Factors Affecting the Rate of Decay of the First Excited Singlet State of Molecular Oxygen $O_2(a^1\Delta_g)$ in Supercritical Fluid Carbon Dioxide

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The photosensitized production and subsequent decay of singlet oxygen in supercritical fluid carbon dioxide has been studied as a function of pressure and temperature. The rate of decay is shown to be a function of the fluid density, demonstrating a quenching effect by the solvent. The observed rate constant for decay is also found to depend on the oxygen concentration, as a result of quenching of singlet oxygen, $O_2(a^1\Delta_g)$, by ground state oxygen. The rate constant for quenching by oxygen is found to be 1.9×10^4 dm^3 mol^{-1} s^{-1}, at 41 °C and at a pressure of 150 kg cm^{-2}, which is compared with previous findings in conventional solvents. The lifetime of singlet oxygen in supercritical fluid carbon dioxide, under these conditions, extrapolated to the value in the absence of ground state molecular oxygen, was found to be 5.1 ms (at 150 kg/cm^2 and 41 °C). The factors determining the lifetime of $O_2(a^1\Delta_g)$, in supercritical fluid carbon dioxide are discussed.

Introduction

Gaseous carbon dioxide becomes supercritical when compressed to a pressure higher than its critical pressure P_c (72 atm) above the critical temperature T_c (32.5 °C). Properties of supercritical fluids (SCFs) are different from ordinary liquids and gases, since they can be made to change substantially by changing temperature and pressure. In particular, density and viscosity change drastically near the critical point. SCF CO_2 has great potential as a solvent in large-scale chemical manufacture as a replacement for conventional organic solvents, since it is abundant, nontoxic, nonflammable, and easily removed from reaction products. Nonpolar compounds show high solubilities in SCF CO_2 and the addition of polar entrainers or surfactants allows the dissolution of polar, ionic, and polymeric species. There has been much activity in attempting to understand solvent effects on reactivity in supercritical fluids, due in the main to the many studies which have shown that local environments around dissolved solutes in supercritical fluids can be very different from the bulk. Effects observed include local density augmentation[1−8] and preferential solvation with addition of cosolvents[9−13] and attraction of dilute solutes for themselves.[14,15] These local solvation effects are in addition to the long-range density fluctuations seen in supercritical fluids near the critical point.

The lifetime of singlet oxygen in normal solvents shows an enormous solvent dependence including a large isotope effect with variations amounting to over 5 orders of magnitude from a few microseconds[16] in water to hundreds of milliseconds[17] in $C_{10}F_{18}$. In the gas phase in the absence of collisions with other molecules the lifetime is in excess of 1 h.[18,19] It is of interest to investigate the lifetime of singlet oxygen in SCF CO_2 since this may prove an environmentally desirable and friendly solvent in which to carry out photosensitized oxidative syntheses.

Molecular oxygen in its ground state is a triplet state $O_2(X^3\Sigma_g^-)$ and its first two, low lying, electronic excited states are singlet states, with energies of 7882 cm^{-1} for the lowest $O_2(a^1\Delta_g)$ and 13 121 cm^{-1} in the case of $O_2(b^1\Sigma_g^+)$. Transitions from the ground state to these two states are forbidden by the selection rules for electric−dipole transitions, but spin−orbit coupling results in magnetic dipole character resulting in phosphorescences from $O_2(a^1\Delta_g)$and $O_2(b^1\Sigma_g^+)$ at 1269 and 760 nm, respectively.[20,21] The radiative rate constants for both transitions are small, varying in solution from 0.10 to 3.11 s^{-1} and from 0.17 to 1.9 s^{-1} for the transitions to the ground state from $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ respectively.[22,23] The lifetime of $O_2(b^1\Sigma_g^+)$ is very short in solution[24,25] owing to the spin-allowed collisional deactivation from $b^1\Sigma_g^+ \rightarrow a^1\Delta_g$. A maximum value for the lifetime of $O_2(b^1\Sigma_g^+)$ in CCl_4 has been reported[26] as 130 ± 10 ns. Deactivation of $O_2(a^1\Delta_g)$, on the other hand, is a spin-forbidden process with lifetimes for this state of 4.2 μs in water[27a] and 34 ms in CS_2.[27b] The decay of $O_2(a^1\Delta_g)$ involves conversion of the electronic excitation energy into energy accepting vibrations of the solvent molecules which depends critically on the highest frequency vibrational modes of the solvent (for detailed discussions see refs 16, 27, and 28). Rodgers[16] suggested that the lifetime can be predicted in a particular solvent by linear combination of “additivity factors”, determined experimentally for each bond type. In this paper we present the first study of the deactivation of singlet oxygen, $O_2(a^1\Delta_g)$, in supercritical fluid carbon dioxide. Results are presented showing a dependence of the observed lifetime on both the concentration of carbon dioxide and the concentration of oxygen. Rate constants for deactivation by both species have been measured. In addition, the rate constant for quenching of singlet oxygen by *N*,*N*,*N′*,*N′*-tetramethyl-1,4-phenylenediamine (TMPD) has been measured in SCF CO_2 and compared with the value obtained in cyclohexane.

Experimental Section

The apparatus used to prepare the supercritical fluid solutions has been described in detail elsewhere.[9] Briefly, carbon dioxide (BOC, water content <20 ppm) at a pressure of 58 bar is liquified by chilling to −5 °C. The liquid CO_2 is pumped using an HPLC pump (Jasco model PU-980) through 1/16 in. stainless steel tubing into a home-built pressure cell (316 stainless steel) with fused silica windows at either end. The tubing is heated to the desired temperature in a gas chromatograph oven (Pye Unicam), and the cell is electrically heated using a home-built

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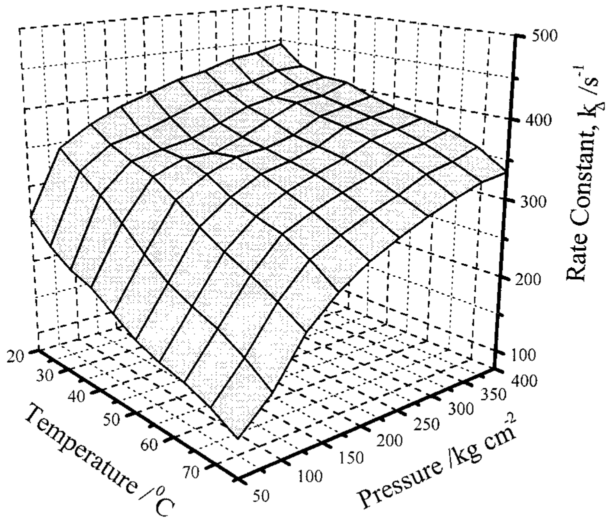

Figure 1. 3D plot showing the dependence of the rate constant for the decay of singlet oxygen ($O_2(a^1\Delta_g)$) in supercritical fluid carbon dioxide, k_Δ, on temperature and pressure.

temperature controller. The cell temperature is monitored using a K series thermocouple. Typical temperature control is ±0.2 °C.

Samples are introduced to the cell as a solution of the desired concentration. The solution is placed in the cell, and the solvent is removed by heating the cell with a slow flow of carbon dioxide gas. Oxygen at the desired concentration is introduced by flushing with mixtures of dry oxygen and dry nitrogen, the ratio of which is controlled using two flow meters (Platon). Calibration of the flow meters was confirmed by measuring oxygen quenching of the fluorescence of 9,10-dimethylanthracene in cyclohexane solution.

The concentration of sensitizer in the cell was determined by measuring the in situ absorbance in the 320−450 nm spectral region using a photodiode array detector (EG&G Princeton Applied Research), which has been described in detail elsewhere,[9] and a xenon arc lamp (275 W, Oriel) as a continuous source. The spectral region of interest was isolated using a colored glass filter with cutoff of all wavelengths above 450 nm.

Excitation of the sensitizer was with the third harmonic of a Lumonics hyperYAG HY200 Nd:YAG laser (355 nm, 8 mJ per pulse, 8 ns fwhm). The excitation energy was attenuated using solutions of sodium nitrite in water. Detection was using an EO-980P liquid nitrogen cooled germanium photodiode detector (North Coast Scientific), with a 1270 nm interference filter (Melles Griot) interposed between sample and detector to reduce detection of laser scatter and sensitizer emission, and to isolate the singlet oxygen phosphorescence. Data capture was with a 250 MS/s digitizing oscilloscope (Tektronix 2432A) and data analysis was using MicroCal Origin.

Phenazine (Aldrich, >97%) was recrystallized from methanol. *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (TMPD) (Aldrich) was recrystallized from water. Cyclohexane (Aldrich, spectrophotometric grade) was used as received.

Results

(a) Pressure and Temperature Effects on Singlet Oxygen Lifetimes. Figure 1 summarizes the data obtained for the variation of singlet oxygen lifetime as a function of temperature and pressure. The measured lifetime was found to be independent of sensitizer identity when quenching of singlet oxygen by different sensitizers to different extents was taken into account. In the case of phenazine as sensitizer the observed lifetime of singlet oxygen was found to be independent of phenazine concentration in the range 2×10^{-5} to 1×10^{-4} mol dm^{-3}, demonstrating that phenazine has a low rate constant for quenching of $O_2(a^1\Delta_g)$. Consequently, phenazine was used as the sensitizer in the data presented here. In each case, the cell was flushed with dry air prior to pressurizing with carbon dioxide. Measurements were performed along a series of isobars from 74 kg cm^{-2} (just above the critical pressure of 72 kg cm^{-2}) to 400 kg cm^{-2}, with temperatures ranging from 22 °C (below the critical temperature of 32.5 °C) to 73 °C.

The slight unevenness of the surface shown in Figure 1 is attributable to experimental error on the measured singlet oxygen lifetime. Also evident from Figure 1 is the fact that there is no abrupt change in lifetime at the transition between liquid and supercritical fluid carbon dioxide. Inspection of the data in Figure 1 shows that along a given isotherm, the rate constant for the decay of singlet oxygen, k_Δ, which equals the inverse of the measured singlet oxygen lifetime increases with increasing pressure. Also, the rate at which the rate constant increases with respect to pressure along a given isotherm, $(dk_\Delta/dP)_T$, decreases with increasing pressure. This clearly shows that the maximum susceptibility of the rate constant to changing pressure occurs in the region just above the critical point. At higher pressures, the rate constant is affected much less by changes in pressure. This trend is independent of the particular isotherm chosen i.e., while the absolute value of the rate constant shows a temperature dependence, the trend in rate constant values with changing pressure does not.

Along a given isobar, the rate constant for the decay of singlet oxygen decreases with increasing temperature, with the rate of decrease of rate constant with temperature, $(dk_\Delta/dT)_P$, showing little variation with temperature over the range studied. The small decrease in rate constant with increasing temperature is more marked at lower pressures, i.e., just above the critical point, than at higher pressures.

(b) Oxygen Quenching of Singlet Oxygen. Using phenazine as a sensitizer and a supercritical fluid temperature and pressure of 41 °C and 150 kg cm^{-2}, respectively, the effect of oxygen concentration on the rate constant for singlet oxygen relaxation k_Δ in supercritical fluid carbon dioxide has been measured. The results are shown in Figure 2. The rate constant, k_Δ, was obtained by an exponential fit to the observed phosphorescence decay traces at 1270 nm. The plot shown in Figure 2 is constructed according to the equation

$$k_\Delta = k_D + k_q^{O_2}[O_2] \qquad (1.1)$$

where k_D includes all the contributions to the decay of singlet oxygen excluding oxygen quenching, discussed in more detail later. The concentration of oxygen is calculated from the initial pressure of oxygen in the system, ${p_{O_2}}^I$, as

$$[O_2] = \frac{{p_{O_2}}^I}{RT} \qquad (1.2)$$

i.e., assuming that oxygen behaves as an ideal gas at low pressures, and that its concentration can be calculated on the basis of its initial pressure at the cell temperature. This assumption appears to be valid on the basis that from the linearity of the plots obtained, the oxygen concentration is directly proportional to its initial pressure. Note that this

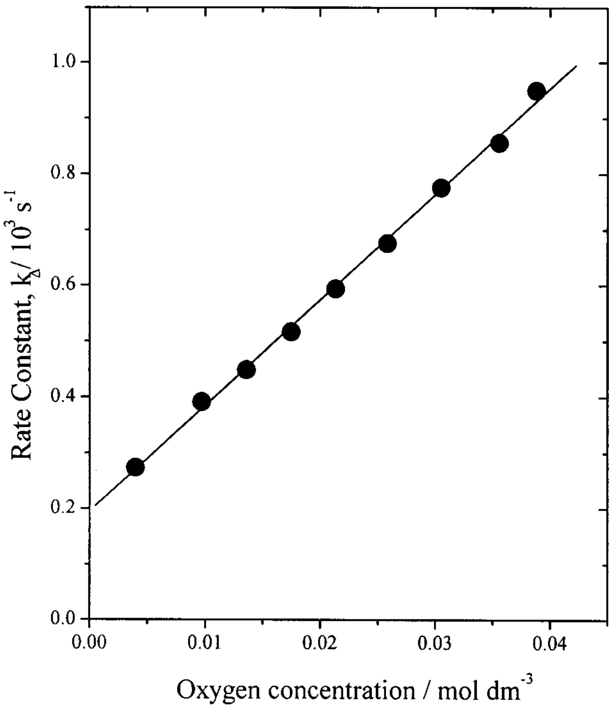

Figure 2. Dependence of the rate constant for the decay of singlet oxygen ($O_2(a^1\Delta_g)$) in supercritical fluid carbon dioxide, k_Δ, on oxygen concentration at 150 kg cm^{-2} and 41 °C.

calculation is to determine the number of moles of oxygen introduced to the cell prior to pressurization with carbon dioxide, and therefore makes no assumptions regarding the concentration of oxygen in SCF CO_2 as a function of its partial pressure. The slope of the plot shown in Figure 2 yields a rate constant for quenching of singlet oxygen by ground state oxygen of $(1.89 \pm 0.04) \times 10^4$ dm^3 mol^{-1} s^{-1} and from the intercept, a limiting lifetime at infinite dilution of oxygen of 5.1 ms is obtained.

(c) Quenching of Singlet Oxygen by TMPD. *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (TMPD) has been used as a singlet oxygen quencher to investigate the rate of this process in supercritical fluid carbon dioxide at 150 kg/cm^2 and 41 °C. The concentration of TMPD in the cell was determined by in situ absorbance measurements assuming invariance of the molar absorption coefficient between cyclohexane and supercritical fluid carbon dioxide. The fact that the spectrum shifts very little (<5 nm) in going between these solvents is support for this assumption. Indeed, we have measured the molar absorption coefficient in a range of solvents and have found a difference of less than 10% in the molar absorption coefficient of TMPD in CCl_4, cyclohexane and *n*-hexane. Where other workers[29] have measured molar absorption coefficients in SCF CO_2 at the densities used here, the values are comparable (±15%) with those values measured for conventional solvents. The data obtained for quenching of singlet oxygen by TMPD in supercritical fluid carbon dioxide is shown in Figure 3, and a rate constant of $(7.6 \pm 1.5) \times 10^7$ dm^3 mol^{-1} s^{-1} is determined from the slope. The intercept of the plot shown in Figure 3 gives a limiting lifetime for singlet oxygen of 4.6 ms, but in this instance the intercept includes some contribution from oxygen quenching and hence is expected to give a limiting rate of decay which is dependent upon oxygen concentration.

Discussion

The pseudo-first-order rate constant for decay of singlet oxygen in supercritical fluid carbon dioxide can be formulated

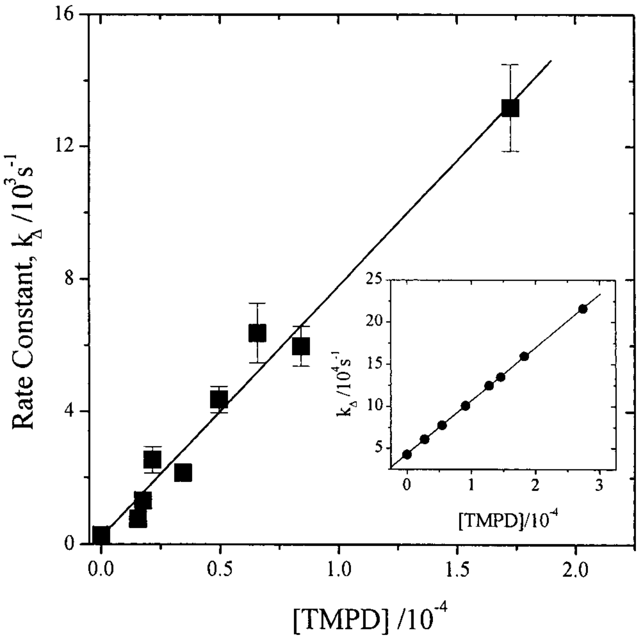

Figure 3. Dependence of the rate constant for the decay of singlet oxygen ($O_2(a^1\Delta_g)$) in supercritical fluid carbon dioxide, k_Δ, on TMPD concentration at 150 kg cm^{-2} and 41 °C. Inset shows the same dependence in cyclohexane.

in terms of a number of contributions:

$$k_\Delta = k_R + k_q^{CO_2}[CO_2] + k_q^{O_2}[O_2] + k_q^{S}[S] + k_q^{Q}[Q] \qquad (1.3)$$

where the superscripts CO_2, O_2, S, and Q indicate quenching by carbon dioxide, oxygen, and sensitizer, respectively, [S] and [Q] are the sensitizer and quencher concentrations, respectively, and k_R is the radiative rate constant. Over the concentration range employed here for phenazine as a sensitizer, changes in its concentration had a negligible effect on the observed rate of decay of singlet oxygen and hence no value for k_q^S was determined.

The diffusion-controlled quenching rate constant in supercritical fluid carbon dioxide at 150 kg cm^{-2} and 50 °C has been determined previously by us[9] as $(1.1 \pm 0.2) \times 10^{11}$ dm^3 mol^{-1} s^{-1}. Hence clearly k_q^Q, where Q = TMPD, and $k_q^{O_2}$ determined here are indicative of reaction-controlled quenching far below the diffusion-controlled limit. The value for $k_q^{O_2}$ depends on the probability of electronic-to-vibrational energy transfer in this spin-allowed process. This rate constant for quenching is comparable with that obtained in CS_2, where a value of 1.3×10^4 dm^3 mol^{-1} s^{-1} was determined,[30] and somewhat higher than the $k_q^{O_2}$ values determined[31] in perfluorodecalin (4.1×10^3 dm^3 mol^{-1} s^{-1}), Freon 113 (3.2×10^3 dm^3 mol^{-1} s^{-1}), perfluorohexane (2.6×10^3 dm^3 mol^{-1} s^{-1}), and tetrachloromethane (3.9×10^3 dm^3 mol^{-1} s^{-1}). The solvent dependence of the $k_q^{O_2}$ values has been proposed to be a function of the packing fraction and has been ascribed as due to variations in the O_2-O_2 collision frequency which depends on the radial pair distribution function,[32] upon which the packing fraction of the solvent is in turn dependent. However, evaluation of the packing fraction in supercritical fluid carbon dioxide under the conditions used here on the basis of the data given by Bondi,[33] and using the density calculated using the equation of state, leads to a packing fraction of 0.35, which can be compared with the values calculated for perhalogenated solvents of between 0.51 for perfluorohexane and 0.57 for perfluorodecalin. Hence the higher value obtained by us in supercritical fluid carbon dioxide for the oxygen quenching of singlet oxygen cannot be explained solely on the basis of the radial pair distribution function through evaluation of the packing fraction.

The quenching rate constant for singlet oxygen by TMPD shows a solvent dependence and has been determined as 1×10^9 dm^3 mol^{-1} s^{-1} in methanol,[34a] and as 5.2×10^9 and 2.6×10^9 dm^3 mol^{-1} s^{-1} in acetonitrile and benzene, respectively.[34b] Darmanyan and Jenks[34b] showed there is a linear correlation between log k_q measured in benzene and cyclohexane and the oxidation potential E_{ox} measured in acetonitrile for a range of aromatic amines, including TMPD, as singlet oxygen quenchers, confirming the involvement of charge transfer interactions and demonstrating that steric effects played little role in determining these quenching rate constants. For comparison, and in light of the known effect of solvent in modifying singlet oxygen quenching rates and the low value obtained in SCF CO_2, we determined the quenching rate constant for $O_2(a^1\Delta_g)$ by TMPD in cyclohexane solution as 6.3×10^8 dm^3 mol^{-1} s^{-1} (see inset in Figure 3). This low value is consistent with the singlet oxygen being quenched via a charge transfer mechanism, with the partially charge separated intermediate being destabilized in a nonpolar solvent. Several observations[35−39] demonstrate that supercritical fluid carbon dioxide behaves more as a nonpolar solvent than a polar solvent. Additionally, the solvent polarity/polarizability (π*) values given for CCl_4 and CS_2 are 0.294 and 0.514, respectively,[40] while that for liquid CO_2 is 0.04,[38] all relative to cyclohexane having a value of 0. However, the fact that the quenching rate constant for $O_2(a^1\Delta_g)$ by TMPD in SCF CO_2 is 8 times lower than the value in cyclohexane demonstrates that solvent polarity is not the only factor involved in determining the quenching rate. If one compares the packing fractions for carbon dioxide and cyclohexane, again calculated from the data of Bondi,[33] it is clear that the packing fraction and thus the collision frequency is higher in cyclohexane (0.55) than in supercritical carbon dioxide (0.35), and this may play a role in determining the rate constants for quenching. Singlet oxygen quenching rates in supercritical fluid carbon dioxide are the subject of on-going studies in our laboratory in order to elucidate these factors.

When considering the pattern of singlet oxygen lifetimes with changing temperature and pressure, the term in the overall equation involving quenching by solvent becomes important. First, we will consider the pattern of rate constant changes along a given isotherm, where in Figure 1 it is clear that the rate constant increases with increasing pressure, and that the rate of increase $(dk_\Delta/dP)_T$ decreases with increasing pressure. This observation can be explained on the basis of the change in fluid density with pressure. This is depicted in Figure 4, where the density is calculated from the equation of state given by Ely.[41] The surface showing the dependence of the rate constant for singlet oxygen decay on pressure and temperature (Figure 1) follows the same pattern as the density, which here clearly equates to the concentration of carbon dioxide in the cell. This points to quenching of the singlet oxygen by the solvent molecules, as is observed for all normal solvents.[27,42−44] Note that supercritical fluids are exceptional since it is possible to vary the solvent density considerably by variations in pressure and temperature and hence to have large influences on the observed rate constant.

On the basis of the work of Ogilby et al.[43,44] and Schmidt and Shafii[35] where solvent-dependent changes in the radiative rate constant have been observed and correlated with solvent refractive index, it is likely that such changes in supercritical fluid carbon dioxide with changing temperature and pressure may also have an effect on the radiative rate constant. However, the radiative rate constant is small in comparison to the observed decay rate constants (vide infra), and the effect of changes in solvent refractive index reported previously is small in comparison with the changes observed here. Also, the absolute magnitude of the initial singlet oxygen signal observed here in SCF CO_2 changes little with changing pressure and temperature, suggestive of little change in the radiative rate constant. Attempts to use eq 3 to calculate a value for k_R based on the previously determined parameters yielded a value of zero to within the error of the determination (which is approximately 15% overall). Hence the changes in rate constant observed in Figure 1 can be assigned as due to quenching by the solvent, in this case carbon dioxide. It may also be anticipated that there may be an effect on the oxygen quenching rate constant as a consequence of changing fluid density, since the viscosity of the fluid also increases. However, this would have the effect of lowering the contribution by oxygen quenching, and hence reducing the apparent effect of the increase in carbon dioxide concentration. A study is currently underway to clarify any changes in the rate constants for oxygen quenching of singlet oxygen due to changes in pressure and temperature.

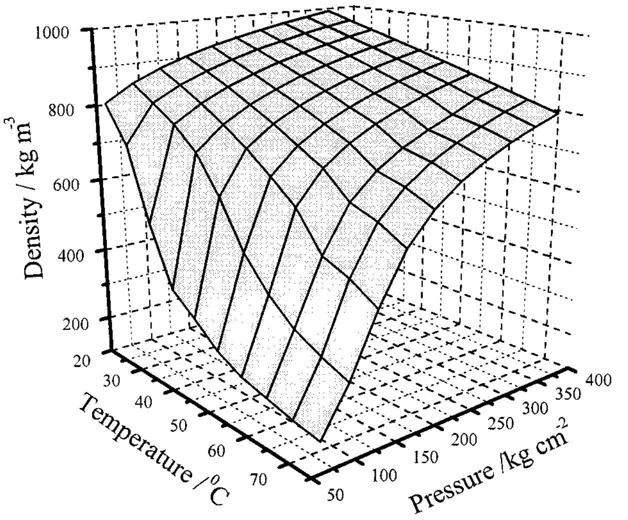

Figure 4. 3D plot showing the change of SCF−CO_2 density with temperature and pressure.

When one considers the variation in the rate constants for singlet oxygen relaxation along a particular isobar, a similar explanation to that used to explain the variation along an isotherm can be invoked. Here again the change in density resulting in a change in carbon dioxide concentration explains the observed pattern, and in fact the change in density with temperature is less at higher pressures, an observation mirrored in the pattern for the rate constants (compare Figures 1 and 4). It should be noted that along a particular isobar, the total oxygen concentration may be expected to decrease as a result of the increase in temperature. However, if the change in oxygen concentration expected over this relatively modest temperature range is calculated, it is clear that the magnitude of the change (typically 14%) is insufficient to perturb the observed rate constant to the extend observed.

Analysis of the data by plotting the observed rate constant against the carbon dioxide concentration along a particular isotherm allows the calculation of a solvent quenching constant at that temperature from the slope of the plot. The carbon dioxide concentration is determined from the density calculated using the equation of state given by Ely,[41] with errors in the latter parameter of less than 3% over the whole range studied.

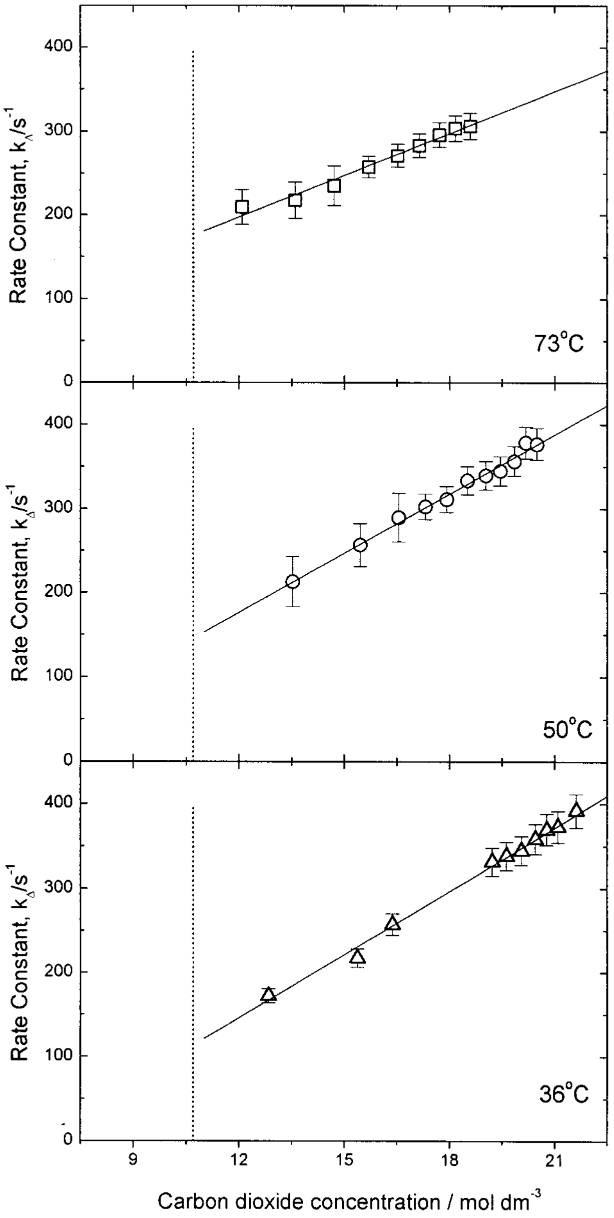

Figure 5. Dependence of the rate constant for the decay of singlet oxygen ($O_2(a^1\Delta_g)$) in supercritical fluid carbon dioxide, k_Δ, on carbon dioxide concentration at 36 °C (△), 50 °C (○), and 73 °C (□). The concentration corresponding to the critical density of CO_2 is indicated by the perpendicular dotted line.

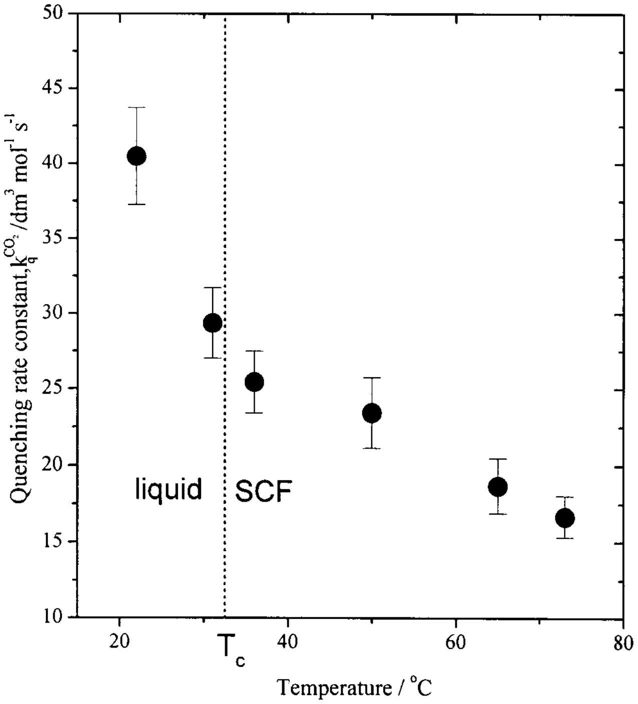

Figure 6. Dependence of the quenching rate constant for singlet oxygen ($O_2(a^1\Delta_g)$) by carbon dioxide, $k_q^{CO_2}$, as a function of temperature. The critical temperature is indicated by the dotted line.

Examples of such a plots are given in Figure 5 for the rate constant for deactivation of singlet oxygen versus carbon dioxide concentration in mol dm^{-3} at three temperatures 36, 50, and 73 °C. Also marked on these plots are the concentrations corresponding to the critical density. The linear correlation between rate constant and concentration is only valid in the supercritical region; extrapolation of these lines to densities corresponding to the liquid region should not be made. Each point in Figure 6 was calculated as the slope of a plot of singlet oxygen decay rate constant at a single temperature against carbon dioxide concentration (varied by varying pressure). [N.B. The partial pressure of oxygen in the cell is approximately constant over this pressure range.] The bimolecular quenching rate constants ($k_q^{CO_2}$) show, within the experimental error, an almost linear correlation with temperature over the range 50−73 °C as shown in Figure 6. The fact that the rate constant decreases with increasing temperature is indicative of a preequilibrium involved in the quenching process with the association between the singlet oxygen and the carbon dioxide having a negative enthalpy. These results are in contrast to the results of Maier et al.,[45] who have previously shown a positive dependence of the rate constant for singlet oxygen relaxation in the low density gas phase, indicating not unexpectedly that the oxygen−oxygen interactions under their conditions are very different from the oxygen−carbon dioxide interaction in the supercritical region of carbon dioxide. It should be noted that the water content of the carbon dioxide used is insufficient to significantly perturb the lifetime of singlet oxygen in this system. The water content even at the highest carbon dioxide pressure is calculated to be at most 9×10^{-4} mol dm^{-3}, leading to a maximum contribution to the overall rate constant of less than 2% based on a value of 4.3×10^3 dm^3 mol^{-1} s^{-1} for the rate constant for quenching of $O_2(a^1\Delta_g)$ by water.[16] Just above the critical temperature (36 °C), the calculated quenching rate constant shows an increase to 25 ± 1 dm^3 mol^{-1} s^{-1}, and below the critical point attains an even greater value. The most likely explanation for this observation is that it is due to the well-known local density enhancements around the critical point in supercritical fluids which have been demonstrated through shifts in absorption[46] and fluorescence[47] spectra, as well as from theoretical considerations based on integral equation theory[48] and molecular dynamics simulations.[49,50] It should be noted that local density augmentation is a solvation effect and is not a critical phenomenon; i.e., it does not correlate with the isothermal compressibility of the solvent. Such local density enhancements may be responsible for the apparent increase in rate of deactivation by the solvent near the critical point relative to that expected on the basis of bulk density, leading to an overestimation of the quenching constant.

Rodgers[16] and Hurst and Schuster[28] have suggested that the rate constants for deactivation of singlet oxygen by conventional solvents can be calculated on the basis of "additivity factors", where the overall quenching rate constant is a linear sum of the rates derived from each bond in the quenching molecule. On this basis, Rodgers suggests a value of 100 dm^3 mol^{-1} s^{-1}for a C=O bond, leading to 200 dm^3 mol^{-1} s^{-1} for CO_2. Clearly,

TABLE 1: Rate Constants for Quenching of Singlet Oxygen by Discreet Bonds in Solution

oscillator	freq/cm^{-1}	k_q/dm^3 mol^{-1} s^{-1}
C−D	2240	10.4[a]
C=O	1750	8[b]
C=S	1520	0.35[a]

[a] From ref 17. [b] This work.

this is a substantial overestimate of the value for a C=O bond of 8 dm^3 mol^{-1} s^{-1} calculated on the basis of our data. However, the value reported by Rodgers was calculated using acetone-d_6 and subtracting the C−D contributions, and Rodgers points out that this single-point determination suffers from a high degree of uncertainty. Hurst and Schuster[28] suggested that there was a correlation between the highest frequency mode of the particular bond and the bimolecular rate constant for quenching of singlet oxygen (see also refs 17 and 27). In Table 1 are gathered data for some low-frequency oscillators indicating that our value obtained for C=O, which is directly measured, is consistent with this hypothesis.

The above additivity factors apply to the summation of isolated bonds in typical organic molecules. In CO$_2$, the two C=O moieties do not behave as isolated oscillators and the asymmetric stretching mode has the highest frequency located at 2350 cm^{-1}, a slightly higher frequency than the C−D highest frequency mode (Table 1). Hence CO$_2$ considered as a single oscillator might be expected to have an additivity factor similar to that of C−D. That this is not observed suggests that a model based solely on the highest frequency vibration is oversimplistic, and higher vibrational energy levels, vibrational energy mismatch, and even specific solvent−solute interactions may all need to be considered. Reasons for the different values for C−D versus CO$_2$ need further investigation.

In the gas phase, there is again some disagreement regarding published values for the rate constants for quenching of singlet oxygen O$_2$(a$^1\Delta_g$) by carbon dioxide. Reported values varying from 220 dm^3 mol^{-1} s^{-1}[51] to $7.8 > k_q > 3.6$ dm^3 mol^{-1} s^{-1},[52] owing mainly to the difficulty associated with measuring such small quenching constants. It is worth noting that the value observed in SCF CO$_2$ is at least twice that reported in the gas phase in ref 52.

Conclusion

We have shown for the first time that singlet oxygen can be efficiently sensitized in supercritical fluid carbon dioxide, and that it has a long lifetime as a result of inefficient quenching by the solvent. This means it has good potential as a solvent in which to carry out synthetic photosensitized oxidations. The dependence of the observed lifetime on the density of the fluid confirms quenching by carbon dioxide. A quenching constant in the supercritical region of 16 ± 2 dm^3 mol^{-1} s^{-1} has been determined over the temperature range of 50−73 °C and at pressures in the range 80−400 kg cm^{-2}, with a slightly higher value being observed near the critical point as a result of local density enhancements.

We have shown that singlet oxygen is quenched by ground state oxygen in supercritical fluid carbon dioxide, and we have measured a rate constant $k_q^{O_2}$ of $(1.89 \pm 0.04) \times 10^4$ dm^3 mol^{-1} s^{-1}, which is comparable with that determined in CS$_2$.[30] Also we present the first measurement of the rate constant for singlet oxygen quenching by an aromatic amine, TMPD, in supercritical fluid carbon dioxide. This quenching rate constant was shown to be a factor of 64 lower than the literature value measured in acetonitrile[34b] and 8 times lower than the value measured in the nonpolar solvent cyclohexane.

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