The Mechanism of the Dye-sensitised Photo-oxygenation of Amines

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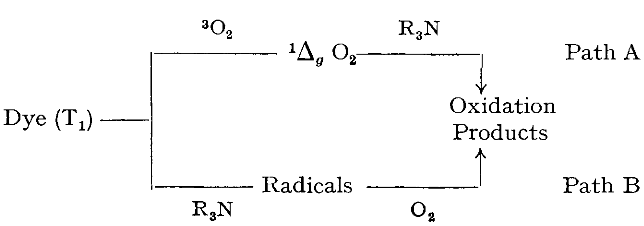
Summary The photo-oxygenation of triethylamine, sensitised by Rose Bengal, is shown to involve both singlet oxygen and radical intermediates; the extent to which these are involved being dependent on amine concentration.

At present there are two suggested mechanisms[1,2] for the dye-sensitised oxygenation of amines. In one (Path A) the amine is oxidised by singlet oxygen and in the other (Path B), radical intermediates are involved. We now show that



the Rose Bengal sensitised photo-oxygenation of triethylamine in aqueous methanol occurs *via* both mechanisms.

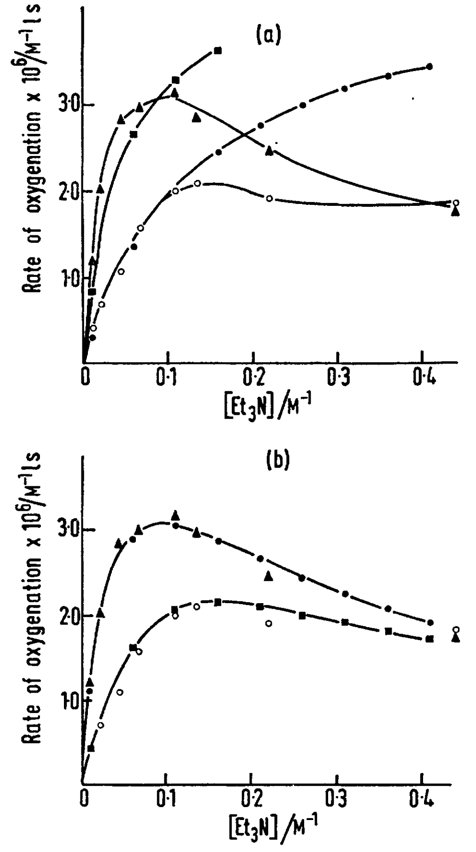


Figure 1. Rates of photo-oxygenation of triethylamine in MeOH–H_2O (50:50) and MeOH–D_2O (50:50) solution. (a) Calculated results using equation (1); (b) calculated results using equation (2). Experimental results ○ (H_2O) and ▲ (D_2O); calculated results ● (H_2O) and ■ (D_2O).

The rates of oxygenation of triethylamine, sensitised by Rose Bengal were measured for various amine concentrations and the results are shown in Figure 1. If reaction occurs solely by Path A, equation (1) describes the rate of oxygenation. It is found that if values of N_0, *e.g.* 0·35, are

$$\text{Rate of oxygenation} = N_0 I_a \Phi_T \; \frac{k_{q_0}[\text{Am}]}{k_d + k_{q_0}[\text{Am}]} \qquad (1)$$

chosen so that the experimental and calculated rates fit using low amine concentrations, a bad fit is obtained using high amine concentrations. Also, the rate of oxygenation does not, as predicted by equation (1), gradually increase and then flatten off as the amine concentration is increased (see Figure 1a). To account for these deviations, and the previous experimental observation that triplet Rose Bengal can react with triethylamine in the presence of oxygen,[2] we derived equation (2) in which account is taken of the following processes.

$$\text{Dye}(S_0) \xrightarrow{I_a} \text{Dye}(S_1)$$

$$\text{Dye}(S_1) \xrightarrow{k_{IC}} \text{Dye}(S_0)$$

$$\text{Dye}(S_1) \xrightarrow{k_F} \text{Dye}(S_0) + h\nu$$

$$\text{Dye}(S_1) \xrightarrow{k_{ISC}} \text{Dye}(T_1)$$

$$\text{Am} + \text{Dye}(S_1) \xrightarrow{k_{q_s}} \text{Am} + \text{Dye}(S_0)$$

$$\text{Am} + \text{Dye}(T_1) \xrightarrow{k_{q_t}} \overset{N_t}{[C_t]} \rightarrow \text{Products}$$

$$^3O_2 + \text{Dye}(T_1) \xrightarrow{k_{O_2}} {}^1\Delta_gO_2 + \text{Dye}(S_0)$$

$$\text{Dye}(T_1) \xrightarrow{k_{d'}} \text{Dye }(S_0)$$

$$^1\Delta_gO_2 \xrightarrow{k_d} {}^3O_2$$

$$\text{Am} + {}^1\Delta_gO_2 \xrightarrow{k_{q_0}} \overset{N_0}{[C_0]} \rightarrow \text{Products}$$

(C_t and C_0 = complexes formed by the processes shown)

Rate of oxygenation =

$$\frac{N_0 I_a \Phi_T}{(1 + k_{q_s}\tau[\text{Am}])} \cdot \frac{k_{O_2}[^3O_2]}{(k_{d'} + k_{O_2}[^3O_2] + k_{q_t}[\text{Am}])} \cdot \frac{k_{q_0}[\text{Am}]}{(k_d + k_{q_0}[\text{Am}]}$$
$$+ \frac{N_t I_a \Phi_T}{(1 + k_{q_s}\tau[\text{Am}])} \cdot \frac{k_{qt}[\text{Am}]}{(k_{d'} + k_{O_2}[^3O_2] + k_{q_t}[\text{Am}])} \qquad (2)$$

$(\Phi_T = k_{ISC}/(k_F + k_{IC} + k_{ISC}), \tau = (k_F + k_{IC} + k_{ISC})^{-1}$

N_0 and N_t = fraction of complex going on to give products).

When values for $N_0 = 0{\cdot}47$, $N_t = 0{\cdot}15$, $k_{q_0} = 2 \times 10^6$ $M^{-1} s^{-1}$ [3] and $k_q = 8 \times 10^7$ $M^{-1} s^{-1}$ are substituted into equation (2) an excellent fit of the calculated to the experimental curve is obtained (see Figure 1b). Unambiguous experimental evidence for the operation of two mechanisms comes from studies on solvent isotope effects.[4]† When the oxygenation of the amine is carried out in a methanol–deuterium oxide mixture (50:50), the rate of reaction is considerably enhanced for low amine concentrations (<0·1 M). At high amine concentrations the isotope effect becomes non-existent. If the reaction was occurring solely by Path A, the rates of reaction in the two solvent systems should not be similar for an amine concentration of 0·4 M (see Figure 1a) and we therefore conclude that at this concentration reaction is occurring to a large extent by Path B. The experimental results do fit equation (2) as can be seen from Figure 1b.

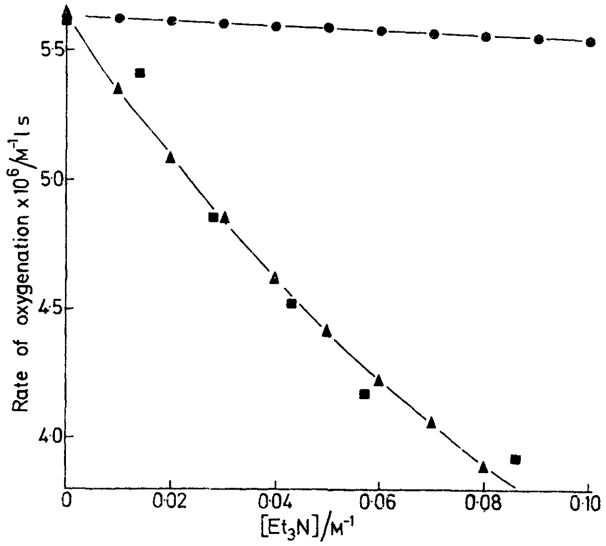


Figure 2. Rate of oxygenation of 2,5-dimethylfuran in the presence of added triethylamine. ● Calculated rates of O_2 absorption (amine acting only as $^1\Delta_g$ O_2 quencher); ▲ calculated rates of O_2 absorption; ■ measured rate of O_2 absorption.

Further proof that the sensitised oxidation of triethylamine occurs by Paths A and B comes from a study of the effect of added triethylamine on the Rose Bengal sensitised oxygenation of 2,5-dimethylfuran. As might be expected, the amine quenches the oxygenation of the furan but the magnitude of the quenching cannot be solely accounted for by the amine acting as a quencher of singlet oxygen (see Figure 2). However, when one takes into account the quenching of singlet and triplet states of the dye by the amine, the experimental and calculated results are in good agreement.

The described results illustrate the point that the concentration of the amine used, is very important in determining the extent to which a dye sensitised oxygenation of an amine occurs by a radical or singlet oxygen pathway.

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† The excited singlet and triplet lifetimes of Rose Bengal are not affected by change from proton to deuterium containing solvents.

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