Pergamon

Tetrahedron, Vol. 53, No. 12, pp. 4469-4478, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00119-1

Photoinduced Electron Transfer Reactions of Benzyl Phenyl Sulfides Promoted by 9,10-Dicyanoanthracene

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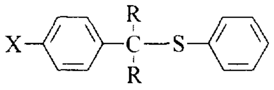
Abstract: The photoinduced oxidation of benzyl phenyl sulfides **1**-**3** has been investigated in MeCN using 9,10-dicyanoanthracene as sensitizer in the presence of O_2. In this reaction a sulfide radical cation is formed, which undergoes one or more of the three main reaction pathways opened to these species: C-S bond cleavage, C-H bond cleavage and S-oxidation. The former route (leading to benzylic products) was observed with all the substrates investigated, whereas the second (leading to benzaldehydes) operates only with **1** and **2**. Formation of sulfoxides was found solely in the photooxidation of **1**. The influence of substrate structures on the relative contribution of the three pathways as well as the role of $O_2^{\cdot-}$ in this respect are discussed. © 1997 Elsevier Science Ltd.

The study of one electron oxidations of sulfides is of relevant interest since it provides information on the three main reaction paths of sulfide radical cations: a) α-C-H bond deprotonation; b) C-S bond cleavage; c) S-oxidation to sulfoxides.[1] Apart from the theoretical and practical aspects, such information is also important with respect to the determination of the actual role played by sulfide radical cations in the biochemical oxidation of sulfur containing compounds.[2]



1 X=H, R=H
2 X=OCH_3, R=H
3 X=H, R=CH_3

Recently, we have studied the electrochemical oxidation of a number of benzyl phenyl sulfides under a variety of conditions[1a] with the aim of acquiring information about the solvent and structure effects upon the competition between the above three reaction routes. In an extension of this investigation, we now report on the photooxidation of benzyl sulfides **1-3** sensitized by 9,10-dicyanoanthracene (DCA) in the presence of oxygen. DCA in its singlet excited state is a relatively strong oxidant (E° ca 2.0 V *vs* SCE)[3] and it should therefore be able to convert the sulfides **1-3** (E° ca 1.6 V *vs* SCE)[4] into the corresponding radical cations, with formation of $DCA^{\cdot -}$. The latter reacts with O_2 to produce ground state DCA and $O_2^{\cdot -}$,[6] thus suppressing the energy wasting back electron transfer (eqs 1-4).

$$\mathrm{DCA} + h\nu \longrightarrow \mathrm{DCA}^{*} \qquad (1)$$

$$\mathrm{DCA}^{*} + \mathrm{ArSR} \longrightarrow \mathrm{DCA}^{\cdot -} + \mathrm{ArSR}^{\cdot +} \qquad (2)$$

$$\mathrm{DCA}^{\cdot -} + O_2 \longrightarrow \mathrm{DCA} + O_2^{\cdot -} \qquad (3)$$

$$\mathrm{DCA}^{\cdot -} + \mathrm{ArSR}^{\cdot +} \longrightarrow \mathrm{DCA} + \mathrm{ArSR} \qquad (4)$$

So far the photochemical oxidation of organic sulfides under homogeneous conditions has been little investigated[7] and moreover the studies with the DCA/O_2 system were limited to dialkyl and diaryl sulfides which when converted to radical cations exhibited only reaction at sulfur by $O_2^{\cdot -}$.[6] Thus, we expected that our study would provide us with interesting information concerning the possibility that in $\mathbf{1}^{+\cdot}$ - $\mathbf{3}^{+\cdot}$, α-C-H deprotonation and C-S bond cleavage compete with sulfoxide formation and on the role of $O_2^{\cdot -}$ and O_2 on the competition between these reaction pathways.

RESULTS AND DISCUSSION

Photolysis experiments were performed at 40 °C (see experimental), by external irradiation (Pyrex filter) of a solution (5×10^{-3} M) of sulfides **1-3** and (5×10^{-4} M) of DCA in CD_3CN saturated with oxygen, in a Rayonet photoreactor. Irradiation time was 15 min for **1** and **2** and 40 min for **3**. Photoreaction products were identified by ^{1}H-NMR and GC-MS (comparison with authentic specimens). Product yields were determined by ^{1}H-NMR and GLC in the presence of an internal standard. All results are reported in Table 1.

In the oxidation of **1** the products observed are benzyl phenyl sulfoxide, benzaldehyde, N-benzylacetamide, benzyl benzenesulfonate, diphenyl disulfide and benzenesulfonic acid, thus clearly indicating that the intermediate radical cation $\mathbf{1}^{+\cdot}$ not only undergoes oxidation at sulfur, but also C-S and C-H bond cleavage.

Table 1. Product Formed in the DCA Sensitized Photolysis of sulfides **1-3**

Substrate	Products (yields %)^a		
1	PhCHO (37)	PhNHCOCD$_3$ (17)	PhCH$_2$SOPh (12)
	PhCH$_2$OSO$_2$Ph (9)	PhSSPh (8)	PhSO$_3$H ^{c}
2	4-OCH$_3$PhCHO (35)	4-OCH$_3$PhCH$_2$NHCOCD$_3$ (34)	
	PhSSPh (14)	PhSO$_3$H ^{c}	
2^b	4-OCH$_3$PhCHO (44)	4-OCH$_3$PhCH$_2$NO$_3$ (43)	
	PhSSPh ^{c}	PhSO$_3$H ^{c}	
3	PhC(CH$_3$)$_2$OH (19)	PhC(CH$_3$)=CH$_2$ (11)	PhCOCH$_3$ (16)
	PhSSPh (6)	PhSO$_3$H ^{c}	

[a] Yields, where determined, are referred to the substrate. Average of at least two determinations. The error is ± 10%.

[b] In the presence of Bu$_4$NNO$_3$ (5×10^{-3}M).

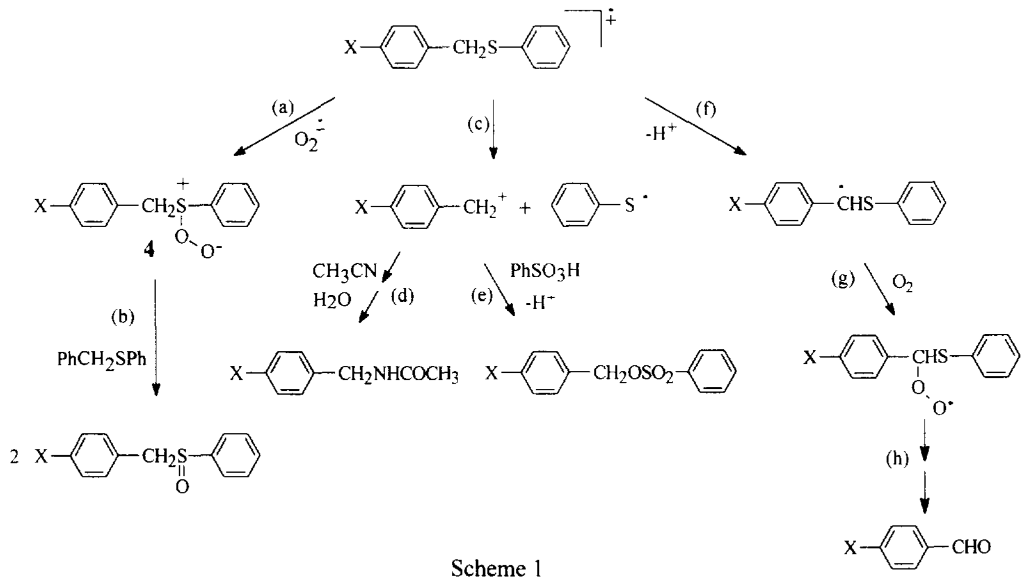
[c] Yield not determined.

The sulfoxide is probably formed by the mechanism already proposed for the DCA photosensitized oxidation of dialkyl and diaryl sulfides: reaction of the radical cation with the superoxide anion, leading to the formation of a persulfoxide intermediate (**4**) that is presumably able to oxidize another sulfide molecule to sulfoxide (Scheme 1, X=H, paths a-b).[6,8] The intervention of singlet oxygen can be excluded since it has been shown that in the DCA promoted photooxidation, formation of sulfoxide is not quenched by β-carotene.[6a,c]

The benzylic products, N-benzylacetamide and benzyl benzenesulfonate should derive from the C-S bond cleavage in $\mathbf{1}^{+\bullet}$; the former product is almost certainly formed by reaction of the benzyl cation with a solvent molecule followed by hydrolysis with traces of water present in the medium (Scheme 3, paths c-d). For the formation of the second product, it can be suggested the reaction of the same cation with benzenesulfonic acid, deriving from the O_2 or $O_2^{-\bullet}$ promoted oxidation of the sulfur containing species also produced in the C-S bond cleavage pathway (phenylthyil radical and its dimerization product, diphenyl disulfide).[9] In line with this suggestion, we found that benzyl benzenesulfonate is also formed in the solvolysis of benzyl chloride in MeCN, in the presence of benzenesulfonic acid.

The formation of benzaldehyde is most probably due to the deprotonation of the radical cation. An α-thiophenoxy carbon radical is formed, which can react with O_2 to give a peroxy radical whose conversion to benzaldehyde can easily be envisaged (Scheme 1, X=H, paths f-g-h). Very likely, the deprotonation of the radical cation is promoted by $O_2^{-\cdot}$, a relatively strong base in MeCN.[10] Accordingly, when $\mathbf{1}^{+\cdot}$ was generated electrochemically in the same solvent, no product deriving from the deprotonation of the radical cation was observed, but only sulfoxide and products of C-S bond cleavage.[1a] This conclusion is in line with recent evidence indicating an important role of $O_2^{-\cdot}$, in the photooxidation of 9,10-dihydroanthracene sensitized by DCA.[12] It might also be suggested that benzaldehyde is derived by the intramolecular α-C-H deprotonation of **4** (the intermediate leading to sulfoxide) as proposed in the singlet oxygen induced oxidations of benzyl sulfides.[13] However, we feel that this possibility is not likely in our case since we observe α-C-H deprotonation also in the photooxidation of **2**, a reaction where no sulfoxide is formed (vide *infra*). Moreover, the base induced deprotonation of benzyl sulfides radical cation is an important reaction also in the absence of oxygen.[1b, 14] Interestingly, no α-C-H deprotonation of the radical cation was observed in the photooxidation of dialkyl sulfides promoted by DCA/O_2, which, as mentioned above, produced only sulfoxides and sulfones.[6a] Reasonably, this can be attributed to the low acidity of the α-C-H bonds in the radical cations of these substrates relatively to that of the benzylic C-H bonds in $\mathbf{1}^{+\cdot}$.

Quite surprisingly, whereas very effective as deprotonating species, $O_2^{-\cdot}$ appears to be a quite weak nucleophile in the reaction at sulfur leading to sulfoxide. Accordingly, the relative amounts of sulfoxide and C-S bond cleavage products are about the same in the electrochemical and in the photochemical oxidation. In the electrochemical oxidation, it was suggested that sulfoxide is formed by reaction of the radical cation with $LiClO_4$, the supporting electrolyte.[1a]



Scheme 1

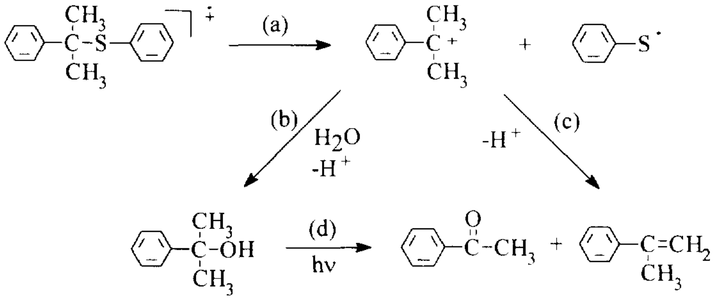
When **2** is the substrate, the same kind of products are formed as with **1**, with the exception of 4-methoxybenzyl phenyl sulfoxide and 4-methoxybenzyl benzenesulfonate.

Absence of sulfoxide was also observed in the electrochemical oxidation of **2**,[1a] and, on the basis of PES experiments, it was suggested that in $\mathbf{2}^{+\cdot}$, differently than in $\mathbf{1}^{+\cdot}$, the SOMO should be mostly localized on the methoxy substituted aromatic ring and not in the sulfur atom.[15] Practically no positive charge should reside on the sulfur atom, thus making path a in Scheme 1 very unlikely, when X=MeO. This explanation could of course also account for the no formation of sulfoxide in the photochemical oxidation of **2**. However, PES experiments are in gas phase and things might go differently in solution. Thus, another possibility is that in $\mathbf{2}^{+\cdot}$ the competing C-H and C-S bond cleavage processes are faster than in $\mathbf{1}^{+\cdot}$ so as to completely overcome path a in the former case.[16]

N-(4-methoxybenzyl)acetamide is formed from $\mathbf{2}^{+\cdot}$ by the C-S bond cleavage and reaction of the benzyl carbocation with the solvent pathway (Scheme 1, paths c-d, X=MeO). As already mentioned, 4-methoxybenzyl benzenesulfonate is not present among the reaction products. A reasonable explanation is that this product undergoes a very fast solvolysis (much faster than with benzyl sulfonate) to acetamide, under the reaction conditions (see Experimental). Interestingly, when the photooxidation of **2** was carried out in the presence of NO_3^-, a much better nucleophile than MeCN, N-(4-methoxybenzyl)acetamide was completely replaced by 4-methoxybenzyl nitrate in the reaction products. However, the ratio between 4-methoxybenzyl nitrate and 4-methoxybenzaldehyde was practically the same (*ca* 1) as that between N-(4-methoxybenzyl)acetamide and 4-methoxybenzaldehyde observed in the photooxidation carried out in the absence of NO_3^-. From this result a very important conclusions can be drawn: the C-S bond cleavage does not require any nucleophilic assistance, otherwise the presence of NO_3^- would have increased contribution of this pathway relatively to the deprotonation route. This conclusion fully confirms the findings of previous work.[1b] In addition, it can also be excluded that 4-methoxybenzylalcohol is also formed, by reaction of the carbocation with adventitious water present in the medium, but it is immediately oxidized to 4-methoxybenzaldehyde under the reaction conditions (see Experimental). Accordingly, in this case too we would expect that the benzylic product/benzaldehyde molar ratio significantly increases when the reaction is carried out in the presence of NO_3^-, due to the fact that the carbocation should be preferentially captured by this anion (present in large amounts) rather than by traces of water.

The formation of 4-methoxybenzaldehyde can again be rationalized, by suggesting the deprotonation of $\mathbf{2}^{+\cdot}$ (Scheme 1, X= MeO, path f). Paths g, h then follow leading to 4-methoxybenzaldehyde. The fundamental role of $O_2^{-\cdot}$ is very clear also in this case since no deprotonation products were observed in the electrochemical in Table 1, it can also be observed that the ratio aldehyde/benzylic products is higher in the oxidation of **1** than of **2**, in agreement with expectations, since the introduction of the ring methoxy group increases the stability of the carbocation formed in the C-S bond cleavage pathway. Relatively to the deprotonation route this pathway should therefore be more important in $2^{+\cdot}$ than in $1^{+\cdot}$. This effect is, however, quite small suggesting that in the transition state of the C-S cleavage no much charge has been transferred to the benzylic carbon atom. Another possibility is that, as mentioned before, the charge distribution in $1^{+\cdot}$ and $2^{+\cdot}$ might be significantly different (most of the charge on sulfur for $1^{+\cdot}$ and on the methoxy substituted ring for $2^{+\cdot}$) so making invalid a comparison between the properties of the two radical cations in this respect.

The irradiation of **3** leads to the formation of 2-phenyl-2-propanol, α-methylstyrene, acetophenone, diphenyl disulfide and benzenesulfonic acid. These products are also rationalised on the basis of the formation of $3^{+\cdot}$, which can, however, follow a unique fragmentation pathway: C-S bond cleavage. A cumyl cation and a phenylthyil radical are formed (Scheme 2, path a), the latter species producing diphenyl disulfide and benzenesulfonic acid, as previously described.



Scheme 2

Preferential reaction of the cumyl cation with adventitious water present in the medium forms 2-phenyl-2-propanol and probably this high selectivity (N-(2-phenyl-2-propyl)acetamide was not observed even though this compound is quite stable under the reaction conditions both in the absence and in the presence of **3**) is due to the high stability of the tertiary benzyl carbocation. Acetophenone and α-methylstyrene are suggested to derive by photolysis of 2-phenyl-2-propanol, under the reaction conditions, as shown by appropriate control experiments (Scheme 2, path d, see experimental). However, at least in part, α-methylstyrene might also be formed by deprotonation of the cumyl cation (Scheme 2, path c).

Finally, a noteworthy result is that no sulfoxide was formed in the DCA photosensitized oxidation of **3**, even though there is little doubt that in $3^{+\cdot}$ the SOMO should be localized on the sulfur atom, like in $1^{+\cdot}$. Thus, the only reasonable explanation is that in $3^{+\cdot}$, the C-S bond cleavage path occurs at a rate much faster than in $1^{+\cdot}$, so that in the former case the process leading to sulfoxide cannot compete.

CONCLUSIONS

The three main reaction paths of sulfide radical cations (α-C-H deprotonation, C-S bond cleavage and S-oxidation) have clearly been observed in the photooxidation of sulfides **1-3** sensitized by DCA in the presence of oxygen. The former path leads to benzaldehyde, the second to benzylic derivatives and the third to sulfoxide. The presence of $O_2^{-\cdot}$ (formed in the reaction between $DCA^{-\cdot}$ and O_2) appears to exert a fundamental role in promoting the deprotonation process of the radical cations $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$. Accordingly deprotonation was not observed when the same radical cations were generated electrochemically in the same solvent.[1a] In contrast, the reaction between the radical cation and $O_2^{-\cdot}$ leading to sulfoxide, does not seem to be a very effective process relatively to the other pathways. For example, with $\mathbf{3}^{+\cdot}$, only products deriving from C-S bond cleavage form, which indicates that the rate of this path is much faster than the sulfoxide forming reaction. When the photooxidation of **2** was carried out in the presence of NO_3^-, 4-methoxybenzyl nitrate completely replaced 4-methoxybenzylacetamide in the reaction products, but the ratio between aldehydic and benzylic products remained practically the same as in the absence of NO_3^-. This indicates that no nucleophilic assistance is required for the C-S bond cleavage path in the radical cation.

EXPERIMENTAL SECTION

Methods. ^{1}H-NMR spectra were recorded on a Bruker WP80SY and a Bruker AC300P spectrometers in $CDCl_3$ and CD_3CN. UV-vis spectra were recorded on a Cary1 spectrophotometer. GC-MS analyses were performed on a HP5890 GC (OV1 capillary column, 12m x 0.2 mm) coupled with a HP5970 MSD. GLC analyses were performed on a Varian 3400 GC (OV1 capillary column, 25m x 0.2mm) and Varian Vista 6000 (OV1701 capillary column, 30m x 0.35 mm). Photochemical experiments were performed by external irradiation in a Rayonet photoreactor, with a bank of 16x24W black light phosphor lamps (centre of emission 360 nm, range of emission 340-380 nm).

Starting Materials. CH_3CN (CARLO ERBA-HPLC grade) was used as obtained or distilled over P_2O_5 and then over K_2CO_3. Tetrabutylammonium nitrate (Fluka) was used as received. Commercial benzyl phenyl sulfide was further purified by recristallizzation from $EtOH/H_2O$. 4-Methoxybenzyl phenyl sulfide was prepared by reaction of 4-methoxybenzyl chloride with thiophenol as previously described.[5,17] 2-Phenyl-2-propyl phenyl sulfide was obtained by acid-catalysed addition of thiophenol on α-methylstyrene.[18] 9,10-Dicyanoanthracene (DCA, KODAK) was purified by recrystallization from CH_3CN.

Photochemical reactions. A solution of DCA ($5x10^{-4}$ M), the substrate **1-3** ($5x10^{-3}$ M) in CD_3CN (5 ml), contained in a Pyrex vessel, was capped with a rubber septum, fluxed with molecular oxygen and irradiated without cooling at the instrumental operating temperature (40 °C) in a Rayonet photoreactor. With **2** the irradiation was carried out also in the presence of *n*-Bu_4NNO_3 ($5x10^{-3}$ M). After irradiation for 15 min (**1** and **2**) or 40 min (**3**), an internal standard was added and the raw photolysate was analyzed by GC-MS and ^{1}H-NMR. Quantitative analysis of reaction products were performed by GLC and ^{1}H-NMR by using an internal standard. A good material balance was obtained in all experiments (>80 %). In the absence of DCA, control experiments, showed no significant photolysis of the substrates.

Reaction Products. All products formed in the photochemical oxidations with DCA of compounds **1-3** were identified by comparison with authentic specimens. Benzaldehyde, benzenesulfonic acid, N-benzylacetamide, diphenyl disulfide, 4-methoxybenzaldehyde, N-(4-methoxybenzyl)acetamide, acetophenone, 2-phenyl-2-propanol, α-methylstyrene, benzyl phenyl sulfoxide and 4-methoxybenzyl phenyl sulfoxide were commercial products or were available from previous works.[1a,5] Benzyl benzenesulfonate was prepared by treating silver benzenesulfonate in dried CH_3CN with benzyl bromide, recrystallized from ether and stored at low temperature.[19] N-(2-Phenyl-2-propyl)acetamide was prepared by reaction of α-methylstyrene with MeCN in the presence of benzenesulfonic acid in glacial acetic acid.[20]

Stability of Photoproducts. The following reactions were performed to determine the stability of some of the reaction products or possible primary photoproducts.

4-Methoxybenzylalcohol. This alcohol exhibited no reactivity when irradiated in the presence of DCA and O_2. However, when a solution of this compound ($8x10^{-4}$ M) and of DCA ($5x10^{-4}$ M) was irradiated in the presence of **2** ($5x10^{-4}$ M), the alcohol was completely oxidized to 4-methoxybenzaldehyde. Clearly, the sulfide acts as an efficient cosensitizer.

2-Phenyl-2-propanol. A solution of this compound ($7x10^{-3}$ M), and of DCA ($5x10^{-4}$ M) in the presence of **1** ($5x10^{-3}$ M, this sulfide was added as mimicking the possible effects of **3** in the photoinduced decomposition of the alcohol) in CD_3CN, was irradiated following the standard procedure. The alcohol was partly converted into α-methylstyrene (40 %) and acetophenone (30 %).

N-(2-phenyl-2-propyl)acetamide. No reaction was observed when a solution of the amide ($2x10^{-3}$ M) and DCA ($5x10^{-4}$ M) in CD_3CN, was irradiated in the absence or in the presence of **3** ($1.5x10^{-2}$ M).

4-X-Benzyl benzenesulfonates (X = H, OCH_3). A solution of 4-X-benzylchloride (0.1 M) in CH_3CN was treated with benzenesulfonic acid (0.1 M) in the presence of Ag_2SO_4 (0.05 M) at 40 °C for 2 h. With benzylchloride the main product (80 %) observed was benzyl benzenesulfonate; with 4-methoxybenzylchloride the substrate was almost completely converted into N-(4-methoxybenzyl)acetamide.

Acknowledgements. Thanks are due to the Ministry for the University and the Scientific and Technological Research (MURST) and to the National Research Council (CNR) for financial support.

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(*Received in UK* 16 *December* 1996; *revised* 29 *January* 1997; *accepted* 30 *January* 1997)