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FORMATION OF SINGLET OXYGEN FROM AROMATIC EXCIMERS AND MONOMERS

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Summary

Singlet oxygen ($^1\Delta_g$) formation is sensitized by excimers of aromatic hydrocarbons as well as by monomers. In methanol the pyrene excimer is a somewhat less efficient sensitizer than is pyrene itself, while the excimer of naphthalene is more efficient than the monomer. An explanation invoking involvement of upper triplet states in oxygen-enhanced intersystem crossing is suggested.

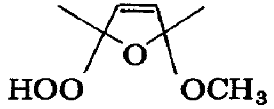
1. Introduction

Recent interest in the role of singlet oxygen ($^1\Delta_g$) as an intermediate in chemical reactions [1 - 3], in biological processes [4] and in air pollution [5] has led to numerous investigations into the production and reactivity of this interesting species. Singlet oxygen is known to be formed by an energy transfer process in which polycyclic aromatic hydrocarbons are efficient sensitizers [1]. To date, however, it has not been reported whether excimers of these compounds may be involved in this process, although many aromatic compounds exhibit excimer-like properties in the solid state (ref. 6, p. 362), as may exist in atmospheric particulate matter. Therefore a study was undertaken to determine to what extent excimers can be involved in singlet oxygen formation.

2. Experimental

2.1. Procedures

Quantum yields were measured using an apparatus similar to that described by Gollnick *et al.* [7]. Light at 313 nm was isolated from a medium pressure mercury lamp by means of a Corning 7-54 filter and a solution containing 0.15 g $KCrO_4$ and 0.004 g NaOH in 25 ml distilled water. This filter solution was replaced daily from stock to avoid decomposition. The light was focused through the filters onto the apparatus which contained 47 ml of solution which was saturated with ogygen by bubbling through a glass frit. The concentration of the sensitizer was kept high enough to ensure that all the light was absorbed in the 2.5 cm cell. Ferrioxalate actinometry using the above filters indicated a light intensity of 9.5×10^{15} quanta s^{-1}. A Corning 7-54 filter was used alone for most of the naphthalene measurements, resulting in an intensity of 1.18×10^{16} quanta s^{-1} (313 nm). Dimethylfuran (DMF) at a concentration of 0.010 mol l^{-1} was used as a singlet oxygen trap. This concentration is sufficient to trap more than 99% of the singlet oxygen generated [8], forming (in methanol) compound I [7].



(I)

The disappearance of DMF was measured by vapor phase chromatography, using 2,2,5-trimethylhexane as an internal standard. Normally four aliquots of each solution were withdrawn at appropriate times and each was analysed by three injections, reproducible to ±0.3%. Consumption of DMF was approximately first order to at least 40% conversion*; maximum conversion for a given run averaged 8.5% and never exceeded 16%. No measurable consumption of DMF occurred in the absence of sensitizer or when the solution was saturated with nitrogen rather than oxygen. Indicated errors in quantum yields (Table 1, Figs. 1 and 2) are standard deviations and reflect scatter of data within an individual run, as analyzed by a least-squares procedure. There is an additional error of probably 5% in the absolute values of the quantum yields.

In addition to quantum yield measurements, the self-quenching of the fluorescence of pyrene and naphthalene in oxygen-saturated methanol was determined. These measurements were performed on the spectrofluorimeter which has been described previously [9]. Round quartz tubes were filled with the sample, saturated with oxygen by bubbling, placed into the spectrofluorimeter and rotated manually to minimize geometrical irregularities. The Stern–Volmer quenching constant K_{SV} was determined from the slope of a plot of ϕ_0/ϕ *versus* concentration for at least four concentrations of naphthalene or pyrene.

2.2. Materials

Reagent grade methanol and "hexanes" were used as solvents, since vapor phase chromatography (VPC) analysis indicated no interfering impurities. 1-Bromonaphthalene, zone refined phenanthrene and reagent grade naphthalene (recrystallized from ethanol) were used as received. Reagent

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*The reaction was well behaved in methanol and in hydrocarbons. In acetonitrile, however, there appeared to be a dark reaction regenerating DMF which made accurate analysis impossible.

TABLE 1

Quantum yields ϕ for O_2 ($^1\Delta_g$) formation at 313 nm

Naphthalene concentration (mol l^{-1})		0.01	0.10	0.20	0.30	0.40	0.50
(Methanol)[a]	ϕ	0.41 ± 0.01	0.45 ± 0.02	0.50 ± 0.01	0.50 ± 0.03	0.55 ± 0.02	
(Hexanes)	ϕ	0.77 ± 0.07					0.70 ± 0.05
Pyrene concentration (mol l^{-1})		0.001	0.004	0.008	0.013	0.018	0.020
(Methanol)	ϕ	0.74 ± 0.01	0.75 ± 0.01	0.67 ± 0.02	0.65 ± 0.04	0.65 ± 0.04	
(Hexanes)	ϕ	0.83 ± 0.05					0.90 ± 0.08
Phenanthrene concentration (mol l^{-1})		0.01	0.13				
(Methanol)	ϕ	0.50 ± 0.02	0.51 ± 0.03				
1-*Bromonaphthalene* concentration (mol l^{-1})		0.01					
(Methanol)	ϕ	0.86 ± 0.03					

[a] The solvent is given in parentheses.

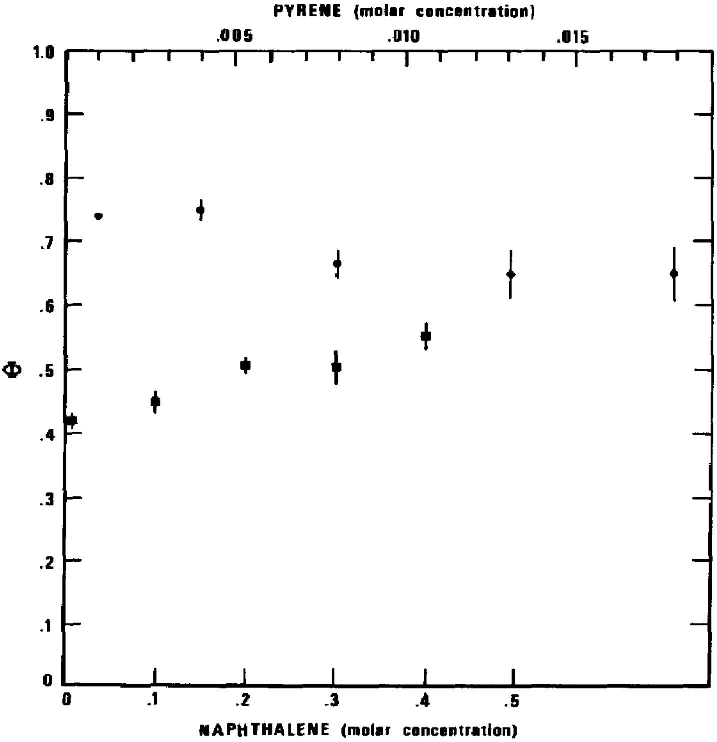

Fig. 1. Quantum yields of singlet oxygen formation in methanol sensitized by pyrene (●) and naphthalene (■).

grade pyrene was sublimed before use (melting point, 144 - 147 °C, literature value, 156 °C [10]). 2,5-Dimethylfuran (99% pure) was passed through a short alumina column immediately before use to remove peroxidic impurities.

3. Results

Pyrene, naphthalene, 1-bromonaphthalene and phenanthrene sensitize singlet oxygen formation in methanol, but at less than 100% efficiency. As shown in Table 1 and in Fig. 1, the quantum yield for pyrene is approximately 0.75 at low concentrations and gradually decreases to about 0.64 at 0.018 mol l^{-1}. The quantum yield for naphthalene increases from 0.41 at low concentrations to 0.55 at 0.4 mol l^{-1}. These changes accompany excimer formation. The Stern–Volmer constant K_{SV} for self-quenching, determined independently, is 38 ± 2 l mol^{-1} for pyrene and 1.0 ± 0.15 l mol^{-1} for naphthalene in oxygen-saturated methanol. In both cases K_{SV} is large enough for significant quenching and excimer formation [11] to occur at the higher sensitizer concentrations used. Similar quantum yield measurements were made on phenanthrene, a compound which does not form excimers [12]. As shown in Table 1, the quantum yield is the same (0.50)

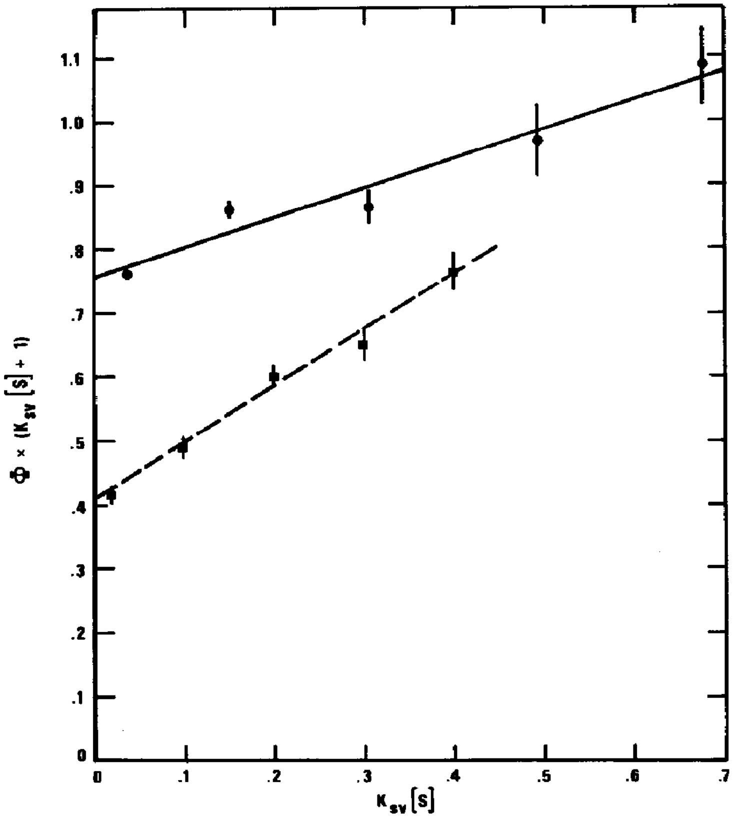

Fig. 2. Quantum yields of singlet oxygen formation in methanol, corrected for the fraction of sensitizer (S) which is self-quenched (see text): ● pyrene; ■ naphthalene.

within experimental error at low and high concentrations. Sensitization by 1-bromonaphthalene was also examined; the quantum yield was 0.86. To investigate the effect of solvent polarity, experiments were also run at low and high concentrations of pyrene and naphthalene in hexanes. These quantum yields are nearer to unity (Table 1) and do not show the concentration dependent trends observed in methanol.

The results in hydrocarbon solvents agree qualitatively with the earlier results which indicate quantum yields of approximately 1 for formation of singlet oxygen from a variety of sensitizers [13]. The reduced quantum yields in methanol agree with the results of Gollnick *et al.* [7] who reported a quantum yield for pyrene of 0.57 - 0.62 (concentration unspecified). However, the quantum yields of 0.41 - 0.55 determined here for naphthalene are considerably larger than the earlier results (0.12 - 0.15) [7].

4. Discussion

There is general agreement that sensitization of singlet oxygen results from interaction of ground state oxygen with the triplet state of the sensitizer [1 - 3]. Thus, spin-allowed energy transfer from the excited singlet to oxygen is normally unimportant, although Stevens and Ors [14] have recently found evidence for this process with highly fluorescent sensitizers. The fact that the quantum yield for naphthalene, pyrene and phenanthrene remains less than 1, however, implies that only one process, energy transfer from the sensitizer triplet, is likely to be important for these molecules.

Quenching of fluorescence by oxygen, however, is a process which results from enhanced intersystem crossing to form the triplet sensitizer [15]. In a system such as this one, the relevant steps may be summarized in scheme I:

Scheme I

$$^1S_0 \xrightarrow{h\nu} {}^1S^* \tag{1}$$

$$^1S^* + O_2 \rightarrow {}^3S^* + O_2 \tag{2}$$

$$^1S^* + O_2 \rightarrow ? \tag{3}$$

$$^1S^* + {}^1S_0 \rightarrow {}^1S_2^* \tag{4}$$

$$^1S_2^* + O_2 \rightarrow {}^3S^* + {}^1S_0 + O_2 \tag{5}$$

$$^1S_2^* + O_2 \rightarrow ? \tag{6}$$

$$^3S^* + O_2 \rightarrow {}^1S_0 + O_2(^1\Delta_g) \tag{7}$$

$$^3S^* + O_2 \rightarrow ? \tag{8}$$

In scheme I, $^1S_0$ represents the ground state sensitizer, $^1S^*$ is the excited singlet, $^3S^*$ is the excited triplet and $^1S_2^*$ is the excimer. Processes (3), (6) and (8) represent modes of decay which may compete with singlet oxygen formation. Excimer formation (process (4)) is represented as an irreversible process for simplicity, although this is not actually the case [16]. The possibility of triplet excimer formation in connection with process (5) cannot be excluded, although Birks [17] has concluded that there is no reliable evidence for emission from triplet excimers of simple aromatic compounds. Spontaneous decay processes such as fluorescence, internal conversion and intersystem crossing have not been included in this scheme. Since oxygen quenches excited states at nearly the diffusion-controlled rate and the lifetimes of excited singlet naphthalene and pyrene are each greater than or equal to 100 ns (ref. 6, pp. 126, 128), these other processes will be unimportant in oxygen-saturated solutions (0.01 mol l^{-1} oxygen in methanol) [18].

Formation of singlet oxygen in hydrocarbon solvents via process (7) is more efficient than are the competing processes (3), (6) or (8), since the quantum yields [13] are nearly unity for sensitization by most aromatic molecules. The lower quantum yields observed in methanol, however, must be due to the occurrence of one or more of these processes. In order to determine the relative importances of these competing reactions, singlet oxygen sensitization by 1-bromonaphthalene was examined.

The energies of the lowest singlet and triplet excited states of this compound are similar to those of naphthalene [19], yet the lifetime of the singlet is less than 1 ns owing to its efficient spontaneous intersystem crossing. The fact that this sensitizer has a quantum yield of nearly 1 suggests that the inefficiency encountered in methanol for naphthalene, pyrene and phenanthrene arises primarily from processes (3) or (6) competing with the oxygen-induced intersystem crossing.

The efficiencies for sensitization by the monomer and the excimer of pyrene or naphthalene can now be determined since the fraction of the excited state quenched to form the excimer is known for each concentration. If one assumes that all the triplets generate singlet oxygen with unit efficiency, scheme I may be simplified to scheme II:

Scheme II

$$^1S^* + O_2 \xrightarrow{k_9} {}^1S_0 + O_2(^1\Delta_g) \tag{9}$$

$$^1S^* + O_2 \xrightarrow{k_3} ? \tag{3}$$

$$^1S^* + {}^1S_0 \xrightarrow{k_4} {}^1S_2^* \tag{4}$$

$$^1S_2^* + O_2 \xrightarrow{k_{10}} 2{}^1S_0 + O_2(^1\Delta_g) \tag{10}$$

$$^1S_2^* + O_2 \xrightarrow{k_6} ? \tag{6}$$

in which k_9 and k_{10} are, of course, composites of several rate constants.

If we let the limiting quantum yield of singlet oxygen formation from the monomer (infinite dilution) be

$$\phi_m = \frac{k_9}{k_9 + k_3}$$

and the limiting quantum yield from the excimer (infinite concentration) be

$$\phi_x = \frac{k_{10}}{k_{10} + k_6}$$

then the total quantum yield will be

$$\phi = \frac{\phi_m + \phi_x K_{SV}[^1S_0]}{K_{SV}[^1S_0] + 1}$$

where K_{SV}, the experimentally determined self-quenching constant, corresponds to $k_4/(k_3 + k_9)[O_2]$. Thus if one plots $\phi(K_{SV}[^1S_0] + 1)$ *versus* $K_{SV} \times [^1S_0]$, the slope is ϕ_x and the intercept is ϕ_m. Such a plot is shown in Fig. 2 for pyrene and naphthalene, and from a least squares analysis of the data in Table 2 it is found that the limiting quantum yields for the sensitization of singlet oxygen by the monomer and excimer of pyrene are 0.76 ± 0.03 and 0.46 ± 0.06, and are 0.41 ± 0.01 and 0.89 ± 0.05 for the monomer and excimer of naphthalene. Therefore, both monomers and excimers do sensitize the formation of singlet oxygen, but they do so with efficiencies which are not at first easy to understand.

An explanation of the differing efficiencies of the monomer and excimer sensitization processes may begin with an understanding of the competing

TABLE 2

Self-quenching and quantum yields in oxygen-saturated methanol

Naphthalene concentration (mol l^{-1})	0.01	0.10	0.20	0.30	0.40
$K_{SV}[S]$	0.01	0.10	0.20	0.30	0.40
$\phi(K_{SV}[S] + 1)$	0.418	0.491	0.604	0.654	0.766
Pyrene concentration (mol l^{-1})	0.001	0.004	0.008	0.013	0.018
$K_{SV}[S]$	0.038	0.151	0.302	0.491	0.677
$\phi(K_{SV}[S] + 1)$	0.762	0.861	0.863	0.966	1.088

processes (3) and (6). Potashnik *et al.* [13] have observed solvent effects in the quenching of excited singlet pyrene by oxygen, which suggest that the quenching in polar solvents (acetonitrile) may be associated with charge-transfer interactions between pyrene and oxygen. This hypothesis was supported by the appearance of the pyrene positive ion in connection with the quenching [13]. Thus it is likely that such a process resulting in ion formation competes with the oxygen-enhanced intersystem crossing in methanol, but is unimportant in hydrocarbon solvents.

Oxygen-enhanced intersystem crossing must thus compete with ion formation in methanol, and the rate of intersystem crossing becomes an important factor in determining the efficiency of monomer or excimer sensitization. The rate of intersystem crossing depends upon the presence of nearby triplet "accepting" states in the molecule. For example, molecules which have a second triplet state slightly below the first excited singlet would be expected to undergo more rapid intersystem crossing than those which do not [20], since a smaller energy gap would result in less vibrational energy to be distributed over the molecule and thus in a larger Franck–Condon factor for the transition [21]. Naphthalene is known to have an upper triplet state at 30 800 cm^{-1}, which is about 1000 cm^{-1} below the excited singlet [22]. Pyrene, however, has its second triplet at 27 200 cm^{-1}, or 400 cm^{-1} above the excited singlet [23], which is still close enough to allow rapid intersystem crossing at room temperature. If one makes the reasonable assumption that these same energy levels are involved in oxygen-enhanced intersystem crossing, one can understand the varying efficiencies of the intersystem crossing by comparing the relevant energy levels of the excimers with those of the monomer.

The lowest excited singlet state of the naphthalene excimer is approximately 2100 cm^{-1} (ref. 6, pp. 354, 357) below that of the uncomplexed naphthalene, and is thus about 1000 cm^{-1} below the second triplet of naphthalene (Fig. 3). Interactions between triplet naphthalene and ground state naphthalene may lower the energy of this upper triplet slightly, causing the energy of the excimer nearly to equal that of the second triplet state and resulting in efficient intersystem crossing from the excimer. In the pyrene singlet, however, the excimer interaction is larger, resulting in a stabilization of about 3500 cm^{-1} (ref. 6, pp. 354, 357). There is thus a large energy

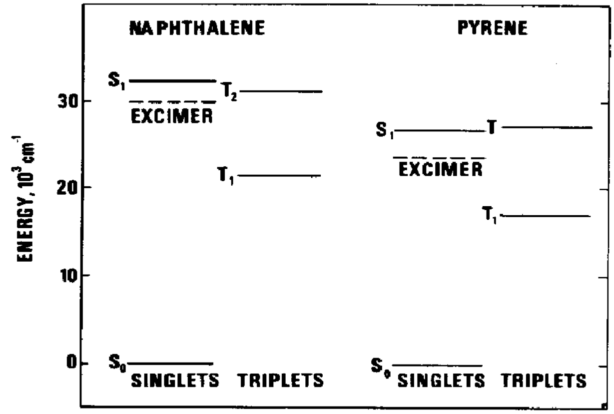

Fig. 3. Energy levels of excimers and monomers of sensitizers: S, singlets; T, triplets.

separation between this excimer and either the first or second triplet states, resulting in less efficient intersystem crossing and singlet oxygen formation than is observed with the monomer.

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