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KINETIC STUDY OF THE PHOTOCHEMICAL REACTION BETWEEN FLUOROXIPERFLUOROMETHANE AND CARBON MONOXIDE *

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RESUMEN

La reacción fotoquímica entre el fluoroxiperfluorometano y el monóxido de carbono, que produce en forma cuantitativa fluoroformiato de perfluorometilo (FFPFM), responde a la ley cinética: $v = (I_{abs}^{1/2})\ [CF_3OF]$ en el intervalo de temperatura entre 35 y 55°. Esta ley es interpretada mediante un esquema de reacción que involucra una cadena corta, cuya terminación es la recombinación de radicales CF_3OCO para producir oxalato de perfluorometilo. Se dan los valores numéricos de k y del rendimiento cuántico. Se presenta el gráfico de Arrhenius y se calcula el factor preexponencial y la energía de activación de la constante total. El agregado de oxígeno inhibe la formación de FFPFM y conduce a la producción de dióxido de carbono.

Fluoroxiperfluoromethane [1] and bis (perfluoromethyl) peroxide are known sources for $CF_3O\cdot$ radicals, which can be generated from the said substances either photochemically or thermally [2, 3].

Although several reactions involving $CF_3O\cdot$ radicals have been described [2, 3], no kinetic study for any of these reactions has been published yet.

We have photolysed fluoroxiperfluoromethane in the presence of carbon monoxide and studied the kinetics of the process. This reaction had already been reported as a convenient preparative route to perfluoromethyl fluoroformate (PFMFF) [4].

* Previous communications on this and the following paper were presented at the 12th Argentine Chemical Meeting held in Córdoba, April 1967. Numerical results have been now corrected for a trivial arithmetic error which did not affect the main conclusions reported at the Meeting.

Final results of the present work have been included in a communication entitled "Some Reactions of Photochemically generated Perfluoromethoxyl and Related Oxygenated Derivatives of the Perfluoromethyl Radical" presented at the International Symposium on Basic Mechanisms in Photochemistry and Photobiology held in Caracas, Venezuela, on December 1967. See: J. Photochem. and Photobiol., in the press.

c) *Analyss of the reaction mixtures*

Reaction mixtures were fractioned by low temperature distillations and components identified by IR spectroscopy. The only products found in this way were PFMFF and minor quantities of fluorophosgene and bis(perfluoromethyl) oxalate [9] (cf. reference 4, which describes work carried out in substantially different experimental conditions).

A typical analysis was perfomed as follows: the "U" tube was cooled with liquid air and residual CO pumped off; condensate was then allowed to warm up and its pressure was measured. Partial pressure of the volatile was then obtained by substraction. Next, the "U" tube was cooled with an EtOH slush at $-130°$, and the volatile transferred quantitatively to an IR cell with a cold finger which was cooled with liquid air. The fluorophosgene

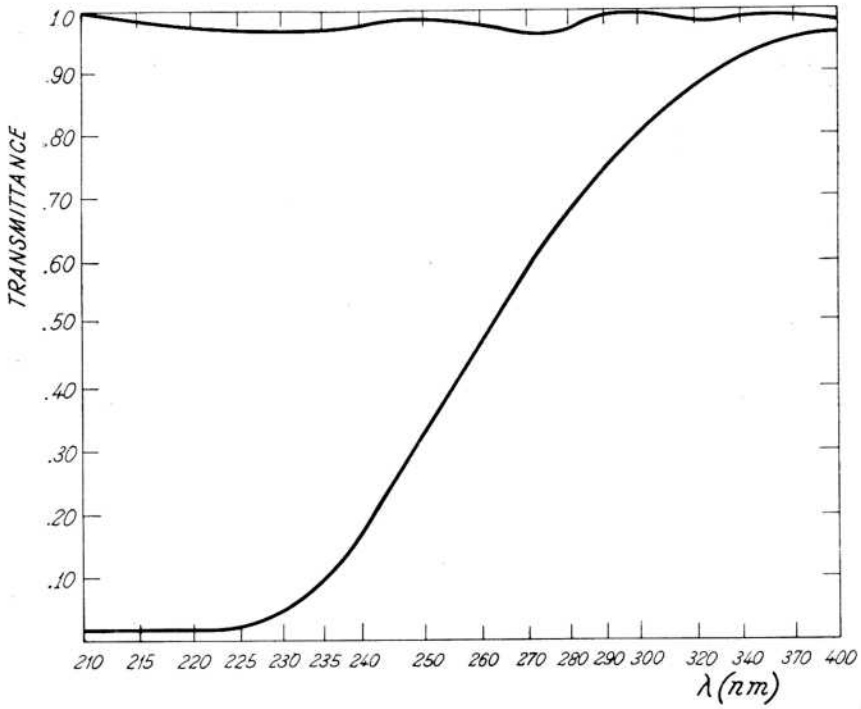

Fig. 1. — The UV absorption spectrum of fluoroxiperfluoromethane

content in this fraction was evaluated from the extinction of the Q-branch of its carbonylic stretching absorption at 1945 cm^{-1} (for calibration purposes a sample of fluorophosgene prepared by direct reaction of fluorine (Allied Chemical Corp.) with CO, as described in reference 16, was used without further purification). The difference of total pressure of this fraction minus fluorophosgene pressure was taken as residual pressure of CF_3OF. The following step was perfomed at $-100°$; the volatile was in this case pure PFMFF; again, its pressure was obtained by difference. The final residue non volatile at $-100°$ was found to be bis(perfluoromethyl) oxalate [9].

Results of some experiments included in Table 1 show that practically all CF_3OF reacted to yield mainly PFMFF, other products amounting in any case to no more than 2 % of CF_3OF consumed. This observation was confirmed in experiments carried out to completion. In these cases, the total pressure drop was equal —within the said percentage— to the initial pressure of the reactant which, according to the stoichiometry of the reaction, was in defect.

TABLE 1

Analytical results of some typical reactions

Exp.	$p^{\circ}_{CF_3OF}$	p°_{CO}	$-\Delta p$	p_{CO}	p_{CF_3OF}	p_{COF_2}	p_{PFMFF}	$p_{Oxalate}$
21	95.3	52.7	51.2	0.6	44.2	1.0	49.9	0.6
25	200.3	188.6	115.9	73.1	82.7	1.7	114.8	1.3
30	73.6	100.1	53.8	45.1	16.5	1.0	52.8	1.1

The superscript ° refers to initial pressures; $-\Delta p$ means total pressure drop at the moment of performing the analysis. Pressures are given in mm Hg.

RESULTS

Rate data were found to fit the following kinetic law:

$$-\frac{\Delta p}{\Delta t} = +\frac{dp_{PFMFF}}{dt} = k\,(I_{abs})^{1/2}\,p_{CF_3OF} = k'(p_{CF_3OF})^{3/2}$$

so that the reaction rate was independent of carbon monoxide partial pressure and of total pressure. The results of some typical experiments are given in Tables 2-8. In these tables initial pressures of reactants and other gases are presented at the heading. Measured pressure change ($-\Sigma\Delta p$), as well as reaction rate ($-\Delta p/\Delta t$) and reactants partial pressures calculated at the end of each interval are tabulated together with the corresponding values of k'. Pressures are measured in mm Hg and time in minutes.

TABLE 2

Experiment Nº 60; T = 35.0°; $p^{\circ}_{CF_3OF} = 60.9$; $p^{\circ}_{CO} = 225.6$

$-\Sigma\Delta p$	$-(\Delta p/\Delta t)\times 10^2$	p_{CF_3OF}	p_{CO}	$k'\times 10^4$ *
5.5	14.3	55.4	220.1	3.47
8.0	12.2	52.9	217.6	3.18
10.4	12.1	50.5	215.2	3.36
12.9	11.2	48.0	212.7	3.38
17.5	8.95	43.4	208.1	3.10
20.7	9.00	40.2	204.9	3.51
25.2	6.37	35.7	200.4	3.00
32.6	5.31	28.3	193.0	3.53
37.1	4.14	23.8	188.5	3.56

$\bar{k}' = 3.34 \times 10^{-4}$ mm $Hg^{-1/2}$ min^{-1}

* Throughout Tables 2 to 8 k' was calculated by means of the expression:

$$k' = \frac{(-\Delta p/\Delta t)}{(p_{CF_3OF})^{1/2}}$$

TABLE 3

Experiment Nº 62 A ; T = 35.0° ; $p°_{CF_3OF}$ = 202.1 ; $p°_{CO}$ = 51.4

$-\Sigma\Delta p$	$-(\Delta p/\Delta t) \times 10^3$	p_{CF_3OF}	p_{CO}	$k' \times 10^4$
11.4	82.4	190.7	40.0	3.12
19.2	77.2	182.9	32.2	3.12
24.9	77.2	177.2	26.5	3.28
31.6	74.8	170.5	19.8	3.36
36.0	71.1	166.1	15.4	3.32
40.9	65.8	161.2	10.5	3.22
35.4	63.4	156.2	5.0	3.24

$$\bar{k}' = 3.24 \times 10^{-4} \text{ mm Hg}^{-1/2} \text{ min}^{-1}$$

TABLE 4

Experiment Nº 63 ; T = 35.0° ; $p°_{CF_3OF}$ = 49.8 ; $p°_{CO}$ = 200.1

$-\Sigma\Delta p$	$-(\Delta p/\Delta t) \times 10^3$	p_{CF_3OF}	p_{CO}	$k' \times 10^4$	I*
6.8	5.56	43.0	193.3	1.97	35
9.4	4.80	40.4	190.7	1.87	35
14.0	4.39	35.8	186.1	2.06	35
18.8	3.36	31.8	181.1	1.87	35
21.8	2.80	28.0	178.3	1.89	35
25.0	4.19	24.8	174.1	3.38	100
29.2	3.13	20.6	170.9	3.34	100
32.8	2.33	17.0	167.3	3.34	100

$$\bar{k}'_{100\%} = 3.35 \times 10^{-4} \; ; \; \bar{k}'_{35\%} = 1.93 \times 10^{-4}$$

$$\bar{k}'_{35\%} \times \left(\frac{100}{35}\right)^{1/2} = 3.26 \times 10^{-4}$$

* Intensity of light in percentage of I_0.

TABLE 5

Experiment Nº 72 ; T = 45.0° ; $p°_{CF_2OF} = 201.5$: $p°_{CO} = 100.7$

$-\Sigma\Delta p$	$-(\Delta p/\Delta t) \times 10$	p_{CF_2OF}	p_{CO}	$k' \times 10^4$
10.3	9.54	191.2	90.4	3.62
15.9	9.96	186.6	84.6	3.94
20.0	9.34	180.5	80.7	3.82
25.0	9.41	176.5	75.7	4.00
29.2	8.41	172.3	71.5	3.71
35.7	8.28	165.8	65.0	3.87
39.6	7.90	161.9	61.1	3.82
44.2	7.59	156.3	56.5	3.84
55.0	6.93	146.5	45.7	3.90
61.2	6.30	140.3	39.5	3.78
68.1	6.22	133.4	32.6	4.04
73.5	5.44	128.0	27.2	3.76
79.6	5.10	121.9	21.1	3.79
85.3	4.71	116.2	15.4	3.74
90.9	4.44	110.6	9.8	3.83

$\bar{k}' = 3.83 \times 10^{-4}$ mm $Hg^{-1/2}$ min^{-1}

TABLE 6

Experiment Nº 80 ; T = 55.0° ; $p°_{CF_2OF} = 93.9$; $p°_{CO} = 48.5$

$-\Sigma\Delta p$	$-(\Delta p/\Delta t) \times 10$	p_{CF_2OF}	p_{CO}	$k' \times 10^4$
8.2	3.83	85.7	40.3	4.85
13.1	3.50	80.8	35.4	4.84
18.1	3.50	75.8	30.4	5.30
22.6	2.71	71.3	25.9	4.49
26.3	2.68	67.6	22.2	4.82
30.2	2.54	63.7	18.3	4.99
34.7	2.12	59.2	13.8	4.64
40.3	1.89	53.6	8.2	4.82
43.6	1.62	50.3	4.9	4.53

$\bar{k}' = 4.81 \times 10^{-4}$ mm $Hg^{-1/2}$ min^{-1}

TABLE 7

Experiment Nº 76 ; T = 35.0° ; p_{CF_3OF} = 102.4 ; p°_{CO} = 199.2 ; p_{CO_2} = 188.5

$-\Sigma\Delta p$	$-(\Delta p/\Delta t) \times 10^4$	p_{CF_3OF}	p_{CO}	$k' \times 10^4$
5.4	32.2	97.0	193.8	3.35
7.6	29.3	94.8	191.6	3.18
11.1	29.5	91.3	188.1	3.38
16.1	25.2	86.3	183.1	3.15
19.2	24.8	83.2	180.0	3.27
21.6	24.6	80.8	177.6	3.39
28.7	20.7	73.7	170.5	3.30
31.7	21.6	70.7	167.5	3.66
43.3	14.6	59.1	155.9	3.21
46.8	12.8	55.6	152.4	3.09
51.0	12.5	51.4	148.2	3.40

$\bar{k}' = 3.30 \times 10^{-4}$ mm $Hg^{-1/2}$ min^{-1}

TABLE 8

Experiment Nº 62 B ; T = 35.0° ; p_{CF_3OF} = 150.7 ; p°_{CO} = 187.9 p°_{PFMFF} = 51.4

$-\Sigma\Delta p$	$-(\Delta p/\Delta t) \times 10^2$	p_{CF_3OF}	p_{CO}	$k' \times 10^4$
10.5	5.71	140.2	177.4	3.34
15.8	5.20	134.9	172.1	3.31
21.5	4.82	129.2	166.4	3.28
26.5	4.65	124.2	161.4	3.37
34.5	4.04	116.2	153.4	3.20
40.7	4.16	110.0	147.2	3.59

$\bar{k}' = 3.35 \times 10^{-4}$ mm $Hg^{-1/2}$ min^{-1}

Table 9 shows the mean value of the rate constant k for each of the temperatures studied, and Figure 2 is the corresponding Arrhenius plot. The overall rate constant k can be expressed in terms of the parameters A and q, as follows:

$$k_{exper} = 10^{(4.5 \pm 1.0)} \exp\left[-(4.200 \pm 1.400/RT\right] \text{ mole}^{-1/2} \text{ cm}^{3/2} \text{ sec}^{-1/2}$$

TABLE 9

Mean values of the rate constant

T (°K)	$\bar{k}$
308.2	29.3
318.2	34.2
328.2	43.0

$\bar{k}$ is given in mole$^{-1/2}$ cm$^{3/2}$ sec$^{-1/2}$, and corresponds to the equation:

$$v = k\,(I_{abs})^{1/2}\,[CF_3OF]$$

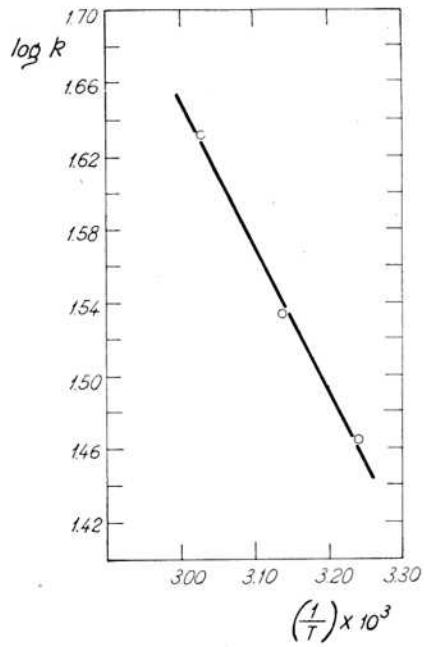

Fig. 2. — Arrhenius plot

The kinetic law found could be explained by postulating the following reaction mechanism:

$$CF_3OF + h\nu \rightarrow CF_3O\cdot + F\cdot \qquad (1)$$

$$CF_3O\cdot + CO \rightarrow CF_3O\dot{C}O \qquad (2\,a)$$

$$CF_3O\dot{C}O + CF_3OF \rightarrow CF_3OC(O)F + CF_3O\cdot \qquad (2\,b)$$

$$2\,CF_3O\dot{C}O \rightarrow (CF_3OCO)_2 \qquad (3)$$

$$F\cdot + CO \rightarrow F\dot{C}O \qquad (4)$$

$$F\dot{C}O + CF_3OF \rightarrow F_2CO + CF_3O\cdot \qquad (5)$$

Step (5) has been included as tthe most likely reaction for FCO radicals; other conceivable reactions would involve less probable radical - radical encounters and would lead either to undetected products (e.g. oxalyl fluoride or the monofluoride of the monoperfluoromethyl ester of oxalic acid) or to PFMFF; in this case however the kinetics of the overall process would be affected because of the consumption of $CF_3O\cdot$ radicals.

Assuming quasi-stationary concentrations of radicals, the usual analysis leads to the following expression for the experimental rate constant:

$$k_{exper} = k_{2b}\, k_3^{-1/2}$$

Chain length can be evaluated inmediatly, because it should be equal to the quantum yield in PFMFF, provided that the quantum yield for the primary process (1) could be taken as unity. In support of this assumption are the high energy of the radiation used (78 kcal/mole against the 47 kcal/mole estimated [10] for the bond strength of the O-F union in CF_3OF) and the type of absorption spectrum shown by CF_3OF (see Fig. 1), which suggests that dissociation is produced instantaneously (i.e., within the time of one vibration) [11].

The expression for the quantum yield corresponding to the given mechanism is:

$$\Phi = \frac{k}{RT\,(2.30\ z\ l\ I_0)^{1/2}}\,(p_{CF_3OF})^{1/2}$$

For $I_o = 4.96 \times 10^{14}$ quanta cm^{-3} sec^{-1},

$$\Phi = 7.6 \times (p_{CF_3OF})^{1/2}$$

This expression should also give the ratio of PFMFF and COF_2 yields, and is in general agreement with the trend found for fluorophosgene production. The same considerations apply to bis(perfluoromethyl) oxalate production.

As stated above, total pressure had no influence on the results. Thus, addition of either PFMFF or carbon dioxide did not alter the value of the rate constant, as shown in Tables 7 and 8. On the other hand, addition of oxygen changed completely the course of the reaction. Two possible different effects are to be expected upon addition of oxygen to analogous systems:

a) The reaction competes with, or even is completely quenched by the sensitized oxidation of carbon monoxide [12];

b) The nature of the reaction product changes, and peroxidic compounds are originated [13, 14].

In the present case the sensitized oxidation of carbon monoxide took place and the original reaction was quenched to the point that CF_3OF was not appreciably consumed. Further study of this system is under way.

DISCUSSION

Two are the most interesting points to be discussed.

The first refers to the activation energy of the overall process. According to the postulated mechanism, the measured value must be attributed to reaction (2b), as reaction (3) should have an activation energy equal or close to zero. The value found is reasonable for the type of reaction involved, i.e. abstraction of the fluorine atom from the O-F bond in CF_3OF by the $CF_3\dot{O}CO$ radical.

The second aspect deserving discussion is the fate of the $CF_3O\cdot$ radicals. According to the given scheme they should react quantitatively with carbon monoxide (step 2a). The following reaction pathways are thus automatically excluded:

a) Recombination:

$$2\ CF_3O\cdot \rightarrow (CF_3O)_2 \tag{6}$$

This reaction would yield undetectet bis(perfluoromethyl) peroxide. Therefore, although Cady [15] found that the peroxide is produced by photolysis of pure CF_3OF, the addition of CO seems to supress completely this reaction of $CF_3O\cdot$ radicals. Recombination is also perhaps an important (possibly chain ending) step of the photochemical formation of CF_3OF from fluorophosgene and fluorine [16]. It should be pointed out that very small quantities of the peroxide could have been observed —if present— in the IR spectra, because of its strong absorption band at 1165 cm^{-1} [17].

b) Loss of fluorine to yield fluorophosgene:

$$CF_3O\cdot \rightarrow CF_2O + F\cdot \tag{7}$$

Fluorophosgene is only a minor secondary product, the origin of which can be traced to reaction (5), because even when instantaneous concentration of $CF_3O\cdot$ was substantially increased (by performing the photolysis with a high intensity light flash) [18], the production of COF_2 was not enhanced.

c) Radical intercombinations:

We have already discussed the reaction:

$$F\dot{C}O + CF_3O\cdot \rightarrow CF_3OC(O)F. \tag{8}$$

Now we can rule out also the following:

$$CF_3O\cdot + CF_3\dot{O}CO \rightarrow (CF_3O)_2CO \tag{9}$$

which would give rise to bis(perfluoromethyl) carbonate [3], and this substance was never found among the reaction products. In fact, this result is in

agreement with those from the photolysis of $(CF_3O)_2$ in the presence of CO; in this reaction the oxalate rather than the carbonate is formed [3, 9], indicating that process (2a) is much faster than reaction (9).

In conclusión, carbon monoxide seems to be a very efficient scavenger for $CF_3O\cdot$ radicals.

Finally, we could mention that the mechanism found in this work sustains the main steps postulated by Pass and Roberts [14] to explain the reaction of CF_3OF with SF_4 and SO_2, although in these cases secondary reactions are apparently more important.

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REFERENCES

1 Named according to recomendations of the ACS Committee on Nomenclature of Highly Fluorinated Molecules. See: J. H. Prager and P. G. Thompson, *J. Am. Chem. Soc.*, *87*, 230 (1965).
2 Ch. J. Hoffman, *Chem. Revs.*, *64*, 91 (1964), and references therein.
3 See for example: E. L. Varetti and P. J. Aymonino, *Chem. Comm.*, 680 (1967).
4 P. J. Aymonino, Chem. Comm., 241 (1965).
5 K. B. Kellogg and G. H. Cady, *J. Am. Chem. Soc.*, *70*, 3986 (1948).
6 P. J. Aymonino, *J. inorg. & nuclear Chem.*, *27*, 2675 (1965).
7 R. Gatti, E. Staricco, J. E. Sicre and H. J. Schumacher, *Z. phys. Chem.*, N. F., *35*, 343 (1962).
8 E. Castellano, N. R. Bergamín and H. J. Schumacher, *Z. phys. Chem.*, N. F., *27*, 112 (1961).
9 E. L. Varetti and P. J. Aymonino, *Anales Asoc. Quím. Argentina*, *55*, 153 (1967).
10 R. S. Porter and G. H. Cady, *J. Am. Chem. Soc.*, *79*, 5628 (1957).
11 J. G. Calvert and J. N. Pitts, "*Photochemistry*", John Wiley, New York, 1966.
12 a) W. Brenschede, *Z. phys. Chem.*, *B 41*, 237, 254 (1938) and references therein; b) R. Gatti and H. J. Schumacher, *Z. phys. Chem.*, *N. F.*, *55*, 148 (1967).
13 J. M. Heras, A. J. Arvía, P. J. Aymonino and H. J. Schumacher, *Z. phys. Chem.*, N. F., *28*, 250 (1961); *Anales Asoc. Quím. Argentina*, *50*, 1 (1962).
14 G. Pass and H. L. Roberts, *Inorg. Chem.*, *2*, 1012 (1963).
15 As quoted in reference 2.
16 P. J. Aymonino, *Proc. Chem. Soc.*, 341 (1964).
17 A. J. Arvía, and P. J. Aymonino, *Spectrochim. Acta*, *18*, 1299 (1962).
18 For experimental details see: C. H. H. Waldow, Ph. D. Dissertation, Facultad de Ciencias Fisicomatemáticas, UNLP, La Plata, 1965.

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