Dye- and Dicyanoanthracene-photosensitized Oxygenations of Sulphur Compounds. Product Selectivity

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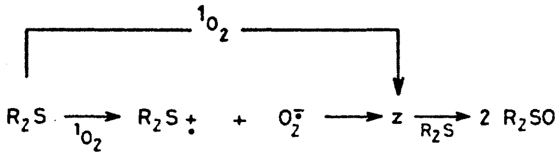
Summary Photo-oxygenation of vinyl sulphides sensitized either by dyes or by 9,10-dicyanoanthracene (DCA) gave products arising from oxidative cleavage of the double bond in closely similar ratios in each case; similarly, dye-photosensitized oxygenation of fluorenyl ethyl sulphide gave fluorenone, 1-hydroxy-9-fluorenone, 9-fluorenyl ethyl sulphoxide, and 9-fluorenyl ethyl sulphone as major products, while DCA-sensitized oxygenation gave the first three products in similar relative yields.

DYE-photosensitized oxygenation of sulphur compounds has been postulated to proceed through an intermediate adduct, **z**, which could be a zwitterionic peroxide, a diradical, or a cyclic peroxide which reacts with a second molecule of sulphide to give the sulphoxide.[1] Photo-oxygenation sensitized by 9,10-dicyanoanthracene (DCA) gives similar products; in this case it was proposed that electron transfer from excited DCA to oxygen gives a superoxide.[2] Electron transfer from sulphur to singlet oxygen was suggested (originally by Foote[3]) as an alternative mechanism but no detailed evidence was reported.



We here report a detailed comparison of the product distribution from oxidation of different types of sulphide by both dye- and DCA-sensitized photo-oxygenation and by means of quenching techniques, and show that, although the latter type of reaction does not involve singlet oxygen, both apparently proceed through the same intermediate.

TABLE 1. Product ratio in the oxygenation of 1-ethylthio-2-ethylhex-1-ene (0.6 mmol) in 25 ml of MeCN–CCl_4 (4:1)

	Product		
Sensitizer	$Bu^nC(:O)Et$	$Bu^nEtC(OH)CHO$	$Pr^nCH:C(Et)CHO$ $+MeCH:CBu^nCHO$
Rose Bengal	70	14	16
DCA with β-carotene	61	14	25

TABLE 2. Product ratio in the oxygenation of 1,1-diphenyl-2-methylthioethylene (2·0 mmol) in 20 ml of solvent

		Product		
Sensitizer	Solvent	3-Phenylbenzo-furan-2-one	Ph_2CO	Sulphoxide
TPP	Benzene	40	60	0
DCA	Acetone	39	61	0

The sensitized photo-oxygenations were carried out in a water cooled immersion irradiation apparatus using a halogen lamp. All the major products were separated by g.l.c., and their properties were consistent in all cases with the structure previously assigned to the photo-oxygenation products.[4]

Quenching experiments by β-carotene showed that singlet oxygen must be the reactive species in dye-sensitized oxygenation. The Figure shows the results for 1-ethylthio-2-ethylhexene. The concentration of added β-carotene was kept below 10^{-3} M.[5] Similar results were observed for other sulphides.

9-Fluorenyl ethyl sulphide was photo-oxygenated in dry benzene with *meso*-tetraphenylporphine (TPP) as sensitizer; *ca.* 1 equiv. of oxygen was absorbed. When the reaction mixture was chromatographed on silica gel, four main products were isolated, and identified as fluorenone, 1-hydroxy-9-fluorenone, 9-fluorenyl ethyl sulphoxide, and 9-fluorenyl ethyl sulphone. Diethyl disulphide was also detected by g.l.c. In a protic solvent such as methanol, considerable amounts of sulphoxides were obtained with

TABLE 3. Product ratio in the oxygenation of 1-ethylthiocyclopentene (0·8 mmol) in 25 ml of $MeCN–CCl_4$ (4:1)

	Product		
Sensitizer	$HC(:O)[CH_2]_3C(:O)SEt$	2-Ethylthio cyclopentanone	2-Ethylthio cyclopent-2-enone
Rose Bengal	98	0	2
DCA with	85[a]	8	7
β-carotene	92[b]	0	8

[a] Irradiation for 3 h. [b] Irradiation for 7 h.

The product distribution from 1-ethylthio-2-ethylhexene, 1,1-diphenyl-2-methylthioethylene, and 1-ethylthiocyclopentene are summarized in Tables 1, 2, and 3. Apparent differences in the product distribution are smaller than the probable error of the analysis, though the solvent and duration of the photolysis may have some effect.

1,1-Diphenyl-2-methylthioethylene gives the same product ratio in each case: a Diels–Alder product, 3-phenylbenzofuran-2-one, and a dioxetan cleavage type, benzophenone. The ratio of Diels–Alder- and dioxetan-type products in DCA-sensitized oxygenation is nearly identical with that obtained in the dye-sensitized oxygenation.

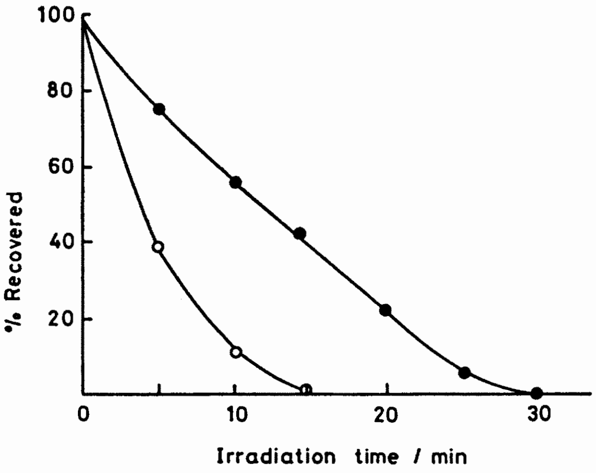
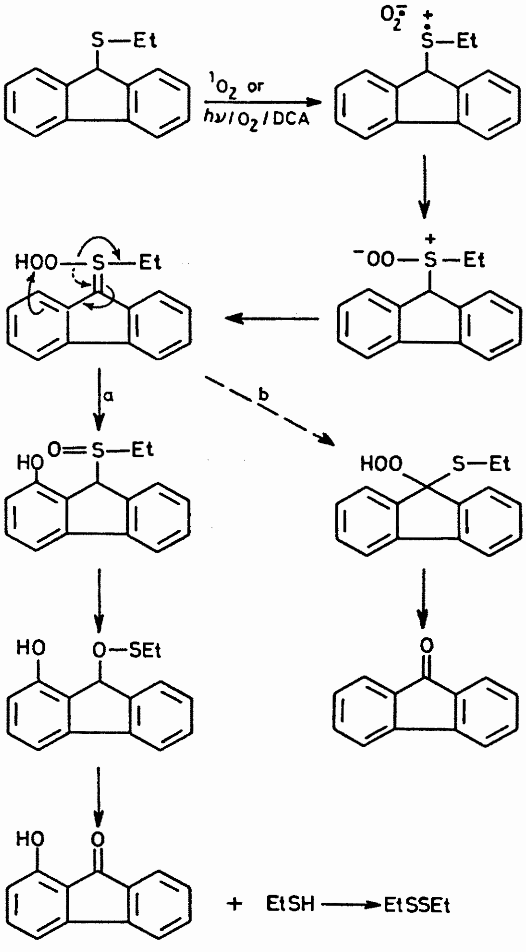


FIGURE. Quenching experiments for the dye-sensitized oxygenation of 1-ethylthio-2-ethylhexene ($3·87 \times 10^{-3}$ M) in $MeCN–CCl_4$ (4:1). ●, with β-carotene ($3·74 \times 10^{-4}$ M); ○ none. [Rose Bengal] = 1·0 mg ml^{-1}, and air was bubbled at a rate of 2·4 ml min^{-1}.



SCHEME

TABLE 4. Product ratio in the oxygenation of 9-fluorenyl ethyl sulphide (1·5 mmol) in 25 ml of solvent

		Product			
Sensitizer	Solvent	Fluorenone	1-Hydroxy 9-fluorenone	Sulphoxide	Sulphone
Methylene Blue	Acetone	51	14	27	8
TPP	Benzene	38	16	36	10
DCA	MeCN–CCl_4 (4 : 1) with β-carotene	40	6	54	0
	Acetone with β-carotene	43	19	38	0

acceleration of the reaction rates, and with consumption of 0·5 equiv. of oxygen.

Also, the DCA-sensitized photo-oxygenation of 9-fluorenyl ethyl sulphide in MeCN–CCl_4 (4 : 1) gave a similar distribution of products after irradiation for 3 h. In this case, β-carotene did not quench the reaction, indicating that singlet oxygen is not the reactive species.

We suggest that the dye-sensitized photo-oxygenation of these sulphides possibly proceeds *via* a superoxide intermediate formed by the reaction of singlet oxygen with the sulphide (Scheme).

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