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EXCIMERS AND EXCIPLEX AS SENSITISERS FOR PHOTO-OXIDATION REACTIONS

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Abstract - Excimers and exciplexes are shown to sensitise the photo-oxidation of both a sulphide (di-t-butyl sulphide) and an alkene (citronellol). Evidence is presented for the intermediacy of singlet oxygen in these photo-oxidation reactions. The ability of excimers and exciplexes to decay to yield triplets, oxygen quenching of which may result in the generation of singlet oxygen, has important consequences for interpreting the mechanisms of photo-oxidation in reactions sensitised by electron acceptors, e.g. 9,10-dicyanoanthracene.

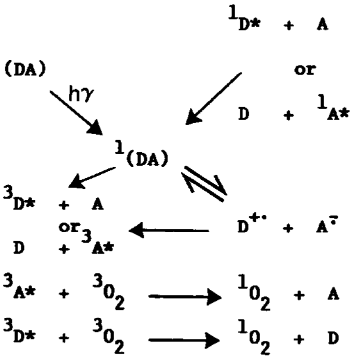
The two main photo-oxidation mechanisms are classified as Type I and Type II processes. The Type I mechanism involves reaction of oxygen with radicals whereas Type II reactions involve singlet molecular oxygen as the oxidising species. Recently there has been a surge of interest in sensitised photo-oxidation reactions mediated by electron transfer processes [1] (Scheme 1).

$$
\begin{aligned}
D + {}^{1}A^{*} &\longrightarrow D^{+\cdot} + A^{\cdot -} \\
A^{\cdot -} + {}^{3}O_2 &\longrightarrow A + O_2^{\cdot -} \\
D^{+\cdot} + O_2 &\longrightarrow \text{oxidation products} \\
D^{+\cdot} + {}^{3}O_2 &\longrightarrow \text{oxidation products}
\end{aligned}
$$

Scheme 1

The most widely used sensitiser for these reactions is 9,10-dicyanoanthracene but methylene blue, a widely used sensitiser for singlet oxygen mediated photo-oxidation reactions, has been found [2] to sensitise the photo-oxidation of trans-stilbene by an electron transfer mechanism. Evidence for the intermediacy of radical ions can be obtained by ESR [3] studies coupled with negative results from tests for the involvement of singlet oxygen. However, in some cases, e.g. the 9,10-dicyanoanthracene sensitised photo-oxidation of 1,4-dimethylnaphthalene [4], product studies have indicated the involvement of both singlet oxygen mediated and electron transfer mechanisms.

Little attention has been paid to the fact that electron transfer reactions of excited singlet states may yield triplets, which can give rise to singlet oxygen production in the presence of oxygen [5,6]. Nevertheless the possibility arises that excimers and exciplexes may behave as sensitisers of singlet oxygen as outlined in Scheme 2. The ability of excited complexes to generate triplet states is dependent upon the efficiency of other non-radiative and radiative



Scheme 2

decay processes, e.g. in polar solvents dissociation to radical ions may be an important process, which lead to their deactivation.

In order to elucidate the utility of excimer and exciplex forming systems as sensitisers of singlet oxygen their ability to sensitise the photo-oxidation of di-t-butyl sulphide and citronellol, which are known to be reactive towards singlet oxygen, was investigated. To test whether singlet oxygen is the species responsible for oxidation, use has been made of the solvent isotope effect upon the life-time of singlet oxygen [7,8]. The magnitude of an observed kinetic solvent isotope effect upon a singlet oxygen mediated photo-oxidation reaction is given by [9,10]:-

$$\frac{\mathrm{Rate}_D}{\mathrm{Rate}_H} = \frac{k_d + (k_r + k_q)\,[\mathrm{Subst.}] + k''\,[\mathrm{Sens.}]}{k_d' + (k_r + k_q)\,[\mathrm{Subst.}] + k''\,[\mathrm{Sens.}]}$$

(where k_d and k_d are the unimolecular decay constants for singlet oxygen in the non-deuterated and corresponding deuterated solvent respectively,

k_r is the rate constant for reaction of singlet oxygen with substrate (Subs.),

k_q and k_q'' are the rate constants for quenching of singlet oxygen by the substrate (Subst.) and the sensitiser (Sens.) respectively)

For the observed kinetic solvent isotope effect to be maximal the concentration of both the substrate and the sensitiser must be kept as low as possible in order that

$k_d \gg ((k_r + k_q)\,[\mathrm{Subs.}] + k''\,[\mathrm{Sens.}])$.

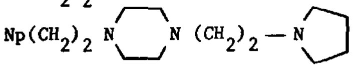
It was necessary to use an aprotic solvent rather than a protic solvent since protic solvents are able to influence the formation of exciplexes derived from amines (and other compounds capable of forming hydrogen bonds). Protic solvents also affect the decay processes of such exciplexes and consequently affect the yield of triplets. We have shown that the quantum yield of triplet production from 1-(N-methyl-anilino)-2-(1-naphthyl)-ethane is larger when MeOD rather than MeOH is used as solvent (0.14 and 0.11 respectively) [6]. If the photophysical properties of the sensitiser are sensitive to the isotopic composition of the solvent, Equation 1 no longer holds. In acetonitrile, which was chosen as the solvent for the photo-oxidation reactions, the lifetime of singlet oxygen has been reported [7] to be between 9 and 22 times shorter than in CD_3CN.

Results and Discussion

In order to determine the magnitude of the kinetic solvent isotope effects upon known singlet oxygen mediated reactions of di-t-butyl sulphide and citronellol, their rose bengal sensitised photo-oxidations were studied in CD_3CN and CH_3CN. Rose bengal is a well known sensitiser of singlet oxygen but observed kinetic solvent isotope effects upon photo-oxidation reactions using rose bengal may be slightly low as a consequence of some quenching of singlet oxygen by the dye [10]. The resultant solvent isotope effects upon the rate of the dye-sensitised photo-oxidation reactions (Table 1) were low but measurable. Consequently, the evaluation of kinetic solvent isotope effects upon excimer and exciplex sensitised photo-oxidations of both the sulphide and the alkene represents a feasible method for determining the role of singlet oxygen in these processes.

Excimers owe most of their stability to exciton resonance and very little to Coulombic interactions. Therefore, excimers are far more likely to decay to yield triplets than radical ions. To determine whether the resultant triplets were capable of sensitising the photo-oxidation of the sulphide and the alkene it was necessary to evaluate the utility of the parent aromatic hydrocarbons as sensitisers. The results in Table 1 indicate that both naphthalene and pyrene are effective sensitisers and the kinetic solvent isotope effects upon these reactions are indicative of the involvement of a diffusional process of singlet oxygen. Both an intramolecular excimer forming system, di-(1-naphthylmethyl) ether (ϕ_f monomer = 0.015, ϕ_f excimer = 0.03, ϕ_T excimer = 0.11) [11], and the intermolecular pyrene excimer sensitised the photo-oxidation of the sulphide and the alkene (Table 1). The concentration of pyrene was sufficiently high that very little fluorescence from the unquenched pyrene monomer singlet state was observed. Consequently most of the singlet oxygen should have been produced

Table 1 Rates of and kinetic solvent isotope effects (in CD_3CN/CH_3CN) upon the photo-oxidation of di-t-butyl sulphide and citronellol (both 5×10^{-3} M) using a range of sensitisers in oxygenated acetonitrile solution (λ_{ex} 300 or 350nm).

Sensitiser System	di-t-butyl sulphide		Citronellol	
	(Rate (M s^{-1})	solvent isotope effect	Rate (M s^{-1})	Solvent isotope effect
Rose bengal (1×10^{-5} M)[a]	3.22×10^{-7}	3.8	3.41×10^{-6}	2.1
Naphthalene[b]	5.68×10^{-7}	4.1	1.47×10^{-6}	2.0
Pyrene monomer[b]	1.28×10^{-6}	4.2	3.04×10^{-6}	c
$NpCH_2OCH_2Np$[b]	8.86×10^{-7}	3.2	2.45×10^{-6}	1.7
Pyrene excimer	1.48×10^{-6}	2.4	5.63×10^{-6}	c
1-Cyanonaphthalene[b]	2.86×10^{-6}	3.2	c	c
Naphthalene (2.5×10^{-2} M)/1-cyanonaphthalene (2.5×10^{-2} M)	3.75×10^{-7}	2.2	c	c
Pyrene[d,e]/1,4-dicyanobenzene (1×10^{-2} M)	3.82×10^{-6}	2.6	c	c
Phenanthrene[e] (1.5×10^{-2} M)/9-cyanophenanthrene (3×10^{-2} M)	3.44×10^{-6}	2.0	5.29×10^{-6}	c
Pyrene[d,e]/triphenylamine (7.5×10^{-2} M)	3.6×10^{-7}	1.3	1.9×10^{-6}	1.0
$Np(CH_2)_2NMePh$[b]	5.31×10^{-7}	2.9	1.14×10^{-6}	1.0
 [b]	7.8×10^{-7}	d	1.34×10^{-6}	1.0

a - using daylight fluorescent lamps and a 2% aqueous potassium chromate light filter solution. b - OD 0.7 @ 300nm. c - not determined.

d - OD 0.42 @ 350nm. e - greater than 90% monomer quenched. Np = 1-naphthyl.

via the pyrene excimer. The di-(1-naphthylmethyl) ether sensitised reactions exhibited solvent isotope effects consistent with the involvement of singlet oxygen. The quantum yields of singlet oxygen production by pyrene monomer and excimer have been reported to be 1.45 and 0.47 respectively in air saturated benzene solution [12]. Oxygen quenching of both the singlet and triplet excited states of pyrene can lead to the generation of singlet oxygen. The singlet-triplet splitting of pyrene excimer (<7880 cm^{-1}) is estimated to be insufficient [12] for oxygen quenching of the singlet excimer to generate singlet oxygen. Scheme 3 illustrates the processes leading to singlet oxygen production from pyrene monomer and excimer.

$$\text{pyrene}_{S_1} + {}^3O_2 \longrightarrow \text{pyrene}_{T_1} + {}^1O_2$$

$$\text{pyrene}_{T_1} + {}^3O_2 \longrightarrow \text{pyrene}_{S_0} + {}^1O_2$$

$$(\text{pyrene excimer})_{S_1} + {}^3O_2 \longrightarrow \text{pyrene}_{T_1} + \text{pyrene}_{S_0}$$

$$(\text{pyrene excimer})_{S_1} \longrightarrow \text{pyrene}_{T_1} + \text{pyrene}_{S_0}$$

Scheme 3

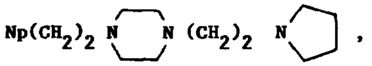
The low solvent isotope effect upon the rate of the pyrene excimer sensitised photo-oxidation of the sulphide may be due to significant quenching of the singlet oxygen as a result of the high concentration of pyrene in solution (triplet pyrene has been reported [13] to quench singlet oxygen via a pyrene-oxygen complex with some charge-transfer character).

In contrast to excimers, exciplexes are mainly stabilised by Coulombic interactions. Consequently triplet production will be in competition with decay to yield radical ions, especially in highly polar solvents like acetonitrile. In aprotic solvents the isotopic composition of the solvent is not expected to affect the rate of an electron transfer process.

It is well known that the fluorescence of many polycyclic aromatic hydrocarbons is quenched by electron donors and acceptors [5, 14]. This was established for the following systems: pyrene/triphenylamine, pyrene/1,4-dicyanobenzene, naphthalene/1-cyanonaphthalene and phenanthrene/9-cyanophenanthrene. These were used to sensitise oxidation reactions under conditions where > 90% of the aromatic hydrocarbon fluorescence was quenched by the electron donor. The low solvent isotope effects upon the rates of photo-oxidations using naphthalene/1-cyanonaphthalene, phenanthrene/9-cyanophenanthrene and pyrene/1,4-dicyanobenzene relative to those obtained for the dye-sensitised reactions may be due to the formation of radical ions in these systems which lead to the formation of the superoxide anion. This species has been shown to be an efficient quencher of singlet oxygen [15]. This quenching process would contribute to a diminution of the solvent isotope effect. Pyrene/1,4-dicyanobenzene has been shown [16], by laser flash photolysis and transient photoconductivity experiments, to undergo ionic dissociation from both the non-relaxed and equilibrium exciplex in acetonitrile solution. However, the results in Table 1 indicate that even this type of intermolecular exciplex forming system yields triplets, oxygen quenching of which leads to the production of singlet oxygen.

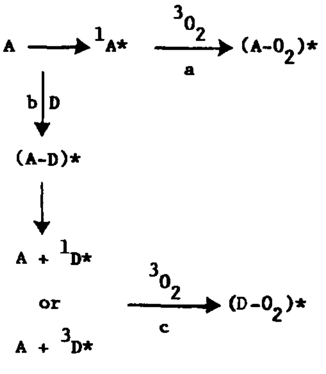
The low kinetic solvent isotope effect observed for the intermolecular exciplex system, pyrene/triphenylamine, sensitised reaction is probably due to both ionic dissociation of the exciplex and quenching of singlet oxygen by the amine, which is present at a high concentration (7.5 x 10^{-2} M)[17]. Laser flash photolysis studies revealed that the quantum yield of pyrene triplets is around ten times greater for the pyrene/triphenylamine system than for pyrene, at the same concentration, in the absence of the amine. The mechanisms of the reactions which utilised intramolecular exciplex forming systems, i.e.

$Np(CH_2)_2NMePh$ and



were, unlike the intermolecular complexes, complicated by competing radical reactions of the sensitisers. These caused the oxidation reactions to exhibit induction periods, which were prolonged in the presence of radical inhibitors e.g. Tinuvin 770. U.V. spectroscopy revealed that the degradation products stabilise the 1-naphthylakylamines to further decomposition. We attribute the observed sensitisation of photo-oxidation reactions by these compounds to singlet oxygen produced by oxygen quenching of the triplet states of the degradation products. One of the products is 1-naphthaldehyde and this was found to be an effective sensitiser for the photo-oxidation of both the sulphide and the alkene. The solvent isotope effects upon the rates of these photo-oxidation reactions were 4.2 and 3.5 respectively indicating that 1-naphthaldehyde can sensitise the production of singlet oxygen. By choosing di-t-butyl sulphide, which does not contain any abstractable α-hydrogens, as an acceptor for singlet oxygen the chance of reactions occuring via radical intermediates of the type RCHSR is minimised.

These experiments have established the feasibility of using intra- and intermolecular excited complexes as sensitisers of singlet oxygen, in polar solvents. In some cases 9,10-dicyanoanthracene sensitised photo-oxidations, e.g. of 1,4-dimethylnaphthalene [4], give rise to products which are consistent with the involvement of both singlet oxygen mediated and electron transfer mechanisms. Our results suggest that intermediate excited complex formation could be responsible for some singlet oxygen production. Excited complexes can result from sensitiser-oxygen (path a), sensitiser-substrate (path b) and/or substrate oxygen (path c) interactions as outlined in Schemes 2 and 4. Foote and co-workers [18] have recently reported that oxygen quenching of both the singlet and triplet excited states of 9,10-dicyanoanthracene gives rise to singlet oxygen production in benzene and acetonitrile solutions. Such behaviour can only be energetically feasible if the singlet-triplet splitting of the sensitiser exceeds the excitation energy of singlet oxygen (7880 cm^{-1}).



Scheme 4

Experimental

UV spectra were recorded on a Perkin Elmer 402 spectrophotometer. Glc analyses were recorded on a Perkin Elmer Sigma 3 gas chromatograph using a Perkin Elmer 10% SE 30, chromosorb W 60-80 mesh column. 9-Cyanophenanthrene, 1,4-dicyanobenzene, di-t-butyl sulphide, pyrene, triphenylamine (all Aldrich) naphthalene, potassium chromate (both BDH), Tinuvin 770 (Ciba-Geigy), rose bengal (Eastman -Kodak), acetonitrile (Fisons AnalaR grade), acetonitrile -d_3 (Goss Intruments Ltd) and 1-naphthaldehyde (Koch-Light) were used as supplied. Citronellol (Aldrich) was distilled prior to use. We thank Dr. R.A. Beecroft for the di-(1-naphthylmethyl) ether and N-(2-(1'-naphthyl)ethyl)-N'-(2-(1-azacyclopentyl)ethyl-1,4-cyclohexane. The N-methyl, N-phenyl(1-naphthyl)ethylamine was prepared by lithium aluminium hydride reduction of N-phenyl-1-naphthyl acetamide. The acetamide was made by reaction of 1-naphthylacetyl chloride with N-methylaniline. The reactions were carried out according to the procedure described by Trethewey [19]. Physical and spectroscopic data confirmed the structure of the N-methyl, N-phenyl(1-naphthyl) ethylamine.

Pyrex photolysis tubes containing the sensitiser and substrate in the appropriae solvent were flushed with a stream of oxygen (dry and carbon dioxide-free) for twenty minutes, stoppered and irradiated within a circular array of fluorescent lamps with a maximum emission at either 300 nm (16 x Rayonet RPR 3000 A) or 350 nm (16 x 8 W Sylvania F8T5/BLB). The rate of loss of substrate was followed by glc analysis. The dye sensitised reactions were carried out as described above using fluorescent daylight lamps (8 x 20 W, Cryselco) and a 2% aqueous potassium chromate light filter solution.

To study the decomposition of sensitisers the photolyses were carried out in 1 cm quartz cuvettes, flushing with oxygen (prior to irradiation) was ceased after five rather than twenty minutes. Laser flash photolysis studies were carried out as previously described [20].

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