We find several possible explanations for the absence of higher order peaks. One is that the structure is columnar but incorporates very large lattice fluctuations3 (with rms motions on the order of a column thickness). A second possibility is that the columns are well-defined but that there is a high degree of intramolecular thermal motion, resulting in an almost sinusoidal charge distribution within one column. In this case, the rationale for forming a columnar structure in the first place is less clear. Finally, the molecules may be essentially linear and organized in layers, with permeation and layer fluctuations as discussed above.

Mertesdorf and Ringsdorf2o have recently studied a closely related cinnamoyl-substituted hexacyclen. On the basis of d-spacings observed in powder X-ray diffraction, as well as optical microscopy observations, they conclude that those compounds form columnar phases. To our knowledge, no measurements on any aza derivative has conclusively proved the existence of hexagonal structure (as manifested for example by (110) X-ray diffraction peaks or a 6-fold single-crystal X-ray pattern). Nevertheless, at the present time the preponderance of evidence for the cinnamoyl derivative indicates a columnar structure, while for 2a a smectic phase is weakly preferred.

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Singlet Oxygen and Electron-Transfer Mechanisms in the Dicyanoanthracene-Sensitized Photooxidation of 2,3-Diphenyl-1,4-dioxene

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Abstract: The 9,10-dicyanoanthracene-sensitized photooxidation of 2,3-diphenyl-1,4-dioxene in CH3CN produces ethylene glycol dibenzoate and small amounts of epoxide. Most of the diester is formed from singlet oxygen via the dioxetane, and only a small amount by electron transfer. The epoxide is a primary electron-transfer product. Various mechanistic possibilities for the electron-transfer process are considered.

Schaap reported that the 9,10-dicyanoanthracene (DCA)-sensitized photooxidation of 2,3-diphenyl-1,4-dioxene (DPD) in acetonitrile gives ethylene glycol dibenzoate (EGDB) as the only isolable product (Scheme I).1 It was assumed that this product is formed by electron transfer, which produces analogous cleavage products from aromatic alkenes with DCA.2,3 However, singlet oxygen can also be formed in large quantities in this reaction,4,5 and it has been suggested that singlet oxygen reacts with DPD to give the dioxetane precursor of EGDB.6 We have reinvestigated the DCA-sensitized photooxidation of DPD to determine whether singlet oxygen, electron transfer, or a combination is responsible for the observed products.

Results

As reported by Schaap, DCA-sensitized photooxidation of DPD in acetonitrile at varying DPD concentrations at 25 °C leads to EGDB as the major isolable product. When the reaction is followed by 1H NMR, an intermediate, shown to be DPD dioxetane, is formed; the dioxetane decomposes completely to EGDB upon heating for 2 h at 60 °C. A minor product in the reaction is also observed, shown to be the unstable 2,3-diphenyl-1,4-dioxene oxide, as discussed below. Reaction of DPD with singlet oxygen generated from polymer-bound Rose Bengal in methylene chloride5 gives EGDB as the major product, also via the dioxetane, as determined by 1H NMR. The epoxide is nearly undetectable in this reaction.

If the singlet oxygen route to EGDB predominates in the DCA-sensitized reaction, product formation should be inhibited


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Photooxidation of 2,3-Diphenyl-1,4-dioxene

Figure 1. Relative rate of ethylene glycol dibenzoate formation vs diphenyldioxene (DPD) concentration in the DCA-sensitized photooxidation of DPD in oxygen-saturated acetonitrile at 25 °C. The solid line is calculated according to the kinetics of Scheme I (see Discussion).

Figure 2. Reciprocal of the relative rate of ethylene glycol dibenzoate (EGDB) formation vs diazabicyclo[2.2.2]octane (DABCO) concentration in the DCA-sensitized photooxidation of DPD in oxygen-saturated acetonitrile at 25 °C. [DPD] = 0.0075 M.

at high DPD concentrations because the electron-transfer route would lead to quenching of 1DCA*. The relative rate of EGDB formation at 25 °C is plotted in Figure 1 as a function of DPD concentration; similar results are obtained at 0 and 50 °C.

A Stern–Volmer plot of quenching of 1DCA* fluorescence (data not shown) gives the quenching rate constant $k_q$ of 1DCA* by DPD as $(2.3 \pm 0.3) \times 10^{-10} \text{M}^{-1} \text{s}^{-1}$ at 25 °C. Independent measurement of $k_q$ by plotting the reciprocal of the relative rate of EGDB formation versus DPD concentration gives the value $(2 \pm 1) \times 10^{-10} \text{M}^{-1} \text{s}^{-1}$ at 25 °C. The value of $k_q$ for reaction of 1DCA* with DPD, determined by 1O2 luminescence quenching(15) is $(1.72 \pm 0.08) \times 10^{-7} \text{M}^{-1} \text{s}^{-1}$.

The kinetics of the DPD photooxidation in the presence of the singlet oxygen quencher 1,4-diazabicyclo[2.2.2]octane (DABCO) were investigated. Acetonitrile solutions 0.0075 M in DPD and with [DABCO] up to $1.1 \times 10^{-5} \text{M}$ were irradiated with DCA as sensitizer at 25 °C; the reciprocal of the relative rate of EGDB formation is plotted versus DABCO concentration in Figure 2. The quenching rate of 1O2 by DABCO in acetonitrile calculated from this plot is $3.5 \times 10^{9} \text{M}^{-1} \text{s}^{-1}$, slightly above the value found in pyridine $(3 \times 10^{9} \text{M}^{-1} \text{s}^{-1})$.

The rate constant appears not to have been measured in polar aprotic solvents.

DPD oxide was synthesized independently from DPD and dimethylidioxirane(13) and characterized by 1H NMR and GC analysis. After this work was completed, Adam reported preparation of several similar epoxides using this reagent. The epoxide is extremely unstable and decomposes in the presence of traces of water to benzil and ethylene glycol.

The ratio of epoxide to EGDB in the DCA-sensitized photooxidation at 25 °C, with concentration of biphenyl 1 M. The solid line is fit to the kinetics of Scheme I (see Discussion).

Discussion

Using the independently determined values of $k_q$ and $k_b$ with $k_b = 6.8 \times 10^{5} \text{M}^{-1} \text{s}^{-1}$ and the lifetime of 1DCA* = 15.2 ns(14) the change in product ratio could be caused by ground-state complexing. However, no shifts in NMR peak positions of either DCA or DPD were observed up to the highest DPD concentration used.

(15) A reviewer has suggested that the change in product ratio could be caused by ground-state complexing. However, no shifts in NMR peak positions of either DCA or DPD were observed up to the highest DPD concentration used.
in the kinetics of Scheme I gives the solid line through the points in Figure 1, which is clearly an excellent fit. This calculation was performed assuming that only singlet oxygen leads to product formation and that all electron-transfer encounters lead to sensitizer quenching. In this scheme, decreasing [DPD] leads to a more rapid production of EGDB because there is relatively less quenching of \( \text{DCA}^* \) by DPD. Since \( \text{O}_2 \) reacts so rapidly with DPD (\( k_3 = 1.72 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \)), \( \text{O}_2 \) trapping is very efficient even at relatively low DPD concentrations. Calculations (Figure 1) indicate that the reaction rate has a maximum at a DPD concentration of \( \sim 2 \times 10^{-3} \text{ M} \), below which product measurement is analytically impractical.

The decrease in reaction rate with increasing DPD concentration strongly suggests that the electron-transfer pathway does not lead to significant product formation but mainly to deactivation of \( \text{DCA}^* \). If this is true, then nearly all of the observed product comes from singlet oxygen and not electron transfer. In agreement, the reciprocal of the relative rate of EGDB formation increases linearly with the concentration of the singlet oxygen quencher 1,4-diazabicyclo[2.2.2]octane (DABCO)\(^1\) at \( 25 \text{ °C} \) (Figure 2), as expected for a pure singlet oxygen reaction. The NMR experiments clearly demonstrate that nearly all the EGDB in the DCA-sensitized process comes from the decomposition of DPD dioxetane, which is the first observable product of the reaction of DPD with independently generated \( \text{O}_2 \).

On the other hand, the near-zero intercepts of the plots in Figure 3 suggest that electron transfer is the only route to the epoxide, consistent with the absence of epoxide in the Rose Bengal-sensitized singlet oxygen reaction. The striking temperature dependence in Figure 3 has a simple explanation in terms of the electron-transfer mechanism. Because the separation of the initially formed DCA\(^{-}/\text{DPD}^+ \) ion pair (Scheme I) has an activation energy, the free ion yield of DCA\(^- \) and DPD\(^+ \) is expected to increase with temperature, leading to larger amounts of the electron-transfer epoxide product at higher temperatures, as observed.

These experiments show that the main route to product formation is reaction of singlet oxygen with DPD to give a dioxetane which cleaves to ethylene glycol dibenzoate. The electron-transfer pathway is minor under normal conditions (nolevated temperature and low DPD concentration) but becomes more important with increasing temperature and DPD concentration.

The inefficiency of product formation by the electron-transfer route suggests that electron back-transfer from DCA\(^- \) to DPD\(^+ \) in the initially formed ion pair is faster than ion pair separation: such competitions are well established in the DCA-sensitized electron-transfer photooxidation of stilbenes.\(^4\) An alternative interpretation is that the free ions are formed, but \( \text{O}_2 \) subsequently trans-fer an electron to DPD\(^+ \) instead of giving oxygenated products; Schaap and co-workers showed that this process is the major reaction of the radical cation of 2,3-bis(p-methoxyphenyl)-1,4-dioxene with added \( \text{O}_2 \).\(^1\)

The experiments using biphenyl as cosensitizer support the conclusion that reaction with DPD leads mainly to deactivation of \( \text{DCA}^* \) and to a low yield of ions. The increase in epoxide formation at high biphenyl concentrations is consistent with a scheme in which \( \text{DCA}^* \) reacts with biphenyl to give biphenyl radical cation, which subsequently reacts with DPD to produce DPD\(^+ \), forcing electron transfer at the expense of the singlet oxygen pathway (Scheme II).\(^6\) The free ion yield of BP\(^+ \) and DCA\(^- \) from \( \text{DCA}^* \) is extremely high (~0.8),\(^2\) and for this reason, cosensitization with BP has been used to increase the efficiency of electron-transfer reactions with low yields of free ions.

At the low (0.006 M) concentration of DPD used, addition of \( \geq 0.2 \text{ M} \) biphenyl converts what was a singlet oxygen reaction (epoxide/EGDB ratio 0.05) into an electron-transfer reaction (epoxide/EGDB ratio 0.25). Because the addition of biphenyl allows the electron-transfer products to be observed, the inefficiency of product formation in the direct electron-transfer reaction must come from the step producing the free ions DCA\(^- \) and DPD\(^+ \) and not in their later reactions.

The increase in the epoxide to EGDB ratio with [DPD] at 1 M biphenyl (Figure 4) shows that the product distribution of the electron-transfer pathway is sensitive to [DPD]. At 1 M biphenyl, all the \( \text{DCA}^* \) is trapped by the cosensitizer, and the observed products arise completely from electron transfer.

One possible mechanism for the electron-transfer process is shown in Scheme III. The uncharacterized intermediate in the scheme could be a biradical or zwitterionic open-chain oxygenated species that closes to dioxetane or reacts with DPD to give two molecules of epoxide. The line through the points in Figure 4 is a curve fit to the kinetics of Scheme III, with the values \( k_1/k_2 = 1.85 \) and \( k_3/k_4 = 0.0096 \text{ M} \). If \( k_2 = 2 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \) (diffusion-controlled), then the lifetime of the intermediate \((1/k_2)\) would be ~5 ns. Figure 4 is not consistent with a mechanism in which \( k_1 = 0 \), because the ratio of epoxide to EGDB would be expected to increase without bound as [DPD] is increased, in contrast to the observed saturation.

Scheme III has DPD dioxetane intermediate in the production of EGDB in the electron-transfer pathway. Analysis by \(^1\text{H} \text{NMR}\) of DPD photolyses in CD\(_2\text{CN}\) in the presence of high (\( \geq 0.5 \text{ M} \)) biphenyl concentrations reveals the presence of DPD dioxetane, showing that this compound is formed to some extent by electron transfer as well as from singlet oxygen and that DPD dioxetane is indeed the precursor of EGDB for the electron-transfer pathway.

Dioxetanes have never before been directly detected as unstable intermediates in an electron-transfer photooxidation. In particular, the dioxetane from \text{trans}-stilbene is unstable under the reaction conditions.\(^5\) We were unable to detect stilbene dioxetane in the DCA-sensitized electron-transfer reaction even using biphenyl cosensitization to increase the reaction rate. Additionally, DPD dioxetane was detected with much more difficulty under the electron-transfer conditions than in the singlet oxygen reaction. The dioxetane appears to decompose more rapidly to EGDB under the electron-transfer conditions, i.e., in the presence of DCA\(^- \) and DPD\(^+ \) than under the singlet oxygen conditions.

In other DCA-sensitized photooxidations such as that of \text{trans}-stilbene,\(^2\) an induction period for epoxide formation has been reported.\(^16\)\(^19\) There is no induction period for the formation


\(^{(18)}\) The benzaldehyde and epoxide from stilbene photooxidation arise completely from the electron-transfer route, not from singlet oxygen.\(^2\)

\(^{(19)}\) On this basis and from other evidence, these researchers\(^2\) suggest that stilbene oxide is produced as a secondary photoproduct from benzaldehyde via an intermediate benzaldehyoxy radical. However, this mechanism predicts equimolar formation of stilbene oxide and benzoic acid, and no benzoic acid was observed in our experiments with stilbenes.
of DPD oxide in the DCA-sensitized photooxidation, which is inconsistent with any electron-transfer mechanism in which the epoxide is a secondary photoproduct, as proposed for stilbene oxide.16

Experimental Section

1H NMR spectra were recorded on a Bruker AF-200 NMR spectrometer with tetrachloromethane (TMS) as internal standard. Melting points are uncorrected.

Materials. DCA (Eastman Kodak) was recrystallized from toluene. Polymer-bound Rose Bengal (Hydron Laboratories, New Jersey) was used as received. 2,3-Diphenyl-1,4-dioxene (DPD) was prepared from benzil and ethylene glycol as previously described. The crude product was chromatographed over silica gel (CHCl3 eluent) and recrystallized from ethanol; mp 92-93 °C (lit. mp 93 °C). 1H NMR of DPD (CDCl3, δ, ppm): 8.06 (s, 1 H), 7.2 (m, 10 H). Biphenyl (MC & B) was recrystallized from methanol. trans-Stilbene (Aldrich) was recrystallized from ethanol. Acetonitrile (Fisher Optima grade) and methylene chloride (Fisher reagent grade) were used as received.

Photochemical Instrumentation. All photolyses were carried out using a Cermax 300-W xenon lamp powered at 16 V. A copper sulfate/sodium nitrite filter solution was used to isolate the wavelengths between 400 and 440 nm absorbed by DCA. Rose Bengal experiments were done without filter solutions.

Irradiation Procedure. All photolyses were performed in 13 x 100 mm Pyrex disposable cuvettes containing 3 mL of solution. Acetonitrile or methylene chloride solutions containing either DCA (10⁻³ M) or polymer-bound Rose Bengal and DPD (0.0025-0.10 M) were saturated with oxygen prior to photolysis and were continuously bubbled during irradiation. Samples were rotated on a merry-go-round apparatus during all kinetic analyses. After irradiation, a standard (biphenyl or anthracene) was added for GC analysis, carried out on a Hewlett-Packard Model 5890A gas chromatograph with tetramethylsilane (TMS) as internal standard. Melting points were determined by a Perkin-Elmer Differential Scanning Calorimeter with biphenyl as standard.

Detection of Intermediate DPD Dioxetane in Electron-Transfer Reaction. A solution of DPD (0.01 M) in acetonitrile or polymer-bound Rose Bengal and DPD (0.04 M) in methylene chloride were irradiated at 25 °C until conversion was complete (about 10 min). The dioxetane was identified by its 1H NMR spectrum (CDCl3, δ, ppm): 4.05 (m, 2 H), 4.25 (m, 2 H), 7.4-7.7 (m, 6 H), 8.10 (dd, 4 H).

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