Tetrahedron Vol. 41, No. 11, pp. 2221 to 2227, 1985
Printed in Great Britain.

0040–4020/85 $3.00 + .00

DICYANOANTHRACENE SENSITIZED PHOTO-OXYGENATION OF OLEFINS

ELECTRON TRANSFER AND SINGLET OXYGEN MECHANISMS

CHRISTOPHER S. FOOTE
Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90024, U.S.A.

(*Received in Japan* 2 *July* 1984)

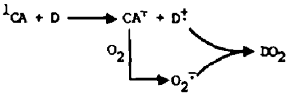
Abstract—Cyanoaromatic sensitizers, in particular 9,10-dicyanoanthracene (DCA), sensitize the photo-oxygenation of olefins by two distinct mechanisms. In the case of aryl substituted olefins (OL), which react extremely slowly (if at all) with singlet oxygen, the reaction proceeds by way of electron transfer to produce discrete radical ions ($DCA^{-\cdot}$ and $OL^{+\cdot}$). In the presence of oxygen, this ionic process results, ultimately, in the cleavage of the olefin to carbonyl compounds along with production of some epoxide and other minor by-products. Aromatic ethers can interfere with this process by reducing the radical cation by electron transfer, resulting in net quenching of the reaction. With simple alkenes the DCA-sensitized reaction takes a different course, producing hydroperoxide products with distributions which are very similar to those obtained with the singlet oxygen ene reaction. Careful study has shown that this reaction does, indeed, proceed by way of singlet oxygen, which is produced by at least two mechanisms: (1) enhanced intersystem crossing, in which ^1DCA is quenched by interaction with the olefin, leading to a low yield of ^3DCA, which subsequently reacts with oxygen to produce singlet oxygen; and (2) direct reaction of ^1DCA with oxygen. At limiting high oxygen concentration, this process produces 2 mol of singlet oxygen for each mol of ^1DCA quenched; the mechanism involves energy transfer to produce ^3DCA and 1 mol of singlet oxygen; the ^3DCA reacts again with oxygen to produce a second mol of singlet oxygen. The complex kinetic behaviour of simple olefins in the presence of DCA can be satisfactorily rationalized by these mechanisms.

Cyanoaromatic (CA) compounds are fluorescent molecules with substantial singlet lifetimes and comparatively high redox potentials. Many react in the excited singlet state (^1CA) with electron donors to transfer electrons. The initial products are the radical anion of the cyanoaromatic and the radical cation of the donor. Several types of chemistry are known to derive from these radical ions.[1–3]

$$^1CA + D \rightarrow CA^{-\cdot} + D^{+\cdot}.$$

Several years ago, our interest was aroused by cyanoaromatic sensitizers because we felt that, by proper choice of sensitizer redox potential, the radical anion should be re-oxidized by oxygen to produce $O_2^{-\cdot}$; we had been interested in the possibility that radical cation–$O_2^{-\cdot}$ pairs were intermediate in the reactions of singlet oxygen with electron-rich olefins such as enamines.[4] We expected superoxide to react with the radical cation of the olefin to give oxygenated products (DO_2) (Scheme 1).

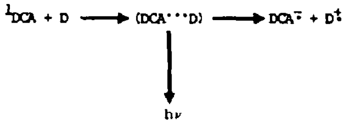
This article summarizes the results of our work showing that this reaction does occur but is not a useful preparative reaction except with a very limited class of olefins, those which are substituted by aromatics and do not react with singlet oxygen.[3] Electron-transfer competes with singlet oxygen formation and the reactions of singlet oxygen may be the only observable outcome in the presence of singlet oxygen acceptors.[5] Others have carried out important work in related systems.[6–8]



Scheme 1.

The sensitizers used in these studies were 9-cyanoanthracene (CNA) and 9,10-dicyanoanthracene (DCA), particularly the latter. The cyanoaromatics are strongly fluorescent and the singlet states can be calculated, by use of the Weller equation,[9] to have very large reduction potentials (of the order of 2 V for DCA and *ca* 1.6 V for CNA, relative to SCE).[10] Quenching of the singlet states of these sensitizers by olefinic and aromatic acceptors follows the Weller relationship[11] to a good approximation; that is, the reaction is diffusion-controlled with electron donors where ΔG^0 for electron transfer from the donor to the singlet cyanoaromatic is more negative than *ca* -5 kcal/mol; when ΔG^0 is more positive than this the reaction is slower and with strongly endothermic electron transfers the rate falls off with a slope near $\log_{10}(k) = -0.017\ (\Delta G^0)$, characteristic of an endothermic process in which the activation energy is solely due to the endothermicity.

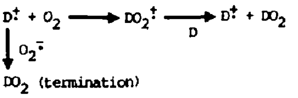
In non-polar solvents, exciplex emission is observed.[10] The emission is much weaker and shifted to longer wavelength in more polar solvents; the most polar solvent in which we have observed it is 1,2-dichloroethane. In acetonitrile and other very polar solvents, no emission is observed because the exciplex, if formed at all, dissociates rapidly. This behaviour is very similar to that observed previously with cyanoaromatic sensitizers and various olefins.[12]



Spectra of radical ions

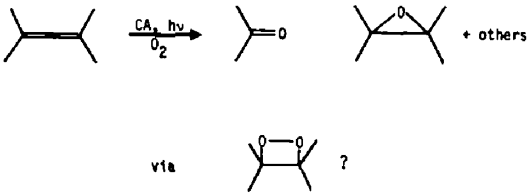
The reaction of ^1DCA and ^1CNA with *trans*-stilbene and other olefins was studied by flash spectroscopy.[13] Clear spectroscopic evidence was obtained for the production of both the stilbene radical cation and the cyanoaromatic radical anion. It was, subsequently, found that a 440 nm shoulder on the $TS^{+\cdot}$ spectrum is due to ^3DCA (see subsequent section). The transient absorptions of the radical ions were observed only in acetonitrile and not in less polar solvents. In the presence of oxygen, the cyanoaromatic anion is rapidly removed, confirming that electron transfer to oxygen is rapid; the disappearance of the radical cation is considerably slower. The characteristic ESR spectrum of $DCA^{-\cdot}$ was observed in the absence of oxygen, as Schaap *et al.*[14] reported simultaneously.

These results provide evidence for radical ions in the photo-oxidation of stilbenes and suggest that the radical anion of the cyanoanthracene is more rapidly oxidized by oxygen than the olefin radical cation. However, they do not require that the product-forming step is the reaction between the radical cation and superoxide anion and they do not rule out the chain process shown below, which is like the Barton–Haynes oxidation of dienes.[15,16] This reaction can also occur with olefins.[17,18] Experiments carried out using electrochemical generation of radical cations with aromatic olefins and with adamantylideneadamantane, suggest that chain oxidation is suppressed in the presence of $O_2^{-\cdot}$, as would be expected (P. Allen, J. Casanova, K. Lee, unpublished).



Products

The major products of reaction with the stilbenes, 1,1-diphenylethylene, and tetraphenylethylene, are the carbonyl compounds which result from cleavage of the double bond.[3] Variable amounts of epoxide are also formed along with some minor products. Some of these derive from the epoxides, but others do not; their source has not been investigated.



The route to the epoxide is also not certain. It is suggestive that epoxide formation becomes increasingly significant at high olefin concentration. The epoxide seems to be produced by reaction of an intermediate with a second olefin in some way.

A small amount of isomerization of the starting olefin accompanies the process. This product may derive either from isomerization of the radical cation or by reversible formation of an intermediate with free rotation around the double bond.

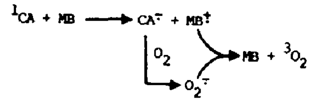
The intermediacy of 1,2-dioxetane in this reaction is likely but not certain. In the case of stilbene, authentic *trans*-3,4-diphenyl-1,2-dioxetane was prepared from *trans*-stilbene by Kopecky's reaction and added to the DCA-sensitized photo-oxygenation (P. Allen, unpublished). After a few minutes, no detectable dioxetane remained. This experiment shows that the dioxetane is unstable under the reaction conditions. Schaap *et al.*[14] reported that a dioxetane can be isolated in good yield from DCA-sensitized photo-oxidation of diphenyldioxene, but this olefin reacts with singlet oxygen and it is not certain whether this is an electron transfer or a singlet oxygen product (see below).

Quenching

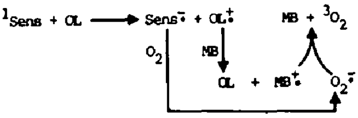
If the mechanism of this reaction is that shown in Scheme 1, reverse electron-transfer from $O_2^{-\cdot}$ to the radical cation should compete with their reaction to give products. This is probably occurring, as suggested by the fact that the quantum yields of all these reactions are less than one, even when extrapolated to infinite substrate concentration where all the excited sensitizer is trapped.[3]

$$D^{+\cdot} + O_2^{-\cdot} \rightarrow D + {}^3O_2.$$

The photo-oxidation of methoxyaromatics (MB) is particularly inefficient. A complicated mixture of products is slowly formed, including a small amount of ring cleavage product.[19] However, the major outcome of the reaction is reverse electron-transfer, resulting in quenching of singlet cyanoaromatic as the only observable outcome.[31]

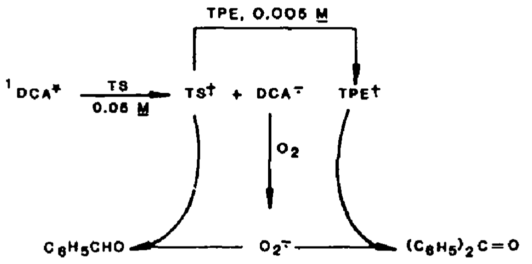


Efficient reverse electron-transfer permits the methoxybenzenes to be used as selective inhibitors of the photo-oxygenation of aromatic olefins. Addition of a small amount of methoxybenzene to a photo-oxidation mixture containing a higher concentration of aromatic olefin and the cyanoaromatic results in inhibition of the photo-oxidation of the olefin. Concentration-dependence and flash photolysis studies confirm that the initially formed olefin radical cation (which is quite long lived under these conditions) is reduced by the methoxybenzene, which has a lower oxidation potential. The $MB^{+\cdot}$ then reacts with $O_2^{-\cdot}$, giving mainly reverse electron-transfer.



Electron transfer studies

The role of electron-transfer in these photo-oxidations is further confirmed by the fact that indirect photo-oxidation reactions can be observed, in which the primary radical cation oxidizes a second substrate to produce a second radical cation, which gives the final product. Experiments were carried out with tetraphenylethylene (TPE) and 1,1-diphenyl-2-methoxyethylene.[20] The electron transfer was conclusively demonstrated by flash photolysis with stilbene (TS) and TPE; the initially formed stilbene radical cation was clearly seen to react with TPE to produce $TPE^{+\cdot}$, which then reacted with the superoxide ion to give benzophenone.[13] This indirect mechanism gives efficient oxidation of TPE which, otherwise, does not react well because it is too insoluble to quench the ^1DCA efficiently.

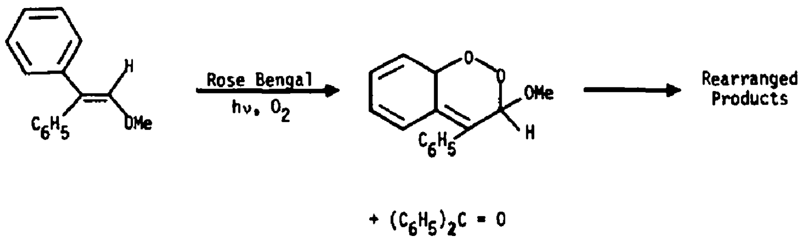


A particularly interesting case of indirect electron-transfer photo-oxidation is provided by the case of diphenylmethoxyethylene (DPME).[20] DPME reacts with singlet oxygen to give an endoperoxide along with a small amount of benzophenone, presumably derived from a dioxetane.

Cyanoaromatic sensitized oxidation of singlet oxygen substrates

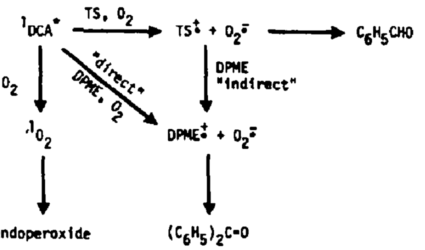
In an attempt to generalize the electron-transfer photo-oxidation reaction, the cyanoaromatic sensitized photo-oxygenation of some simple olefins was studied. 1-Methylcyclohexene (**1**), limonene, cholesterol (**3**), 1,2-dimethylcyclohexene (**2**) and 2-methyl-2-pentene have all been used frequently as substrates for singlet oxygen and their characteristic product distributions are well known. To our surprise, the cyanoaromatic sensitized photo-oxygenation of these substrates all gave product distributions which were indistinguishable from those of reaction with singlet oxygen.[5]

The products from **1**–**3** from Rose Bengal and DCA-sensitized oxygenation (after reduction of hydroperoxides) are shown below. The products of radical-initiated autoxidation are included for contrast.

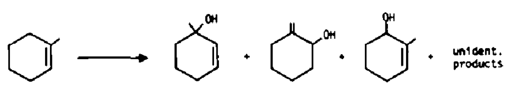


We had expected the dioxetane to predominate in the DCA-sensitized photo-oxygenation. However, to our surprise, the endoperoxide derived products predominated, although benzophenone was formed in larger amounts. When stilbene was present at 10 times the concentration of DPME, benzophenone made up 90% of the product. The ratio of endoperoxide derived products to benzophenone depended on the ratio of TS–DPME; at high enough ratios, the product is almost exclusively benzophenone. The explanation for this behaviour is that a singlet oxygen pathway competes with the electron transfer process; at the low DPME concentrations used, ^{1}DCA is inefficiently trapped by DPME, and singlet oxygen production predominates. When a high concentration of TS is added, DCA is trapped completely by TS to give TS$^{+\cdot}$, which oxidizes DPME to the radical cation, which reacts with the superoxide ion to form benzophenone (Scheme 2).

This was the first hint that singlet oxygen could be a significant product from the cyanoaromatic sensitizers. Shortly thereafter, Santamaria[21] also suggested that singlet oxygen was an important intermediate in some cases. This suggestion received strong support from the studies reported in the next sections.

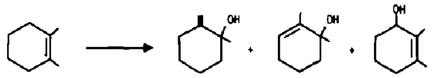


Scheme 2.



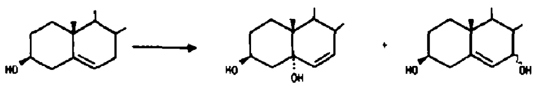
1

DCA-sensitized	53%	40%	7%	—
Rose Bengal-sensitized	45%	41%	14%	—
Radical autoxidation	12%	36%	40%	12%



2

DCA-sensitized	92%	8%	0%
Rose Bengal-sensitized	89%	11%	0%
Radical autoxidation	7%	39%	54%



3

DCA-sensitized	> 90%	< 10%
Rose Bengal-sensitized	> 90%	< 10%
Radical autoxidation	not detected	major

To characterize these reactions more fully, a series of kinetic investigations was carried out in which the dependence of product yield on oxygen and substrate concentration, and on solvent were determined. The results were difficult to interpret and indicated that the reaction was more complex than we had initially believed. Plots of product yield versus substrate concentration had complex curvature (Z. Q. Jiang, Y. Araki, unpublished). The olefins quench ^{1}DCA at rates which are consistent with their redox potential; the rates fall on the curve defined by the Weller equation for quenching rate versus redox potential, just as the aromatic olefins had. It was clear that the olefins could interact with ^{1}DCA at high rates, but it was not clear that this interaction leads directly to products.

This confusing situation was clarified using laser spectroscopy, monitoring the production of singlet oxygen by its 1.27 μm luminescence with a sensitive photodiode in a time resolved system.[22] It was found that cyanoaromatic sensitizers in the absence of substrate produce large amounts of singlet oxygen; the intensity of the luminescence is concentration dependent and is stronger under oxygen than under air.[23] Thus, it was certain that singlet oxygen is produced from cyanoaromatic sensitizers, but there was a question regarding the mechanism of its production.

Mechanisms of singlet oxygen production from cyanoaromatic sensitizers

There are a number of possible mechanisms for production of singlet oxygen from DCA and other aromatic sensitizers.[24–27] Direct production of ^{3}DCA from ^{1}DCA by ordinary intersystem crossing would be one mechanism; however, the fluorescence quantum yields of the cyanoaromatics are very large and flash photolysis studies (see below) show that the direct production of triplet from the singlet is extremely inefficient. Therefore, other mechanisms for the production of singlet oxygen need to be considered. If ^{3}DCA is produced by any mechanism, by analogy with other anthracenes, it should be quantitatively trapped by oxygen to produce singlet oxygen.

$$^3\text{DCA} \xrightarrow[\text{O}_2]{} {}^1\text{O}_2$$

The following mechanisms for singlet oxygen production were considered.

Substrate enhanced intersystem crossing. In this mechanism, interaction of ^{1}DCA with substrate leads to an exciplex which could relax to ^{3}DCA with varying degrees of efficiency.

$$^1\text{DCA} + \text{S} \rightarrow (\text{DCA}\cdots\text{S}) \rightarrow {}^3\text{DCA} + \text{S} \qquad (1)$$

Oxygen enhanced intersystem crossing. Interaction of ^{1}DCA with oxygen could lead to a paramagnetic charge-transfer complex with oxygen, which would also relax intersystem crossing restrictions and give enhanced production of singlet oxygen.

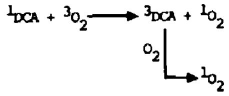
$$^1\text{DCA} + {}^3\text{O}_2 \rightarrow (\text{DCA}\cdots\text{O}_2) \rightarrow {}^3\text{DCA} + {}^3\text{O}_2 \qquad (2)$$

Energy transfer. In addition, two possible modes of energy transfer from ^{1}DCA to oxygen need to be considered.

(a) Direct energy transfer, giving ground state DCA and 1 mol of singlet oxygen. This is a spin-forbidden process, but might proceed via a DCA–oxygen complex.

$$^1\text{DCA} + {}^3\text{O}_2 \longrightarrow (\text{DCA}\cdots\text{O}_2) \longrightarrow \text{DCA} + {}^1\text{O}_2 \qquad (3a)$$

(b) Energy transfer from ^{1}DCA to oxygen, producing ^{3}DCA and 1 mol of singlet oxygen; subsequent energy transfer from ^{3}DCA to oxygen would produce a second mol.



$$^1\text{DCA} + {}^3\text{O}_2 \longrightarrow {}^3\text{DCA} + {}^1\text{O}_2,\quad {}^3\text{DCA} \xrightarrow{\text{O}_2} {}^1\text{O}_2 \qquad (3b)$$

Mechanisms (1)–(3a) would produce a maximum of 1 mol of singlet oxygen per quantum of light absorbed; mechanism (3b) could produce a maximum of 2 mol of singlet oxygen. In order to clarify the mechanism, laser flash studies of the yield of singlet oxygen and ^{3}DCA were carried out as a function of substrate and oxygen. The results show that at least mechanisms (1) and (3b) occur.

Substrate enhanced intersystem crossing

Flash photolytic studies of the reaction of *trans*-stilbene with DCA under nitrogen in the presence of various substrates reveal that, in addition to the well known absorption of *trans*-stilbene radical cation at 473 nm, a shoulder at *ca* 440 nm is formed (425 nm for CNA), close to the known absorption of the triplet anthracenes.[28] This band is frequently produced along with the radical cation and always has the same absorption maximum, regardless of the substrate. It is oxygen sensitive and we have assigned it to the triplet.

The most efficient production of the triplet transient absorption occurs when singlet cyanoaromatic is quenched by a heavy-atom containing substrate, iodoxylene. Under these conditions, intersystem crossing is rapid and efficient and a good absorption spectrum of the triplet can be obtained. Trapping with 2-methyl-2-pentene of the singlet oxygen produced by iodoxylene-enhanced intersystem crossing in the presence of oxygen confirmed that singlet oxygen is produced in this reaction in quantitative yield. Other substrates catalyse the enhanced intersystem crossing with lower efficiencies; substrates with no heavy atoms (such as the stilbenes and simple olefins) produce a relatively low yield of intersystem crossing.

The quantum yield of direct intersystem crossing of ^{3}DCA (in the absence of other quenchers and oxygen) was found to be only *ca* 0.2%; this is reduced proportionately if ^{1}DCA undergoes other fates. Because of the overlapping absorption of *trans*-stilbene radical cation, it was not possible to measure the yield of ^{3}DCA accurately in the presence of *trans*-stilbene. However, with 2-methyl-2-pentene, it was possible to determine that 4.8% of the ^{1}DCA eventually produces ^{3}DCA (and thus singlet oxygen) in an air saturated solution with 0.1 M 2-methyl-2-pentene. This is close to the maximum production possible with this olefin since almost all the ^{1}DCA is being quenched at this concentration. This path is not very efficient with simple olefins; most of the quenching leads to deactivation of excited ^{1}DCA.

In order to determine whether energy transfer processes (3a) or (3b) occur, the intensity of the singlet oxygen emission was monitored at 1.27 μm and compared with the intensity produced with other sensitizers of known quantum yields of $^1\text{O}_2$ production.[28] The quantum yield determined this way was confirmed by trapping the singlet oxygen with 2-methyl-2-pentene. It was found that singlet oxygen production is a function of oxygen concentration and, on extrapolation to infinite oxygen concentration (where all the ^{1}DCA is trapped by oxygen), the quantum yield is very close to two. Double energy transfer mechanism (3b) is, therefore, the major mechanism for the production of singlet oxygen. Only at extremely high olefin concentrations or very low oxygen concentrations does this mechanism become

Table 1. Relative rates of DCA-sensitized photo-oxygenation of 1–3 in benzene and acetonitrile

Olefin	Concentration (M)	$\frac{\phi_p(CH_3CN)}{\phi_p(C_6H_6)}$ (observed)[a]	$\frac{\phi_p(CH_3CN)}{\phi_p(C_6H_6)}$ (calculated)
1	0.0634	0.43 ± 0.06[b] (3)	0.46
1	0.0211	1.59 ± 0.06[b] (2)	1.13
2	0.0560	0.22 ± 0.02[b] (3)	0.67
2	0.0423	0.24 ± 0.03[b] (2)	0.72
3	0.00100	4.2 ± 0.3 (6)	> 3.1

[a] The number of determinations is shown in parentheses.
[b] Errors are standard deviations.

unimportant and the olefin-quenching mechanism becomes measurable.

Kinetics of olefin reactions

The kinetic studies carried out with several olefins were complex and difficult to interpret. These experiments were of three types: (1) solvent polarity effects; (2) solvent isotope effects; and (3) substrate concentration dependence. Since the system was now well characterized by the laser flash work, it was decided to see whether the earlier data were consistent with what had been learned about the system. All the parameters necessary for the complete calculation of the behaviour of three olefins (1-methylcyclohexene, **1**, 1,2-dimethylcyclohexene, **2**, and cholesterol, **3**) in response to the parameters had already been determined, and the observed behaviour could be compared with that calculated.[5]

Effect of solvent polarity. As mentioned above, the DCA-sensitized electron-transfer photo-oxygenation of phenyl-substituted olefins takes place only in polar solvents, such as acetonitrile and methanol.[3] This behaviour is expected for a process with an intermediate ion pair which is too poorly solvated to diffuse apart in a non-polar solvent. In contrast, singlet oxygen reactions show only a very small response to changes in solvent polarity.[29,30] All three olefins were found to react nearly as rapidly in benzene as in acetonitrile, a strong indication that radical ions are not intermediate in the photo-oxidation of these olefins.

If reaction of these olefins proceeds via singlet oxygen, the relative rates of reaction in acetonitrile and benzene should equal the ratio of quantum yields of product formation in the two solvents. The ratios calculated from the known rate are shown in Table 1. The observed and calculated ratios agree within a small factor. The differences are probably due to uncertainties in the large number of parameters required. The agreement is particularly compelling by contrast with the effect with phenyl substituted olefins, where the ratios are immeasurably large.

Solvent isotope effect. It is now well known that the lifetime of singlet oxygen is significantly longer in deuterated than in protiated solvents.[22,31,32] This effect causes large solvent deuterium isotope effects on the rates of singlet oxygen reactions. In contrast, an electron-transfer mechanism would not be expected to exhibit a solvent isotope effect unless the lifetime of $^{1}\mathrm{DCA}^{*}$ were affected. The lifetime of $^{1}\mathrm{DCA}^{*}$ was measured by single photon counting and found to be the same in deuterated and protiated acetonitrile. The fact that deuterated acetonitrile also does not cause a rate enhancement for the DCA-sensitized photo-oxygenation of *trans*-stilbene is consistent with the suggestion that electron-transfer reactions should not exhibit a solvent isotope effect.[5]

The solvent isotope effect on the reaction is given by the ratio of quantum yields in deuterated and protiated solvents, which can also be calculated for a singlet oxygen reaction from the known rate parameters. It is important to note that the solvent isotope effect is not merely the ratio of the lifetimes of singlet oxygen in the two solvents, since the effective lifetime is modified by the olefin with which singlet oxygen reacts. Table 2 lists observed solvent isotope effects on the rate of DCA-sensitized photo-oxygenation of **1** and **3** along with values calculated using the known rates of reaction and decay of singlet oxygen with the olefins in the two solvents. The observed isotope effects are again in remarkably good agreement with the calculated values.

Table 2. Solvent isotope effects on the rate of sensitized photo-oxygenation of 1–3

Olefin	Concentration (M)	Solvent	Sensitizer	$\frac{\phi_p(D)}{\phi_p(H)}$ (observed)[a]	$\frac{\phi_p(D)}{\phi_p(H)}$ (calculated)
1	0.0634	CD_3CN–CH_3CN	DCA	1.5 ± 0.3[b] (4)	1.8
1	0.0211	CD_3CN–CH_3CN	DCA	2.4 ± 0.5[b] (2)	2.9
1	0.0634	C_6D_6–C_6H_6	DCA	2.7 ± 0.7[b] (2)	2.7
1	0.0211	C_6D_6–C_6H_6	DCA	5.1 ± 2.1[b] (2)	5.3
3	0.0010	CD_3CN–CH_3CN	DCA	8 ± 2 (6)	8.9
3	0.0010	CD_3CN–CH_3CN	Rose Bengal	10 ± 3 (6)	8.9

[a] The number of determinations is shown in parentheses.
[b] Errors are ranges.

Table 3. Quantum yields of product formation for the DCA-sensitized photo-oxygenation of **1–3** in acetonitrile at 25°

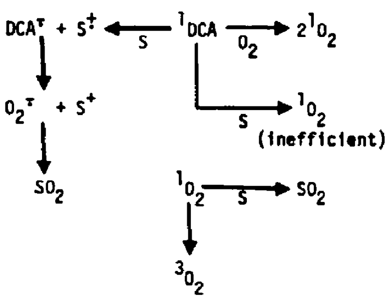
Olefin	Concentration (M)	ϕ_P (observed)	ϕ_P (calculated)
1	0.025	0.054	0.10
2	0.025	0.19	0.25
3	0.00091	0.0023	0.0037

Quantum yields. The quantum yields of product formation for the DCA-sensitized photo-oxygenations of **1–3** were determined using the DCA-sensitized photo-oxygenation of 1,1-diphenylethylene (DPE) as a chemical actinometer. The experimental quantum yields are shown in Table 3 along with calculated values and are again in good agreement with a singlet oxygen mechanism.

Summary

The products of DCA-sensitized photo-oxygenation of olefins **1–3** are the same as those formed by reaction with singlet oxygen. Compounds **1–3** all react at appreciable rates in benzene as well as acetonitrile. As discussed above, this behaviour is inconsistent with an electron-transfer mechanism. Compounds **1** and **3** exhibit solvent isotope effects which are in close agreement with those expected for a singlet oxygen mechanism. Finally, the quantum yields of product formation for **1–3** are close to the values expected for a singlet oxygen reaction. The inescapable conclusion is that these olefins are reacting by a singlet oxygen mechanism.

The results of these studies illustrate very clearly that the mechanism of reaction of excited singlet cyanoaromatics with substrates in the presence of oxygen is a sensitive function of the concentrations of substrate and oxygen. With substrates which can undergo electron-transfer to give radical ions, the radical ion mechanism will predominate at high substrate and low oxygen concentration. With substrates which can undergo only singlet oxygen reactions, this mechanism will become most efficient at high oxygen and low substrate concentration. Higher substrate concentrations lead to quenching of the sensitizer, but only inefficient production of singlet oxygen unless the substrate has a heavy atom. This inhibition of the photo-oxidation by substrate quenching of ^{1}DCA appears to be the major cause of the curved plots of product formation versus substrate concentration which we have repeatedly observed in these cases.



The competitive processes shown above all need to be considered. With the aromatic olefins, singlet oxygen reactions appear not to be important since the olefins do not react and the ionic pathways appear to be efficient; oxygen actually inhibits the electron-transfer photo-oxygenation of stilbenes because routes leading to singlet oxygen produce no product. With simple olefins, sensitizer–donor interactions do not produce free ions (we have never been able to detect any by flash photolysis); they seem to lead only to inefficient production of singlet oxygen. With these substrates, energy transfer to oxygen is the major oxidation pathway.

The results of these studies emphasize that compounds which can react with cyanoaromatics both by electron-transfer mechanisms and by singlet oxygen reactions are likely to prove very complex mechanistically and the outcome may not be easy to predict in advance.

Acknowledgements—This work was carried out over several years by many different co-workers, whose contributions are credited individually in the text and was supported by grants from the NSF and the Petroleum Research Fund.

REFERENCES

[1] S. L. Mattes and S. Farid, in *Organic Photochemistry* (Edited by A. Padwa), Vol. 6, p. 233. M. Dekker, New York (1983).

[2] D. R. Arnold and R. A. Neunteufel, *J. Am. Chem. Soc.* **95**, 4080 (1973).

[3] J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.* **102**, 6083 (1980).

[4] C. S. Foote, A. A. Dzakpasu and J. W.-P. Lin, *Tetrahedron Lett.* 1247 (1975).

[5] Y. Araki, D. C. Dobrowolski, T. Goyne, D. C. Hanson, Z. Q. Jiang, K. J. Lee and C. S. Foote, *J. Am. Chem. Soc.* **106**, 4570 (1984).

[6] S. L. Mattes and S. Farid, *J. Am. Chem. Soc.* **104**, 1454 (1982).

[7] K. Mizuno, N. Kamiyama and Y. Otsuji, *J. Am. Chem. Soc.* 477 (1983).

[8] A. P. Schaap, S. Siddiqui, S. D. Gagnon and L. Lopez, *J. Am. Chem. Soc.* **105**, 5149 (1983).

[9] A. Weller and K. Zachariasse, *J. Chem. Phys.* **46**, 4984 (1967).

[10] J. Eriksen and C. S. Foote, *J. Phys. Chem.* **82**, 2659 (1978).

[11] D. Rehm and A. Weller, *Isr. J. Chem.* **8**, 259 (1970).

[12] N. C. Yang, D. M. Shold and J. K. McVey, *J. Am. Chem. Soc.* **97**, 5004 (1975).

[13] L. T. Spada and C. S. Foote, *J. Am. Chem. Soc.* **102**, 391 (1980).

[14] A. P. Schaap, K. A. Zaklika, B. Kaskar and W.-M. Fung, *J. Am. Chem. Soc.* **102**, 389 (1980).

[15] D. H. R. Barton, R. K. Haynes, G. Leclerc, P. D. Magnus and I. D. Menzies, *J. Chem. Soc. Perkin Trans. 1* 2055 (1975).

[16] R. K. Haynes, *Aust. J. Chem.* **31**, 121 (1978).

[17] E. L. Clennan, W. Simmons and C. W. Almgren, *J. Am. Chem. Soc.* **103**, 2098 (1981).

[18] S. F. Nelsen and R. Akaba, *J. Am. Chem. Soc.* **103**, 2096 (1981).

[19] J.-J. Liang and C. S. Foote, *Tetrahedron Lett.* **23**, 3039 (1982).

[20] D. S. Steichen and C. S. Foote, *J. Am. Chem. Soc.* **103**, 1855 (1981).

[21] J. Santamaria, *Tetrahedron Lett.* **22**, 4511 (1981).

[22] P. R. Ogilby and C. S. Foote, *J. Am. Chem. Soc.* **105**, 3423 (1983).

[23] D. C. Dobrowolski, P. R. Ogilby and C. S. Foote, *J. Phys. Chem.* **87**, 2261 (1983).

[24] A. P. Darmanyan, *Chem. Phys. Lett.* **91**, 396 (1982).

[25] K. C. Wu and A. M. Trozzolo, *J. Phys. Chem.* **83**, 2823 (1979).

[26] B. Stevens, K. L. Marsh and J. A. Barltrop, *J. Phys. Chem.* **85**, 3079 (1981).

[27] B. Stevens, S. R. Perez and J. A. Ors. *J. Am. Chem. Soc.* **96**, 6846 (1974).

[28] L. E. Manring, C.-L. Gu and C. S. Foote, *J. Phys. Chem.* **87**, 40 (1983).

[29] L. E. Manring and C. S. Foote, *J. Am. Chem. Soc.* **105**, 4710 (1983).

[30] F. Wilkinson and J. G. Brummer, *J. Phys. Chem. Ref. Dat.* **10**, 809 (1981).

[31] J. R. Hurst and G. B. Schuster, *J. Am. Chem. Soc.* **105**, 5756 (1983).

[32] P. R. Ogilby and C. S. Foote, *J. Am. Chem. Soc.* **104**, 2069 (1982).