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## Solution Reactivity of Thiyl Radicals with Molecular Oxygen : Unsensitized Photooxidation of Dimethyldisulfide.

Evelyne Banchereau<sup>(a)</sup>, Sylvie Lacombe<sup>(a)\*</sup>, Jean Ollivier<sup>(b)</sup>

(a) Laboratoire de Physico-Chimie Moléculaire, associé au CNRS, Université de Pau, 64000 Pau, France
 (b) Groupement de Recherches de Lacq, Elf, Elf Atochem, BP n°34, 64170 Artix, France

Abstract : Irradiation of dimethyldisulfide in a protic solvent in the presence of molecular oxygen leads to the formation of sulfonic and sulfuric acids as major products. The addition of molecular oxygen on the thiyl radical formed by S-S bond cleavage is postulated.

The photooxidation of sulfur containing compounds in solution, in the presence of singlet oxygen has been extensively studied in the last decades. The common way is the addition of singlet oxygen on either sulfide or disulfide leading to intermediate peroxy sulfoxide or peroxy thiosulfinate respectively, producing sulfoxide and sulfone or thiosulfinate and thiosulfonate<sup>1,2,3</sup>.

In the following, we report a study of the photolysis of dimethyldisulfide in the presence of molecular oxygen, without sensitizer, which reveals the formation of sulfonic and sulfuric acids as major products in a protic solvent<sup>4</sup>.

Solutions of disulfide were irradiated with a medium pressure mercury lamp (Hanovia 679A36) between 30 and 40°C. Oxygen was bubbled continuously through the solution during the photolysis. The formation of acidic products was monitored both potentiometrically in alcoholic medium and by Ion Exchange Chromatography and that of non-acidic products by GC and GC-MS after extraction of aliquot samples by chloroform.

Irradiation of 1 ( $\lambda_{max}=254$  nm,  $\varepsilon=398^5$ ) without Pyrex filter results in the formation of sulfonic acid 2 and sulfuric acid as major oxygenated products in methanol (Table 1). Methanolic solutions remain clear and uncolored.

 $\begin{array}{c} CH_3-S-S-CH_3 & \xrightarrow{h_{U}, O_2} & CH_3-SO_3H & + & H_2SO_4 \\ 1 & MeOH & methanesulfonic acid \\ 2 & \end{array}$ 

In this case, other reaction products, arising from solvent photolysis, have been identified: formic acid, methyl formate and dimethoxymethane. The production of formaldehyde (either further oxidized to formic acid or acetalized by methanol in acidic medium to give dimethoxymethane) has already been reported upon

photolysis of methanol<sup>6,7</sup> and its rate enhancement in the presence of oxygen was noticed<sup>7</sup>.

solvent	methanol	methanol *	cyclohexane	acetonitrile
concentration of 1	0,56 M	0,49 M	0.56 M	0.56 M
irradiation time (h)	14	9,5	11.5	5.25
% conversion	99	21	50	40
% sulfonic acid 2	65	7.1	4	5.7
% total sulfuric acid	18	1.1	0.3	0.3
% 3	0	6.2	1.2	5.6

Table 1. Relative Molar Yields of Products Formed During the Photooxidation of 1 in Various Solvents in a Quartz Vessel ( $\lambda > 220$  nm) except \* with a Pyrex Filter (( $\lambda > 320$  nm).

In methanol, methyl methanethiosulfonate 3 and methyl methanesulfinate 4 are detected during the reaction course by GC, but have disappeared at the end of the irradiation. It should be pointed out that sulfonic acid 2 is not esterified into methyl methanesulfonate 5 in methanol under our conditions, although some trace amounts of this latter product are actually detected. However sulfuric acid is esterified into methylsulfuric acid CH<sub>3</sub>OSO<sub>3</sub>H <sup>8</sup>.

$$\begin{array}{cccc} CH_3 - SO_2 - S - CH_3 & CH_3 - SO - OCH_3 & CH_3 - SO_2 - OCH_3 \\ 3 & 4 & 5 \end{array}$$

The rate of disulfide consumption and of acids formation has been followed during the irradiation in methanol. While disulfide concentration regularly decreases with time, a sharp acidity increase is observed when the conversion rate of disulfide reaches ca. 80%. This enhanced acidity is observed together with a marked increase of oxygen uptake.

When a Pyrex filter is used ( $\lambda > 320$  nm) the reaction is much more sluggish (only 21% of 1 consumed after 9 hours of irradiation) : sulfonic acid 2 and methyl methanethiosulfonate 3 are the main reaction products.

In cyclohexane or acetonitrile, **3** is obtained in the reaction products, together with low yields of acids and with important amounts of sulfur by-products (CH<sub>3</sub>-S<sub>n</sub>-CH<sub>3</sub>, n=3,4, CH<sub>3</sub>SCH<sub>2</sub>SCH<sub>3</sub>, CH<sub>3</sub>S<sub>2</sub>CH<sub>2</sub>SCH<sub>3</sub>, CH<sub>3</sub>S<sub>2</sub>CH<sub>2</sub>S<sub>2</sub>CH<sub>3</sub>). A strong coloration and the inhomogeneization of the medium are evidenced.

The best yields of acids are thus obtained in methanol without Pyrex filter.

Irradiation of a mixture of dimethyldisulfide 1 and diethyldisulfide 6 in solution without oxygen leads to the formation of the mixed disulfide 7, and indicates that the S-S bond cleavage, leading to thiyl radicals, is the first step in photolysis under our conditions.

$$\begin{array}{cccc} CH_{3}-S-S-CH_{3}+C_{2}H_{5}-S-S-C_{2}H_{5} & \xrightarrow{h_{0}} & CH_{3}-S-S-C_{2}H_{5} + 6 + 1 \\ 1 & 6 & N_{2} & 7 \end{array}$$

The formation of sulfonic and sulfuric acids may thus be accounted for by the photochemical S-S bond cleavage ( $\lambda$ =254 nm<sup>9</sup>) and the addition of oxygen on thiyl radicals 8 to form thiylperoxyl radicals 9.

$$CH_3-S-S-CH_3 \longrightarrow 2 CH_3-S \xrightarrow{O_2} CH_3-SOO \xrightarrow{\cdots} 2 + H_2SO_4$$

An intermediate such as 9 has already been postulated in the oxidation under air of sulfides and disulfides, as atmospheric pollutants, where oxygenated products like SO<sub>2</sub> and sulfonic acid 2 are observed among others 10.11.12.

The formation of the thiosulfonate 3 may be rationalized through dimerisation of sulfinyl radicals  $10^{13}$ , issued from the reaction between thiyl 8 and thiylperoxyl 9 radicals<sup>14</sup>:

$$8 + 9 \longrightarrow 2 CH_3 \cdot SO \longrightarrow CH_3 \cdot SO_2 \cdot S \cdot CH_3$$
  
10 3

We have indeed verified that methyl methanethiosulfinate  $CH_3$ -SO-S- $CH_3$ , likely to produce a sulfinyl radical 10 upon homolysis of the S-S bond<sup>15</sup>, gave rise within a few minutes under irradiation without oxygen, to 1 and 3 in quantitative yields.

We have moreover observed that a synthetic sample of thiosulfonate 3 ( $\lambda_{max}=239$  nm,  $\epsilon=60$ ) under our irradiation conditions, in the presence of oxygen, also leads to the formation of sulfonic acid 2 as major product:

$$3 \xrightarrow{h_{\mathcal{V}}} CH_3 - SO_2 + 8 \xrightarrow{O_2} 2 + H_2SO_4$$
  
MeOH 11 72% 8%

It thus follows that sulfonic acid formation very likely occurs by oxidation of the sulfonyl radical 11<sup>14</sup>. These radicals are known to easily cleave into SO<sub>2</sub> and alkyl radicals<sup>16</sup>, which can further be oxidized into sulfuric and carboxylic acid (i.e. formic acid from 1, also issued from solvent photolysis) respectively in the reaction medium.

The formation of trace amounts of methyl methanesulfonate 4 and methyl methanesulfinate 5 from 1 further supports the eventual formation of sulfinyl 10 and sulfonyl 11 radicals.

These results display a close similarity with those reported for paraffins photosulfoxidation<sup>17</sup>. In these reactions, photochemically excited SO<sub>2</sub> reacts with an alkane to produce an alkyl radical which first adds to SO<sub>2</sub> to produce a sulfonyl radical RSO<sub>2</sub>. This radical further adds oxygen and leads to a peroxy sulfonyl

radical RSO<sub>2</sub>OO', giving rise to a persulfonic acid RSO<sub>4</sub>H. The fate of RSO<sub>4</sub>H is highly dependant on the reaction medium: in an anhydrous solvent, sulfonic acid is obtained, whereas a mixture of sulfonic and sulfuric acids is produced in the presence of water.

Although these first tentative proposals appear consistent with our results, they don't provide any satisfactory explanation either for the oxygen uptake increase at the end of the irradiation, or for the need for a protic solvent.

Additional studies designed to explore the photooxidation mechanism of disulfides are currently in progress and will be reported in the near future.

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