Photosensitized Generation of Singlet Molecular Oxygen with Near-infrared Radiation

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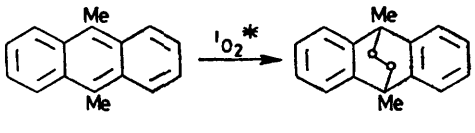
Summary Singlet oxygen has been generated with near i.r. radiation in the presence of sensitizers and trapped with 9,10-dimethylanthracene.

OXYGEN is one of the few simple molecules known which exists as a triplet in its electronic ground state. However, it has a low-lying electronic singlet state 22·544 kcal mol^{-1} above the ground state. Singlet oxygen has been implicated in many photo-oxidation processes and so has been well studied.[1] Theoretically, light of wavelength 1·268 μm or shorter should have sufficient energy to effect the transition of ground-state triplet oxygen to its excited singlet level. While singlet oxygen has been generated with visible light many times, including once with a laser,[2] there is no report of doing so with near-i.r. radiation.

The ability of potential sensitizers to generate singlet oxygen upon irradiation with near-i.r. radiation was evaluated qualitatively in solution using 9,10-dimethylanthracene



(I) (II)

(I) as a probe since it is well known to react efficiently with singlet oxygen in solution to give the 9,10-*endo*-peroxide (II).

The reaction can be followed by monitoring the two u.v. absorptions at 245 and 265 nm for compound (I) which are absent for compound (II). The *endo*-peroxide (II) was also characterized by n.m.r. spectroscopy.

TABLE 1. Production of singlet oxygen with near-i.r. sensitizers; 30 min irradiation.

Sensitizer[a] (mg/100 ml)	[Compound (I)] (mg/100 ml)	Solvent	% Reaction[b]
(A) (0·53)	2·1	Dioxan	51
(B) (3)	1	$ClCH_2CH_2Cl$	25
(C) (4)	1	$ClCH_2CH_2Cl$	10

[a] In Tables 1 and 2, (A) ≡ 1,1′-diethyl-2,2′-tricarbocyanine iodide; (B) ≡ xenocyanine; (C) ≡ 3,3′-diethyl-9,11,15,17-dineopentylenethiapentacarbocyanine iodide. [b] Measured by the decrease in the 263 nm absorption band and corrected for absorption of (II); average of 3 runs.

A solution of sensitizer and (I) in an appropriate solvent was irradiated with a Varian Eimac 150X8S xenon lamp. The emitted light was filtered with a Corning CS 7-56 filter so as to exclude wavelengths shorter than *ca.* 0·9 μm. The results with several sensitizers are summarized in Table 1.

Three sensitizers, 1,1-diethyl-2,2′-tricarbocyanine iodide, xenocyanine, and 3,3-diethyl-9,11,15,17-dineopentylenethiapentacarbocyanine iodide, generated singlet oxygen in this manner; *p*-chloranil bis-(4-dimethylaminodithiobenzil)-nickel, 3,3′-diethylthiatricarbocyanine iodide, neocyanine, napthacene, and 4-{6-[*N*-methylpyridin-4(1*H*)-ylidene]hexa-2,4-dienylidene}-3-phenylisoxazol-5(4*H*)-one did not. Control photolyses in the absence of both sensitizer and oxygen and in the absence of each alone resulted in no reaction. These sensitizers were then investigated with laser irradiation at 0·95, 1·06, and 1·15 μm similarly (see Table 2). None were effective at 1·15 μm, but all three were at 0·95 μm.

TABLE 2. Production of singlet oxygen with near-i.r. sensitizers (laser illumination). For footnotes see Table 1.

	% Reaction (*t*/min)[b]		
Sensitizer[a]	0·95 μm (40 mW)	1·06 μm (40 mW)	1·15 μm (25 mW)
(A)	7·5 (30)	0	0
	10 (60)		
(B)	8·5 (30)	9·5 (30)	0
	14 (60)	13 (60)	
(C)	5 (30)	3 (30)	0
	22 (60)	9 (60)	

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[1] See, *e.g.*, D. R. Kearns, *Chem. Rev.*, 1971, **71**, 395.
[2] D. F. Evans, *Chem. Comm.*, 1969, 367.
[3] See, *e.g.* G. W. Lundeen and A. H. Adelman, *J. Amer. Chem. Soc.*, 1970, **92**, 3914.