

PHOTOSENSITIZED OXYGENATION INITIATED BY ELECTRON-TRANSFER.¹

A NEW TYPE OF PHOTOOXYGENATION OF ALKYL BENZENES

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The photosensitized oxygenation with 9,10-dicyanoanthracene has led to the selective oxidation of the alkyl side-chain of alkylbenzenes. The photooxygenation has been shown to be initiated by an electron-transfer via exciplex followed by a radical chain process.

Recently there has been considerable practical and mechanistic interest in the photooxygenation of alkenes via a non-singlet-oxygen mechanism.² This type of photooxygenation can be accomplished by sensitized oxygenation with α -diketones³ or with 9,10-dicyanoanthracene (DCA).⁴ We report here a new type of photooxygenation using DCA as sensitizer leading to the selective side-chain oxidation of alkylbenzenes which are inert toward singlet oxygen. Noteworthy is the mildness of the conditions, in contrast to rather drastic conditions for usual metal salts-catalyzed⁵ or free-radical⁶ oxidations of alkylbenzenes. In addition, we show (1) the photooxygenation is initiated by an electron-transfer via exciplex and (2) superoxide ion is not involved at least as the oxidizing species.

In a typical experiment a solution of *p*-xylene (3 mmol) and DCA (0.03 mmol) in acetonitrile (180 ml) was irradiated with a high-pressure mercury lamp under oxygen bubbling at room temperature for 7 h. Preparative tlc of the mixture gave *p*-tolualdehyde (47%) and *p*-methylbenzoic acid (50%).⁷ The sensitizer DCA was recovered unchanged after the reaction. In control experiments no products were formed if oxygen or DCA was absent. The substrates except hexamethylbenzene⁸ listed in table I were not oxidized by rose bengal- or methylene blue-sensitized photooxygenation irradiated at $\lambda > 500$ nm, indicating that singlet oxygen is not involved in the oxidation.

Fluorescence of DCA in nitrogen saturated acetonitrile was quenched by a series of methyl-

benzenes. The quenching rate constants (k_q)⁹ of hexamethylbenzene, pentamethylbenzene and durene are close to a diffusion-controlled rate ($1.82 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in CH_3CN at 20°C) (Table I). There is a linear relation between $\log k_q$ and the half-wave oxidation potentials¹¹ ($E_{1/2}^{\text{ox}}$) with a slight deviation of mesitylene (Fig. 1a). These results indicate that exciplex formation between $^1\text{DCA}^*$ and methylbenzenes plays an important role at the initial stage of the photo-reaction.¹² In highly polar solvents such as acetonitrile the exciplex may well dissociate to a radical ion pair. In the presence of oxygen the radical ions are expected to react with O_2 .¹³ However, the mechanism of the oxidation is more complicated. As shown in Fig. 1b, semilog plots of the relative rates (K_{rel}) of oxidation *vs.* $E_{1/2}^{\text{ox}}$ did not give a straight line, suggesting that an electron-transfer process is not necessarily a rate-limiting step of the oxidation.

Foote and his coworkers^{4a} have proposed that superoxide ion (O_2^-) is formed from an electron-transfer from DCA^- to O_2 and that the recombination of O_2^- and a donor radical cation may produce the products in DCA-sensitized photooxygenation of alkenes. However, in the present case methylbenzenes did not react with potassium superoxide (KO_2) dissolved by complexation with a crown ether in acetonitrile either in a dark reaction or under the photooxygenation conditions in the presence of DCA. More importantly, DCA was rapidly destroyed by KO_2 in the dark reaction. In an attempt to trap O_2^- , we have carried out the photooxygenation of mesitylene in the presence of large excess of phenyl *n*-caprylate.¹⁴ The expected phenol and *n*-caprylic acid have not been detected under the conditions. The results strongly suggest that O_2^- is not generated in appreciable amounts during the photooxygenation.

DCA-sensitized photooxygenation of *p*-cymene gave a mixture of products as shown in Table I. The ratio of the oxidation of methyl group to isopropyl was 1 : 1.3. The ratio (P/T) of the formation of benzylic primary radical (P) to tertiary radical (T) is often used as a measure to discriminate a classical free-radical mechanism from an electron-transfer mechanism. The reactivity of methyl group *vs.* isopropyl in free-radical oxidation is 1 : 3.2,^{6a} whereas Co (III)-catalyzed oxidation of *p*-cymene, a process which has been interpreted to involve an electron-transfer process, gives products with 19 : 1 P/T ratio.⁵ Proton transfer from *p*-cymene to photoexcited α,α,α -trifluoroacetophenone possibly through a charge transfer process gives products with 3.4 : 1 P/T ratio.¹⁵ The small P/T value in the present case is much closer to that for a free-radical oxidation and not be explained by a simple electron-transfer mechanism. We, therefore, propose following mechanism involving a radical chain process (Scheme 1). The substrate radical cation formed from the exciplex may lose proton to give a benzylic radical

Table I Product Distribution, Relative Rates and Quenching Rate Constants in the DCA-Sensitized Photooxygenation of Alkylbenzenes

Substrate	Rel rate ^a	k_q M ⁻¹ s ⁻¹	Products (%) ^b
<i>m</i> -Xylene	0.07	3.06×10^7	<chem>c1ccc(C=O)cc1</chem> (27), others
<i>o</i> -Xylene	0.13	5.80×10^7	<chem>c1ccccc1C=O</chem> (25), others
<i>p</i> -Xylene	0.54	6.38×10^8	<chem>c1ccc(C=O)cc1</chem> (47), <chem>c1ccc(C(=O)O)cc1</chem> (50)
Mesitylene	0.48	4.21×10^9	<chem>c1cc(C=O)cc1</chem> (85), <chem>c1cc(C(=O)O)cc1</chem> (15)
Durene	0.82	1.08×10^{10}	<chem>c1cc(C=O)cc1</chem> (35), <chem>c1cc(C(=O)O)cc1</chem> (47)
Petamethylbenzene	0.82	1.31×10^{10}	} complex mixture of unidentified products
Hexamethylbenzene	1	1.33×10^{10}	
<hr/>			
<i>p</i> -Cymene			<chem>c1ccc(C=O)cc1</chem> (43) <chem>c1ccc(C(=O)C)cc1</chem> (19)
<i>p</i> -Ethyltoluene			<chem>c1ccc(C(=O)C)cc1</chem> (38)
			<chem>c1ccc(C(=O)O)cc1</chem> (54)
			<chem>c1ccc(C(O)C)cc1</chem> (12) <chem>c1ccc(C(O)C)cc1</chem> (17)
Tetralin			α -Tetralone (100)

^a[Substrate] = 0.1 M, [DCA] = 3×10^{-4} M. In CH₃CN at 25 °C. The relative rates were determined by GLC. ^b[Substrate] = 16.7 mM, [DCA] = 0.17 mM. In CH₃CN at 20 °C. Isolated yield. Under the conditions toluene gave benzaldehyde (29%) slowly.

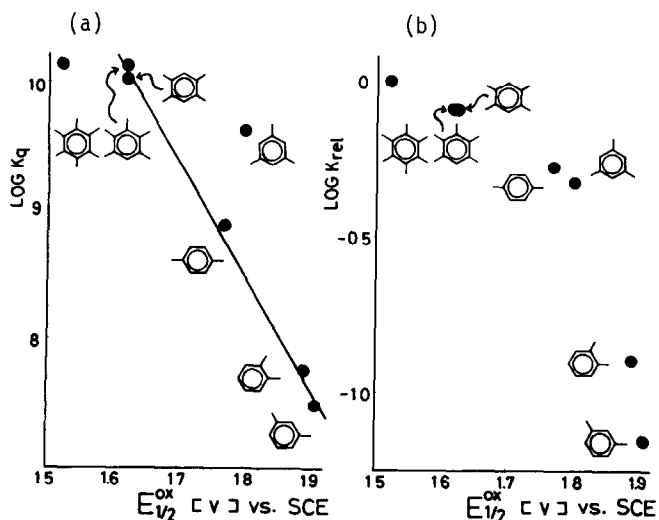
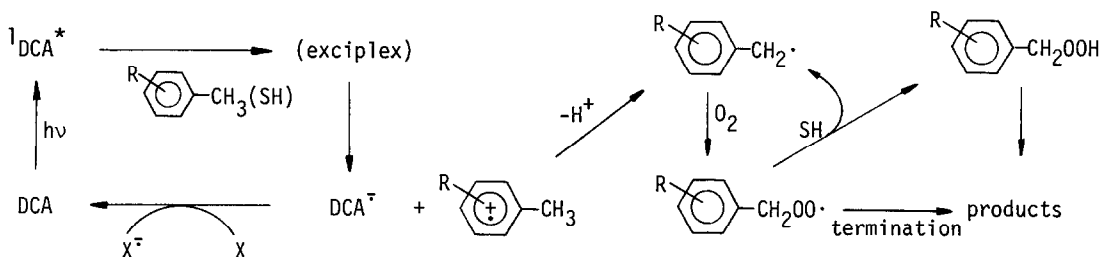


Figure 1. (a) Plot of $\log K_q$ vs. $E_{1/2}^{ox}$ (SCE) for the quenching of DCA fluorescence by methylbenzenes. (b) Plot of $\log K_{rel}$ vs. $E_{1/2}^{ox}$ (SCE) in the DCA-sensitized photooxygenation of methylbenzenes.

which undergoes a classical free-radical chain autoxidation. Superoxide ion, if formed from an electron-transfer from $\text{DCA}^{\cdot-}$ to O_2 , may well be a proton acceptor. An alternative route for the regeneration of DCA from $\text{DCA}^{\cdot-}$ is an electron-transfer between $\text{DCA}^{\cdot-}$ and peroxy radicals in the chain termination step.

Scheme 1



Following additional evidence has been obtained in support of the free-radical mechanism.

(1) Addition of small amount of CCl_4 greatly accelerated the photooxygenation as has been observed with alkene photooxidation.^{2,4a} (2) Photoreaction of DCA with methylbenzenes under nitrogen conditions was negligibly slow compared to the fast photoreaction in the presence of O_2 ($\phi = 0.08$).^{16,17}

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