THE PHOTOLYSIS OF BIS(FLUOROXY)DIFLUOROMETHANE ($CF_2(OF)_2$) AND ITS PHOTOCHEMICAL REACTION WITH CARBON MONOXIDE

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Summary

The photochemical decomposition of bis(fluoroxy)difluoromethane ($CF_2(OF)_2$) and its reaction with CO at 253.7 nm was studied in a static system at temperatures between −20 and 30 °C. At low conversion the decomposition of pure $CF_2(OF)_2$ proceeds according to the reaction stoichiometry

$$CF_2(OF)_2 = CF_2O + F_2 + \tfrac{1}{2}O_2$$

with a quantum efficiency ϕ of 0.65 ± 0.03 molecules quantum^{-1} independent of the experimental conditions. The addition of a sufficiently large concentration of CF_2O produces a change in the reaction mechanism and trifluoromethyl peroxide $(CF_3O)_2$ is observed among the reaction products. An increase in the oxygen pressure tends to increase the quantum efficiency to an upper limit of 1 molecule quantum^{-1}.

In the presence of CO the reaction stoichiometry is

$$CF_2(OF)_2 + 2CO \rightarrow 2CF_2O + CO_2 \qquad \Delta n = 0$$

and ϕ = 1.0 ± 0.1 molecules quantum^{-1} for all experimental conditions. The addition of oxygen changes the reaction mechanism, and a decrease in the total pressure accompanied by the formation of bis(monofluorocarbonyl)-peroxide $(FCO)_2O_2$ was observed.

1. Introduction

We have recently studied the kinetics of the gas phase thermal reaction between bis(fluoroxy)difluoromethane ($CF_2(OF)_2$) and CO at temperatures between 110 and 140 °C [1]. The experimental results were interpreted by a

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chain mechanism similar to that proposed by Schumacher and coworkers [2] for the thermal reaction between F_2O and CO. The chain length γ was 2.5 and was independent of the experimental conditions.

In the present work the photolysis of pure $CF_2(OF)_2$ and its photochemical reaction with CO at 253.7 nm in the range −20 to +30 °C was studied.

2. Experimental details

2.1. Apparatus

A conventional apparatus for the study of photochemical reactions in static systems described by Müller and Schumacher [3] was used with minor modifications. The reactor vessel was a quartz cylinder 10 cm long and 5 cm in diameter with flat optical windows. It was connected to a Bodenstein quartz spiral manometer used as a null instrument which in turn was connected to a mercury manometer and, via a U-trap used for low temperature separations, to a standard vacuum line for gas handling. Stainless steel needle valves with Teflon seats were used. A 500 W Osram HBO 500 superpressure mercury lamp was employed as the light source. A set of quartz lenses and diaphragms was used to produce a parallel homogeneous light beam 4.5 cm in diameter. A filter 4.5 cm long containing 2 atm of chlorine was used in conjunction with a filter 3 cm long containing aqueous 1 M nickel sulphate–1 M cobalt sulphate to isolate the 254 nm region. The incident light intensity was measured with a Hatchard and Parker [4] ferrioxalate actinometer. The ratio of the intensity of the transmitted light to the intensity of the incident light was measured at 30 °C for the working wavelength in the reaction vessel. A correction for absorption and reflection by the windows was applied. The fractions of absorbed light intensity calculated for several $CF_2(OF)_2$ pressures are given in Table 1.

TABLE 1

$CF_2(OF)_2$ (Torr)	I_a/I_0
51.9	0.29
51.9	0.27
103.0	0.50
103.0	0.51
149.4	0.61
150.0	0.64
166.6	0.66
229.8	0.75

T = 30 °C.

2.2. *Materials*

$CF_2(OF)_2$ was prepared by the method described by Cauble and Cady [5]. It was purified by filtration [6] at liquid oxygen temperature followed by trap-to-trap low temperature distillation and was stored in a liquid-air-cooled trap or, in gaseous form, in a 2 l Pyrex flask.

99.9% CO, 97% COF_2 and 99.7% CF_4 obtained from Matheson Gas Products (U.S.A.) were passed through cooled traps (−140 °C) and stored in Pyrex flasks. Cylinder nitrogen and oxygen obtained from La Oxígena S.A. (Buenos Aires) were passed through a liquid-oxygen-cooled trap and stored in Pyrex flasks.

3. Results

3.1. *Photolysis of pure $CF_2(OF)_2$*

Preliminary experiments showed that the reaction occurs with an increase in the total concentration. Accordingly, its progress can be followed at constant volume by measuring the pressure increase after different time intervals. The results are summarized in Table 2. When the reaction products were distilled at −183 °C a non-condensable fraction identical in amount with the total pressure increase was obtained. This fraction showed no IR absorption. The IR spectra of the condensable fraction showed the characteristic bands of $CF_2(OF)_2$ and COF_2. The consumption $[CF_2(OF)_2]_c$ of $CF_2(OF)_2$ determined iodometrically [7] was identical with the amount $[COF_2]_f$ of COF_2 formed which was determined spectrophotometrically from the 1944 cm^{-1} band in the IR spectrum. Both concentration changes were equal to two-thirds of the total pressure increase. These results suggest the reaction stoichiometry

$$CF_2(OF)_2 \rightarrow COF_2 + F_2 + \tfrac{1}{2}O_2 \qquad \Delta n = +1.5$$

from which $[CF_2(OF)_2]_c = [COF_2]_f = \frac{2}{3}\Delta p$.

TABLE 2

Experiment	*T* (°C)	$[CF_2(OF)_2]_i$ (Torr)	Δp (Torr)	[A][a] (Torr)	$\frac{2}{3}\Delta p$	$[CF_2(OF)_2]_c$ (Torr)	$[CF_2O]_f$ (Torr)
104	30	98.6	10.0	—	6.7	6.2	—
105		98.8	10.8	—	7.3	7.3	—
6		28.4	4.1	4.0	2.7	—	2.7
2		53.9	7.1	7.0	4.7	—	4.9
90		99.5	7.8	7.7	5.2	—	5.3
150		104.8	10.7	11.4	7.1	—	7.2
205		102.0	5.4	5.2	3.6	—	3.6
156	20	95.9	12.5	12.6	8.3	—	8.3
153	−20	84.8	10.7	11.4	7.1	—	6.9

[a] Non-condensable fraction at −183 °C.

In order to prove that fluorine was present in the reaction products some experiments were carried out in which oxygen and CO were added to the system at the end of an illumination period. A thermal reaction was observed with a decrease in total pressure accompanied by the formation of bis(monofluorocarbonyl)peroxide ($(FCO)_2O_2$) [8]. This compound, which was not formed in the absence of fluorine, was isolated from the reaction products as a distillation residue at −115 °C and was characterized by its IR spectrum. This behaviour confirms the reaction stoichiometry given above.

In an attempt to establish the mechanism of the photolytic decomposition of pure $CF_2(OF)_2$ numerous experiments were carried out in which the experimental conditions were systematically varied as follows: light intensity, 0.41×10^{17} - 3.16×10^{17} quanta min^{-1}; initial $CF_2(OF)_2$ pressure, 16 - 150 Torr; total pressure, 16 - 600 Torr; fluorine pressure, 0.5 - 100 Torr; COF_2 pressure, 0.5 - 100 Torr; oxygen pressure, 0.25 - 300 Torr; temperature, between −20 and +30 °C.

In all cases the quantum efficiency $\phi = [CF_2(OF)_2]_c/I_{abs}$ was 1 molecule $quantum^{-1}$ or less. Increasing the oxygen pressure tended to increase ϕ to the upper limit of unity but produced no change in the reaction stoichiometry. The oxygen effect was more pronounced at lower temperatures. Some of the data obtained at 0 and 30 °C are given in Table 3.

TABLE 3

Experiment	T (°C)	$[CF_2(OF)_2]_i$ (Torr)	Δp (Torr)	$[O_2]$ (Torr)	ϕ (molecules $quantum^{-1}$)
13	30	100.5	2.0	0.38	0.68
79	30	101.1	11.6	1.9	0.67
54	30	99.4	13.1	23.4	0.73
34	30	101.9	2.6	44.1	0.81
129	30	98.9	7.3	244.6	1.02
128	30	105.8	7.5	268.2	0.93
161	0	91.1	5.8	0.5	0.81
162	0	92.5	7.9	15.4	0.92
163	0	92.9	9.7	72.7	0.99

A change in the reaction mechanism was observed in the presence of a sufficiently high concentration of COF_2. When 100 Torr of COF_2 was added at 30 °C, the reaction occurred without any pressure change and tri(fluoromethyl)peroxide ($(CF_3O)_2$) was obtained in the reaction products. However, for $[O_2] \leqslant 5$ Torr and $[COF_2] \leqslant 6$ Torr the effects of COF_2 on ϕ were negligible. Accordingly most of the experiments were carried out at a low conversion of $CF_2(OF)_2$. In these conditions $\phi = 0.65 \pm 0.03$ molecules $quantum^{-1}$, independent of the other experimental conditions. Some of the results are shown in Table 4.

TABLE 4

Experiment	*T* (°C)	$[CF_2(OF)_2]_i$ (Torr)	Δt (min)	Δp (Torr)	$I_0 \times 10^{-17}$ (quanta min^{-1})	ϕ (molecules $quantum^{-1}$)
13	30	100.5	600	2.0	0.414	0.68
51	30	99.1	240	2.6	1.35	0.68
100	30	98.6	428	9.5	2.92	0.66
102	30	99.3	277	6.5	3.16	0.64
19	30	99.7	390	2.5	0.86	0.63[a]
85	30	102.1	238	5.0	2.76	0.64[b]
41	30	16.2	526	1.7	2.02	0.67
6	30	28.4	763	4.1	2.14	0.63
7	30	28.4	495	2.5	2.01	0.62
8	30	26.7	478	1.2	1.00	0.64
1	30	53.5	210	4.4	4.96	0.62
2	30	53.9	210	4.1	4.52	0.63
12	30	100.9	370	2.9	1.00	0.66
5	30	152.5	185	4.3	2.46	0.63
79	30	101.1	405	11.6	3.87	0.63
76	30	99.7	451	10.1	3.31	0.59[c]
82	30	99.2	230	4.7	3.35	0.61[d]
83	30	97.2	250	5.1	3.19	0.66[e]
114	−10	91.3	450	6.4	1.86	0.69

[a] In the presence of 407 Torr of CF_4.
[b] In the presence of 434 Torr of CF_4.
[c] In the presence of 4.8 Torr of COF_2; apparent value of ϕ.
[d] In the presence of 100 Torr of fluorine.
[e] In the presence of 109 Torr of fluorine.

3.2. *The photochemical reaction with CO*

Preliminary experiments carried out at 30 °C in the dark showed no observable thermal reaction. The photochemical reaction occurs without any change in the total pressure. Low temperature separations were carried out by means of the U-trap attached to the reaction vessel. The IR spectra of the fraction condensed at −183 °C showed characteristic $CF_2(OF)_2$, COF_2 and CO_2 bands. The IR spectra of the non-condensable fraction showed CO bands only. The relation (Table 5)

$$[COF_2]_f = 2[CF_2(OF)_2]_c = [CO]_c$$

was obtained between the amount $[COF_2]_f$ of COF_2 formed which was measured spectrophotometrically, the consumption $[CF_2(OF)_2]_c$ of $CF_2(OF)_2$ which was determined iodometrically and the amount $[CO]_c$ of CO consumed which was determined as the difference between the initial CO pressure $[CO]_i$ and the pressure of the non-condensable fraction at −183 °C. This result shows without any doubt that the reaction stoichiometry is

$$CF_2(OF)_2 + 2CO = 2COF_2 + CO_2 \qquad \Delta n = 0$$

TABLE 5

Experiment	$[CO]_c$ (Torr)	$[CF_2(OF)_2]_c$ (Torr)	$[CO]_c/2$ (Torr)	$[CF_2O]_f$ (Torr)
182	12.5	6.8	6.3	—
183	10.3	5.3	5.1	—
186	10.2	5.4	5.1	—
188	15.8	8.6	7.9	—
189	11.5	6.3	5.7	—
195	9.4	—	—	8.9
174	12.8	—	—	13.0
175	12.2	—	—	13.2

T = 30 °C.

Therefore the reaction rate can be obtained by measuring the non-condensable fraction at −183 °C after a known photolysis time.

In order to determine the rate law numerous experiments were carried out in which the variables were systematically varied as follows: light intensity, 0.7×10^{17} - 2×10^{17} quanta min^{-1}; total pressure, 130 - 600 Torr; initial $CF_2(OF)_2$ pressure, 50 - 230 Torr; initial CO pressure, 30 - 500 Torr; temperature, 0 - 30 °C. Some experiments were also carried out in the presence of up to 65 Torr of COF_2.

In all cases the quantum efficiency for $CF_2(OF)_2$ consumption was 1 ± 0.1 molecules $quantum^{-1}$, independent of the experimental conditions (Table 6). A change in the reaction mechanism was observed in the presence of oxygen: there was a decrease in the total pressure accompanied by the formation of bis(monofluorocarbonyl)peroxide ($(FCO)_2O_2$).

4. Discussion

$CF_2(OF)_2$ shows a continuum absorption spectrum at wavelengths below 300 nm. Consequently the primary process must be molecular dissociation. Radiation of wavelength 254 nm has enough energy (113 kcal mol^{-1}) to break either an O—F bond (about 47 kcal mol^{-1}) or a C—OF bond (about 70 kcal mol^{-1}). Therefore there are two possibilities for the primary process:

$$CF_2(OF)_2 + h\nu_{254} \rightarrow \dot{C}F_2\text{—}OF + OF \qquad (1)$$

$$CF_2(OF)_2 + h\nu_{254} \rightarrow CF_2\begin{matrix} \diagup O^{\cdot} \\ \diagdown OF \end{matrix} + F \qquad (2)$$

In order to account for a ϕ value of less than unity, as observed in the photolysis of pure $CF_2(OF)_2$, it is reasonable to assume that one or both recombination reactions operates:

TABLE 6

Experiment	T (°C)	$[CF_2(OF)_2]_i$ (Torr)	$[CO]_i$ (Torr)	Δt (min)	$[CO]_c$ (Torr)	$I_0 \times 10^{-17}$ (quanta min^{-1})	ϕ
179	30	165.3	117.9	603	10.4	0.71	1.1
198	30	159.8	123.9	182	7.6	2.00	1.0
178	30	99.9	79.2	321	8.3	2.15	0.97[a]
180	30	101.1	79.3	395	12.6	2.15	0.97[b]
200	30	51.2	79.6	548	9.2	2.00	0.98
182	30	99.7	76.0	348	11.5	2.24	0.97
187	30	99.5	75.9	385	11.2	1.94	0.98
189	30	98.0	81.6	430	11.7	1.68	1.1
198	30	159.8	123.9	182	7.6	2.00	1.0
201	30	166.8	97.4	196	7.9	1.66	1.1
202	30	167.4	99.4	184	7.2	1.66	1.1
203	30	229.8	77.3	186	7.7	1.66	1.0
99	30	99.7	28.5	337	16.5	3.21	1.0
101	30	100.0	29.2	277	12.5	3.17	0.93
172	30	100.9	25.7	234	8.8	2.21	1.1
187	30	99.5	75.9	385	11.2	1.81	1.05
189	30	98.0	81.6	430	11.7	1.63	1.1
145	30	98.3	100.6	460	14.5	2.19	0.96
151	30	104.9	130.5	619	18.4	1.94	0.98
181	30	99.7	162.8	258	10.0	2.24	1.1
169	30	100.5	252.2	282	10.0	2.22	1.0
190	30	98.7	492.1	388	10.2	1.58	1.1
204	30	162.0	51.4	203	6.1	1.45	1.0[c]
214	30	105.1	97.3	379	8.1	1.40	0.96[d]
184	3.5	88.8	78.9	378	7.3	1.94	0.97
185	3.5	88.7	89.7	368	7.3	1.94	0.97

[a] In the presence of 405 Torr of nitrogen.
[b] In the presence of 401 Torr of nitrogen.
[c] In the presence of 8.6 Torr of COF_2.
[d] In the presence of 65.1 Torr of COF_2.

$$\dot{C}F_2{-}OF + OF \rightarrow CF_2(OF)_2 \tag{1a}$$

$$CF_2\begin{matrix} \diagup O^{\cdot} \\ \diagdown OF \end{matrix} + F \rightarrow CF_2(OF)_2 \tag{2a}$$

Since the addition of fluorine atoms resulting from the photolysis of F_2 added to the system leaves the ϕ value unchanged, it must be concluded that all the fluorine atoms eventually produced by dissociation (2) are consumed by the recombination reaction (2a).

The above conclusion is supported by the observed effect of oxygen on ϕ. It is well known that oxygen catalyses the recombination of fluorine atoms [9]:

$$F + O_2 \rightarrow FO_2 \tag{3}$$

$$FO_2 \rightarrow F + O_2 \tag{3a}$$

$$F + FO_2 \rightarrow F_2 + O_2 \tag{4}$$

Reaction (3a) has an activation energy of about 15 kcal mol^{-1}, whereas the activation energy of (3) is probably near to zero and that of (4) must also be small (probably between 2 and 5 kcal mol^{-1}). Therefore we can expect an increasing effect of oxygen at decreasing temperatures as is observed.

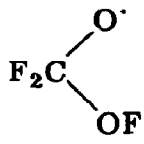
In the photolysis of pure $CF_2(OF)_2$ at low conversion and with no added oxygen the effective primary process must consist of reactions (1), (2) and (2a), and the value $\phi = 0.65$ molecules $quantum^{-1}$ is a measure of the occurrence of reaction (1). The OF radicals produced can react [10] to form F_2 and O_2:

$$OF + OF \rightarrow 2F + O_2 \rightarrow F_2 + O_2 \tag{5}$$

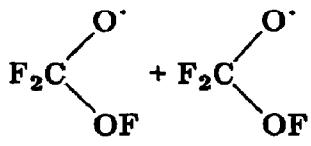
Since ϕ is independent of the experimental conditions, the set of reactions that follows is highly speculative. However, it seems reasonable to assume that there is a reaction between two $\dot{C}F_2OF$ radicals produced in reaction (1)

$$\dot{C}F_2OF + \dot{C}F_2OF \rightarrow 2CF_2O + F_2 \tag{6}$$

resulting in the formation of end products. In the presence of oxygen some of the fluorine atoms produced in reactions (2) and (5) are consumed in reactions (3) and (4). Consequently the



radicals can also react to produce end products



$$\rightarrow 2CF_2O + F_2 + O_2 \tag{7}$$

and the quantum efficiency increases.

In the presence of CO the quantum efficiency is $\phi = 1.0 \pm 0.1$ molecules $quantum^{-1}$, independent of the widely varying experimental conditions. The well-known fast reaction between fluorine atoms and CO [8]

$$F + CO \rightarrow FCO \tag{8}$$

then removes the fluorine atoms, making reaction (2a) unimportant. In this case the ϕ value increases to the upper limit of 1 molecule $quantum^{-1}$.

In the thermal reaction mechanism [1] the step

$$FCO + CF_2(OF)_2 \rightarrow COF_2 + CF_2\begin{matrix} O^{\cdot} \\ OF \end{matrix}$$

gives rise to a short chain. Since $\phi = 1$ molecule quantum^{-1} in the photochemical reaction this step can be ruled out. From the effect observed when oxygen is added, the reaction between two OF radicals to form O_2 can also be neglected in the presence of CO. Accordingly it must be accepted that these OF radicals also react with CO. There are several possibilities for this reaction, one of which is

$$OF + CO \rightarrow FO\dot{C}O \tag{9}$$

followed by

$$FO\dot{C}O + CO \rightarrow F\dot{C}O + CO_2 \tag{10}$$

or

$$OF + CO \rightarrow CO_2 + F \tag{11a}$$

followed by reaction (8) or

$$OF + CO \rightarrow F\dot{C}O + O \tag{11b}$$

followed by

$$O + CO + M \rightarrow CO_2 + M \tag{12}$$

all of which lead to the formation of FCO and CO_2.

The radicals produced in steps (1) and (2) must also react with CO in order to maintain the stoichiometry of the photochemical reaction with CO. One possibility is

$$CF_2\begin{matrix} O^{\cdot} \\ OF \end{matrix} + CO \rightarrow \dot{C}F_2OF + CO_2 \tag{13}$$

$$\dot{C}F_2OF + CO \rightarrow F\dot{C}O + CF_2O \tag{14}$$

$$F\dot{C}O + \dot{C}F_2OF \rightarrow 2CF_2O \tag{15}$$

The effect of oxygen can be explained by the well-known fast reaction [8]

$$FCO + O_2 \rightarrow FCO\cdot O_2$$

followed by

$$FCO\cdot O_2 + FCO\cdot O_2 \rightarrow (FCO)_2O_2 + O_2$$

which explains the observed $(FCO)_2O_2$ formation.

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