Photo-oxygenation *via* Electron Transfer and its Susceptibility to Catalysis

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Summary The photo-oxygenation of diphenylacetylene (**1**) is efficiently sensitized (*via* electron transfer) with dicyanoanthracene (Φ = *ca.* 0·15), but is sensitized very poorly ($\Phi < 0{\cdot}001$) with tetracyanoanthracene (TCA); catalysis by acids and nucleophiles substantially increases the quantum yield of photo-oxygenation through reactions competing with the reverse electron transfer between $(\text{TCA})^{-\cdot}$ and $(\mathbf{1})^{+\cdot}$.

Photo-oxygenation *via* electron transfer is attracting considerable interest.[1–6] We have reported the first example of such a reaction, the photo-oxygenation of diphenylacetylene.[1] This communication deals with the mechanism of this reaction.

Several photo-induced electron transfer reactions are sensitized with 9,10-dicyanoanthracene (DCA), which has a reduction potential of −0·88 V (in MeCN *vs.* saturated calomel electrode, S.C.E.) and a 0–0 singlet excitation energy of 2·94 eV. Diphenylacetylene (**1**), which has an oxidation potential of 1·85 V (in MeCN *vs.* S.C.E.), quenches the fluorescence of DCA at a diffusion-controlled rate as expected for an exothermic electron transfer.[7]

$\text{PhC}{\equiv}\text{CPh}$ (**1**) $\quad$ PhCOCOPh (**2**) $\quad$ PhCO_2H (**3**)

In the absence of oxygen, no products are isolated from the irradiation of an acetonitrile solution of DCA and (**1**).† When oxygen or air is bubbled during the irradiation of such a solution, benzil (**2**) and benzoic acid (**3**) are obtained in the ratio of *ca.* 2·9 : 1 [Φ(products) = *ca.* 0·15]. The ratio of these products is constant, within experimental error, from the earliest stage of the reaction (*ca.* 0·1% conversion) to *ca.* 10% conversion. This constant ratio and the linear increase of both products with the irradiation time in this conversion range show that, under selected reaction conditions [*ca.* 0·5 mM DCA, 0·1—0·5 M (**1**), λ = 405 and 436 nm], (**3**) is formed concurrently with (**2**).

Oxygen (reduction potentials: −0·75, −0·82 V in MeCN

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† The related photoreaction of phenylacetylene sensitized with tetracyanoanthracene gives a dimer, 1-phenylnaphthalene, and a solvent-incorporated product, 2-methyl-3,6-diphenylpyridine (S. L. Mattes and S. Farid, *J. Chem. Soc., Chem. Commun.*, **1980**, 126).

vs. S.C.E.)[8] is more readily reduced than DCA. Secondary electron transfer from DCA$^{-\cdot}$ to O_2 giving $O_2^{-\cdot}$ should, therefore, be an efficient process. The oxidation products could result from the reaction of **(1)**$^{+\cdot}$ with $O_2^{-\cdot}$ and/or with O_2. The involvement of **(1)**$^{+\cdot}$ in oxidation is clearly shown by quenching the reaction with compounds which have lower oxidation potentials than **(1)**. 1,4-Dimethoxybenzene and 1,4-dimethoxynaphthalene, at concentrations as low as 10^{-4}M, almost completely suppress the formation of **(2)** and **(3)**.

$$\begin{aligned}
{}^{1}\mathrm{DCA}^{*} + \mathbf{(1)} &\longrightarrow \mathrm{DCA}^{-\cdot} + \mathbf{(1)}^{+\cdot}\\
\mathrm{DCA}^{-\cdot} + \mathrm{O_2} &\longrightarrow \mathrm{DCA} + \mathrm{O_2}^{-\cdot}\\
\mathbf{(1)}^{+\cdot} + \mathrm{O_2}^{-\cdot} &\longrightarrow \text{oxidation products}
\end{aligned}$$

2,6,9,10-Tetracyanoanthracene (TCA) has a singlet energy (2·9 eV) similar to that of DCA, but it is much easier to reduce (E_{red} −0·45 V in MeCN *vs.* S.C.E.). In a reaction of **(1)** sensitized with TCA, no $O_2^{-\cdot}$ can be formed because electron transfer from TCA$^{-\cdot}$ to O_2 would be highly unfavourable. In fact, the quantum yield of the photo-oxygenation of **(1)** sensitized by TCA is very low ($\Phi < 0{\cdot}001$) which indicates either that virtually none of the radical cation **(1)**$^{+\cdot}$ escapes out of the cage of the geminate pair, (TCA)$^{-\cdot}$/**(1)**$^{+\cdot}$, owing to an exceptionally efficient reverse electron transfer (which is unlikely), or that the reaction of **(1)**$^{+\cdot}$ with O_2 is too slow to compete with the diffusion-controlled recombination of (TCA)$^{-\cdot}$ and **(1)**$^{+\cdot}$.

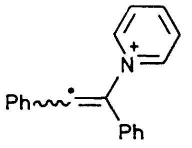
The following experiments show that the latter is the correct explanation, and we have also found that acids catalyse the TCA-sensitized photo-oxygenation of **(1)**. Quantum yields for the formation of **(2)** and **(3)**‡ of *ca.* 0·05 are measured when trifluoroacetic acid (10^{-3} to 10^{-2}M) is added to the reaction mixture.

This observation can be best explained in terms of protonation of (TCA)$^{-\cdot}$ formed from the reaction of ^{1}(TCA)* with **(1)**. The protonation of the radical anion will prolong the lifetime of **(1)**$^{+\cdot}$ by eliminating the reverse electron transfer from (TCA)$^{-\cdot}$ to **(1)**$^{+\cdot}$ and, therefore, allowing **(1)**$^{+\cdot}$ to react slowly with O_2 to give **(2)** and **(3)**.

$$\begin{aligned}
{}^{1}\mathrm{TCA}^{*} + \mathbf{(1)} &\longrightarrow \mathrm{TCA}^{-\cdot} + \mathbf{(1)}^{+\cdot}\\
\mathrm{TCA}^{-\cdot} + \mathrm{H}^{+} &\longrightarrow \mathrm{TCA{-}H}\\
\mathbf{(1)}^{+\cdot} + \mathrm{O_2} &\longrightarrow \text{oxidation products}
\end{aligned}$$

Interestingly, the TCA-sensitized reaction can also be induced by pyridine. This effect is probably due to nucleophilic addition of pyridine to **(1)**$^{+\cdot}$. The resultant intermediate **(4)** in which the positive charge is removed from the reactive site should have a higher affinity for O_2 than **(1)**$^{+\cdot}$, and its reaction with (TCA)$^{-\cdot}$ could give the corresponding biradical, which would be more reactive to molecular oxygen.‡ Unlike the acid-catalysed reaction, the effect of pyridine cannot be regarded as a true catalysis since it is consumed in the reaction. These pyridine-derived products have not yet been identified.

A measure for the reactivity of other nucleophiles relative to that of pyridine is determined by comparing the intercept/slope ratio of the linear plot of the reciprocal quantum yield of **(2)** with the reciprocal of the nucleophile concentration. As expected, the nucleophilic addition of the sterically hindered 2-t-butylpyridine to **(1)**$^{+\cdot}$ is estimated to be more than two orders of magnitude slower than that of pyridine.



(4)

Also, the poorer nucleophile, 4-cyanopyridine, has only one-third the reactivity of 4-picoline. It is interesting to note that similar intercepts for the aforementioned plot were obtained for the 4-picoline- and the cyanopyridine-induced reactions. From this intercept, the maximum quantum yield for oxidation in these TCA-sensitized reactions is estimated to be *ca.* 0·05, which is similar to that obtained from the acid-catalysed reaction. This quantum yield probably reflects the efficiency of the dissociation of the geminate pair (TCA)$^{-\cdot}$–**(1)**$^{+\cdot}$ to the separated radical ions.

$$\begin{aligned}
\mathbf{(1)}^{+\cdot} + \text{pyridine} &\longrightarrow \mathbf{(4)}\\
\mathbf{(4)} + \mathrm{O_2} &\longrightarrow \text{oxidation products}
\end{aligned}$$

In these reactions **(2)** is probably formed *via* the dioxete; the mechanism for benzoic acid formation, however, is not certain but the product ratio is very marginally, if at all, affected by the concentration of oxygen in the range between *ca.* 10^{-2} and *ca.* 4×10^{-4}M. It is thus tempting to speculate that the precursor for **(3)** is the *E*-isomer of the 1,4-biradical or the 1,4-radical cation formed by the addition of $O_2^{-\cdot}$ or O_2, respectively, to **(1)**$^{+\cdot}$. Unlike the *Z*-isomer, which can cyclize to the dioxete, the *E*-isomer could lead to benzoic acid in several steps (which might include addition of another O_2 molecule and hydrogen abstraction). Obviously more work is required to test such a hypothesis.

In conclusion, in the DCA-sensitized reaction, the oxidation is primarily *via* the reaction of **(1)**$^{+\cdot}$ with $O_2^{-\cdot}$. The reaction of **(1)**$^{+\cdot}$ with O_2 is too slow to compete with that of $O_2^{-\cdot}$, in spite of the large difference in concentration of O_2 and $O_2^{-\cdot}$. In the TCA-sensitized reaction where no $O_2^{-\cdot}$ is formed, the reaction can be efficient only if the reverse electron transfer reaction of (TCA)$^{-\cdot}$ with **(1)**$^{+\cdot}$ is suppressed. This is accomplished by protonation of the radical anion, or *via* nucleophilic addition of pyridine to **(1)**$^{+\cdot}$. In these reactions, oxidation is achieved by the reaction of **(1)**$^{+\cdot}$ or **(4)** with molecular oxygen.

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‡ The ratio of (2)/(3) using (TCA) as a sensitizer in the presence of CF_3CO_2H is *ca.* 2·1. In the presence of pyridine this ratio varies from *ca.* 2·7 to *ca.* 5·7 at pyridine concentrations of 0·001 M and 0·1 M, respectively.

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[8] *Cf.* C. L. Mann and K. K. Barnes, 'Electrochemical Reactions in Nonaqueous Systems,' Dekker, New York, 1970, p. 505, and references therein.