



## Unsensitized Photooxidation of Sulfur Compounds with Molecular Oxygen in Solution

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**Abstract** : The short wavelength irradiation of aliphatic disulfides, sulfides and of n-butanethiol in alcohols or aqueous acetonitrile in the presence of oxygen was investigated : the corresponding sulfonic acids are produced in good yields for short alkyl chain compounds, together with smaller amounts of sulfuric and carboxylic acids. In acetonitrile, the influence of added water on the reaction course is evidenced : increased reaction rate and acid yields, control of sulfuric acid formation. Intermediates such as sulfinic acid and thiosulfonate were detected and their rates of formation were monitored. The reaction appears to involve thiyl radicals giving rise to sulfonyl radicals in the presence of oxygen. A first tentative hypothesis concerning the mechanism is advanced.

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### INTRODUCTION

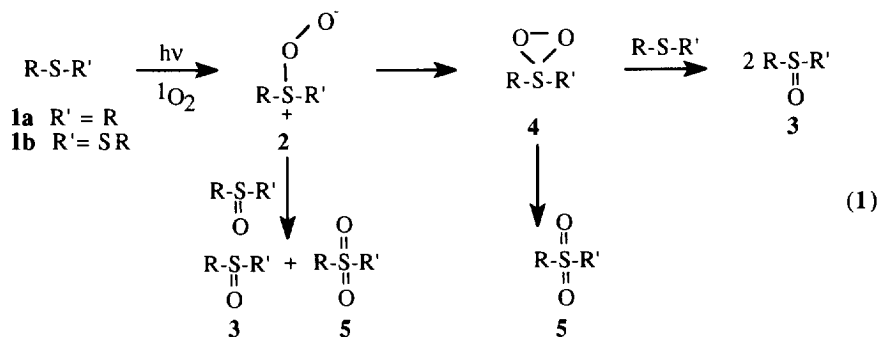
The photooxidation of organosulfur compounds has been extensively studied in the last decades<sup>1,2</sup>. In solution, the common way is the addition of singlet oxygen, generated by photoconversion of triplet oxygen, on sulfur compounds.

Sulfides are known to produce the corresponding sulfoxide and sulfone by this reaction and the former is usually the major product<sup>3-6</sup>. Two intermediates have often been proposed :

- a nucleophilic "peroxysulfoxide" **2a** stabilized in protic solvents. **2a** is able to oxidize trapping agents such as sulfoxides leading to one mole of sulfoxide **3a** and one mole of sulfone **5a**.
- an electrophilic "thiadioxirane" **4a**, formed in non-protic solvents and which reacts with starting sulfide to produce two moles of sulfoxide **3a**.

Although oxygen labeling experiments suggest a unimolecular pathway starting from thiadioxirane **4** for sulfone formation<sup>7</sup>, these results are difficult to reconcile with other sulfoxide trapping experiments<sup>4</sup>. Moreover recent computational investigations indicate that in the gas phase, the two intermediates located at the MP2/6-31G\* level, are almost isoenergetic but separated by an activation energy close to 84 kJ.mol<sup>-1</sup>, inconsistent with the previously accepted reaction mechanism<sup>4</sup>.

According to current investigations, it is quite likely that the actual explanation is more complex<sup>8</sup> and that other sulfurane-type intermediates are involved in protic solvents<sup>1,9</sup>.



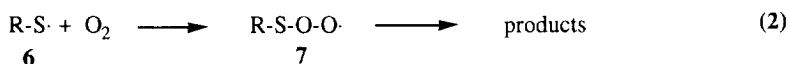
Similar intermediates (namely a "peroxythiosulfinate" **2b** and a thiadioxirane **4b**) are also postulated in the photosensitized oxidation of disulfides for which the formation of the corresponding thiosulfinate **3b** and thiosulfonate **5b** is observed<sup>10-11</sup>.

To the best of our knowledge, only three studies report the direct photooxidation of sulfides with molecular oxygen in solution : a charge transfer mechanism has been postulated to explain the formation of the corresponding sulfoxide<sup>12-14</sup>. The self photoinduced oxidation of alkyl 4-nitrophenyl sulfides, in the absence of any sensitizer, follows a different course : excitation of the alkyl aryl sulfide sensitizes the conversion of <sup>3</sup>O<sub>2</sub> to <sup>1</sup>O<sub>2</sub> which reacts with ground-state sulfide to produce the peroxythiosulfinate **2a**. In this case, besides sulfoxide formation, **2a** undergoes heterolytic C-S bond-cleavage leading to a variety of products including sulfonates and carbonyl compounds<sup>15</sup>.

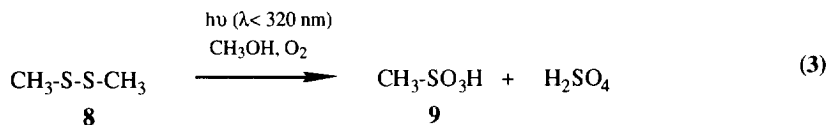
The direct irradiation of sulfur compounds in the presence of oxygen has been mostly studied in the gas phase and is related to the atmospheric chemistry of dimethyldisulfide and dimethylsulfide : oxygenated products such as sulfur dioxide and sulfonic acid are observed among others<sup>16-18</sup>.

In aqueous solution, ESR studies of oxygen addition on radicals derived from biological compounds such as cysteine, glutathione and penicillamine have also been performed<sup>19-23</sup>.

Both in the gas phase and in solution, the postulated intermediate for these reactions is a thiylperoxy radical **7** formed by addition of ground state oxygen on a thiyl radical **6**.



In a previous note<sup>24</sup>, the unsensitized irradiation ( $\lambda < 320$  nm) of dimethyldisulfide **8** in methanol and in the presence of molecular oxygen leading to sulfonic **9** and sulfuric acids in good yields has been described.



Irradiation in other solvents such as acetonitrile or cyclohexane only leads to poor yields of oxygenated products and to numerous polysulfide compounds.

The exploration of this unsensitized photooxidation mechanism was further investigated. Dimethyldisulfide **8** ( $\epsilon_{254\text{nm}} = 400 \text{ l cm}^{-1} \text{ mol}^{-1}$ ) is used as a model for the reaction study.

## RESULTS

### Solvent effect

From our previous experiments<sup>24</sup>, it is clear that the solvent plays a crucial role on the reaction course. Moreover at the high disulfide concentrations used (about 0,5 M), a transitory (methanol) or persistent (acetonitrile) turbidity of the irradiated mixture is observed. We further studied the influence of the solvent at lower disulfide concentrations, thus avoiding this phenomenon and shortening the irradiation times.

Alcohols and acetonitrile, likely to dissolve both the starting organic disulfide and the acidic reaction products, have been tested. The results are reported in Table I. For the sake of comparison, our previous results<sup>24</sup> for methanol and acetonitrile have been added.

Table I - Photooxidation of Disulfide **8** in Several Solvents

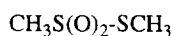
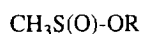
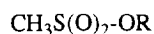
Experiment number	1	2	3	4	5	6	7	8
Solvent	methanol <sup>24</sup>	ethanol	2-propanol	butanol	2-methyl 2-propanol	anhydrous acetonitrile <sup>24</sup>	anhydrous acetonitrile	aqueous acetonitrile (96/4)
Concentration of <b>8</b> (mol/l)	0.56	0.2	0.2	0.2	0.2	0.56	0.2	0.2
Irradiation time (hour)	14	2.5	3.75	12.75	14.75	5.25	4.25	3.25
Conversion rate of <b>8</b>	99	100	100	100	75	40	100	100
Sulfonic acid yield <sup>a</sup> %	65	48	36	8.2	13	5.7	44.2	66
Sulfuric acid yield <sup>a</sup> %	18 <sup>b</sup>	6	12	8.8	1.5	0.3	1.2	19
Observations on the crude product <sup>c</sup>	homogeneous clear	homogeneous brown	homogeneous clear	two-phase clear	two-phase opaque yellow droplets	two-phase brown	two-phase brown	two-phase clear

<sup>a</sup> yield as the following molar ratio : number of moles of compounds / 2 × number of moles of disulfide; <sup>b</sup> esterified and non-esterified; <sup>c</sup> obtained after evaporation of the solvent

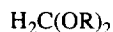
*Alcohols* : We verified that under these conditions methanesulfonic acid **9** did not esterify. Conversely, it is known that in alcohols and mainly in methanol, sulfuric acid quickly reacts to give its monoester<sup>25</sup>.

The best yields of sulfonic acid are obtained in methanol (entry 1), in ethanol (entry 2) and in 2-propanol (entry 3). However a constant decrease in total acid yields is observed as the alkyl chain of the alcohol changes from methyl (83 %) to butyl (17 %). A parallel increase in irradiation times is noticed from ethanol (2.5 hours) to 2-methyl 2-propanol (14.75 hours for a conversion rate less than 100 %). Comparison with methanol cannot be made (entry 1), as at 0.56 M the transitory turbidity of the medium lengthens the irradiation time.

In all these experiments, methyl methanethiosulfonate **10** and sulfur dioxide are detected by GC/MS and alternatively by <sup>1</sup>H NMR. The formation of sulfinate **11** (experiments 1, 2 and 4) and sulfonate **12** (experiments 1 and 2) is also observed.

**10**R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>4</sub>H<sub>9</sub>**11**R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>**12**

The production of acetals **13** (experiments 1, 2, 3 and 5) and methanoic esters **14** (experiments 1, 2, 3 and 4) is indicative of the oxidation of the methyl radicals derived from **8** either to methanal or to methanoic acid and of their further reaction with the solvent.

R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, <sup>1</sup>C<sub>3</sub>H<sub>7</sub>, <sup>1</sup>C<sub>4</sub>H<sub>9</sub>**13**R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, <sup>1</sup>C<sub>3</sub>H<sub>7</sub>, C<sub>4</sub>H<sub>9</sub>**14**

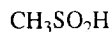
The presence of different oxidation products from the alcohols such as methanoic acid in methanol, ethanal and its ethylacetal in ethanol, butanal and butylester of butanoic acid in butanol imply the photolysis of the solvent<sup>26, 27</sup>. In 2-propanol, numerous products arising from the reaction of the solvent were detected. However their structure could not be clearly determined. In 2-methyl 2-propanol, no product arising from direct solvent photolysis was detected. Instead large amounts of different polysulfides (CH<sub>3</sub>S<sub>n</sub>CH<sub>3</sub>, n=3, 4, CH<sub>3</sub>SCH<sub>2</sub>SSCH<sub>3</sub>, CH<sub>3</sub>SSC<sub>4</sub>H<sub>9</sub>), most of which have already been reported in cyclohexane or acetonitrile<sup>24</sup>, and a thiol CH<sub>3</sub>SCH<sub>2</sub>SH are observed.

In experiments 1 to 4, a substantial increase in oxygen consumption is observed when the conversion rate is about 80%.

*Acetonitrile* : A lower concentration of **8** in anhydrous acetonitrile (experiments 6 and 7) favors the formation of the oxygenated products in spite of the production of large amounts of the usually observed polysulfides<sup>24</sup> (CH<sub>3</sub>S<sub>n</sub>CH<sub>3</sub>, n=3, 4, CH<sub>3</sub>SCH<sub>2</sub>SSCH<sub>3</sub>, CH<sub>3</sub>SSCH<sub>2</sub>SSCH<sub>3</sub>, CH<sub>3</sub>SCH<sub>2</sub>SCH<sub>3</sub>) and of a mixed compound CH<sub>3</sub>SSCH<sub>2</sub>CN. At the lowest concentration (experiment 7), the sulfonic acid yield is 44% for a still low production of sulfuric acid (1.2 %). In both cases, the crude reaction product is a two-phase, strongly colored and bad-smelling mixture.

The addition of a small amount of water to acetonitrile accelerates the reaction since total conversion is reached after 3.25 hours (experiment 8) for 4.25 hours without added water (experiment 7). The total yield of acids significantly increases and can be compared with that obtained in methanol : 66 % in sulfonic acid **9** and 19 % in sulfuric acid. The medium remains homogeneous, clear and odorless. Only minute amounts of the usually observed polysulfides are present.

As in alcoholic solvents, the formation of methyl methanethiosulfonate **10** and sulfur dioxide is also detected in these three experiments. As in alcohols, oxidation products derived from methyl radicals (methanal, methanoic acid) are observed. Moreover a weakly acidic product, identified as methanesulfinic acid **15** by comparison with an independently prepared pure sample, is detected both by potentiometric method and by Ion Exchange Chromatography (see experimental part).

**15**

*Choice of the solvent for the study of the reaction* : These first results clearly indicate that the best yields in sulfonic and sulfuric acids are obtained in methanol or in aqueous acetonitrile. However due to the numerous by-products of the alcohol reaction either with sulfuric acid or by direct photolysis, we chose to complete the mechanism study with 0.2 M disulfide concentration in aqueous acetonitrile.

#### *Influence of water on the acids yields*

We controlled the amount of water added to acetonitrile in order to determine its influence on the yields of acids (Figure 1). Irradiation of these solutions is performed until total conversion of **8** is obtained. As already inferred from Table I, these experiments confirm both the increase in the reaction rate and the increase in yields of acids with added water. For low amounts of added water (less than two moles of water per mole of introduced sulfur), water concentration controls the sulfuric acid yield. For larger amounts of water, the sulfuric acid yield remains roughly constant (around 20 %). The presence of water improves to a lesser extent the sulfonic acid yield (maximum 70 % for 15 moles of water per mole of introduced sulfur), but an excess of water (more than 15 moles of water per mole of introduced sulfur) decreases it. It is important to note that for small amounts of added water (less than one mole of water per mole of introduced sulfur), the reaction medium becomes brown and heterogeneous, while for larger amounts of added water it remains clear and homogeneous. In the former case, after evaporation of the solvent, the crude reaction product contains, besides an acidic water-soluble phase, an important organic phase essentially made up of the already mentioned polysulfides and of methyl methanethiosulfonate **10**. In the latter case, the crude reaction product is a clear acidic phase.

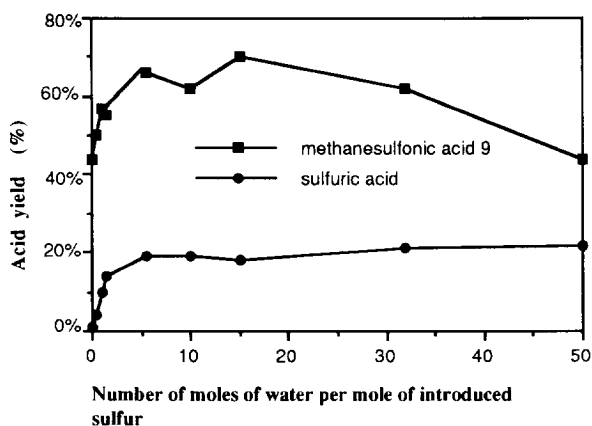


Figure 1 : Influence of added water on the formation of sulfuric and sulfonic acids in acetonitrile

The conclusion of these observations is that an hydroxylated or a protic solvent is needed in the photooxidation of dimethyldisulfide **8** to obtain good yields of oxygenated products. The presence of water (or alcohol) is essential for the formation of sulfuric acid and noticeably improves the production of sulfonic acid.

#### *Kinetic study of the photooxidation of 8 in acetonitrile*

In order to better understand the reaction, the evolution of the previously described products during the photolysis of 0.2 M solutions was studied in both anhydrous (Figure 2) and aqueous (one mole of water per mole of introduced sulfur) acetonitrile (Figure 3).

Sulfinic, sulfonic, sulfuric and methanoic acids are monitored by Ion Exchange Chromatography and the non-acidic products (except sulfur dioxide) by GC after extraction of aliquot samples by chloroform.

As already mentioned, the reaction is slower in anhydrous acetonitrile : the global rate of disappearance of **8** is  $1.9 \cdot 10^{-4} \text{ mol mn}^{-1}$  and  $3.6 \cdot 10^{-4} \text{ mol mn}^{-1}$  respectively in the absence and in the presence of water, that is about two times slower in an anhydrous medium.

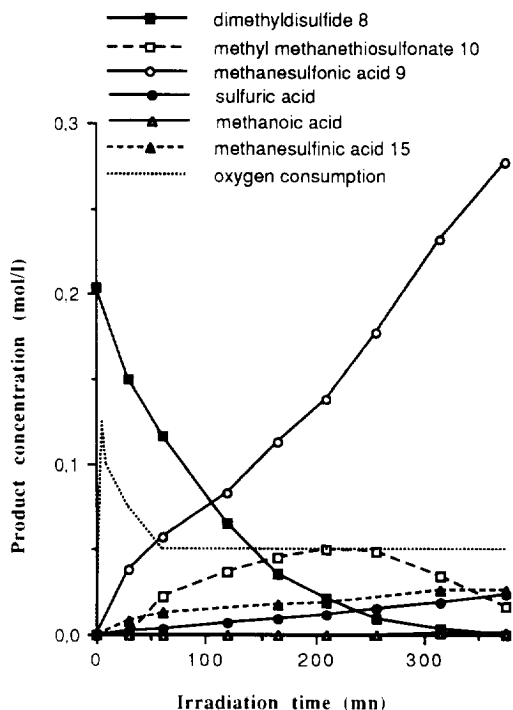


Figure 2 : Photooxidation of dimethyldisulfide **8** in anhydrous acetonitrile

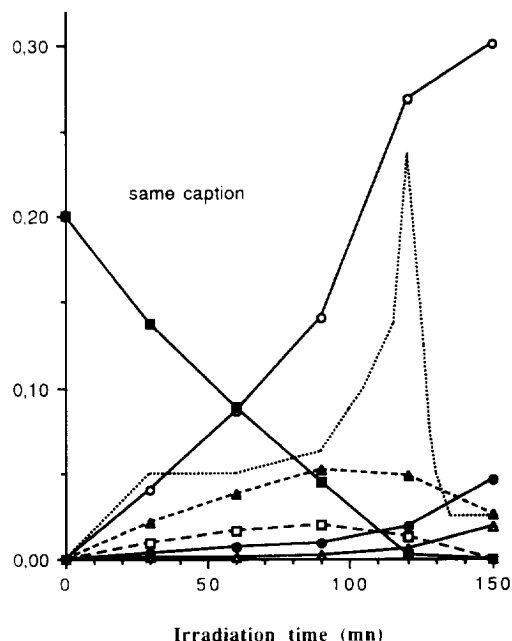


Figure 3 : Photooxidation of dimethyldisulfide **8** in aqueous acetonitrile

In both solvents, the identified compounds are identical but follow a different course :

- the concentration of disulfide **8** decreases, while the concentration of sulfonic acid **9** increases.
- the fate of thiosulfonate **10** confirms its intermediate participation, as its concentration increases and then decreases at the end of the reaction. Its production is more important in anhydrous than in aqueous acetonitrile.
- the concentration of sulfinic acid **15** increases until the end of the irradiation in anhydrous medium while, in aqueous medium, it is greater and decreases at the end of the reaction.
- sulfuric and methanoic acids appear in low concentrations in anhydrous acetonitrile. In an aqueous solvent, their concentration quickly increases at the end of the reaction.

During the irradiation, the production of polysulfides is only observed in anhydrous acetonitrile (traces in aqueous acetonitrile).

An important difference between these two solvents is the marked increase in oxygen consumption only observed in aqueous acetonitrile (as in alcoholic solvents) when the conversion rate of **8** reaches about 80 %.

This increase parallels the modification of the rate of acids. An increase in the production of sulfonic, sulfuric and methanoic acids and a decrease in the concentration of sulfinic acid is observed, together with a slight temperature increase (about five degrees).

From these results, it may be concluded that at least intermediate species such as thiosulfonate **10** and sulfinic acid **15** are involved during the photooxidation of disulfide **8** to sulfonic and sulfuric acids.

#### *Extension to heavier aliphatic disulfides, to sulfides and thiols*

The photooxidation reaction has been applied to several sulfur compounds in order to compare their reactivity (Table II).

Table II - Photooxidation of Disulfides, Sulfides and Thiols in Aqueous Acetonitrile

Experiment number	Disulfides R-S-S-R					Sulfides R-S-R		Thiols R-SH
	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>	<b>13</b>	<b>14</b>	<b>15</b>	<b>16</b>
R	C <sub>2</sub> H <sub>5</sub>	C <sub>3</sub> H <sub>7</sub>	C <sub>4</sub> H <sub>9</sub>	<sup>1</sup> C <sub>4</sub> H <sub>9</sub>	C <sub>8</sub> H <sub>17</sub>	CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub>	C <sub>4</sub> H <sub>9</sub>
Number of moles of water per mole of introduced sulfur	1	1	1	1	<i>a</i>	<1	2	2
Initial concentration of sulfur compound	0,2	0,2	0,2	0,2	0,2	0,1	0,2	0,2
Irradiation time	4 h 30	4 h	4 h 30	6 h	11 h 45	2 h 30	3 h	3 h
conversion rate of sulfur compound	100 % (after 3h30)	100 % (after 3 h)	100 % (after 3h 30)	100 %	89 %	100 %	100 % (after 2 h)	100 % (after 2 h)
Sulfonic acid yield <sup>b</sup> %	49	46	56	50	49	50	50	63
Sulfuric acid yield <sup>b</sup> %	17,1	16	13	16	7	10	10,4	21

<sup>a</sup> solvent 2-propanol ; <sup>b</sup> yields as the following molar ratio : number of moles of compound / 2 × number of moles of disulfide.

*Disulfides* : Irradiation of symmetric alkyl disulfides in aqueous acetonitrile leads to sulfonic and sulfuric acids with yields varying respectively from 46 to 56 % and from 7 to 17% according to the alkyl chain (experiment 9 to 13).

(Here yields of sulfuric acid are maxima because the irradiation has been performed beyond total conversion of the disulfide : we have shown that the yield in sulfuric acid quickly increases at the end of the reaction.)

The behaviour of diethyldisulfide, dipropyldisulfide and dibutyldisulfide (experiments 9 to 11) parallels that of dimethyldisulfide **8** with roughly similar reaction rates, homogeneous and clear crude products and increase of oxygen consumption at the end of the irradiation. The reaction is more sluggish with dibutyldisulfide (experiment: 12) and very slow with dioctyldisulfide (experiment 13). (In this case, the reaction is performed in 2-propanol because of disulfide insolubility in acetonitrile).

The formation of thiosulfonate RS(O)<sub>2</sub>SR and sulfur dioxide is detected in all these experiments while polysulfides (RS<sub>n</sub>R, n = 3, 4) are observed in experiments 10 to 12. In experiment 12, the corresponding thiosulfinate (RS(O)-SR) and sulfone RS(O)<sub>2</sub>R are also found. It may be recalled that aliphatic thiosulfonates

are rather unstable compounds<sup>28</sup>, which could explain why they are not observed for R = methyl, ethyl, propyl and butyl.

The presence of carboxylic acids such as ethanoic, propanoic and butanoic acids respectively in experiments 9 to 11 suggests the oxidation of the alkyl radicals derived from the disulfide, as already observed with dimethyldisulfide **8**. Moreover, the hydrolysis of acetonitrile is indicated by the observation of either ethanamide in experiment **9** or ethanoic acid in experiments **10** and **11**. This solvent hydrolysis has not been observed previously during the irradiation of **8**. These different results may tentatively be accounted for by the increased irradiation times (beyond 100 % conversion of disulfide) in experiments 9 to 11 and by the hydrolysis of the solvent in a strongly acidic medium. The formation of *t*-butylethanamide (CH<sub>3</sub>CONHC(CH<sub>3</sub>)<sub>3</sub>) in experiment 12 follows a different course : this compound is detected by GC from the very beginning of the irradiation.

*Sulfides* : Two sulfides were studied : dimethylsulfide (experiment 14) and dibutylsulfide (experiment 15). The corresponding sulfonic acid (about 50 % yield) and sulfuric acid (about 10 % yield) are produced by photolysis of these two compounds in aqueous acetonitrile. The intermediate formation of sulfoxide followed by sulfone, and of sulfur dioxide is observed in both case. The corresponding disulfide is only present in experiment 14. The production of methanoic and butanoic acids is accounted for by the oxidation of the corresponding alkyl radicals.

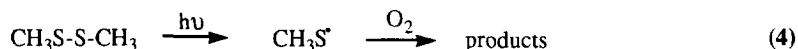
*Thiols* : When a solution of butanethiol in aqueous acetonitrile is photolysed in the presence of oxygen (experiment 16), butanesulfonic acid is obtained in good yield (63%) and sulfuric acid is produced in substantial amount (21%) for only traces of butanoic acid. The presence of the sole disulfide is intermediately detected.

Comparison of the results obtained for dibutylsulfide (experiment 11), dibutylsulfide (experiment 15) and butanethiol (experiment 16) indicates that the greatest yield in sulfonic acid is observed with the thiol : 63% against 50% for the sulfide and 56% for the disulfide. The production of sulfuric acid is also greater during the photolysis of the thiol (21%) than in the case of the disulfide (13%) or of the sulfide (10,4%). In summary, the thiol leads to better results than the other sulfur compounds.

#### ***Photooxidation mechanism of dimethyldisulfide : some experimental arguments***

The formation of sulfonic acids from the photolysis of disulfides implies a sulfur-sulfur bond cleavage. At this stage of our analysis, two assumptions can be made :

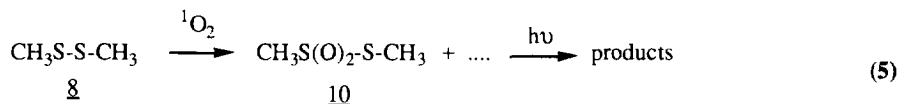
- the sulfur-sulfur bond cleavage takes place before the reaction with oxygen, implying the reaction of a primarily formed thiyl radical :



This assumption is supported by our previous results concerning the formation of the mixed ethylmethyldisulfide during the irradiation of **8** and diethyldisulfide without oxygen under the same conditions<sup>24</sup> and by the known photolysis of dimethyldisulfide at 254 nm<sup>29</sup>.



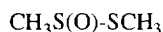
- the addition of molecular oxygen on disulfide precedes the photolysis of species derived from this addition. This reaction can only be expected if the participation of singlet oxygen is effective<sup>10,11</sup> or if a charge transfer between oxygen and disulfide is observed.



From the absence of any modification of the UV absorption spectrum when acetonitrile solutions of disulfide are bubbled with oxygen, we can rule out the occurrence of a charge transfer process. On the other hand, the presence of thiosulfonate (and alternatively thiosulfinate from di-*t*-butyldisulfide) can support the hypothesis of the participation of singlet oxygen since they are known to form in this way<sup>10,11</sup>.

*Singlet oxygen* : However, we have determined that singlet oxygen was not the reagent under our conditions, and did not add to disulfide **8** to give thiosulfonate **10**. Actually, the irradiation of a solution of **8** in acetonitrile in the presence of DABCO (quencher of singlet oxygen<sup>30</sup>) leads to the formation of sulfonic and sulfuric acids with the same yield as in its absence. Moreover the formation of thiosulfonate **10** is also detected under these conditions. A mechanism involving thiyl radicals is thus the only possible reaction pathway.

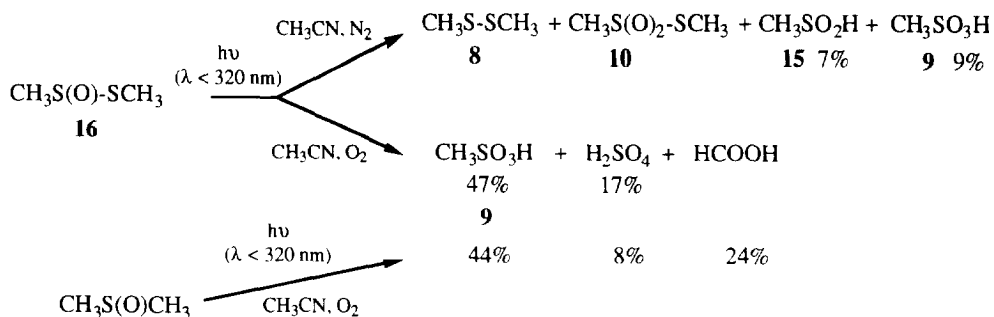
*Involvement of sulfinyl radicals* : From literature data, sulfinyl radicals may be postulated as intermediate between thiylperoxy radicals **7** (derived from the addition of triplet oxygen on thiyl radicals) and sulfonyl radicals<sup>22,23</sup>. In order to check the possible occurrence of these radicals under our conditions, we performed the photolysis of methyl methanethiosulfinate<sup>31</sup> **16** ( $\epsilon_{254\text{nm}} = 2300 \text{ l cm}^{-1} \text{ mol}^{-1}$ ) and of dimethyldisulfoxide<sup>32</sup> ( $\epsilon_{213\text{nm}} = 1580 \text{ l cm}^{-1} \text{ mol}^{-1}$ ) either without or with oxygen bubbling (scheme 1).



**16**

Irradiation of acetonitrile solution of **16** without oxygen leads, as already observed by Block, to the formation of disulfide **8** and thiosulfonate **10**<sup>28b</sup>. However methanesulfinic acid **15** (7%) and methanesulfonic acid **9** (8%) are also produced, while sulfuric acid is not. Under the same conditions, but in the presence of oxygen, **8**, **10** and **15** are intermediately detected, but the final products are sulfonic acid (47%), sulfuric acid (17%) and methanoic acid (traces). In both cases, sulfur dioxide is observed during the reacting course by UV spectroscopy.

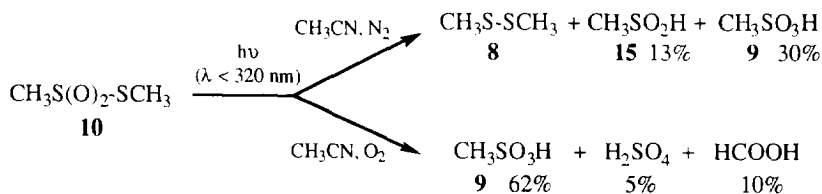
The presence of **8**, **10** and sulfonic acid **9** is also observed when dimethylsulfoxide is irradiated without oxygen<sup>32</sup>. In the presence of oxygen, we obtained sulfonic acid **9** (44%), sulfuric acid (8%) and methanoic acid (24%). In this case, thiosulfonate **10** is not detected as an intermediate, but instead dimethylsulfone is. It is worth noting that a charge transfer complex between dimethylsulfoxide and oxygen has been reported<sup>33</sup>.



From these experiments we conclude that besides their known coupling leading to disproportionation products such as disulfide and thiosulfonate<sup>34</sup>, sulfonyl radicals are able to produce either sulfinic and sulfonic acids in the absence of oxygen, or sulfonic and sulfuric acids in its presence and that thiosulfonate is an intermediate in this latter case.

*Involvement of sulfonyl radicals* : We further investigated the photochemical reactivity of thiosulfonate **10** ( $\epsilon_{236\text{nm}} = 72 \text{ l cm}^{-1} \text{ mol}^{-1}$ ) in order to identify precisely its behaviour first as an intermediate in the photooxidation of disulfide **8**, and second as a source of sulfonyl radicals<sup>35</sup>.

Photolysis of acetonitrile solutions of **10** without oxygen produces besides disulfide **8** and minor amounts of the previously mentioned polysulfides, sulfinic (13%) and sulfonic (30%) acids. In the presence of oxygen, the final products are sulfonic (62%), sulfuric (5%) and methanoic (10%) acids (identical results to those obtained in methanol<sup>24</sup>). Sulfur dioxide is detected during the reaction course by UV spectroscopy in both cases (Scheme II).



The similarity of these results with those obtained from thiosulfinate **16** (Scheme I) strongly suggests that thiosulfonate **10** (or its sulfonyl radical precursor) is the active species during the photolysis of **16**. Moreover, the formation of acids originates from sulfonyl radicals, and their distribution (sulfinic + sulfonic) or (sulfonic + sulfuric) only depends on the presence of oxygen. Sulfonyl radicals can also dissociate by carbon - sulfur bond cleavage into sulfur dioxide and alkyl radicals<sup>36</sup> likely to give rise to carboxylic acid in the presence of oxygen.

*Sulfur dioxide* : Atmospheric oxidation of sulfur dioxide is known and accounts for acid rains<sup>37-38</sup>. It is suggested that sulfur dioxide is quickly oxidized into sulfur trioxide, which then forms a cluster with water molecules. This cluster can isomerize into sulfuric acid.

We verified that :

- sulfuric acid does not arise from the photooxidation of methanesulfonic acid **9**.
- a solution of sulfur dioxide in acetonitrile irradiated with oxygen bubbling under our conditions only leads to sulfuric acid in the presence of water. This reaction is noticeably faster in an acidic medium.

*Occurrence of a persulfonic acid* : This compound ( $\text{RSO}_4\text{H}$ ) is postulated in the sulfoxidation of paraffins<sup>39</sup> and in the autooxidation of arenesulfinic acids<sup>40</sup>. It arises from the addition of oxygen on sulfonyl radicals. We made some attempts to identify this compound with potassium iodide in acetic anhydride<sup>40</sup>. Although an iodine coloration, indicative of the presence of peracidic species, was observed both from thiosulfonate or disulfide irradiation in the presence of oxygen, no conclusive evidence for the formation of this persulfonic acid as the sole peroxidic compound can be drawn.

## DISCUSSION

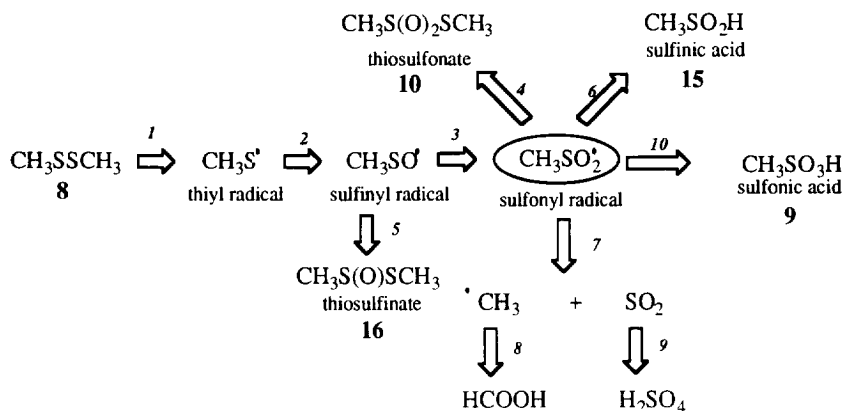
Our results show that in either alcoholic or aqueous acetonitrile solutions, aliphatic thiols, sulfides and disulfides are able, under short wavelength irradiation ( $\lambda < 320$  nm), and in the presence of oxygen, to give rise to the corresponding sulfonic acid in good yields (between 36 and 65% depending on the alkyl chain of the organosulfur compound). For a preparative purpose, the major drawback of this reaction is the presence of by-products such as sulfuric acid and carboxylic acids arising from the oxidation of the alkyl chain of the sulfur compound. In alcohols, moreover, we observed oxidation products from the solvent (acetals from the reaction of the corresponding aldehyde in acidic medium, carboxylic acids or their esters). Acetonitrile appears to be less reactive under irradiation. However, when the reaction times are lengthened, hydrolysis products of acetonitrile in an acidic medium are observed (ethanamide, ethanoic acid).

As a result of these shortcomings, the major interest of this work is to point out a new reactivity of organosulfur compounds in solution towards oxygen. Our results parallel those already obtained in the gas phase with dimethyldisulfide<sup>16,18</sup> or dimethylsulfide<sup>16,17</sup> for which the formation of methanesulfonic acid, sulfuric acid and sulfur dioxide together with methanol, methanal and, in one case, methylhydroperoxide has been reported. We have moreover identified intermediate compounds such as thiosulfonate, sulfinic acid and alternatively thiosulfinate from di-*n*-butyldisulfide.

The detailed analysis of the reaction course with dimethyldisulfide **8** allows the following conclusions to be made :

- the presence of water in acetonitrile controls sulfuric acid formation, whereas sulfonic acid is always obtained whatever the amount of water.
- a radical mechanism starting with the formation of a thiyl radical is most probably involved.
- sulfonyl radicals, possibly derived from sulfinyl radicals, control the acid formation. The reaction of sulfonyl radicals in acetonitrile, without oxygen bubbling, gives a mixture of sulfinic and sulfonic acids. In the presence of oxygen, no more sulfinic acid is obtained, but sulfuric acid is produced.
- sulfur dioxide is always detected. Its photochemical reaction in an acidic aqueous medium leading to sulfuric acid has been checked.

According to these observations a tentative mechanism proposal for the reaction of dimethyldisulfide **8** can be made (Scheme III).



Scheme III

In this scheme, the arrow means "is linked to", i. e. some of these reactions are probably balanced (arrows 4 and 5). However a number of questions remain to be answered in such a process :

- there is probably a reaction between sulfinic acid (or its precursor) and oxygen leading to sulfonic and sulfuric acids,
- the role of water (or alcohol) is not clearly obvious,
- the increased oxygen consumption rate in alcohols or aqueous acetonitrile when dimethyldisulfide conversion rate is about 80% is not explained.

If such a scheme could apply for sulfides, i.e. if sulfinyl radicals were involved, their rapid transformation into thiosulfonate would be at least competitive with the observation of sulfoxide, transiently detected, while thiosulfonate is not. From this result and from the known occurrence of a charge transfer mechanism between sulfides and oxygen<sup>14</sup>, it may be supposed that another mechanism is operative for sulfides. However, further investigations are clearly needed to better understand these results.

On the other hand, the results obtained with butanethiol are very interesting as :

- only traces of carboxylic acid are detected,
- no other intermediate product than dibutyldisulfide is observed,
- the reaction rate is faster than with the corresponding disulfide.

This strongly suggests that in solution oxygen addition on thiyl radicals is at least as efficient as their recombination into disulfide.

## CONCLUSION

To the best of our knowledge, this work provides the first attempt to extend the known gas phase reactivity of sulfur compounds towards oxygen to their behaviour in solution. Thiyl radicals are thus able to add ground-state molecular oxygen in solution. In alcohol or aqueous acetonitrile, sulfonic and sulfuric acids are produced, together with carbonyl compounds arising from alkyl radical oxidation. The determination of acid yields according to the reaction conditions and the search for reaction intermediates have been performed. These results provide additional data relevant to the atmospheric chemistry of dimethylsulfide and

dimethyldisulfide<sup>16-18</sup> and to the aqueous photooxygenation of biological thiols<sup>19-23</sup>. Some arguments have been proposed to understand the complex mechanism of disulfide photooxidation, which highlight the crucial role of sulfonyl radicals in this process. Further studies aimed at a more precise analysis of the reaction mechanism are in progress and will be reported in the near future.

## EXPERIMENTAL SECTION

Analytical gas chromatographic measurements were carried out on a Fisons 8000 series gas chromatograph equipped with a flame ionization detector and a J&W 30 m \* 0,541 mm \* 3  $\mu$ m DB1 megabore column. The GC/MS were collected on a Hewlett Packard instrument consisting of a 5890 series GC (HP PONA 50 m \* 0,22 mm \* 0,5  $\mu$ m) and a 5970 series mass selective detector. Proton NMR spectra were obtained on a BRUKER AM 300 MHz and are referenced to internal TMS. UV spectra were performed on a Hewlett Packard 8450A Diode Array Spectrophotometer. Potentiometric titrations were carried out on a Mettler DK Electrode Potentiometer Amplifier and with a Metrohm Calomel Electrode. Ion Exchange Chromatographic analysis were performed on a 2020I Dionex instrument equipped with a AS9SC column and a AG9SC precolumn, and with a conductimeter CTM1 Dionex.

Methanol, ethanol, 2-propanol (SDS, 99% analytical grade), 2-methyl 2-propanol (Janssen, 99,5%) and acetonitrile (Standa, HPLC quality 99,9%) are used without purification. Anhydrous acetonitrile is distilled from P<sub>2</sub>O<sub>5</sub> and dried over molecular sieves under nitrogen. After such a treatment, the water content of acetonitrile determined by Karl Fischer titration is less than 200 ppm, i.e. for a 0.2 mol l<sup>-1</sup> disulfide solution 0.03 moles of water per mole of sulfur.

*t*-Butyl ammonium hydroxyde (TBAOH) is obtained from SDS. *m*-chloro perbenzoic acid (MCPBA) is used as received from Sigma. Acetic acid, hydrogen peroxide and chloroform (Analytical grade) are obtained from Prolabo. Dimethyldisulfide, dioctyldisulfide and dimethylsulfide are obtained from Elf Atochem and used without further purification. The other disulfides, sulfides and *n*-butanethiol are purchased from Aldrich and used as received.

*Methyl methanethiosulfinate 16* is synthesized by oxidation of dimethyldisulfide by *m*-chloroperbenzoic acid in chloroform at low temperature according to the method of Small and coworkers.<sup>41</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.6 (s, 3H), 2.9 (s, 3H)<sup>10</sup>.

*Methyl methanethiosulfonate 10* is synthesized by oxidation of dimethyldisulfide **8** by hydrogen peroxide in acetic acid at room temperature according to the method of Scholz<sup>42</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.65 (s, 3H), 3.2 (s, 3H)<sup>10</sup>.

*Sodium salt of methanesulfinic acid 15* is synthesized by hydrolysis of methyl methanethiosulfonate with sodium hydroxide<sup>43</sup>: 0,8 ml of 40% aqueous NaOH (80 mmol) were added to 1 g (79,4 mmol) of methyl methanethiosulfonate at 0°C under efficient stirring for one hour. The progress of the reaction is monitored by GC on aliquot samples extracted with chloroform: the appearance of dimethyldisulfide and methyl methanethiosulfinate is observed, followed by the disappearance of methyl methanethiosulfonate and methyl methanethiosulfinate. The resulting mixture is washed with chloroform to remove the disulfide and traces of sulfinate and the aqueous layer is evaporated to give the sodium salt. <sup>1</sup>H NMR (D<sub>2</sub>O)  $\delta$  2.2 (s, 3H)<sup>44</sup>. This

sodium salt is analysed by Ion Exchange Chromatography and by potentiometric titration after careful reacidification for comparison with a reaction sample.

*Photolysis conditions* : 250 ml of a sulfur compound solution in a quartz immersion-well reactor are irradiated with a medium pressure mercury lamp (Hanovia 679A36) between 30 and 35°C. Oxygen (or nitrogen) is bubbled continuously through the solution during photolysis. The reactor is equipped with two outlets fitted with rubber septa to take aliquot samples either of the solution or of the gaseous stream and a third outlet for a temperature probe. Oxygen consumption is roughly estimated as a differential measure between two flowmeters, one located at the entrance of the reactor and the other at the outlet of the reactor. Aliquot samples (1 ml) are regularly taken to follow the reaction course and analyzed by four methods :

- potentiometric titration by TBAOH in 2-propanol<sup>45</sup> to determine the concentration of strong acids (sulfonic and first acidity of sulfuric acid) and weak acids (second acidity of sulfuric acid, carboxylic acid and sulfinic acid<sup>46</sup>).
- Ion Exchange chromatography (determination of each acid)
- UV spectroscopy
- GC and or GC/MS after extraction of the aliquot sample by 1 ml chloroform. Organic products concentrations are determined by GC by the internal standard method.

When the reaction is completed, the solvent is evaporated under vacuum and the crude reaction product can be analyzed by <sup>1</sup>H NMR (solvent CD<sub>3</sub>OD or D<sub>2</sub>O) and titrated by potentiometry (TBAOH in 2-propanol) and by gravimetry (precipitation of BaSO<sub>4</sub> with BaCl<sub>2</sub>) to determine the final yields respectively in sulfonic and sulfuric acids. In acetonitrile, these two latter titrations are sufficient to determine these two yields. However in methanol, the presence of the strong acid CH<sub>3</sub>OSO<sub>2</sub>OH arising from the monoesterification of sulfuric acid, requires the determination of its concentration by <sup>1</sup>H NMR (internal standard method) : δ 3.68 (s, 3H) (CD<sub>3</sub>OD). The sulfuric and sulfonic acid contents are then obtained by double potentiometric / gravimetric titration.

*Photolysis of 8 in the presence of DABCO* : A 0,1 M solution of **8** in acetonitrile containing DABCO (0.1 % on the number of moles of introduced sulfur) was irradiated under the usual conditions but with a pyrex filter to avoid DABCO photolysis. A control experiment was also performed without DABCO : sulfonic acid yield : 35 % - sulfuric acid yield : 2.8 and 1.7 % respectively.

*Photolysis of methyl methanethiosulfinate 16, methyl methanethiosulfonate 10 and dimethylsulfoxide* : 250 ml of 0.1 mol l<sup>-1</sup> solutions of these compounds in acetonitrile (used without drying treatment; water content less than 1000 ppm i.e. 0.5 mole of water per mole of sulfur compound) are irradiated and analyzed under the same conditions as previously described.

#### *Sulfur dioxide oxidation*

Acetonitrile is bubbled with sulfur dioxide during the photolysis reaction. The solution is then irradiated under the same conditions as before. Sulfuric acid is determined by gravimetry.

*Persulfonic acid (RSO<sub>4</sub>H)* determination was performed according to the method of Horner and Basedow<sup>40</sup>.

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