

## AN INVESTIGATION INTO THE ROLE OF CO-SENSITIZERS IN 9,10-DICYANOANTHRACENE-SENSITIZED REACTIONS

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### Summary

The ability of biphenyl to enhance dramatically the rate of 9,10-dicyanoanthracene-sensitized photo-oxidation reactions is investigated. Evidence is presented in favour of this phenomenon being due to the biphenyl increasing the yield of singlet oxygen.

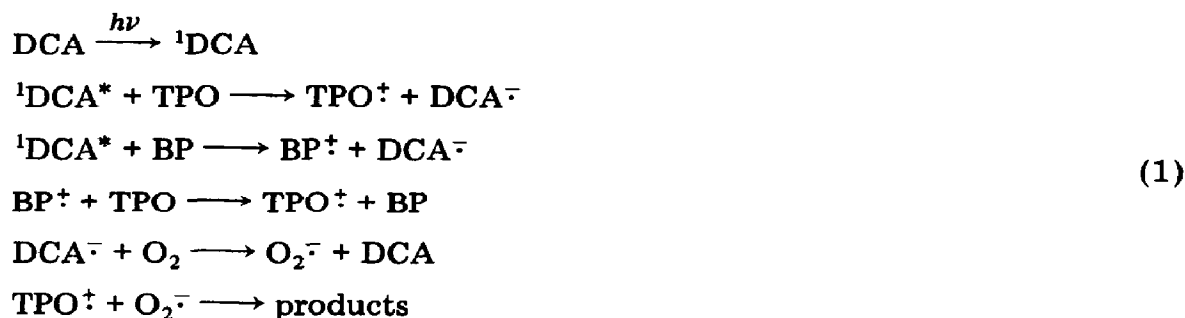
### 1. Introduction

Schaap *et al.* [1] have reported a very interesting 9,10-dicyanoanthracene DCA-sensitized photo-oxidation reaction in which the rate of oxidation of the tetraphenyloxirane 1 (TPO) is dramatically enhanced in the presence of biphenyl (BP).



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In order to account for the observed rate enhancement the following scheme was proposed [1]:



The main drawback to this mechanism is the highly endothermic nature of the key electron transfer from the substrate to  $\text{BP}^\ddagger$  (4th step in (1)). The inefficiency of the reaction in the absence of BP was attributed to the inability of TPO to effectively quench the fluorescence of DCA. In contrast with the substrate, BP readily quenches DCA fluorescence. In the above scheme it has been assumed that quenching by BP leads exclusively to the

generation of radical ions. However, it is well known [2] that excited state complexes can also decay to yield triplets. We have recently shown [3] that as a consequence of their ability to decay to yield triplets, exciplex-forming systems can sensitize singlet oxygen production.

## 2. Experimental details

The following chemicals were used as supplied: 4-chlorobiphenyl, 1-bromonaphthalene, 9-cyanoanthracene (CA) and xanthone (all Aldrich); 4-bromobiphenyl and naphthalene (both BDH); 1-chloronaphthalene (Ralph N. Emanuel); DCA (Eastman Kodak). BP (BDH) was recrystallized from acetonitrile prior to use, and the acetonitrile was Aldrich Gold Label spectrophotometric grade.

Fluorescence quenching experiments were performed on a Perkin-Elmer MPF-4 spectrofluorometer using acetonitrile solutions of CA and DCA having an optical density of 0.1 at the excitation wavelength (353 nm). Each solution was degassed by flushing with a stream of argon for 5 min and stoppering the cell. The effect of adding increasing amounts of the aromatic hydrocarbon quencher was determined by monitoring the resultant change in the intensity of the uncorrected fluorescence spectra.

Laser flash photolysis experiments were carried out with an excimer laser (Oxford Lasers) using a procedure which has been previously described [4]. For the laser flash photolysis experiments, acetonitrile stock solutions of CA and DCA were made up having an optical density of 1.0 ( $3.8 \times 10^{-4}$  M) at the excitation wavelength (353 nm, xenon fluoride). Appropriate amounts of aromatic hydrocarbon were added to each solution so as to quench a similar proportion of the fluorescence of each cyanoanthracene compound. The solutions were degassed by three freeze-pump-thaw-shake cycles.

In order to evaluate the quantum yield of triplet formation of the aromatic hydrocarbon in each case, xanthone was used as the triplet counter. Laser flash photolysis of degassed acetonitrile solutions of xanthone (having the same optical density as the cyanoanthracenes, *i.e.* 1.0 at 353 nm) containing the aromatic hydrocarbon produced the triplet aromatic hydrocarbon in each case. The optical density of these species at their respective triplet-triplet  $\lambda_{\text{max}}$  and at zero time were determined.

Since the triplet yield of xanthone in acetonitrile is virtually unity, the ratio of the optical densities of the triplet aromatic hydrocarbon formed in the reactions with xanthone and the cyanoanthracenes respectively gives the triplet yield of the aromatic hydrocarbon as shown in Tables 1 and 2.

## 3. Results and discussion

Utilizing the technique of laser flash photolysis we have been able to evaluate the effect of the addition of BP on the quantum yield of triplet

production. The results revealed that in the presence of BP ( $10^{-2}$  M) the optical density of the observed triplet-triplet absorption spectrum of DCA increases from 0.023 to 0.032 at 465 nm. However, although decay of the intermediate charge transfer species to yield triplet DCA is more energetically favourable than decay to produce triplet BP the latter decay route is also found (Table 1) to be operative.

Furthermore, the results in Table 1 reveal that such behaviour is not confined to BP but also occurs when DCA is irradiated in the presence of a range of other aromatic hydrocarbons. In all cases DCA was the only species which absorbed the incident light and generation of the triplet aromatic hydrocarbons could not have occurred via energy transfer. In some cases (Table 1) any enhancement of triplet DCA production was found to be minimal. A possible explanation for the finding that decay of the intermediate exciplex yields predominantly the triplet state of higher energy involves consideration of the energy gap between the exciplex and each of the possible localized triplet states. As this gap increases, radiationless transitions from a given energy level of the exciplex will be to an increasingly high vibrational level of the localized triplet state and the probability of energy transfer will be correspondingly decreased. Consequently, energy transfer from the exciplex to form the triplet state of higher energy will effectively compete with decay to yield the triplet state of lowest energy. It can be seen from the results in Table 2 that CA behaves in a similar manner to DCA.

On the basis of the results in Table 1 it would appear that the rate of photo-oxidation of TPO is enhanced under conditions where the overall yield of triplets, of whatever nature, is increased. In the presence of oxygen these triplets can act as progenitors of singlet oxygen. This would suggest that the photo-oxidation of TPO can occur, albeit slowly, via a singlet oxygen mechanism. Consequently, we propose that the mechanism outlined in reactions (2) provides an alternative explanation for the ability of BP to act as a cosensitizer in DCA-sensitized photo-oxidation reactions.

TABLE 1

Quantum yields  $\phi_T(\text{sens})$  of triplet production from aromatic hydrocarbons ( $10^{-2}$  M) as a consequence of their interaction with excited DCA ( $3.8 \times 10^{-4}$  M) in degassed acetonitrile solution

| Hydrocarbon         | Triplet-triplet absorption $\lambda_{\text{max}}$<br>(nm) | $\phi_T(\text{sens})$ |
|---------------------|---|-----------------------|
| BP                  | 358   | 0.146                 |
| 4-Chlorobiphenyl    | 372   | 0.042                 |
| 4-Bromobiphenyl     | 375   | 0.050                 |
| Naphthalene         | 412   | 0.070                 |
| 1-Chloronaphthalene | 414   | 0.090                 |
| 1-Bromonaphthalene  | 420   | 0.088                 |

Xanthone was used as the triplet counter.

TABLE 2

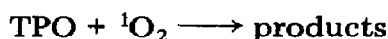
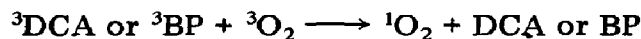
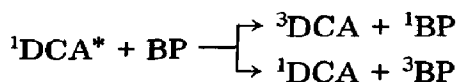
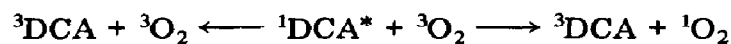
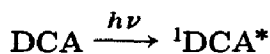
Quantum yields of triplet production  $\phi_T(\text{sens})$  from aromatic hydrocarbons as a consequence of their interaction with excited CA and excited DCA (both  $3.8 \times 10^{-4}$  M) in degassed acetonitrile solution

| Hydrocarbon <sup>a</sup> | Triplet-triplet absorption $\lambda_{\text{max}}$ (nm) | Fs <sup>b</sup> (%) | $\phi_T(\text{sens})^b$ | Fs <sup>c</sup> (%) | $\phi_T(\text{sens})^c$ |
|--------------------------|--|---------------------|-------------------------|---------------------|-------------------------|
| Biphenyl                 | 358  | 47                  | 0.066                   | 34                  | 0.146                   |
| Naphthalene              | 412  | 64                  | 0.043                   | 72                  | 0.065                   |

<sup>a</sup>The concentration of the aromatic hydrocarbons ( $10^{-1}$  M in the CA solution,  $10^{-2}$  M in the DCA solution) were such that they quenched a similar proportion Fs of the fluorescence from each cyanoanthracene compound.

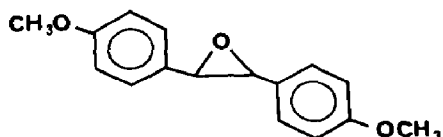
<sup>b</sup>CA results.

<sup>c</sup>DCA results.



Although TPO was chosen as a substrate which exhibits low reactivity towards singlet oxygen, this does not preclude reaction occurring by this route under circumstances where alternative mechanisms are even less efficient. The oxidation which was observed [1] in the absence of BP is not inconsistent with a singlet oxygen mechanism since Dobrowlski *et al.* [5] have demonstrated the ability of DCA to behave as a sensitizer of singlet oxygen. In the absence of reported quantum yields it is impossible to comment on the apparent stability of TPO when Rose Bengal is used as sensitizer [1].

The slightly different product distribution in the presence of BP indicates that more than one mechanism is operative, *i.e.* both electron transfer and singlet oxygen mediated processes. In order for the mechanism outlined in reactions (2) to be valid the efficiency with which TPO reacts with singlet oxygen must exceed the probability of endothermic electron transfer from TPO to BP<sup>+</sup>. A recent report by Clawson *et al.* [6] suggests that the proposed electron transfer from TPO to BP<sup>+</sup> is not efficient. They found that BP is ineffective as a co-sensitizer in the DCA-sensitized C—C bond cleavage of a similar oxirane 2.



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In this reaction the initial electron transfer was followed by bond cleavage to yield an intermediate which could be trapped by a suitable dipolarophile. It would therefore seem reasonable to conclude that the addition of BP to a DCA-sensitized photo-oxidation reaction will not have a marked effect on any electron transfer process but can dramatically affect the yield of triplets, and consequently the rate of any reaction which occurs via a singlet oxygen intermediate.

### Acknowledgments

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