We find several possible explanations for the absence of higher order peaks. One is that the structure is columnar but incorporates very large lattice fluctuations[3] (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 Ringsdorf[20] 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.

(20) Mertesdorf, C.; Ringsdorf, H. Private communication.

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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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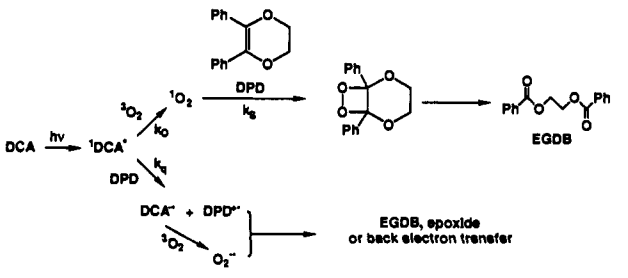
Abstract: The 9,10-dicyanoanthracene-sensitized photooxidation of 2,3-diphenyl-1,4-dioxene in CH_3CN produces ethylene glycol dibenzoate and small amounts of epoxide. Most of the diester is formed from singlet oxygen via the dioxetane, and only a small amount by electron transfer. The epoxide is a primary electron-transfer product. Various mechanistic possibilites 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,[4-6] and it has been suggested that singlet oxygen reacts with DPD to give the dioxetane precursor of EGDB.[7] 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.

Scheme I



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 ^{1}H 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 chloride[8] gives EGDB as the major product, also via the dioxetane, as determined by ^{1}H 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

(1) Schaap, A. P.; Zaklika, K. A.; Kaskar, B.; Fung, W.-M. *J. Am. Chem. Soc.* **1980**, *102*, 389-391.
(2) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083-6088.
(3) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290-4301.
(4) Dobrowolski, D. C.; Ogilby, P. R.; Foote, C. S. *J. Phys. Chem.* **1983**, *87*, 2261-2263.
(5) Foote, C. S. *Tetrahedron* **1985**, *41*, 2221-2227.
(6) Kanner, R. C.; Foote, C. S. *J. Am. Chem. Soc.* **1991**, in press.
(7) Spada, L. T.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 391-393.
(8) Schaap, A. P.; Thayer, A. L.; Blossey, E. C.; Neckers, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 3741-3745.

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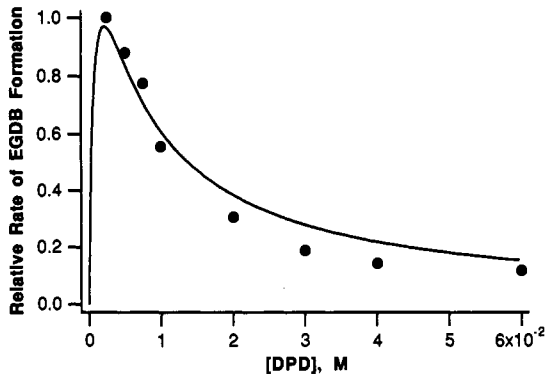

Figure 1. Relative rate of ethylene glycol dibenzoate formation vs diphenyldioxene (DPD) concentration in the DCA-sensitized photooxidation of DPD in oxygen-saturated acetonitrile at 25 °C. The solid line is calculated according to the kinetics of Scheme I (see Discussion).

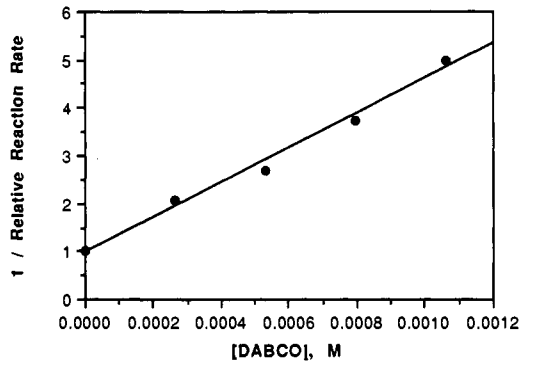

Figure 2. Reciprocal of the relative rate of ethylene glycol dibenzoate (EGDB) formation vs diazabicyclo[2.2.2]octane (DABCO) concentration in the DCA-sensitized photooxidation of DPD in oxygen-saturated acetonitrile at 25 °C. [DPD] = 0.0075 M.

at high DPD concentrations because the electron-transfer route would lead to quenching of ^{1}DCA*. 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 ^{1}DCA* fluorescence (data not shown) gives the quenching rate constant k_q of ^{1}DCA* by DPD as $(2.3 \pm 0.3)^9 \times 10^{10}$ M^{-1} 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 $(2 \pm 1) \times 10^{10}$ M^{-1} s^{-1} at 25 °C. The value of k_S (for reaction of $^1O_2$ with DPD, determined by $^1O_2$ luminescence quenching[10]) is $(1.72 \pm 0.08) \times 10^7$ M^{-1} s^{-1}.

The kinetics of the DPD photooxidation in the presence of the singlet oxygen quencher 1,4-diazabicyclo[2.2.2]octane (DABCO)[11] were investigated. Acetonitrile solutions 0.0075 M in DPD and with [DABCO] up to 1.1×10^{-3} 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 $^1O_2$ by DABCO in acetonitrile calculated from this plot is 5.5×10^8 M^{-1} s^{-1}, slightly above the value found in pyridine (3×10^8 M^{-1} s^{-1}).[12] The rate constant appears not to have been measured in polar aprotic solvents.

DPD oxide was synthesized independently from DPD and dimethyldioxirane[13] and characterized by ^{1}H NMR and GC analysis. After this work was completed, Adam reported preparation of several similar epoxides using this reagent.[14] The

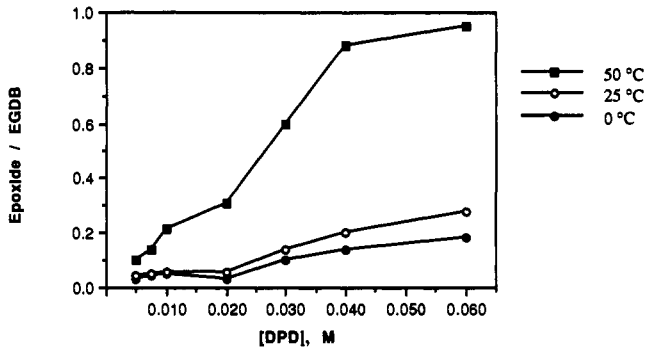

Figure 3. Ratio of DPD oxide to EGDB vs DPD concentration in the DCA-sensitized photooxidation of DPD in oxygen-saturated acetonitrile at 0, 25, and 50 °C. Product ratios are uncorrected for GC response factors.

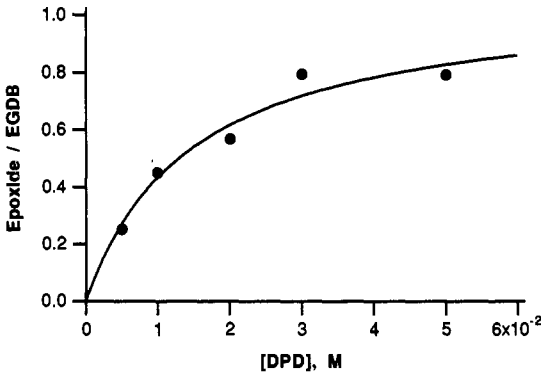

Figure 4. Ratio of DPD oxide to EGDB vs DPD concentration in the DCA-sensitized photooxidation of DPD in oxygen-saturated acetonitrile at 25 °C, with concentration of biphenyl 1 M. The solid line is fit to the kinetics of Scheme III (see Discussion).

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 in acetonitrile at 0, 25, and 50 °C is plotted versus DPD concentration in Figure 3. The fraction of epoxide increases monotonically with DPD concentration at all temperatures and is larger at higher temperatures.[15]

Addition of biphenyl to DCA-sensitized photooxidations leads to a cosensitization process that forces electron transfer at the expense of the singlet oxygen pathway (see Discussion).[16] At constant DPD concentration (0.006 M), the overall rate of product formation remains approximately constant as the biphenyl concentration is increased from 0 to 1 M, at which concentration no $^1O_2$ is formed. However, the ratio of epoxide to EGDB increases significantly from 0.05 to 0.25 on going from 0 to 0.2 M biphenyl and then remains nearly constant up to 1 M (data not shown).

The ratio of epoxide to EGDB in the DCA-sensitized photooxidation at 25 °C in the presence of 1 M biphenyl is plotted versus DPD concentration in Figure 4. The ratio increases strongly at first and then saturates.

By irradiation of CD_3CN solutions of DPD containing DCA and 0.5 M biphenyl, DPD dioxetane was shown to be an intermediate in the formation of EGDB by ^{1}H NMR. Since all the ^{1}DCA* reacts with biphenyl at this high concentration, no singlet oxygen is formed, and all the observed products must arise from electron transfer (see Discussion).

Discussion

Using the independently determined values of k_q and k_S with $k_O = 6.8 \times 10^9$ M^{-1} s^{-1} [17] and the lifetime of ^{1}DCA* = 15.2 ns[2]

(9) 95% confidence level.
(10) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423–3430.
(11) Foote, C. S. In *Quenching of Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; pp 139–173.
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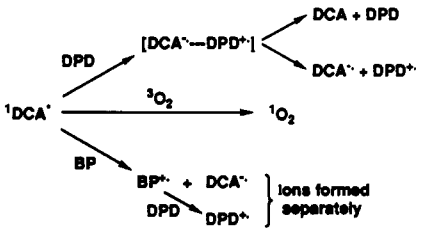
(13) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847–2853.
(14) Adam, W.; Hadjiarapoglou, L.; Wang, X. *Tetrahedron Lett.* **1991**, *32*, 1295–1298.

(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.
(16) Lewis, F. D.; Bedell, A. M.; Dykstra, R. E.; Elbert, J. E.; Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 8055–8064.

Scheme II



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 more rapid production of EGDB because there is relatively less quenching of ^{1}DCA* by DPD. Since $^1O_2$ reacts so rapidly with DPD ($k_S = 1.72 \times 10^7$ M^{-1} s^{-1}), $^1O_2$ 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 $\sim 2 \times 10^{-3}$ 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 ^{1}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)[11] at 25 °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 $^1O_2$.

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•⁻/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.

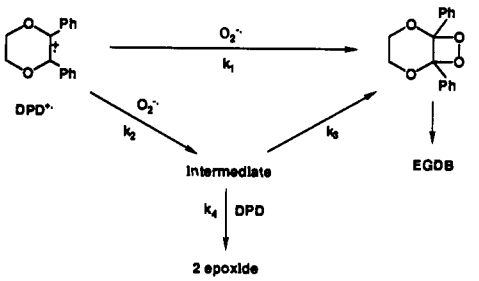
These experiments show that the main route to product formation is reaction of singlet oxygen with DPD to give a dioxetane which cleaves to ethylene glycol dibenzoate. The electron-transfer pathway is minor under normal conditions (nonelevated temperature and low DPD concentration) but becomes more important 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.[16] An alternative interpretation is that the free ions are formed, but O_2•⁻ subsequently transfers 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 O_2•⁻.[1]

The experiments using biphenyl as cosensitizer support the conclusion that reaction with DPD leads mainly to deactivation of ^{1}DCA* and to a low yield of ions. The increase in epoxide formation at high biphenyl concentrations is consistent with a scheme in which ^{1}DCA* reacts with biphenyl to give biphenyl radical cation, which subsequently reacts with DPD to produce

(17) Kanner, R. C. Ph.D. Dissertation, University of California, Los Angeles, 1990.

Scheme III



DPD•⁺, forcing electron transfer at the expense of the singlet oxygen pathway (Scheme II).[16] The free ion yield of BP•⁺ and DCA•⁻ from ^{1}DCA* is extremely high ($\sim$0.8),[3] 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 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 ^{1}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 $k_3/k_4 = 0.0096$ M. If $k_4 = 2 \times 10^{10}$ M^{-1} s^{-1} (diffusion-controlled), then the lifetime of the intermediate ($1/k_3$) would be $\sim$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}H NMR of DPD photolyses in CD_3CN in the presence of high ($\geq$0.5 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 *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 *trans*-stilbene,[2,18] 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[16] suggest that stilbene oxide is produced as a secondary photoproduct from benzaldehyde via an intermediate benzoylperoxy 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

^{1}H NMR spectra were recorded on a Bruker AF-200 NMR spectrometer with tetramethylsilane (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.[20] The crude product was chromatographed over silica gel (CH_2Cl_2 eluent) and recrystallized from ethanol; mp 92–93 °C (lit.[20] mp 93 °C). ^{1}H NMR of DPD ($CDCl_3$, δ, ppm): 4.33 (s, 4 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[2] 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 × 100 mm Pyrex disposable cuvettes containing 3 mL of solution. Acetonitrile or methylene chloride solutions containing either DCA (10^{-4} 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 5890 with a HP-1 methyl silicone gum capillary column or a HP 5880A with a DB17-30N medium-polarity capillary column. All GC analyses were performed in triplicate and the results averaged. Photolysis times were 0.5–5 min in most cases; the conversion of substrate was kept below 10% for all analytical photolyses.

Determination of Rate Constants. ^{1}DCA* quenching rate constants were determined by Stern–Volmer quenching on a Spex Fluorolog spectrofluorometer equipped with a photon-counting detection system. Singlet oxygen quenching rate constants were determined by luminescence quenching.[10]

DABCO Quenching Experiment. Acetonitrile solutions of 0.0075 M in DPD and with [DABCO] up to 1.1×10^{-3} M were irradiated as described above. Under these conditions, the quenching of ^{1}DCA* by DABCO is negligible compared to the reaction of ^{1}DCA* with DPD and with O_2.

Synthesis of DPD Oxide. DPD oxide was generated by reaction of DPD with dimethyldioxirane in acetone at room temperature.[13,14] The reaction was monitored by GC and was complete in <30 s; the yield of epoxide was 97% from DPD, calculated from the GC peak areas. Evaporation of the solvent left a white solid residue, which when prepared for NMR analysis decomposed significantly to benzil and ethylene glycol, requiring 1 mol of water/mol of epoxide. A chloroform solution of DPD oxide completely decomposed to benzil overnight in a freezer. ^{1}H NMR of DPD oxide ($CDCl_3$, δ, ppm): 4.05 (m, 2 H), 4.25 (m, 2 H), 7.4–7.7 (m, 6 H), 8.10 (dd, 4 H).

Detection of Intermediate DPD Dioxetane in DCA- and Rose Bengal-Sensitized Reactions. Solutions containing DCA and 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 ^{1}H NMR spectrum (($CDCl_3$, δ, ppm) 4.40 (m, 2 H), 4.94 (m, 2 H), 7.5 (m, 6 H), 8.06 (dd, 4 H)) and ^{13}C NMR spectrum (($CDCl_3$, δ, ppm) 60.2, 109.5, 126.7, 127.8, 129.2, 135.6). Some EGDB was found in the product, presumably from sensitized decomposition of the dioxetane. Upon heating at 60 °C for 2 h, the dioxetane was completely decomposed to EGDB. ^{1}H NMR ($CDCl_3$, δ, ppm): 4.67 (s, 4 H), 7.5 (m, 6 H), 8.08 (dd, 4 H). ^{13}C NMR ($CDCl_3$, δ, ppm): 62.8, 128.4, 129.7, 133.2, 166.4. ^{1}H NMR reported:[21] 4.67 ppm. The spectra were identical with those of an authentic sample independently prepared from ethylene glycol and benzoyl chloride.

Biphenyl Cosensitization Experiments. Acetonitrile solutions of DCA (10^{-4} M), DPD (up to 0.06 M), and biphenyl (up to 1 M) were irradiated as described above. The solutions were analyzed by GC.

Detection of Intermediate Dioxetane in Electron-Transfer Reaction. A solution of DPD (0.005 M) and biphenyl (0.5 M) in CD_3CN in an NMR tube was irradiated for 3 min at 25 °C, after which time conversion was 100% by GC; ^{1}H NMR of the solution revealed the presence of DPD dioxetane as well as EGDB in approximately equal amounts. Upon heating at 60 °C for 2 h, the dioxetane signals completely disappeared and the EGDB signal grew in intensity.

Acknowledgment. This work was supported by NSF Grant No. CHE89-11916. We thank James W. Arbogast for measurement of singlet oxygen quenching rate constants.

Registry No. DPD, 4344-45-0; EGDB, 94-49-5; DCA, 1217-45-4; DABCO, 280-57-9.

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(21) Lopez, L.; Calo, V.; Aurora, R. *J. Photochem.* **1986**, *32*, 95–104.