

## PHOTOCHEMICAL DECOMPOSITION OF SF<sub>5</sub>OF IN THE PRESENCE OF CARBON MONOXIDE: KINETICS AND MECHANISM

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### Summary

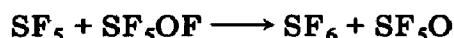
The photochemical decomposition of SF<sub>5</sub>OF in the presence of CO has been investigated at 253.7 nm. CO<sub>2</sub> and SF<sub>6</sub> are the main products. Small amounts of S<sub>2</sub>F<sub>10</sub>, COF<sub>2</sub>, SF<sub>5</sub>OCOF and SF<sub>5</sub>COF are also formed.

The reaction follows a chain mechanism whose rate is proportional to both the square root of the absorbed light intensity and the SF<sub>5</sub>OF pressure.

The proposed mechanism leads to the expression

$$\Phi_{\text{CO}} - 2 = \frac{k[\text{SF}_5\text{OF}]}{I_{\text{ab}}^{1/2}}$$

From the temperature dependence of  $k$ , an activation energy of  $7 \pm 1$  kcal mol<sup>-1</sup> for



can be estimated.

### 1. Introduction

It is known [1] that SF<sub>5</sub>OF reacts thermally with CO, the main products being CO<sub>2</sub> and SF<sub>6</sub>. The results can be represented by the following mechanism:



and the rate law obtained is

$$\frac{d[\text{CO}_2]}{dt} = 2k_c \left( \frac{k_a}{k_e} \right)^{1/2} [\text{SF}_5\text{OF}]^{3/2} [\text{CO}]^{1/2}$$

In this paper the photochemical reaction between  $\text{SF}_5\text{OF}$  and  $\text{CO}$  at 253.7 nm is investigated.

## 2. Experimental details

The absorption spectrum of  $\text{SF}_5\text{OF}$  was recorded using a Cary 14 spectrophotometer. It may be seen (Fig. 1) that the spectrum is continuous. The absorption begins at 350 nm and increases towards shorter wavelengths. The absorption coefficient at 253.7 nm is  $\epsilon(24.2^\circ\text{C}) = 2.03 \times 10^{-4} \text{ Torr}^{-1} \text{ cm}^{-1}$ .

The experimental arrangement was the same as that described previously [2]. The reactor was an optical quartz cell 10 cm long with plane windows and a diameter of 4.8 cm. It was located on a Lauda thermostat in which the temperature could be held constant within  $\pm 0.1^\circ\text{C}$ . A sensitive quartz spiral manometer was used as the zeroing instrument.

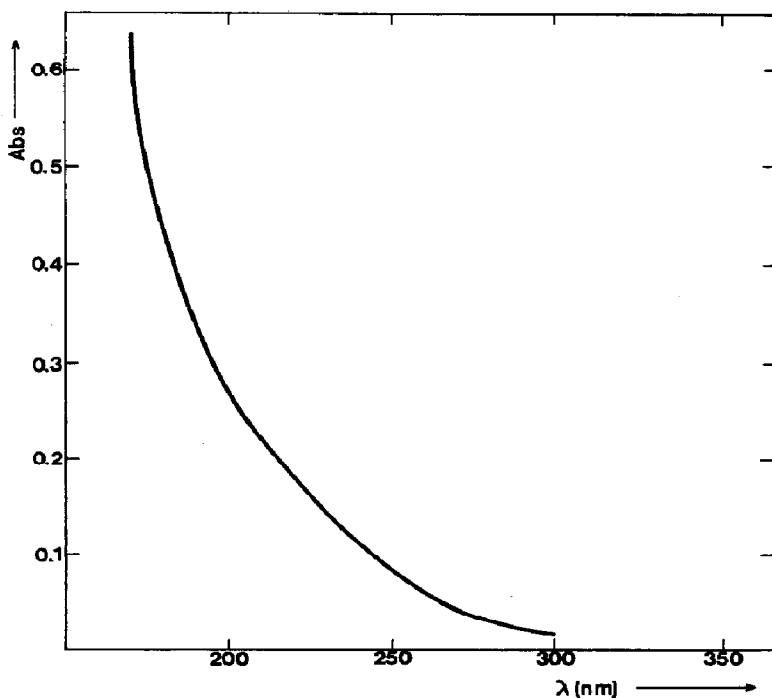


Fig. 1. UV absorption spectrum of  $\text{SF}_5\text{OF}$  ( $p(\text{SF}_5\text{OF}) = 115.9 \text{ Torr}$ ;  $l = 10 \text{ cm}$ ;  $T = 24.2^\circ\text{C}$ ).

In order to separate the reaction products by distillation, a small U-tube was placed between the reaction cell and the valve which connected it to the pumping system.

A 500W Osram HBO mercury lamp was used as the light source. A system of quartz lenses combined with a chlorine filter and cobalt and nickel sulphate filter produced a well-defined homogeneous and approximately parallel light beam at 253.7 nm. The intensity  $I_0$  of the incident light was measured periodically with a potassium ferrioxalate actinometer [3] and the absorbed light was calculated using the absorption coefficient of  $SF_5OF$ .

### 2.1. Preparation and purification of the reactants

$SF_5OF$  was prepared according to the method of Ruff and Lustig [4] by the reaction of  $SOF_2$  with  $F_2$  in the presence of CsF as a catalyst. The fluorination was carried out in a nickel reactor at 100 °C.  $SOF_2$  was prepared by the reaction of  $Cl_2SO$  with  $SbF_3$  in the presence of  $SbCl_5$  as a catalyst [5].  $SF_5OF$  was purified by low temperature distillation, its purity was tested by IR spectroscopy and it was then stored in a trap cooled with liquid air.

CO was a commercial product. It was purified according to the standard method and stored in a 5 l bulb.

## 3. Experiments and results

Preliminary experiments on the photolysis of  $SF_5OF$  with 253.7 nm light showed no pressure change. The IR spectra taken after the  $SF_5OF$  had been photolysed showed only the characteristic bands of this compound.

The experiments were performed at 20, 26.6 and 43.6 °C. The  $SF_5OF$  pressure was varied between 180 and 300 Torr and the CO pressure between 120 and 400 Torr. Several experiments were carried out in the presence of the reaction products, and in others the light intensity was reduced to one-third by inserting a blackened mesh into the light path. Under these conditions no dark reaction was detected.

A slow pressure change was observed during the reaction. However, it was decided to follow its course by interrupting the reaction after a certain time and then separating the CO by distillation on cooling the U-tube with liquid air.

The reaction products were identified by IR spectroscopy using a Perkin-Elmer type 325 spectrometer.

In some experiments the reaction mixture was distilled at -120 °C. Two fractions were obtained. In the non-volatile fraction the following bands were observed: 826  $cm^{-1}$  belonging to  $S_2F_{10}$ ; 1898 and 1190  $cm^{-1}$  belonging to both  $SF_5OCOF$  and  $SF_5COF$ . By comparing the intensity of these bands with those of the literature spectra [6] it was possible to estimate that the amount of  $SF_5OCOF$  plus  $SF_5COF$  formed during the reaction was about 5% of the  $SF_5OF$  consumed. The other bands overlapped with those of the  $SF_5OF$ .

TABLE 1

COF<sub>2</sub> and S<sub>2</sub>F<sub>10</sub> formed at 26.6 °C

Experiment number	$\Delta p$ (Torr)	$\Delta t$ (min)	$I_{ab}$ (Torr min <sup>-1</sup> )	$\Delta t I_{ab}$ (Torr)	[COF <sub>2</sub> ] (Torr)	[S <sub>2</sub> F <sub>10</sub> ] (Torr)
20	4.4	180	0.0190	3.4	2.0	2.0
21	4.7	185	0.0184	3.4	2.2	2.0
22	4.0	183	0.0182	3.3	2.5	2.3
23	4.4	181	0.0228	4.1	2.8	2.6
25	3.0	303	0.0208 × 0.33	2.1	1.5	1.7 <sup>a</sup>

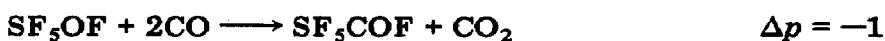
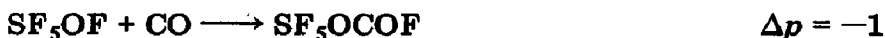
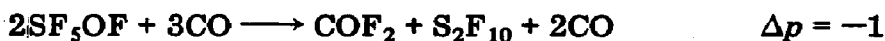
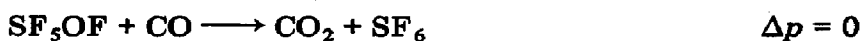
<sup>a</sup>Experiment with a blackened mesh.

In the volatile fraction it was possible to observe the characteristic bands corresponding to CO<sub>2</sub> and SF<sub>6</sub>. These substances are without doubt the main products. Furthermore, two bands (1928 and 1238 cm<sup>-1</sup>) belonging to COF<sub>2</sub> were observed. The CO<sub>2</sub> formed was estimated from these spectra and was similar to CO consumed ( $\pm 10\%$ ).

The amounts of S<sub>2</sub>F<sub>10</sub> and COF<sub>2</sub> were determined spectroscopically by their IR absorption at 826 cm<sup>-1</sup> and 1928 cm<sup>-1</sup> respectively, using calibrated spectra of both substances (see Table 1).

The amount of SF<sub>5</sub>OF consumed, measured by iodometric titration [7, 8] was found to be identical with the CO consumed.

The products were formed according to the following equations:



Knowing the stoichiometry of the reaction, its progress could be followed by determining the amount of CO consumed during the reaction time.

The reproducibility of the experiments was good. They showed that the pressure of carbon monoxide, and the reaction products, had no effect on the quantum efficiency  $\Phi(\text{CO})$  of CO consumption. The dependence of  $\Phi(\text{CO})$  on  $I_{ab}$  and  $[\text{SF}_5\text{OF}]$  can be expressed by the expression

$$\Phi_{\text{CO}} - \Phi_{\Delta p} - 2 = \frac{k[\text{SF}_5\text{OF}]}{I_{ab}^{1/2}} \quad (\text{I})$$

where

$$\Phi_{\Delta p} = \frac{\Delta p}{\Delta t I_{ab}}$$

The experimental results are summarized in Tables 2 - 4.  $\Delta t$  is the reaction time in minutes and  $[\text{SF}_5\text{OF}]$  and  $[\text{CO}]$  are the corresponding

TABLE 2  
Experiments at 20 °C

Experiment number	[SF <sub>5</sub> OF] <sub>i</sub> (Torr)	[CO] <sub>i</sub> (Torr)	[CO] (consumed) (Torr)	Δp (Torr)	Δt (min)	I <sub>ab</sub> (Torr min <sup>-1</sup> )	Φ <sub>CO</sub>	Φ <sub>Δp</sub>	k̄ (M <sup>-1/2</sup> s <sup>-1/2</sup> )
6	200.6	119.7	10.5	2.3	60	0.0267	6.5	1.4	0.046
	190.1	119.5	11.2	2.2	60	0.0258	7.2	1.4	0.056
	178.9	117.4	6.6	1.2	41	0.0250	6.4	1.2	0.051
	172.3	116.3	10.6	1.8	64	0.0242	6.8	1.2	0.060
	161.7	116.8	4.6	0.9	32	0.0235	6.1	1.2	0.049
7	198.0	191.8	11.0	2.7	60	0.0265	6.9	1.7	0.047
10	209.1	396.9	13.2	3.6	66	0.0265	7.5	2.0	0.049
11	221.9	119.9	17.2	2.2	76	0.0282	8.0	1.0	0.068
	204.7	118.3	15.0	2.7	71	0.0269	7.8	1.4	0.064
	189.7	119.4	16.9	2.8	84	0.0255	7.9	1.3	0.070
12	253.1	294.1	18.4	3.4	70	0.0295	8.9	1.6	0.064
	234.7	298.2	19.7	3.4	85	0.0282	8.2	1.4	0.062
	215.0	293.0	12.5	2.9	67	0.0270	6.9	1.6	0.046
14	195.1	268.9	14.3	2.9	111	0.0161	8.0	1.6	0.052

$$\bar{k} = 0.056 \text{ M}^{-1/2} \text{ s}^{-1/2}$$

TABLE 3

Experiments at 26 °C

Experiment number	[SF <sub>5</sub> OF] <sub>i</sub> (Torr)	[CO] <sub>i</sub> (Torr)	[CO] (consumed) (Torr)	Δp (Torr)	Δt (min)	I <sub>ab</sub> (Torr min <sup>-1</sup> )	Φ <sub>CO</sub>	Φ <sub>Δp</sub>	k (M <sup>-1/2</sup> s <sup>-1/2</sup> )
21	214.2	193.2	32.3	4.7	180	0.0187	9.2	1.3	0.072
22	210.7	148.3	31.6	4.0	183	0.0185	9.3	1.2	0.076
23	306.2	199.0	45.2	4.4	181	0.0229	10.9	1.1	0.074
26	214.1	294.2	32.0	5.0	207	0.0180	8.6	1.3	0.063
27	201.1	195.5	35.3	4.5	213	0.0171	9.7	1.2	0.081
28	206.7	145.2	33.5	3.8	200	0.0176	9.5	1.1	0.079
29	300.2	197.0	47.3	5.1	198	0.0216	11.1	1.2	0.074
30	288.5	201.0	36.3	2.5	303	0.0140 × 0.33	17.0	1.2	0.076 <sup>a</sup>

 $\bar{k} = 0.074 \text{ M}^{-1/2} \text{ s}^{-1/2}$ .<sup>a</sup>Experiment with a blackened mesh.

TABLE 4

Experiments at 43.6 °C

Experiment number	[SF <sub>5</sub> OF] <sub>i</sub> (Torr)	[CO] <sub>i</sub> (Torr)	[CO] (consumed) (Torr)	Δp (Torr)	Δt (min)	I <sub>ab</sub> (Torr min <sup>-1</sup> )	Φ <sub>CO</sub>	Φ <sub>Δp</sub>	k (M <sup>-1/2</sup> s <sup>-1/2</sup> )
31	205.9	196.8	44.0	3.8	180	0.0162	15.1	1.3	0.148
32	299.1	199.7	30.6	2.2	96	0.0190	16.8	1.2	0.119
33	189.2	196.9	23.0	2.1	114	0.0144	14.0	1.3	0.131
35	203.3	199.4	16.7	1.9	155	0.0139 × 0.33	23.5	2.7	0.119 <sup>a</sup>
36	223.8	213.9	30.4	2.6	125	0.0145	16.8	1.4	0.140

 $\bar{k} = 0.131 \text{ M}^{-1/2} \text{ s}^{-1/2}$ .<sup>a</sup>Experiment with a blackened mesh.

pressures of the gases in torrs. The index  $i$  indicates the initial pressure.  $k$  ( $M^{-1/2} s^{-1/2}$ ) is the rate constant calculated using eqn. (I).

The following mean values of the rate constant at different temperatures were obtained:  $\bar{k}(20^\circ C) = 0.056 M^{-1/2} s^{-1/2}$ ,  $\bar{k}(26.6^\circ C) = 0.074 M^{-1/2} s^{-1/2}$  and  $\bar{k}(43.6^\circ C) = 0.131 M^{-1/2} s^{-1/2}$ .

The apparent energy of activation derived from these values is  $E = 7 \pm 1$  kcal mol $^{-1}$ .

#### 4. Discussion of the results

On the basis of the experimental results and considering previous data it is possible to deduce the reaction mechanism. The primary process which consists, without doubt, in the dissociation of  $SF_5OF$  molecules into fluorine atoms and  $SF_5O$  radicals, is followed by the very fast reaction between  $SF_5O$  and CO [2, 9] which leads to the formation of  $CO_2$  and  $SF_5$  radicals. The fluorine atoms are also trapped by CO to form COF radicals [10].

The fact that the CO pressure does not appear in the rate equation proves that under the experimental conditions all  $SF_5O$  radicals are removed according to reaction (2) before they can participate in other reactions.

The radicals  $SF_5$  and COF react with  $SF_5OF$  molecules producing the stable products  $SF_6$  and  $COF_2$  respectively and at the same time regenerating  $SF_5O$  radicals. Consequently,  $SF_5$  and COF must be considered as the participants of a short chain reaction ( $5 \leq \Phi \leq 15$ ) although the small amount of  $COF_2$  formed shows that reaction (6) is slower than reaction (4). Furthermore, it is possible that COF radical reacts with CO producing FCOCO radical [11] which may react with  $SF_5OF$  to produce the stable molecule  $SF_5OCOF$  and regenerate COF radical. Finally, the radicals FCOCO and  $SF_5$  can disappear by reactions (7) and (9), forming the products  $S_2F_{10}$  and  $SF_5COF$ .

The following reaction mechanism is obtained:



When a steady state is assumed for the reactive intermediates the proposed set of reactions leads to

$$I_{ab} = k_7[\text{SF}_5]^2 + k_9[\text{FCOCO}][\text{SF}_5] \quad (\text{II})$$

and

$$I_{ab} = k_6[\text{SF}_5\text{OF}][\text{COF}] + k_9[\text{FCOCO}][\text{SF}_5] \quad (\text{III})$$

Moreover

$$\frac{\Delta p}{\Delta t} = k_7[\text{SF}_5]^2 + k_8[\text{SF}_5\text{OF}][\text{FCOCO}] + k_9[\text{SF}_5][\text{FCOCO}] \quad (\text{IV})$$

and in consequence the rate of  $\text{SF}_5\text{OCOF}$  formation can be expressed as

$$\frac{\Delta p}{\Delta t} - I_{ab} = k_8[\text{SF}_5\text{OF}][\text{FCOCO}] \quad (\text{V})$$

and hence

$$k_7[\text{SF}_5]^2 = k_6[\text{SF}_5\text{OF}][\text{COF}]$$

However, the mechanism leads to the rate equation

$$-\frac{d[\text{CO}]}{dt} = I_{ab} + k_2[\text{CO}][\text{SF}_5\text{O}] + k_8[\text{SF}_5\text{OF}][\text{FCOCO}] \quad (\text{VI})$$

Using eqn. (V) and rearranging gives

$$\Phi_{\text{CO}} - \Phi_{\Delta p} = \frac{k_2[\text{CO}][\text{SF}_5\text{O}]}{I_{ab}}$$

and furthermore

$$k_2[\text{CO}][\text{SF}_5\text{O}] = k_4[\text{SF}_5\text{OF}][\text{SF}_5] + 2k_7[\text{SF}_5]^2 + k_9[\text{FCOCO}][\text{SF}_5]$$

From eqns. (V) and (II) we find

$$[\text{SF}_5] = \frac{1}{2} - B \pm \left( B^2 + \frac{4I_{ab}}{k_7} \right)^{1/2}$$

where

$$B = k_9(\Phi_{\Delta p} - 1) \frac{I_{ab}}{k_7 k_8 [\text{SF}_5\text{OF}]}$$

If  $B \ll 1$  (this is possible if we consider that  $\Phi_{\Delta p}$  is between 1 and 2,  $I_{ab}$  is between  $1.5 \times 10^{-2}$  and  $2 \times 10^{-2}$  Torr min<sup>-1</sup> and the  $\text{SF}_5\text{OF}$  pressure is between 180 and 300 Torr, and taking  $k \approx 10^7$  M<sup>-1</sup> s<sup>-1</sup> [9, 12],  $k_9 \ll 10^9$  M<sup>-1</sup> s<sup>-1</sup> and  $k_8 \approx k_4 \approx 10^8$  M<sup>-1</sup> s<sup>-1</sup>) then

$$[\text{SF}_5] = \frac{I_{ab}^{1/2}}{k_7^{1/2}}$$



and substituting this value into the rate equation gives

$$\Phi_{\text{CO}} - \Phi_{\Delta p} - 2 = \frac{k_4[\text{SF}_5\text{OF}]}{k_7^{1/2}I_{\text{ab}}^{1/2}}$$

If reactions (5), (8) and (9) are ignored, we obtain the following rate law:

$$\Phi_{\text{CO}} - 2 = \frac{k_4[\text{SF}_5\text{OF}]}{k_7^{1/2}I_{\text{ab}}^{1/2}}$$

which also reproduces the experimental results. However, these reactions are necessary for explaining the product formation.

From the temperature dependence of  $k = k_4/k_7^{1/2}$  the apparent heat of activation can be calculated:  $E = E_4 - (1/2)E_7$ . The activation energy  $E_7$  of radical recombination can be considered to be zero, and so  $E_4 = 7 \pm 1$  kcal mol<sup>-1</sup>. This is a typical value for such a reaction. Colussi and Schumacher [1] estimated the value of 4 kcal mol<sup>-1</sup> for  $E_4$ , and using this they obtained the value of 28 kcal mol<sup>-1</sup> for the activation energy of the reaction between CO and SF<sub>5</sub>OF. Recalculating this energy using the  $E_4$  value obtained in this work, the latter is now 22 kcal mol<sup>-1</sup>, which is in good agreement with the value for other similar reactions [13, 14].

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