

THE MECHANISM OF QUENCHING OF SINGLET OXYGEN $O_2^*(^1\Delta_g)$ BY MOLECULAR IODINE[†]

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Summary

The pseudo-first-order constants for the decay of singlet oxygen $O_2^*(^1\Delta_g)$ in aerated benzene have been measured from a kinetic analysis of the disappearance of a small proportion of a fixed concentration of the singlet oxygen acceptor, diphenylisobenzofuran, following nanosecond laser photolysis to produce singlet oxygen via the sensitizer, triplet anthracene, in the absence and presence of increasing concentrations of iodine. Iodine is shown to give rise to a non-linear quenching of singlet oxygen with the quenching constant at low concentrations being $(1.4 \pm 0.2) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ whilst at higher concentrations of iodine (about $10^{-4} \text{ mol dm}^{-3}$) quenching levels off. It is suggested that quenching of singlet oxygen by iodine is due to endothermic electronic energy transfer to produce a triplet state of iodine with an estimated energy corresponding to $8500 \pm 500 \text{ cm}^{-1}$ and that the non-linear quenching is consistent with dissociative quenching by a second iodine molecule of a complex of $O_2^*(^1\Delta_g)$ and molecular iodine which at low concentrations leads to efficient quenching.

1. Introduction

There has been considerable recent interest in the kinetics of energy transfer processes which occur in gas phase mixtures containing excited molecular oxygen and iodine partly stimulated by the development of the chemically pumped atomic iodine laser [1]. In contrast, in dilute solution, although quenching of excited singlet oxygen $O_2^*(^1\Delta_g)$ by some alkyl iodides [2, 3] and the iodide ion [3 - 5] has been investigated, quenching by molecular iodine has not previously been reported [6] despite the fact that molecular iodine quenches excited triplet [7] and singlet states [8] of aromatic hydrocarbons with high efficiency. We report here our attempts to

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investigate quenching of excited singlet oxygen by molecular iodine in benzene solution.

2. Experimental details

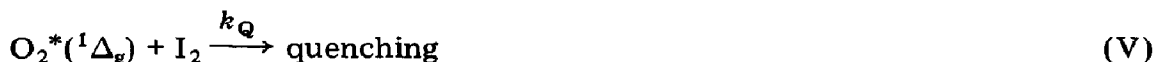
Laser flash photolysis studies were carried out using a frequency-doubled *Q*-switched ruby laser which gives a pulse of about 25 mJ at 347 nm with a half-peak duration of 25 ns as the excitation source. Transient absorption within a quartz spectroscopic cell 10 mm × 10 mm was monitored at right angles to the unfocused excitation pulse using part of the light from the laser pumping flash-lamp as the analysing light source. The analysis wavelength was selected using a Bausch and Lomb grating monochromator with an RCA 931 A photomultiplier at its exit slit. The output of the photomultiplier was displayed on a Tektronix 585 A oscilloscope triggered by a 2 V pulse from a photodiode activated by the red laser light following the operation of the passive *Q* switch. The complete apparatus has been described in detail previously [9]. The oscilloscope traces were recorded photographically on Kodak RX-120 film and kinetic analysis of these decay traces gave rate constants for repeated events which agreed to within 5%.

Absorption spectra were measured on a Perkin-Elmer EPS-3T spectrophotometer and emission spectra and intensity measurements were made using a Farrand mark I spectrofluorometer. Anthracene was Hopkins and Williams microanalytical reagent and 1,3-diphenylisobenzofuran (DPBF) was from the Aldrich Chemical Co. Ltd. and was recrystallized from ethanol. BDH all-*trans*- β -carotene was recrystallized from benzene-methanol. Benzene BDH AnalaR reagent was purified according to the procedure outlined by Vogel [10].

3. Results

Let us consider the following mechanism for the production and decay of singlet oxygen:





where S and A represent the singlet oxygen sensitizer (anthracene) and acceptor (DPBF) respectively. In this work excitation was with a 25 ns laser pulse and $k_T[\text{O}_2]$ in aerated benzene solution was measured from the decay of triplet anthracene alone in aerated benzene solutions as $(5.0 \pm 0.5) \times 10^6 \text{ s}^{-1}$. Thus steps (I) and (II) are more than 99% complete after 1 μs . Thus according to this mechanism for times of more than 1 μs the singlet oxygen concentration is given by

$$[^1\text{O}_2^*] = [^1\text{O}_2^*]_0 \exp\left\{-\left(k_d t + k_Q[\text{Q}]t + \int_0^t k_A^r[\text{A}] dt\right)\right\} \quad (1)$$

where k_A^r represents the rate constant for reactive quenching by DPBF, and

$$-\frac{d[\text{A}]}{dt} = k_A^r[\text{A}][^1\text{O}_2^*] \quad (2)$$

Following the approach of Merkel and Kearns [11] for analysing these equations which has been shown to give the same answers within experimental error ($\pm 5\%$) as more rigorous approaches [9, 12] we replace

$$\int_0^t k_A^r[\text{A}] dt$$

in eqn. (1) by $k_A^r[\text{A}]_{\text{av}}$ and since [A] changes by about 10% this introduces little error; thus eqn. (1) becomes

$$\begin{aligned} [^1\text{O}_2^*] &= [^1\text{O}_2^*]_0 \exp\{-(k_d + k_A[\text{A}]_{\text{av}} + k_Q[\text{Q}])t\} \\ &\equiv [^1\text{O}_2^*]_0 \exp(-k_D t) \end{aligned} \quad (3)$$

where

$$k_D = k_d + k_A[\text{A}]_{\text{av}} + k_Q[\text{Q}] \quad (4)$$

Substitution of $[\text{A}] = [\text{A}]_{\text{av}}$ and eqn. (3) into (2) gives

$$\Delta[\text{A}] = \frac{k_A^r[\text{A}]_{\text{av}}[^1\text{O}_2^*]_0}{k_D} \exp(-k_D t) \quad (5)$$

where $\Delta[\text{A}]$ is the change in the concentration of A (DPBF) at times greater than 1 μs . $\Delta[\text{A}]$ is directly proportional to ΔA the measured change in absorbance by DPBF in the laser flash photolysis experiments. Plots of $\ln \Delta A$ versus t are linear yielding values of k_D . Keeping [A] constant and measuring k_D as a function of increasing concentration of a quencher Q allows values of k_Q to be determined. Figure 1 shows a plot of the change in k_D , obtained in this way for aerated benzene solution, versus [Q] for the singlet oxygen quencher β -carotene which quenches by the mechanism of electronic energy transfer [13]. The concentration of the sensitizer

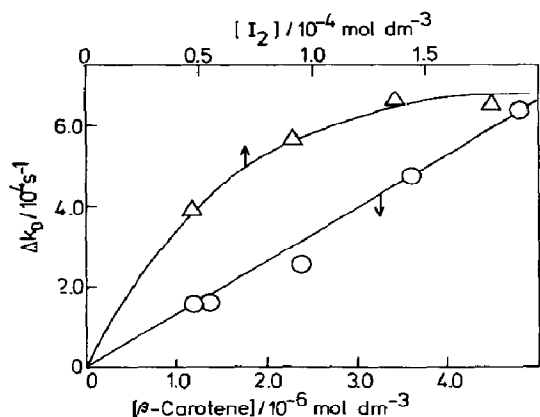


Fig. 1. Quenching plots showing the change Δk_D in the singlet oxygen decay constant in benzene solution as a function of the quencher concentration for β -carotene and molecular iodine.

anthracene was $3 \times 10^{-4} \text{ mol dm}^{-3}$ and $[\text{DPBF}]_0 = 3.5 \times 10^{-5} \text{ mol dm}^{-3}$ throughout. The slope of this plot gives a value for the quenching of singlet oxygen by β -carotene of $(1.4 \pm 0.2) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. In contrast with the results with β -carotene as quencher, a plot of Δk_D versus $[\text{I}_2]$ in aerated benzene solution with identical conditions for the sensitizer and DPBF gives the curve shown in Fig. 1. The initial slope of the curve given in Fig. 1 gives a quenching constant for molecular iodine of $1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ or more at low concentrations.

Absorption spectra of mixtures of DPBF, the sensitizer and the quenchers were within experimental error equal to those expected from the superimposition of the spectra of the separate components. Laser photolysis of concentrated solutions of molecular iodine alone in benzene gave the well-characterized [14] transient ($\dot{\text{I}}$ -solvent) as a weak transient absorption. However, in the presence of the sensitizer anthracene even at the highest concentration of iodine used in these studies (namely $1.8 \times 10^{-4} \text{ mol dm}^{-3}$) the portion of the exciting light absorbed by molecular iodine was negligible.

We have measured the rate constants for quenching of triplet phenanthrene and anthracene by iodine in benzene solution with our equipment and obtained values of $(1.4 \pm 0.1) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in each case. Porter and Wilkinson [7] report a value of $(1.4 \pm 0.6) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for quenching of triplet phenanthrene in hexane. Their reported value of $2.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for quenching of triplet anthracene by iodine was later shown to be erroneous because of complications due to iodine photolysis and a revised value for this constant of more than $3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ can be derived from their data.

4. Discussion

The results for quenching by iodine presented here may be considered as presenting two problems, firstly the mechanism of quenching by iodine at

low concentrations where $k_Q \geq 1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and secondly why the quenching effect levels off at higher iodine concentrations. As far as the mechanism of quenching is concerned we may consider the following: (a) heavy atom quenching; (b) charge transfer quenching; (c) energy transfer.

Heavy atom quenching is most unlikely since the rate constant for quenching of singlet oxygen by iodoethane is only $2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [2]. Quenching by iodide ions is also considerably less efficient than that for iodine found here (see refs. 3 - 5).

The rate constants for iodine quenching of the triplet states of nine organic molecules show little or no correlation with the ionization potentials or electron affinities of the triplet states being quenched but show a correlation with triplet energy [15] as would be expected if the mechanism of quenching is due to electronic energy transfer as was suggested by Porter and Wilkinson [7] who first observed quenching of triplet states by iodine. Figure 2 gives the gas phase energy levels of interest adapted from ref. 1. The precise energy levels for iodine in the complexing solvent benzene [16] are questionable. The rate constant for quenching of triplet anthracene by molecular iodine of $1.4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is consistent with essentially diffusion-controlled quenching as expected for exothermic triplet-triplet energy transfer. A rate constant of $1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ or more as observed for iodine quenching of singlet oxygen at low iodine concentrations is consistent with endothermic energy transfer to an accepting triplet level with an energy level corresponding to $8500 \pm 500 \text{ cm}^{-1}$. The accepting level is probably the ${}^3\Pi_{2u}$ state of iodine but unfortunately we do not have direct evidence for the sensitized production of this state.

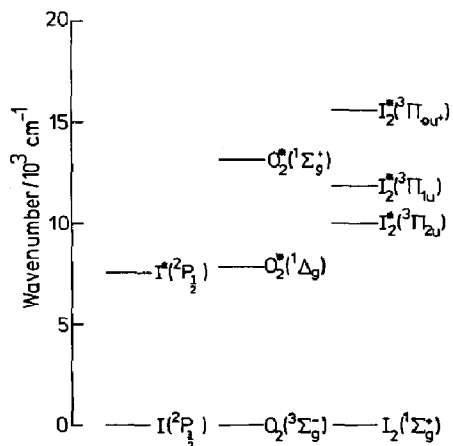
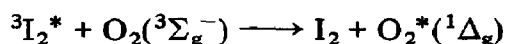


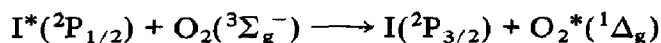
Fig. 2. Low-lying energy levels of iodine and oxygen.

Olmsted and Karal [17] have reported that IR excitation of iodine in hexane solution sensitizes the production of $O_2^*(1\Delta_g)$ which they explain by the reaction



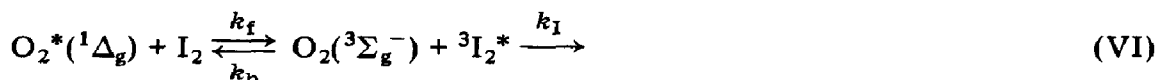
For such a reaction to take place under the conditions they used, the lifetime of $^3\text{I}_2^*$ would have to be 10^{-5} s or more. We therefore subjected aerated benzene solutions containing 10^{-3} mol dm^{-3} of molecular iodine and 5×10^{-5} mol dm^{-3} of DPBF to laser photolysis at 694 nm but we found no detectable photo-oxygenation of the DPBF. We have also been unable to detect any transient absorption changes which we can associate with a long-lived $^3\text{I}_2^*$.

If in any of these studies excited iodine atoms are produced then the process

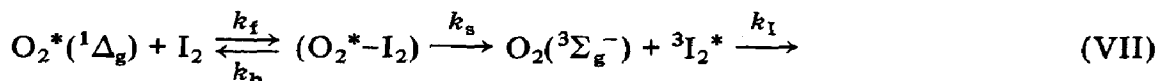


may occur. In the gas phase this reaction occurs at almost every collision [1]. It is possible that some such reaction could explain the findings of Olmsted and Karal [17]. The close proximity of the energies of $\text{I}^*(^2\text{P}_{3/2})$ and $\text{O}_2(^1\Delta_g)$, see Fig. 2, could mean that the reaction shown above is reversible and could result in a mechanism for quenching of singlet oxygen in the presence of iodine atoms. In this work the concentration of iodine used in the quenching experiments was restricted to minimize the production of iodine atoms due to direct excitation of molecular iodine.

Figure 1 shows that once the concentration of iodine is greater than 10^{-4} mol dm^{-3} a further increase in iodine concentration leads to no further increase in the decay of singlet oxygen. Writing step (V) as a reversible reaction, *i.e.*



does not explain the curve shown in Fig. 1, since this simply requires $k_Q = k_f k_I / (k_b + k_I)$, *i.e.* k_Q is a composite second-order constant. What is needed is a mechanism in which iodine inhibits its own quenching. For example, we can propose that singlet oxygen forms a complex with molecular iodine which leads either to quenching or to an iodine-catalysed dissociation to give back singlet oxygen. Thus we can replace step (V) by the further steps



Applying the steady state approximation to the complex gives

$$[(\text{O}_2^*-\text{I}_2)] = \frac{k_f [^1\text{O}_2^*] [\text{I}_2]}{k_b + k_s + k_{QC} [\text{I}_2]} \quad (6)$$

Consideration of steps (III) and (IV) with (VII) and (VIII) after 1 μs gives

$$-\frac{d \ln[^1\text{O}_2^*]}{dt} = k_d + k_A [A]_{\text{av}} + k_f [\text{I}_2] \left(1 - \frac{k_b}{k_b + k_s + k_{QC} [\text{I}_2]} \right)$$

or

$$k_D = k_D^0 + \frac{k_f[I_2](k_s + k_{QC}[I_2])}{k_b + k_s + k_{QC}[I_2]} \quad (7)$$

where k_D^0 is the decay constant in the absence of quencher. Rearrangement putting $\Delta k_D = k_D - k_D^0$ gives

$$\frac{1}{\Delta k_D} = \frac{k_b + k_s}{k_f k_s [I_2]} + \frac{k_{QC}}{k_f k_s} \quad (8)$$

Figure 3 shows that a plot of Δk_D^{-1} versus $[I_2]^{-1}$ is a straight line (within experimental error). According to eqn. (8)

$$(\text{slope})^{-1} = \frac{k_f k_s}{k_b + k_s}$$

which is equal to the net quenching constant when $[I_2] \rightarrow 0$. From Fig. 3 the initial quenching constant is $(1.4 \pm 0.2) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and

$$\begin{aligned} \frac{\text{intercept}}{\text{slope}} &= \frac{k_{QC}}{k_b + k_s} \\ &= (1.5 \pm 0.5) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \end{aligned}$$

Taking the maximum value for k_{QC} as $3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ it follows that $(k_b + k_s)^{-1} \geq 0.5 \mu\text{s}$. This is quite a long lifetime for such a complex and, as mentioned earlier, we have no direct evidence for such a relatively long-lived species although it is unlikely that such a complex would absorb strongly in the regions we are able to study.

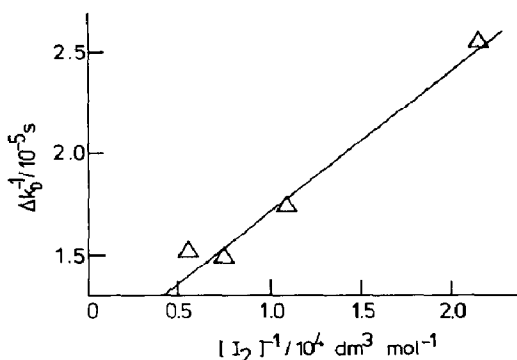


Fig. 3. Plot showing the inverse $1/\Delta k_D$ of the change in the singlet oxygen decay constant in benzene solution vs. the inverse of the iodine concentration.

5. Conclusions

Molecular iodine has been shown to quench singlet oxygen $O_2^*(^1\Delta_g)$ in benzene solution with high efficiency, *i.e.* with $k_Q = (1.4 \pm 0.2) \times 10^9 \text{ dm}^3$

$\text{mol}^{-1} \text{s}^{-1}$ at low molecular iodine concentrations. This is consistent with endothermic electronic energy transfer to form a triplet state of iodine, with an estimated energy of $8500 \pm 500 \text{ cm}^{-1}$, as the quenching mechanism. At higher molecular iodine concentrations the quenching effect levels off. A possible mechanism, in which an iodine-(singlet oxygen) complex which leads to quenching at low molecular iodine concentrations is intercepted at high molecular iodine concentrations by a second iodine molecule which catalyses the dissociation of this complex to give back unquenched singlet oxygen, is shown to be consistent with the results obtained.

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