Explorative and Mechanistic Studies of the Photooxygenation of Sulfides

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The results of recent work on the dye-sensitized photooxygenation of sulfides is discussed. In the case of dialkyl sulfides, the weakly bonded adduct initially formed with singlet oxygen (the persulfoxide) decays unproductively unless protonation by an acid (an alcohol or a carboxylic acid) facilitates its conversion to the sulfoxide. The effect is proportional to the strength of the acid (*eg.*, less than 0.1% chloroacetic acid in benzene is sufficient for maximal efficiency) and corresponds to general acid catalysis, suggesting that protonation of the persulfoxide occurs. On the other hand, with sulfides possessing an activated hydrogen in α position (*eg.*, benzyl and allyl sulfides), hydrogen transfer becomes an efficient process in aprotic media and yields a *S*-hydroperoxysulfoniumm ylide, possibly arising from a conformation of the persulfoxide that is different from the one protonated in the presence of acids. Calculations on some substituted sulfides support this hypothesis. This process, which leads to C–S bond fragmentation with formation of an aldehyde, may be viewed as a general method for the preparation of aryl and heteroaryl aldehydes. In this effort, mechanistic studies offered new hints on the structure of the intermediate persulfoxide.

key words: photooxygenation, sulfides, persulfoxide, oxidation, acid catalysis

INTRODUCTION

The oxidation of sulfides is field of continuing interest, in view of the many mechanistic implications and of the significance both for biological systems and for organic synthesis [1-5]. We have been involved since some years in a work on the field, and in particular, as it is traditional in our research, in the photoinduced oxidation. The work has been concerned with various mechanisms of photooxidation, but at the moment the side that we have most developed, and in fact has been much more extensively investigated in the literature, is the dye-sensitized reaction via singlet oxygen.

Sulfides have a peculiar role in the reaction with singlet oxygen. With a rough simplification, we may subdivide the reactions of organic molecules with $^1O_2$, a strong electrophile and an oxidant, in two groups, electrophilic addition, with its various concerted versions, and single electron transfer. The ene reaction with alkenes is an example of the first group, while the electron transfer interaction with amines, which finally leads to physical quenching, not to chemical reaction (eq. 1), is a typical case for the second group.

$$R_3N + {}^1O_2 \rightarrow (R_3N^{\delta+} \cdots O_2^{\delta-}) \rightarrow R_3N + O_2 \qquad (1)$$
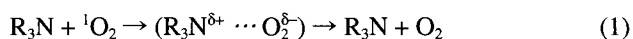
Thus, with alkenes, formation of the initial adduct, the perepoxide, leads to the final products through a path complex and perhaps controversial, but at any rate with little dissociation to the components, while with amines no bonded intermediate

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is formed and there is no room for chemical reaction.

Sulfides are in an intermediate position. They are not sufficiently good donors for entering in a charge transfer path, but at the same time the S-O bond they form in the primary adduct is no strong bond. As a result, they show the uncommon characteristics of a *high-* and, as it generally happens with singlet oxygen, solvent-independent – *total rate* for quenching, but a *low-* and unusually highly solvent-dependent – *rate for chemical reaction*.

The current rationalization for this peculiar behavior is based on the properties of the first formed adduct, the persulfoxide (**1** in Figure 1), for which there is practically no direct experimental evidence. This intermediate, contrary to the perepoxide from alkenes, is, as hinted above, very weakly bonded and in solvents such as benzene or acetonitrile for the most part decays to the components (k_d in the Figure). However, it behaves like a nucleophile and its role can be indirectly assessed by oxygen transfer to sulfoxides. A fraction of the persulfoxide rearranges (k_x) to a second intermediate, that behaves like an electrophile and transfers oxygen to sulfides, and for which a thiadioxirane (**2**) structure has been considered.

On the other hand, in methanol the reaction is much more efficient and involves a single intermediate (quenched by both sulfides and sulfoxides), for the structure of which either a hydrogen bonded complex of the persulfoxide (**3**) or an alkoxyhydroperoxysulfide (**3′**) have been proposed. This intermediate arises again via the persulfoxide and leads to a much more efficient conversion of the sulfide to the sulfoxide. This mechanism is based on a kinetic study by Foote and further extensive experimental investigations by Foote and by
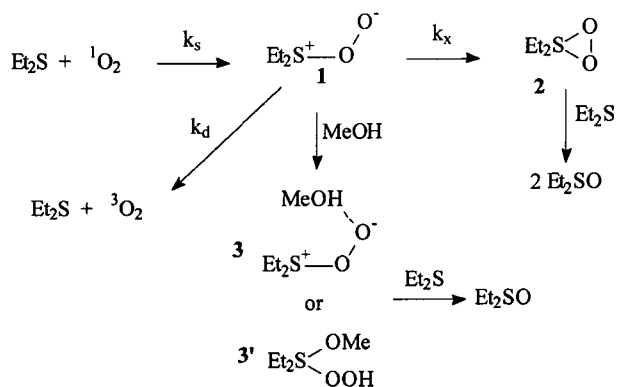
Figure 1.

Clennan [6-8].

Recent computational work by Jensen *et al.* [9] and by McKee [10] supports the role of the persulfoxide (1) – though of insignificant stability – while disfavoring the structure of thiadioxirane (2) for the second intermediate. Another possible conversion of the persulfoxide seems to be that to a sulfonium ylide (structure 4).
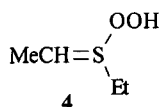

Figure 2.

The equally interesting electron transfer photooxidation of sulfides has been at the moment less extensively investigated, but Baciocchi [11] showed that such a pathway occurs in the photosensitization of phenyl sulfides when using cyanoaromatics. The electron transfer path may be also relevant as a model for the biochemical oxidation.

In the frame of our interest for photooxidation processes, we became interested in this field. The themes of this ongoing study are on one hand a reconsideration of some aspects of the singlet oxygen process, in particular of sulfides that differ in reactivity from the extensively studied alkyl sulfides, as well as of the conditions that may increase the efficiency of the oxidation, and on the other the comparison of the singlet oxygen with the electron transfer oxygenation. The main results obtained at the moment are summarized in the following.

DISCUSSION

Effect of proticity on the photooxygenation of dimethyl sulfide

One of the questions we confronted was the effect of alcohols on the dye-sensitized photooxidation of diethyl sulfide [12]. As mentioned above, the reaction is much more efficient in methanol and appears to involve a different intermediate. In this solvent, the oxidation occurs with close

to unitary efficiency, viz almost two moles of sulfoxide are formed for every mole of singlet oxygen quenched. This does not require using neat alcohol as the solvent. Clennan showed that the addition of 1.5% methanol to benzene leads to a 10-fold increase of the rate of photooxidation [13]. The question is, which is the effect of alcohols on the reaction, and reasonably on the first-formed intermediate, the persulfoxide. This is an important point because the constancy of the overall quenching rate fits with the idea that a weakly bonded adduct (the persulfoxide) is formed with a medium-independent efficiency (k_s in Figure 1) and then the alcohol prevents its decay to the components. Investigations by Clennan, mainly based on intramolecular reactions, substantiated the hypothesis that the alcohol adds to the persulfoxide formig an alkoxyhydroperoxysulfide. However, the same author extended the study to different alcohols, used as cosolvents in benzene, and found that their effect was not related to their nucleophilicity, with trifluoroethanol having a stronger activating effect than non-fluorinated alcools. This led him to suggest a concerted addition, in which protonation of the oxygen atom and nucleophilic addition to the sulfur atom both had a role (see structure 5) [13].
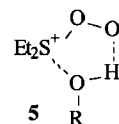

Figure 3.

We extended the study to protic additives different from alcohols and to different solvents and found that much smaller amounts (<0.05 M) of carboxylic acids caused the same increase in the rate of formation of sulfoxides [12].

If k_H is the rate constant of the additive-induced path (Figure 4) and the other constants are as defined in Figure 1, the concentration of sulfoxide formed in a given irradiation time is provided in equation (2), where K is the amount of singlet oxygen formed in that time, a quantity that does not change significantly in the media tested as we checked by carrying out the oxidation of octaline under the same conditions.

$$[Et_2SO] = K \frac{k_s[Et_2S]}{k_d + k_s[Et_2S]} \frac{2k_x + 2k_H[HA]}{k_x + k_q + k_H[HA]} \tag{2}$$

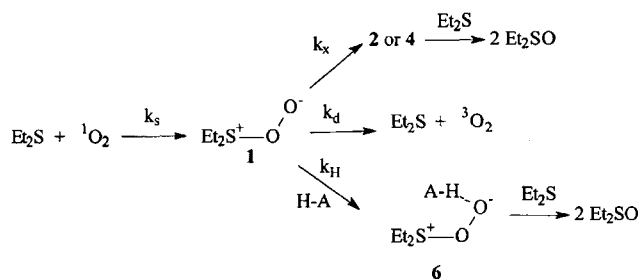With the small amounts of additives we used, k_s and k_d also

Figure 4.

Table 1. Increase in the rate of photooxygenation of diethyl sulfide in the presence of protic additives in various solvents, as evaluated through the ratio k_H/k_q (see Eq. 4)

Additive	k_H/k_q, M		
	in benzene	in acetone	in acetonitrile
CH_2ClCO_2H	1200	250	950
CH_3CO_2H	420	26	39
m-$O_2NC_6H_4OH$	410	18	
CF_3CH_2OH	43	0.65	3.8
CH_3OH	3.6	0.03	0.3
H_2O		0.06	0.6

do not change and the above expression leads to equation (3) in reciprocal form.

$$[Et_2SO]^{-1} = (1/K')^{-1} \frac{k_x + k_q + k_H[HA]}{2k_x + 2k_H[HA]} \qquad (3)$$

By further considering that the observed increase in oxygenation is large, viz $k_H[HA] \gg k_x$, the expression reduces to the simple form below (Eq. 4).

$$[Et_2SO]^{-1} = (\tfrac{1}{2}K')^{-1}(1 + (k_q/k_H[HA]^{-1})) \qquad (4)$$

We observed indeed the predicted linear doubly reciprocal plots of the yield of sulfoxide versus the additive concentration. The intercept vs slope ratio in such plots is k_H/k_q and the values obtained in benzene are reported in Table 1, where it is apparent that they depend on the acidity of the additive.

Extension of the study to methanol and acetone as solvent in the place of benzene showed that also in this case a similar dependence applied. Logarithmic correlation of the k_H/k_q values vs the gas phase acidities ($\Delta G°$) of the additives followed linear correlations with slope -0.06, -0.078, and -0.093 for benzene, acetonitrile and acetone, respectively. Since there is no reason to expect that the persulfoxide decay rate (k_q) changes significantly upon addition of the small amounts of additives used, the data can be taken to be proportional to k_H. These span over three orders of magnitude for a change of 70 kcal/mol in the $\Delta G°$ scale, corresponding to ca. 15 pK_a units.

The simplest rationalization of these results is that the activation of persulfoxide is due to hydrogen bonding. The persulfoxide is a mesomeric zwitterion, but shows some basic character on the outer oxygen. As seen above, the k_H/k_q vs $\Delta G°$ plot exhibits a small slope, consistently with the idea that hydrogen bonding is weak and/or reversible. The hydrogen-bonded persulfoxide (6 in Figure 4) is involved in a fast equilibrium with the solvent-proton donor complex (Solvent $\cdots$ H, notice that the slope appears to depend on the solvent basicity), and the equilibrium is shifted progressively when passing from a weak acid such an alcohol to a stronger one such as chloroacetic acid.

In order to further characterize the action of the acid, we studied the co-photooxgenation of diphenylsulfoxide. As demonstrated by Foote [6], this compound is insensitive to singlet oxygen, but is co-oxidized in the presence of diethyl sulfide and the ratio $[Et_2SO]/[Ph_2SO_2]$ is linearly dependent on $[Ph_2SO]^{-1}$ both in benzene and in methanol, though with different slopes.

We carried out a similar study in benzene containing 0.05 M acetic acid, viz under conditions where the oxidation of diethyl sulfide proceeds completely via the acid activated mechanism, and found again a linear behavior, with a slope of 0.16 which is closer to the value in methanol than to that in benzene. This further strengthens the proposed model, since hydrogen bonding of the persulfoxide enhances the electrophilic character of the sulfur atom and makes formation of a cyclic adduct (structure 7), and from this of the two co-oxidized products, easier (see Figure 5).
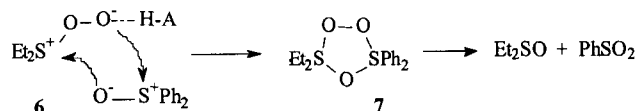

Figure 5.

Thus, we feel that general acid catalysis operates on the photooxygenation of diethyl sulfide and is due to hydrogen bonding with the persulfoxide. Under these conditions, the oxidation proceeds efficiently, with limiting quantum yield for formation of the sulfoxide equal to 2 (since $k_H[HA] \gg k_x$ +k_q, and the observed rate of oxidation coincides with $2k_s$), thus overcoming the limitation that the 'spontaneous' reaction of the persulfoxide to give the sulfoxide (k_x) is slow. The advantage of reaching this value by using a small amount (0.1% or less) of a strong acid rather than carrying out the reaction in a neat alcohol, is that the method is now much more flexible, and one can avoid other effects of that medium that may be undesirable under certain circumstances, such as nucleophilicity.

A question that we are now confronting is whether a similar effect extends to further sulfides. With non branched dialkyl sulfides such as diethyl sulfide k_s is high (in the order of 10^7 $M^{-1}s^{-1}$) and the problem is that, as discussed above, unproductive decay of the persulfoxide to the components overcomes chemical reaction ($k_q \gg k_x$). However, with branched alkyl sulfides, e.g. di-$tert$-butyl sulfide, and with diaryl sulfides, the quenching of singlet oxygen (k_q) becomes low and the reactivity is probably still lower, so that such substrates are often considered stable to singlet oxygen. This makes it more interesting to 'catalyze' the photooxygenation in order to explore whether, under suitable conditions, reluctant substrates can undergo preparatively useful photooxygenations. The first results we have in the field support this view. It may be interesting to note that there are only a few cases of catalysis in organic photochemical reactions, and, as we pointed out
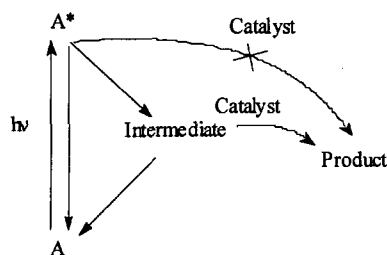
Figure 6.

some years ago [14], virtually all of these do not involve an interaction of the catalyst with the excited state. This can be often justified for kinetic reasons because the catalyst is present in a low concentration, and the steady state concentration of the short-lived excited state is obviously minimal. Greater possibilities exist for activating a high-energy, ground state intermediate which is likely to be longer lived and could otherwise decay unproductively (see Figure 6).

Here, the persulfoxide intermediate must decay with a rate constant equal or lower than 1×10^7 s^{-1}, considering that it is quenched by chloroacetic acid at very low concentrations (for this acid $k_H/k_q = 1.2 \times 10^3$ M) and is not necessarily longer-lived that the relevant excited state, singlet oxygen. Nevertheless, also in this case the acid seems effective in activating the intermediate by transforming the weak bond formed in the singlet oxygen attack to the sulfide in a strong bond, whereas it has certainly no effect on singlet oxygen itself. This is a point that possibly merits further elaboration. At any rate, the catalytic effect is useful for the mechanistic point of view (it affords indirect evidence for an intermediate that is not otherwise detected, apparently due to unfavorable spectroscopic characteristics rather than for a short lifetime), and of course for directing the reaction in view of preparative applications.

Photooxygenation of benzyl sulfides

In what has been presented up to now there is no variation in the chemical reaction, and indeed the photooxygenation of dialkyl (as well as aryl alkyl) sulfides leads, though with quite different efficiency, to a single chemical product, the sulfoxide. Variable, but generally low, amounts of sulfone are formed, and this may be an indication that a different path operates in some cases (obviously referring to low conversion experiments, where further oxidation of the sulfoxide is insignificant). Thus, any inference on the mechanism must be limited on variations on the rate of reaction, not on a change in the chemical path followed. More clear evidence may be obtained where a different chemistry takes place. In this sense a report by Corey and Ouannès from 1976 is interesting [15]. They reported that dye-sensitized oxygenation of some benzyl sulfides yields benzaldehyde. Further investigations on benzyl sulfides or related substrates such as fluorenyl sulfides and thiazolidines have followed, but the scope of the reaction and its mechanism have not been fully clarified [16].

We therefore studied benzyl ethyl sulfide and a number of

related substrates [17]. This compound exhibits a solvent-dependent photooxygenation, yielding benzaldehyde with a minor amount of the sulfone and very little sulfoxide in benzene and in acetonitrile, but mainly the sulfoxide in methanol or in methanol containing benzene. The efficiency of the reaction increases also in this case in going from aprotic to protic media, but the increase is only by a factor of 2, not 20 as with diethyl sulfide. The rate of singlet oxygen quenching remains almost constant around $k_s = 1 \times 10^7$ M^{-1}s^{-1} in benzene, in the same order as that of diethyl sulfide, and the rate of overall chemical reaction varies from $k_r = 0.55 \times 10^7$ M^{-1}s^{-1} in benzene to $k_r = 1.2 \times 10^7$ M^{-1}s^{-1} in methanol, and this is accompanied by the above mentioned change in the product distribution.

It seems reasonable to think that the initial interaction is the same as with aliphatic sulfides, forming the persulfoxide. In protic media, in fact, the reaction is just the same and we could carry out the co-photooxygenation of both diphenyl sulfide an diphenyl sulfoxide obtaining results quantitatively close to those obtained with diethyl sulfide under the same conditions.

On the contrary, in benzene only Ph$_2$SO and not Ph$_2$S could be co-oxidized; noteworthy, in the presence of the first additive the yield of benzaldehyde does not change, some sulfoxide is formed and the yield of sulfone grows considerably.

Furthermore, we found again that small amounts of acidic additives could change the course of the reaction. Addition of 0.07 M trifluoroethanol to a benzene solution makes the sulfoxide, negligible in the neat solvent, as abundant as benzaldehyde and as low as 0.007 M chloroacetic causes the same effect. Larger amounts of both additives make the sulfoxide the main product, but the lowering in the yield of benzaldehyde is much less than proportional and becomes
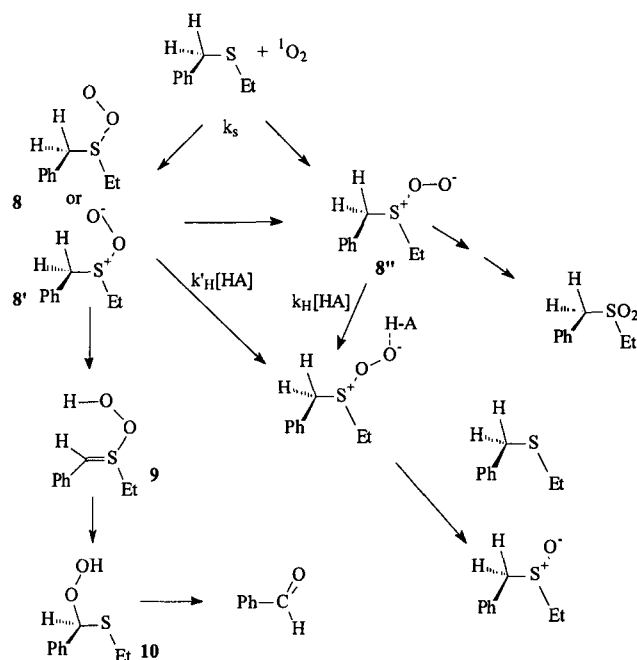

Figure 7.

important only at much higher concentrations of the acids.

All of these pieces of evidence point to two intermediates in aprotic solvents. Our rationalization is that these are a weak exciplex (**8**) or a diradicalic *syn* persulfoxide (**8′**) and a second intermediate that has the properties usually assigned to the persulfoxide, and may be the *anti* rotamer (**8″**) (see Figure 7).

The latter one in fact is not different in its chemistry from aliphatic persulfoxides, and either decays to the components, or, under protic or acid catalysis gives the sulfoxides; likewise it co-oxidizes diphenyl sulfoxide as seen above. The first one is much less easily protonated and leads to benzaldehyde. In fact, in the presence of the strongest acid we used, chloroacetic acid, the second intermediate was wholly protonated (and the sulfoxide had reached a plateau value) at *ca.* 0.02 M, while the former one was only three fourths protonated at a 0.1 M concentration of the same additive, as judged from the benzaldehyde yield, and was not quenched by Ph_2SO.

The former intermediate had a diradicalic character and in the presence of an activated (benzylic) hydrogen atom undergoes hydrogen transfer to give a *S*-hydroperoxysulfonium ylide (**9**), a process for which the *syn* conformation may be determining. As a matter of fact, when mono-α-deuterobenzyl ethyl sulfde was used, α-deuterobenzaldehyde was formed in a proportion larger that 50% (ratio PhCDO/CHO 3.63 in benzene), consistently with the notion that the O-H bond is formed to a considerable degree in the transition state and that the reaction is no proton transfer but rather follows a concerted or radical pathway. The hydroperoxyl ylide has found support from recent calculations [9,10] as a more appropriate stucture for Foote's second intermediate in the diethyl sulfide photooxygenation in aprotic solvents (**4** rather than **2**) and we suggest that its role is more important when benzylic hydrogens make its reaction easier, as here in the conversion to intermediate **9**. The ylide then undergoes a Pummerer type rearrangement to give an α-hydroperoxylsulfide (**10**) that cleaves to benzaldehyde, a path again supported by recent calculations.

On the other hand, quenching experiments by acids and diphenyl sulfoxide do not suggest that the sulfone arises for the ylide, but rather from the persulfoxide. In particular, with the latter additive a cyclic adduct (**11**) may be formed, which decays according to two modes, to yield diphenyl sulfone and the benzyl sulfoxide or, the other way around, diphenyl sulfoxide and the benzyl sulfone (see Figure 8, analogous for the first part to Figure 5).
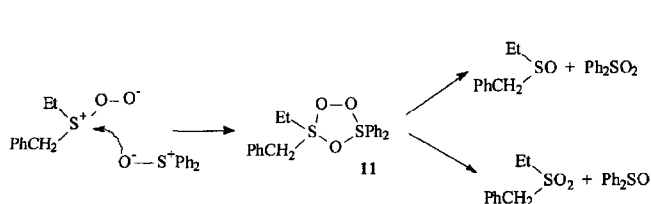
Hydrogen transfer in the persulfoxide

The role of the geometrical arrangement in the first formed intermediate on the following course of the reaction and in particular in the formation of the ylide appeared a point worth further investigation. We made some attempt in this direction through PM3 calculations on the conversion of the persulfoxide to the ylide for which this method had shown to give results comparable to those of *ab initio* calculations [18]. With dimethyl sulfide we found a sizeable barrier ($\Delta H^{\neq} = 19$ kcal mol^{-1}) and, interestingly, the minimum was located for a conformation with the O-O bond roughly bisecting the Me-S-Me angle, just as indicated by more advanced calculations [9, 10]. With benzyl ethyl sulfide, two conformers were found with a considerably smaller $\Delta H^{\neq}$ (16 kcal mol^{-1}), both of which smoothly converted to the ylide.

As an example, the intramolecular O-H interaction was apparent in conformation **12** ($d_{OH}=2.90$ Å) and led to bonding in transition state **13** ($d_{OH}=1.33$ Å) which in turn gave easily the ylide **14** with essentially C=S double bond character ($d_{C-S} =2.60$ Å, see Figure 9).

We considered further α-substitution, with α-methylbenzyl ethyl sulfide ad benzhydryl ethyl sulfide and found that while the $\Delta H^{\neq}$ for the conversion to the ylide decreased monotonically with the decrease of the C-H bond strength (13.8 and 12.2 kcal mol^{-1}, respectively) for the *best* conformation, α-substitution also increased the number of conformers unsuitable for the rearrangement. This on one hand was a further support for the diradicalic or concerted path of the rearrangement and on other hand showed that substitution on the α position led to the contrary effect, the balance of which would have determined the final result.

In the actual experiments (in benzene) it turned out that the photooxygenation of the methylbenzyl sulfide was one half as effcient as that of benzyl sulfide and gave as the main product the sulfoxide, showing that in this case the hydrogen transfer path was disfavored, while with the benzhydryl sulfide the rate increased somewhat and the main process returned fragmentation, to give in this case benzophenone, though accompanied by an unusually high proportion of the sulfone. Thus, the final result is determined by a quite delicate balance based on the number of suited and unsuited conformations for intramolecular hydrogen transfer, and on the competition of this group of processes with the other ones, viz (acid-catalzed) insertion to the sulfoxide and decay to the starting components.
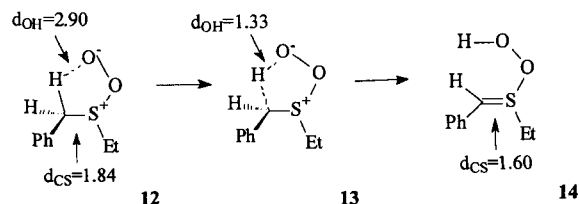

Figure 8.

Figure 9.

α-(Hetero-arylalkyl and allyl sulfides)

The investigation was extended in order to determine the scope of the oxidative carbon-sulfur bond cleavage [19]. The effect of substituents was first ascertained, and showed to be not a major one. 4-Methoxy, 4-nitro and 2-nitrobenzyl sulfides all gave the corresponding benzaldehydes in apolar solvents. The procedure could be easily carried out in a gram scale and may be considered a convenient way to prepare aromatic aldehydes when one considers the mild conditions (visible light is used) the absence of overoxidation to acids and the easy work up (distillation of the raw photolysate). As for the mechanistic point of view, one should notice that both the total rate for the quenching of singlet oxygen and the rate of reaction changed little with the methoxy group (actually this rate constant maintained the characteristic solvent dependence, and slightly increased with respect to the parent substrate in each solvent), while both rates diminished with the nitro group, which also hindered the conversion to sulfoxides, so that oxidative cleavage to 4-nitrobenzaldehyde remained the main process also in methanol (compare the preparative results shown in Figure 10).

This was consistent with the notion that the initial interaction wit singlet oxygen was an electrophilic attack, but the following rearrangement to the hydroperoxylsulfonylylide was a radicalic hydrogen transfer rather than proton transfer. Of the effect of substituents in position α, some mechanistic indications have been given in the previous section, and some illustrative preparative results are shown in Figure 11.

The reaction was also extended to heteroaryl sulfides, with good results from 2-pyridinylmethyl ethyl sulfide, which exhibited the same solvent proticity-dependent photochemistry of carbocyclic analogues, and poor results with 3-indolylmethyl ethyl sulfide, in the case of which some indole-3-carboxaldehyde was nevertheless formed in benzene (10% isolated yield), a result that shows that the oxidative cleavage of the sulfide group still competes to some degree even in the presence of a moiety highly reactive with singlet oxygen as is the indole ring.

Furthermore, allylic derivatives also reacted in this way. 2-Cyclohexenyl ethyl sulfide gave at least some cyclohexencarboxyladehyde and cynnamyl ethyl sulfide gave a good yield of the aldehyde in benzene and the sulfoxide in methanol (see Figure 12).

Further studies

We have determined the condition for a previously little known reaction, the photooxidative cleavage of sulfides to carbonyl
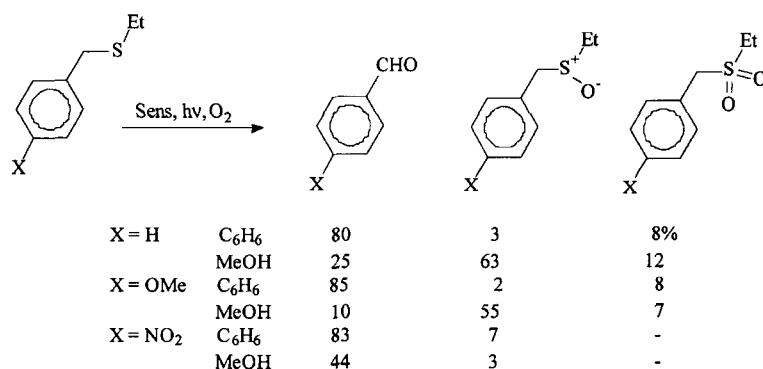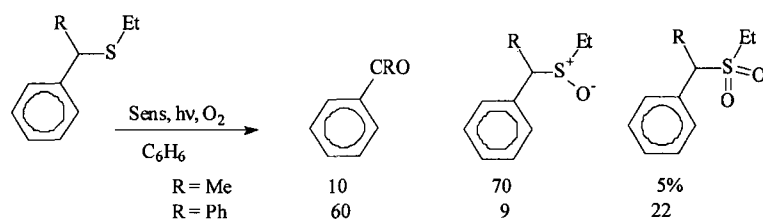

X = H	C6H6	80	3	8%
	MeOH	25	63	12
X = OMe	C6H6	85	2	8
	MeOH	10	55	7
X = NO2	C6H6	83	7	-
	MeOH	44	3	-

Figure 10.

R = Me	10	70	5%
R = Ph	60	9	22

Figure 11.

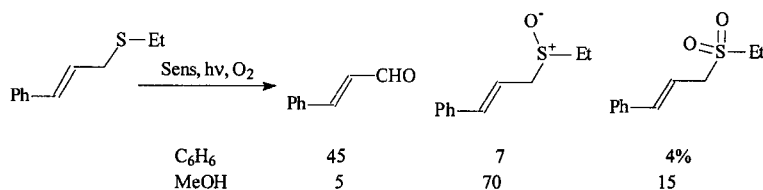| C6H6	45	7	4%
MeOH	5	70	15

Figure 12.

derivatives, occurring in connection wit intramolecular hydrogen transfer in the persulfoxide, and have explored its mechanism and synthetic significance. Along with the ascertainment of general acid catalysis of the photooxygentation of sulfides, via protonation of the persulfoxide, this works contributes to the present debate on a reaction of singlet oxygen, that with sulfides, which probably has still much to add to the knowledge of the chemistry of this species, along with much more largely investigated reactions, such as that with alkenes and dienes.

Besides than on the advancement of this theme, our attention is now addressed to the electron transfer photosensitized oxygenation, a reaction that, from what appears in the initial investigations, is exactly complementary with the dye-sensitized, singlet oxygen process, and completes the available entries to the selective oxidation of these class of substrates.

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