Factors affecting Dye-sensitised Photo-oxygenation Reactions

By **R. Stephen Davidson** * and **Kenneth R. Trethewey**, Department of Chemistry, The University, Leicester LE1 7RH

The kinetics of dye-sensitised oxidation reactions are considered. Utilisation of rate of oxygen absorption measurements to provide information on light intensity and the quantum yield of triplet formation of the dye, is discussed. The way in which solvent isotope effects, sensitiser–substrate triplet–triplet energy transfer processes, and quenching of the sensitiser excited singlet state by the substrate affect the kinetics is considered. Quantitative measurements on the quenching of the excited singlet states of Methylene Blue and Rose Bengal by anions, β-carotene, and 2,5-diphenylisobenzofuran are reported. A comprehensive rate expression is obtained for oxidation reactions in which the substrate interacts with the excited singlet and triplet states of the sensitiser, and with singlet oxygen.

THE ability of many compounds to act as photosensitisers for the oxygenation of a wide variety of compounds has been recognised for years.[1] Of recent, a particular interest has been the role of singlet molecular oxygen ($^1\Delta gO_2$) in these reactions. A number of methods have been devised to demonstrate the intermediacy of this species. These have included the mimicking of the photoreactions by producing singlet oxygen *via* a chemical process [2a-d] (*e.g.* from a sodium hypochlorite–hydrogen peroxide mixture,[2a] by thermal decomposition of the triphenyl phosphite–ozone adduct,[2b] and 9,10-diphenylanthracene 9,10-*endo*-peroxide [2c]) or by passing oxygen through a radiofrequency discharge.[2d] Direct methods used for studying photosensitised oxygenation reactions usually involve kinetic studies. Thus, information from the rate of oxidation of a compound of known reactivity in the presence of a compound of unknown reactivity,[3] and from the rates of oxidation of compounds in the presence of a quencher (*e.g.* 1,4-diazabicyclo[2.2.2]octane [4] or β-carotene [5]) has been obtained. More recently, solvent isotope effects have been shown to be of value in such studies.[6a,b] Many of these kinetic methods are not without their pitfalls and furthermore do not help to delineate whether oxidation is occurring *via* singlet oxygen or a radical process. Because of the enigma concerning the mechanism of photo-oxygenation of amines we have made a study of these kinetic treatments and now summarise the findings.

Production of singlet oxygen *via* energy transfer from a photosensitiser involves processes (1)—(3b). By a

$$\mathrm{Sens}_{S_0} \xrightarrow{I_a} \mathrm{Sens}_{S_1} \qquad (1)$$

$$\mathrm{Sens}_{S_1} \xrightarrow{k_F} \mathrm{Sens}_{S_0} + h\nu \qquad (2a)$$

$$\mathrm{Sens}_{S_1} \xrightarrow{k_{IC}} \mathrm{Sens}_{S_0} \qquad (2b)$$

$$\mathrm{Sens}_{S_1} \xrightarrow{k_{ISC}} \mathrm{Sens}_{T_1} \qquad (2c)$$

$$\mathrm{Sens}_{T_1} \xrightarrow{k_d^1} \mathrm{Sens}_{S_0} \qquad (3a)$$

$$^3O_2 + \mathrm{Sens}_{T_1} \xrightarrow{k_{O_2}} \mathrm{Sens}_{S_0} + {}^1O_2 \qquad (3b)$$

---

[1] K. Gollnick, *Adv. Photochem.*, 1968, **6**, 1; C. S. Foote, *Science*, 1968, **162**, 963; *Accounts Chem. Res.*, 1968, **1**, 104; J. Bourbon and B. Schnuriger, ' Physics and Chemistry of the Organic Solid State,' New York, 1967, vol. III, p. 97.

[2] (*a*) C. S. Foote, S. Wexler, W. Ande, and R. Higgins, *J. Amer. Chem. Soc.*, 1968, **90**, 975; (*b*) M. E. Brennan, *Chem. Comm.*, 1970, 956; P. D. Bartlett and G. D. Mendenhall, *J. Amer. Chem. Soc.*, 1970, **92**, 6055; (*c*) H. H. Wasserman, J. R. Schaffer, and J. L. Cooper, *ibid.*, p. 4891; H. H. Wasserman, F. J. Vinick, and Y. C. Chang, *ibid.*, p. 7180; (*d*) R. Chapelon and B. Pouyet, *Bull. Soc. chim. France*, 1974, 2367.

[3] R. H. Young, K. Wehrly, and R. L. Martin, *J. Amer. Chem. Soc.*, 1971, **93**, 5774.

[4] C. Ouannes and T. Wilson, *J. Amer. Chem. Soc.*, 1968, **90**, 6527.

[5] C. S. Foote, Y.C. Chang, and R. W. Denny, *J. Amer. Chem. Soc.*, 1970, **92**, 5218.

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

steady state kinetic treatment it can be shown that equation (4) applies where $\Phi_T = k_{\mathrm{ISC}}/(k_{\mathrm{F}} + k_{\mathrm{IC}} + k_{\mathrm{ISC}})$. Since in most cases $k_{\mathrm{O_2}}$ *ca.* 2×10^9 l $\mathrm{mol^{-1}\ s^{-1}}$

$$\mathrm{d}[{}^1\mathrm{O_2}]/\mathrm{d}t = I_{\mathrm{a}}\Phi_T \frac{k_{\mathrm{O_2}}[{}^3\mathrm{O_2}]}{k_{\mathrm{d^1}} + k_{\mathrm{O_2}}[{}^3\mathrm{O_2}]} \qquad (4)$$

and $k_{\mathrm{d^1}}$ *ca.* $10^4\ \mathrm{s^{-1}}$ it can be seen that equation (4) reduces to (5). Introduction of a substrate into the reaction,

$$\mathrm{d}[{}^1\mathrm{O_2}]/\mathrm{d}t = I_{\mathrm{a}}\Phi_T \qquad (5)$$

which reacts with the singlet oxygen means that processes (6) and (7) have also to be taken into account.

$$ {}^1\mathrm{O_2} \xrightarrow{k_\mathrm{d}} {}^3\mathrm{O_2} \qquad (6)$$

$$ {}^1\mathrm{O_2} + \mathrm{A} \xrightarrow{k_\mathrm{r}} \mathrm{AO_2} \qquad (7)$$
$$\mathrm{AO_2} = \text{product}$$

Assuming that there is no build up of singlet oxygen in solution, the following equations can be derived: $-\mathrm{d}[{}^1\mathrm{O_2}]/\mathrm{d}t = (k_\mathrm{d} + k_\mathrm{r}[\mathrm{A}])[{}^1\mathrm{O_2}]$ and hence $I_\mathrm{a}\Phi_T = (k_\mathrm{d} + k_\mathrm{r}[\mathrm{A}])[{}^1\mathrm{O_2}]$. The rate of loss of A is given by equation (8). This simple equation has been used in numerous

$$\begin{aligned} -\mathrm{d}(\mathrm{A})/\mathrm{d}t &= k_\mathrm{r}[\mathrm{A}][{}^1\mathrm{O_2}] \\ &= I_\mathrm{a}\Phi_T k_\mathrm{r}[\mathrm{A}]/(k_\mathrm{d} + k_\mathrm{r}[\mathrm{A}]) \qquad (8)\end{aligned}$$

kinetic examinations of photo-oxygenation reactions.

Examination of equation (8) shows that if very low concentrations of A are used, it can be simplified to (9).

$$-\mathrm{d}(\mathrm{A})/\mathrm{d}t = I_\mathrm{a}\Phi_T k_\mathrm{r}[\mathrm{A}]/k_\mathrm{d} \qquad (9)$$

When equation (9) holds, a linear dependence of the rate of photo-oxygenation upon the substrate concentration will be observed. However, departure from linearity will occur as the values of k_d and $k_\mathrm{r}[\mathrm{A}]$ become similar and when $k_\mathrm{r}[\mathrm{A}] \gg k_\mathrm{d}$ no further increase in the rate will be observed on addition of substrate. Under these conditions equation (8) reduces to (10). It can be

$$-\mathrm{d}(\mathrm{A})/\mathrm{d}t = I_\mathrm{a}\Phi_T \qquad (10)$$

clearly seen that if rate constants for photo-oxygenation are to be determined accurately, one has to ensure that one is working under conditions in which $k_\mathrm{r}[\mathrm{A}] \ll k_\mathrm{d}$.

Equation (8) has been used in form (11), for the

$$\left(\frac{-\mathrm{dA}}{\mathrm{d}t}\right)^{-1} = \frac{I_\mathrm{a}\Phi_T}{\mathrm{I}}\left\{1 + \frac{k_\mathrm{d}}{k_\mathrm{r}} \cdot \frac{1}{[\mathrm{A}]}\right\} \qquad (11)$$

determination of β values $(k_\mathrm{d}/k_\mathrm{r})$.[1,3,7] Recently methods have been developed for determining k_d values [8a,b] and consequently quite a number of k_r values are now known.

A useful application of equation (8) is for the determination of values of $I_\mathrm{a}\Phi_T$. The range of solvents for which Φ_T values for common dye sensitisers is known, is relatively limited. By measuring the rate of oxygenation of a compound having a known k_r value, under conditions in which $k_\mathrm{r}[\mathrm{A}] \gg k_\mathrm{d}$ [*i.e.* equation (10) holds] the value is obtained directly. We have found that 2,5-dimethylfuran ($k_\mathrm{r} = 4 \times 10^8$ l $\mathrm{mol^{-1}\ s^{-1}}$[6b]) is a particularly useful substrate. The furan has also found recent application for the determination of the quantum yield of singlet oxygen production by Methylene Blue.[9] Determination of $I_\mathrm{a}\Phi_T$ values in this way neatly sidesteps the problems which occur when the absorption spectrum of the dye is solvent sensitive. If an independent method is available for determining I_a, quantum yields of triplet formation are readily obtained.

The importance of using the correct substrate concentration range for making kinetic measurements is relevant to the use of solvent isotope effects as a criterion for the participation of singlet oxygen.[6a,b] Merkel and Kearns have noted that the lifetime of singlet oxygen is increased from 3.5 to 11 μs on change from methanol–water (50 : 50) to methanol–deuterium oxide (50 : 50).[6b] This increase in lifetime will only manifest itself when $k_\mathrm{d} \gg k_\mathrm{r}[\mathrm{A}]$. The isotope effect disappears when $k_\mathrm{d} \approx k_\mathrm{r}[\mathrm{A}]$ (where k_d refers to lifetime of singlet oxygen in the deuteriated solvent) and this can be seen by inspection of Table 1. Thus, to observe the *maximal* effect, the concentration of A has to be carefully selected.

TABLE 1

Calculated relative quantum yields of oxygenation for a compound having k_r 4×10^8 l $\mathrm{mol^{-1}\ s^{-1}}$ in methanol–water (50 : 50) and methanol–deuterium oxide (50 : 50) [a]

[compound]/M	Φ in MeOH–H_2O	Φ in MeOH–D_2O	$\frac{\Phi\mathrm{MeOH{-}D_2O}}{\Phi\mathrm{MeOH{-}H_2O}}$
10^{-1}	0.993	0.998	1.005
10^{-2}	0.932	0.977	1.05
10^{-3}	0.580	0.815	1.40
10^{-4}	0.121	0.305	2.52

[a] Lifetime of singlet oxygen in the two solvent systems has been previously determined.[6b] The useful quantity ' relative quantum yield ' can be defined as the rate of reaction divided by $I_\mathrm{a}\Phi_T$ assuming that term A in equation (32) can be neglected.

It will be realised that these isotope effects will be difficult to observe for highly reactive compounds, *i.e.* those having k_r values in the 10^8—10^9 l $\mathrm{mol^{-1}\ s^{-1}}$ range. One must also add a cautionary note with regard to ascribing the observation of an isotope effect as being due to participation of singlet oxygen in a reaction since it may be due to Φ_T and Φ_S varying with change in solvent composition.

A quantitative examination of a photosensitised reaction can also be complicated by the occurrence of triplet–triplet energy transfer from the sensitising dye to the substrate. We have found this process to occur in the Rose Bengal sensitised oxidation of anthracenes. When 9-methylanthracene was employed it was found that the maximal observed rate of oxidation did not correspond to $I_\mathrm{a}\Phi_T$. When degassed solutions of Rose Bengal containing 9-methylanthracene were examined

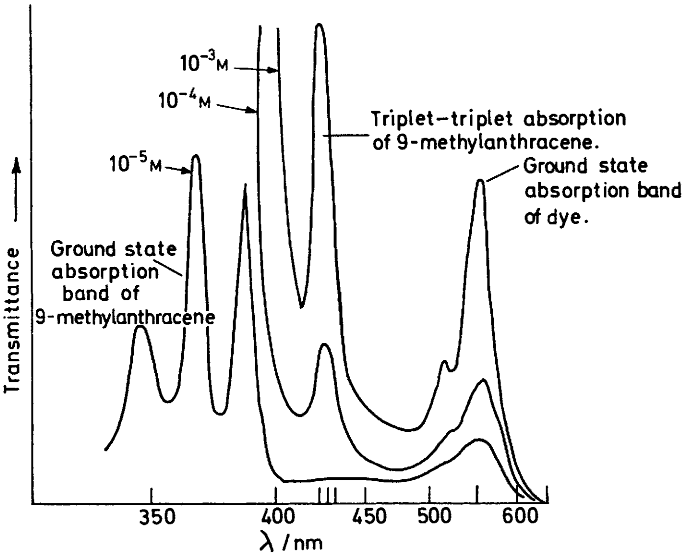
---

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

[8] (*a*) D. R. Adams and F. Wilkinson, *J.C.S. Faraday II*, 1972, 586; P. B. Merkel and D. R. Kearns, *J. Amer. Chem. Soc.*, 1972, **94**, 1029; (*b*) I. B. C. Matheson and J. Lee, *Chem. Phys. Letters* 1972, **14**, 350.

[9] Y. Usui and K. Kamogawa, *Photochem. Photobiol.*, 1974, **19**, 245.

by the technique of flash photolysis, the triplet–triplet absorption of the anthracene was easily visible (Figure). Since the hydrocarbon did not directly absorb any of the exciting light, triplet energy transfer from the dye to the anthracene had occurred. Similar results were obtained when tris-(2,2′-bipyridyl)ruthenium(II) chloride, eosin, and fluorescein were used as sensitisers.[10] The occurrence of triplet–triplet energy transfer from the sensitiser to the substrate will affect the kinetics of oxidation because Φ_T will be altered. It is true that the substrate triplet may also act as a progenitor of singlet oxygen, but the sensitisation process, which involves two excited sensitiser molecules, will be far less efficient than the process involving one.



Flash absorption spectra of 10^{-5}M-Rose Bengal solutions, in MeOH (degassed) in the presence of added 9-methylanthracene after 8 μs delay

Interaction of the excited singlet state of the sensitiser with a substrate has also to be taken into account with some systems. This has been shown to be the case for the Rose Bengal sensitised oxidation of triethylamine.[11] It is also a process which should not be neglected when amines are used as physical quenchers of singlet oxygen in photo-oxygenation reactions.[12] Many other compounds, which are frequently added to photo-oxygenation reactions to aid mechanistic studies, *e.g.* azides [13] and β-carotene,[14] efficiently quench the fluorescence of dyes such as Rose Bengal and Methylene Blue (see Table 2). Several anions quench the fluorescence of these dyes and the efficiency of quenching increases as the oxidation potential of the anion decreases. This observation strongly indicates that the quenching process is a redox reaction. It has been previously noted that anions quench the fluorescence of fluorescein,[15] several aromatic hydrocarbons,[16] and heterocyclic compounds.[17] The more efficient quenching by anions of Methylene Blue fluorescence compared with that of Rose Bengal fluorescence is no doubt due to the unfavourable coulombic interaction which will develop as the anion approaches the latter dye which contains an anionic group. A similar result has been obtained for the quenching of triplet states of dyes by anions, *i.e.* triplet state of the cationic dye thionine is much more efficiently quenched by anions than the triplet state of

TABLE 2

Stern–Volmer constants [a] for quenching of the fluorescence of Rose Bengal and Methylene Blue

	K_{SV}/mol l^{-1}	
Substrate	Rose Bengal	Methylene Blue
Sodium iodide	2.0 [b]	14.6 [b]
Sodium bromide	0.1 [b]	0.8 [c]
Sodium chloride		0.2 [c]
Sodium azide	0.6 [b]	3.6 [c]
β-Carotene		57 [d]
2,5-Diphenylisobenzofuran		57 [e]

[a] Calculated from $\Phi_0/\Phi = 1 + K_{SV}[Q]$ where Φ_0 = quantum yield of fluorescence in absence of quencher, Φ = quantum yield of fluorescence when quencher is present at concentration [Q] and $K_{SV} = K_q\tau$ where k_q = bimolecular quenching rate constant and $\tau \doteq$ fluorescence lifetime of dye. In all cases aerated solutions were used. Maximum error in K_{SV} estimated at ±10%. [b] Methanol–water (50 : 50 v/v). [c] Methanol–water (20 : 80 v/v). [d] Methanol–benzene (20 : 80 v/v) corrections applied for absorption by β-carotene at $\lambda_{excit.}$ and $\lambda_{emis.}$ of dye. [e] Methanol.

---

[10] R. S. Davidson and K. R. Trethewey, unpublished results. Further work is underway to obtain quantitative data.

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

[12] R. S. Davidson and K. R. Trethewey, 1976, 178.

[13] C. S. Foote, T. T. Fujimoto, and Y. C. Chang, *Tetrahedron Letters*, 1972, 45; N. Hasty, P. B. Merkel, P. Radlick, and D. R. Kearns, *ibid.*, p. 49.

[14] C. S. Foote and R. W. Denny, *J. Amer. Chem. Soc.*, 1968, **90**, 6233; P. B. Merkel and D. R. Kearns, *ibid.*, 1972, **94**, 7244; A. Farnulo and F. Wilkinson, *Photochem. Photobiol.*, 1973, **18**, 447.

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

[16] A. R. Watkins, *J. Phys. Chem.*, 1974, **78**, 1885; C. A. G. Brooks and K. M. C. Davis, *J.C.S. Perkin II*, 1972, 1649.

[17] T. G. Beaumont and K. M. C. Davis, *J. Chem. Soc. (B)*, 1970, 456.

the anionic dye eosin.[18] Azide ions are quite efficient quenchers of the fluorescence of Methylene Blue. It is therefore not surprising that addition of a high concentration of azide ions to the Methylene Blue sensitised oxidation of olefin diverts the course of reaction and α-azido-hydroperoxides are isolated instead of the usual olefinic α-hydroperoxides.[19] Formation of the azido-hydroperoxide can be rationalised as occurring *via* initial electron transfer from the azide ion to the excited dye to give azide radicals. These radicals react with the olefin in the presence of oxygen to give the observed products. That azide radicals react in this way has been recently demonstrated by Gollnick.[20] The finding that β-carotene is a very efficient quencher of the fluorescence of Methylene Blue shows that extreme care has to be exercised when the compound is added to photo-oxygenation reactions in the hope that it will act purely as a physical quencher of singlet oxygen.[21] From the K_{SV} value it would appear that the carotenoid concentration ought to be kept well below 10^{-3}M.

2,5-Diphenylisobenzofuran is another remarkably efficient quencher of Methylene Blue fluorescence. In theory this reaction should not invalidate measurements of rate constants for reaction of singlet oxygen with acceptors made by the methods of Wilkinson and Kearns.[8a] Similarly, the measurement made by the method of Young *et al.*[22] should be free from error since the concentration of isobenzofuran used in these experiments is kept very low. For all the compounds shown in Table 2 we propose that quenching occurs *via* a redox process. In no case is singlet–singlet energy transfer likely to occur.

Another complication in the kinetics of oxidation reactions arises when the substrate acts as a good physical quencher of singlet oxygen but reacts to give chemical products, relatively inefficiently. Sulphides[23] and amines[11,24] have been shown to fall into this category. Account has to be taken of the partitioning of the electronic energy of singlet oxygen when oxygen absorption measurements are made. When the comparative method of Young and Martin[3] is employed, no information is gained on the efficiency of chemical reaction.

Perhaps one of the most difficult situations to handle is the one in which the substrate reacts with the sensitiser to give oxidation products by a radical process and also reacts with singlet oxygen to give oxidation products. Both amines[11,24] and phenols[25] have been shown to react in this way. A kinetic scheme has been developed, which takes into account reaction of the substrate with the excited singlet and triplet states of the dye and with singlet oxygen. For convenience the substrate is considered as being an amine (Am) since the equation is used in the accompanying paper to investigate the mechanism of oxidation of these compounds. In addition to processes shown in equations (1)—(3b), (6), and (7), we have also to consider (12)—(20).

$$\mathrm{Sens}_{S_1} + \mathrm{Am} \xrightarrow{k_{\mathrm{q_s}}} [\mathrm{Sens}_{S_1}\text{–}\mathrm{Am}]^\dagger \qquad (12)$$

$$[\mathrm{Sens}_{S_1}\text{–}\mathrm{Am}]^\dagger \xrightarrow{k'_{\mathrm{cd}}} \mathrm{Sens}_{S_0} + \mathrm{Am} \qquad (13)$$

$$[\mathrm{Sens}_{S_1}\text{–}\mathrm{Am}]^\dagger \xrightarrow{k'_{\mathrm{cr}}} \mathrm{Radicals} \qquad (14)$$

$$\mathrm{Sens}_{T_1} + \mathrm{Am} \xrightarrow{k_{\mathrm{q_t}}} [\mathrm{Sens}_{T_1}\text{–}\mathrm{Am}]^\dagger \qquad (15)$$

$$[\mathrm{Sens}_{T_1}\text{–}\mathrm{Am}]^\dagger \xrightarrow{k''_{\mathrm{cd}}} \mathrm{Sens}_{S_0} + \mathrm{Am} \qquad (16)$$

$$[\mathrm{Sens}_{T_1}\text{–}\mathrm{Am}]^\dagger \xrightarrow{k''_{\mathrm{cr}}} \mathrm{Radicals} \qquad (17)$$

$$[{}^1\mathrm{O}_2] + \mathrm{Am} \xrightarrow{k_{\mathrm{q_0}}} [{}^1\mathrm{O}_2\text{–}\mathrm{Am}] \qquad (18)$$

$$[{}^1\mathrm{O}_2\text{–}\mathrm{Am}] \xrightarrow{k_{\mathrm{cr}}} \mathrm{Products} \qquad (19)$$

$$[{}^1\mathrm{O}_2\text{–}\mathrm{Am}] \xrightarrow{k_{\mathrm{cd}}} {}^3\mathrm{O}_2 + \mathrm{Am} \qquad (20)$$

Consideration of the excited singlet state of the sensitiser under steady state conditions gives equation (21). For the

$$I_{\mathrm{a}} = [S_1](k_{\mathrm{F}} + k_{\mathrm{IC}} + k_{\mathrm{ISC}} + k_{\mathrm{q_s}}[\mathrm{Am}]) \qquad (21)$$

triplet state of the sensitiser equations (22) and (23)

$$\mathrm{d}(T_1)/\mathrm{d}t = \frac{I_{\mathrm{a}}k_{\mathrm{ISC}}}{(k_{\mathrm{F}} + k_{\mathrm{IC}} + k_{\mathrm{ISC}} + k_{\mathrm{q_s}}[\mathrm{Am}])} \qquad (22)$$

$$-\mathrm{d}(T_1)/\mathrm{d}t = (k_{\mathrm{d}^1} + k_{\mathrm{O_2}}[{}^3\mathrm{O}_2] + k_{\mathrm{q_t}}[\mathrm{Am}])[T_1] \qquad (23)$$

apply leading to (24) under steady state conditions.

$$[T_1] = \frac{I_{\mathrm{a}}k_{\mathrm{ISC}}}{(k_{\mathrm{F}} + k_{\mathrm{IC}} + k_{\mathrm{ISC}} + k_{\mathrm{q_s}}[\mathrm{Am}])} \cdot \frac{1}{(k_{\mathrm{d}^1} + k_{\mathrm{O_2}}[{}^3\mathrm{O}_2] + k_{\mathrm{q_t}}[\mathrm{Am}])} \qquad (24)$$

Since $\Phi_T = k_{\mathrm{ISC}}/(k_{\mathrm{F}} + k_{\mathrm{IC}} + k_{\mathrm{ISC}})$ and $\tau = 1/(k_{\mathrm{F}} + k_{\mathrm{IC}} + k_{\mathrm{ISC}})$ this equation may be reduced to (25).

$$[T_1] = \frac{I_{\mathrm{a}}\Phi_{T_1}}{(1 + k_{\mathrm{q_s}}\tau[\mathrm{Am}])} \frac{1}{(k_{\mathrm{d}^1} + k_{\mathrm{O_2}}[{}^3\mathrm{O}_2] + k_{\mathrm{q_t}}[\mathrm{Am}])} \qquad (25)$$

Consideration of processes involving singlet oxygen gives equations (26) and (27) leading to (28) under steady

$$\mathrm{d}[{}^1\mathrm{O}_2]/\mathrm{d}t = k_{\mathrm{O_2}}[{}^3\mathrm{O}_2][T_1] \qquad (26)$$

$$-\mathrm{d}[{}^1\mathrm{O}_2]/\mathrm{d}t = (k_{\mathrm{d}} + k_{\mathrm{q_0}}[\mathrm{Am}])[{}^1\mathrm{O}_2] \qquad (27)$$

$$[{}^1\mathrm{O}_2] = [T_1]k_{\mathrm{O_2}}[{}^3\mathrm{O}_2]/(k_{\mathrm{d}} + k_{\mathrm{q_0}}[\mathrm{Am}] \qquad (28)$$

---

[18] L. Kraljić and L. Lindqvist, *Photochem. Photobiol.*, 1974, **20**, 351.

[19] W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, 1969, **91**, 7771.

[20] K. Gollnick, D. Haisch, and G. Schade, *J. Amer. Chem. Soc.*, 1972, **94**, 1747.

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

[22] R. H. Young, K. Wehrly, and R. L. Martin, *J. Amer. Chem. Soc.*, 1971, **93**, 5774.

[23] C. S. Foote and J. W. Peters, *J. Amer. Chem. Soc.*, 1975, **95**, 3795; R. Ackerman, I. Rosenthal, and J. N. Pitts, *J. Chem. Phys.*, 1971, **54**, 4966.

[24] G. O. Schenck and K. O. Gollnick, *J. Chim. phys.*, 1958, **55**, 892; W. F. Smith, *J. Amer. Chem. Soc.*, 1972, **94**, 186.

[25] K. A. Muszkat and M. Weinstein, *J.C.S. Chem. Comm.*, 1975, 143.

state conditions. Considering the rate of consumption of amine by the three types of reaction, *via* the singlet state of the sensitiser, the triplet state of the sensitiser, and singlet oxygen, respectively, we obtain expressions (29)—(31).

$$\begin{aligned}-\mathrm{d}[\mathrm{Am}]/\mathrm{d}t &= k_{\mathrm{q_s}}[\mathrm{Am}][S_1] - k'_{\mathrm{cd}}[\mathrm{Am}\text{–}S_1]^{\dagger} \\ &= N_{\mathrm{S}}k_{\mathrm{q_s}}[\mathrm{Am}][S_1] \qquad (29) \\ N_{\mathrm{S}} &= k'_{\mathrm{cr}}/(k'_{\mathrm{cd}} + k'_{\mathrm{cr}})\end{aligned}$$

$$\begin{aligned}-\mathrm{d}[\mathrm{Am}]/\mathrm{d}t &= N_{\mathrm{t}}k_{\mathrm{q_t}}[\mathrm{Am}][T_1] \qquad (30) \\ N_{\mathrm{t}} &= k''_{\mathrm{cr}}/(k''_{\mathrm{cd}} + k''_{\mathrm{cr}})\end{aligned}$$

$$\begin{aligned}-\mathrm{d}[\mathrm{Am}]/\mathrm{d}t &= N_0k_{\mathrm{q_o}}[\mathrm{Am}][^1\mathrm{O}_2] \qquad (31) \\ N_{\mathrm{o}} &= k_{\mathrm{cr}}/(k_{\mathrm{cd}} + k_{\mathrm{cr}})\end{aligned}$$

Substitution can be made into these equations for $[S_1]$, $[T_1]$, and $[^1\mathrm{O}_2]$ and hence expression (32) follows which describes the rate of loss of amine as a result of

$$\begin{aligned}\frac{-\mathrm{d}[\mathrm{Am}]}{\mathrm{d}t} = N_{\mathrm{S}}I_{\mathrm{a}}\frac{k_{\mathrm{q_s}}\tau[\mathrm{Am}]}{(1 + k_{\mathrm{q_s}}\tau[\mathrm{Am}])} + \\ \frac{N_{\mathrm{t}}I_{\mathrm{a}}\Phi_T}{(1 + k_{\mathrm{q_s}}\tau[\mathrm{Am}])}\cdot\frac{k_{\mathrm{q_t}}[\mathrm{Am}]}{(k_{\mathrm{d^1}} + k_{\mathrm{O_2}}[^3\mathrm{O}_2] + k_{\mathrm{q_t}}[\mathrm{Am}])} + \\ \frac{N_0I_{\mathrm{a}}\Phi_T}{(1 + k_{\mathrm{q_s}}\tau[\mathrm{Am}])}\cdot\frac{k_{\mathrm{O_2}}[^3\mathrm{O}_2]}{(k_{\mathrm{d^1}} + k_{\mathrm{O_2}}[^3\mathrm{O}_2] + k_{\mathrm{q_t}}[\mathrm{Am}])}\cdot \\ \cdot\frac{k_{\mathrm{q_o}}[\mathrm{Am}]}{(k_{\mathrm{d}} + k_{\mathrm{q_o}}[\mathrm{Am}])} \qquad (32)\end{aligned}$$

all three processes. This equation is of the form (33)

$$-\mathrm{d}[\mathrm{Am}]/\mathrm{d}t = A + B + C \qquad (33)$$

where A—C represent the contributions made by reaction of the excited singlet and triplet state of the sensitiser and of singlet oxygen, respectively. Thus if $k_{\mathrm{q_s}}$ is small, term A disappears. The part played by terms A and B will also be very dependent upon amine concentration. It has recently been shown that for low concentrations of amines the major contribution comes from reaction *via* singlet oxygen whereas at high amine concentrations terms A and B dominate the oxidation process. For many photo-oxygenation reactions it is possible to neglect some of the processes contributing to equation (32) and in the extreme it simplifies to equation (8).

EXPERIMENTAL

Materials.—Rose Bengal (B.D.H.) was purified by t.l.c. on alumina. Methylene Blue (Aldrich) was used as supplied. Methanol was dried over calcium hydride and distilled to use.

Spectroscopic Measurements.—Fluorescence measurements were made with Baird Atomic SF 100E and Perkin-Elmer MPF4 instruments. In all cases the optical density of the dye solution at the excitation wavelength was 0.1. The flash photolysis apparatus has been previously described.[26]

We are grateful to the S.R.C. for financial assistance (to K. R. T. and for the purchase of equipment).

[6/685 *Received, 7th April,* 1976]

---

[26] R. S. Davidson and M. Santhanam, *J.C.S. Perkin II*, 1972, 2355.