0.020×10^{-19} cm^3 spins^{-1}, respectively. These intercepts are probably equal to zero within the experimental uncertainty of the data. The solid lines represent values calculated from the slope and intercept determined by the least-squares method. The slopes were 0.143×10^{-19} and 0.0899×10^{-19} cm^3 spin^{-1} min$^{-1/2}$ for the 18.7- and 39.8-Mrad experiments. Assuming r_0 is 4×10^{-7} in both cases, diffusion coefficients of the individual species ($\frac{1}{2}D$) are calculated to be 3.31×10^{-19} and 1.31×10^{-19} cm^2/s which are of the same order of magnitude of $\frac{1}{2}D$ equal to 1.7×10^{-19} cm^2/s as given above for the required value of $1/2D$ to make the term in eq 2 $2r_0/(\pi Dt)^{1/2}$ at t equal to 100 min ten times greater than unity.

It is interesting to note at the higher dose where there would be expected to be more cross links produced by the irradiation and, therefore, less chain mobility that the allyl radical diffusion coefficient is only about half as great as at the lower dose.

Details of the experimental work[4] and further application of eq 1 to other systems will be given in the full paper. The relationship of this treatment to the kinetics of decay involving two simultaneous second-order reactions observed by us[5] and others will also be clarified.

Acknowledgments. This research was supported by the U.S. Energy Research and Development Administration and by income from the chain in chemistry at Baylor University endowed by The Robert A. Welch Foundation. The extended chain polyethylene was generously provided by Professor B. Wunderlich of Rensselaer Polytechnic Institute. Chak Gupta assisted with some of the calculations.

References and Notes

(1) M. W. Smoluchowski, *Z. Phys. Chem.*, **92**, 192 (1917).
(2) T. R. Waite, *Phys. Rev.*, **107**, 463 (1957).
(3) W. Y. Wen, D. R. Johnson, and M. Dole, *J. Phys. Chem.*, **78**, 1798 (1974).
(4) Gordon Patel, V. M. Patel, C. S. Hsu, N. Gvozdic, and M. Dole, unpublished work.
(5) M. Dole, C. S. Hsu, V. M. Patel, and G. N. Patel, *J. Phys. Chem.*, **79**, 2473 (1975).

Malcolm Dole,* J. Salik
Department of Chemistry, Baylor University
Waco, Texas 76703
Received May 31, 1977

Photosensitized Oxygenation of Alkenes and Sulfides via a Non-Singlet-Oxygen Mechanism

Sir:

A number of electron-rich compounds react with singlet oxygen in a different way from less electron-rich compounds. Enamines[1] and vinyl ethers[2] produce dioxetanes, phenols[3] give hydroperoxydienones, and sulfides[4] react to give sulfoxides or quench singlet oxygen, depending on the conditions. There are indications that several of these reactions may go by way of electron transfer from the electron-rich molecule (D) to singlet oxygen.[1a] Because of its excitation energy, singlet oxygen should have an $E_{1/2}$ 1 V higher than ground-state oxygen ($E_{1/2} = -0.57$ V).[5] The resulting ion pair could react either to give product (DO_2) or to quench singlet oxygen.

$$D + {}^1O_2 \longrightarrow D^{\cdot+} + O_2^{\cdot-} \rightleftharpoons \begin{matrix} DO_2 \\ D + {}^3O_2 \end{matrix}$$

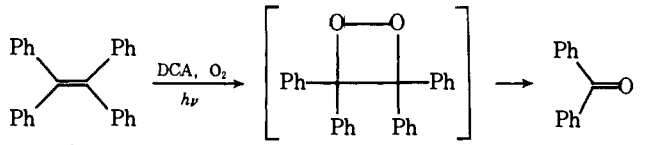
We now report that 9,10-dicyanoanthracene (DCA) sensitizes the photooxygenation of certain substrates in oxygen-saturated CH_3CN solution. The reactions do not seem to involve singlet oxygen, and we propose the following mechanism involving a donor radical cation and DCA radical anion which subsequently reduces O_2 to superoxide. The ultimate products are similar to those of electron-rich substrates with $^1O_2$. Our

$$DCA \xrightarrow{h\nu} {}^1DCA^* \xrightarrow{D} [DCA^{\cdot-} + D^{\cdot+}] \xrightarrow{{}^3O_2} DCA + O_2^{\cdot-} + D^{\cdot+} \longrightarrow DO_2$$

rationale for this mechanism was the use by Shigemitsu and Arnold[6] of electron-deficient sensitizers to add alcoholic solvents to electron-rich olefins, and by Evans and Farid et al. and Roth and Manion[7] to dimerize alkenes. With $E_{1/2}(R/R^-)$ for DCA of -0.82 V[8] and -0.57 V for oxygen,[5] the electron transfer from $DCA^{-}\cdot$ to O_2 should be exothermic ($\Delta G^\circ = -5$ kcal/mol). Our preliminary evidence is described below.

DCA Fluorescence Quenching. Diffusion-controlled rate constants were found for the quenching of DCA fluorescence in nitrogen-saturated CH_3CN and C_6H_6 by 1,3-cyclohexadiene, 1,4-dimethyl-1,3-cyclohexadiene, 1,4-dimethoxy-1,4-cyclohexadiene, diphenyl sulfide, tetraphenylethylene, and *trans*-stilbene.[9] Near-diffusion-controlled rate constants have also been obtained by Ware, Holmes, and Arnold[10] for the quenching of DCA fluorescence in the same solvents by substituted 1,1-diphenylethylenes. From the reduction potential and singlet excitation energy (2.89 eV, 66.6 kcal/mol)[11] of DCA, an electron-transfer mechanism[12] should be possible for substrates with oxidation potentials less than ~2.0 V. All of the substrates mentioned above comply with this requirement: e.g., *trans*-stilbene, $E_{1/2}(R^+/R) = +1.51$ V;[13] diphenyl sulfide, +1.45 V; and tetraphenylethylene, +1.33 V.[14]

Tetraphenylethylene (1) and *trans*-Stilbene (2). Irradiation[15,16] of **1** in CH_3CN containing DCA (10^{-4} M) gave 2 equiv of benzophenone (**3**, 57%), triphenylmethanol (14%), benzopinazolone (8%), tetraphenyloxirane (1.5%), an unidentified product (~1%), and small amounts of benzoic acid and benzaldehyde. All products were identified by comparison with authentic samples. The presence of water (0.3%) results in an increased yield of **3** at the expense of the other products. Addition of small amounts of CCl_4 greatly speeds up the reaction without changing the product distribution appreciably. This result is similar to that obtained by Bartlett and Landis.[17] No products were formed (0.5% of **3** would have been detected) if oxygen or DCA was absent, and addition of 7.7×10^{-5} M of the singlet oxygen quencher bis(2,3-dithiolato-2-butene)nickel(II)[18] ($k_q = 2.8 \times 10^{10}$ M^{-1} s^{-1}) did not quench the formation of **3**.[19] Reaction was slower in CH_2Cl_2 and acetone and no products were detected in benzene, diethyl ether, cyclohexane, *p*-dioxane, CCl_4, or ethyl acetate. More importantly, no products were formed in an oxygen-saturated CH_3CN solution of **1** containing the singlet oxygen sensitizers, rose bengal or methylene blue, irradiated at $\lambda > 500$ nm.[20] Thus, it appears that the DCA photooxygenation of **1** does not involve singlet oxygen, but involves an initial reaction of substrate with *singlet* excited DCA to give a polar intermediate, as in the electron-transfer mechanism above. The initial product is presumably 3,3,4,4-tetraphenyl-1,2-dioxetane; under the reaction conditions, this dioxetane would be expected to decompose to **3** by direct photolysis at the wavelength used.



1 3

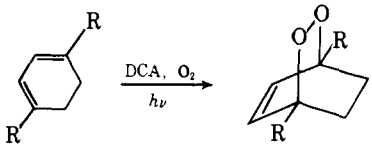
This possibility and the mode of formation of the intriguing by-products are currently under investigation. Some of the products may be formed by a mechanism analogous to that

suggested by Bartlett and Landis.[17]

Similarly, DCA sensitized irradiation of **2** gave 2 equiv of benzaldehyde (**4**) and ~2% of *cis*-stilbene (**5**), identified by comparison with authentic samples. Again, rose bengal or methylene blue sensitized photooxygenation of **2** did not lead to **4**[20] (0.5% would have been detected) or **5** (detection limit not established). Formation of **4** or **5** was not a result of direct light absorption by **2** under the reaction conditions; **5** could have been formed either by sensitization by triplet **4** (from decomposition of the corresponding dioxetane) or by bond rotation in the radical cation of **2** followed by back-transfer of the electron. Triplet sensitization by **4** to form **5** from **2** is a very facile reaction, as determined in a separate irradiation at 350 nm in oxygen-saturated CH_3CN.

Sulfides. DCA sensitized photooxygenation of diphenyl sulfide (**6**) gave diphenyl sulfoxide, while diethyl sulfide (**7**) gave a mixture of diethyl sulfoxide and diethyl sulfone. Addition of β-carotene at concentrations up to 10^{-4} M did not quench the formation of the photoproducts.[19] It was found that **6** was three times as reactive as **7**, whereas **6** is 2800 times *less* reactive than **7** toward singlet oxygen (in CH_3OH[4a]). It appears, therefore, that singlet oxygen is not involved (at least in the major pathway) in the DCA sensitized photooxygenation of **6**.

1,3-Cyclohexadienes. DCA sensitized photooxygenation of 1,3-cyclohexadiene (**8**) and 1,4-dimethyl-1,3-cyclohexadiene (**9**) gave the endoperoxides **10** and **11**, respectively. Since **8** and **9** react with singlet oxygen to give the same products, a careful kinetic study is necessary to establish whether the DCA sensitization involved singlet oxygen or not. Preliminary quenching studies indicate that a non-singlet-oxygen pathway is involved at least to some extent.



8, R = H; **9**, R = Me — **10**, R = H; **11**, R = Me

It is noteworthy that this reaction permits oxidation of substrates such as **1** and **2** which are too electron poor to react with singlet oxygen, and we expect that the oxidation will be limited by the oxidation potential of the substrate as described above.

Two very recent papers have discussed a similar mechanism in different systems.[21]

Acknowledgment. Supported by National Science Foundation Grant No. CHE73-08502.

References and Notes

(1) (a) C. S. Foote, A. A. Dzakpasu, and J. W.-P. Lin, *Tetrahedron Lett.*, 1247 (1975); (b) C. S. Foote and J. W.-P. Lin, *ibid.*, 3267 (1968).

(2) P. D. Bartlett and A. P. Schaap, *J. Am. Chem. Soc.*, **92**, 3223 (1970); S. Mazur and C. S. Foote, *ibid.*, **92**, 3225 (1970); A. P. Schaap and P. D. Bartlett, *ibid.*, **92**, 6055 (1970); P. D. Bartlett, G. D. Mendenhall, and A. P. Schaap, *Ann. N.Y. Acad. Sci.*, **171**, 79 (1970).

(3) T. Matsuura, N. Yoshimura, A. Nishinaga, and I. Saito, *Tetrahedron*, **28**, 4933 (1972); C. S. Foote, M. Thomas, and T.-Y. Ching, *J. Photochem.*, **5**, 172 (1976).

(4) (a) C. S. Foote and J. W. Peters, *J. Am. Chem. Soc.*, **93**, 3795 (1971); (b) C. S. Foote and J. W. Peters, *Int. Congr. Pure Appl. Chem., Spec. Lect., 23rd*, **4**, 129 (1971).

(5) All potentials are vs. SCE for $R_{ox} + e^- \rightarrow R_{red}$. The reduction potential for oxygen is somewhat obscure; we have used the equation $E_{1/2}(SCE) = E^0(NHE) - 0.24$ V and taken the value $E^0 = -0.33$ V as the most reasonable for our conditions, since this value has been obtained both by polarographic, voltametric, and equilibrium measurements. Most of these measurements have been in aqueous solution. Values in CH_3CN range from -0.75[5d] to -0.82.[5e] For almost all reduction potentials reported for O_2 the electron-transfer reaction $DCA^{-\cdot} + O_2 \rightarrow DCA + O_2^{-\cdot}$ is calculated to be exothermic. For a discussion on the $O_2/O_2^{-\cdot}$ system, see (a) Y. Sawada, T. Iyanagi, and I. Yamazaki, *Biochemistry*, **14**, 3761 (1975); (b) J. Divisek and B. Kastening, *J. Electroanal. Chem.*, **65**, 603 (1975); (c) D. Bauer and J.-P. Beck, *ibid.*, **40**, 233 (1972); (d) M. E. Peover and B. S. White, *Electrochim. Acta*, **11**, 1061 (1966); (e) J. F. Coetzee and I. M. Kolthoff, *J. Am. Chem. Soc.*, **79**, 6110 (1957).

(6) Y. Shigemitsu and D. R. Arnold, *J. Chem. Soc., Chem. Commun.*, 407 (1975).

(7) (a) T. R. Evans, R. W. Wake and O. Jaenicke, *Exciplex, Proc. Meet., 1974*, 345 (1975); (b) S. Farid, S. E. Hartman, and T. R. Evans, *ibid.*, 327 (1975); (c) H. D. Roth and M. L. Manion, *Int. Conf. Photochem., 7th, 1975*, Abstracts, U2 (Aug. 1975).

(8) E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, **47**, 2557 (1967).

(9) The quenching rate constants were obtained from the slopes of Stern–Volmer plots using the singlet lifetime of DCA in nitrogen-saturated acetonitrile ($\tau_S = 15.2$ ns[10]) and benzene (12.4 ns[10]). Exciplex emission could not be detected in either acetonitrile or benzene at quencher concentration up to 0.1 M.

(10) W. R. Ware, J. D. Holmes, and D. R. Arnold, *J. Am. Chem. Soc.*, **96**, 7861 (1974).

(11) Calculated from the absorption and fluorescence spectra in acetonitrile.

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

(13) L. Eberson and K. Nyberg, *J. Am. Chem. Soc.*, **88**, 1686 (1966).

(14) J. D. Stuart and W. E. Ohnesorge, *J. Am. Chem. Soc.*, **93**, 4531 (1971).

(15) A 1-cm path-length filter solution consisting of 27.0 g of $CuSO_4 \cdot 5H_2O$, 30.0 g of $NaNO_2$, and 50 mL of concentrated NH_4OH diluted with water to 1000 mL was used. This filter isolates the Hg lines at 404–408 and 436 nm from a 1200-W medium-pressure Hanovia lamp in a water-cooled immersion well.

(16) Solution of 10^{-2} M substrates in oxygen-saturated dry CH_3CN were used, unless stated otherwise.

(17) P. D. Bartlett and M. E. Landis, *J. Am. Chem. Soc.*, **99**, 3033 (1977).

(18) A. Zweig and W. A. Henderson, *J. Polym. Sci., Part A-1*, **13**, 717 (1975).

(19) Addition of the quencher actually *increased* the conversion of starting material for reasons yet unknown.

(20) Very slow reaction of **1** and **2** with singlet oxygen to give **3** and **4**, respectively, has been reported: G. Rio and J. Berthelot, *Bull. Soc. Chim. Fr.*, 3609 (1969).

(21) C. P. Anderson, D. J. Salmon, T. J. Meyer, and R. C. Young, *J. Am. Chem. Soc.*, **99**, 1980 (1977); F. D. Saeva and G. R. Olin, *J. Chem. Soc., Chem. Commun.*, 943 (1976).

J. Eriksen, C. S. Foote,* T. L. Parker

Contribution No. 3827 from the Department of Chemistry University of California, Los Angeles, California 90024

Received May 13, 1977

One-Step Preparation of Vitamin K_1 or K_2 Analogues by Cyclodextrin Inclusion Catalysis

Sir:

One of the most important and interesting, although uninvestigated, aspects of the rapidly developing field of cyclodextrin chemistry is application to the highly selective synthesis of bioactive compounds[1] by inclusion catalysis. Reactions modeling enzymatic processes by the use of cyclodextrins have been extensively studied mostly from the mechanistic viewpoint, particularly once cyclodextrins were found to behave as hydrolytic enzyme models toward their own pyrophosphate[2] or carboxylate ester substrates.[3]

In this communication, we wish to report the first successful application of cyclodextrin to the one-step synthesis of a bioactive compound, i.e., the highly selective preparation of vitamin K_1 (or K_2) analogues in dilute aqueous alkaline solution.

Vitamin K_1 was first synthesized from 2-methylhydronaphthoquinone-1,4 and phytol via the Friedel-Crafts reaction by Fieser,[4] and thereafter many modifications of the original preparation have been reported.[5] However, these Friedel-Crafts-type preparations seem to have the serious and inevitable disadvantage that they are accompanied by the formation of undesirable products from alkylation on the C_2 position and further cyclization to naphthotocopherol.

In the present communication, we wish to report a novel preparation of vitamin K_1 (or K_2) analogues by use of β-cyclodextrin. Thus, a solution of 8.505 g (7.5 mmol) of β-cyclodextrin, 3.630 g (30 mmol) of allyl bromide, and 261 mg (1.5 mmol) of 2-methylhydronaphthoquinone-1,4 in a mixture of 105 mL of borate buffer solution (pH 9.0) and 45 mL of