

## Short Communication

---

### Photolysis of SO<sub>2</sub> at 123.6 nm in the presence of H<sub>2</sub>\*

C. LALO and C. VERMEIL

*Equipe de Recherche du C.N.R.S., E.S.P.C.I., 10 rue Vauquelin, Paris V<sup>o</sup> (France)*

(Received July 21, 1972)

The photodecomposition of SO<sub>2</sub> in the vacuum–u.v. range, has been studied at the krypton resonance line of 123.6 nm, sulfur trioxide formation being observed.

At this wavelength, the adsorption coefficient value of SO<sub>2</sub> is high (1000 cm<sup>-1</sup> atm<sup>-1</sup>)<sup>1</sup> as can be seen in Fig. 1 which shows the adsorption spectrum of SO<sub>2</sub>. The energy is high enough to dissociate the molecule SO<sub>2</sub> giving either S + O<sub>2</sub> fragments with the sulfur atom in the <sup>1</sup>S, <sup>1</sup>D or <sup>3</sup>P states and the oxygen molecule in the b<sup>1</sup>Σ<sub>g</sub><sup>+</sup>, a<sup>1</sup>Δ<sub>g</sub> or X<sup>3</sup>Σ<sub>g</sub><sup>-</sup> states, or SO + O fragments, the oxygen atom being in the <sup>1</sup>S, <sup>1</sup>D or <sup>3</sup>P states and the radical SO in the b<sup>1</sup>Σ, a<sup>1</sup>Δ or X<sup>3</sup>Σ states. The energy levels corresponding to the dissociation processes (Δ*H*<sub>SO-O</sub> = 125 kcal/mole) described above are shown in Fig. 1.

#### *Experimental*

The experimental apparatus is a mercury-free and greaseless flow system. The pressure can be varied between 5 × 10<sup>-1</sup> and 760 Torr, the flow rate between 10 and 200 cm<sup>3</sup> sec<sup>-1</sup> and hence the residence time between 1 and 10 sec.

The gases (SO<sub>2</sub>) Matheson anhydrous grade 99.98%; H<sub>2</sub>, Air Liquide “U” 99.995%) have been used first without purification. Some experiments performed with H<sub>2</sub> flowing through Pd powder and P<sub>2</sub>O<sub>5</sub>, and SO<sub>2</sub> through P<sub>2</sub>O<sub>5</sub>, gave identical results. The higher oxygen concentration in the flowing gases, coming from insufficient strength of the links is evaluated to be of the order of 1<sup>o</sup>/100. The effluent gases are trapped at 77K. After the photolysis, the trap is heated, the gases are carried away by a flow of H<sub>2</sub> and SO<sub>3</sub> is collected in a 4:1 isopropanol–water mixture. The amount of SO<sub>3</sub> formed is determined as SO<sub>4</sub><sup>2-</sup> using a barium perchlorate and thoron titrimetric method<sup>2</sup>. The validity of the method has been carefully checked with blank runs.

---

\* Paper presented at the Tenth Informal Photochemistry Conference, Stillwater, Oklahoma, May 15–18, 1972.

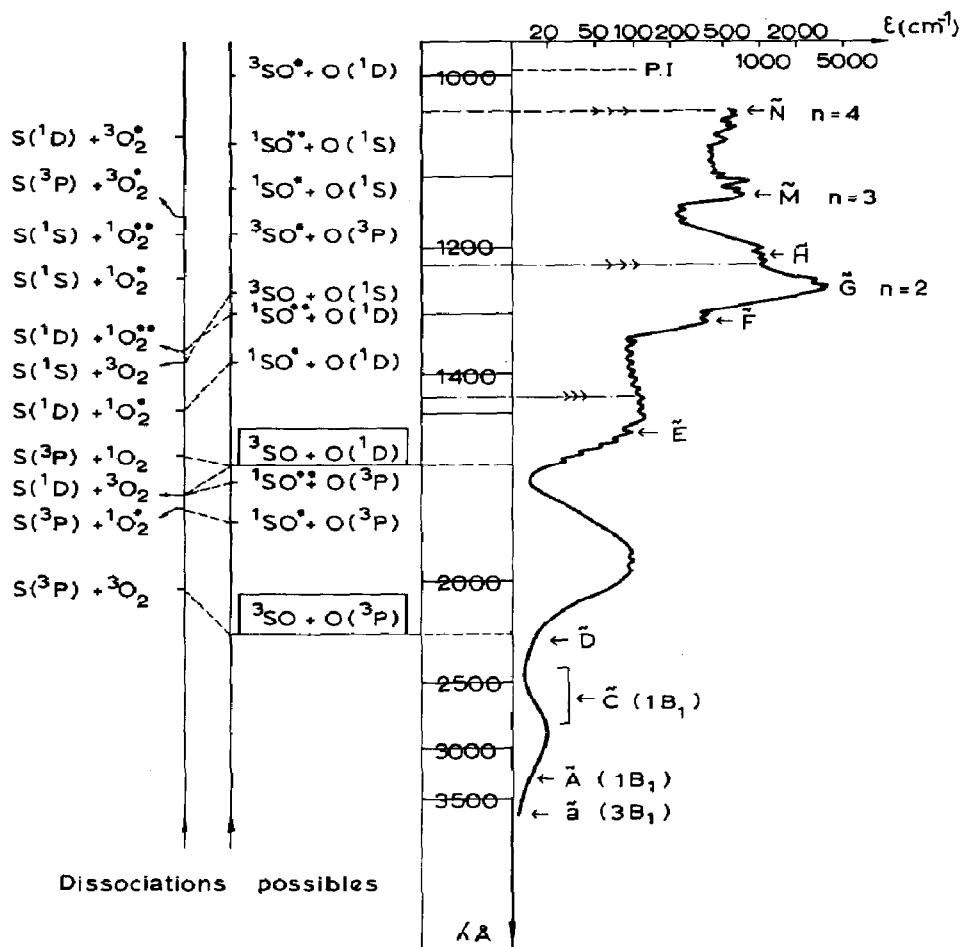


Fig. 1. Absorption spectrum and thresholds for all possible modes of dissociation of SO<sub>2</sub>.

The number of photons flowing into the cell at  $\lambda = 123.6$  nm, the lamp being filled with krypton (4 Torr) excited by a microwave discharge and sealed by a lithium fluoride window, is  $5 \times 10^{14}$  photons sec<sup>-1</sup>. This value has been measured by means of the photolysis of CO<sub>2</sub> taking  $\Phi_{\text{CO}_2} = 1^3$ .

### Results

The photolysis of pure SO<sub>2</sub>, even at the lowest pressure and shortest residence time used, is immediately followed by the appearance of a solid deposit upon the inner surface of the window. This deposit is essentially formed of solid sulfur since it has a yellow colour and is soluble in CS<sub>2</sub>.

This deposit is still formed when SO<sub>2</sub> is diluted in argon at a concentration of 3% or less, but is completely suppressed when diluted in hydrogen in the same concentration range. H<sub>2</sub> is transparent to 123.6 nm and 147.0 nm radiation.

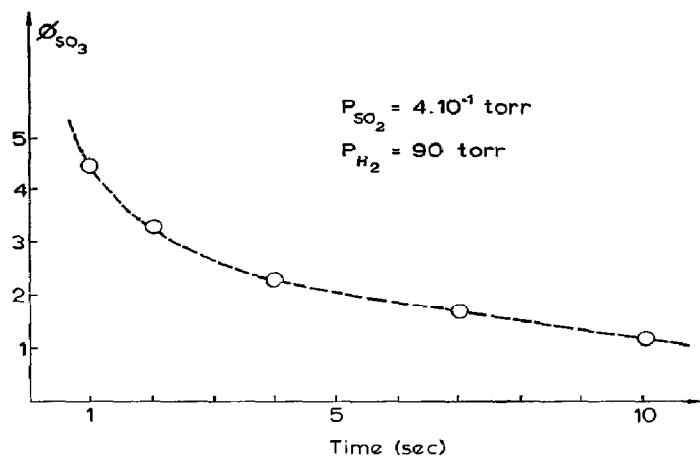


Fig. 2.  $SO_3$  photochemical yields in a mixture of  $SO_2$  and  $H_2$  (Kr lamp, LiF window) as a function of the residence time in seconds.

Some experiments have been done when the photolysis of  $SO_2$  is performed at 147.0 nm (xenon resonance line). If the concentration of  $SO_2$  in hydrogen is as high as 10% without any fogging of the window, the same deposit as at 123.6 nm is obtained with higher concentration of  $SO_2$ .

At 123.6 nm, one can make the following observations: for a given residence time and  $p_{SO_2} = 0.4$  Torr,  $\Phi_{SO_3}$  is constant for  $p_{H_2}$  varying from 15 to 200 Torr;  $\Phi_{SO_3}$  is a decreasing function of the residence time (Fig. 2) extrapolated to flow rates  $\rightarrow \infty$ ,  $\Phi_{SO_3}$  is greater than unity at every pressure of  $SO_2$  studied; for a given residence time,  $\Phi_{SO_3}$  increases as  $p_{SO_2}$  increases:  $\Phi_{SO_3} = 1$  ( $p_{SO_2} = 0.05$  Torr) and  $\Phi_{SO_3} = 5$  ( $p_{SO_2} = 2$  Torr).

As is shown later, these oxidation quantum yields are too high because they are only related to the photonic intensity at 123.6 nm.

The absorption spectrum of  $SO_2$  revealing the existence of weak absorption bands at  $\lambda < 390$  nm, a photolysis of this compound by the near u.v. lines emitted by the lamp must be considered. The near u.v. spectrum of the emission has been recorded and shows well defined bands between 250 nm and 450 nm with a strong one at 388 nm. Consequently some irradiations have been performed with the same krypton lamp but sealed by a quartz window. The  $SO_3$  quantities obtained are half that with a LiF window, with the same pressure conditions. This is probably due to the low lying excited states (or state) of  $SO_2$ . When using a quartz window the yield of  $SO_3$  is increased by increasing the partial pressure of  $H_2$ . No explanation can be proposed at this moment to account for this effect.

On the other hand, an explanation of the relation between quantum yields of  $SO_3$  and residence time can be found in a secondary photolysis of this compound. To clarify this point, the absorption spectrum of  $SO_3$  which is only known<sup>4</sup> in the wavelength range  $220 < \lambda < 300$ , has been determined down to 145 nm at the

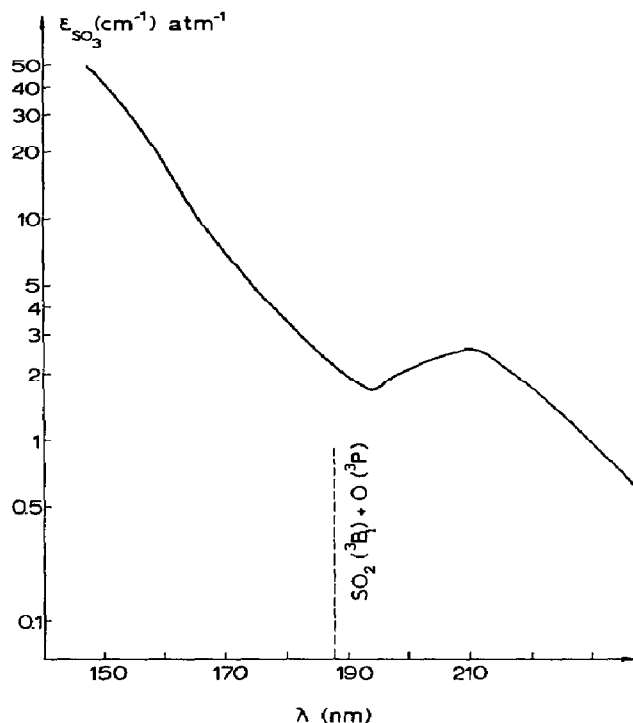
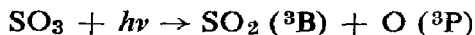


Fig. 3. Absorption spectrum of  $\text{SO}_3$ .

Laboratoire des Hautes Pressions (CNRS) at Bellevue with the kind assistance of Mlle M.C. Castex (Fig. 3).

This spectrum is composed of two continua, the onset of the second continuum (190 nm or 150 kcal/mole) corresponding most probably to the dissociative process:



(calculated threshold 156 kcal/mole).

The adsorption coefficient values of  $\text{SO}_3$  at shorter wavelengths are of the same order of magnitude as those observed for  $\text{SO}_2$ . The secondary photolysis of  $\text{SO}_3$  may lead to the low lying triplet state of  $\text{SO}_2$ .

### Discussion

#### *Sulfur formation by direct dissociation $\text{S} + \text{O}_2$*

Sulfur atoms are formed in the photolysis; they are most likely directly produced in the  $^1\text{D}$  state by a primary dissociative process, because  $\text{S}(^1\text{S})$  is quenched by  $\text{H}_2$  to give  $\text{S}(^3\text{P})$  and  $\text{S}(^3\text{P})$  does not react with  $\text{H}_2$ . On the contrary, the reaction:

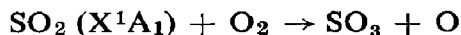


is very efficient.  $k = 2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  (5).

It can be noted that this process is less probable at 147 nm.

*SO<sub>3</sub> formation by the photodissociation of SO<sub>2</sub>*

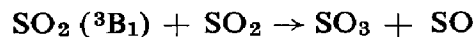
The reaction:



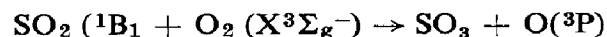
is energetically possible if and only if O<sub>2</sub> is in its (<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) state. On the other hand, if fragmentation in SO + O occurs, oxygen atoms are not expected to be formed in the O(<sup>1</sup>D) state since O(<sup>1</sup>D) is known to react very quickly with H<sub>2</sub> giving OH radicals, presumably less efficient than O(<sup>1</sup>D) for SO<sub>3</sub> formation. This will lead to a strong diminution of Φ<sub>SO<sub>3</sub></sub> as the SO<sub>2</sub>/H<sub>2</sub> ratio decreases by a factor of 10<sup>3</sup>.

*SO<sub>3</sub> formation below the SO<sub>2</sub> dissociation threshold*

The occurrence of the reaction:



has been postulated by Calvert and coworkers<sup>6</sup>. This reaction seems to offer a more probable mechanism to explain SO<sub>3</sub> formation at λ > 250 nm than the following reaction involving the first excited singlet state:



since the O<sub>2</sub> concentration in the gas mixture is rather low.

*Conclusion*

At 123.6 nm, the primary process of photodecomposition leading to the S + O<sub>2</sub> fragments is important. Sulfur atom is probably produced in the <sup>1</sup>D state. At 147 nm, this process though less probable, is still occurring. The observation of high oxidation quantum yields can be explained by formation of low lying triplet state of SO<sub>2</sub> produced by the near u.v. Kr lines emitted by the lamp.

1 D. Golomb, K. Watanabe and F. F. Marmo, *J. Chem. Phys.*, 36 (1962) 958.

2 R. S. Fielder and G. H. Morgan, *Anal. Chim. Acta*, 23 (1960) 538.

3 B. H. Mahan, *J. Chem. Phys.*, 33 (1960) 959.

4 E. Fajans and C. F. Goodeve, *Trans. Faraday Soc.*, 32 (1936) 511.

5 R. J. Donovan, L. J. Kirsch and D. Husain, *Trans. Faraday Soc.*, 66 (1970) 774.

6 H. W. Sidebottom, C.C. Badcock, J. G. Calvert, G. W. Reinhart, B. R. Rabe and E. K. Damon, *J. Am. Chem. Soc.*, 93 (1971) 2587.