Quenching of Singlet ($^1\Delta_g$) Oxygen by 2,2,6,6-Tetramethylpiperidine Derivatives

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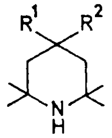
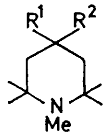
Summary 2,2,6,6-Tetramethylpiperidine-*N*-oxyls (III) efficiently quench singlet oxygen generated by dye sensitisation or by sodium hypochlorite–hydrogen peroxide, whereas the parent 2,2,6,6-tetramethylpiperidines exhibit only low activity.

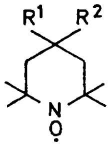
THE possibility that singlet oxygen in its $^1\Delta_g$ state is involved in oxidative photodegradation of polymers has been suggested by several authors.[1] The effectiveness of 2,2,6,6-tetramethylpiperidines (I) and their *N*-oxyls (III) and *N*-methyl derivatives (II) in light-stabilisation of polyolefins[2] implies possible quenching of singlet oxygen in these systems. Although it is well established that aliphatic amines quench singlet oxygen,[3–5] no evidence, so far, exists for quenching by paramagnetic *N*-oxyl radicals, as has been reported for other paramagnetic molecules such as ground state (Σ_g^-) oxygen and nitric oxide.[6]



(I)



(II)



(III)

a ; $R^1 = R^2 = H$, b ; $R^1 = H, R^2 = OH$, c ; $R^1 = OH, R^2 = P(O)(OEt)_2$

We have measured the inhibiting efficiency of (I)—(III) on the photo-oxygenation of the singlet oxygen acceptors: 2-methylpent-2-ene (IV) and 9,10-dimethoxymethylanthracene (V).† A well known[3,5] and efficient quencher of singlet ($^1\Delta_g$) oxygen, 1,4-diazabicyclo[2,2,2]octane (DABCO), was used. Rates of isobaric photo-oxygenation of (IV) and (V) (see Table) were measured in a thermostated (25°) system, containing benzene–methanol (1 : 1) solutions (8×10^{-3}M oxygen acceptor, (IV) or (V); 5×10^{-2}M quencher; $2{\cdot}5 \times 10^{-4}$M sensitiser, Rose Bengal). The concentration of (V) after a certain time of irradiation was checked by u.v. spectroscopy (absorbance at 391 nm).

In our experiments piperidines (I) show only low quenching efficiency in comparison to the more efficient quencher of singlet oxygen (DABCO); this might be due to the difference in ionisation potentials‡ [*i.e.* (Ia) : i.p. = 7·85 eV;[4] DABCO : i.p. = 7·23 eV[7]].

TABLE. *Relative rates of oxygen uptake and decrease of concentration during sensitised photo-oxidation of* (IV) *and* (V) *in the presence of quenchers of singlet oxygen.*

Quencher	(IV), rel. rate of O_2 uptake	(V), rel. rate of O_2 uptake	(V), rel. decrease of concentration	Oxidation of quencher[a]
None	1	1	1	—
(Ia)	0·94	0·95	0·92	no
(Ib)	1·02	0·98	0·96	no
(IIa)	—	>1[b]	0·47[b]	yes[c]
(IIb)	>1[b]	>1[b]	—	yes[c]
(IIIb)	0·50	0·58	0·51	no
(IIIc)	0·52	0·68	0·66	no
DABCO	0·37	0·64	0·59	no

[a] Control, without (IV) or (V). [b] Due to simultaneous reaction of quencher with singlet oxygen; see text. [c] Quantitative demethylation to (Ia) and (Ib), respectively, occurred; see text.

Data for *N*-methylpiperidines (IIa) (*e.g.* i.p. = 7·65 eV[2]) and (IIb) reflect no actual quenching of singlet oxygen. In a set of separate control runs it was verified that under the conditions of the experiments an uptake of 1 mole oxygen per mole of (IIa) or (IIb) occurred. The only detectable reaction products were the *N*-demethylated piperidines (Ia) and (Ib) in quantitative yields (> 98% by g.l.c.). In competitive experiments with 9,10-dimethoxymethylanthracene (V) the rate of *N*-demethylation of (IIa) was found to be roughly equal to the rate of photo-oxygenation of (V).

$$\text{(IIa) (IIb)} \xrightarrow[\text{O}_2,\ \text{methanol–benzene}]{h\nu,\ \text{Rose Bengal}} \text{(Ia) (Ib)}$$

These clean conversions are probably due to absence of any other α-hydrogen atoms in (IIa) and (IIb). Other *N*-methyl amines bearing additional α-hydrogen atoms usually give lower yields (60—75%) of *N*-demethylated products.[8]

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† The solubility of (V)[10] in methanol–benzene 1 : 1 was about 40 times that of anthracene. A concentration (10^{-4}—10^{-5}M) *vs.* absorbance plot of (V) obeyed Beer's Law. M.p. of endoperoxide: 139—140° (decomp.); i.r. (CCl_4): 1462, 1121, 997, 910 cm^{-1}.

‡ The ionisation potentials of aliphatic amines were reported to be indirectly proportional to their efficiency to quench singlet oxygen.[4]

We find that *N*-oxyls (IIIb) and (IIIc) are nearly as effective quenchers in the sensitised photo-oxygenation of (IV) and (V) as DABCO. In order to substantiate a singlet-oxygen quenching mechanism, 2,3-dimethylbut-2-ene ($2\cdot5 \times 10^{-3}$ mol) was oxygenated with singlet oxygen, generated from the sodium hypochlorite–hydrogen peroxide reagent.[9] In duplicate runs, yields of 3-hydroperoxy-2,3-dimethylbut-1-ene decreased by 1·6 in the presence of (IIIb) (10^{-2} mol).

These data, however, do not completely exclude the possibility that *N*-oxyls quench excited sensitiser molecules. Comparison of fluorescence intensities of a Rose Bengal solution (benzene–methanol 1 : 1) in the presence of (IIIb) ($4\cdot5 \times 10^{-2}$M) showed a 15% decrease over that obtained in the absence of (IIIb) [corrected for absorption of (IIIb) at the wavelength of excitation at 550 nm]. This experiment indicates that only weak quenching of the lowest sensitiser singlet state occurs. Although we have not excluded the possibility that Rose Bengal triplets may be quenched, the similarity between the decrease in yields from chemically-generated singlet oxygen oxidations (where no triplet states are involved) and those from the dye-sensitised oxidations suggests that this mechanism is not of major significance.§

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§ Simultaneously with our work, singlet-oxygen quenching with certain 2,2,6,6-tetramethylpiperidine derivatives has been observed in some methylene blue-sensitised photo-oxidations.[11] We thank the authors for a prepublication manuscript.

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