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Photosensitized production of singlet oxygen and factors governing its decay in xenon and carbon dioxide supercritical fluids

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Abstract

The photosensitized generation and subsequent decay of singlet oxygen in supercritical fluid xenon has been studied as a function of pressure and temperature. It has been found that the rate constant for quenching of singlet oxygen by ground state oxygen, k_q^O, increases as the pressure increases and decreases as the temperature increases. At 298 K, the value of k_q^O increases from (1.27 to 1.76) × 10^3 dm^3 mol^{-1} s^{-1} as the pressure increases from 9.8 to 39.2 MPa; at 355 K the values of k_q^O drop to 6.2×10^2 and 1.54×10^3 dm^3 mol^{-1} s^{-1} at these same pressures. It has also been found that the fractional contribution of the oxygen quenching to the overall singlet oxygen decay rate increases with increasing pressure, showing greater variations at high temperatures, and decreases with increasing temperature. The measured volume of activation was found to decrease with increasing pressure, and shows a small but systematic decrease with decreasing temperature, particularly at lower pressures.

Keywords: Singlet oxygen; Supercritical fluids; Quenching; Effect of pressure; Effect of temperature; Activation volume

1. Introduction

Supercritical fluids (SCFs) are of considerable interest as solvents for a number of reasons, mainly since their physical properties such as density and viscosity can be influenced appreciably by changes in temperature and pressure, allowing the investigation of the effects of fundamental solvent properties on the rates of reactions without changing the chemical identity of the solvent [1,2]. In addition, around the critical point phenomena such as solvent clustering and local density augmentation are apparent, and these effects have been probed in a number of studies involving the measurement of fluorescence quenching, triplet–triplet annihilation rates, and shifts in emission and absorption spectra [2–24].

Molecular oxygen in its ground state is a triplet state $O_2(X^3\Sigma_g^-)$ and its first two, low lying, electronically excited states are singlet states, with energies of 94 and 157 kJ mol^{-1} for $O_2^*(a^1\Delta_g)$ and $O_2^*(b^1\Sigma_g^+)$, respectively. 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 762 nm, respectively [25,26]. The radiative rate constants for both transitions are small, varying in solution from 0.21 to 3.1 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 [27,28]. The lifetime of $O_2^*(b^1\Sigma_g^+)$ is very short in solution [29,30] 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 [31] 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 3.1 μs in water [32] and 79 ms in CS_2 with oxygen concentrations $\leq 10^{-5}$ mol dm^{-3} [33]. 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. [29,34]).

As early as the 1970s, several investigators studied the lifetime of singlet oxygen in solution, and bimolecular rate constants for the quenching of singlet oxygen were determined

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[35–37]. Later Rodgers [38] and Hurst and Schuster [39] discussed in detail the deactivation of singlet oxygen $O_2^*(a^1\Delta_g)$ by solvent molecules, followed by the studies of Schmidt et al. [34,40,41]. According to these studies the deactivation of singlet oxygen $O_2^*(a^1\Delta_g)$ by solvent molecules can be understood on the basis of a collisional electronic-to-vibrational energy transfer, which occurs by coupling of the highest fundamental vibrational mode of the acceptor molecule with an O_2 $(^1\Delta_g, \nu = 0) \rightarrow (^3\Sigma_g{}^-, \nu = m)$ transition. Previously, we published [42] a detailed investigation into the behaviour of singlet oxygen in supercritical fluid carbon dioxide, and showed that singlet oxygen was quenched by electronic-to-vibrational energy transfer both to carbon dioxide and to ground state oxygen, although no evidence for self-quenching by singlet oxygen was found under our experimental conditions. Okamoto et al. [43] also studied this system, but did not separate contributions from ground state oxygen quenching from that of the solvent. We have also published [44] data regarding the deactivation of singlet oxygen in supercritical fluid xenon, and showed a very long limiting lifetime at 325 K and 8.8 MPa of 22 ms, the observed lifetime being limited by the concentration of ground state oxygen. We also showed that activation volumes for the quenching of singlet oxygen by xenon could be extracted from the pressure dependence of the quenching rate. Following the model of Schmidt and Afshari [34], we showed that in supercritical fluid xenon, although the Frank–Condon factors and off-resonance terms are unfavourable, the electronic factor, perturbed by the heavy atom effect, is significant and contributes to effective quenching by xenon despite the lack of accepting vibrational modes in the solvent.

In this publication, we extend our treatment of radiationless deactivation of singlet oxygen in supercritical fluids to cover an extensive range of temperature and pressures in both supercritical fluid xenon and carbon dioxide, and demonstrate temperature and pressure dependencies of activation volumes in both solvents.

2. Experimental

The apparatus used to prepare the supercritical fluid solutions has been described in detail elsewhere [20,42,44]. Briefly, xenon (BOC) is condensed first at 77 K in an external cylinder (25 cm^3) to achieve a pressure of >50 bar at 268 K, then either the xenon or CO_2 (BOC, 58 bar) is liquefied by chilling to −5 °C. The resulting liquid Xe or CO_2 is then 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 temperature controller. The cell temperature, typically controlled in these experiments to ±1 K, is monitored using a K series thermocouple and the pressure monitored using the pressure transducer in the HPLC pump head.

Phenazine (Aldrich, >97%) was recrystallised from methanol. Cyclohexane (Aldrich, spectrophotometric grade) was used as received. Samples were introduced into the cell as a cyclohexane solution of the desired concentration. The solution was placed in the cell, and the solvent removed with a slow flow of dry nitrogen gas whilst heating the cell. Oxygen at the desired concentration was introduced by flushing with mixtures of dry oxygen and nitrogen, the ratio of which was controlled using two calibrated flow meters (Platon).

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 aqueous sodium nitrite solution. Detection of $O_2^*(a^1\Delta_g)$ was with an EO-980P liquid nitrogen cooled germanium photodiode detector (North Coast Scientific), with a 1270 nm interference filter (Melles Griot) interposed between sample and photodiode to isolate the singlet oxygen phosphorescence and to reduce detection of laser scatter and sensitizer emission. Data capture was with a 250 MS/s digitising oscilloscope (Tektronix 2432A) and data analysis were done using MicroCal Origin 6.1.

3. Results and discussion

The pseudo-first order rate constant, k_Δ, for decay of $O_2^*(a^1\Delta_g)$ in SCF-Xe or CO_2 can be formulated in terms of a number of contributions: i.e.,

$$k_\Delta = k_P + k_q^X[X] + k_q^O[O_2] + k_q^S[S] + k_q^\Delta[\Delta] \qquad (1)$$

where k_p is the rate constant for phosphorescence from $O_2^*(a^1\Delta_g)$, k_q^X represents the bimolecular rate constants for the quenching of $O_2^*(a^1\Delta_g)$ by quencher X, equal to xenon (X = Xe) or carbon dioxide (X = CO_2), k_q^O represents quenching by ground state molecular oxygen (O_2) and $k_q^S[S]$ represents quenching by the sensitizer (S), phenazine in this instance. The rate of the radiative transition from $O_2^*(a^1\Delta_g)$ to $O_2(X^3\Sigma_g{}^-)$ is on average [45] 6×10^{-4} times less than that from $O_2^*(b^1\Sigma_g{}^+)$ to $O_2^*(a^1\Delta_g)$ and since Fink et al. [46] have measured the bimolecular constant for this latter transition, collisionally induced by Xe in the gas phase, as 46.8 $dm^3\ mol^{-1}\ s^{-1}$ it follows that k_p is likely to be <1% of the values of k_Δ measured here. Values of k_p in a variety of different solvents given previously [45,47,48] support this suggestion, for example k_p equals 3.1 s^{-1} in CS_2. Changes in the phenazine concentration from 2 to 10×10^{-5} mol dm^{-3} had a negligible effect on the observed rate of decay of $O_2^*(a^1\Delta_g)$ in SCF-Xe or in SCF-CO_2, and hence in both of these systems the value of $k_q^S[S]$ when phenazine is the sensitizer is negligible. k_q^Δ describes self-quenching of $O_2^*(a^1\Delta_g)$ by $O_2^*(a^1\Delta_g)$, a reaction previously observed in CS_2 [49]. Under the conditions used here the singlet oxygen phosphorescence decay traces are monoexponential and the observed singlet oxygen lifetime is independent of the excitation energy over a range of 0.05–8 mJ/pulse, demonstrating that there is no dependence of the observed singlet oxygen decay rate on the concentration of $O_2^*(a^1\Delta_g)$ under these conditions; in addition, changing the amount of singlet oxygen produced by varying the sensitiser concentration did not change the observed k_Δ· Therefore, self-quenching, i.e., $k_q^\Delta[\Delta]$ is negligible under our conditions. Hence the observed rate of decay of the singlet oxygen is determined under these conditions by the concentrations of solvent molecules and of ground state oxygen, and the rate constants for quenching by these molecules.

3.1. Quenching of singlet oxygen by ground state oxygen

The effect of oxygen concentration on the rate constant for singlet oxygen decay, k_Δ, in the supercritical fluids carbon dioxide and xenon has been measured. Under the conditions used in these studies Eq. (1) simplifies to the following equation:

$$k_\Delta = k_D + k_q^O[O_2] \tag{2}$$

Plots according to Eq. (2) (Fig. 1) give slopes of k_q^O and intercepts $k_q^X[X]$. These intercepts give lifetimes of singlet oxygen at infinite dilution of oxygen of between 25 and 27 ms, the value decreasing with increasing pressure due to quenching of singlet oxygen by solvent molecules, observations consistent with our previously reported results [44]. The concentration of oxygen is calculated from the initial pressure and the final cell temperature, i.e., $[O_2] = P_{O_2}/RT$, assuming that oxygen is behaving as an ideal gas.

In a previous publication [42], we reported in SCF-CO$_2$ a value for the quenching of singlet oxygen by ground state molecular oxygen of $(1.89 \pm 0.04) \times 10^4$ dm^3 mol^{-1} s^{-1} at 314 K and 14.7 MPa, and we commented that this value required further investigation since it was somewhat higher than in other solvents. We have subsequently re-measured this value using very high purity carbon dioxide and well-dried oxygen and nitrogen and have obtained a value of $(1.62 \pm 0.16) \times 10^3$ dm^3 mol^{-1} s^{-1}, which is comparable with the k_q^O values determined [33] in perfluoro-decalin (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}), and is slightly higher than the value obtained by us [44] of 1.2×10^3 dm^3 mol^{-1} s^{-1} for quenching in supercritical fluid xenon at 14.7 MPa and 308 K. Hence we can conclude on the basis of this data that quenching of singlet oxygen by ground state oxygen in these systems shows very little dependence on the identity of the solvent.

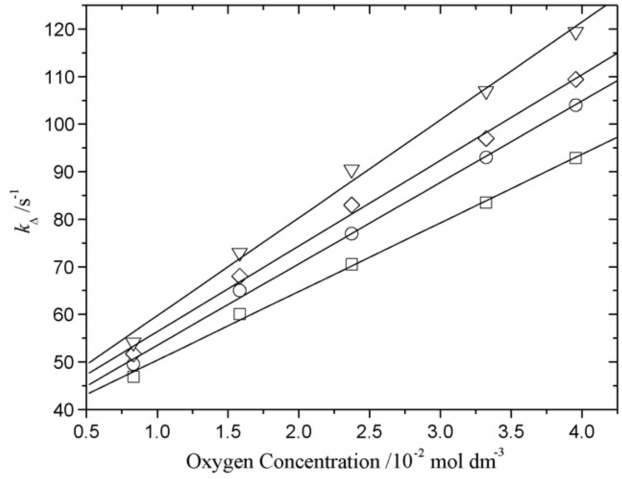

Fig. 1. Dependence of the rate constant, k_Δ, for the decay of singlet oxygen, O$_2$($^1\Delta_g$), in supercritical fluid xenon at 308 K at: 7.84 (□); 12.25 (◯); 17.15 (◇); 24.5 (▽) MPa.

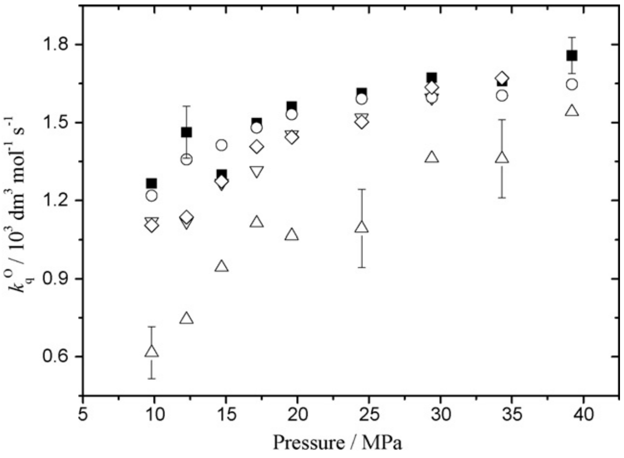

Fig. 2. Quenching constant for quenching of singlet oxygen by ground state oxygen k_q^O as a function of temperature and pressure in SCF-Xe: 25 °C (■); 35 °C (▽); 50 °C (◯); 60 °C (◇); 82 °C (▲).

In a previous publication [44], we used an approximation in the calculation of activation volumes (*vide infra*) that the contribution of oxygen quenching to the overall deactivation rate constant of singlet oxygen in supercritical fluid xenon was a constant fraction of 15%. We have now measured in detail the effect of both temperature and pressure on the oxygen-quenching rate constant in supercritical fluid xenon, the results of which are summarized in Fig. 2. As can clearly be seen, the rate constant for quenching by oxygen increases with increasing pressure, and decreases with increasing temperature. Note that the data from which the quenching constants have been calculated have been corrected for the different oxygen concentrations at the different temperatures used. Using this data, we have now assessed the contribution of the ground state oxygen-quenching rate constant as a function of temperature and pressure to the overall singlet oxygen deactivation rate constant, which we have now also measured over a wide range of temperature and pressure. These results are summarized in Fig. 3. As can be seen, the approximation of a constant fraction is valid to within 5% at lower temperatures, although the average value is slightly higher than our previous estimate of 15%; *N.B.*: the contribution is significantly less at 82 °C. There is clearly a systematic change in the contribution of oxygen quenching with both increasing temperature and, to a lesser extent, pressure. Also, the fractional contribution of the oxygen quenching to the overall singlet oxygen decay rate increases with increasing pressure, and decreases with increasing temperature. The actual contribution of ground state oxygen quenching to the overall observed rate determined here can therefore be used to extract the real quenching rate constant by xenon at each temperature and pressure.

In terms of the quenching mechanism, the fact that the rate of collisional quenching of the singlet oxygen by ground state oxygen shows an increase with increasing pressure can be interpreted in terms of the formation of an encounter or collision complex, the dissociative and associative steps showing different pressure dependences [50]. The overall rate constant

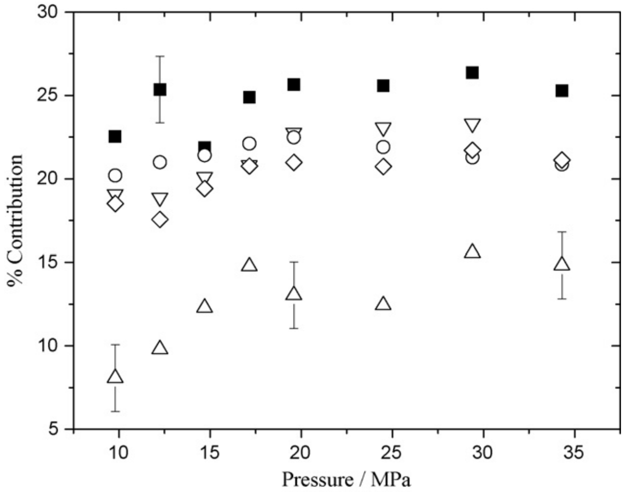

Fig. 3. Contribution of oxygen quenching to the overall deactivation rate of singlet oxygen in supercritical fluid xenon as function of pressure at temperatures: 25 °C (■); 35 °C (▽); 50 °C (◯); 60 °C (◇); 82 °C (▲).

for the spin-allowed reaction out of the encounter complex to give ground state products is less than the rate of dissociation of the encounter complex back to reactants, and any perturbation of the equilibrium constant will therefore have an effect on the observed rate constant. Under these pre-equilibrium conditions, the observed quenching rate constant will be, as seen experimentally, much less than diffusion controlled.

$$^1O_2^* + {}^3O_2 \underset{k_{-\text{diff}}}{\overset{k_{\text{diff}}}{\rightleftharpoons}} {}^3(O_2\cdots O_2)^* \xrightarrow{k_f} {}^3O_2 + {}^3O_2$$

Application of the steady state approximation leads to the following expression for the rate constant, k_q^O:

$$k_q^O = \frac{k_{\text{diff}}k_f}{k_{-\text{diff}} + k_f} \tag{3}$$

Under conditions where the dissociation constant is much larger than the reaction rate from the encounter complex, the overall rate constant observed will be the product of the equilibrium constant and the forward rate constant out of the encounter complex; i.e., $k_q^O = k_{\text{diff}}\,k_f/k_{-\text{diff}}$. The observed pressure dependence on the oxygen-quenching rate constant may suggest a negative reaction volume associated with the encounter complex formation, although this parameter has not been calculated in this work since more accurate values for the pressure and temperature dependence of k_q^O are required to avoid large errors in the extracted parameters; this is the subject of current study. Such a differential pressure dependence of the associative and dissociative steps also explains the relatively greater contribution of oxygen quenching as a proportion of the overall deactivation rate at higher pressures, where the rate of oxygen quenching is enhanced relative to that by the solvent as a result of this pressure dependence.

The observed temperature dependence can similarly be explained on the basis of this pre-equilibrium model, where an exothermic collision complex formation step would act to retard the quenching reaction as the temperature is increased, even though the collision rate may be expected to increase. Similar negative correlations between quenching rate and temperature have been observed for oxygen quenching of organic species, and have been ascribed as arising due to the formation of an intermediate (exciplex) with a finite binding energy [51–54].

3.2. *Activation volumes in supercritical fluid xenon and carbon dioxide*

In a recent publication [42], we showed that data regarding the pressure dependence of the singlet oxygen deactivation rate constant could be used, utilising activated complex theory, to determine volumes of activation. Having determined the oxygen-quenching rate constants as a function of temperature and pressure, it is possible to separate out the contribution of oxygen quenching, $k_q^O[O_2]$ in Eq. (1), from the overall decay rate. Then since k_p and $k_q^S[S]$ are negligible under these conditions (*vide supra*), the observed singlet oxygen decay rate $k_\Delta = k_q^X[X]$. Hence to calculate the value of k_q^X, the value of k_Δ, corrected for the contribution of oxygen quenching, is divided by the bulk concentration of solvent determined from the density calculated in the case of xenon by interpolation of the data collected by Sifner and Klomfar [55], or in the case of carbon dioxide from the equation of state given by Ely et al. [56].

As discussed in Ref. [57], the mechanism for quenching of $O_2^*(a^1\Delta_g)$ by xenon may be written as

$$^1O_2^* + \text{Xe} \underset{k_{-\text{diff}}}{\overset{k_{\text{diff}}}{\rightleftharpoons}} {}^1(O_2\cdots\text{Xe}) \xrightarrow{k_{\text{isc}}} {}^3(O_2\cdots\text{Xe}) \rightarrow {}^3O_2 + \text{Xe}$$

Based on this scheme, the rate constant for the quenching of $O_2^*(^1\Delta_g)$ by xenon is given by

$$k_q^{\text{Xe}} = \frac{k_{\text{diff}}k_{\text{isc}}}{k_{-\text{diff}} + k_{\text{isc}}} \tag{4}$$

For this reaction $k_{-\text{diff}} \gg k_{\text{isc}}$, i.e., the observed kinetics are dominated by the pre-equilibrium and the quenching rate is seen as less than diffusion controlled. Therefore,

$$k_q^{\text{Xe}} = \frac{k_{\text{diff}}}{k_{-\text{diff}}}k_{\text{isc}} = K_{\text{diff}}k_{\text{isc}} \tag{5}$$

where K_{diff} is the equilibrium constant of contact complex formation [58].

As we have shown [44], it is necessary to consider the fluid as a hard-sphere fluid rather than taking a classical continuum approach. K_{diff} is proportional to $g(\sigma_{\text{OX}})$, the radial distribution function at closest approach of $O_2^*(a^1\Delta_g)$ and Xe which is given by Yoshimura and Nakahara [59] as

$$g(\sigma_{\text{OX}}) = \frac{1}{1-\eta} + \frac{3\sigma_O\eta}{2\sigma_{\text{OX}}(1-\eta)^2} + \frac{\sigma_O^2\eta^2}{2\sigma_{\text{OX}}^2(1-\eta)^3} \tag{6}$$

where $\eta = \pi\sigma_x^3 N/6V_m$ is the packing fraction of the solvent, σ_O and σ_X are the hard-sphere diameters of $O_2^*(a^1\Delta_g)$ and of Xe, taken as 0.346 and 0.432 nm, respectively [57] and $2\sigma_{\text{OX}} = (\sigma_O + \sigma_X)$. The pressure and temperature dependence of the oxygen-quenching rate constant is qualitatively reproduced by the behaviour of the radial distribution function [59] at the

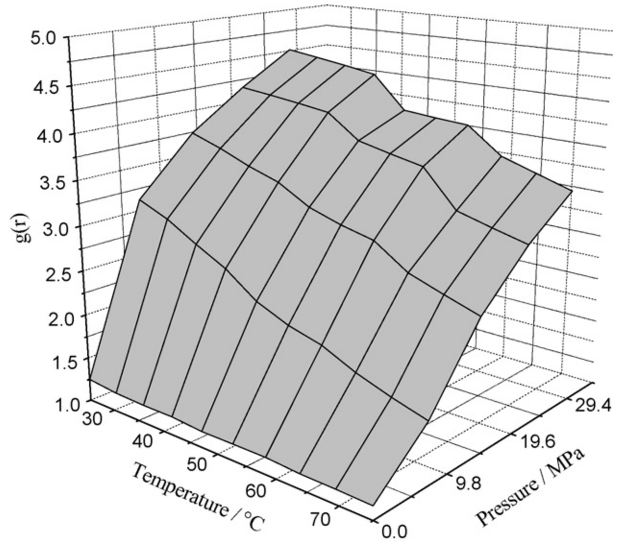

Fig. 4. Temperature and pressure dependence of the radial distribution function $g(\sigma_{\mathrm{OX}})$ on temperature and pressure in supercritical fluid xenon.

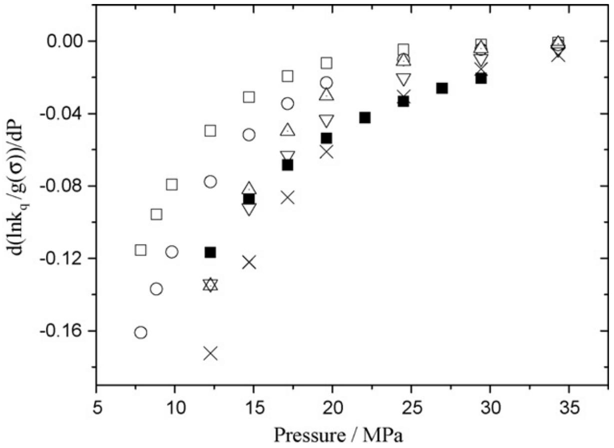

Fig. 5. Comparison of observed activation volumes in supercritical fluid carbon dioxide and xenon; Xe 25 °C (□); Xe 35 °C (○); Xe 50 °C (△); Xe 60 °C (▽); Xe 82 °C (×); CO_2 41 °C (■).

collision radius between oxygen and xenon, which is a measure of the molecular packing and hence of the constraints on the volume change and is shown in Fig. 4. Where a hard-sphere molecule of diameter σ_A and a hard-sphere molecule of diameter σ_B form a contact complex, statistically the number of contact complexes can be expressed in terms of the radial distribution function. The radial distribution function is an explicit function of the solvent packing fraction and the driving force for molecular association is the many-body and cooperative pushing effect of the surrounding solvent molecules, i.e., it cannot be accounted for in a dielectric continuum model.

The pressure dependence of K_{diff} can be described as

$$\left(\frac{\partial \ln K_{\mathrm{diff}}}{\partial P}\right)_{\mathrm{T}} = \frac{-\Delta V_{\mathrm{en}}}{RT} - \kappa \tag{7}$$

where ΔV_{en} is the change in volume associated with the encounter complex formation and κ equal to the isothermal compressibility of the solvent, defined as $-\partial \ln(V_{\mathrm{m}})/\partial P$. It, therefore, follows that the pressure dependence of $k_{\mathrm{q}}^{\mathrm{Xe}}$ is given by

$$\left(\frac{\partial \ln k_{\mathrm{q}}^{\mathrm{Xe}}}{\partial P}\right)_{\mathrm{T}} = \frac{-\Delta V_{\mathrm{en}}}{RT} - \frac{\Delta V_{\mathrm{isc}}}{RT} - \kappa \tag{8}$$

The reaction volume associated with a hard-sphere encounter complex formation can be described as [59]

$$\Delta V_{\mathrm{en}}^{\mathrm{HS}} = -RT\left(\frac{\partial \ln g(\sigma_{\mathrm{ox}})}{\partial P}\right)_{\mathrm{T}} - \kappa RT \tag{9}$$

and therefore:

$$\left(\frac{\partial \ln(k_{\mathrm{q}}^{\mathrm{Xe}}/g(\sigma_{\mathrm{OX}}))}{\partial P}\right)_{\mathrm{T}} = \frac{-\Delta V_{\mathrm{en}} + \Delta V_{\mathrm{en}}^{\mathrm{HS}}}{RT} - \frac{\Delta V_{\mathrm{isc}}}{RT} = \frac{\Delta V_{\mathrm{c}}^{\neq}}{RT} \tag{10}$$

where $\Delta V_{\mathrm{en}}^{\mathrm{HS}}$ is the change in volume associated with hard-sphere contact complex formation; ΔV_{isc} the activation volume associated with the intersystem crossing from $^1(O_2\ldots Xe)$ to $^3(O_2\ldots Xe)$; $\Delta V_{\mathrm{c}}^{\#}$ is the observed reaction volume. On the basis that ΔV_{isc} is small [57,60], then according to Eqs. (8)–(10) if the pressure dependence of $k_{\mathrm{q}}^{\mathrm{Xe}}$ is equal to that of $g(\sigma_{\mathrm{OX}})$ then ΔV_{en} is equal to $\Delta V_{\mathrm{en}}^{\mathrm{HS}}$ and $\Delta V_{\mathrm{c}}^{\#}$ is approximately zero. Therefore, if the hard-sphere model applies, then $\partial(\ln k_{\mathrm{q}}^{\mathrm{Xe}}/g(\sigma_{\mathrm{OX}}))/\partial P)_{\mathrm{T}}$ is expected to be small and approximately equal to $-\Delta V_{\mathrm{isc}}$.

In applying the same theoretical treatment to quenching of singlet oxygen by carbon dioxide in supercritical fluid carbon dioxide, we have followed others [43,61] in using the work of Bondi [62] to calculate a hard-sphere diameter for CO_2 of 0.402 nm. In the case of CO_2, the intersystem crossing in the encounter complex is followed by electronic-to-vibrational energy transfer with, according to the theoretical treatment of Schmidt and Afshari [34] applied by us in Ref. [44], 76% of the electronic energy ending up as vibrational energy in the CO_2 with the remainder resulting in ground-state vibrational excitation in oxygen with some off-resonance energy taken up as translational energy. In the case of xenon, having no receiving vibrational modes, the excess energy partitions between vibrational modes on ground state oxygen and translational energy in the xenon.

Results are shown in Fig. 5. Here it can be clearly seen that the measured volume of activation decreases in magnitude with increasing pressure, and shows a small but systematic decrease with decreasing temperature, particularly at lower pressures. This temperature dependence emerges from the data once the temperature dependence of the radial distribution function and oxygen-quenching rates have been accounted for, and therefore represent a genuine temperature dependence of the activation volume. Such a diminution of activation volume with increasing temperature and pressure has been described previously for thermal ring closure reactions of $W(CO)_5$(Phen) [63], where this effect is ascribed mainly to the temperature and pressure dependence of the isothermal compressibility, which magnifies the effects due to attractive and repulsive solvent interactions. Therefore we may expect larger values where the isothermal compressibility is larger. In a similar study to ours by Okamoto et al. in supercritical fluid CO_2 [43], activation volumes were determined without correcting for the radial distribution function, and large negative volumes of activation were obtained. However, these authors did not take any account of the quenching of singlet oxygen by ground state oxygen in this calculation. They calculated that their determined activiation volumes were nearly equal to the hard-sphere activation volumes given by the pressure dependence of the radial distribution function; however, the errors associated with their calculated values were relatively large, and based on a single point determination. In our treatment, we account for this pressure dependence in the determination of the reaction volumes.

From inspection of the data presented in Fig. 5, there are clearly non-zero values for the measured reaction volumes, which vary systematically with pressure and temperature and which are more pronounced at higher temperatures and lower pressures. This clearly suggests that either (a) the pressure dependence of k_q^{Xe} is not equal to that of $g(\sigma_{OX})$ or (b) that ΔV_{isc} has a finite value and that this shows a pressure and temperature dependence. Fig. 5 suggests that if (b) is the case, then ΔV_{isc} has a small positive value at lower pressures. Positive activation volumes in this context can be ascribed to a greater perturbation to the solvent packing fraction as a result of intersystem crossing in the contact complex as compared to initially formed encounter complex [58]. However, a perhaps more attractive explanation is given in (a) above, which may arise due to the hard-sphere approximation not being an accurate description of the system, particularly where the compressibility is large. Such a deviation from hard-sphere behaviour may be ascribable to specific solvent–solute interactions, which perturb the distribution of solvent molecules, which would be expected to be more pronounced near to the critical point where, as discussed in Section 1, solvent clustering has been observed by a variety of methods. The pressure dependence of the radial distribution function leads then to the change in volume associated with hard-sphere contact complex formation, ΔV_{en}^{HS}, being an overestimate of ΔV_{en}, which may be rationalised on the basis of attractive solvent–solute interaction leading to a greater solvent packing than the radial distribution function suggests.

This hypothesis is supported by inspection of the data in supercritical fluid carbon dioxide, also shown in Fig. 5. Here, a similar dependence is seen as in the case of xenon, except the measured activation volumes are apparently larger than at the corresponding temperature and pressure in xenon; here, this does not arise from the temperature and pressure dependence of the radial distribution functions since these are taken into account. If we assume, as others have done (*vide supra*) that the work of Bondi provides an accurate basis for calculating the radial distribution functions, then this leads to the conclusion that in the case of carbon dioxide ΔV_{en}^{HS} is a greater overestimate of ΔV_{en} than in the case of xenon, suggestive of greater specific solvent–solute interactions in the case of carbon dioxide relative to xenon. In both cases, far from the critical point where the packing fraction is large and the compressibility is small, these specific effects have less of an influence on the solvent packing and consequently the hard-sphere treatment becomes a better approximation to the system and ΔV_{en}^{HS} becomes a better estimate of ΔV_{en}.

4. Conclusions

We have shown that for singlet oxygen produced in both supercritical fluid xenon and carbon dioxide, solvent mediated deactivation plays a dominant role in determining the observed lifetime. The quenching kinetics are shown to involve a pre-equilibrium, the rates of deactivation being much less than would be expected were the reaction diffusion controlled. In previous publications [42,44], we showed the quenching of singlet oxygen by ground state oxygen was a significant component of the overall observed deactivation rate. In this paper, we have shown that oxygen-quenching rate constants are a function of fluid properties, and the proportion of the total deactivation rate attributable to oxygen quenching is itself a function of temperature and pressure. This dependence is interpreted as arising from perturbation of the initially formed encounter complex in the quenching process. The volume of activation associated with quenching by the solvent was found to decrease with increasing pressure, and shows a small but systematic decrease with decreasing temperature, particularly at lower pressures. The volumes associated with the quenching process calculated for carbon dioxide and xenon supercritical fluids, corrected for the effects of the radial distribution functions, are comparable although demonstrate that ΔV_{en}^{HS} is not equal to ΔV_{en}, particularly near the critical point. This observation can be rationalised on the basis of the presence of specific solvent–solute interactions, which are not taken account of in the hard-sphere model.

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