

A Steady-State and Time-Resolved Fluorescence Study of Quenching Reactions of Anthracene and 1,2-Benzanthracene by Carbon Tetrabromide and Bromoethane in Supercritical Carbon Dioxide

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Abstract: This paper reports on the solvent effect on energy transfer reactions in supercritical CO₂. The energy transfer reactions are studied by steady-state and time-resolved fluorescence spectroscopy and the fluorophor/quencher reaction pairs are chosen to vary the reactions from diffusion-controlled to kinetically-controlled. In particular, the fluorescence quenching of anthracene by CBr₄, 1,2-benzanthracene by CBr₄, and anthracene by C₂H₅Br in supercritical CO₂ at 35 °C has been reported. Experimental rate constants for the first two reaction pairs, anthracene/CBr₄ and 1,2-benzanthracene/CBr₄, follow the predicted diffusion control limit at all pressures from 77.9 to 160.6 bar, indicating that local solvation does not enhance the reaction rate nor substantially impede the diffusion process in supercritical CO₂. The rate constants for the third reaction, the quenching of anthracene by C₂H₅Br, are several orders of magnitude below the diffusion control limit, indicating that the reaction is kinetically controlled, as it is in liquids. In supercritical CO₂ the apparent rate constants (i.e., those based on bulk concentrations of the reactants) for the anthracene/C₂H₅Br reaction decrease dramatically with increasing pressure. We believe that this apparently large pressure effect on the reaction rate is primarily due to the local composition enhancement of the quencher molecules around the dilute anthracene solute. This analysis is supported by fluorescence spectra and solvatochromic shift data of anthracene in pure CO₂ and in mixtures of CO₂ with C₂H₅Br at 35 °C that indicate both local density augmentation and local composition increases around the anthracene.

Introduction

There is great interest in the development of supercritical fluids as possible alternatives to common organic solvents as reaction media. This requires a detailed mechanistic knowledge of the specific factors that can influence and control chemical reactivity under supercritical conditions. In addition, supercritical fluids are attractive because many of their properties, including the viscosity, diffusivity, density, and other density-dependent properties, change dramatically with small changes in temperature or pressure. Thus, one can control or tune the reaction environment simply by adjusting the pressure or temperature, without actually changing the solvent.

A significant number of experimental, theoretical, and simulation works have established that the local environment about a dilute solute in a supercritical fluid (SCF) or SCF/cosolvent mixture can be significantly different than the bulk. The local density of the solvent around a dilute solute can be enhanced by as much as twice the bulk density in regions near and below the critical point.^{1–11} The local composition of cosolvent in the cybotactic sphere about a solute can be as much

as eight times the bulk cosolvent composition in SCF/cosolvent mixture.^{12–15} While preferential solvation exists in liquid solutions as well, the unique feature of supercritical fluid solutions is that the local environments can be changed substantially simply by adjusting the temperature and pressure. This provides the additional capabilities of influencing and manipulating reactivity in SCFs. As a result, the effect of local solvent structure has been the subject of many studies of a variety of reactions in supercritical fluids.^{14–30}

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In studies of kinetically controlled reactions in supercritical fluids,^{15,22,23,28–30} it was reported that the local composition enhancement can affect how reaction rates vary with pressure by influencing the concentration of one reactive specie around the other. Conversely, in a study of benzophenone triplet–triplet annihilation and the benzyl radical self-termination reaction in pure and 1 mol % acetonitrile doped supercritical CO₂, ethane, and CHF₃, Roberts et al.^{24,25} observed that both reactions occurred essentially at the diffusion control limit when spin statistical factors were taken into account. Thus, no evidence was found for the diffusion-controlled reactions being influenced by the enhanced solute–solute interactions. Other researchers have reported similar results for diffusion-controlled reactions in supercritical fluids.^{19–21} However, in a recent study of the fluorescence quenching reaction of 9,10-bis(phenylethynyl)anthracene (BPEA)/CBr₄ in supercritical CO₂, Bunker and Sun²⁷ reported that the rate constant was unusually efficient at lower pressures when the results were compared to Stokes–Einstein/Debye predictions, and the authors have attributed this to the local composition enhancement of CBr₄ around BPEA molecules. This suggests that diffusion controlled reactions can be enhanced by local solvation, in contrast to previous experimental reports and the explanations by Randolph and co-workers³¹ that increased local concentrations of one reactant about another do not exist in systems where the reaction occurs at the diffusion controlled limit.

The purpose of this study is to investigate local solvation effects on a single type of reaction as that reaction is varied from diffusion controlled to kinetically controlled. Energy transfer reactions afford the unique opportunity to do this because the reaction rate constants can be anywhere from diffusion controlled to many orders of magnitude below diffusion control dependent upon the choice of the energy donor (fluorophor) and the energy acceptor (quencher). The energy transfer reactions that we investigate do not have any thermodynamic limitations, i.e., they are not equilibrium limited reactions. By “kinetically controlled” reactions we mean those reactions that have a significant activation barrier and, thus, have rate constants far below the diffusion controlled limit. “Diffusion controlled” reactions are those that do not have an activation barrier, i.e., that react as soon as the species come together. In liquid solutions, Leite and Naqvi³² showed that the quenching constant of aromatic molecules by quenchers of heavy atoms depends largely on electron affinities and energy levels of the reacting species. Even though the reactions of interest are energy transfer (as opposed to electron transfer), as

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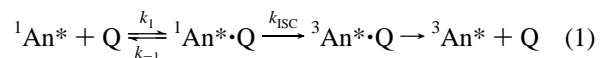
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is discussed in detail in the next section, their reaction rates depend on donor energy levels and acceptor electron affinities. We have taken advantage of this feature of energy transfer reactions and chosen two reaction pairs that are diffusion controlled in liquids and one that is well below the diffusion controlled limit. Specifically, the quenching reactions of anthracene by carbon tetrabromide (CBr₄) and 1,2-benzanthracene (1,2-BA) by CBr₄ are diffusion controlled in liquids,^{32–35} whereas the reaction of anthracene with bromoethane (C₂H₅-Br) is kinetically controlled in normal liquids.³² In this paper, we present the results of these three quenching reactions in supercritical CO₂ at 35 °C and various pressures. In addition, we present solvatochromic shifts of steady-state fluorescence spectra of anthracene in CO₂ and CO₂/C₂H₅Br mixtures and use the shifts to obtain estimates of local densities and local compositions. These data are vital in the interpretation of the rates of the anthracene/bromoethane reaction.

Mechanism of Fluorescence Quenching

It is important that reaction mechanisms be carefully considered when using reaction intermediates as spectroscopic probes of SCF solvent effects on chemical reactivity and reaction kinetics. This is especially true when considering the potential importance of the influence of SCF solvation on transition states and reaction intermediates. The structural and electronic nature of these species may, or equally well may not, have a dominating influence on observed reaction kinetics. Therefore, below we recall some relevant literature regarding fluorescence quenching of aromatic hydrocarbons by alkyl bromides and other heavy-atom quenchers.

There is considerable experimental evidence that indicates that fluorescence quenching of anthracene by CBr₄ and C₂H₅Br occurs by heavy-atom induced intersystem crossing (ISC) of the initially formed excited state donor/acceptor singlet complex. That is, the mechanism involves a diffusive encounter of the excited singlet state of anthracene (¹An*) with the quenching reactant bromide (Q) that forms the initial excited singlet state encounter complex (¹An*•Q) that subsequently undergoes heavy-atom spin–orbit coupling induced ISC to an excited triplet state complex (³An*•Q).



The triplet complex may then dissociate to excited state triplet anthracene (³An*), which will subsequently deactivate to ground-state anthracene and the bromide quencher. Wilkinson and Medinger³⁶ have demonstrated that the triplet state (³An*) is indeed the product of the fluorescence quenching of anthracene by bromobenzene by measurement of triplet state quantum yields. They found no effect on the mechanism in going from a low to a moderate dielectric constant solvent and no evidence for charged species. Ware and Novros³⁴ have reported similar results in their investigation of the diffusion-controlled fluorescence quenching of anthracene with CBr₄.

In more general terms, Thomaz and Stevens³⁷ have presented a detailed description of external heavy-atom effects in aromatic hydrocarbon fluorescence quenching. They have presented convincing experimental evidence that measured rate constants of fluorescence quenching will depend on two factors: (1) the

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extent of spin-orbit coupling in the initial encounter complex and (2) the stability of the complex toward dissociation as determined by the donor/acceptor properties of the quenching partners. The fluorescence quenching of pyrene (Py) with 29 chlorine, bromine, and iodine containing species was investigated and the observed quenching rate constants (k_q) were related to spin-orbit coupling parameters and electron-acceptor properties of the quenching species. Just as there is an internal effect of heavy atoms on the unimolecular ISC probability of isolated molecules, there is also an external heavy atom influence on the probability of ISC in the ${}^1\text{Py}^*\cdot\text{Q}$ complex caused by the heavy atom quencher. k_q and the ISC process are related to the matrix element of the spin-orbit perturbation operator between the singlet and triplet states of the complex.^{38,39}

The second factor that influences k_q is the dissociation of ${}^1\text{Py}^*\cdot\text{Q}$. In the work of Thomaz and Stevens³⁷ no fluorescence of the ${}^1\text{Py}^*\cdot\text{Q}$ complex was observed. This corroborated the findings of Wilkinson and co-workers³⁶ that the heavy atom quenching produces exclusively the hydrocarbon triplet state. Therefore, k_q may be represented by $k_q = k_1 \cdot k_{\text{ISC}}/k_{-1}$ for the cases where k_q is appreciably less than the diffusion limit. The complex dissociation frequency k_{-1} may be related to its dissociation energy (E) by $k_{-1} = A \exp(-E/RT)$, where A is a constant and E is expressed, for a purely charge transfer interaction, in terms of the ionization potential (I_D) of the donor and the electron affinity (E_A) of the acceptor, and the Coulomb attraction energy ($C(r)$) at the equilibrium donor-acceptor separation (r), according to $-E = I_D - E_A - C(r)$. A plot relating k_q and the two factors of spin-orbit coupling parameters and acceptor properties (half-wave potentials) of the 29 heavy atom quenchers was remarkably linear considering the vast difference in the chemical composition of the quenchers. This result reinforces that the most likely mechanism for the reactions presented in the present study is heavy atom induced ISC of the initially formed encounter pairs, i.e., ${}^1\text{An}^*\cdot\text{Q}$, and that the magnitude of k_q should be related to I_D of anthracene (or 1,2-benzanthracene) and E_A of CBr_4 and $\text{C}_2\text{H}_5\text{Br}$, as is observed experimentally in our results.

Experimental Section

Materials. Anthracene (Aldrich, zone-refined, 99+%), carbon tetrabromide (Aldrich, 99%), bromoethane (Aldrich, 99+%), 1,2-benzanthracene (Aldrich, 99%), acetonitrile (Aldrich, 99.9+%, HPLC grade), hexane (Aldrich, 99+%), and cyclohexane (Aldrich, 99.9+%, HPLC grade) were used as received. Carbon dioxide (Scott Specialty Gases, SFC grade, <2 ppm O_2) was also used as received.

Procedure. Fluorescence spectra and fluorescence lifetimes were obtained with a Photon Technology International fluorescence system. This system includes two main components: a steady-state spectrofluorometer and a laserstrobe lifetime instrument. The steady-state spectrofluorometer consists of a 75-W xenon arc lamp with LPS-220 power supply, lenses, emission monochromator, excitation monochromator, and PMT for detection. The laserstrobe lifetime instrument uses a pulse method for the lifetime measurement. It includes a PL-2300 nitrogen laser coupled with a PL-202 high-resolution dye laser to provide the desired excitation wavelength. The detection system for the lifetime system consists of the high efficiency emission monochromator followed by a gated and pulsed photomultiplier tube. Time resolved detection is achieved with a stroboscopic approach similar to boxcar techniques. Fluorescence decay data are acquired by measuring the fluorescence intensity at a large number of points in time from before the excitation light pulse to a terminal point that is generally five to seven times the measured lifetime. With the 2 ns nitrogen laser pulse as the dye laser pump and the iterative reconvolution technique

used in the software, this system has the capability of measuring lifetimes from 0.5 ns to several tens of microseconds. The steady state spectrofluorometer and the laserstrobe lifetime instrument share one sample compartment. All data acquisition functions except slit widths are under direct computer control. Excitation and emission slits were typically set at a 0.5–2 nm resolution for the steady state fluorescence measurements. Emission slits were typically of 3-nm resolution for the lifetime measurements. A PTI laser dye (PLD 366) was used to generate the laser pulse at the desired wavelength of 366 nm for the experiments involving anthracene. The direct N_2 laser pulse at 337 nm was used for the 1,2-benzanthracene study.

The high-pressure optical cells used in this study were fitted with suprasil quartz windows, were equipped for 90° detection, and were of approximately 2.5-mL capacity. They have been described previously.²⁴

Sample preparation for the anthracene/ CBr_4 / CO_2 system involved placing a known amount of an anthracene/hexane stock solution and an appropriate amount of a CBr_4 /hexane solution into the high-pressure cell. The hexane was allowed to evaporate and the cell was evacuated with a vacuum pump and then filled with pure CO_2 from an Isco Model 260D high-pressure syringe pump. The typical anthracene concentration was 3×10^{-6} M. The quencher (CBr_4) concentration varied from 7.06×10^{-4} to 3.53×10^{-3} M. The experiments were conducted at a constant molarity of the quencher as the pressure was varied from low to high by adding pure CO_2 to the optical cell at 35 °C. The sample was equilibrated for over 2 h before taking any data to ensure that the components were fully dissolved. This was ascertained by a constant intensity of the fluorescence signal. The constant molarity experiments have been verified by separate experiments conducted at a constant mole fraction of the quencher.

The reaction rate experiments for the anthracene/ $\text{C}_2\text{H}_5\text{Br}$ / CO_2 system were carried out at a constant mole fraction of quencher and involved a slightly different procedure since $\text{C}_2\text{H}_5\text{Br}$ is a liquid. Mixtures of CO_2 / $\text{C}_2\text{H}_5\text{Br}$ were prepared in an Isco Model 260D high-pressure syringe pump with use of a Reodyne HPLC injection loop for addition of liquid quencher ($\text{C}_2\text{H}_5\text{Br}$). Pure CO_2 was flowed through the injection loop containing the desired amount of quencher and was condensed in the Isco pump, which was maintained at 7 °C. Sample preparation involved placing an appropriate amount of the anthracene/hexane stock solution into the high-pressure optical cell, letting the hexane evaporate, evacuating the cell, and filling it with the above $\text{C}_2\text{H}_5\text{Br}/\text{CO}_2$ mixture from the Isco pump. All experiments were performed from low pressure to high pressure by adding more $\text{C}_2\text{H}_5\text{Br}/\text{CO}_2$ mixture into the optical cell. Quencher concentrations were determined with use of pure CO_2 densities calculated from the analytic equation of state used by Angus et al.⁴⁰ in the construction of the IUPAC CO_2 density data.

The 1,2-BA/ CBr_4 / CO_2 experiments were also carried out at a constant mole fraction of the quencher in a manner similar to the one described for anthracene/ $\text{C}_2\text{H}_5\text{Br}/\text{CO}_2$. Because CBr_4 is a solid, a U-tube assembly, rather than the injection loop, was used to introduce it into the Isco pump. The U-tube was primed with the desired amount of CBr_4 , and pure CO_2 was passed through it, carrying the quencher into the pump. After filling the pump, the U-tube was rinsed thoroughly with acetone into a beaker to check for residual CBr_4 . The acetone was allowed to evaporate, leaving, in each case, no CBr_4 . The 1,2-BA was injected into the cell in the same manner described above for anthracene, and the experiments were performed from low to high pressure. The 1,2-BA concentration used was typically 3.0×10^{-6} M, and the CBr_4 mole fractions were between 3.50×10^{-5} and 1.20×10^{-4} , which yielded CBr_4 concentrations between 3.11×10^{-4} and 2.08×10^{-3} M. The 1,2-BA/ CBr_4 / CO_2 samples could have been prepared by using the method described above for anthracene/ CBr_4 / CO_2 . This procedure, making up a CO_2 / CBr_4 sample in the Isco pump, was developed to ascertain that the concentration of CBr_4 was the intended value. However, anthracene/ CBr_4 / CO_2 samples prepared by both methods produced the same results, indicating that both techniques are reliable.

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The solvatochromic shift data were carried out in the same high-pressure optical cell and with the same steady-state fluorescence spectrometer described above. The local density measurements (anthracene/CO₂ data) involved depositing an appropriate amount of anthracene into the cell and filling the cell with CO₂ from an Isco Model 260D pump. The experiments were performed at constant molarity by adding pure CO₂ from the Isco pump. The local composition measurements (anthracene/C₂H₅Br/CO₂ data) were also taken at constant molarity of both the anthracene and the bromoethane. Liquid bromoethane was introduced into an evacuated cell containing anthracene through the Rheodyne injection loop with use of pure CO₂ from the Isco pump. The experiments were conducted from low pressure to high pressure by adding pure CO₂. Thus, the spectra were taken at various pressures with constant concentrations of anthracene and bromoethane of 6.78×10^{-6} and 0.268 M, respectively. This corresponds to bromoethane mole fractions that range from 4 mol % at low pressures to 1.4 mol % at high pressures.

For all experiments, the temperature within the high-pressure optical cell was monitored and controlled with a platinum resistance thermometer that made direct contact with the supercritical fluid mixtures, and an Omega (Model CS-6071A) temperature controller equipped with a Watlow Firerod cartridge heater. Pressure was monitored at the optical cell with a Heise (Model 901A) pressure gauge. The optical cell temperature and pressure were typically maintained at ± 0.1 °C and ± 0.1 bar, respectively. All normal liquid experiments were conducted with use of 1 cm quartz cells at room temperature.

Results

The experimental results are divided into four sections. The first section describes the steady-state fluorescence of anthracene in supercritical CO₂ and supercritical CO₂/C₂H₅Br mixtures. Both excitation and emission spectra were obtained for anthracene in pure CO₂ at 35 °C from 57.6 to 160.7 bar and the observed spectral shift with pressure is analyzed in terms of the local density augmentation. In the supercritical CO₂/C₂H₅Br mixture the excitation and emission spectra of anthracene were obtained at 35 °C from 76.4 to 155.6 bar and analyzed to obtain local compositions. The next three sections give the results for the quenching reactions of anthracene/CBr₄, 1,2-BA/CBr₄, and anthracene/C₂H₅Br, respectively. The three different reactions were studied in CO₂ at 35 °C and in liquids at room temperature with time-resolved and/or steady-state fluorescence spectroscopy. To obtain the bimolecular rate constants, either fluorescence lifetimes (τ) or fluorescence intensities (I) of the fluorophor (anthracene or 1,2-BA) were measured at different pressures and different quencher concentrations. Then Stern–Volmer plots were constructed and the Stern–Volmer constants, K_{sv} , were determined by reading the slopes, according to the well-known Stern–Volmer relationships. τ_0 and I_0 are the fluorescence lifetime and intensity, respectively, of the fluorophor in the absence of added quencher.

$$\tau_0/\tau = 1 + K_{sv}[\text{quencher}] \quad (2a)$$

or

$$I_0/I = 1 + K_{sv}[\text{quencher}] \quad (2b)$$

The bimolecular quenching rate constant, k_{bi} , was calculated from the following relationship.

$$k_{bi} = \frac{K_{sv}}{\tau_0} \quad (3)$$

1. Steady-State Fluorescence of Anthracene in Supercritical CO₂ and Supercritical CO₂/C₂H₅Br Mixtures. For comparison with SCF experiments, we first measured the excitation and emission spectra of anthracene in acetonitrile at

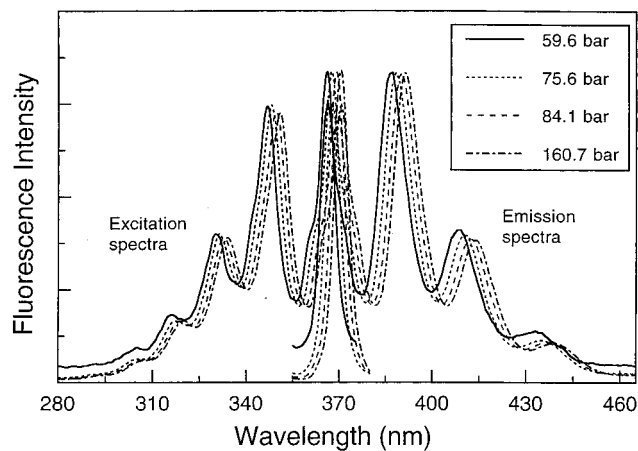


Figure 1. Excitation and emission spectra of anthracene fluorescence in pure CO₂ at 35 °C at various pressures. The excitation wavelength for the emission spectra measurements was 347 nm and the excitation spectra were obtained by monitoring the fluorescence at 389 nm. The fluorescence intensity at different pressures has been normalized for a clear comparison.

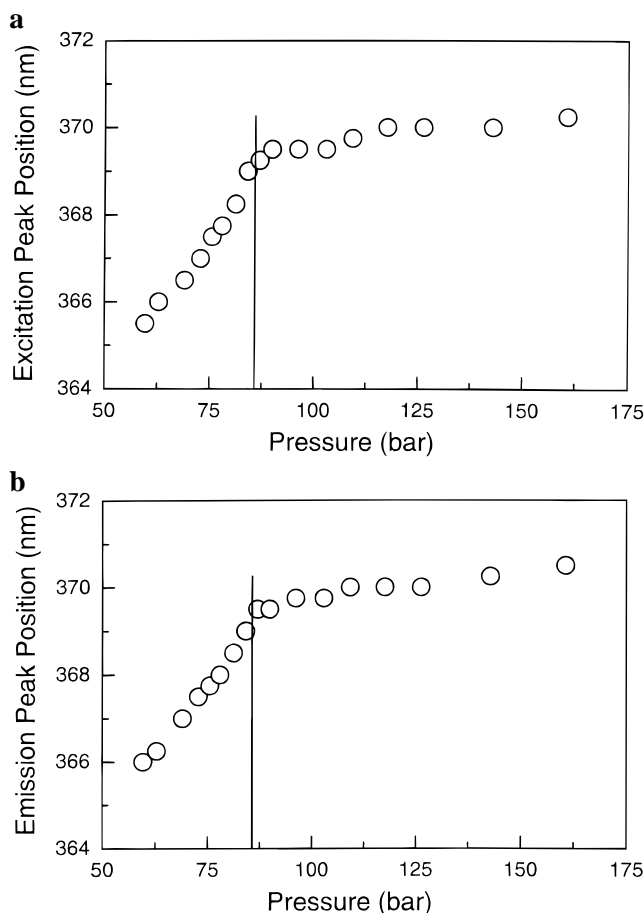


Figure 2. Change of peak positions with pressure for excitation (a) and emission spectra (b) of anthracene fluorescence in CO₂ at 35 °C. The vertical line is positioned where the wavelength increase changes slope.

room temperature. Then, both the fluorescence excitation and emission spectra of anthracene were measured from 57.6 to 160.7 bar at 35 °C in pure CO₂, and these results are shown in Figure 1. Both spectra shifted about 6 nm at high pressures in CO₂ at 35 °C, relative to liquid acetonitrile. The spectra also shift about 5 nm when changing the pressure from 57.6 to 160.7 bar at 35 °C. Thus, a significant change in solvating power can be achieved by simply varying the pressure of the CO₂.

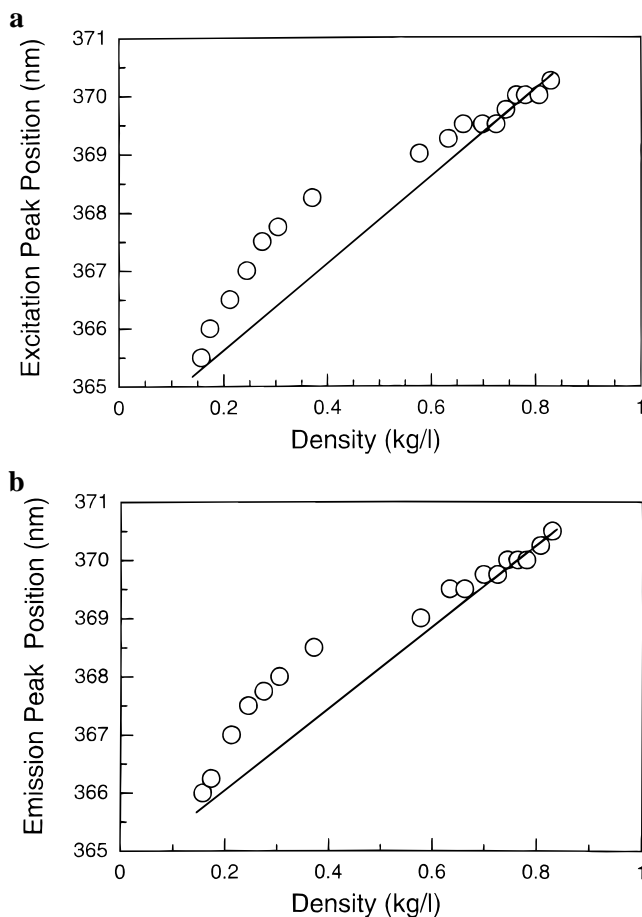


Figure 3. Change of peak positions with density for excitation (a) and emission spectra (b) of anthracene fluorescence in CO₂ at 35 °C. The solid line is a linear least-squares fit to the high-pressure data.

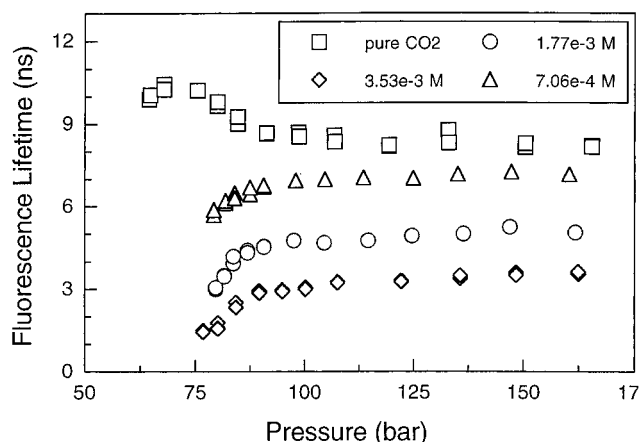


Figure 4. Measured fluorescence lifetimes of anthracene in CO₂ at 35 °C as a function of pressure in pure CO₂ and for several CBr₄ concentrations.

Figure 2 shows the change of spectral position with pressure. For a clear comparison of the pressure effect on the excitation and emission spectra, we present the 0–0 transition for anthracene, i.e., the longest wavelength peak of the excitation spectra (S_0 – S_1) and the shortest wavelength peak of the emission spectra (S_1 – S_0) in Figure 2. The spectra shift more rapidly with increasing pressure at low pressures; however, this change is less dramatic after reaching a pressure of about 89 bar, which is marked with a vertical line as a guide. To show the dependence on bulk density, the same data are plotted against the density of CO₂ in Figure 3.

Both the excitation and emission spectra of anthracene were

Table 1. Solvatochromic Shifts of the S_1 – S_0 Emission Peak and the S_0 – S_1 Excitation Peak of Anthracene at 35 °C in Pure CO₂ and a Mixture of CO₂ and C₂H₅Br^a

pressure (bar)	S_1 – S_0 emission peak max (nm)		S_0 – S_1 excitation peak max (nm)	
	pure CO ₂	mixture	pure CO ₂	mixture
76.4	367.75	369.5	367.5	368.75
80.0	368.25	370	368	369.5
84.1	368.75	370.25	368.5	369.5
88.2	369.5	370.25	369	369.5
94.1	369.75	370.25	369.5	369.75
101.0	369.75	370.25	369.75	370
111.0	370	370.25	369.75	370
128.4	370	370.25	370	370.25
155.6	370.25	370.5	370	370.25

^a Note: The maxima for the S_1 – S_0 emission peak and the S_0 – S_1 excitation peak occur at 379 and 378.5 nm, respectively, in pure bromoethane.

measured from 76.4 to 155.6 bar at 35 °C in the mixture of CO₂/C₂H₅Br, and the S_0 – S_1 excitation band and the S_1 – S_0 emission band are listed in Table 1 as a function of pressure. The peak positions change about 3 nm in going from low to high pressure, which is small but measurable with the instrument accuracy of about ± 0.25 nm.

2. The Reaction of Anthracene with CBr₄ in CO₂. To study potential effects of local solvation on fluorescence quenching reactions in supercritical fluids, we performed time-resolved fluorescence experiments on the system of anthracene/CBr₄ in CO₂ at 35 °C over a pressure range of 80.3 to 160.7 bar.

To verify that the quenching reaction of anthracene by CBr₄ is a diffusion-controlled reaction in liquids, as reported in the literature,^{32,34} we performed time-resolved fluorescence experiments for this quenching reaction in acetonitrile at room temperature. The fluorescence decay of anthracene was very well fitted to a single exponential equation by deconvolution from the instrument response function (IRF). The Stern–Volmer plot of the lifetime ratio of τ_0/τ versus quencher concentration is linear over the concentration range studied and gives a Stern–Volmer constant, K_{sv} , of 110.7 M^{-1} . The lifetime of anthracene in pure acetonitrile at room temperature was determined to be 5.1 ns (which is in reasonable agreement with the literature value of $4.83 \pm 0.4 \text{ ns}$ ³⁴), and this gives a bimolecular rate constant of $2.17 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. This bimolecular rate constant is in excellent agreement with the prediction of the Stokes–Einstein based Debye equation, which gives a value of $1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. This confirmed that the quenching reaction of anthracene by CBr₄ is diffusion controlled in liquids.

The pressure dependence of the fluorescence lifetime of anthracene in pure CO₂ was measured and is shown as the top curve in Figure 4. It is interesting to notice that the anthracene lifetime decreases with increasing pressure and levels off at high pressures. This trend is the same as the fluorophor BPEA in CO₂,²⁷ but different from another fluorophor, 9-cyanoanthracene, in several supercritical fluids.⁴¹ It has been suggested that the radiative rate of the fluorescence decay should be proportional to the square of the refractive index of the solvents.⁴² To identify the factors which affect the anthracene fluorescence lifetime in CO₂, a plot of $(\tau \times n^2)$ versus pressure is given in Figure 5, where n is the refractive index of CO₂ calculated from

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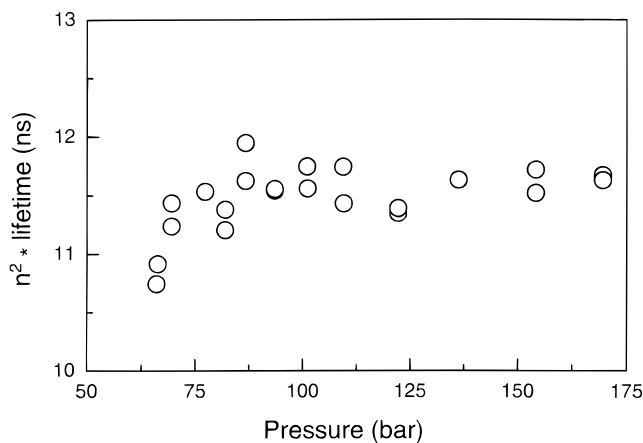


Figure 5. Plot of the fluorescence lifetime (τ) times the square of the refractive index (n^2) as a function of pressure for anthracene in pure CO_2 at 35 °C.

an empirical equation.⁴³ The plot shows that $\tau \times n^2$ is constant from 165.4 bar to about 78 bar. This suggests that the refractive index is the main factor responsible for the lifetime change in this pressure range. However, the situation becomes more complicated at pressures below about 78 bar. In addition to the dramatic change of refractive index, the changes of fluorescence quantum yield, extinction coefficient, and absorption spectral shift all become important and prohibit any conclusion without tackling all these influencing factors separately.

To construct Stern–Volmer plots, the fluorescence lifetimes of anthracene were measured at different quencher concentrations. The CBr_4 concentration in CO_2 ranged from 0.71 to 3.53 mM. At all conditions the fluorescence decays of anthracene were well fit to a single exponential. In fact, attempts to fit the decay to a double exponential equation did not improve the fit significantly and gave essentially the same lifetime as fitting to a single exponential equation. The experimental fluorescence lifetime results are presented in Figure 4 for anthracene in CO_2 at 35 °C and several concentrations of quencher. In contrast to the trend of lifetime change with pressure in pure CO_2 , the fluorescence lifetime of anthracene increases with increasing pressure in the presence of the quencher. The change in the lifetime is more dramatic at low pressures. This indicates that the high efficiency quenching of anthracene by CBr_4 is greater than the effect of refractive index on the lifetime.

The Stern–Volmer plot is presented in Figure 6 for anthracene/ CBr_4 in CO_2 at 35 °C and at several pressures. The Stern–Volmer constants were obtained by reading the slopes in Figure 6. These values decrease from 1382 M^{-1} at 80.3 bar to 361 M^{-1} at 160.7 bar, a 3.8-fold change over this pressure range. According to eq 3, the bimolecular rate constants for this quenching reaction were calculated from the Stern–Volmer constants and the fluorescence lifetime of anthracene in pure CO_2 measured at the pressure and temperature of the individual quenching experiments. The bimolecular rate constants are shown in Figure 7 as a function of pressure. Also shown in the plot are the predicted bimolecular rate constants from the well-known Stokes–Einstein based Debye equation, $k_{\text{diff}} = 3RT/\eta$, where η is viscosity of the solvent, which is estimated by the Jossi–Stiel–Thodos method^{44,45} for CO_2 .

3. The Reaction of 1,2-Benzanthracene with CBr_4 in CO_2 . The fluorescence quenching of 1,2-BA by CBr_4 was also

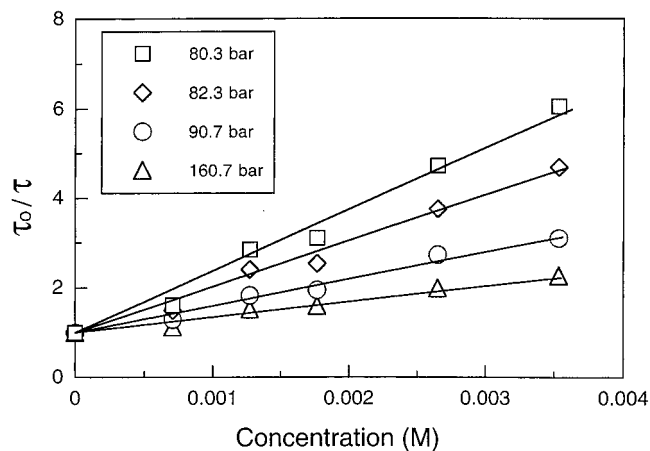


Figure 6. Stern–Volmer plot for anthracene/ CBr_4 in CO_2 at 35 °C at several pressures.

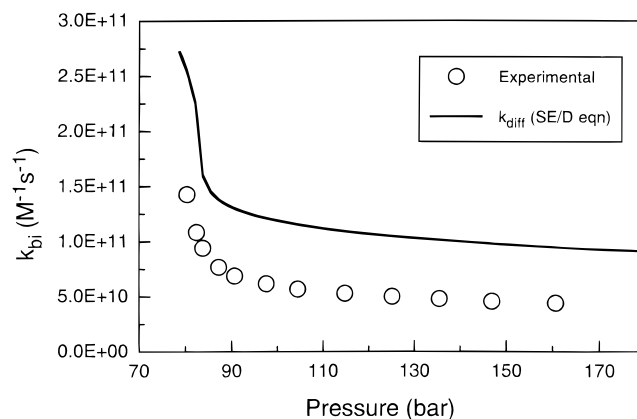


Figure 7. Plot of the pressure dependence of the bimolecular rate constants for the fluorescence quenching reaction of anthracene/ CBr_4 in CO_2 at 35 °C, compared to predictions from the Stokes–Einstein based Debye equation.

examined. This reaction was determined³⁵ to be diffusion controlled in liquid 1,2-propanediol. To confirm diffusional reactivity, we performed time-resolved quenching experiments for this reaction in liquid hexane at room temperature. The Stern–Volmer plot of τ_0/τ versus quencher concentration is linear over the concentration range studied and gives a Stern–Volmer constant, K_{sv} , of 1113 M^{-1} . This, along with a value of 55.9 ns for the fluorescence lifetime of 1,2-BA in pure hexane, gives a bimolecular rate constant of $1.99 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The value for this rate constant from the Stokes–Einstein based Debye equation is $2.15 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which confirms that the reaction is diffusion controlled in liquids at room temperature.

The quenching experiments in CO_2 at 35 °C were performed at various constant mole fractions of quencher over a pressure range from 77.9 bar to 158.6 bar. With use of these fluorescence lifetimes and the densities of pure CO_2 , Stern–Volmer plots were constructed at each pressure at 35 °C and these are shown in Figure 8. The Stern–Volmer plots are linear over the concentration range examined, and the Stern–Volmer constants were determined at each pressure from the slope of the lines according to eq 2a. Using the Stern–Volmer constants and the lifetimes of 1,2-BA in pure CO_2 , the bimolecular quenching rate constants were determined from eq 3 and are plotted in Figure 9, along with the rate constants calculated from the Stokes–Einstein based Debye equation. With increasing pressure, the bimolecular rate constants k_{bi} decrease from $1.18 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ at 77.9 bar to $5.19 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ at 158.6 bar, a 2.3-fold change over the pressure range studied.

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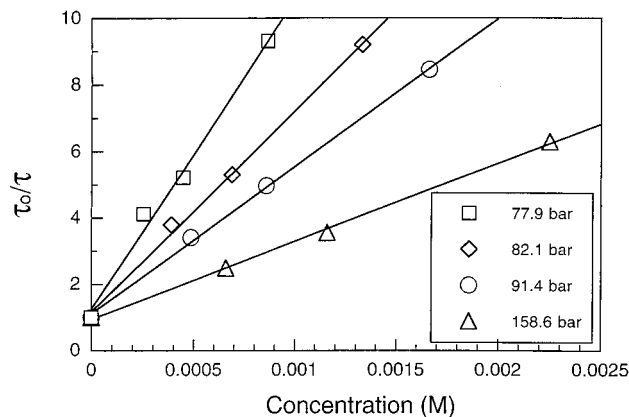


Figure 8. Stern–Volmer plot for 1,2-benzanthracene/CBr₄ in CO₂ at 35 °C at several pressures.

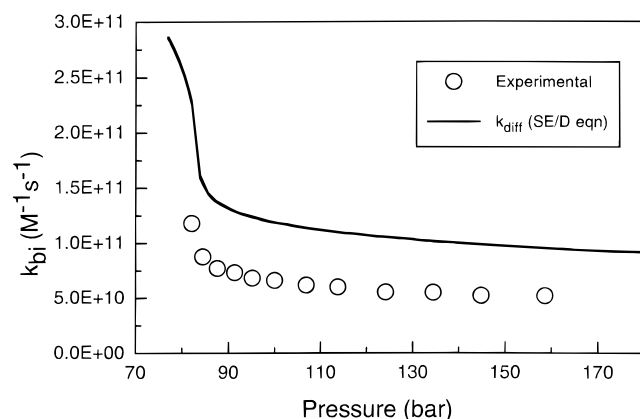


Figure 9. Plot of the pressure dependence of the bimolecular rate constants for the fluorescence quenching reaction of 1,2-benzanthracene/CBr₄ in CO₂ at 35 °C, compared to predictions from the Stokes–Einstein based Debye equation.

4. The Reaction of Anthracene with C₂H₅Br in CO₂. We have presented experimental results for the diffusion-controlled reactions between anthracene and CBr₄ and 1,2-benzanthracene and CBr₄ in supercritical CO₂. Here we give results for the kinetically controlled reaction of anthracene with C₂H₅Br in supercritical CO₂. We chose a quencher (C₂H₅Br), which contains the same heavy atom (Br) as in the previous quencher (CBr₄), but which has a reduction potential of -2.08 V.³² Since the reduction potential of the quencher is close to that of the energy donor (the reduction potential of anthracene is -1.96 V), one would expect this reaction to be kinetically controlled, as will be discussed later.³²

The fluorescence quenching reaction of anthracene by C₂H₅Br has been reported in the literature.³² To verify that this reaction is kinetically controlled and not strongly influenced by solvent polarity or viscosity, we conducted both steady-state and time-resolved fluorescence experiments in hexane, cyclohexane, and acetonitrile at room temperature. The results for cyclohexane are shown in Figure 10 (top). The fluorescence intensity results are in excellent agreement with the lifetime results in all three solvents. The Stern–Volmer plots are linear over the concentration range studied, and yield a Stern–Volmer constant (the slope) of 1.06 M⁻¹ for hexane, 1.09 M⁻¹ for cyclohexane, and 1.11 M⁻¹ for acetonitrile. The fluorescence lifetime of anthracene has been determined to be 5.7 ns in hexane, 5.3 ns in cyclohexane, and 5.1 ns in acetonitrile, which are in good agreement with the literature.^{46,47} Thus, we determined the

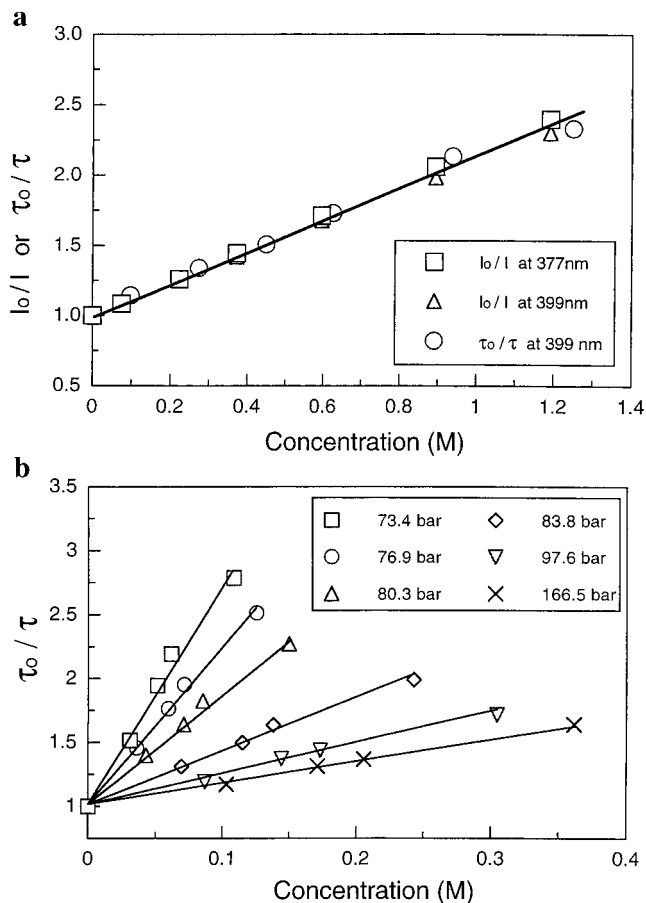


Figure 10. Stern–Volmer plot for the quenching reaction of anthracene/C₂H₅Br in cyclohexane (top) and CO₂ at 35 °C and various pressures (bottom). The data obtained with CO₂ as the solvent were obtained from fluorescence lifetime measurements. The cyclohexane data were obtained from both fluorescence lifetime and steady-state intensity measurements.

Table 2. Rate Constants for the Reaction of Anthracene with C₂H₅Br in Various Solvents, Along with Their Physical Properties

solvent	refractive index	dielectric const	viscosity (cP)	rate const (M ⁻¹ s ⁻¹)
CO ₂ (73.5 bar) ^e	1.05 ^a	1.14 ^b	0.0221 ^c	1.63×10^9
CO ₂ (166.5 bar) ^e	1.19 ^a	1.51 ^b	0.0731 ^c	2.17×10^8
hexane	1.3749 ^{d,f}	1.88 ^{d,g}	0.313 ^{d,f}	1.87×10^8 ^f
cyclohexane	1.4262 ^{d,f}	2.02 ^{d,f}	1.0 ^{d,f}	2.06×10^8 ^f
acetonitrile	1.344 ^{d,f}	37.5 ^{d,f}	0.38 ^{d,h}	2.18×10^8 ^f

^a Reference 43. ^b Reference 71. ^c References 44 and 45. ^d Reference 72. ^e All data for CO₂ are taken at 35 °C. ^f Liquid data at 20 °C. ^g Liquid data at 25 °C. ^h Liquid data at 15 °C.

bimolecular rate constants to be 1.87×10^8 , 2.06×10^8 , and 2.18×10^8 M⁻¹ s⁻¹ for hexane, cyclohexane, and acetonitrile, respectively. The rate constants are about two orders of magnitude lower than the diffusion control limit and independent of the viscosity of the solvents (see Table 2). As previously demonstrated,³² the quenching reaction of anthracene by C₂H₅Br is kinetically controlled in liquids (i.e., it has an activation barrier). As such, it is a good probe to study the solvation effects on kinetically controlled quenching reactions in supercritical fluids.

All fluorescence quenching experiments were performed under constant mole fraction conditions for this reaction. The measured lifetime of anthracene, in the presence of quencher, increased with increasing pressure and then leveled off at high pressures. From the measured fluorescence lifetimes and the densities of pure CO₂, we constructed the Stern–Volmer plots

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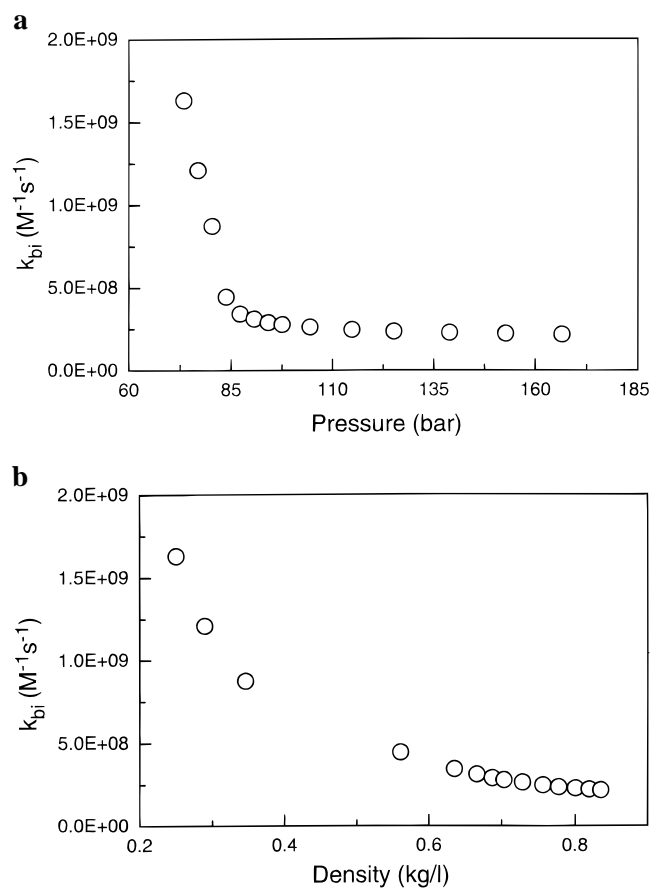


Figure 11. Bimolecular rate constants plotted vs pressure (top) and density (bottom) for the quenching reaction of anthracene with C_2H_5Br at $35\text{ }^\circ C$.

at each pressure at $35\text{ }^\circ C$ using the bulk concentrations of the quencher, and these are shown in Figure 10 (bottom). The Stern–Volmer plots are linear at all pressures over the bulk quencher concentrations studied. The Stern–Volmer constants were obtained by reading the slopes at each pressures in Figure 10 (bottom). From the Stern–Volmer constant and lifetime in pure CO_2 , the quenching rate constants based on bulk concentrations, k_{bi}^{bulk} , were determined for each pressure, according to eq 3, and are plotted versus both pressure and density in Figure 11, parts a and b. With increasing pressure, k_{bi}^{bulk} decreased from $1.63 \times 10^9\text{ }M^{-1}\text{ }s^{-1}$ at 73.4 bar to $2.17 \times 10^8\text{ }M^{-1}\text{ }s^{-1}$ at 166.5 bar, about a 7.5-fold difference over the pressure range studied.

Discussion

To interpret the experimental results, we will first use the fluorescence wavelength shifts to determine local density augmentation around anthracene in supercritical CO_2 and the local composition of bromoethane around anthracene in a CO_2/C_2H_5Br mixture. The next section includes a discussion of the estimation of diffusion coefficients in supercritical fluids. Then we will show how this applies to the two diffusion controlled reactions of anthracene and 1,2-benzanthracene with CBr_4 and provide an alternative interpretation of the data previously presented for the reaction of BPEA with CBr_4 . Finally, we will discuss the kinetically controlled reaction of anthracene with bromoethane (C_2H_5Br).

1. Interpretation of Fluorescence Wavelength Shifts. Local density augmentation of the solvent around dilute solute molecules in supercritical fluids has been studied for some time due to its important influence on solvation, physiochemical

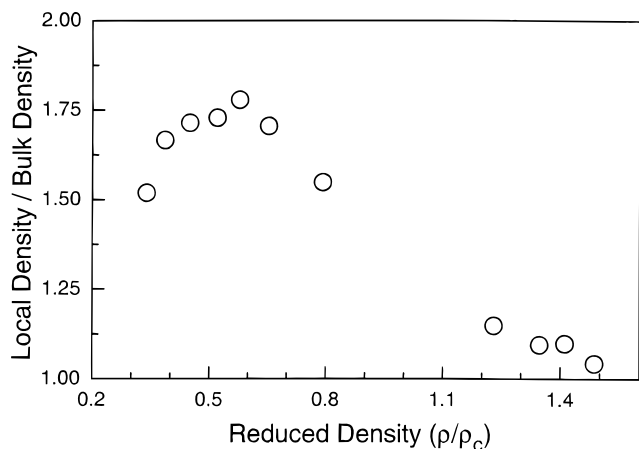


Figure 12. Ratio of local density to bulk density of CO_2 around anthracene molecules in CO_2 at $35\text{ }^\circ C$ as a function of reduced density. These data were obtained from the spectral shift measurements shown in Figure 3.

properties of solute molecules, and the potential effects on reactions in supercritical fluids. Researchers have quantitatively characterized local solvent density using different techniques, which include absorption solvatochromic shifts,¹² pyrene fluorescence peak ratios (I_1/I_3),^{4,9,48} solvatochromic shifts of fluorescence spectra,^{10,49} and measurement of rotational correlation time of solute molecules.⁵⁰ In this study we can determine local densities from the fluorescence wavelength shifts for the anthracene/ CO_2 system. This system is important since anthracene is a well-known and widely used molecular probe and CO_2 is the most widely used supercritical fluid and has potential as an environmentally benign replacement for many organic solvents.

We obtained quantitative estimates of the local density of CO_2 around anthracene using the data in Figure 3. These curves exhibit a characteristic linear portion at high pressures and an upward deviation from that trend at intermediate pressures, spanning through and extending well below the critical density. These trends bear close resemblance to the peak ratio measurement of pyrene fluorescence in supercritical fluids reported previously.^{4,9,48} The upward deviation from the linear trend established at high pressures was used to estimate local densities, following procedures similar to those used previously.^{4,6,9} The local density values were obtained by finding the density that a given peak position corresponds to on a linear least-squares line fit through the high-pressure points in Figure 3. The local density results are shown in Figure 12. The implied assumption made is that there is no local density enhancement at high pressures and the dependence of the spectral shift on density should be the same at both low and high pressures if there is no local density augmentation. The maximum in the ratio of local to bulk density occurs at about a reduced density of 0.58, well below the critical density, which is in qualitative agreement with some recent studies.^{7,9,51,52} Although the ratio of local to bulk density can be as high as 1.8 at about half the critical density, the local density at any given pressure does not exceed the local density at a higher pressure over the whole pressure range studied.

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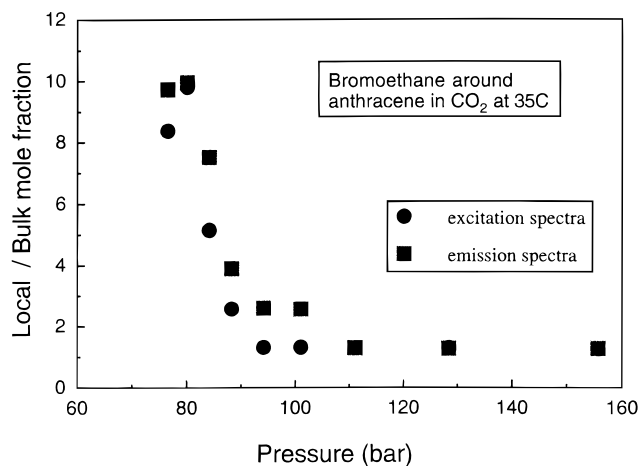


Figure 13. Ratio of local composition to bulk composition of C_2H_5Br around anthracene in CO_2 at 35 °C. These values were determined from the solvatochromic shift data shown in Table 1. Equivalent results were obtained from the excitation spectra (●) and the emission spectra (■).

Local compositions around dilute solutes in supercritical fluid mixtures have also been studied by a number of researchers using solvatochromic shift data.^{12–15} Kim and Johnston¹² developed a model to calculate local compositions by assuming that the shift in the mixture is due to a linear contribution of the pure component shifts weighted by the local mole fractions and the coordination numbers. Using this technique, we obtained local compositions of the bromoethane around the dilute anthracene solute using the solvatochromic shift data in Table 1, and these results are shown in Figure 13. For the coordination number ratios we used molar density ratios, where the density of liquid bromoethane is 1.46 kg/L (13.4 M), the density of pure CO_2 at each pressure was obtained from the IUPAC equation of state,⁴⁰ and the density of the mixture was approximated with the density of pure CO_2 . Excitation and emission spectra data gave equivalent results, and both are plotted in Figure 13. Since the experiments were done at constant molarity of the bromoethane rather than constant mole fraction, the results are plotted as a ratio: local mole fraction/bulk mole fraction. This presentation relies on the reasonable assumption^{12,14,15} that at a particular temperature and pressure the ratio of local to bulk mole fraction is not sensitive to concentration over the small range of mole fractions used (0.014 to 0.04). The ratio of local to bulk mole fraction ranges from close to unity at high pressures to about ten at low pressures. This trend and these values are similar to those obtained for other solvatochromic probe/cosolvent systems in supercritical CO_2 .^{12–15} We will use these data to help in the analysis of the reaction rates for anthracene with bromoethane in CO_2 in section 4 of the discussion below.

2. Estimation of Diffusion Coefficients in Supercritical Fluids. Diffusion data in supercritical fluids are often modeled by Stokes–Einstein based equations, which state that the diffusivity is inversely proportional to viscosity of solvent ($D_{12} \propto \eta^{-1}$). However, it has been frequently found that the Stokes–Einstein based equations do not apply to the low viscosity region.^{53–57} After reviewing diffusivity data for noncomplexing systems in normal liquids, Hayduk and Cheng⁵³ found that the slope of the $\log D$ vs $\log \eta$ relationship appears to depend on the diffusivity itself; i.e., the lower the diffusivity the greater

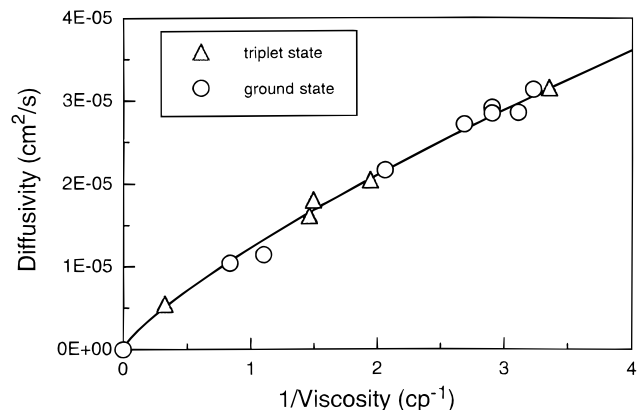


Figure 14. Plot of diffusion coefficients versus the inverse of viscosity for anthracene in different liquid solvents. The solid line is a power law fit of the form $D_{12} = (1.228 \times 10^{-5})\eta^{-0.777}$.

the slope. Thus, a power law expression has been suggested, $D_{12} \propto \eta^{-\alpha}$. Hayduk and Minhas⁵⁴ conducted a critical review of liquid diffusivity data and found that an exponent of 0.78 worked best based on 254 values of diffusivities in nonpolar solvents. An exponent of 0.8 was the best fit for 436 data points in both polar and nonpolar liquid solvents. Even in a study of the diffusivity of naphthalene in supercritical CO_2 , Lamb et al.⁵⁸ found that a power law, $D(\eta/T)^{0.75} = \text{constant}$, represented their experimental data well. On the basis of this observation, the fact that supercritical CO_2 viscosities are rather low (typically falling between 0.02 and 0.1 Cp), and some comparisons between experimental diffusivities in supercritical fluids,^{56,57} one might expect the Stokes–Einstein equation to overestimate the diffusivity at supercritical conditions.

Experimental diffusion coefficient data of anthracene in CO_2 are not available in the literature to our knowledge. However, experimental diffusion data are available for both the anthracene ground and triplet states in normal liquids,^{59–64} and they are plotted in Figure 14. Anthracene triplet diffusion coefficients do not show any noticeable difference from the ground state values. A fit of the Stokes–Einstein based equation to the experimental liquid diffusion data shown in Figure 14 gives $D_{12} = (1.03 \times 10^{-5})\eta^{-1}$, with a fairly good fit. A better fit is obtained with a power law equation, $D_{12} = (1.228 \times 10^{-5})\eta^{-0.777}$, and this is the solid curve shown in Figure 14. This agrees with the comprehensive study of diffusion coefficients in normal liquids mentioned above.⁵⁴ The question that remains is which equation fit to the experiment diffusion data in liquids should best represent the diffusivity of anthracene in supercritical CO_2 . When extrapolated to supercritical fluid conditions, the Stokes–Einstein based equation gives significantly larger values than the power law expression, as shown in Figure 15. Also shown in Figure 15 are the experimental diffusion coefficients of molecules similar to anthracene in supercritical CO_2 obtained from literature.^{56,58,65,66} The power law equation obtained from the liquid data gives remarkably good predictions when

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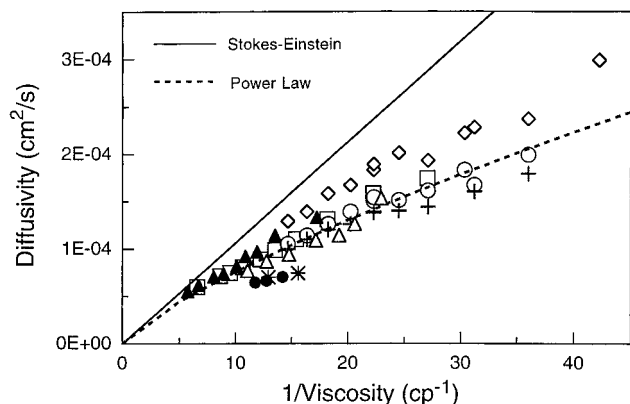


Figure 15. Plot of diffusion coefficients versus the inverse of viscosity for various aromatic molecules in supercritical CO₂. The solid and dashed lines are the extrapolations of the Stokes–Einstein model and the power law equation, respectively, fitted to diffusion coefficient data of anthracene in liquids. The data are for the following solutes and conditions: (Δ) naphthalene, 35 °C;⁵⁵ (\blacktriangle) naphthalene, 35 °C;⁵⁴ (\square) naphthalene, 55 °C;⁵⁴ (\bullet) 2-naphthol, 35 °C;⁴⁶ ($*$) 2-naphthol, 45 °C;⁴⁶ (\diamond) benzene, 40 °C;⁵⁶ (\circ) *n*-propylbenzene, 40 °C;⁵⁶ and (+) 1,3,5-trimethylbenzene, 40 °C.⁵⁶ The Stokes–Einstein and power law extrapolations from the liquid data at room temperature are corrected to 35 °C for better comparison with the supercritical data.

extrapolated to the supercritical region (Figure 15). The difference between the extrapolation of the Stokes–Einstein based equation and the power law equation (up to about a factor of 2) demonstrates why the Stokes–Einstein based equation has been observed to somewhat overpredict diffusion coefficients in low viscosity supercritical fluids, even though it does an excellent job of predicting diffusivities in liquids. Failure of the Stokes–Einstein equation at low density (which corresponds to low viscosity in SCFs) may be due to a violation of the theory's assumption that the solute diffuses through a continuum that exerts a uniform force on the molecule or to clustering of the solvent around the solute leading to a larger effective size of the diffusing species.⁵⁵ This is an area that warrants further investigation. Nevertheless, an overestimation of the diffusion coefficient by the Stokes–Einstein equation leads directly to an overprediction of the diffusion control limit of reaction rate constants by the SE/D equation.

3. The Reactions of Anthracene with CBr₄ and 1,2-Benzanthracene with CBr₄. On the basis of the above discussion, we conclude that the reactions of both anthracene/CBr₄ and 1,2-BA/CBr₄ occur at the diffusion control limit at all pressures studied in CO₂ at 35 °C. This is in agreement with other diffusion controlled reaction studies^{24,25} and the revised analysis^{10,67} of several studies of pyrene excimer formation in supercritical fluids.^{19–21} In this study there is no indication of increased rate constant due to the enhanced molecular interaction between the anthracene or 1,2-BA molecule with the CBr₄. This may be due to the equilibrium distribution of quencher molecules (CBr₄) around the anthracene or 1,2-benzanthracene not having sufficient time to be established for the fast diffusion process.³¹ The initial equilibrium distribution of the CBr₄ around the ground state anthracene may lead to a greater chance of static quenching, but this would occur at a much shorter time scale than the diffusion process and would not be detected in a nanosecond scale lifetime measurement. In other words, the diffusional bimolecular rate constants determined from fluorescence lifetime measurements do not reflect static quenching effects if they are present. These

experiments indicate that the reactions of both anthracene/CBr₄ and 1,2-BA/CBr₄ occur at the expected diffusion control limit in supercritical CO₂.

However, these results do not agree with those published recently for a very similar reaction, the fluorescence quenching of 9,10-bis(phenylethynyl)anthracene (BPEA) with CBr₄ in both liquid hexane and supercritical CO₂.²⁷ In their paper Bunker and Sun²⁷ described the BPEA/CBr₄ reaction as diffusion controlled but concluded that the reaction was enhanced by the local composition enhancement of CBr₄ around BPEA, thus suggesting that a diffusion-controlled reaction can be influenced by the enhanced molecular interactions between the reacting species. This is in striking contrast to the results for anthracene/CBr₄ and 1,2-benzanthracene/CBr₄ quenching reported above. Bunker and Sun reached their conclusions for the BPEA/CBr₄ system by comparing their experimental data to the SE/D prediction multiplied by a factor of 0.18. They did this to force the theory to match the experimental data at high pressures. However, when this multiplier was used the experimental data fell above the SE/D prediction at lower pressures, and this deviation was attributed to enhanced local compositions of the CBr₄ around the BPEA.²⁷ The discrepancy between our anthracene/CBr₄ and 1,2-benzanthracene/CBr₄ results presented above and the results for the BPEA/CBr₄ reaction²⁷ motivated additional examination of the BPEA/CBr₄ system.

The BPEA/CBr₄ quenching reaction was described as diffusion controlled and was analyzed with use of the Stokes–Einstein/Debye equation.²⁷ However, the bimolecular rate constants were only about 34% of the value predicted from the SE/D equation in liquid hexane, and only 18% of the value predicted in CO₂ at a reduced density of 1.9 at 35 °C. We have confidence in these data since we have reproduced them in our laboratory. Since the rate constants for BPEA/CBr₄ are significantly below the SE/D predictions in both liquids and supercritical CO₂, there is some concern as to whether this reaction is really diffusion controlled. This concern is further strengthened by examining the reduction potentials and electronic energies of the involved species. Leite and Naqvi³² studied various quenching reactions and their results indicate clearly that the important effect on the reaction rate is the reduction potential difference between the two reacting species. The quenching reaction can be shifted from a diffusion controlled reaction to a kinetically controlled reaction by choosing quenchers of different reduction potential or electron affinity. The reduction potential of anthracene is -1.96 V,⁶⁸ compared to -0.81 V for BPEA.⁶⁹ The reduction potential is -0.30 V for CBr₄ and, for comparison, -2.08 V for C₂H₅Br.³² The closer the reduction potentials of the energy donor and acceptor, the slower the reaction. The reduction potentials for anthracene and CBr₄ are very different, and the energy transfer reaction between them is diffusion controlled. Conversely, anthracene and C₂H₅Br have similar reduction potentials and, subsequently, react at a rate several orders of magnitude below diffusion control (i.e., it is a kinetically controlled reaction—one with an activation barrier). The BPEA/CBr₄ reaction falls between these two extremes. Another measure of the donor's willingness to transfer energy to the quencher is the donor's electronic energy. The electronic energy of anthracene in its first excited state is 3.3 eV³² while it is 2.66 eV for BPEA,⁶⁹ so the driving force is greater for the anthracene/CBr₄ reaction than for the BPEA/CBr₄ reaction. Thus, the reaction of BPEA with CBr₄ may not be diffusion controlled. The local composition enhancement obtained by Sun et al.²⁷ may be from solvation

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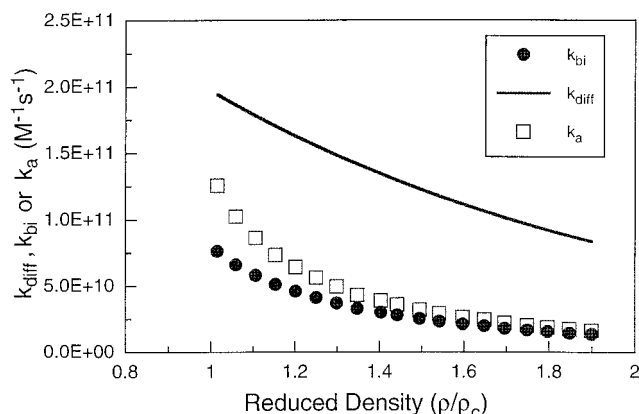
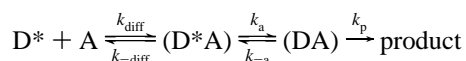


Figure 16. Different contributions to the observed bimolecular rate constants, k_{bi} , for the reaction of BPEA with CBr_4 in CO_2 at 35 °C. The experimentally measured bimolecular rate constants, k_{bi} , are the solid circles.²⁷ The solid line is the diffusion controlled limit predicted from the SE/D equation. The squares are the rate constants for the activated step of the reaction, determined from the measured k_{bi} and the SE/D predictions of the diffusion control limit using eq 4 (see text).

effects on the intrinsic activation process of a kinetically controlled reaction step.

The following general reaction scheme for quenching reactions^{70–72} involves the donor and acceptor diffusing together, followed by an activated step.



If $k_{-a} \ll k_a$ and $k_{diff} = k_{-diff}$, the following relationship is obtained.⁷⁰

$$\frac{1}{k_{bi}} = \frac{1}{k_a} + \frac{1}{k_{diff}} \quad (4)$$

Thus, a measured bimolecular rate constant for fluorescence quenching can contain both diffusional and activated contributions. If there is no activation barrier then $k_a \rightarrow \infty$ and $k_{bi} = k_{diff}$. This is the case for the reactions of anthracene/ CBr_4 and 1,2-BA/ CBr_4 reported above. If there is a large activation barrier, which would make k_a substantially less than k_{diff} , then $k_{bi} \rightarrow k_a$. This is the case for the anthracene/ C_2H_5Br reaction reported above. Also, one can have the case where k_a and k_{diff} are comparable, and we believe that this may be the situation for the BPEA/ CBr_4 reaction. Since Bunker and Sun reported experimental measurements of the bimolecular rate constant (k_{bi}) for the BPEA/ CBr_4 reaction in CO_2 and SE/D gives estimates of k_{diff} , we can use eq 4 to get k_a and examine the relative magnitude of each of these rate constants. This is what is shown as a function of reduced density in Figure 16. Clearly, the measured rate constants, k_{bi} , are well below the diffusion controlled limit, k_{diff} . The rate constant for the activated portion of the reaction, k_a , does appear to increase at lower pressures, and it is possible that this increase in the activated reaction rate may actually be due to an increase in the local concentration of the CBr_4 around the BPEA, as is discussed in much more detail for the anthracene/ C_2H_5Br reaction in the next section.

Our results presented above for the diffusion controlled reactions of anthracene/ CBr_4 and 1,2-BA/ CBr_4 in supercritical CO_2 do not show any indications of being enhanced by increased local compositions, as had been suggested by Bunker and Sun²⁷

for the BPEA/ CBr_4 reaction. Since the BPEA/ CBr_4 reaction is noticeably below diffusion control, we believe that the interpretation presented here of both diffusional and activated contributions to the measured rate may be an alternative explanation of the Bunker and Sun²⁷ data. Also, this analysis demonstrates that there may be mechanistic explanations for deviations from the expected diffusion control limit that may be more apparent in supercritical fluids than in liquid solutions.

4. The Reaction of Anthracene with C_2H_5Br . The experimental results showed that there is a dramatic pressure effect on the reaction of anthracene with C_2H_5Br in supercritical CO_2 . There are several factors that could contribute to this trend, such as changes in the bulk solvation properties as reflected in changes in the solvent refractive index and dielectric constant, the thermodynamic pressure effect on the rate constant due to general molecular interactions, the formation of a highly polar transition state, the local density augmentation, and the local composition enhancement of the quencher around the anthracene.

To analyze the possible effect of changing bulk solvent properties on the rate constant, as reflected in the solvent refractive index and dielectric constant, we make a simple comparison of the rate constants in CO_2 , hexane, cyclohexane, and acetonitrile, as shown in Table 2. Although the dielectric constants and refractive indices are significantly different in the three liquid solvents and in CO_2 at high pressure, the bimolecular rate constants for this quenching reaction are very similar, indicating that this reaction is not affected much by these properties. So, we can reasonably assume that the small change of the refractive index and dielectric constant in CO_2 from low pressure to high pressure cannot account for any significant change in the bimolecular rate constant.

The thermodynamic pressure effect due to general molecular interactions can be estimated from transition state theory and the Peng–Robinson equation of state.^{15,26} It predicts that the bimolecular rate constants should increase very slightly with increasing pressure, which is opposite to the trend observed for the experimental bimolecular rate constants based on bulk concentrations. The partial molar volumes are negative. Like the C_2H_5Br , the transition state would most likely be polar since the encounter complex does have charge-transfer characteristics, as discussed in the section on the Mechanism of Fluorescence Quenching. If the transition state were ionic or an ion pair (as would occur in actual electron transfer), the transition state complex would have an even larger negative partial molar volume. The evidence given in the mechanism section indicates that this reaction does not involve electron transfer, and this is corroborated by the fact that the rate of this reaction is the same in nonpolar hexane and highly polar acetonitrile. In fact, the complete insensitivity of this reaction to various solvents suggests that the transition state and the reactants are equally solvated so that the pressure effect on this reaction should, in fact, be very small. Nonetheless, a hypothetical ionic or ion pair transition state would result in a more negative activation volume than that predicted from the Peng–Robinson equation, and this would make the rate constants have an even greater increase with increasing pressure. Thus the thermodynamic pressure effect on the rate constant cannot explain the observed trends of the rate constants based on bulk concentrations. Local solvent density augmentation would make the solvent environment more like that at higher pressures, as well as increase the local concentration of the quencher around the anthracene by as much as a factor of 1.8, as shown in Figure 12. A solvent environment more like that at higher pressures would serve to depress the reaction rate since the rate constants are lower at

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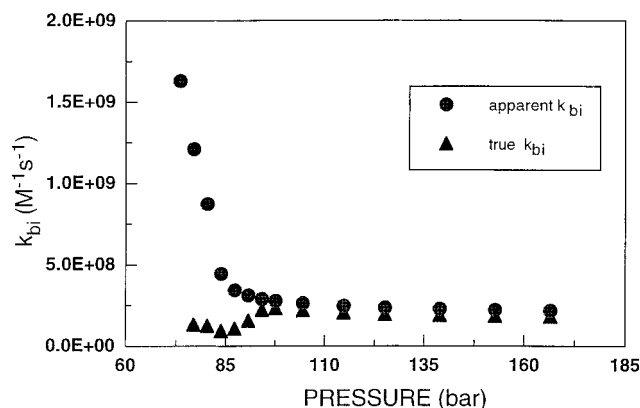


Figure 17. Bimolecular rate constants plotted vs pressure for the quenching reaction of anthracene with C_2H_5Br at 35 °C: (●) rate constants based on the bulk concentrations of the reactants; (▲) rate constants based on the local concentration of the C_2H_5Br around the anthracene (see text).

the higher pressures. The 1.8-fold increase in the local concentration of quencher around the anthracene due to local density enhancement would serve to increase the apparent rate at lower pressures but cannot account for the full 7.5-fold increase observed.

There is strong theoretical⁹ and experimental evidence^{1,12–15,23,26,29} that the local compositions of cosolvents around dilute solute molecules in supercritical fluids are greater than the bulk values. Moreover, we have used solvatochromic shift data and shown in Figure 13 that the local composition of C_2H_5Br around anthracene in CO_2 increases to about ten times the bulk value at pressures around 75 bar. Previously, the apparently dramatic pressure effects on the reaction rates of several kinetically controlled reactions have been attributed to local composition enhancement of the reacting cosolvents around the reacting solute in supercritical fluids.^{14,15,23,26,28} On the basis of the above analysis, we suggest that, for the quenching reaction of anthracene by C_2H_5Br , local composition enhancement of C_2H_5Br around anthracene is an important factor in the dramatic pressure effect observed experimentally. To show this more clearly, we have recalculated the bimolecular rate constants for the reaction of anthracene with C_2H_5Br in CO_2 , using local concentrations, as indicated by the values in Figure 13, instead of the bulk values (i.e., rate = $k_{bi}^{local}[\text{anthracene}][C_2H_5Br]^{local}$ instead of rate = $k_{bi}^{bulk}[\text{anthracene}][C_2H_5Br]^{bulk}$). These rate constants, k_{bi}^{local} , are shown in Figure 17 and are relatively insensitive to pressure. This is in agreement with the liquid data that indicate that this reaction is completely solvent insensitive.

In conclusion, the quenching reaction of anthracene by C_2H_5Br is kinetically controlled in both liquids and supercritical CO_2 . The quenching rate is almost an order of magnitude higher in low-density supercritical CO_2 than it is in a variety of liquids or in high-density CO_2 , and this can be explained by the increased local concentration of the C_2H_5Br around the anthracene.

Conclusions

Steady-state and time-resolved fluorescence has been used to study three different quenching reactions in supercritical CO_2 . Experimental results show that the rate constants for the reactions of anthracene with CBr_4 and 1,2-benzanthracene with CBr_4 decreased with increasing pressure, and the trend closely followed the diffusion control limit under all conditions studied. There is no indication of the enhanced molecular interactions between anthracene or 1,2-BA and CBr_4 molecules affecting these diffusion controlled reactions in supercritical CO_2 .

The rate constant of the kinetically controlled quenching reaction between anthracene and C_2H_5Br decreases dramatically with increasing pressure in CO_2 at 35 °C when bulk concentrations of the reactants are used. Since this reaction is relatively solvent insensitive and solvatochromic shift measurements indicate preferential solvation of anthracene by C_2H_5Br at lower pressures, the apparent pressure effect on the reaction rate has been attributed mainly to the increased local concentration of the quencher molecules around the dilute anthracene.

Thus, by studying both diffusion controlled and kinetically controlled quenching reactions, we have shown two distinct solvation effects on energy transfer reactions in supercritical CO_2 . Moreover, we have suggested how supercritical fluids may affect reactions where the diffusion and activated rate constants are comparable in magnitude. Since diffusion is faster in supercritical fluids than in liquids, the activated portion of these reactions is more apparent, providing the opportunity to better investigate the energetics and mechanisms of these energy transfer reactions.

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