

FACTORS INFLUENCING THE QUANTUM YIELDS FOR ROSE BENGAL FORMATION OF SINGLET OXYGEN

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Summary

The ϕ for $^1\text{O}_2$ formation obtained via the relative actinometric method is dependent on the quencher concentration when photo-oxidations in different solvents are compared; a method to determine the appropriate quencher concentration is described.

1. Introduction

Singlet oxygen ($^1\text{O}_2$) has been used in synthetic [1] and therapeutic [2] applications for decades. The most common method of generating singlet oxygen is photochemically, via the so-called Kautsky method [3]. In this method energy transfer from the triplet state of a dye to molecular oxygen produces the excited state of the acceptor. Rose bengal (A comprehensive survey of the photochemical properties of rose bengal and its derivatives can be found in ref. 4.) gives among the highest efficiencies of singlet oxygen formation ($\phi = 0.76$ in MeOH [5]) in polar solvents. Its use is limited in non-polar solvents by solubility, though non-polar derivatives have been recently prepared which circumvent this problem [6]. Polymer rose bengal is also used in non-polar solvents [7]. Polymer rose bengal is commercially available as Sensitox 1 [8].

2. Results and discussion

The most important quantitative measure of sensitizer effectiveness is the quantum yield of singlet oxygen formation. This is usually obtained by a relative actinometric method [7] which eliminates the concern of non-radiative relaxation of singlet oxygen in solution by using a high concentration of quencher. In this method one uses the known quantum yield of $^1\text{O}_2$ formation in methanol and the measured rate of disappearance of a singlet oxygen trap under conditions where it is presumed that all singlet oxygen is trapped by the quencher:

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$$\phi(^1\text{O}_2)(\text{derivative}) = \phi(^1\text{O}_2)(\text{rose bengal}) \frac{V(^1\text{O}_2)(\text{derivative})}{V(^1\text{O}_2)(\text{rose bengal in MeOH})} \quad (1)$$

The use of this relative method appears trivial at first glance. If one takes into account the changes in lifetime of $^1\text{O}_2$ in different solvents, it is simply a matter of arithmetic to calculate the proper concentration of quencher required to trap all of the singlet oxygen formed in the energy transfer process.

Unfortunately a number of factors make a simple matter of arithmetic more difficult. First, there are some substantial differences in singlet oxygen lifetimes in the literature. The lifetime in CHCl_3 is $60 \pm 15 \mu\text{s}$ according to Long and Kearns [9], $228 \mu\text{s}$ according to Young and Brewer [10] and $250 \mu\text{s}$ according to Hurst and Schuster [11]. Second, the reactivity of the various quenchers with singlet oxygen also depends on the solvent [12, 13]. If the singlet oxygen is physically quenched either by the chemical trap or by the sensitizer in the solvents employed, this also introduces a factor of uncertainty in "routine arithmetic calculations" [12]. Under these conditions, the general equation describing the rate of singlet oxygen formation becomes much more complex:

$$V(^1\text{O}_2) = I_a \phi(^1\text{O}_2) \frac{k_r[\text{A}]}{k_d + k_q^s[\text{Sens}] + k_q^s[\text{A}] + k_r[\text{A}]} \quad (2)$$

where I_a is the number of light quanta absorbed, $k_d = 1/\tau_{s0}$, k_q^s and k_q^a are the rates of physical quenching by A and by the sensitizer and k_r is the rate of reaction between the quencher and $^1\text{O}_2$.

In order to eliminate the influence of k_d , $k_q^s[\text{Sens}]$ and $k_q^s[\text{A}]$ on the efficiency of A photo-oxidation, zero-order reaction conditions are necessary. It is very easy to eliminate k_d and $k_q^s[\text{Sens}]$ from eqn. (2) by using a high concentration of quencher A. That is

$$k_r[\text{A}] + k_q^a[\text{A}] \gg k_q^s[\text{Sens}] + k_d$$

Employing the data from ref. 14, the rate constants of quenching of $^1\text{O}_2$ by rose bengal are approximately the same as the values of the rate of quenching of $^1\text{O}_2$ for 1,2-diphenyl-*p*-dioxene (DPDO). Since the concentration of rose bengal used in our experiments was 1×10^{-4} M or 2×10^{-4} M, and the concentration of DPDO varied from 1×10^{-2} to 7×10^{-2} M, under our conditions $k_r[\text{A}]$ is about 100 times higher than $k_q^s[\text{Sens}]$. The latter is therefore negligible.

After this approximation the equation describing the rate of photo-oxidation becomes

$$V(^1\text{O}_2) = I_a \phi(^1\text{O}_2) \frac{k_r[\text{A}]}{k_q^a[\text{A}] + k_r[\text{A}]} \quad (3)$$

and

$$\phi(^1\text{O}_2) = \frac{V(^1\text{O}_2)}{I_a} \left(1 + \frac{k_q^a}{k_r} \right) \quad (4)$$

The value of the $\phi(^1\text{O}_2)(\text{solvent})$ is given by

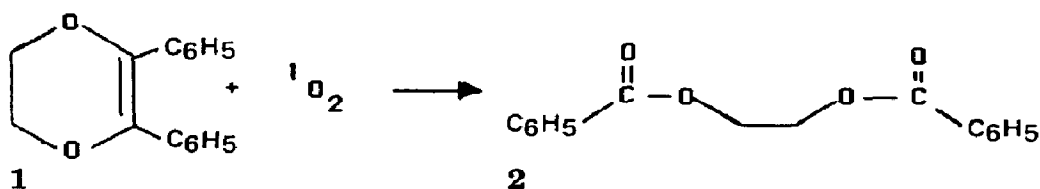
$$\phi(^1\text{O}_2)(\text{solvent}) = \phi(^1\text{O}_2)(\text{MeOH}) \frac{V_{\text{AO}_2}(\text{solvent})}{V_{\text{AO}_2}(\text{MeOH})} \frac{(1 + k_q^a/k_r)(\text{solvent})}{(1 + k_q^a/k_r)(\text{MeOH})} \quad (5)$$

if $I_a(\text{MeOH}) \approx I_a(\text{solvent}) \approx I_o$. Gollnick and Griesbeck [12] have shown for cycloaddition reactions that the value of k_q^a/k_r is negligible with respect to 1, so eqn. (5) has the form

$$\phi(^1\text{O}_2)(\text{solvent}) = \phi(^1\text{O}_2)(\text{MeOH}) \frac{V_{\text{AO}_2}(\text{solvent})}{V_{\text{AO}_2}(\text{MeOH})} \quad (6)$$

Since the values of k_d and k_q^a vary widely with different solvents and k_q^a may vary with different solvents we deemed it necessary to quantitate the critical quencher concentration. Concentrations greater than critical [A] must be used in order to obtain accurate values of quantum yields for $^1\text{O}_2$ formation by using the relative actinometric method in common solvents, *i.e.* solvents in which the lifetime of singlet oxygen has been measured.

The $^1\text{O}_2$ quencher DPDO (1) was used in these studies, and its photo-oxidation to the dibenzoate 2 was monitored in various solvents by vapour phase chromatography.



Rose bengal, solubilized when necessary by crown ether, was used as the sensitizer. A plot of per cent product formed *versus* time gave straight lines (with monitoring up to 35% conversion) indicating zero-order kinetics were initially followed. The resultant slopes are proportional to the rates of photo-oxidation; therefore, the ratios of these slopes were substituted for the ratio of the rates in eqn. (1). The differences in non-radiative relaxation of singlet oxygen and physical quenching of singlet oxygen by quencher and sensitizer should be reflected in a plot of [DPDO] *versus* $V_{\text{AO}_2}(\text{solvent})/V_{\text{AO}_2}(\text{MeOH})$ where $\phi(^1\text{O}_2)(\text{MeOH}) = 0.76$ and $\phi(^1\text{O}_2)(\text{solvent})$ was derived from eqn. (1). The results are shown in Fig. 1. At low [DPDO], large deviations in the ratio of the two values of ϕ for $^1\text{O}_2$ formation are apparent, with the solvents that support a longer lifetime having the greatest deviation. The ratio of the two eventually become constant at a [DPDO] which can be called the critical concentration (critical [A]). The conditions of irradiation as well as the critical quencher concentrations and values are given in Table 1.

The critical quencher concentration also has an additional significance. It indicates when the same non-chemical quenching processes occur in different solvents. Thus it yields information about the influence of the solvent on all the photo-oxidation processes. This information not only takes into

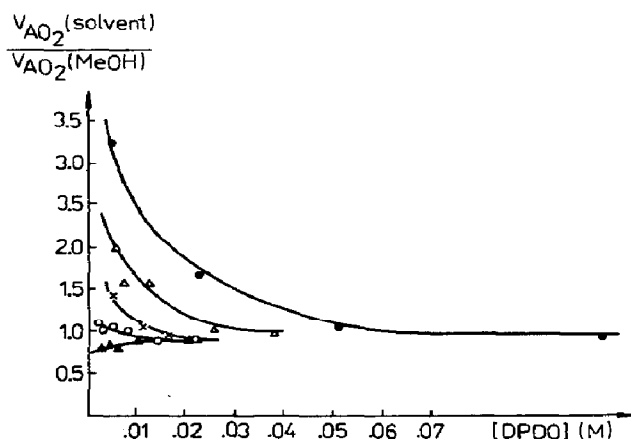


Fig. 1. Effect of [DPDO] on $^1\text{O}_2$ calculations in various solvents: ●, CHCl_3 ; △, CH_2Cl_2 ; ×, acetone; ○, EtOH; ▲, spectral grade EtOH.

TABLE 1

Experimental conditions and critical concentration values

Solvent	Rose bengal (M)	λ_{irr} (nm)	Critical [A] (M)	$\phi(^1\text{O}_2)$
EtOH (spectral grade)	1×10^{-4}	555	1.2×10^{-2}	0.68
EtOH	1×10^{-4}	555	1.2×10^{-2}	0.68
Acetone	1×10^{-4}	557	1.6×10^{-2}	0.70
CH_2Cl_2	2×10^{-4}	559	2.8×10^{-2}	0.76
CHCl_3	2×10^{-4}	559	5.8×10^{-2}	0.76

account the different lifetimes of $^1\text{O}_2$ and the differing rates of physical quenching by the chemical quencher and by the sensitizer, but the different rates of the photo-oxidation process as well.

Knowledge of the critical [A] is of great practical importance. Its value indicates when the photo-oxidation process has the highest efficiency of photo-oxidation product formation. Under these conditions all the singlet oxygen produced is used for product formation. It is important to emphasize that no relationship between the critical [A] and the lifetime of singlet oxygen in the various solvents was found. Also no relationship was observed between critical [A] and solvent polarity.

We have shown the necessity of knowing the critical concentration of quencher when extending the use of the relative actinometric method for singlet oxygen quantum yield measurements with one sensitizer in different solvents. Critical quencher values will vary with different quenchers owing to different rates of reaction with $^1\text{O}_2$. Thus, similar studies must be performed for each quencher used.

3. Experimental details

Rose bengal (Aldrich) was dissolved in various solvents at the concentrations listed in Table 1. Acetone, CH_2Cl_2 and CHCl_3 required 1 equivalent, 15 equivalents and 10 equivalents respectively of dicyclohexano-18-crown-6 ether for complete solubilization. Various amounts of DPDO were dissolved in these stock solutions. These solutions were then irradiated and monitored for product formation as previously reported [9]. Each run was compared with photo-oxidation performed in MeOH with the same [DPDO].

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