The Photosensitised Oxidation of Amines

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Summary Benzophenone, Methylene Blue, and Rose Bengal have been shown to photosensitise the oxidation of a number of amines, and from product studies it is concluded that the reactions occur by abstraction of hydrogen from the amines by the excited sensitiser, followed by reaction of the amine radicals with oxygen.

THERE are two important mechanisms by which aerobic photosensitised oxidation of organic compounds can occur.[1a,b] The first involves interaction of the excited sensitiser with substrate (Path A) whereas the second involves its interaction with oxygen (Path B).

$$\begin{tikzcd}
\text{Products} & \text{Radicals} \arrow[l, "O_2"] & \text{Sens}^{*}_{T_1} \arrow[l, "S(k_S)", "\text{Path A}"'] \arrow[d, "O_2(k_{O_2})"] \\
 & \text{Products} & {}^1\Delta_g O_2 \arrow[l, "S", "\text{Path B}"']
\end{tikzcd}$$

S = Substrate

The efficiency of each path depends upon the relative rates of reaction of the sensitiser with the substrate and with oxygen.[1a] The photo-oxidation of aliphatic amines sensitised by dyes[2a] and carbonyl compounds[2b] has been assumed to occur *via* Path B. More recently, the benzophenone-sensitised oxidation of aniline[3a] and diphenylamine[3b] has been postulated as occurring *via* the triplet state of the amine.

We have found that irradiation of oxygenated benzene solutions of benzophenone containing amines, with light of wavelength >300 nm, leads to products derived by oxidation of the amine (see Table). The oxidation of *N*-ethyl-*NN*-di-isopropylamine and 1,4-diazabicyclo[2,2,2]octane are particularly interesting since it is known that these amines quench singlet oxygen without undergoing chemical change.[4] This suggests that the oxidations listed in the Table occur by Path A. Furthermore, the high bimolecular rate constants (k_S) for hydrogen abstraction from

Products obtained by irradiation of oxygenated benzene solutions of amines containing benzophenone

Amine	Initial amount of amine (mmol)	Time (h)	Amine reacted (mmol)	Benzophenone recovered (%)	Products (yield in mmol)
NN-Dimethylaniline[a]	15·1	14	14·8	90	*N*-Methylformanilide (7·4) *N*-Methylaniline (2·9) Aniline (0·7)
NN-Diethylaniline[a]	15·0	7	12·0	90	Acetaldehyde (15·5) Aniline (4·0) *N*-Ethylaniline (3·1) Acetanilide (0·3)
Triethylamine[b]	24·0	2[d]	7·7	70	Acetaldehyde (4·6) Diethylacetamide (trace)
Tri-*N*-propylamine[b]	24·0	2[d]	12·0	80	Propionaldehyde (4·8) EtCH=NPr (2·4)
Di-*N*-propylamine[b]	24·1	2[d]	[c]	90	Propionaldehyde (1·9) EtCH=NPr [c]
N-Propylamine[b]	24·0	2[d]	[c]	80	Propionaldehyde (2·0)
N-Ethyl-*NN*-di-isopropylamine[a]	7·5	8	7·2	80	Acetone (3·5) Acetaldehyde (1·0)
1,4-Diazabicyclo[2,2,2]octane[a]	55·4	14	37·0	40	1 : 1 Adduct (6·1) Together with oxygenated amine derivatives.

[a] Solution 0·05 M in benzophenone.
[b] Solution 0·3 M in benzophenone.
[c] Amount produced could not be estimated.
[d] Light intensity higher by a factor of 10.

amines by triplet benzophenone (*ca.* 10^{8} M^{-1} s^{-1})[5a,b] should favour reaction by Path A compared with Path B by a factor of 10.[1a] Quantum-yield studies on the reactions showed that tertiary amines were oxidised with yields $\gg 1$, whereas secondary and primary amines all had yields of *ca.* 1 or less. Presumably the presence of the N–H bond in primary and secondary amines facilitates a terminating reaction in which an imine is produced. The formation of imines $R^{1\bullet} + R^{2\bullet}CH\cdot NHR^{2} \rightarrow R^{1}H + R^{2}CH{=}NR^{2}$ has also been observed in the photoreduction of benzophenone by primary and secondary aliphatic amines.[6]

The question as to whether the dye-photosensitised oxidation of amines occurs *via* Path A has also been investigated. This mechanism is certainly a possibility for tertiary amines since these have been shown to react with dyes in their lowest triplet states at diffusion-controlled rates.[7] Methylene Blue and Rose Bengal have been found to photosensitise the oxidation of a number of tertiary amines, *e.g.* tri-n-propylamine, *N*-ethyl-*NN*-di-isopropylamine, and triethylamine, with the formation of the same products as those obtained in the benzophenone-sensitised reactions. Furthermore, oxidation only occurred in those cases in which, under anaerobic conditions, the amines photoreduced the dye efficiently. These observations are in accord with the conclusion that the benzophenone- and dye-sensitised reactions occur *via* a common mechanism, *i.e.* Path A. Primary and secondary amines were found to be relatively unreactive; oxidation only occurred in those cases where, under anaerobic conditions, the amines photoreduced the dyes. The fact that the products of the dye- and benzophenone-sensitised reactions are the same suggests a common mechanism, *i.e.* Path A.

The finding that the photo-oxidation of pseudopelletierene and tropinone to substituted formamides "is sensitised" by naphthalene and triphenylene[2b] is difficult to, interpret in terms of the mechanism shown by Path A. The reactions with tropinone have been repeated, and it was found that the amount of oxidation taking place in the presence of the sensitisers was proportional to the amount of light absorbed by the tropinone. Thus, when two solutions of tropinone, one containing a sensitiser and one without, were irradiated simultaneously under identical conditions, the solution without the sensitiser was found to have undergone more oxidation than the one with sensitiser. The photo-oxidation of the two amino-ketones can be readily understood in terms of rapid hydrogen abstraction from the *N*-methyl group by the triplet carbonyl group. The fact that neither naphthalene nor triphenylene quenched the reaction is not surprising in the light of the high bimolecular rate constants for the hydrogen-abstraction reaction.[5a,b]

We conclude that the sensitised oxidation of primary secondary, and tertiary amines by benzophenone and of tertiary amines by dyes, occurs by the mechanism outlined in Path A and that singlet oxygen is not the reactive species in these reactions.

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[1] (a) C. S. Foote, *Science*, 1968, **162**, 963; (b) J. Bourbon and B. Schnuriger, "Physics and Chemistry of the Organic Solid State," vol. III, Interscience, New York, 1967, 97.

[2] (a) K. Gollnick, *Adv. Photochem.*, 1968, **6**, 111; (b) M. H. Fisch, J. C. Gramain, and J. A. Oleson, *Chem. Comm.*, 1970, 13.

[3] (a) M. Santhanam and V. Ramakrishnan, *Chem. Comm.*, 1970, 344; (b) M. Santhanam and V. Ramakrishnan, *Indian J. Chem.*, 1970, **8**, 374.

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

[5] (a) S. G. Cohen and A. D. Litt, *Tetrahedron Letters*, 1970, 837; (b) R. S. Davidson and P. F. Lambeth, *Chem. Comm.*, 1968, 511.

[6] S. G. Cohen and R. J. Baumgarten, *J. Amer. Chem. Soc.*, 1965, **87**, 2996; S. G. Cohen and R. J. Baumgarten, *ibid.*, 1967, **89**, 3471; S. G. Cohen and H. M. Chao, *ibid.*, 1968, **90**, 165.

[7] V. Kasche, *Photochem. and Photobiol.*, 1967, **6**, 643; V. Kasche and L. Lindquist, *ibid.*, 1965, **4**, 923.