

Short Communication

Photolysis of oxygen difluoride in the presence of carbonyl sulfide and carbonyl sulfide/oxygen mixtures

D. SORIA, O. SALINOVICH, E. RAMONDELLI DE STARICCO and E. H. STARICCO
Departamento de Físico-Química, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Córdoba (Argentina)

(Received October 23, 1973)

Some time ago it was discovered in this laboratory that carbonyl sulfide reacts with fluorine [1] in rather a complex manner and that addition of oxygen drastically changes the course of the reaction. In order to obtain details of the mechanism of the process, the reaction of carbonyl sulfide and oxygen difluoride [2], and the influence of oxygen on the reaction between carbonyl sulfide and fluorine [3] has been studied. The present paper reports results of the study of the photolysis of oxygen difluoride in the presence of carbonyl sulfide and carbonyl sulfide/oxygen mixtures.

Experimental

Materials

Carbonyl sulfide was prepared by the reaction of H_2SO_4 with SCN NH_4 . It was condensed at -100°C , distilled at temperature between -100°C and -193°C , identified by IR spectroscopy and its purity checked by gas chromatographic analysis.

Oxygen difluoride was prepared by bubbling fluorine diluted with nitrogen into a 2% aqueous solution of NaOH at 0°C . It was then condensed in liquid nitrogen, the oxygen pumped off and the product distilled from trap to trap between -186°C and -193°C . Oxygen could not be completely eliminated by this method, however, so runs were performed with two types of $\text{F}_2\text{O}/\text{O}_2$ mixture, one with 1% of oxygen and the other with 3% of oxygen. Oxygen difluoride free from oxygen was obtained by photolysis of an $\text{F}_2\text{O}/\text{O}_2$ mixture in the presence of SCO until the oxygen was totally consumed, then F_2O was separated from the reaction products by distillation.

Oxygen (99.8%) was obtained from a cylinder and dried by bubbling through sulfuric acid. All reactants were stored in Pyrex bulbs.

Runs were carried out using a conventional vacuum system. The reactor consisted of a cylindrical quartz cell, 10 cm long and 4 cm in diameter, connected to a quartz spiral manometer which was used as a null instrument. The pressure was read on a mercury manometer.

A 366 nm parallel light beam was obtained by using an Osram HBO 500 lamp, a quartz lens, diaphragms and Schott filters. The intensity of the incident light was $1.29 \times 10^{15} h\nu \text{ cm}^{-3} \text{ Torr}^{-1}$, as determined by the photolysis of oxygen difluoride alone [4].

Procedure

After illumination for a given time, the gas mixture was transferred to a U-trap cooled with liquid nitrogen and the condensable compounds identified by IR spectroscopy and quantified by GC analysis using a Varian Aerograph 202B fitted with a Gow Mac gas density detector in conjunction with a stainless-steel column 130 cm long and 0.55 cm diameter filled with Porapak Q. The carrier gas was nitrogen and the flow ratio column/reference was 1:3. The column temperature was 60 °C.

The reactant pressures employed were 9 - 34 Torr for SCO, 100 - 300 Torr for F₂O and 1 - 300 Torr for oxygen. All runs were carried out at -2 °C.

Results

No change in the total pressure occurs during the course of the reaction, the reaction products being F₂SO and CO. Sulfur dioxide was not detected in runs carried out with oxygen-free F₂O even when these were taken to total conversion. If irradiation was continued after total conversion of SCO, the further products F₄SO, F₂SO₂, F₂CO, CF₃OF and (CF₃)₂O₂ were formed.

Above room temperature a thermal reaction occurs between F₂O and SCO but at -2 °C this reaction is negligible for the length of the irradiation employed for most of the runs.

The experimental results obtained in the presence of oxygen are shown in Table 1. The first four runs were undertaken with the same initial reactant pressure but at different illumination times and show that while the quantum yield of thionyl fluoride remains constant at around unity, the quantum yield of sulfur dioxide clearly decreases with time.

Run 5 was performed in order to check the dependence of the quantum yield of F₂SO on the light intensity and was conducted with a neutral filter of known transmission inserted into the light beam. It was observed that the quantum yield of F₂SO depends on the first power of the intensity of the absorbed light. Runs 3, 5 and 6 show that the formation of F₂SO and SO₂ is independent of the initial pressure of SCO. The other runs demonstrate the dependence of the quantum yields of products on the oxygen pressure, the respective quantum yields being $\phi_{\text{F}_2\text{SO}} = 1$ and $\phi_{\text{SO}_2} = 4$. A quantum yield of less than 4 for SO₂ indicated that the quantity of oxygen present in the system was insufficient. The reduced value for this quantum yield obtained in runs 2, 3 and 4 (in which the same pressure of oxygen was used as in run 1) may be attributed to the longer irradiation time. The amount of SO₂ detected in these runs (2.3, 2.0, 2.2 and 2.4 Torr) is constant to within experimental error, and in all cases the oxygen in the system was totally consumed within approximately the first 30 min.

If the results of runs 14 and 15 are compared with those of 13, 16, 17,

TABLE 1

Data associated with the photolysis of F_2O in the presence of SCO and O_2

Run No.	Time (min)	P_{SCO} (Torr)	\dot{P}_{F_2O} (Torr)	\dot{P}_{O_2} (Torr)	P_{SO_2}	P_{F_2SO}
1	30	33.5	288.0	3.0	3.83	1.3
2	60	30.7	317.4	3.0	1.53	0.8
3	120	33.6	289.0	3.0	0.92	1.1
4	240	32.2	291.7	3.0	0.52	0.8
5	240	32.1	291.2	3.0	0.90	0.8
6	120	10.2	295.8	2.9	1.22	0.8
7	120	21.3	287.4	3.0	0.96	0.9
8	120	17.8	296.4	8.8	2.80	—
9	120	8.9	275.5	8.5	3.10	—
10	120	31.0	275.8	3.0	1.25	1.2
11	120	34.2	194.0	2.0	0.85	0.9
12	120	32.4	145.3	1.5	1.16	1.2
13	120	32.0	102.3	1.1	1.19	1.3
14	120	30.4	287.8	9.2	3.60	0.6
15	60	32.0	574.6	18.0	3.23	0.6
16	120	33.4	145.3	4.5	3.70	0.6
17	120	31.5	285.3	11.3	3.50	1.0
18	120	32.8	291.0	23.0	4.00	0.9
19	120	33.2	282.8	324.2	3.45	0.6
20	120	31.1	276.5	169.0	4.30	0.6

18 and 19, it may be concluded that the quantum yield of SO_2 is independent of the initial pressure of F_2O and solely dependent on the first power of the light intensity.

The same conclusion also applies to F_2SO . In the absence of oxygen (in which no SO_2 was formed), the quantum yield of F_2SO was also found to be around unity.

Discussion

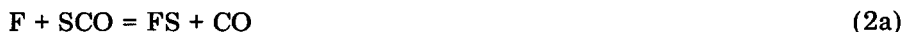
Carbonyl sulfide, SCO , does not absorb at the wavelength (366 nm) at which the runs were carried out. Accordingly [4] the primary process is



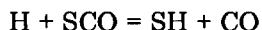
Since photolysis of F_2O in the presence of SCO , but in the absence of oxygen, produces only F_2SO and CO , although kinetic data alone do not permit a mechanism to be assigned unequivocally, it is reasonable to assume that an F atom attacks SCO



Another possibility is



a reaction which is comparable to



as postulated [5] as the mode of attack of hydrogen atoms on SCO. Reaction (2a) can however be neglected, principally on the grounds that FS radicals should react with oxygen to produce FSO₂ radicals, which might reasonably react further to give F₂SO₂ [3]. This product could not be detected, however, even at a trace level.

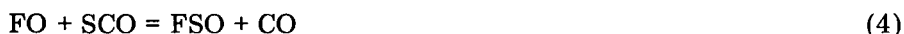
Reaction (2) is probably followed by



although another route to the formation of F₂SO, especially in view of the influence of oxygen as mentioned below, may be



In the presence of oxygen, reactions (1) and (2) may be followed by the steps:



Reaction (6) should explain the increase in the rate of conversion of SCO following the addition of O₂ as is evidenced by the quantum yield of SO₂. Reactions (7) and (8) explain the observation that addition of oxygen does not inhibit the rate of production of F₂SO, which is not unexpected if the FSCO radical is a common precursor to both SO₂ and F₂SO.

The formation of F₄SO, F₂SO₂, F₂CO, CF₃OF and (CF₃)₂O₂ in those runs where irradiation was continued after total conversion of SCO may be readily explained in terms of the above mechanism. Thus it is well known that reaction of F and FO with F₂SO [6] yields F₄SO and F₂SO₂, and that, in addition, F₂CO is formed by the reaction of F atoms with CO [7]. Finally, CF₃OF and (CF₃)₂O₂ are the products of the fluorination of F₂CO [8].

References

- 1 O. Salinovich, E. A. R. de Staricco and E. H. Staricco, *Inorg. Nucl. Chem. Lett.*, 2 (1966) 157.
- 2 D. Soria, E. A. R. de Staricco and E. H. Staricco, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 35.
- 3 O. Salinovich, R. Andía, E. A. R. de Staricco and E. H. Staricco, *Anales Asoc. Quím. Arg.*, 59 (1971) 215.
- 4 R. Gatti, E. H. Staricco, J. E. Sicre and H. J. Schumacher, *Z. Phys. Chem. (Frankfurt)*, 35 (1963) 343.
- 5 G. A. Oldershaw and D. A. Porter, *J. Chem. Soc. (Faraday Trans. I)*, 68 (1972) 709.
- 6 E. Castellano and H. J. Schumacher, *Z. Phys. Chem. (Frankfurt)*, 40 (1964) 51.
- 7 J. M. Heras, A. J. Arvía, P. J. Aymonino and H. J. Schumacher, *Z. Phys. Chem. (Frankfurt)*, 28 (1961) 250.
- 8 P. J. Aymonino, *Proc. Chem. Soc.*, (1964) 341.