

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

Ayman A. Abdel-Shafi^{a,*}, David R. Worrall^{b,**}

^a Department of Chemistry, Faculty of Science, Ain Shams University, Abbassia, 11566 Cairo, Egypt

^b Chemistry Department, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK

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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 $(1.27 \text{ to } 1.76) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ 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 $1.54 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ 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.

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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 $130 \pm 10 \text{ ns}$. Deactivation of $O_2^*(a^1\Delta_g)$ on the other hand, is a spin-forbidden process with lifetimes for this state of $3.1 \mu\text{s}$ in water [32] and 79 ms in CS_2 with oxygen concentrations $\leq 10^{-5} \text{ mol dm}^{-3}$ [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

* Corresponding author. Present address: Faculty of Science, King Faisal University, Al Hufuf 31982, Al Hassa, Saudi Arabia.

** Corresponding author. Tel.: +44 1509 222567; fax: +44 1509 223925.

E-mail addresses: aaashafi@yahoo.com (A.A. Abdel-Shafi), d.r.worrall@lboro.ac.uk (D.R. Worrall).

[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 cm³) to achieve a pressure of >50 bar at 268 K, then either the xenon or CO₂ (BOC, 58 bar) is liquefied by chilling to –5 °C. The resulting liquid Xe or CO₂ 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 CO₂ can be formulated in terms of a number of contributions: i.e.,

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

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=CO₂), k_q^O represents quenching by ground state molecular oxygen (O₂) 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 $46.8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ 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 CS₂. Changes in the phenazine concentration from 2 to $10 \times 10^{-5} \text{ mol dm}^{-3}$ had a negligible effect on the observed rate of decay of $O_2^*(a^1\Delta_g)$ in SCF-Xe or in SCF-CO₂, 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 CS₂ [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 sensitizer 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

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