Tetrahedron Letters,Vol.23,No.36,pp 3729-3732,1982 0040-4039/82/363729-04$03.00/0
Printed in Great Britain

DYES AS QUENCHERS OF SINGLET OXYGEN

R. Stephen Davidson* & Julie E Pratt
(Department of Chemistry, The City University, London EC1V 0HB)

Summary The magnitude of solvent isotope effects on the rate of the dye sensitised photo-oxidation of alkenes is dependent upon the nature and concentration of the dye An explanation, involving quenching of singlet oxygen by the dye, is proposed

Generation of singlet oxygen, for both preparative and kinetic studies, is often accomplished by the use of dyes as sensitisers Kinetic studies, using steady state and transient methods enable the determination of the lifetime of singlet oxygen and the rate constant for its reaction with a substrate Values for the lifetime of singlet oxygen in a range of solvents are now available, but there are discrepancies between the values obtained from different investigations[1,2,3,4] Recently[3,4] lifetimes of singlet oxygen were determined by monitoring the decay of its luminescence, at 1270nm, after illumination of a dye solution by a laser pulse It was pointed out[3] that high dye concentrations led to erroneous results We now show that the neglect of the fact that many dyes are capable of quenching singlet oxygen is a source of error in determining its lifetime

The lifetime of singlet oxygen is generally longer in a deuterated than the corresponding non-deuterated solvents, therefore solvent isotope effects on the rate of photo-oxidation reactions have been used as evidence for the participation of singlet oxygen[5] Solvent isotope effects on the rate of oxidation of (+)-limonene, using a range of photo-sensitisers, at various concentrations, were measured The results are shown in Table 1. Similar experiments were carried out using citronellol as substrate, and the results are shown in Table 2.

Table 1 Solvent isotope effects on the photo-oxidation of (+)-limonene (5×10^{-3}M) in CH_3CN/D_2O and CH_3CN/H_2O (1 1 v/v)

Sensitiser	Sensitiser Concentration (M)	Solvent Isotope Effect
Rose Bengal	7.86×10^{-4}	2.18
(Eastman-Kodak)	1.0×10^{-5}	3.2
Methylene Blue	2.14×10^{-3}	1.79
(Aldrich)	1.0×10^{-5}	3.68
Thionine	2.78×10^{-3}	2.12
(Koch-Light	5.0×10^{-5}	6.08
Tris-ruthenium(II)-	1.0×10^{-3}	2.75
(2,2'-bipyridyl)-chloride,	1.0×10^{-4}	5.32
hexahydrate		

Table 2 Solvent isotope effects on the photo-oxidation of citronellol (5×10^{-3}M) in CH_3CN/D_2O and CH_3CN/H_2O (1 1 v/v)

Sensitiser	Sensitiser Concentration (M)	Solvent Isotope effect
Methylene Blue	$2\ 14 \times 10^{-3}$	1 59
	1.0×10^{-5}	2 4
Thionine	$2\ 78 \times 10^{-3}$	1.45
	$5\ 0 \times 10^{-5}$	2.5

From Tables 1 and 2 it can be seen that the measured solvent isotope effects are dependent upon the nature and concentration of the sensitiser The lower solvent isotope effects observed at high dye concentrations can be explained if the sensitising dyes are behaving as quenchers of singlet oxygen The following equation[6] describes the solvent isotope effect under conditions where the ground state dyes can act as quenchers -

$$\frac{\text{Rate}_D}{\text{Rate}_H} = \frac{k_d + k_r\ [\text{Subst.}] + k_q\ [\text{Sens }]}{k_d' + k_r'\ [\text{Subst }] + k_q'\ [\text{Sens.}]}$$

Where k_d = unimolecular decay constant for singlet oxygen,

k_r = rate constant for reaction of singlet oxygen with substrate at a concentration [Subst.]

k_q = bimolecular rate constant for quenching of singlet oxygen by the sensitiser at a concentration [Sens]

k_d', k_r' and k_q' refer to reaction in the deuterated solvent

For the solvent isotope effect to be maximal -

$$k_d > k_r\ [\text{Subst }] + k_q\ [\text{Sens }]$$

The dependence of the observed solvent isotope effect on sensitiser concentration suggests that the value of k_q [Sens] at high dye concentrations is too large for the above condition to hold Obviously, when solvents are used in which the lifetime of singlet oxygen is particularly long the term k_q [Sens.] may well dominate k_d or k_d' Hence, the quenching reaction will have a more dominant effect on the rate of photo-oxidation in the deuterated solvent It was indeed observed that the increase in rate of oxidation on raising the dye concentration, as a consequence of absorption of a higher proportion of incident photons, was more marked in the protic solvent.

The ruthenium complex, used as sensitiser, is of interest because its photophysical properties e.g. $\phi_{\text{Lumin}} + \tau_{\text{Lumin}}$ are affected by solvent deuteration[7] Consequently, solvent isotope effects observed using this dye should differ from those obtained using sensitisers whose photo-physical properties remain unchanged e.g Rose Bengal. However, a sensitivity of photo-physical parameters to solvent deuteration cannot explain the dependency of the observed solvent isotope effects upon concentration of the ruthenium complex.

Since the triplet states of the sensitisers used are higher in energy than singlet oxygen, quenching of the latter by the ground state dyes is unlikely to be an energy transfer process As all the sensitisers in this study are potential electron donors (particularly methylene blue and thionine which are both aromatic amines) the quenching may be due to an electron transfer process Recently, it has been shown that singlet oxygen can be quenched, via an electron transfer process, e g. by azide ions.[8] The observation[9] that 'oil soluble' chlorophyll quenches singlet oxygen can also be rationalised in these terms It is probable that the efficiency of quenching i e. $k_q[\text{Sens}]$ by the dyes, via such a process, will be affected by solvent deuteration Solvent isotope effects have recently been observed for intramolecular charge transfer reactions.[10]

We conclude that for kinetic investigations of dye-sensitised photo-oxidation reactions, involving singlet oxygen, it is essential to keep the dye concentration to a minimum As a consequence dyes with high extinction coefficients in the visible region will be of particular use

Acknowledgements We thank the S E R.C for a maintenance grant to J E P.

References

1 P R Ogilby & C.S Foote, J Amer. Chem. Soc , 1981, 103, 1219

2. G. Peters & M A J Rodgers, J Amer. Chem. Soc , 1981, 103, 6759

3 P R Ogilby & C S Foote, J Amer. Chem. Soc., 1982, 104, 2069

4 J R Hurst, J D McDonald & G B Schuster, J Amer Chem Soc 1982, 104, 2065.

5. R Nilsson, P B Merkel & D R Kearns, Photochem Photobiol , 1972, 16, 117

6 R S Davidson & K R Trethewey, J.C S Perkin II, 1977, 169.

7. J Van Houten & R J Watts, J Amer Chem. Soc , 1975, 97, 3843

8 J R Harbour & S L Issler, J Amer Chem Soc., 1982, 104, 903

9 C Tanielian & L Golder, Photochem. Photobiol , 1981, 34, 411

10 R A Beecroft, R S Davidson, D Goodwin & J.E Pratt, Pure & Appl Chem , 1982, 53, in the press.

(Received in UK 24 June 1982)