

PHOTOINDUCED ELECTRON TRANSFER REACTIONS: OXIDATION OF ELECTRON-RICH DIOXENES AND 2,3,5,6-TETRAPHENYL-*p*-DIOXIN INDUCED BY 2,4,4,6-TETRABROMOCYCLOHEXA-2,5-DIENONE[†]

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Summary

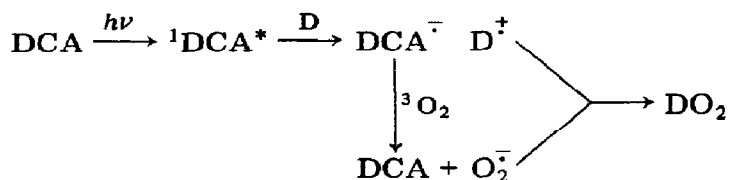
2,4,4,6-Tetrabromocyclohexa-2,5-dienone (TBCHD) sensitizes the photo-oxygenation of dioxenes and 2,3,5,6-tetraphenyl-*p*-dioxin by electron transfer to yield ethane-1,2-diol dibenzoates and (*Z*)-stilbenediol dibenzoate respectively, together with small quantities of the corresponding α -diketones. A preliminary investigation of the physical properties of TBCHD supports a radical cation chain mechanism in which the active oxygen species involved is molecular oxygen. A comparison with the photo-oxygenation of the same substrates sensitized by 9,10-dicyanoanthracene is also reported.

1. Introduction

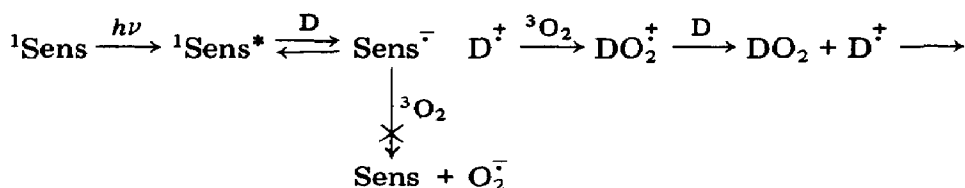
Recently, electron-transfer photo-oxygenation has received considerable attention [1 - 3]. Olefins, acetylenes, dioxenes, epoxides, cycloalkanes, aziridines and sulphides are oxidized upon irradiation in oxygen-saturated polar solvents in the presence of electron-deficient sensitizers. Much of the research has been conducted using cyano-substituted aromatic hydrocarbons such as 9,10-dicyanoanthracene (DCA) ($E^{\text{red}} = -0.98$ V versus the standard calomel electrode (SCE); $\Delta E_{0-0} = 2.98$ eV) as the photosensitizer, under conditions in which superoxide anions are formed and in which the oxygenated products arise from the coupling of O_2^- and the radical cation of the donor (Scheme 1).

However, there are only a few examples in which it is likely that the electron-transfer photo-oxygenation occurs by reaction of a radical cation with molecular oxygen through a radical-cation chain mechanism [4, 5] (Scheme 2; Sens, sensitizer).

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Scheme 1.

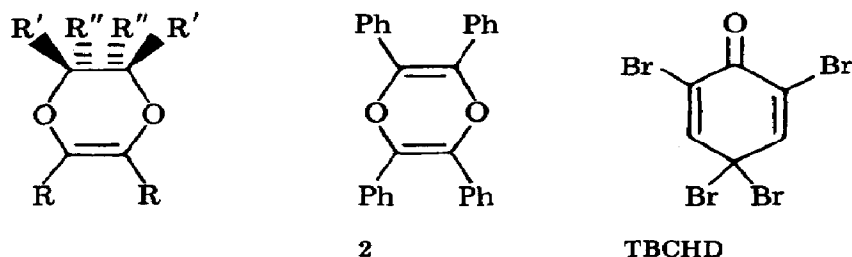


Scheme 2.

For these cases, in which for thermodynamic reasons the superoxide anion cannot be formed, the reverse electron-transfer process prevails over the reaction of the intermediate radical cation with molecular oxygen, and consequently there is a low conversion of starting materials into products [6].

The chemical devices introduced by Farid [4] in the photo-oxygenation of diphenylacetylene (DPA) sensitized by 2,6,9,10-tetracyanoanthracene (TCA; $E^{\text{red}} = -0.45 \text{ V(SCE)}$; $\Delta E_{0-0} = 2.94 \text{ eV}$), clearly show that the main aims in photosensitized electron-transfer oxidation experiments should be to prolong the lifetime of the intermediate radical cation, maximizing the cage escape efficiency, and to liberate the radical cation species from the radical ion pair, thus allowing its reaction with molecular oxygen.

In order to explore these suggestions, we have studied, on the basis of the unusual physical properties of 2,4,4,6-tetrabromocyclohexa-2,5-dienone (TBCHD), the photosensitized oxidation of dioxenes (1a, 1b and 1c) and tetraphenyl-*p*-dioxin (2) induced by TBCHD which in the past has widely been used as a mild and selective brominating agent [7].



1a $\text{R} = \text{C}_6\text{H}_5$; $\text{R}' = \text{R}'' = \text{H}$

1b $\text{R} = p\text{-MeO-C}_6\text{H}_4$; $\text{R}' = \text{R}'' = \text{H}$

1c $\text{R} = \text{R}' = \text{C}_6\text{H}_5$; $\text{R}'' = \text{H}$

2. Experimental details

2.1. General details

Melting points were determined using electrical apparatus and are uncorrected. IR spectra were recorded using a Perkin-Elmer 681 spectrometer (KBr pellets). The proton nuclear magnetic resonance spectra (^1H NMR; CDCl_3 , tetramethylsilane) were recorded using Varian XL 200 MHz, Varian 90 MHz EM 360A or Nicolet 300 MHz instruments. Gas chromatography (GC) analyses were run on a Hewlett-Packard 5750 instrument using columns of dimension 6 ft \times 1/4 in packed with 10% SP 2100 on acid-washed dimethylchlorosilane-treated Chromosorb. Mass spectra were recorded using a Kratos MS 80 instrument. Elemental analyses were performed using Hewlett-Packard apparatus.

2.2. Materials

2,3-Diphenyl-1,4-dioxene (melting point, 93 °C), 2,3-di(methoxyphenyl)-1,4-dioxene (melting point, 102 °C), *cis*-2,3,5,6-tetraphenyl-1,4-dioxene (melting point, 165 °C) and 2,3,5,6-tetraphenyl-*p*-dioxin (melting point, 214 °C) were prepared by reported methods [8 - 10]. TBCHD was freshly prepared and carefully purified as reported in ref. 7. DCA was prepared by reaction of 9,10-dibromoanthracene (Aldrich) with CuCN in boiling quinoline and was crystallized as reported in ref. 11. Acetonitrile (Carlo Erba RS grade) was purified by distillation with CaH_2 and P_2O_5 and was stored over molecular sieves. Dichloromethane was purified by following standard procedures.

2.3. General procedure and results

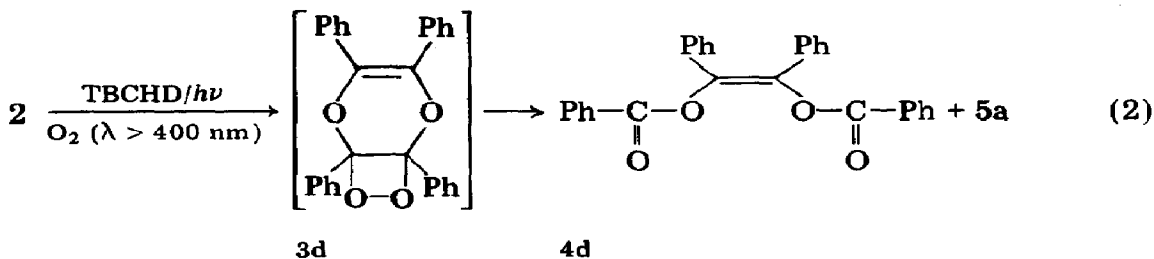
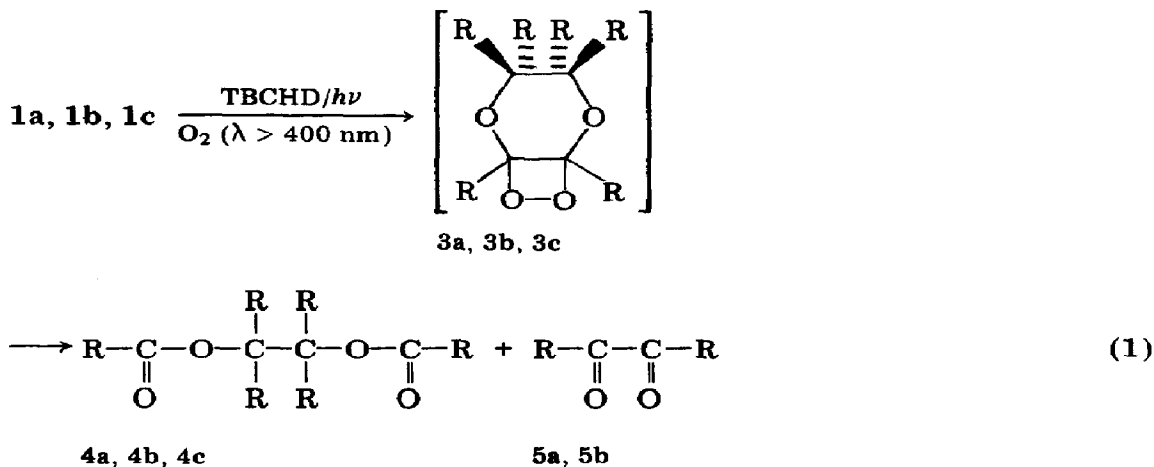
The photo-oxygenations were carried out using either a 700 W high pressure lamp or a 450 W medium pressure mercury lamp surrounded by CuSO_4 filter solution. "Dry" oxygen was further dried by passing through a bed of drierite before it was bubbled through the solution. A photolysing tube containing the appropriate substrates (1a, 1b, 1c and 2) (10^{-2} M) and TBCHD (10^{-3} M) in dry acetonitrile or an acetonitrile-dichloromethane mixture (depending on the solubility of the substrates) was fitted with a gas inlet tube and placed in a water bath at 10 °C. An aliquot of the mixture was taken out prior to irradiation for GC analysis. The remaining solution was irradiated while maintaining the flow of oxygen. Small aliquots were taken out at predetermined times and were analysed. Typical irradiation periods varied as reported in Table 1. Reactions (1) and (2) were monitored by thin-layer chromatography, GC and ^1H NMR and, through the plausible intermediate dioxetanes (3a, 3b, 3c and 3d), give the corresponding cleavage products, *i.e.* ethane-1,2-diol dibenzoates (4a, 4b, 4c) and (*Z*)-stilbenediol dibenzoate (4d) together with small amounts of α -diketones (5a, 5b).

The reaction products were isolated by means of column chromatography over silica gel (eluant, hexane-diethyl ether) and were characterized by their spectral properties and by comparison with authentic commercial

Photosensitized oxygenation of dioxenes and dioxin induced by TBCHD and DCA

Substrates	E^{ox} (V)	Irradiation time (h)	Sens	Product yields (%)	Melting point (°C)	1H NMR δ ($CDCl_3$)	IR ν (KBr) (cm^{-1})
1a	0.928 ^{a,b}	2	TBCHD	4a 75 ^c 5a 20	72 - 73 ^d 94	4.668 s 8.0 - 7.249 m	1712, 1340 1670, 1440
1a	0.928 ^{a,b}	1	DCA	4a ^e			
1b	0.726 ^a	3	TBCHD	4b 80 5b 20	117 - 118 ^d 132 - 133	4.606, 3.847 s 3.874 s	1730, 1175 1652, 1160
1b	0.726 ^a	1.5	DCA	4b			
1c	1.065 ^f	8	TBCHD	4c 55 5a 40	247 - 248 ^g	6.459 s	1708, 1448
1c	1.065 ^f	2.5	DCA	4c ^e			
2	0.89 ^h	2	TBCHD	4d 48 5a 52	159 - 160 ⁱ	8.055 - 7.203 m	1738, 1444
2	0.89 ^h	1/2	DCA	4d 73% 5a 27%			

^aFrom cyclic voltammetry; see refs. 2 and 12.^bThe reaction with added TBABr (10^{-3} - 10^{-4} M) is not quenched.^cMinor quantities of 2-phenyl-2-benzoyl-1,3-dioxolane and 1,6-diphenyl-2,5,7,10-tetraoxabicyclo [4.4.0]decane have been also observed; see refs. 9 and 10.^dSee ref. 2.^eThe reaction products were characterized using 1H NMR.^fFrom cyclic voltammetry; platinum electrode, tetraethylammonium perchlorate (0.1 M) in MeCN versus SCE.^gSee ref. 13.^hThe reactions were carried out in acetonitrile-dichloromethane.ⁱSee ref. 14.



or synthesized samples (Table 1). DCA-sensitized photo-oxygenations on the same substrates were carried out simultaneously in order to compare the reaction rate and the products with those sensitized by TBCHD. The DCA-photosensitized oxidations of 1a, 1b, 1c and 2 are faster and they give, with the exception of 2, only the cleavage products 4a, 4b and 4c with no traces of the α -diketones 5a and 5b. On the contrary, the DCA-sensitized photo-oxygenation of 2 leads to 4d together with 5a.

3. Discussion

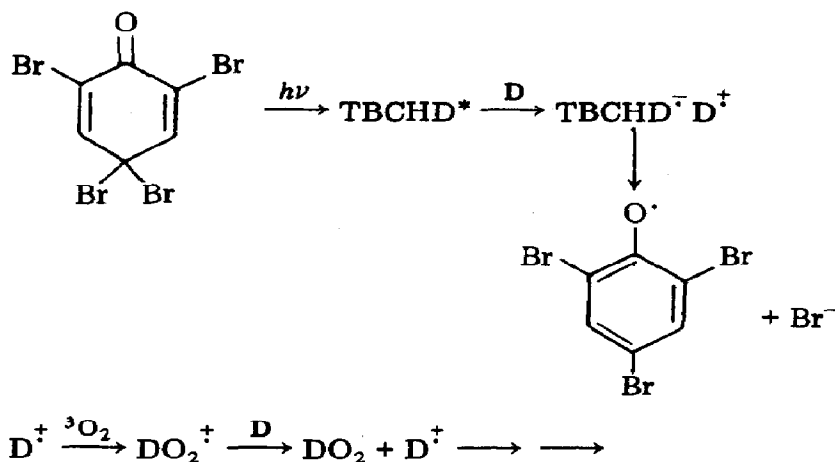
The feasibility of an electron-transfer process can be predicted on the basis of the simple equation derived by Knibbe *et al.* [15], in which the free energy change is calculated from the oxidation potential of the donor, the reduction potential of the electron acceptor, the singlet (triplet) energy of the excited acceptor and a coulombic term $e^2/a\epsilon$, *i.e.* the energy gained by bringing the two radical ions to an encounter distance a in a solvent of dielectric constant ϵ ($\epsilon = 0.06$ eV in CH_3CN) (eqn. (I)).

$$\Delta G \text{ (kcal mol}^{-1}\text{)} = 23.06(E(\text{D}/\text{D}^{\ddagger}) - E(\text{sens}^-/\text{sens}) - e^2/a\epsilon) - \Delta E_{0-0} \quad (I)$$

In this respect, cyclic voltammetry experiments on TBCHD show that it is reducible through an irreversible process at $E^{\text{red}} = 0.29 \text{ V(SCE)}$ at a platinum electrode in CH_3CN containing tetrabutylammonium tetrafluoroborate (TBABF_4) (0.1 M). This exceedingly low reduction potential together with its singlet excitation energy ($\Delta E_{0-0} = 2.94 \text{ eV}$) and the oxidation potential of the donors (1a, 1b, 1c and 2) substantiate that an electron-transfer process is compatible with the nature of our reagents. Furthermore, no superoxide anion can be formed in the medium, owing to the highly unfavourable electron transfer from the radical anion (TBCHD^-) to molecular oxygen (endothermic by 1.21 eV). On this basis, our conditions in the TBCHD-sensitized photo-oxygenations of 1a, 1b, 1c and 2 closely resemble the photo-oxygenation of *trans*-stilbene (TS) sensitized by methylene blue (MB^+) ($E^{\text{red}} = -0.25 \text{ V(SCE)}$) and the TCA-sensitized photo-oxygenation of DPA [4] in which no superoxide anion can be formed in the medium.

Anyway, our reaction proceeded readily compared with the examples cited above, leading to results similar to those obtained in the DCA-sensitized photo-oxygenations of the same substrates [2, 12].

In the light of our experimental results, we believe that the driving force operating under our conditions is the aromatization of the TBCHD^- radical anion, presumably into tribromophenoxy radical and bromide anion. This process, which frees the radical cation and/or reduces the extent of reverse electron transfer, allows the reaction of the radical cation with molecular oxygen through a radical cation chain mechanism (Scheme 3).

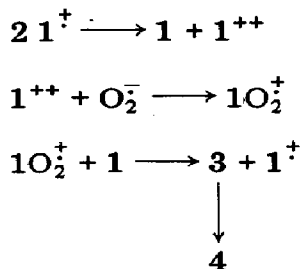


Scheme 3.

The voltammogram of TBCHD gives an insight into this mechanism. The irreversibility of the process is based upon the observations: (i) no oxidation wave for the radical anion (TBCHD^-) is observable; (ii) the reduction wave is extremely broad; (iii) the current function decreases significantly for each scan; (iv) the broad oxidation waves at $E_p = 0.67 \text{ V}$ and 0.93 V result from

the oxidation of bromide anion. (10^{-3} M tetrabutylammonium bromide (TBABr) in acetonitrile exhibits two peaks with $E_p = 0.67$ V and $E_p = 0.93$ V [16].) Furthermore, there is experimental proof to support this mechanism: (a) the TBCHD-photosensitized oxidation of 1a is not quenched by benzoquinone, which is a good quencher for superoxide anion [17], in contrast to what occurs in the DCA-sensitized photo-oxygenation of the same substrate where superoxide anion is involved [18]; (b) we can exclude the involvement of singlet oxygen, although all the listed substrates support a reaction with singlet oxygen [19], since substrates such as TS, DPA and many others which are totally unreactive towards singlet oxygen, readily react in the TBCHD-sensitized photo-oxygenation to give the expected carbonyl compounds [12]; (c) no reaction takes place after a long irradiation time in the absence of the electron acceptor; (d) the reaction of 1a carried out with added TBABr (10^{-3} - 10^{-4} M) is not quenched; (e) the action of TBCHD as an electron acceptor can also be substantiated in the thermal reaction of 1a, 1b and 1c in acetonitrile solution (10^{-2} M) with one equivalent of TBCHD to give the corresponding compounds 5a and 5b (yield, 95%) together with some byproducts such as *meso*-dihydrobenzoin (6) from 1c.

All these experimental results suggest that the α -diketones could arise from a different mechanism involving the dioxene cation radicals as key intermediates. Schaap and coworkers [2], in discussing the photo-oxidation of dioxenes in the presence of DCA as a sensitizer in terms of Foote's mechanism, suggested that even a chain mechanism involving disproportionation of the dioxene cation radicals was conceivable on the basis of thermodynamic considerations. The disproportionation of dioxene cation radicals could be substantiated by cyclic voltammetry studies since they show a second irreversible oxidation wave with a peak potential 0.2 - 0.5 V more positive than the half-wave potential for one-electron oxidation. Anyway, this thermodynamically supported mechanism could not be favoured kinetically.

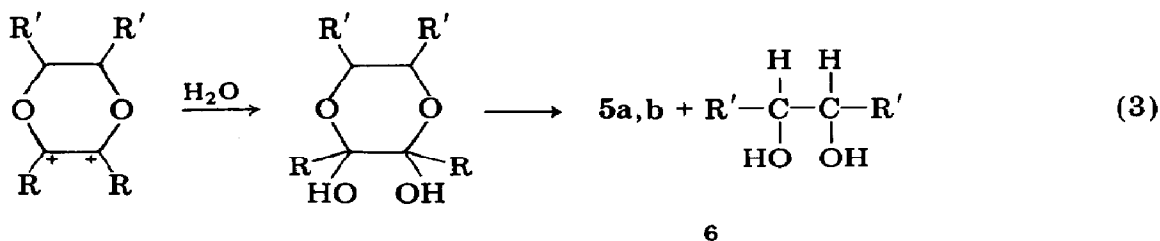


Scheme 4.

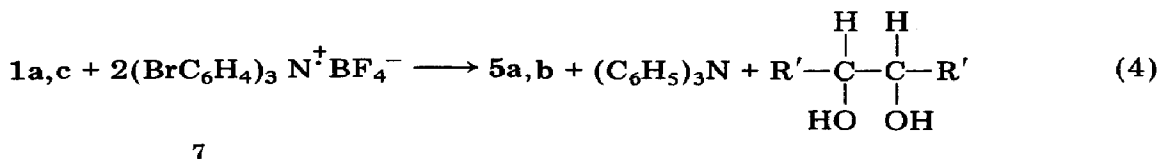
All our experimental results seem to confirm this conclusion. Therefore when the cation radicals find superoxide anion in the reaction medium in DCA-sensitized photo-oxygenations of 1a, 1b and 1c only the cleavage products (4a, 4b and 4c) can be formed. But this might not be so when the

same cation radicals react more slowly with molecular oxygen or when the delocalization prolongs the lifetime of the cation-radical DCA-sensitized photo-oxygenation of **2** making the disproportionation a viable mechanism.

In these cases the question arises: what is the fate of the dicationic species? In our opinion they give the corresponding α -diketones **5a** and **5b** through a fast reaction with traces of water, followed by fragmentation of the corresponding diacetals:



To confirm this mechanism we have recently provided clear chemical and spectroscopic evidence for disproportionation of dioxene cation radicals in the chemical oxidation of **1a**, **1b** and **1c** with *tris*-(*p*-bromophenyl)ammoniumyl tetrafluoroborate (**7**) [20]:



The stoichiometric requirement and the synthetic results, together with the spectroscopic evidence, strongly support the disproportionation mechanism.

Recent observations [21] on the DCA-sensitized photo-oxygenation of **2** and dioxenes show that *p*-benzoquinone exhibits a modest effect, as a superoxide anion quencher, which is not consistent with the exclusive involvement of O_2^- as the oxygen active species in this process.

4. Conclusions

Although the intermediate species formed during the TBCHD-sensitized photo-oxygenation of dioxenes and *p*-dioxin, such as radical cations and 1,2-dioxetanes, have not been characterized by ^1H NMR or chemiluminescence, we believe that our results can be rationalized on the basis of an electron-transfer mechanism between the excited electron acceptor (TBCHD*) and the donors, followed by the reaction of the radical cation with molecular

oxygen. Furthermore, the formation of α -diketones could be interpreted on the basis of a disproportionation mechanism for the intermediate radical cations. Studies on photosensitized and thermal oxidations of dioxin are in progress.

Acknowledgments

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