyl radical, which is expected to be on the order of micromolar.

The lack of increased local solvent and cosolvent concentration effects on these reactions is in contrast to the recently published work of Zagrobelny and Bright.[15,16] In a series of articles, they examined the influence of solvent on the kinetics of pyrene excimer formation. They found that excimer formation was diffusion controlled in SC CO_2 and C_2H_4 but was up to an order of magnitude below diffusion control in SC CHF_3 and SC CO_2 with less than 1 mol % of CH_3CN or CH_3OH added. Moreover, the lifetime of the excimer was up to three orders of magnitude longer in CH_3OH doped CO_2 and three orders of magnitude shorter in CH_3CN doped CO_2 than in pure CO_2. Unlike the excimer formation kinetics, we do not see any anomalous behavior in the TTA of ^3BP or the benzyl radical recombination in SC CHF_3 or the CH_3CN/CO_2 mixture. The inconsistency is shown in Figure 1 (middle), where the rate constants for the TTA of ^3BP in CHF_3 (this work) are shown with the data of Zagrobelny and Bright[15] for pyrene excimer formation in CHF_3 at 35 °C. Taking the spin statistical factors into account, the excimer formation data should match the k_{diff} curve and the TTA data should match the $^5/_9k_{diff}$ curve. As shown in Figure 1 (middle), and in all the cases presented in previous sections, the TTA and recombination reaction occur at the diffusion control limit (with spin factors), as expected. Also, we do not observe any cage effects in the photodecomposition of DBK or the decarbonylation of phenylacetyl radical. This corroborates our previous observations[17] that the reaction must occur on a time scale comparable to the time scale that the local environment maintains its integrity for it to be influenced by that environment. Furthermore, we conclude that the influence of local solvent or cosolvent density on diffusion controlled reactions may be specific to the reaction involved.

We believe that there may be several possibilities to explain the discrepancy between the results presented here and the results of the pyrene excimer formation. First, one might envision specific chemical interactions between pyrene or pyrene excimer and the CHF_3, CH_3CN, or CH_3OH. This might dramatically affect the kinetic parameters extracted from the global analysis of the fluorescence data. However, a complex with the monomer should be readily apparent from the absorption spectrum. Second, there has been significant discussion recently on the effect of the time dependence of the bimolecular rate constant and the importance of the geminate pair decomposition (reversibility) of the excimer on the kinetic parameters extracted from fluorescence data,[47-53]

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both of which are neglected in the standard Birks[54] analysis. It has been shown that neglect of these effects can result in apparent bimolecular rate constants that are an order of magnitude or more off from the true values.[49,53] The contribution from the time dependence of the rate constant is most pronounced in viscous solutions so one would not readily anticipate this to be a problem in SCFs, where the diffusion coefficients are generally greater than in normal liquids. Conversely, the distinction between excited monomers formed by light and those formed by dissociation of the excimer is most pronounced in dilute solutions, which is certainly the case for most experiments conducted in SCFs. Therefore, it may be possible that the difference in distributions of ground-state monomers about excited monomers formed from light absorption versus excimer dissociation and/or the short-time time dependence of the rate constant is responsible for the discrepancy between the work presented here and the data of Zagrobelny and Bright.[15,16]

In conclusion, the TTA of ^{3}BP and the benzyl radical termination reaction occur essentially at the diffusion-controlled limit in SC CHF_3 and a 1 mol % CH_3CN/CO_2 mixture when the appropriate spin statistical factors are taken into account. We do not see any influence of solute/solute interactions or increased local solvent density on the rate constants. In addition, there are no cage effects on the photodecomposition of DBK or the decarbonylation of phenylacetyl radical. From these results we conclude that the local CHF_3 environment is not significantly different than CO_2 or C_2H_6 in influencing these simple diffusion-controlled reactions and the addition of a small amount of cosolvent has no significant effect on these reactions.

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