Concerning the Use of Amines as Probes for Participation of Singlet Oxygen in Dye-sensitised Oxygenation Reactions

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Amines quench the excited singlet states of Methylene Blue and Rose Bengal. Aromatic amines are particularly potent quenchers. Quenching of dye-sensitised oxygenation reactions by amines involves interaction of the amine with singlet oxygen and the excited singlet and triplet states of the dye. An equation is developed which describes the rate of oxygenation of a compound in the presence of an amine. The use of amines as probes for the participation of singlet oxygen in dye-sensitised oxygenation reactions has a number of pitfalls. These may be minimised by keeping the amine concentration below 10^{-3}M. Oxygenation reactions sensitised by tris-(2,2'-bipyridyl)-ruthenium(II) chloride are also quenched by amines establishing that these reactions involve singlet oxygen. The kinetics of these reactions are simpler than those of the dye-sensitised reactions since only one excited state of the complex is involved.

In the last few years the need has arisen for a simple test to determine whether or not singlet oxygen ($^1\Delta gO_2$) is an intermediate in an oxygenation reaction. The most elegant method, developed by Merkel and Kearns,[1a,b,2] relies upon the fact that the lifetime of singlet oxygen is solvent dependent and hence, when singlet oxygen is involved a change of solvent has a profound effect upon the rate of oxygenation. Examples have been reported in which change from a methanol–water mixture to a methanol–deuterium oxide mixture has a large effect upon the rate of oxygenation (*e.g.* of tryptophan [1a]). An alternative test involves the addition of a physical quencher of singlet oxygen to an oxidation reaction.[3] If singlet oxygen is involved, retardation in the rate of reaction should be observed and for a dye-sensitised reaction, relationship (1) should hold. Amines [4] and β-carotene [5] have been used as quenchers.[5]

$$\text{Rate of oxygenation} = I_a\Phi_T k_r[\text{A}]/(k_d + k_q[\text{Q}] + k_r[\text{A}]) \quad (1)$$

k_r = bimolecular rate constant for reaction of substrate [A] with oxygen
k_d = rate constant for unimolecular decay of singlet oxygen
k_q = bimolecular rate constant for quenching singlet oxygen by Q.

In a recent study on the dye-sensitised photo-oxidation of triethylamine [6a,b] it became apparent that the amine not only reacts with the triplet state of the dye but also quenches the excited singlet state of the dye. Thus addition of an amine such as triethylamine to a dye-sensitised oxygenation reaction may cause a retardation for reasons other than it acting as a quencher of singlet oxygen, *i.e.* the interactions between the amine and the excited states of the dye may over-ride the quenching of singlet oxygen. We now report a study on the efficiency of quenching of excited singlet and triplet states of Rose Bengal and Methylene Blue by amines and assess the value of the method for testing for the participation of singlet oxygen in dye-sensitised reactions, which relies upon the use of amines as physical quenchers of singlet oxygen.

RESULTS AND DISCUSSION

The fluorescence of Rose Bengal and Methylene Blue is quenched by a variety of amines and Stern–Volmer

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[1] (*a*) R. Nilsson, P. B. Merkel, and D. R. Kearns, *Photochem. and Photobiol.*, 1972, **16**, 117; *J. Amer. Chem. Soc.*, 1972, **94**, 1030; (*b*) P. B. Merkel and D. R. Kearns, *ibid.*, p. 7244.

[2] For a discussion of the kinetics of these reactions see R. S. Davidson and K. R. Trethewey, *J.C.S. Perkin II*, 1976, 169.

[3] C. S. Foote in ' Free Radicals and Biological Systems,' ed. W. A. Pryor, Academic Press, New York, 1975.

[4] R. H. Rynbrandt and F. E. Dulton, *J. Org. Chem.*, 1975, **40**, 3079; I. Saito, M. Imuta, S. Matsugo, and T. Matsuura, *J. Amer. Chem. Soc.*, 1975, **97**, 7191.

[5] N. A. Evans and I. H. Leaver, *Austral. J. Chem.*, 1974, **27**, 1797.

[6] R. S. Davidson and K. R. Trethewey (*a*) *J.C.S. Chem. Comm.*, 1975, 674; (*b*) preceding paper.

constants (K_{SV}) for these reactions are shown in Table 1. The efficiency of quenching increases as the ionisation potential of the amine decreases. Since the excited singlet states of the amines are of far higher energy than those of the dyes, the quenching process cannot involve singlet–singlet energy transfer. A more likely process involves a redox reaction.

$$\mathrm{Dye}_{S_1} + \mathrm{Am} \longrightarrow \mathrm{Dye}^{-\bullet} + \mathrm{Am}^{+\bullet}$$

$$\mathrm{Am} = \text{amine}$$

The quenching of fluorescence of dyes by anions [2,7] and β-carotene [2] has been proposed as occurring by a similar mechanism. That quenching of the excited singlet states of dyes by amines is an important process when amines are added to dye-sensitised photo-oxygenation reactions becomes immediately apparent when one tries to quantify the retarding effect of the amine on these reactions on the basis that they only occur *via* singlet oxygen. From equation (1) and using the following rate constants, k_r 4 × 10^8 l mol^{-1} s^{-1},[1b] k_d = 1.4 × 10^5 s^{-1},[1b] and k_q 2 × 10^6 l mol^{-1} s^{-1},[8] one would anticipate that triethylamine should quench the Rose Bengal sensitised oxygenation of 2,5-dimethylfuran relatively inefficiently (see Figure 2 of ref. 6*a*). However the degree of quenching is much greater than is calculated.

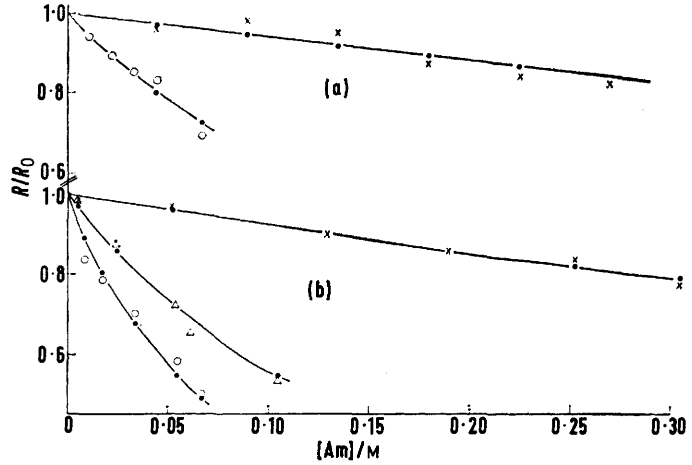

FIGURE 1 Quenching of the sensitised oxygenation of 2,5-dimethylfuran by (a) triethylamine and (b) 1,4-diazabicyclo[2.2.2]octane: ●, calculated rate; ×, △, ○, observed rates utilising Ru(bipy)$_3$Cl$_2$, Rose Bengal, and Methylene Blue as sensitisers

It therefore appears that the addition of amines is causing quenching by additional processes. Since we know that the excited singlet and triplet states of the dyes can be quenched by the amines we have developed equations (2) and (3).

$$\begin{aligned}\text{Rate} = {} & \frac{I_a\Phi_T}{(1 + k_{q_s}\tau[\mathrm{Am}])}\cdot\frac{k_{\mathrm{O_2}}[\mathrm{O_2}]}{(k_{d'} + k_{\mathrm{O_2}}[\mathrm{O_2}] + k_{q_t}[\mathrm{Am}])}\cdot\frac{k_r[\mathrm{A}]}{(k_d + k_{q_o}[\mathrm{Am}] + k_r[\mathrm{A}])}\\ & + \frac{N_oI_a\Phi_T}{(1 + k_{q_s}\tau[\mathrm{Am}])}\cdot\frac{k_{\mathrm{O_2}}[\mathrm{O_2}]}{(k_{d'} + k_{\mathrm{O_2}}[\mathrm{O_2}] + k_{q_t}[\mathrm{Am}])}\cdot\frac{k_{q_o}[\mathrm{Am}]}{(k_d + k_{q_o}[\mathrm{Am}] + k_r[\mathrm{A}])}\\ & + \frac{N_tI_a\Phi_T}{(1 + k_{q_s}\tau[\mathrm{Am}])}\cdot\frac{k_{qt}[\mathrm{Am}]}{(k_{d'} + k_{\mathrm{O_2}}[\mathrm{O_2}] + k_{q_t}[\mathrm{Am}])}\end{aligned} \quad (2)$$

$$\text{Rate} = \frac{I_a\Phi_T}{(1 + k_{q_s}\tau[\mathrm{Am}])}\cdot\frac{k_{\mathrm{O_2}}[\mathrm{O_2}]}{(k_{d'} + k_{\mathrm{O_2}}[\mathrm{O_2}] + k_{q_t}[\mathrm{Am}])}\cdot\frac{k_r[\mathrm{A}]}{(k_d + k_{q_o}[\mathrm{Am}] + k_r[\mathrm{A}])} \quad (3)$$

Equation (2) is the rate of oxygenation of a substrate when an amine (*e.g.* triethylamine) is added which absorbs oxygen. Equation (3) is for the rate of oxygenation of a substrate when an amine (*e.g.* DABCO) is added which does not absorb oxygen.

TABLE 1

Stern–Volmer constants (K_{SV}) for quenching of the fluorescence of Rose Bengal and Methylene Blue by amines in methanol

Substrate	K_{SV}/mol l^{-1} Rose Bengal	K_{SV}/mol l^{-1} Methylene Blue
NN-Dimethylaniline	32.5	23
N-Methylaniline	30	22
Aniline	18.5	19
Diphenylamine	29	33
Tribenzylamine		5.0
1,4-Diazabicyclo[2.2.2]octane	6	2.6
Triethylamine	1.1	1.0

Estimated error ±10%.

Unfortunately these equations contain unknown rate

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[7] D. K. Majumdar, *Z. phys. Chem.* (*Leipzig*), 1961, **217**, 200.

[8] I. B. C. Matheson and J. Lee, *J. Amer. Chem. Soc.*, 1972, **94**, 7244.

constants and partition factors (N_o and N_t) and therefore are not directly solvable. In order to abstract the relevant data attempts were made to simulate the experimental curve by substitution of good guesses for the unknown values. By a process of trial and error a good fit was obtained and the rate constants, *etc.*, derived in this way are shown in Table 2. In order to rigorously test the validity of equation (2), the quenching of the photo-oxygenation of furan and 2,5-dimethylfuran (sensitised by Rose Bengal and Methylene Blue) by triethylamine and 1,4-diazabicyclo[2.2.2]octane (DABCO) were studied (see Figure 1). For the Rose Bengal sensitised reactions, run in the presence of triethylamine it will be seen that there is fair agreement between the values for k_{qt}, N_o, and N_t and those previously obtained by studying the dye-sensitised oxygenation of the amine.[6b] Although a relatively small change in these values leads to a bad fit between the experimental and computed curves it must be stated that we are not advocating the use of this curve-fitting method to determine accurate rate constants. What the results do show is that when amines are added to photo-oxygenation reactions account has to be taken of the interactions between the amine and singlet oxygen and the excited states of the dye. We can say with certainty that the use of amines to test for the participation of singlet oxygen in oxygenation reactions has a number of pitfalls. These may be minimised by keeping the amine concentration below 10^{-3}M. Because of this restriction amines cannot be used as quenchers for the oxidation of highly reactive compounds unless a rigorous kinetic treatment is applied.

TABLE 2

Values for N_o, N_t, and k_{qt} derived by fitting experimentally determined data to equations (2)—(5)

Substrate	Quencher	Dye[a]	N_o	N_t	k_{qt}/l mol^{-1} s^{-1}
2,5-Dimethylfuran	Triethylamine	RB	0.15	0.15	8×10^7
2,5-Dimethylfuran	Triethylamine	MB	0.15	0.07	8×10^7
2,5-Dimethylfuran	Triethylamine	Ru	0.15	0.05	1×10^7
2,5-Dimethylfuran	DABCO	RB			1×10^7
2,5-Dimethylfuran	DABCO	MB			1.8×10^8
2,5-Dimethylfuran	DABCO	Ru			1×10^6
2,5-Dimethylfuran	*NN*-Dimethylaniline	RB			7.5×10^8
Furan	Triethylamine	RB	0.15	0.07	2×10^8
Furan	Triethylamine	MB	0.15	0.07	2.5×10^8
Furan	Triethylamine	Ru	0.14	0.07	1.7×10^8
Furan	DABCO	RB			6×10^7
Furan	DABCO	MB			1.8×10^8
Furan	DABCO	Ru			2×10^6

[a] RB = Rose Bengal, MB = Methylene Blue, Ru = tris-(2,2′-bipyridyl)ruthenium(II) chloride. For all reactions, methanol was used as solvent.

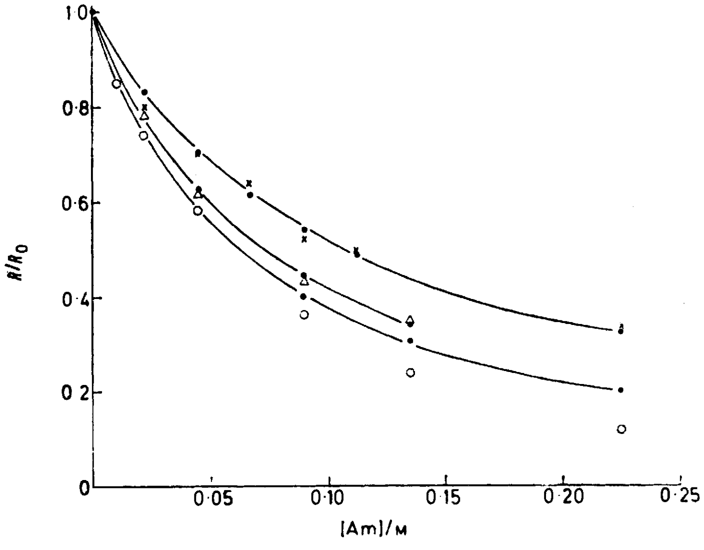

FIGURE 2 Quenching of the sensitised oxygenation of furan by triethylamine: ●, calculated rate; ×, △, ○, observed rates utilising Ru(bipy)$_3$Cl$_2$, Rose Bengal, and Methylene Blue as sensitisers

It will be seen from Figures 2 and 3 that the efficiency of quenching by amines is affected by the type of dye that is employed. This, of course, should not be the case if the amines were acting purely as quenchers of singlet oxygen. From Table 2 it can be seen that for a particular amine, the rate constant for quenching triplet Methylene Blue is greater than that for quenching triplet Rose Bengal. This is not surprising in the light of the recent finding that many amines quench triplet thionine more efficiently than triplet eosin.[9]

So far, an issue which has been avoided is the question as to whether the excited singlet states of the dyes react with amines to give products. We have found this particularly difficult to assess because at the high amine concentrations employed chemical reaction *via* the triplet state occurs relatively efficiently. Thus if chemical reaction does occur from the excited singlet state it will only be a small percentage of the total reaction. Consequently our omitting to take account of chemical reaction *via* this pathway probably involves little error.

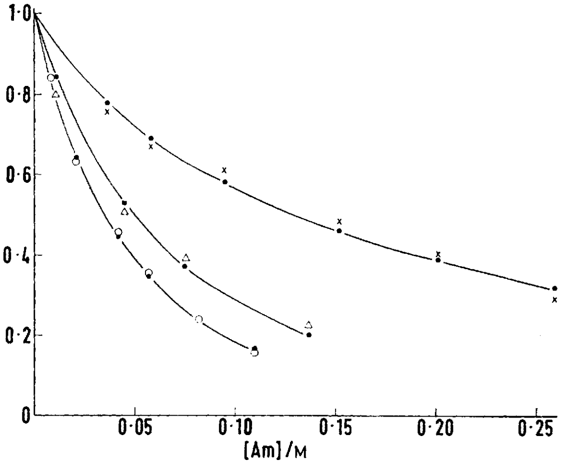

FIGURE 3 Quenching of the sensitised oxygenation of furan by 1,4-diazabicylo[2.2.2]octane: ●, calculated rate; ×, △, ○, observed rates utilising $Ru(bipy)_3Cl_2$, Rose Bengal, and Methylene Blue as sensitisers

The quenching of the excited triplet states of dyes by aromatic amines has been the subject of quantitative studies [9,10] whereas quenching of the excited singlet states of dyes has only received scant attention.[11] As can be seen from Table 1, this process is remarkably efficient and not surprisingly when an amine like *NN*-dimethylaniline is added to a photo-oxygenation reaction, quenching of the excited singlet state of the dye by the amine is very important (see Figure 4). One cannot therefore conclude [12] that the ability of an amine, particularly an aromatic amine, to quench a sensitised oxygenation reaction is evidence for the amine being a quencher of singlet oxygen. However it will be appreciated that a major factor which controls the efficiency of quenching singlet and triplet states of dyes by amines, namely the oxidation potential of the amine, is also a major factor in determining the efficiency with which the amine reacts with singlet oxygen. Thus, the better an amine is at quenching singlet oxygen, the better it will be at quenching the excited states of dyes. It has been previously noted that the efficiency with which amines quench the fluorescence of aromatic hydrocarbons can be related to the efficiency with which amines quench singlet oxygen.[13]

We have previously shown that the complex tris-(2,2′-bipyridyl)ruthenium(II) chloride sensitises the photo-oxygenation of triethylamine and that reaction involves singlet oxygen and reaction of the excited state of the complex with the amine.[6b] The kinetics of oxygenation reactions sensitised by the complex are somewhat simpler than those for reaction sensitised by dyes since only one excited state is involved. We find the complex to be a good sensitiser for photo-oxygenations of 2,5-dimethylfuran and furan, which complements the previous finding that it sensitises the oxidation of 2,3-dimethylbut-2-ene and cyclohexa-1,3-diene efficiently.[14] These reactions are quenched by triethylamine and 1,4-diazabicyclo[2.2.2]octane (Figures 1—3).

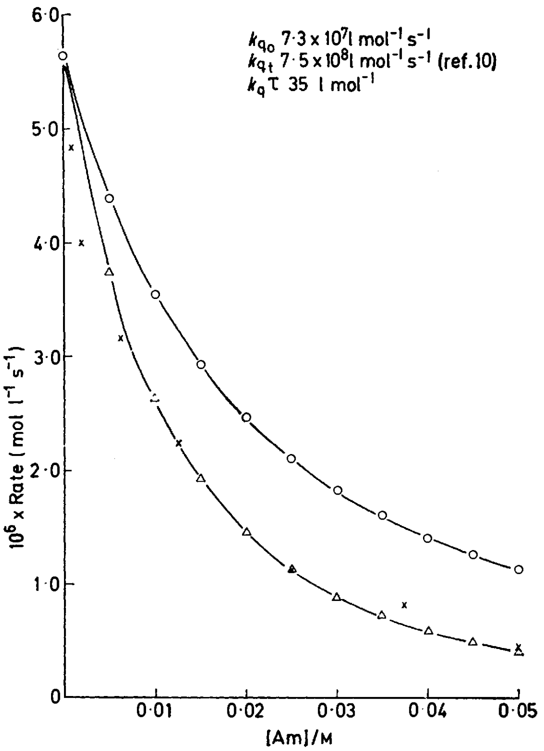

FIGURE 4 Quenching of the photo-oxygenation of 2,5-dimethylfuran by *NN*-dimethylaniline (Rose Bengal as sensitiser): ×, observed rate; △, calculated rate; ○, calculated rates when quenching of the excited singlet state of the dye by the amine is not included.

The degree of quenching was greater than that calculated for the amines acting solely as physical quenchers of singlet oxygen. Equations (4) and (5) were derived by modifying equations (2) and (3). Equation (4) is for

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[9] I. Kralijc and L. Lindqvist, *Photochem. and Photobiol.*, 1974, **20**, 351.

[10] R. H. Young, D. Brewer, R. Kayser, R. Martin, D. Feriozi, and R. A. Keeler, *Canad. J. Chem.*, 1974, **52**, 2889.

[11] W. F. Smith, *J. Amer. Chem. Soc.*, 1972, **94**, 186; R. H. Young, R. L. Martin, D. Feriozi, B. Brewer, and R. Kayser, *Photochem. and Photobiol.*, 1973, **17**, 233.

[12] W. F. Smith, W. G. Herkstroeter, and K. L. Eddy, *J. Amer. Chem. Soc.*, 1975, **97**, 2764.

[13] R. H. Young and R. L. Martin, *J. Amer. Chem. Soc.*, 1972, **94**, 5183.

[14] J. N. Demas, D. Diemente, and E. W. Harris, *J. Amer. Chem. Soc.*, 1973, **95**, 6864.

the rate of oxygenation of a substrate (sensitised by the ruthenium complex) when an amine (*e.g.* triethylamine) is added which absorbs oxygen. Equation (5) is for the rate of oxygenation of a substrate (sensitised by the ruthenium complex) when an amine (*e.g.* DABCO) is added which does not absorb oxygen.

$$\begin{aligned}\text{Rate} = {} & I_a\Phi \frac{k_{O_2}[O_2]}{(k_E + k_{q_E}[Am] + k_{O_2}[O_2])} \cdot \frac{k_r[A]}{(k_d + k_r[A] + k_{q_0}[Am])} \\ & + N_0 I_a\Phi \frac{k_{O_2}[O_2]}{(k_E + k_{q_E}[Am] + k_{O_2}[O_2])} \cdot \frac{k_{q_0}[Am]}{(k_d + k_r[A] + k_{q_0}[Am])} \\ & + N_E I_a\Phi \frac{k_{q_t}[Am]}{(k_E + k_{q_E}[Am] + k_{O_2}[O_2])} \qquad (4)\end{aligned}$$

$$\text{Rate} = I_a\Phi \frac{k_{O_2}[O_2]}{(k_E + k_{q_E}[Am] + k_{O_2}[O_2])} \cdot \frac{k_r[A]}{(k_d + k_r[A] + k_{q_0}[Am])} \qquad (5)$$

k_E = rate constant for unimolecular decay of excited state of sensitiser

The modifications take into account the fact that only one excited state of the sensitiser is involved and that this is severely quenched by oxygen. Fits of calculated to experimental curves were obtained when the rate constants shown in Table 2 were used. These experiments verify the previous finding that the complex is an efficient source of singlet oxygen and that the excited state of the complex can react with the amine even in the presence of oxygen.

EXPERIMENTAL

The photo-oxygenation apparatus and the purification of Rose Bengal have been previously described.[6b] Methylene Blue (Aldrich) was used as received. 2,5-Dimethylfuran and furan (Fison) were distilled prior to use. Fluorescence measurements were made on a Perkin-Elmer MPF-4 spectrofluorimeter.

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