POSSIBLE FORMATION OF SINGLET OXYGEN FROM VIBRATIONALLY EXCITED WATER[†]

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Summary

Tryptophan decomposition is observed in aerated aqueous solutions and in solutions under 10 MPa oxygen, on irradiation at 990 nm and at 1.06 μm. The decomposition at 990 nm and in the aerated solution at 1.06 μm is greater in H_2O than in D_2O. This is attributed to the formation of singlet oxygen on energy transfer from vibrationally excited water. However, the decomposition of the solution under 10 MPa oxygen at 1.06 μm is greater in D_2O than in H_2O because of the direct optical excitation of oxygen to singlet oxygen.

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1. Introduction

Observations of optical transitions from the triplet ground state of oxygen ($^3\Sigma_g^-$) to the two low-lying singlet states ($^1\Delta_g$ and $^1\Sigma_g^+$) have been reported by several workers [1 - 9]. Enhanced optical absorption by oxygen at high concentrations (*e.g.* under high pressures, 15 MPa or less) has been used by several workers to produce singlet oxygen for time-resolved and steady state reactions in halocarbon solvents and water [10 - 20].

In solutions in Freon-113 and carbon tetrachloride, the intensities of the various visible and IR absorption bands of oxygen are greater than those in gaseous oxygen [21]. However, in aqueous solutions, only the $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ transition at 762 nm is observed [21]. The other bands in the visible region are not observed and the two bands in the IR region ($^1\Delta_{g+v}$ and $^1\Delta_g$ at 1066 and 1266 nm) are masked by the strong absorption by water in this region [22]. Our results on tryptophan (TRP) solutions [18, 19], where the solutions under high pressures of oxygen were exposed to visible and IR radiation, can be explained by the initial formation of $O_2(^1\Sigma_g^+)$ by absorption at 762 nm, followed by its conversion to $O_2(^1\Delta_g)$ [23, 24]. However, formation of singlet oxygen is suggested on exposure of solutions in D_2O, under high

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pressures of oxygen, to an Nd–YAG laser (1.06 μm) [13, 25, 26]; at this wavelength, absorption by oxygen in these solutions is too small to be measured.

The present investigation was undertaken to clarify the mechanisms of formation of singlet oxygen in aqueous solutions under high pressures of oxygen (15 MPa or less), on exposure to IR radiation. In particular, the work was aimed at investigating the possibility that vibrationally excited water at $\lambda \leqslant 1266$ nm [22] produces singlet oxygen by energy transfer to oxygen.

2. Experimental details

The materials and methods used have been described [17 - 19]. TRP was purified by passing a 10^{-1} mol dm^{-3} solution in water through a Whatman M.9 Partisil 10 ODS preparative high performance liquid chromatography (HPLC) column (25 cm; inside diameter, 9.4 mm). The TRP peak was separated and the solvent was evaporated in the dark under partial vacuum. The purified TRP was stored in the dark in a refrigerator. Heavy water (99.76% D_2O supplied by Chalk River Nuclear Laboratories) was distilled before use.

To reduce the elution time, only one analytical HPLC column (LiChrosorb RP 18; 7μ; Unimetric–Knauer) was used in the present studies. The yield of N-formylkynurenine (FK) was taken as a measure of the TRP decomposition. The irradiations were done with a 1600 W xenon arc lamp [19] (dose rate, 6.5×10^{-3} J s^{-1} at 990 nm with Corning 0-51 + Corion SS-99-00-2 filters between the lamp and the sample), or with a Quant-Ray Nd–YAG laser (1.06 μm; model DCR 1A; energy per pulse, 0.5 - 0.8 J).

3. Results

Preliminary work showed that, on irradiation of aqueous solutions of 1,3-diphenylisobenzofuran (DPBF) containing about 1% acetonitrile under 10 MPa oxygen at 990 nm, the DPBF bleaching was greater in H_2O than in D_2O. However, because of the relatively large dark reaction (about 50%) in this case, further work was done with TRP.

3.1. 990 nm irradiations
3.1.1. Aerated solutions
FK is formed on irradiation of aqueous aerated solutions of TRP. The yield of FK is greater in H_2O than in D_2O (Table 1).

3.1.2. 10 MPa oxygen
The FK yield from solutions of TRP under 10 MPa oxygen is also greater in H_2O than in D_2O (Table 1). The presence of sodium azide protects TRP against decomposition and the FK yields are reduced by about 70% in both H_2O and D_2O (Table 1).

TABLE 1

Irradiation of 4×10^{-4} mol dm^{-3} solutions of tryptophan: relative yields of N-formyl-kynurenine

Number	Wavelength	Cover gas	Additive	Relative yields of FK^a	
				H_2O^b	D_2O^b
1	990 nm^c	Air	—	98 (NA)	1 (1)
2	990 nm^d	10 MPa O_2	—	850 (650)	88 (71)
3	990 nm^d	10 MPa O_2	10^{-3} mol dm^{-3} NaN_3	61 (30)	13 (9)
4	1.06 μm^e	Air	—	64 (27)	16 (5)
5	1.06 μm^e	10 MPa O_2	—	1630 $(200)^f$	3600 (400)
6	1.06 μm^e	10 MPa O_2	10^{-3} mol dm^{-3} NaN_3	55 (1)	NA (28)

NA, not available.

[a]Error, ±20% or less for yields greater than 10; the yields given are the measured peak heights (100 = 0.02OD, where OD $\equiv$ optical density).

[b]The data in parentheses are for unheated samples; the data outside the parentheses are for irradiated samples heated at 60 °C for 10 min. Heating the samples converts hydroperoxides to FK and other products [19]. Since the hydroperoxides decompose spontaneously on standing, the differences between the heated and unheated samples would be expected to be greater for irradiations at 1.06 μm.

[c]Dose rate, 6.5×10^{-3} J s^{-1}. The data for H_2O are for 16 h irradiation; the data for D_2O are those expected for 16 h irradiation on the basis of results from 64 h irradiation.

[d]Dose rate, 6.5×10^{-3} J s^{-1}; 17 h irradiation.

[e]Dose rate, 0.5 J $pulse^{-1}$; total number of pulses, 18000; time of irradiation, 20 min or less.

[f]Based on the data obtained with 36000 pulses; time of irradiation, 40 min or less

3.2. Nd–YAG laser

3.2.1. Aerated solutions

FK formation at low yields is observed on exposure of aerated aqueous solutions of TRP to pulsed beams of 1.06 μm from an Nd–YAG laser. Again, the FK yield is greater in H_2O than in D_2O (Table 1).

3.2.2. 10 MPa oxygen

The TRP decomposition increases markedly when the solutions under 10 MPa oxygen are exposed to pulsed beams from the Nd–YAG laser (Table 1). In this case, however, the FK yield is greater in D_2O than in H_2O. Sodium azide protects TRP against decomposition (Table 1).

4. Discussion

The TRP decomposition is most likely due to one or all of the following mechanisms.

(A) Direct formation of $O_2(^1\Delta_g)$ by absorption of light by oxygen in its 1066 and 1266 nm bands:

$$O_2 \xrightarrow{h\nu} O_2(^1\Delta_g) \tag{1}$$
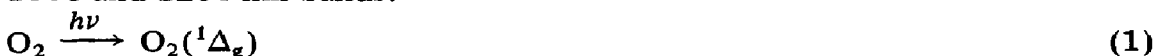
(B) Formation of $O_2(^1\Delta_g)$ by energy transfer from vibrationally excited water to oxygen:

$$\text{water} \xrightarrow{h\nu} \text{water}^{*v} \xrightarrow{O_2} O_2(^1\Delta_g) \tag{2}$$

(C) Formation of vibrationally excited TRP by energy transfer from vibrationally excited water followed by reaction with oxygen:

$$\text{water}^{*v} + \text{TRP} \longrightarrow \text{TRP}^{*v} \xrightarrow{O_2} \text{FK} \tag{3}$$

Their roles in the TRP decomposition at 990 nm and at 1.06 μm are considered below.

4.1. 990 nm irradiations

The optical densities of H_2O and D_2O and the expected optical densities of oxygen in air and under 10 MPa pressure are given in Table 2. The optical density of H_2O is higher than that of D_2O; thus, if the TRP decomposition is brought about by vibrationally excited water, the decomposition may be expected to be greater in H_2O than in D_2O, as is the case (Table 1). In this case, three factors would combine to give the observed results: (i) greater light absorption in H_2O would result in a greater yield of vibrationally excited H_2O than vibrationally excited D_2O, (ii) the efficiencies of energy transfer from vibrationally excited H_2O and vibrationally excited D_2O to oxygen or TRP may be different and (iii) the lifetime of $O_2(^1\Delta_g)$ formed would be longer [29] in D_2O than in H_2O. If, however, the TRP decomposition were due to direct light absorption by oxygen, the decomposition would be greater in D_2O.

As pointed out above, vibrationally excited water can lead to TRP decomposition via two routes: singlet oxygen formation (reaction (2)) or formation of vibrationally excited TRP (reaction (3)) and its reaction with oxygen. In our case, the concentrations of oxygen and TRP at atmospheric pressures are 2.9×10^{-4} mol dm^{-3} [30] and 4×10^{-4} mol dm^{-3} respectively. Thus reaction (3) could take place under these conditions. However, at

TABLE 2

Relevant optical densities of water [22] and oxygen dissolved in water

Absorber[a]	Optical density	
	990 nm	*1.06 μm*
H_2O	1.19	0.58
D_2O	0.16	0.18
O_2 (10 MPa)[b]	$\approx 1 \times 10^{-6}$	$\approx 4 \times 10^{-5}$
O_2 (air)[c]	$\approx 4 \times 10^{-12}$	$\approx 2 \times 10^{-10}$

[a] 5 cm path length.
[b] Based on the observed optical density of oxygen in Freon-113 [27] and assuming dependence of the optical density of oxygen on the square of its concentration [28].
[c] Extrapolated from the 10 MPa values.

10 MPa, the concentration of oxygen is much greater (about 0.1 mol dm^{-3} [21]), so that, in these solutions, reaction (3) would be negligible.

The observed decomposition of TRP is greater in H_2O than in D_2O (Table 1). This suggests that it is via vibrationally excited water (reaction (2)) rather than direct optical excitation of oxygen (reaction (1)). Thus, it would seem that the efficiency of vibrational energy transfer from vibrationally excited H_2O to oxygen is greater than from vibrationally excited D_2O, which just about compensates for the larger lifetime of singlet oxygen in D_2O. Protection of TRP against decomposition by added sodium azide in the solutions under 10 MPa oxygen (Table 1) is consistent with the formation of $O_2(^1\Delta_g)$ via reaction (2).

4.2. Nd–YAG laser

Although the energy absorbed in these runs in aerated solutions is greater than those irradiated at 990 nm (9000 J compared with 400 J) the FK yield in H_2O is smaller. This rules out any need to consider multiphoton excitation of either oxygen or TRP. The FK yield is still greater in H_2O than in D_2O, consistent with the results at 990 nm and with the $O_2(^1\Delta_g)$ formation mechanism via reaction (2). The lower yield compared with that at 990 nm suggests that the efficiency of $O_2(^1\Delta_g)$ formation decreases with decreasing energy of vibrational excitation of water. This result also appears to favour the $O_2(^1\Delta_g)$ mechanism (reaction (2)) rather than the vibrationally excited TRP mechanism (reaction (3)).

Under 10 MPa oxygen, there is a very large increase in TRP decomposition and now the order of decomposition has changed, being greater in D_2O than in H_2O. This suggests that $O_2(^1\Delta_g)$ is being formed by direct light absorption by oxygen itself (reaction (1)). At 990 nm, there is about a ninefold increase in the yield of FK in going from aerated solution to the solution under 10 MPa oxygen. If we assume a similar increase for 1.06 μm irradiations, we can estimate that about two-thirds of the FK formation is due to directly produced $O_2(^1\Delta_g)$. Comparing the FK yields in air at 1.06 μm, we conclude that in the D_2O solution under 10 MPa oxygen, about 96% of the FK formation is due to directly produced $O_2(^1\Delta_g)$. On the basis of these data at 1.06 μm and those in Table 2, the quantum yield for $O_2(^1\Delta_g)$ formation from vibrationally excited water can be calculated to be 3×10^{-5}.

5. Concluding remarks

Our work suggests that singlet oxygen is formed by energy transfer from vibrationally excited water. Since production of vibrationally excited water, mainly due to sunlight, is a process occurring constantly in rivers, lakes, oceans and water vapour in the atmosphere during daytime, singlet oxygen at low levels becomes a ubiquitous species.

Acknowledgments

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