# PRODUCTION AND QUENCHING OF SINGLET OXYGEN BY THE SENSITIZER IN DYE-SENSITIZED PHOTO-OXYGENATIONS†

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## Summary

The production and quenching of singlet oxygen $O_2(^1\Delta_g)$ by the sensitizer in dye-sensitized photo-oxygenations are studied. The quantum yield $\gamma_\Delta$ of $O_2(^1\Delta_g)$ formation is equal to the intersystem crossing yield $\gamma_{is}$ for dyes such as Rose Bengal, eosin and methylene blue which do not exhibit fluorescence quenching by $O_2(^3\Sigma)$. For these dyes the efficiency of $O_2(^1\Delta_g)$ production from the $O_2(^3\Sigma)$ quenching of the triplet state is about 100%. For dyes such as chlorophyll a and tetraphenylporphine which do exhibit fluorescence quenching, $\gamma_\Delta > \gamma_{is}$ and it is shown that the $O_2(^3\Sigma)$-catalysed intersystem crossing of their singlet state is operative. Moreover it appears that the quenching of $O_2(^1\Delta_g)$ by the dyes themselves is a rather general process. Thus the values of the rate constants for Rose Bengal and eosin in acetonitrile are $5.0 \times 10^7$ $M^{-1}$ $s^{-1}$ and $7.2 \times 10^7$ $M^{-1}$ $s^{-1}$ respectively compared with that of chlorophyll a in benzene ($7.3 \times 10^8$ $M^{-1}$ $s^{-1}$). The consequences of these results are discussed.

## 1. Introduction

The combined action of light and oxygen on suitable sensitizer S and acceptor A mixtures is the oldest technique for studying the reactions of singlet oxygen $O_2(^1\Delta_g)$ and is also in a general way the most convenient. The sensitizer is critical to the success of any sensitized photo-oxygenation and dyes such as xanthenes (Rose Bengal (RB) and eosin), thiazines (methylene blue (MB)) and porphyrins (chlorophyll a (Chl a) and tetraphenylporphine (TPP)) have been used.

However, some significant gaps remain in both our qualitative and our quantitative knowledge of fundamental parameters. Thus it is in general implicitly assumed that the quantum yield $\gamma_\Delta$ of $O_2(^1\Delta_g)$ production is equal
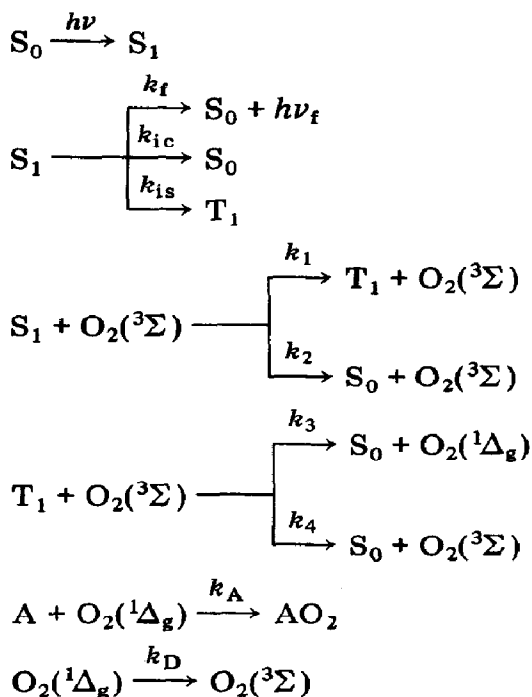
to the intersystem crossing efficiency $\gamma_{is}$. If this equality seems to be established for some xanthenes [1], its extension to other dyes [2, 3] has to be proved. However, the sensitizer itself may cause quenching of $O_2(^1\Delta_g)$ as we have shown for Chl a [4] and "oil-soluble chlorophyll", a commercial mixture containing a low percentage of pure chlorophyll [5]. It is important to consider this quenching as a general process for a better understanding of the photosensitized oxygenations. Neglect of sensitizer quenching has led to erroneous results in the determination of the lifetime of $O_2(^1\Delta_g)$ and of the rate constant for its reaction with acceptors.

## 2. Procedure

For all the dyes investigated, the excitation energy of $O_2(^1\Delta_g)$ (7880 cm$^{-1}$) exceeds the energy separation $\Delta E_{ST}$ of sensitizer excited singlet ($S_1$) and triplet ($T_1$) states and hence the energy transfer processes

$$S_1 + O_2(^3\Sigma) \longrightarrow T_1 + O_2(^1\Delta_g)$$
$$S_1 + O_2(^3\Sigma) \longrightarrow S_0 + O_2(^1\Delta_g)$$
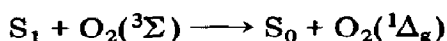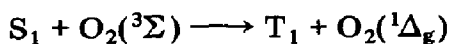
are prohibited respectively by energetic and spin conservation requirements. In this case the overall mechanism in the absence of physical quenching of $O_2(^1\Delta_g)$ by the acceptor may be described as follows:

$$S_0 \xrightarrow{h\nu} S_1$$

$$S_1 \longrightarrow \begin{cases} \xrightarrow{k_f} S_0 + h\nu_f \\ \xrightarrow{k_{ic}} S_0 \\ \xrightarrow{k_{is}} T_1 \end{cases}$$

$$S_1 + O_2(^3\Sigma) \longrightarrow \begin{cases} \xrightarrow{k_1} T_1 + O_2(^3\Sigma) \\ \xrightarrow{k_2} S_0 + O_2(^3\Sigma) \end{cases}$$

$$T_1 + O_2(^3\Sigma) \longrightarrow \begin{cases} \xrightarrow{k_3} S_0 + O_2(^1\Delta_g) \\ \xrightarrow{k_4} S_0 + O_2(^3\Sigma) \end{cases}$$

$$A + O_2(^1\Delta_g) \xrightarrow{k_A} AO_2$$

$$O_2(^1\Delta_g) \xrightarrow{k_D} O_2(^3\Sigma)$$

In this scheme the relaxation process $T_1 \rightarrow S_0$ is not considered as its rate is very low with respect to $(k_3 + k_4)[O_2]$.

From this mechanism the quantum yield $\phi_{O_2}$ of oxygen consumption is given by

$$\phi_{O_2} = \gamma_\Delta \phi_A$$

where $\gamma_\Delta$ is the quantum yield of $O_2(^1\Delta_g)$ production and $\phi_A = k_A[A]/(k_A[A] + k_D) = [A]/([A] + \beta)$, with $\beta = k_D/k_A$, the efficiency of $O_2(^1\Delta_g)$ addition to the acceptor A.

Under conditions where $[A] \gg \beta$, $\phi_A \approx 1$, and it is possible to obtain $\gamma_\Delta$ values as

$$(\phi_{O_2})_{[A] \rightarrow \infty} = \gamma_\Delta$$

The experimentally accessible $\gamma_\Delta$ may be expressed as the product of the quantum yield $\gamma_T$ of formation of the sensitizer triplet state and the probability $\epsilon = k_3/(k_3 + k_4)$ that oxygen quenching of the triplet state produces $O_2(^1\Delta_g)$. If the sensitizer triplet state is produced by intersystem crossing with yield $\gamma_{is} = k_{is}/(k_f + k_{ic} + k_{is})$ (in the absence of oxygen) and by oxygen quenching of $S_1$ with efficiency $\delta = k_1/(k_1 + k_2)$ then $\gamma_T$ and $\gamma_\Delta$ are given by

$$\gamma_T = \gamma_{is}(1 - P_{O_2}) + \delta P_{O_2}$$

$$\gamma_\Delta = \epsilon\{\gamma_{is} + P_{O_2}(\delta - \gamma_{is})\}$$
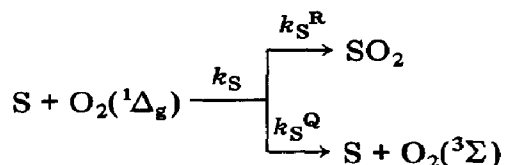
where

$$P_{O_2} = \frac{(k_1 + k_2)[O_2]}{(k_1 + k_2)[O_2] + k_f + k_{is} + k_{ic}}$$

$$= \frac{K[O_2]}{1 + K[O_2]}$$

denotes the oxygen quenching probability of $S_1$; $K$ is independently available as the Stern–Volmer quenching constant.

If the sensitizer also interacts with $O_2(^1\Delta_g)$ with a rate constant $k_S = k_S^R + k_S^Q$, i.e.

$$S + O_2(^1\Delta_g) \xrightarrow{k_S} \begin{cases} \xrightarrow{k_S^R} SO_2 \\ \xrightarrow{k_S^Q} S + O_2(^3\Sigma) \end{cases}$$

the efficiency $\phi_A$ of $O_2(^1\Delta_g)$ addition becomes

$$\phi_{A,S} = \frac{k_A[A] + k_S^R[S]}{k_A[A] + k_S[S] + k_D}$$

Since the dyes investigated have a relatively low tendency to bleach [2, 5, 6], the quenching of $O_2(^1\Delta_g)$ by the sensitizer S is essentially physical or

$k_A[A] \gg k_S^R[S]$. Hence

$$\phi_{A,S} = \frac{[A]}{[A] + \beta_{app}}$$

where $\beta_{app} = \beta(1 + k_S\tau_\Delta[S])$ with $\tau_\Delta = k_D^{-1}$. Thus

$$\gamma_\Delta\phi_{O_2}^{-1} = (\phi_{O_2})_{[A] \to \infty}\phi_{O_2}^{-1} = 1 + \beta_{app}[A]^{-1}$$

and the variation in $\gamma_\Delta\phi_{O_2}^{-1}$ as a function of $[A]^{-1}$ leads to the value of $\beta_{app}$.

If quenching of $O_2(^1\Delta_g)$ by the sensitizer S is significant, $\beta_{app}$ should change with $[S]$ and a plot of $\beta_{app}$ against $[S]$ should give a straight line with intercept $\beta$ and a slope-to-intercept ratio of $k_S\tau_\Delta$.


## 3. Experimental details

### 3.1. Sensitizers and $O_2(^1\Delta_g)$ acceptors

TPP, RB, MB (Fluka), rubrene (Aldrich), eosin Y (Merck) and oil-soluble chlorophyll (Roth) were used as received after spectrophotometric control.

Chl a was extracted from spinach leaves and purified according to the method described by Omata and Murata [7].

2-Methyl-2-pentene (2M2P) and tetramethylethylene (TME) were obtained from Fluka and their purity was tested by means of gas chromatography.

### 3.2. Quantum yields of $O_2(^1\Delta_g)$ formation

Measurements of the quantum yields of $O_2(^1\Delta_g)$ formation in oxygen-saturated solutions were performed in a cylindrical photoreactor equipped with a device to monitor the oxygen consumption; the concentration of the substrate (TME) was sufficiently high so that $\phi_A \approx 1$. The sensitizer concentration ensured absorption of more than 99% of the incident radiation at 535, 546 and 577 nm provided by a mercury halogen lamp Hanau TQ 150 Z2 with a liquid filter of $K_2Cr_2O_7$ (5 g $l^{-1}$) in water. For all the sensitizers used, we checked that the concentration employed was low enough to avoid self-quenching.

### 3.3. Quenching of $O_2(^1\Delta_g)$ by sensitizers

Kinetic studies related to the quenching of $O_2(^1\Delta_g)$ by sensitizers were carried out in a photo-oxidation reactor similar to that described by Gollnick et al. [8]. Oxygen-saturated solutions of 2M2P at various concentrations were irradiated with the light of an Osram 200 W mercury lamp (glass filter MTO J 385 a). The least-squares method was used for interpretation of data involving linear relationships.

## 4. Results and discussion

### 4.1. Quantum yield of $O_2(^1\Delta_g)$ production

The values of $\gamma_\Delta$ are obtained by comparison with that corresponding to MB in methanol taken as 0.50; for this system we have measured $\gamma_{is}$ = 0.50 [6] and have assumed that $\epsilon = 1$ as for MB in aqueous and ethanolic solutions [9, 10]. Indeed, the $\gamma_\Delta$ values obtained using this reference compound and presented in Table 1 are in excellent agreement with the corresponding literature data for RB in methanol, MB in ethanol, TPP in toluene and rubrene in benzene.

TABLE 1

Quantum yields $\gamma_\Delta$ in the dye-photosensitized production of $O_2(^1\Delta_g)$

| Sensitizer | Solvent | $[O_2] \times 10^3$ (M)[a] | $\gamma_\Delta$(lit) | $\gamma_{is}$ | Fluorescence quenching by oxygen |
|---|---|---|---|---|---|
| RB | Methanol | 10.6 | 0.79 (0.80) [8] | 0.80 [8] | No |
| Eosin | Methanol | 10.6 | 0.42 | 0.3 [1] - 0.66 [12] | No |
|  | Ethanol | 9.9 | 0.42 | 0.42 [13] | No |
| MB | Methanol | 10.6 | 0.50[b] | 0.50 [6] | No |
|  | Ethanol | 9.9 | 0.50 (0.52) [10, 13] | 0.52 [13] | No |
| Chl a | Benzene | 9.1 | 0.60 | 0.46 [6] | Yes |
|  | Toluene | 8.5 | 0.68 | 0.57 [14] | Yes |
| TPP | Benzene | 9.1 | 0.89 |  | Yes |
|  | Toluene | 8.5 | 0.88 (0.88) [3][c] | 0.82 [15] | Yes |
| Oil-soluble chlorophyll | Benzene | 9.1 | 0.50 |  |  |
| Rubrene | Benzene | 9.1 | 0.90 [16] (0.88 [17] - 0.91 [18]) | 0.03 [16] - 0.012 [19] | Yes |
|  |  | 4.6 | 0.64 [16] |  |  |
|  |  | 1.8 | 0.36 [16] (0.30) [17] |  |  |

[a]From ref. 11.
[b]Taken as the reference.
[c]The value of 0.88 indicated by Olmsted as that of $\gamma_{is}$ corresponds indeed to $\gamma_\Delta$.

In addition $\gamma_{is}$ values are reported in Table 1 for comparison with $\gamma_\Delta$. The dyes may be classified into two groups depending on whether their fluorescence is quenched by oxygen or not, i.e. on whether $P_{O_2}$ is finite or zero. In the latter case exemplified by RB, eosin and MB, it is found that $\gamma_\Delta \approx \gamma_{is}$. As the yield $\gamma_\Delta$ is given by $\gamma_\Delta = \epsilon\gamma_{is}$ it can be deduced that $\epsilon \approx 1$. Thus the process

$$T_1 + O_2(^3\Sigma) \longrightarrow S_0 + O_2(^1\Delta_g)$$
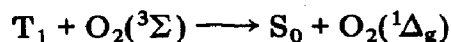
is solely responsible for the oxygen quenching of the triplet state of these dyes.

However, when the fluorescence of the dye is quenched by oxygen, it is observed that the yield $\gamma_\Delta$ is always greater than $\gamma_{is}$, in contrast with the implicit assumption [2, 3]. Since $\epsilon \leqslant 1$ this requires that
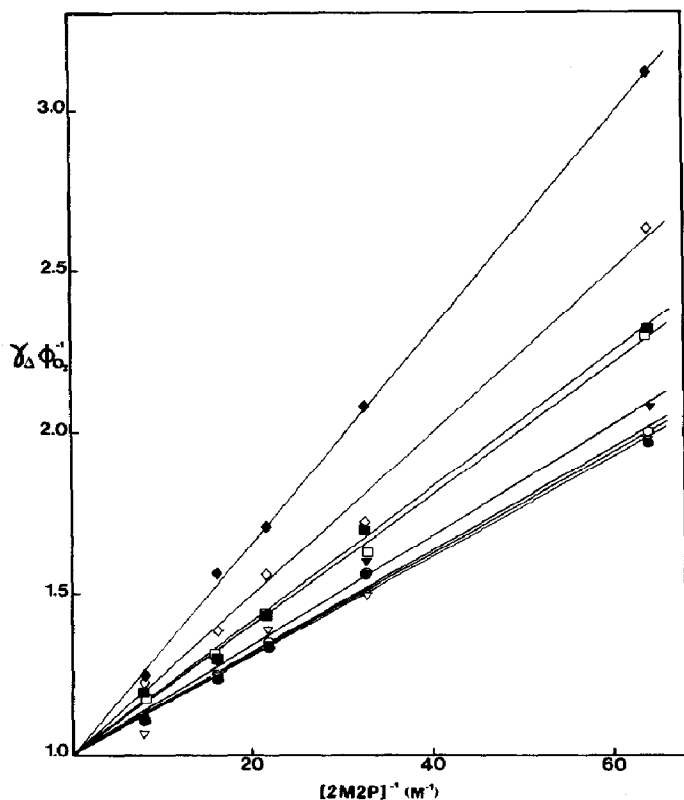
Fig. 1. RB-photosensitized oxygenation of 2M2P in oxygen-saturated acetonitrile: ●, 1 × $10^{-5}$ M RB; ▽, 2 × $10^{-5}$ M RB; ○, 4 × $10^{-5}$ M RB; ▼, 5 × $10^{-5}$ M RB; ■, 10 × $10^{-5}$ M RB; □, 12 × $10^{-5}$ M RB; ◇, 24 × $10^{-5}$ M RB; ◆, 40 × $10^{-5}$ M RB.

$$\frac{\gamma_\Delta}{\epsilon} \geqslant \gamma_\Delta > \gamma_{is}$$
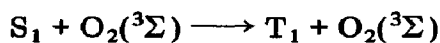
or

$$\gamma_{is} + P_{O_2}(\delta - \gamma_{is}) > \gamma_{is}$$

and

$$P_{O_2}(\delta - \gamma_{is}) > 0$$

Since $P_{O_2} > 0$ it is concluded that $\delta > \gamma_{is}$.

As for the dyes investigated the value of the intersystem crossing yield $\gamma_{is}$ is high and this indicates that the process

$$S_1 + O_2(^3\Sigma) \longrightarrow T_1 + O_2(^3\Sigma)$$

is predominantly responsible for the oxygen quenching of the dye singlet state. This result for these dyes is similar to that for aromatic hydrocarbons. To our knowledge this is the first report of this behaviour for dyes of this type.
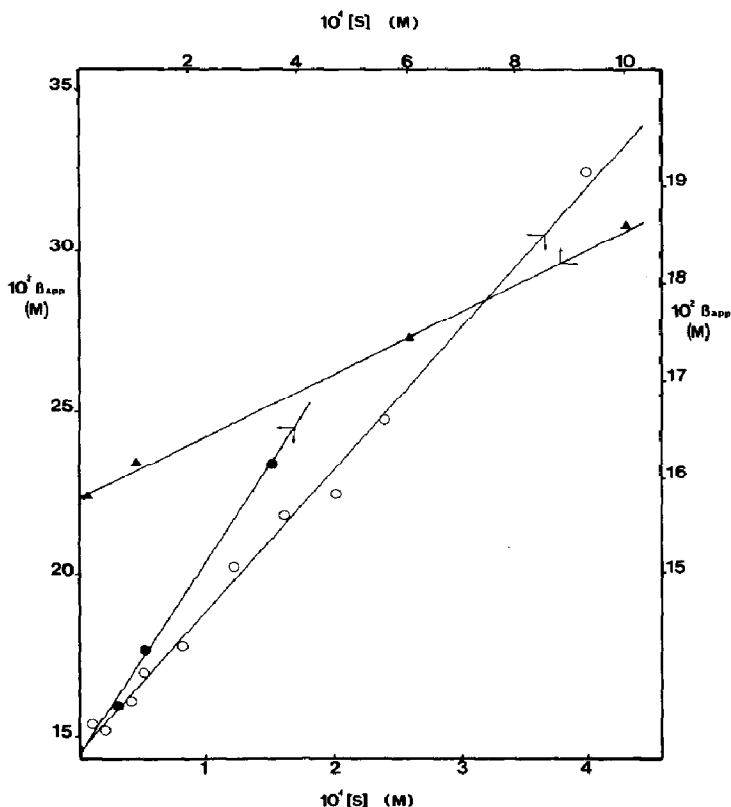
Fig. 2. Plots of $\beta_{app}$ vs. [S] for the dye-sensitized photo-oxygenation of 2M2P: ▲, RB in methanol; ○, RB in acetonitrile; ●, eosin in acetonitrile.

In oil-soluble chlorophyll, the presence of compounds which can absorb the incident light may explain the lower value of $\gamma_\Delta$ compared with that of pure Chl a, i.e. 0.50 instead of 0.60. Carotenoids and degradation products of chlorophyll for instance were found in the commercial mixture; however, this very cheap mixture is remarkably stable compared with pure chlorophyll and may be advantageously used for preparative purposes.

## 4.2. Quenching of $O_2(^1\Delta_g)$ by the sensitizer

Figure 1 is a typical plot of $\gamma_\Delta\phi_{O_2}^{-1}$ against $[A]^{-1}$ for different concentrations of the sensitizer for the system RB–2M2P in acetonitrile; the straight lines $\beta_{app} = f([S])$ obtained for 2M2P in acetonitrile with two sensitizers (RB and eosin) are presented in Fig. 2.

This evidence for quenching of $O_2(^1\Delta_g)$ by RB in acetonitrile has led us to reinvestigate RB in methanol, for which a first estimate based on a narrow range of dye concentration provided a variation in $\beta_{app}$ within the experimental error limits with $\beta_{app} = 0.18 \pm 0.02$ M [5]. Further experiments lead finally to the values presented in Fig. 2 which shows that RB also quenches $O_2(^1\Delta_g)$ in methanol. The same conclusion was reached for eosin in methanol.

TABLE 2

Rate constants of $O_2(^1\Delta_g)$ quenching by the sensitizer in dye-sensitized photo-oxygenations

| Sensitizer | Solvent | $\beta \times 10^2$ (M) | $k_S \times 10^{-7}$ [a] $(M^{-1} s^{-1})$ |
|---|---|---|---|
| RB | Methanol | 15.8 | 2.0 |
| | Acetonitrile | 1.45 | 5.0 |
| Eosin | Methanol | 15.5 | 2.4 |
| | Acetonitrile | 1.43 | 7.2 |
| Chl a | Benzene | 4.8 [4] | 73 [4] |
| Oil-soluble chlorophyll | Benzene | 4.4 [5] | $< 100^b$ |

[a]By taking $\tau_\Delta = 9$ $\mu$s, 25 $\mu$s and 60 $\mu$s respectively in methanol, benzene and acetonitrile.
$^b k_S = 5.4 \, 10^4$ l s$^{-1}$ g$^{-1}$ of oil-soluble chlorophyll [5].

Table 2 summarizes the results for the various dyes examined. The $\beta$ values for 2M2P are in agreement with literature data; thus the values of 0.014 M and 0.046 M in acetonitrile and benzene respectively compare well with those obtained very recently by Mauring and Foote [20] of 0.013 M and 0.047 M respectively. From Table 2 it appears that the quenching of $O_2(^1\Delta_g)$ by the dyes is a rather general process. The rate constant $k_S$ for Chl a is at least one order of magnitude higher than for xanthenes where $k_S$ is lower in methanol than in acetonitrile. Moreover the quenching efficiency is slightly higher for eosin than for RB. Since energy transfer is an unlikely mechanism, the physical quenching of $O_2(^1\Delta_g)$ by the dyes may be attributed to charge transfer promoted by the high electron affinity of $O_2(^1\Delta_g)$ as substantiated by experiments on porphyrins [21]. This process must be taken into account in the determination of $\beta$ values since with $\beta = \beta_{app}/(1 + k_S\tau_\Delta[S])$ a knowledge of $k_S$ is required; this is also the case for the measurement of $O_2(^1\Delta_g)$ lifetimes $\tau_\Delta$ since the experimental decay constant $k_{Dapp}$ obtained is in fact $k_D + k_S[S]$. The quenching of $O_2(^1\Delta_g)$ by dyes explains, at least partially, the discrepancies between the literature data $k_A$ and $\tau_\Delta$ for various acceptors and solvents [22].

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