Photosensitised Oxidation of Amines: Mechanism of Oxidation of Triethylamine

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The rates of photo-oxygenation of triethylamine sensitised by Rose Bengal have been measured for a variety of amine concentrations utilising methanol, methanol–water, and pyridine as solvents. In order to explain the results a kinetic scheme is used in which account is taken of chemical reaction occurring *via* singlet oxygen and interaction of the excited triplet state of the dye and the amine. The excited singlet state of Rose Bengal is quenched by the amine. That the oxidation of the amine can occur by two concurrent mechanisms is supported by a study of solvent isotope effects. Oxygenation reactions using tris-(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate as sensitiser are less complicated since only one excited state of the sensitiser is involved in the reactions. The effect of change in oxygen concentration upon the rate of oxygenation reactions involving both singlet oxygen and radical pathway is discussed. Calculations show that whether the change causes retardation or acceleration is dependent upon the magnitude of the various rate constants and the efficiency with which the singlet oxygen and radical pathways lead to products.

THE question as to the mechanism by which the photosensitised oxygenation of amines occurs is a matter of controversy. In many cases it has been tacitly assumed that singlet oxygen ($^1\Delta gO_2$) is the oxidising species. Evidence has started to accumulate which indicates that amines can be oxidised by this species. When oxygen is flowed through a microwave discharge and the exit gases passed over codeine on a suitable support, demethylation occurs.[1] Other work includes a kinetic study of the oxidation of aniline [2] in which care was taken to account for all the physical quenching processes. Recently, Leaver has shown that the oxidation of pyrazolines displays a solvent isotope effect and this is particularly convincing evidence.[3]

We have previously advocated the view that dye-

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[1] J. H. E. Lindner, H. J. Kuhn, and K. Gollnick, *Tetrahedron Letters*, 1972, 1705.

[2] R. Chapelon, G. Perichet, and B. Pouyet, *Mol. Photochem.*, 1973, **5**, 77.

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

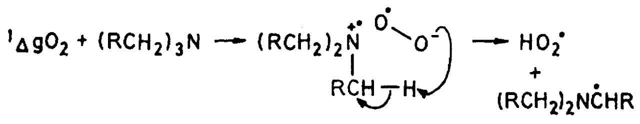
sensitised oxygenation reactions occur *via* a radical process.[4] Evidence presented in favour of this mechanism was that dye–amine interactions could be detected

$$\mathrm{Dye}_{T_1} + \mathrm{R_3N} \longrightarrow \text{Radicals}$$
$$\text{Radicals} + \mathrm{O_2} \longrightarrow \text{Oxidation products}$$

in oxygenated solutions. It also seemed reasonable to propose this mechanism because of the analogy with the carbonyl compound-sensitised oxidation of amines in which quantum yields of greater than unity were observed.[5] Furthermore, experiments which established that amines are good quenchers of singlet oxygen suggested that the quenching was mainly physical.[6a,b]

It has recently been reported[7] that 1,2-diamino-*NNN'N'*,4,5-hexamethylbenzene undergoes photo-oxidation to give products by addition of oxygen to the ring (a typical singlet oxygen reaction) and oxidation of the *N*-methyl group. The efficiency of competition between these two processes is dependent upon the dye and whether the dye is bound to a polymer or not. These results suggest that the two types of products are being formed by different mechanisms.

Unfortunately one cannot use the nature of the products formed in the oxidation of aliphatic amines to distinguish between the singlet oxygen and radical mechanism. Reaction of amines with singlet oxygen involves a charge transfer process and we can anticipate that this will lead to formation of aminoalkyl radicals (1). The excited state of the dye can react in a similar way to give the same radical. Thus trapping of radical (1) or reactive species derived from it does not shed any light on their genesis.



(1)

It therefore appears that, to distinguish between the two mechanisms, a detailed kinetic study is necessary. Such a study has been made of the photo-oxidation of triethylamine and the conclusion reached that reaction occurs *via* singlet oxygen.[8] By use of pyridine as solvent, reaction by this pathway is particularly favoured because the lifetime of singlet oxygen is reasonably long (42 μs) in this solvent.[9] The radical mechanism was dismissed from consideration because plots of the reciprocal of the rates of oxygenation *versus* the reciprocal of the amine concentration were apparently linear. We have shown[10] in the preceding paper that use of equation (1) is a very sensitive test for assessing whether the reactions wholly involve singlet oxygen.[11] Other reasons given for discounting the radical mechanism were (1) the rate of reaction was not sensitive to change in oxygen concentration (a change from oxygen to air) and (2) photobleaching of Rose Bengal by triethylamine in pyridine was not observed upon flash photolysing such a solution.

$$\text{Rate of oxygenation} = N_0 I_a \Phi_T k_{q_e}[\mathrm{Am}]/(k_d + k_{q_e}[\mathrm{Am}]) \qquad (1)$$

N_0 = Fraction of molecules undergoing oxidation
I_a = Light intensity
Φ_T = Quantum yield of triplet formation for the sensitising dye
k_{q_e} = Rate constant for reaction of the acceptor with singlet oxygen
k_d = Rate constant for decay of singlet oxygen in the solvent used
[Am] = Amine concentration

RESULTS AND DISCUSSION

Rose Bengal has been used as a sensitiser, in preference to Methylene Blue since the latter dye can undergo permanent photobleaching on reaction with amines. This makes it difficult to obtain reproducible kinetic measurements.

Rose Bengal is a fluorescent dye, λ_{max} 560—570 nm, and its fluorescence is quenched by triethylamine. The efficiency is very solvent dependent and Stern–Volmer quenching constants are given in Table 1. The magnitude of these constants is such that correction has to be made for quenching of the excited singlet state of the dye in order to get a true value of the quantum yield of singlet oxygen production.

TABLE 1

Stern–Volmer constants[a] for the quenching of Rose Bengal fluorescence by triethylamine in various solvents

Solvent	K_{SV}/mol l^{-1}
Ethanol	1.5
Methanol	1.1
Methanol–water (50 : 50 v/v)	1.4
Methanol–deuterium oxide (50 : 50, v/v)	1.8
Water	4—5 [b,c]
Pyridine	0.25
Acetone	0.4
Acetonitrile	~1.5[c]

[a] Calculated from $\Phi_0/\Phi = 1 + K_{SV}$ [Q] (see ref. 11). [b] Minimum amount of methanol added to aid solubility (*ca.* 1%). [c] Some curvature was observed in the Stern–Volmer plot.

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[4] R. F. Bartholomew and R. S. Davidson, *J. Chem. Soc.* (*C*), 1971, 2347.

[5] R. F. Bartholomew and R. S. Davidson, *J. Chem. Soc.* (*C*), 1971, 2342.

[6] (*a*) C. Ouannes and T. Wilson, *J. Amer. Chem. Soc.*, 1968, **90**, 6527; K. Furukawa and E. A. Ogryzlo, *Chem. Phys. Letters*, 1971, **12**, 370; E. A. Ogryzlo and C. W. Tang, *J. Amer. Chem. Soc.*, 1970, **92**, 5031; G. A. Hollinden and R. B. Tinimons, *ibid.*, p. 4181; R. H. Young and R. L. Martin, *ibid.*, 1972, **94**, 5183; (*b*) I. B. C. Matheson and J. Lee, *Chem. Phys. Letters*, 1970, **7**, 475; *J. Amer. Chem. Soc.*, 1972, **94**, 3310.

[7] I. Saito, S. Abe, G. Takahashi, and T. Matsuura, *Tetrahedron Letters*, 1974, 4001.

[8] W. F. Smith, *J. Amer. Chem. Soc.*, 1972, **94**, 186.

[9] R. S. Davidson and K. R. Trethewey, unpublished results. *Cf.* R. H. Young, D. Brewer, and R. A. Keller, *J. Amer. Chem. Soc.*, 1973, **95**, 375.

[10] R. S. Davidson and K. R. Trethewey, *J.C.S. Chem. Comm.*, 1975, 674.

[11] For a discussion of the kinetics of dye-sensitised oxygenation reactions please see R. S. Davidson and K. R. Trethewey, preceding paper.

The rate of oxygenation of methanolic solutions of triethylamine sensitised by Rose Bengal has been studied utilising a wide range of amine concentrations (see Figure 1). The most striking fact to emerge is that a low limiting quantum yield is attained at a fairly low amine concentration. If equation (1) is a true description of the process the rate of reaction should increase as the amine concentration is increased and then flatten off. What is actually observed is that the rate is maximal at *ca.* 0.12M-amine and then starts to decrease as the amine concentration is increased. When correction is made for quenching of the excited singlet state of the dye by the amine one finds that an over-correction has been applied (Figure 1), *i.e.* more reaction is occurring *via* the excited singlet state of the dye and/or the excited triplet state of the dye. From photoreduction studies we know that chemical reaction between the triplet state of the dye and the amine is extremely efficient. For this reason, equation (2) was developed[10,11] in which oxygenation is described as occurring *via* singlet oxygen and the excited triplet state of the dye whereas interaction of the amine with the excited singlet state of the dye leads to quenching.

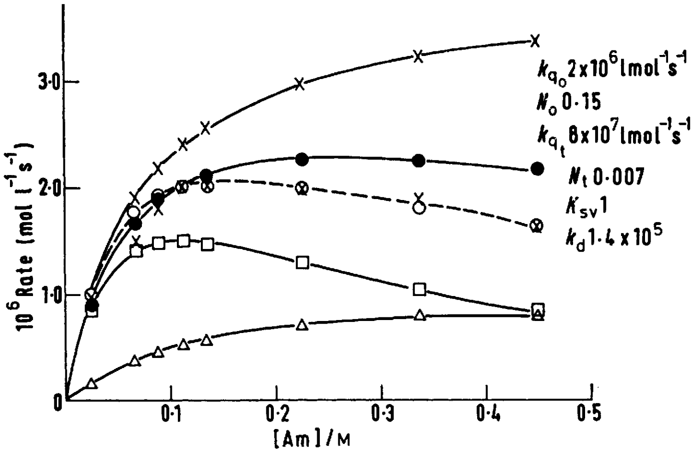

FIGURE 1 Rates of photo-oxygenation of triethylamine in methanol solution sensitised by Rose Bengal: -×-, experimentally observed values; ○, calculated values taking all parameters into consideration; —×—, calculated values for reaction only occurring *via* singlet oxygen; ●, calculated values for reaction involving singlet oxygen and quenching of the excited singlet state of the dye by the amine; □, calculated component of reaction occurring *via* singlet oxygen; △, calculated component of reaction occurring *via* triplet dye

$$\text{Rate of oxygenation} = \frac{N_o I_a \Phi_T}{(1 + k_{q_s}\tau[\text{Am}])} \cdot \frac{k_{o_2}[^3\text{O}_2]}{(k_{d'} + k_{o_2}[^3\text{O}_2] + k_{qt}[\text{Am}])} \cdot \frac{k_{q_o}[\text{Am}]}{(k_d + k_{q_o}[\text{Am}])} + \frac{N_t I_a \Phi_T}{(1 + k_{q_s}\tau[\text{Am}])} \cdot \frac{k_{qt}[\text{Am}]}{(k_{d'} + k_{o_2}[^3\text{O}_2] + k_{qt}[\text{Am}])} \quad (2)$$

In this equation there are four unknowns, N_o, N_t, k_{qt}, and k_{o_2}. The latter can be assumed to be diffusion controlled since the triplet energy of the dye (E_T 39 kcal mol^{-1}) [12] is far greater than the energy of singlet oxygen (22 kcal mol^{-1}).[13] The value of 2×10^6 l mol^{-1} s^{-1} obtained by Matheson and Lee[5] was used for k_{q_o}. A good fit of the calculated to the experimental curve is obtained when the values shown in Table 2 are substituted.

Change in solvent from methanol to aqueous methanol (50 : 50 v/v) causes a large change in the way in which rate of oxygenation varies with amine concentration. The difference in lifetime of singlet oxygen in the two solvents[14] has an effect but this does not account for all the change. Fluorescence quenching is more efficient in the aqueous solvent and when this is taken into account a good fit of the experimental to the calculated curve is obtained with the values shown in Table 2. It will be seen that the greater efficiency in oxygenation is mainly due to more chemical reaction ensuing from the complexes formed between singlet oxygen and the amine and the excited triplet state of the dye and the amine.

Recently Merkel and Kearns[14,15] have devised a very elegant test for the participation of singlet oxygen in oxygenation reactions. This relies on the fact that the lifetime of singlet oxygen is very different in deuteriated compared with the related non-deuteriated solvents. Since the lifetime of singlet oxygen is different in aqueous methanol (50 : 50 v/v) and methanol–deuterium oxide mixtures (50 : 50 v/v) (3.5 and 11 μs respectively), a method was available, not only for checking whether singlet oxygen was participating in the amine oxygenation reactions, but also for checking the validity of equation (2). The results of the reaction run in methanol–deuterium oxide mixture have been described[10] and from these it can be seen that an increase in rate and limiting quantum yield for the reaction is observed on change to the deuteriated solvent. However, apart from the use of a different lifetime for singlet oxygen, all the rate constants used for the methanol–water system can be used for the methanol–deuterium

TABLE 2

Rate constants and partition factors derived by fitting calculated rates of oxygenation of triethylamine [using equation (2)] to the experimentally observed rates

Rose Bengal as sensitiser Solvent	N_o	N_t	k_{qt}/l mol^{-1} s^{-1}
Methanol	0.15	0.07	8×10^7
Methanol–water (50 : 50 v/v)	0.47	0.15	8×10^7
Methanol–deuterium oxide (50 : 50 v/v)	0.47	0.15	8×10^7
Pyridine	0.6	0.06	4×10^8
Tris-(2,2′-bipyridyl)ruthenium(II) chloride as sensitiser			
Methanol	0.15	0.04	4×10^7
Pyridine	0.14	0.09	6×10^7

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[12] K. Gollnick, *Adv. Photochem.*, 1968, **6**, 1.

[13] C. S. Foote, *Accounts Chem. Res.*, 1968, **1**, 104.

[14] P. B. Merkel and D. R. Kearns, *J. Amer. Chem. Soc.*, 1972, **94**, 7244.

[15] R. Nilsson, P. B. Merkel, and D. R. Kearns, *Photochem. and Photobiol.*, 1972, **16**, 117; *J. Amer. Chem. Soc.*, 1972, **94**, 1030.

oxide system. That the rate differences in the two solvent systems are not due to changes in physical parameters of the excited states of the dye is attested to by the fact that the singlet and triplet lifetime of the dye are unaffected by use of deuterium containing solvents. The latter point was evaluated by showing that the rate of photoreduction of the dye by the amine (very low concentration) is the same in CH_3OH, CD_3OD, and CH_3OD.

It is interesting to note that the deuterium isotope effect is most marked at low amine concentrations and becomes non-existent at high amine concentrations. Such behaviour is to be anticipated by a reaction which occurs solely by singlet oxygen, and for which the rate constant for reaction of the substrate with singlet oxygen is particularly high. However one would not expect a decrease in rate as amine concentration is increased as is observed at amine concentrations >0.11M. At this and higher amine concentrations the radical reaction takes over from reaction *via* singlet oxygen but the overall rate is decreased because of increased quenching of the excited singlet state of the dye and also because reaction of the excited triplet state of the dye with the amine leads inefficiently to chemical reaction. If reaction had been occurring solely by singlet oxygen, the rate of oxygenation in the two solvent system should not have been the same at an amine concentration of 0.4M.

Use of pyridine as solvent for the oxygenation reaction also affects the relationship between rate of oxygenation and amine concentration (see Figure 2). The increased lifetime of singlet oxygen in this solvent compared with methanol, is reflected in the large increase in rate of reaction over a small change in amine concentration. The radical reaction and fluorescence quenching process assert themselves at high amine concentrations although the latter has a relatively small effect due to the K_{SV} value (Table 1) being so low. In Smith's study[8] on the oxidation of the amine in pyridine, the operation of the radical mechanism was dismissed on the grounds that the rate of reaction was not sensitive to change in oxygen concentration. By means of equation (2) and the derived rate constant k_{qt} and partition factors N_o and N_t it is possible to calculate what effect change in oxygen concentration will have on the rate. The results for pyridine are shown in Figure 3 and the surprising finding is that a decrease in oxygen concentration leads to a reduction in rate at high amine concentrations and an increase in rate at low concentration (<7 × 10^{-3}M). The actual magnitude of the differences is affected by the light intensity. Calculations were also made for the reaction in aqueous methanol solution and the results are shown in Figure 4.

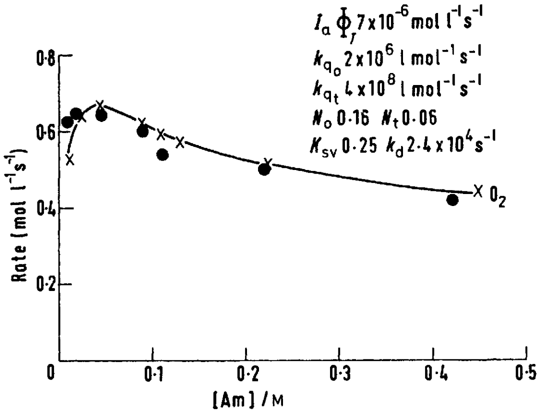

FIGURE 2 Rates of photo-oxygenation of triethylamine in pyridine sensitised by Rose Bengal: ●, experimentally observed values; ×, calculated values

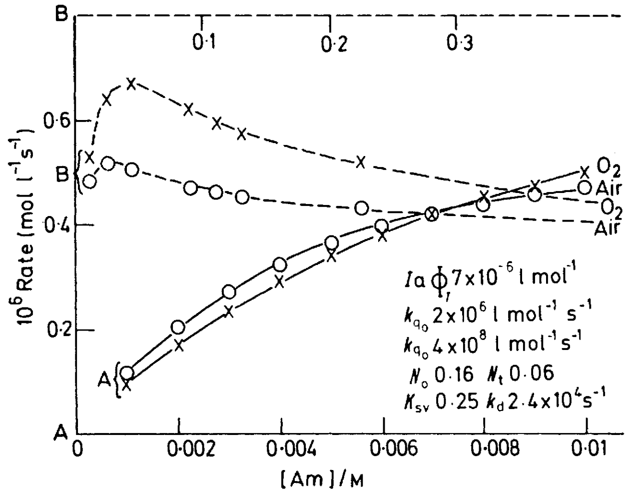

FIGURE 3 Calculated rates of photo-oxygenation of triethylamine in air-saturated and oxygen-saturated pyridine solution sensitised by Rose Bengal

Qualitatively the result is the same as for pyridine solution but the change over from retardation to rate enhancement occurs at a higher amine concentration (*ca.* 7.5 × 10^{-2}M). Change of solvent to a methanol–deuterium oxide mixture also has a profound effect upon the change over concentration (see Figure 4). These results show that to predict whether a reduction in oxygen concentration for a reaction involving singlet oxygen and radical pathways will retard the reaction is very difficult and requires precise knowledge of all the relevant rate constants and partition factors. What can be concluded is that since a reaction involving only singlet oxygen will show little sensitivity to oxygen concentration (unless extremely low concentrations of oxygen are employed) a rate enhancement or retardation by decrease in oxygen concentration may indicate a radical pathway. This conclusion would be verified if that rate difference increased with increase in light intensity and if it varied over a change in substrate concentration. The effect of decreasing oxygen concentration upon rate of consumption of starting material will also be dependent upon the extent to which the reaction is allowed to proceed. Thus, for a very small percentage conversion a retardation may be observed whereas for a higher percentage conversion an acceleration may be observed. This has been found for the oxidation of triethylamine in methanol solution.[4]

Use of Rose Bengal as a sensitiser for oxidation of amines is complicated by the excited singlet state of the dye being quenched by the amine. It appeared that this difficulty could be overcome by use of tris-(2,2′-bipyridyl)ruthenium(II) chloride as a sensitiser since this complex has been shown to be an effective sensitiser for singlet oxygen production and it also has a very high quantum yield of triplet formation.[16b] Oxidation of triethylamine, using this complex, was studied in both methanol and pyridine solution. Good fits between experimental and calculated curves (Figure 5) for the dependence of rate of oxygenation upon amine concentration are obtained when the values shown in Table 2 are utilised.* Fits could not be obtained to equation (1). Values which give a good fit for low amine concentrations lead to an abysmal fit at high amine concentrations and therefore it appears that with the complex as sensitiser reaction is occurring by two mechanisms.

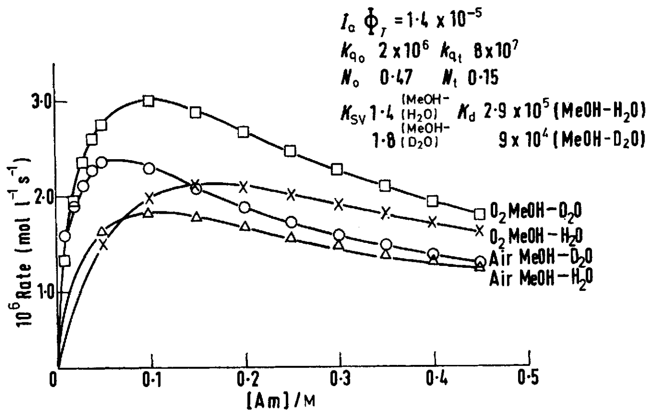

FIGURE 4 Calculated rates of photo-oxygenation of triethylamine in oxygen and air-saturated aqueous–methanol and deuterium oxide–methanol mixtures (sensitised by Rose Bengal)

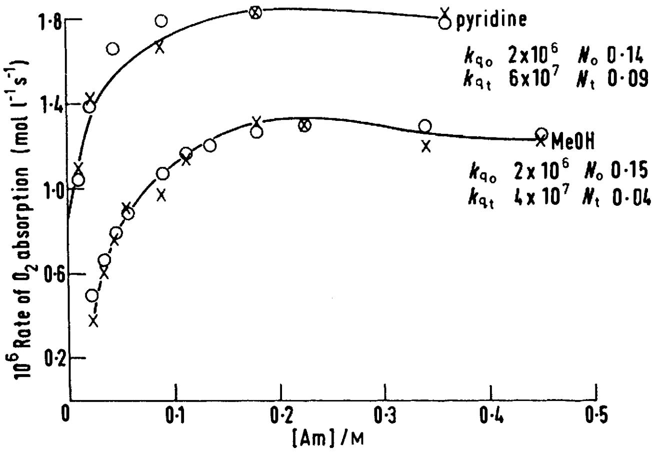

FIGURE 5 Rates of photo-oxygenation of triethylamine in pyridine and methanol solution sensitised by $Ru(bipy)_3Cl_2$

The described results show how the photo-oxygenation of triethylamine, which can be taken as a typical aliphatic amine, is dependent upon the solvent and the type of sensitiser employed. Thus determination of rate constants for reaction of singlet oxygen with amines by comparing rates of oxidation of amines with a standard singlet oxygen acceptor, is fraught with difficulties.[17] Presumably the only reliable technique is the one in which the effect of amines upon the lifetime of singlet oxygen is assessed.[5b,18]

EXPERIMENTAL

All solvents were dried and distilled prior to use. Rose Bengal (B.D.H. technical) was purified by thick-layer chromatography on alumina plates.

Fluorescence measurements were made on a Baird Atomic SF100E instrument.

The oxygenation apparatus was constructed to a design supplied by Dr. A. K. Davies and is sufficiently sensitive to record rates of 0.1 μmol l^{-1} s^{-1}.[19] For all reactions an aqueous solution of potassium chromate was interposed between the tungsten lamp (1 kW) and the reaction cell in order to eliminate light of <460 nm. A Balzers interference filter transmitting between 510 and 640 nm was used for reactions involving Rose Bengal.

Actinometry was carried out by measuring the rate of photo-oxygenation of 2,5-dimethylfuran. Since the rate constant for reaction of singlet oxygen with this acceptor and k_d values for singlet oxygen in the various solvents are known, values for $I_a\Phi_T$ were readily evaluated.

APPENDIX

Since tris-(2,2′-bipyridyl)ruthenium(II) chloride has effectively only one excited state which is responsible for

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* See appendix.

[16] (*a*) J. N. Demas, D. Diemente, and E. W. Harris, *J. Amer. Chem. Soc.*, 1973, **95**, 6864; (*b*) J. N. Demas and A. W. Adamson, *ibid.*, 1971, **93**, 1800.

[17] R. H. Young, R. L. Martin, D. Feriozi, D. Brewer, and R. Kayser, *Photochem. and Photobiol.*, 1973, **17**, 233.

[18] D. R. Adams and F. Wilkinson, *J.C.S. Faraday II*, 1975, 586; P. B. Merkel and D. R. Kearns, *J. Amer. Chem. Soc.*, 1972, **94**, 1029.

[19] G. O. Phillips, A. K. Davies, and J. F. McKellar, *Lab. Practice*, 1970, **19**, 1037.

reaction with oxygen and the amine, a modified form of equation (2) has to be used. This equation is of the from Rate $= A + B$ where $A =$ portion of reaction *via* singlet oxygen and $B =$ portion of reaction *via* a sensitiser–amine interaction.

Rate of oxygen absorption

$$= \frac{N_{\mathrm{o}} I_{\mathrm{a}} \Phi k_{\mathrm{o_2}}[\mathrm{O_2}]}{(k_{\mathrm{E}} + k_{\mathrm{qE}}[\mathrm{Am}] + k_{\mathrm{o_2}}[\mathrm{O_2}])} \cdot \frac{k_{\mathrm{q_o}}[\mathrm{Am}]}{(k_{\mathrm{d}} + k_{\mathrm{r}}[\mathrm{A}] + k_{\mathrm{q_o}}[\mathrm{Am}])}$$

$$+ N_{\mathrm{E}} I_{\mathrm{a}} \Phi \frac{k_{\mathrm{qE}}[\mathrm{Am}]}{(k_{\mathrm{E}} + k_{\mathrm{qE}}[\mathrm{Am}] + k_{\mathrm{o_2}}[\mathrm{O_2}])}$$

k_{E} = rate constant for unimolecular decay of excited state of sensitiser

k_{qE} = rate constant for quenching excited state of the sensitiser by amine

N_{E} = partition factor describing amount of chemical reaction which takes place from the quenching process

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