J. Phys. Chem. A **1999,** *103,* 6591−6598

Laser Flash Photolysis Investigation of the Triplet−Triplet Annihilation of Anthracene in Supercritical Water

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Received: March 30, 1999; In Final Form: July 1, 1999

The effects of the supercritical water environment on the triplet−triplet annihilation of anthracene, a simple, well-characterized reaction that is known to be diffusion controlled in normal liquids, was investigated at temperatures from 375 to 450 °C and pressures from 50 to 350 bar. The reaction was found to occur just slightly above the diffusion-control limit, which was estimated from the Stokes−Einstein based Debye equation, when spin statistical factors are taken into account. This is in qualitative agreement with previous studies of diffusion-controlled reactions in lower temperature supercritical fluids (SCFs). Thus, the supercritical water environment is similar to that of lower temperature SCFs for diffusion-controlled reactions of nonpolar hydrocarbon species. There is no evidence of solvent clustering and any influence of solute/solute interactions is small. Finally, the mechanism of the reaction appears to be the same as in nonpolar liquid solvents.

Introduction

A fundamental issue in understanding the influence of supercritical fluids (SCFs) on reactions has been the effect on reactions that would normally occur at the diffusion-controlled limit in liquids or gases. Numerous experimental, theoretical, and simulation studies have been conducted to address this issue.[1−25] Much of the work points to the conclusion that reactions that would normally occur at the diffusion-control limit in liquids also occur at the normal diffusion-control limit in SCFs. For instance, in studies of the triplet−triplet annihilation (TTA) of benzophenone and benzyl radical recombination in supercritical (SC) ethane, fluoroform, CO_2, and a CO_2−acetonitrile mixture, we found the experimental rate constants to follow those predicted from the Stokes−Einstein based Debye equation (SE/D) within the ability of the Stokes−Einstein equation to represent diffusivities in SCFs (about ±40−50%).[11,12] This was corroborated with fluorescence quenching studies of anthracene and 1,2-benzanthracene with CBr_4 in SC CO_2.[13] Of course, the rates measured are about an order of magnitude greater in SCFs than in liquids because bulk viscosities of SCFs are lower than those in liquids. Moreover, the viscosity is a function of density, so diffusion-controlled rate constants are greater at lower pressures where the bulk viscosities are lower. Diffusion-controlled rate constants and mutual diffusion coefficients[26,27] tend to track bulk thermodynamic properties even though there is significant evidence that local densities and local compositions around dissolved solutes in supercritical fluid solutions can be much higher than bulk values.[2,10,28−40]

The goal of the present study is to determine whether the conclusions about diffusion-controlled reactions in lower temperature supercritical fluids also apply to reactions in supercritical water (SCW). The critical point of water is 374 °C and 221 bar, and at these conditions the dielectric constant has been greatly reduced.[41] There have been extensive investigations of reactions in SCW, many of which have been targeted at the efficient destruction of hazardous organic compounds by oxidation in the homogeneous supercritical water medium.[41,42] To our knowledge, this is the first investigation in SCW of a single, relatively simple, nonionic reaction that would normally be diffusion-controlled in liquids.

We present results for the triplet−triplet annihilation of anthracene in supercritical water at temperatures between 375 and 450 °C and pressures of 50−350 bar. This reaction has been well-studied in liquids[43,44] and, as expected, was found to be second order in the concentration of anthracene triplet. Saltiel and co-workers studied the reaction in toluene and benzene between 208 and 323 K at concentrations on the order of 10^{-5} M. The TTA rates ($2k_{TTA}$) were found to be linear versus T/η (η = viscosity), which indicates a diffusion-controlled process.

In particular, we present measurements of the observed rate constant, k_{obs}, which is related to the true bimolecular rate constant, $2k_{TTA}$, by $k_{obs} = (2\,k_{TTA}/\epsilon b)$, where ϵ is the extinction coefficient of anthracene triplet and b is the path length. We also present measurements of the density dependence of the extinction coefficient of the anthracene triplet, ϵ, to determine the bimolecular rate constants, $2k_{TTA}$, at various temperatures and pressures in the supercritical region. Experimentally determining the extinction coefficients was important because various spectroscopic studies of solutes in SCFs have found that the absorption extinction coefficient at the maximum in absorbance can change significantly with changes in temperature and pressure.[12,13,45] In addition, in this study, the triplet absorbance was detected at a fixed wavelength, 408 nm. Since the wavelength of maximum absorbance can shift with temperature and pressure,[37,38] this could result in a significant change in the extinction coefficient at a particular wavelength.

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10.1021/jp991097i CCC: $18.00

In SCW, we find the reaction rate constants for the triplet−triplet annihilation of anthracene to be essentially at the expected diffusion-control limit. This corroborates results for similar reactions that have been measured in lower temperature supercritical fluids such as carbon dioxide, ethane, and fluoroform.[12,13] There is no evidence of enhanced solute/solvent interactions, and any influence of enhanced solute/solute interactions is small. In other words, like in lower temperature SCFs, diffusion-controlled reactions of organic compounds in SCW occur as expected, and the rates can be easily predicted from the bulk solvent viscosity.

Experimental Section

Materials. Anthracene (Aldrich, zone refined 99+%) was used as received. Water was filtered to 16 $\mathrm{M\Omega}$ using a Millipore Reagent Water System at the Notre Dame Radiation Laboratory. Cyclohexane (Baker, ACS Reagent grade) and methylene chloride (Fisher, Spectranalyzed) were used as received.

Apparatus. Two different high-pressure, high-temperature optical cells were used for these experiments. Both were modeled after a functioning version used by Tester and co-workers.[46−48] The main body of the first cell, which was used for the measurements of the observed rate constants for the TTA of anthracene, was a 2.5 in. cube of Inconel 625, a high-nickel alloy chosen for corrosion resistance. The optical path length was 0.5 cm. The main body of the second cell, which was used for confirmation of the kinetics and the measurements of the extinction coefficient of anthracene triplet in SCW, was a 4 in. cube of Inconel 718. This material was chosen since it is corrosion resistant and has greater high-temperature strength than Inconel 625. After approximately 50 temperature cycles of the smaller cell, the window plugs "bowed," causing leakage and window breakage, prompting the use of the larger cell. The type of windows, sealing mechanism, temperature control, and pressure measurements on the two cells were the same. The details for the larger cell are given below.

Ports were machined into the block to accept three window closure assemblies, two pressure ports, and a thermocouple adapter. The volume of the large water cell was determined to be 7.0 mL, and the path length of the cell was verified to be 1.00 in. The top and bottom pressure ports were equipped with $^{1}/_{8}$" stainless steel valves to facilitate the exchange of liquid solutions. These ports were sealed into the cell with a jam screw and disposable copper gaskets (0.846" o.d. × 0.648" i.d. × 0.050" thick). Gasket seats machined into the cell body positioned the gaskets about the port such that, when the jam screws were tightened, the compression was uniform.

The window closure is a two-part assembly: a window flange and a window cap. The window flange is necessary to seal the combined device into the cell body with the disposable copper gaskets, while the window cap threads onto the window flange and contains the sapphire window ($^{3}/_{8}$" diameter × 3/16" thick). Sapphire was chosen for its high-temperature strength and durability, as well as the fact that it has an approximately 80% transmittance for all wavelengths of interest (260−700 nm). The actual window seal is made with the aid of an Inconel 718 spring washer (0.344" o.d. × 0.168" i.d. × 0.025" thick) available from Solon Manufacturing and a copper foil gasket (0.378" o.d. × 0.190" i.d.). The spring washer was placed on the water side of the window and the copper foil helps to seal the window against the polished metal face of the window flange. Tightening the window assembly until the spring washer is fully compressed made reliable window seals.

The cell was connected with 1/16" o.d. tubing to a High-Pressure Equipment Co. (HIP) pressure generator (HIP 87-6-5 or HIP 50-6-15) or an ISCO syringe pump (ISCO 260D) and a Heise pressure gauge (PM1H) with a pressure transducer (PPM2) rated to 7500 psi. Isolation valves were positioned at the pressure gauge and near the cell. These valves allowed the cell and all lines to be evacuated before filling with water or cyclohexane for an experiment.

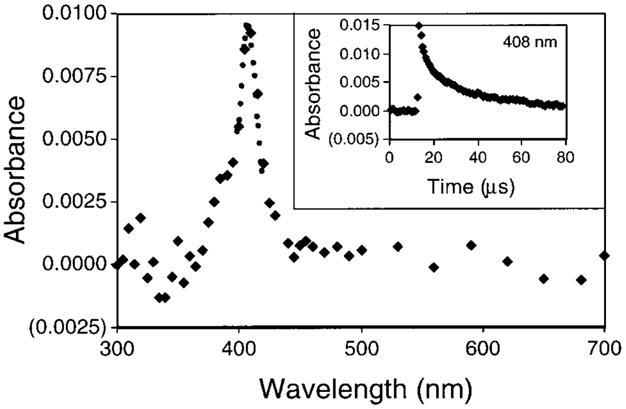

Figure 1. Absorbance spectrum of triplet anthracene in SCW at 400 °C and 267 bar (diamonds) and at 450 °C and 206 bar (circles). Inset shows a typical decay trace at 408 nm.

An Omega temperature controller, model MCS 6081-K, equipped with a type K inconel sheathed thermocouple (Omega KMTIN-062U-6) and two Watlow Firerod cartridge heaters, was used to heat the cell at a rate of approximately 2−2.5 °C per minute. A box composed of Zircar type ECO-1200A silica alumina insulation was used to cover the cell to a thickness of 2 in. to prevent excessive heat losses. To add a measure of safety, the cell, pressure gauge, and temperature controller, when set up at the laser flash photolysis (LFP) apparatus, were enclosed in a $^{1}/_{2}$" thick Plexiglas box to provide protection from any leaks of high-temperature, high-pressure fluid.

The LFP apparatus has been described in detail elsewhere.[49] Briefly, these experiments were performed using laser excitation perpendicular to a pulsed 1000 W xenon lamp monitoring source. Laser excitation was provided by a Quanta Ray DCR-1 Nd:YAG (355 nm; ~10 mJ; pulse width ~6 ns) laser system. Transient absorption signals were digitized with a Tektronix 7912 AD digitizer. For experimental control and computer analysis, a VAX-11/780 was used.

Method. For SCW experiments, a known amount of solute (anthracene) was added to methylene chloride and a known quantity of this solution was introduced into the cell through the top port. Typically, about 100 μL of a 0.01 M solution was used; i.e., enough to yield an optical density at experimental conditions of between 0.2 and 0.8 at 355 nm. The cell was evacuated with a vacuum pump to remove all methylene chloride and any air present. Then, an appropriate amount, determined from the equation of Hill,[50] of filtered, deionized, deoxygenated water was added from the ISCO syringe pump or the HIP hand pump to generate pressures of 275−350 bar when heated to reaction temperatures. The concentration of the anthracene in SCW was approximately millimolar (1.8×10^{-5} to 4.7×10^{-6} mole fraction). Experiments were conducted at 375, 400, 420, and 450 °C and pressures between 50 and 350 bar.

Laser excitation at 355 nm generates the anthracene excited state singlet, which undergoes intersystem crossing to the triplet (^{3}anthracene).[44,51] Two triplets undergo a bimolecular encounter. A typical absorbance spectrum of the anthracene triplet in SCW is shown in Figure 1. The second order decay of the triplet signal was monitored at 408 nm, where the triplet exhibits a maximum in SCW; an example is shown in the insert in Figure 1. The observed rate constants for the TTA are obtained from these decays, at all the temperatures and pressures of interest. The maximum absorbance of the triplet, which is needed to determine the triplet extinction coefficient, was also measured in SCW at 408 nm. The absorption maximum shifted slightly from high-density to low-density SCW. The primary spectrum in Figure 1 (the diamonds) is at 400 °C and 267 bar, which corresponds to a density of 0.220 kg/L. Superimposed on this spectrum in the region of maximum absorbance is the absorbance of anthracene triplet at 450 °C and 206 bar (circles), which corresponds to a density of just 0.084 kg/L. At the lower density, the absorption maximum has shifted about 1.5 to 2 nm. Since the peak is sharp, this slight shift may account for some of the apparent decrease in the extinction coefficient at 408 nm, as discussed below. All SCW experiments were performed at constant mole fraction from high to low pressure by release of homogeneous solution.

In addition to the triplet maximum absorbance, determination of the triplet extinction coefficient in SCW required measurements of the absorbance of the ground state anthracene solutions in SCW. Since the large water cell was too large to fit into a conventional UV−vis spectrometer, the LFP apparatus was used as a normal absorbance spectrophotometer by attaching a voltmeter to the photomultiplier tube and measuring the voltage (or intensity, I). The ground-state absorbance was determined at 355 nm, the wavelength of the laser excitation and a maximum in the absorbance of ground-state anthracene, at each temperature and pressure of interest. The absorbance (A) is the intensity of light passing through a sample (I) and through a reference solution (I_0), where $A = \ln(I_0/I)$.

The extinction coefficient of ^{3}anthracene in SCW was determined relative to a liquid solution in which the ^{3}anthracene extinction coefficient was known. This was done with matched SCW and liquid experiments, in which the laser excitation system was identical. After an SCW experiment, the remaining solution was vented and the cell allowed to cool overnight; neither the cell and its components nor the laser setup were altered or moved in any way. When the cell was cool, it was rinsed several times to remove any solute that may have fallen out of solution in the cell when it was depressurized.

The cell was then rinsed with cyclohexane and evacuated, and an appropriate concentration of anthracene−cyclohexane solution was introduced to the cell. The triplet and ground-state absorbances were recorded as described above, but now at room temperature and pressure in the liquid solvent cyclohexane. Successive experiments were performed using solutions of increasing solute concentration. The mole fractions of anthracene in cyclohexane ranged from 1.6×10^{-5} to 3.3×10^{-5}. These concentrations were chosen to match the anthracene ground state absorbances in SCW at 355 nm, and the reason for this is described below. After all liquid experiments were performed, the cell was taken apart and carefully cleaned in an effort to remove any residual solute or other impurities.

Theory

Laser excitation of an anthracene solution at 355 nm generates an anthracene excited state singlet which then undergoes intersystem crossing (ISC) to the triplet state (^{3}anthracene).[44,51] Two triplets undergo a bimolecular encounter, as shown in eq 1. This is a simplified version of the full scheme that is described in the discussion section. Exceptional care was taken to remove oxygen from the system, since even small quantities of reactive impurities could result in mixed order kinetics. The decays were monitored at 408 nm, where ^{3}anthracene has a strong absorbance. As mentioned previously, Figure 1 shows the transient absorption spectrum of ^{3}anthracene in SCW at 400 °C and 267 bar.

$$\begin{gathered}\text{anthracene} \xrightarrow{h\nu} {}^{*1}\text{anthracene} \xrightarrow{\text{ISC}} {}^{3}\text{anthracene} \\ {}^{3}\text{anthracene} + {}^{3}\text{anthracene} \xrightarrow{k_{\text{TTA}}} \text{deactivation}\end{gathered} \tag{1}$$

Because the reaction proceeds in a bimolecular fashion, the TTA reaction of anthracene is known to be second order, giving a rate law as follows:

$$\text{rate} = \frac{-\mathrm{d}C_{(^3\mathrm{A})}}{\mathrm{d}t} = 2k_{\mathrm{TTA}}{C_{(^3\mathrm{A})}}^2 \tag{2}$$

By integrating the above equation, it can be seen that the concentration of ^{3}anthracene is a function of the bimolecular rate constant ($2k_{\mathrm{TTA}}$),

$$\Delta\frac{1}{C_{(^3\mathrm{A})}} = 2k_{\mathrm{TTA}}\Delta t \tag{3}$$

Substituting the Beer−Lambert law ($A = \epsilon bC$) into this rate law, one is left with

$$\Delta\frac{1}{A} = \left[\frac{2k_{\mathrm{TTA}}}{\epsilon b}\right]\Delta t = k_{\mathrm{obs}}\Delta t \tag{4}$$

where A is the absorbance, ϵ is the extinction coefficient in M^{-1} cm^{-1}, b is the path length in cm, Δt is the time after the laser pulse excitation that forms the anthracene triplet, and $2k_{\mathrm{TTA}}$ is the bimolecular rate constant in M^{-1} s^{-1}. The computer interface measured absorbance as a function of time and plotted the reciprocal, giving k_{obs} in s^{-1} as the slope of the line. To determine the actual bimolecular rate constant, $2k_{\mathrm{TTA}}$, the unknown ϵ, the extinction coefficient of ^{3}anthracene in SCW, had to be determined. All other variables in eq 4 were known.

The extinction coefficients of ^{3}anthracene in SCW as a function of density (i.e., temperature and pressure) were determined relative to a liquid solution at room temperature where the value of ϵ is known. This was done with experiments that matched the identical physical apparatus and operating parameters for the SCW and liquid cyclohexane experiments. The basic assumption is that Beer's law, $A = \epsilon bC$, holds for both the ground state anthracene and triplet anthracene in both a liquid solvent and in SCW. Furthermore, it is assumed that for a given laser and optical configuration the same fraction of ground state molecules which absorb will be promoted to the triplet state (i.e., that the concentration of triplet is proportional to the absorbance of the ground state molecules). These assumptions yield

$$\frac{A_{\mathrm{W}}}{A_{\mathrm{L}}} = \frac{\epsilon_{\mathrm{W}} b_{\mathrm{W}} Y A_{\mathrm{w}}}{\epsilon_{\mathrm{L}} b_{\mathrm{L}} Y A_{\mathrm{l}}} \tag{5}$$

where A_{w} and A_{W} are the absorbance of the ground state and the triplet, respectively, in SCW, A_{l} and A_{L} are the absorbance of the ground state and the triplet, respectively, in liquid cyclohexane, and ϵ_{W} and ϵ_{L} are the extinction coefficients of the triplet in SCW and cyclohexane, respectively. Since the SCW and cyclohexane experiments were both done in the high-pressure optical cell, the path lengths, b_{W} and b_{L}, are equal. Y is the fraction of absorbing ground-state anthracene molecules that are excited to the triplet state in a particular system configuration. Since the laser configuration and optical cell position were identical for both SCW and cyclohexane experiments and yielded the same intensity of light from the xenon lamp, the values of Y cancel, as well. Finally, the cyclohexane solution is chosen so that its ground-state absorbance matches that in SCW so $A_w = A_l$. This yields

$$\epsilon_W = \frac{A_W}{A_L}\epsilon_L \qquad (6)$$

Thus, by measuring the triplet absorbance in liquid cyclohexane and in SCW at various temperatures and pressures, we were able to determine the extinction coefficient of ^{3}anthracene in SCW as a function of density. The triplet absorbances were measured in both cyclohexane and in SCW at 408 nm. This is where the triplet exhibits an absorption maximum in SCW and where all the decay kinetics were measured. Excellent decays were observed in liquid cyclohexane at this wavelength even though it is not at the absorption maximum in the liquid. In liquid cyclohexane, the triplet absorbance maximum is in the range of 422.5 to 425 nm, and the extinction coefficient is reported at this maximum in the literature.[52,53] The ground state absorbances were matched at 355 nm, which is the excitation laser wavelength and a maximum in the ground state absorbance of anthracene. Absorbances were determined as described above, where I_0 was the intensity of light passing through pure SCW or pure cyclohexane (no anthracene present). In SCW, I_0 was found to be relatively insensitive to temperature or pressure over the ranges investigated. The generally accepted value of the extinction coefficient of the triplet anthracene in cyclohexane at room temperature at the absorption maximum is 64 700 M^{-1} cm^{-1}.[52,53] From our measurements of the anthracene triplet spectrum, we determined that the triplet absorbance at 408 nm in cyclohexane is a factor of 5.6 less than the value at the absorption maximum, so we used 11 550 M^{-1} cm^{-1} as the extinction coefficient of the triplet in cyclohexane at 408 nm. It should be pointed out that there is significant variability in the values of ϵ_{max} in liquids reported in the literature. For example, in cyclohexane, the reported values range from 19 800 to 85 700 M^{-1} cm^{-1}.[52,53] Although we are using the generally accepted value of 64 700 M^{-1} cm^{-1} for ϵ_{max} (and, subsequently, 11 250 M^{-1} cm^{-1} for $\epsilon_{408\ nm}$), we recognize the uncertainty of ϵ_L as an additional source of uncertainty in the final values of $2k_{TTA}$ presented below.

Results and Discussion

Observed rate constants, $k_{obs} = (2k_{TTA}/\epsilon b)$, for the triplet−triplet annihilation of anthracene in SCW were measured along four isotherms, 375, 400, 420, and 450 °C, at pressures from 50 to 350 bar. These values were obtained from second-order fits to the decay of the absorbance of ^{3}Anthracene at 408 nm as a function of time. The decays were second order, which was ascertained by fitting the data to combined first and second order kinetics and determining that the first order contribution was less than 5−10%.[11,54] This confirmed that there were no impurities or contaminants, like oxygen, present in the system. The k_{obs} at the four temperatures are shown in Figure 2 as a function of pressure. The error in the values of k_{obs} is approximately ±10%. The observed rate constants increase with decreasing pressure, which is what one would anticipate for a diffusion-controlled reaction since the solvent viscosity is lower at lower pressures. The observed rate constants at 450 °C are slightly below those at 420 °C at a particular pressure, which is contradictory to what one might expect for a diffusion-controlled reaction. However, when compared at constant density, which is perhaps the more appropriate variable, the difference between the two isotherms is quite small. Moreover, the extinction coefficient of the ^{3}anthracene is not expected to be a constant over the range of temperatures and pressures investigated.

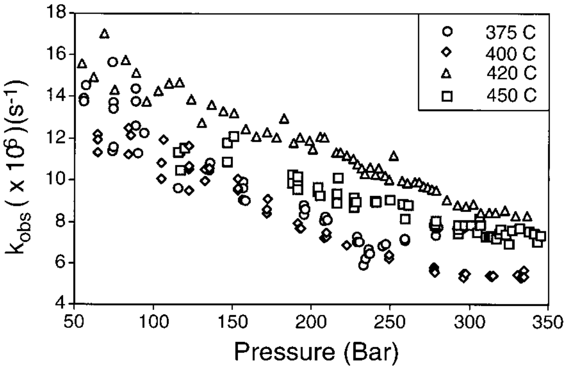

Figure 2. k_{obs} as a function of pressure for triplet anthracene in SCW at 375, 400, 420, and 450 °C.

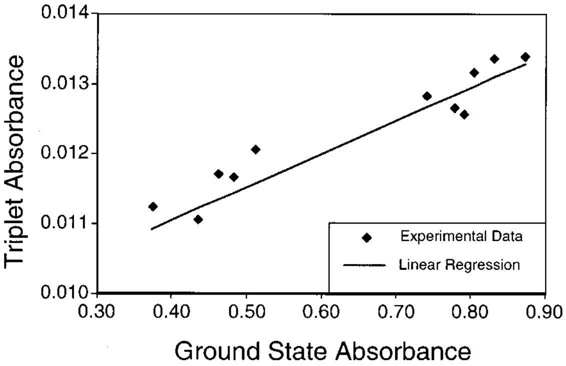

Figure 3. Plot of the absorbance of triplet anthracene as a function of the absorbance of ground state anthracene in liquid cyclohexane at room temperature.

Obtaining the bimolecular rate constant, $2k_{TTA}$, from k_{obs} required the extinction coefficients of ^{3}anthracene in SCW at various temperatures and pressures. We obtained these values for ^{3}anthracene in SCW at temperatures of 375, 420, and 450 °C and pressures between 180 and 290 bar. The matching method described above, where the ground state absorbance of the liquid solution was made to match that of the SCW solution, was used. Unfortunately, it was difficult to exactly match the ground state absorbances of the cyclohexane and the SCW solutions. Because of this, we made liquid solutions with a variety of ground state absorbances, bracketing the range of the ground state absorbances of the SCW solutions. A plot, shown in Figure 3, was constructed of ^{3}anthracene absorbance as a function of ground state absorbance for the liquid solutions and a line was fit to the data. From this fit, it was possible to determine the triplet absorbance for a liquid solution with a ground state absorbance the same as the absorbance of a SCW solution. With this slight modification to the method described above, it was possible to obtain values for the extinction coefficient (ϵ) of ^{3}anthracene in SCW.

We found that the ^{3}anthracene extinction coefficients (at 408 nm) were primarily a function of density. This is most easily seen from a plot of all the ϵ values as a function of density, as shown in Figure 4. The data for the various isotherms are identified to show that ϵ is only a weak function of temperature. The lack of data at intermediate densities reflects the difficulties associated with operation near the critical density of 0.31 kg/L.

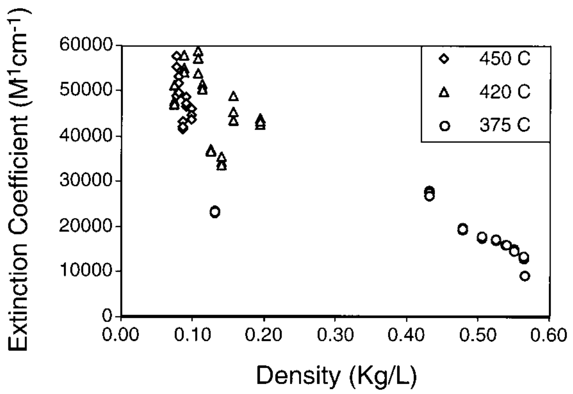

Figure 4. Extinction coefficient of triplet anthracene in SCW at 408 nm as a function of density.

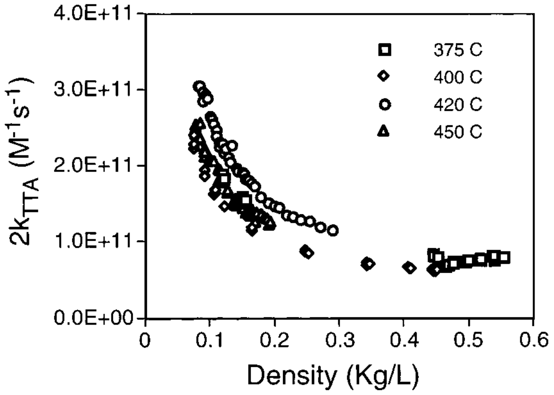

Figure 5. Experimental bimolecular rate constants, $2k_{\mathrm{TTA}}$, for anthracene triplet−triplet annihilation in SCW at 375, 400, 420, and 450 °C.

The extinction coefficients increase substantially, by about 500−600%, with decreasing density. These values for $\epsilon_{\max}$ are the same order of magnitude as those in liquid solvents (64 700 $\mathrm{M}^{-1}\mathrm{cm}^{-1}$ at $\epsilon_{\max}$ in cyclohexane). To determine the value of ϵ at any particular density, a curve was fit to the data, as shown in eq 7, where ϵ is in $\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ and ρ is the density of SCF in kg/L.

$$\epsilon = 11550(1.331\rho^{-0.485}) \tag{7}$$

From the values obtained from eq 7, it was possible to determine values for the bimolecular rate constants using eq 4 and the experimental values of k_{obs} shown in Figure 2. The bimolecular rate constants, $2k_{\mathrm{TTA}}$, obtained from these data at all four temperatures are shown in Figure 5. The densities shown in Figure 5 correspond to the pressure range from 180 to 290 bar, since this is the range in which the extinction coefficient measurements were obtained. At a given temperature, increasing density corresponds to increasing pressure. Along all the isotherms, the bimolecular rate constants increase with decreasing density, as one would expect for a diffusion-controlled reaction.

A more quantitative comparison between the experimental bimolecular rate constants and what one would expect for diffusion-controlled reactivity can be made with the Stokes−Einstein based Debye (SE/D) equation:

$$k_{\mathrm{diff}} = \frac{8RT}{3\eta} \tag{8}$$

where the viscosity, η, was taken from the literature[55] using densities taken from the equation of Hill.[50] For a self-annihilation reaction, one actually measures $2k_{\mathrm{TTA}}$ since two molecules disappear for every reaction. Moreover, for TTA, a spin statistical factor must be used to account for all possible deactivation pathways, according to $2k_{\mathrm{TTA}} = \sigma k_{\mathrm{diff}}$, where σ is the spin statistical factor.[44] This factor accounts for the fact that not all triplets decay immediately to the ground state upon collision, due to spin selection rules. The full deactivation scheme for anthracene triplet−triplet annihilation in liquid benzene and toluene has been reported by Saltiel and coworkers,[44] and is shown above. This results in a spin statistical factor of 0.27 ± 0.02.[44] The scheme includes rapid internal conversion of doubly excited triplet pairs to fully dissociative triplet excimers and dissociation of quintet pair states back to triplets.[44] Since spin statistical factors have been shown to be fairly independent of temperature in various cases,[56,57] and since values have been reported between 0.27 and 0.30,[58] the value of 0.28 is used for the current work.

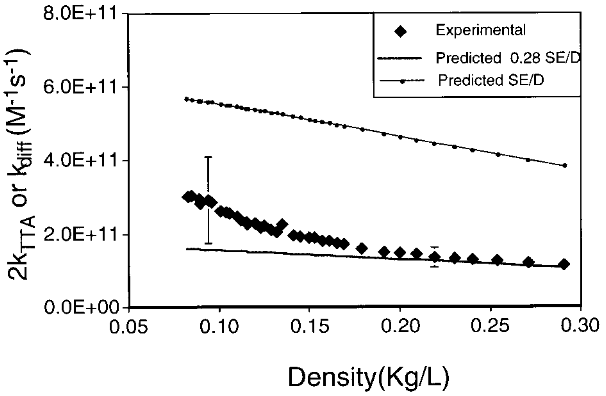

Figure 6. Experimental $2k_{\mathrm{TTA}}$ and k_{diff} predicted by 0.28 SE/D and SE/D at 420 °C as a function of density.

SCHEME 1: Mechanism for Anthracene Triplet−Triplet Annihilation[44]

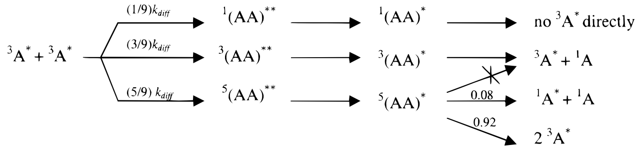

Figure 6 shows $2k_{\mathrm{TTA}}$ as a function of density along just one of the isotherms, 420 °C, as well as the k_{diff} predicted by the SE/D equation, with and without the spin statistical factor taken into account. This isotherm is typical of all isotherms. The uncertainty in the measurements is substantial, as seen from the error bars included with the data. At higher densities, the uncertainty is approximately 20%; at lower densities it is approximately 40%. Most of the experimental error can be traced to the measurement of the extinction coefficient. Specifically, the experimental uncertainty in I_0 for the triplet in SCW is accentuated when the triplet absorbance is small. This occurs at low pressure (i.e., density) because the experiments were performed at constant mole fraction. Every reasonable effort was taken to minimize these experimental uncertainties, which are a particular challenge for high-temperature, high-pressure optical experiments.

From Figure 6, it can be seen that the experimental data increase somewhat with decreasing density, as is expected for a diffusion-controlled reaction. However, the data fall slightly *above* the predicted 0.28 SE/D limit, especially at lower densities, but match it within experimental error. The error bars give the experimental uncertainty in our measurements but do not reflect the additional uncertainty in the value of the triplet extinction coefficient in liquid cyclohexane that was taken from the literature. Previous studies performed by Roberts and co-workers[12,13] of the triplet−triplet annihilation of benzophenone in SC carbon dioxide, ethane, fluoroform, and a carbon dioxide−acetonitrile mixture showed that the reaction occurred close to the expected diffusion-controlled limit, when the spin statistical factor was taken into account. Thus, these results for anthracene TTA in SCW are in qualitative agreement with the earlier study. However, in the studies of benzophenone TTA, the measured rate constants were about 50% *below* the predictions from the SE/D equation, even after the spin statistical factor was taken into account. That seemed reasonable since there are many cases in which the Stokes−Einstein equation slightly *over*predicts mutual diffusion coefficients in supercritical fluids.[26] Therefore, the fact that the measured values for anthracene TTA in SCW are somewhat above the SE/D equation predictions (with spin statistical factor) warrants some further discussion.

The first question is whether the Stokes−Einstein based Debye equation is an adequate estimate of diffusion-controlled rate constants in SCW. While supercritical water oxidation has been of interest for quite some time, investigations of transport properties in supercritical water are rather limited. The *self*-diffusion coefficient of compressed sub- and supercritical water has been reported by several researchers,[59−61] with the most extensive work in the supercritical region being reported by Lamb and co-workers,[61] who measured diffusion constants by NMR spin echo techniques. Mutual diffusion coefficients have been limited to iodide ions and hydroquinone in near-critical subcritical water[62] and inorganic nitrates in subcritical[63] and supercritical[64] water. Lamb and co-workers[61] reported that the Stokes−Einstein equation breaks down for the self-diffusion of SCW at densities below the critical density of about 0.31 kg/L. Goemans et al.[63] found that the Stokes−Einstein equation slightly underpredicted the diffusion coefficients of inorganic nitrates when liquid size parameters were used but found that it yielded predictions within 10% of the experimental values if the structure of the diffusion species could be estimated. It should also be noted that, in a concentrated (1 M) solution of $NaNO_3$ solution, Butenhoff et al.[64] observed a decrease in the diffusion coefficients near the phase separation pressure, frequently referred to as the “critical slowing down” of the diffusion coefficient. Molecular simulations and theoretical modeling of SCW and SCW solutions[65−81] shed some light on the necessity to estimate the structure of the diffusing species in order to obtain good results from the Stokes−Einstein equation. Balbuena et al.[80] shows that for ions in SCW the effective Stokes−Einstein radius is essentially constant over a relatively wide solvent density range and reflects a first solvation shell that is tightly coupled to the ion. Molecular simulations of pure water using either rigid or flexible simple point charge models reproduce self-diffusion coefficients within experimental error. Thus, although the measurements of diffusivities in SCW are limited, the work described above suggests that the Stokes−Einstein equation should prove a reasonable first estimate of diffusivity in SCW, as it does in lower temperature supercritical fluids. However, it should be emphasized that the temperatures and pressures studied here yield solution densities that are, in many cases, well below the critical density of water. At these conditions we would not expect the Stokes−Einstein equation to be very accurate. In the lower temperature studies,[7−9,11−13] reduced densities less than one were generally inaccessible due to solubility limitations.

Although there is uncertainty in the predictions of the diffusion-controlled rate constants in SCW from the SE/D equation, there does not seem to be any fundamental difference in the ability of the SE/D equation to estimate these rate constants in SCW compared to lower temperature SCFs. Thus, we are left with the observation that the measured rate constants are slightly above the SE/D equation estimates in SCW but slightly below the SE/D equation estimates in lower temperature SCFs. Although one cannot draw any firm conclusions from the small difference between the measurements of the rate of anthracene TTA in SCW and the SE/D equation estimates, it is possible that solute/solvent or solute/solute interactions might be affecting the reaction rates. These are discussed below. Also, we present some discussion to further support the reaction mechanism described earlier in this paper.

Solute−Solute Interactions. Several research groups have suggested that enhanced solute−solute interactions might enhance reaction rates in supercritical fluids. For instance, Randolph and co-workers[82] studied the enzyme-catalyzed reaction of cholesterol in SC CO_2. They found that the reaction rates were faster than what had been observed in liquids; furthermore, the addition of butanols to the solution yielded up to 4-fold increases in reaction rates. They attributed this to the fact that the added cosolvent had a strong effect on the nature of cholesterol aggregation and that there is a strong correlation between the amount of cholesterol aggregation and the rate of oxidation. Combes and co-workers[83] studied the photodimerization of cyclohexenone and examined the selectivity of head-to-head (HH) to tail-to-tail (TT) dimers. They found a decrease in the selectivity with increasing solvent density, a result that was counterintuitive based on previous liquid experiments. They attributed this occurrence to large solute−solute fluctuations, which increase the number of encounters between reacting species. Combes and co-workers concluded that this investigation provided experimental evidence that solute−solute interactions can increase reaction rate constants and selectivities near the critical point. Rhodes and co-workers studied the Michael addition of piperidine to methyl propiolate in SC fluoroform and ethane.[84] Although better stabilization of the zwitterionic-like transition state would be expected at higher densities, high rates were observed at low densities, near the critical point. This observed rate enhancement was attributed to solute−solute interactions. Theoretical studies corroborate the existence of density and concentration inhomogeneities in supercriticial fluids solutions.[24]

For our system, such concentration inhomogeneities might result in the average distance that had to be traversed by each anthracene triplet being less than if the solute molecules were evenly distributed. Conversely, actual anthracene triplet aggregates are unlikely since the solution is millimolar (1.8×10^{-5} to 4.7×10^{-6} mole fraction) and the concentration of anthracene triplets is several orders of magnitude below this. In addition, solute aggregates would result in static quenching, which could occur on a time scale much shorter than that used to measure the kinetics of the TTA (i.e., static quenching would occur within the time of the laser pulse). Nonetheless, if solute−solute interactions are strong, it is possible that the average distance traveled by a solute molecule could be less than if they were uniformly distributed through the solution, resulting in a reaction rate apparently greater than the diffusion-controlled one. This might be occurring in our system, but the effect would have to be small since the rate of anthracene TTA in SCW is just slightly above the expected diffusion-controlled limit.

Solute/Solvent Interactions. Another way in which the supercritical fluid environment might affect these reactions is the increased local density of the solvent around the solute. As mentioned above, in SC solvents, it is well-known that density inhomogeneities exist.[2,10,28−40] Tucker[23,24] has shown that there are regions of high density surrounded by regions of lower density. Most of the solvent molecules exist in the clusters of relatively high density, with a small fraction of the solvent molecules residing in the lower density regions between these clusters. Moreover, if a solute is attractive, most of the solute molecules will reside in the regions of high density. For SCW, this idea is corroborated by the work of Balbuena et al.,[80] who showed that for ions in SCW the effective Stokes−Einstein radius is essentially constant over a relatively wide solvent density range, and reflects a first solvation shell that is tightly coupled to the ion. If this were occurring for anthracene in SCW, this would mean that the effective Stokes−Einstein radius for diffusion would be larger than the reaction radius and they would no longer cancel in the SE/D equation. A larger diffusion radius means slower diffusion so, if this were occurring in our system, the rates should be less than those predicted from the SE/D equation. Since this is not the case, we conclude that there is *no* evidence of solvent clustering, i.e., a tightly bound first solvent shell, affecting the rate of the reaction of TTA of anthracene in SCW. Perhaps this is not surprising since anthracene is neutral and nonpolar; diffusion-controlled reactions of ionic species may show different results.

Mechanism. There is some previous evidence of reaction rates somewhat faster than the predicted diffusion-control limit for the triplet−triplet annihilation of anthracene and other arenes. Saltiel and co-workers[44] report reaction rates for 1,2-benzanthracene in polar solvents such as methanol (room-temperature dielectric constant of 32.63)[85] and ethylene glycol that were 2−3 times faster than those predicted by diffusion control (without including a spin statistical factor) over the entire temperature range studied. In another review of spin-statistical factors, the same author[51] stated that TTA of arenes could produce cation−anion radical pairs in polar solvents, indicating a change in mechanism, e.g., charge-transfer or full electron transfer. Thus, it is possible that the mechanism of the reaction is different in SCW than in organic solvents such as cyclohexane, benzene, and toluene (room-temperature dielectric constants of 2.023, 2.284, and 2.379).[85] In the range of temperatures and pressure investigated, the dielectric constant of water is between 1 and 10. Since the measured rate constants are just slightly above SE/D, including the spin statistical factor, yet still well below SE/D without the spin statistical factor, we conclude that the experimental results support the mechanism discussed earlier and shown in Scheme 1. In other words, the mechanism in SCW appears to be the same as it is in nonpolar liquid organic solvents.

Conclusions

The triplet−triplet annihilation reaction of anthracene in supercritical water at temperatures between 375 and 450 °C and pressures from 50 to 350 bar was studied to elucidate the effects of the supercritical water environment on a reaction that is known to be diffusion-controlled in most liquids. Observed rate constant and anthracene triplet extinction coefficient data were taken in order to determine the bimolecular rate constants as a function of temperature and pressure. Bimolecular rate constants were calculated at four isotherms and compared to the predicted diffusion-controlled values. The reaction rates occur just slightly above the diffusion-controlled limit predicted by the Stokes−Einstein based Debye equation, when the appropriate spin statistical factors are taken into account. Therefore, there is no evidence that this reaction is influenced by enhanced solute/solvent interactions, and any effect of solute/solute interactions is small. Moreover, the mechanism of the reaction appears to be the same as it is in nonpolar liquid solvents. In general, this work corroborates the findings of studies of benzophenone TTA in lower temperature SCFs that concluded that these reactions occur at the diffusion-controlled limit that can be calculated from bulk viscosities.[12,13]

Acknowledgment. The work described herein was supported by the Army Research Office. We also thank the National Science Foundation, the Clare Boothe Luce Foundation, and the American Association of University Women for fellowship support. In addition, acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Finally, we thank the Notre Dame Radiation Laboratory, which is supported by the Office of Basic Energy Sciences of the U. S. Department of Energy, for use of their facilities.

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