

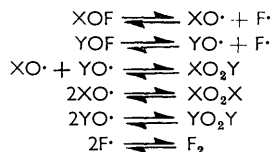
### 267. *The Thermal Decomposition of Fluorine Fluorosulphonate.*

By F. B. DUDLEY.

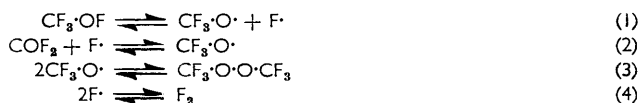
In the temperature range of 509—536°K fluorine fluorosulphonate undergoes homogeneous, quantitative thermal decomposition to sulphuryl fluoride and oxygen. The decomposition is catalysed by fluorine and then follows first-order reaction kinetics, but, in the presence of added fluorine, the observed first-order rate constant is proportional to the square root of the fluorine pressure. These facts can be explained by the assumption of a fluorine molecule-fluorine atom equilibrium, and a bimolecular reaction mechanism involving an activated complex  $\text{SO}_3\text{F}_3^*$ . Decomposition of each molecule of complex liberates a fluorine atom, hence the fluorine pressure remains unchanged. Under these conditions the bimolecular reaction appears to be of the first order.

In the absence of added fluorine, the decomposition follows 4/3-order kinetics, again explained in terms of a fluorine atom-fluorine fluorosulphonate interaction, the fluorine resulting from the reversible equilibrium,  $2\text{SO}_3\text{F}_2 \rightleftharpoons 2\text{SO}_3\text{F}\cdot + \text{F}_2$ , for which  $K_p'$  values have been obtained.

A NUMBER of very reactive compounds of hypofluorite type, XOF, have been synthesised by Cady and his co-workers. Well-known closely related symmetrical and unsymmetrical peroxy-compounds may be considered to be formed in accordance with the reversible equilibria:



The only previous quantitative investigation suggestive of such equilibria is by Porter and Cady,<sup>1</sup> who found that, when equimolar amounts of carbonyl fluoride and trifluoromethyl hypofluorite were heated to 560°K and then cooled, the products contained bistrifluoromethyl peroxy, whose formation requires the transitory existence, at least, of a trifluoromethoxy-radical, and probably the following reversible stages:



<sup>1</sup> Porter and Cady, *J. Amer. Chem. Soc.*, 1957, **79**, 5628.

The absence of tetrafluoromethane and oxygen from the products indicates that in trifluoromethyl hypofluorite the C-O is stronger than the O-F bond.

Porter and Cady observed that at 510°K the pressure of a mixture of carbonyl fluoride and trifluoromethyl hypofluorite began unexpectedly to decrease. This is consistent with the commencement of dissociation of the hypofluorite and establishment of equilibria 1-4. They also record that bistrifluoromethyl peroxide, on being heated in a nickel vessel, started to decompose at 500°K, decomposition being complete at 600°K. Since they examined the equilibrium above 600°K, and since the peroxide is completely decomposed at this temperature, equilibrium (3) can be ignored. If, therefore, one writes  $K_1$ ,  $K_2$ , and  $K_4$  for the equilibrium constants corresponding to equations (1), (2), and (4), then

$$K_1 = [\text{CF}_3\cdot\text{O}\cdot][\text{F}\cdot]/[\text{CF}_3\cdot\text{OF}]; \quad K_2 = [\text{COF}_2][\text{F}\cdot]/[\text{CF}_3\cdot\text{O}\cdot]; \quad K_4 = [\text{F}_2]/[\text{F}\cdot]^2;$$

from which it follows that

$$K_1 K_2 K_4 = [\text{COF}_2][\text{F}_2]/[\text{CF}_3\cdot\text{OF}].$$

The equilibrium constant determined by Porter and Cady could thus be a combined equilibrium constant for a series of interdependent equilibria.

Similar equilibria are involved between fluorine atoms, fluorosulphonate free radicals, and fluorine fluorosulphonate, namely:



Good evidence for the existence of fluorosulphonate free radicals has been provided by Roberts and Cady<sup>2</sup> who prepared a number of non-metallic fluorosulphonates by treating both fluorine fluorosulphonate and peroxodisulphuryl difluoride with bromine, iodine, nitrogen dioxide, sulphur dioxide, and sulphur tetrafluoride. In the present work it has also been established that passage of peroxodisulphuryl difluoride through a hot section of glass tube produces an intense brownish-yellow colour which persists only in the hot zone. As the difluoride is obtained unchanged after this treatment the phenomenon is probably due to reversible dissociation into fluorosulphonate radicals. It has also been shown that fluorine fluorosulphonate with sulphur trioxide yields peroxodisulphuryl difluoride, a reaction analogous to that of trifluoromethyl hypofluorite with carbonyl fluoride. Obviously the addition of fluorine to either of these systems would repress the dissociations (5) and (1), respectively.

*The Fluorine-catalysed Decomposition.*—The only previous kinetic studies of the thermal decomposition of hypofluorite-type compounds have been on fluorine monoxide,<sup>3</sup> fluorine dioxide,<sup>4</sup> fluorine nitrate,<sup>5</sup> and trifluoroacetyl hypofluorite.<sup>6</sup> In several of these cases, the authors commented on the marked catalytic effect of fluorine, and this was also observed in the thermal decomposition of fluorine fluorosulphonate. In the presence of added fluorine, although first-order rate curves were invariably obtained, the rate constant was dependent on the square root of the fluorine pressure. This behaviour not only requires that

$$-d[\text{SO}_3\text{F}_2]/dt = k[\text{SO}_3\text{F}_2], \quad (8)$$

but that

$$k = k'[\text{F}_2]^{\frac{1}{2}}. \quad (9)$$

These equations can only be consistent if

$$-d[\text{SO}_3\text{F}_2]/dt = k'[\text{F}_2]^{\frac{1}{2}}[\text{SO}_3\text{F}_2],$$

<sup>2</sup> Roberts and Cady, *J. Amer. Chem. Soc.*, 1960, **82**, 352, 353, 354.

<sup>3</sup> Koblitz and Schumacher, *Z. phys. Chem.*, 1933, *B*, **20**, 460.

<sup>4</sup> Ruff and Menzel, *Z. anorg. Chem.*, 1933, **211**, 204.

<sup>5</sup> Skiens and Cady, *J. Amer. Chem. Soc.*, 1958, **80**, 5640.

<sup>6</sup> Stewart and Cady, *J. Amer. Chem. Soc.*, 1955, **77**, 6110.

so that the decomposition is a bimolecular reaction involving fluorine atoms and fluorine fluorosulphonate molecules, and the reaction rate is given by

$$-d[\text{SO}_3\text{F}_2]/dt = k''[\text{F}\cdot][\text{SO}_3\text{F}_2]. \quad (10)$$

In the temperature range used, dissociation of fluorine molecules is appreciable. The equilibrium constants, which Wise<sup>7</sup> determined by an effusion method, range from  $1.16 \times 10^{-5} \text{ atm.}^{\frac{1}{2}}$  at  $513^\circ\text{K}$  to  $2.10 \times 10^{-3} \text{ atm.}^{\frac{1}{2}}$  at  $900^\circ\text{K}$ . Hence, at a constant pressure of fluorine, equations (8) and (10) are compatible.

The bimolecular reaction indicated by equation (10) therefore appears to be of the first-order, with a rate constant  $k$  dependent on the square root of the fluorine pressure. This is emphasised in Fig. 1, where many of the points correspond to rate constants

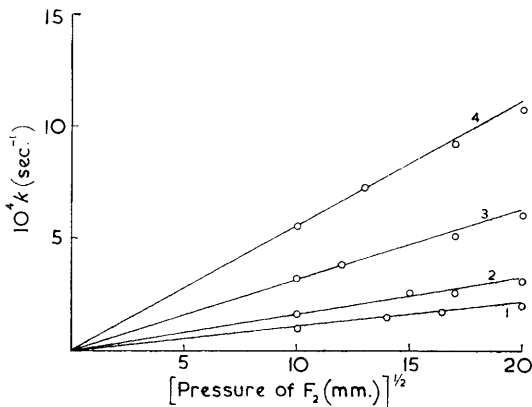
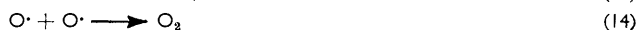


FIG. 1. Variation of first-order rate constant with the square root of the fluorine pressure. Curve 1,  $509^\circ$ ; curve 2,  $516^\circ$ ; curve 3,  $527^\circ$ ; curve 4,  $536^\circ\text{K}$ .

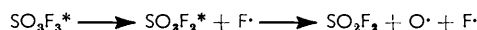
determined at a variety of fluorine fluorosulphonate pressures. It therefore appears that the rate-determining step in the decomposition is the formation of an activated complex:



and that this undergoes rapid decomposition either by reactions (12—15)



or by the reactions:



followed by (14) and (15). In either case the concentration of both fluorine molecules and fluorine atoms remains unchanged throughout.

*The Decomposition in the Absence of Added Fluorine.*—In the absence of added fluorine, decomposition was homogeneous in the temperature range investigated— $509$ — $536^\circ\text{K}$ —the rates being identical (within the limits of experimental error) in packed and unpacked vessels. The decomposition was found to be of a fractional order,  $4/3$ , which suggests a chain reaction. However, there was no indication of an induction period, the rate being greatest at the beginning and decreasing steadily with time. Moreover, the unusual fractional order can be explained in terms of the fluorine atom—fluorine fluorosulphonate mechanism used to explain the fluorine-catalysed decomposition. This requires the assumption of reversible equilibria corresponding to reactions (5—7). That an equilibrium corresponding to reaction (5) is reasonable is shown by the feasibility of such an equilibrium in the analogous case of trifluoromethyl hypofluorite, by the use of fluorine fluorosulphonate

<sup>7</sup> Wise, *J. Phys. Chem.*, 1954, **58**, 389.

or peroxodisulphuryl difluoride in the preparation of numerous non-metallic fluorosulphonates, and by the preparation of symmetrical and unsymmetrical peroxy-compounds containing fluorosulphonate groups.

Moreover, the dissociation of peroxodisulphuryl difluoride appears to be complete at temperatures well below those at which the decomposition of fluorine fluorosulphonate was studied. This being assumed, it follows that  $[F\cdot] = \text{Constant} \times [SO_3F_2]^{\frac{1}{2}}$ . If the decomposition proceeds by the same mechanism as when it is fluorine-catalysed, the decomposition rate becomes of 4/3 order with respect to fluorine fluorosulphonate.

For a largely undissociated dimeric peroxy-compound the equilibrium would be represented by:



Since each mole of fluorine formed would also result in a mole of the peroxy-compound, the concentration of fluorine atoms would now be proportional to the square root of  $[SO_3F_2]$ , and the rate of decomposition would be of 3/2 order with respect to that compound. This situation is ruled out for two reasons: (1) an equilibrium such as that represented by equation (16) leaves the total number of molecules unchanged and therefore does not account for the observed departure of the initial pressure from that theoretically required for an ideal gas; and (2) the observed order for the thermal decomposition is 4/3 and not 3/2.

Now, since several minutes elapse before fluorine fluorosulphonate comes into equilibrium with fluorosulphonate free radicals and fluorine atoms and molecules, the initial rate of pressure increase will be fast, but once this equilibrium has been attained the rate-determining step will be the interaction of fluorine atoms and fluorine fluorosulphonate molecules to form activated complexes. At any time  $t$  after attainment of the equilibria, the pressure of fluorine fluorosulphonate would be equal to

$$2[(\text{Final observed pressure}) - (\text{Observed pressure at time } t)].$$

This permits calculation of the 4/3 order rate constant and hence evaluation of the expected fluorine fluorosulphonate pressure at zero time for the condition that equilibration was instantaneous. (The maximum time interval for equilibration was about 15 minutes and occurred at low temperatures and pressures. Obviously some decomposition due to formation of activated complexes  $SO_3F_3^*$  will also have occurred during this time, but that does not affect the above argument.)

Calculations made on this basis show that the decompositions are consistent with a 4/3 order for up to 90% of the reaction. This conclusion is further emphasised by a consideration of Fig. 2 where the same results are plotted for 4/3 and 3/2 order.

*Degree of Dissociation of Fluorine Fluorosulphonate.*—If we have an equilibrium,  $SO_3F_2 \rightleftharpoons SO_3F\cdot + \frac{1}{2}F_2$ , and if  $\alpha$  is the degree of dissociation at an initial fluorine fluorosulphonate pressure of  $p$  mm., then for small values of  $\alpha$  it follows that

$$\alpha \propto (1/p)^{\frac{1}{2}} \quad (17)$$

If this equilibration is faster than the rate-determining step for the decomposition to sulphuryl fluoride and oxygen, then the observed initial pressure  $p_e$  will be greater than the calculated initial pressure  $p_c$  and the degree of dissociation  $\alpha$  will be given by

$$\alpha = 2(p_e - p_c)/p_c \quad (18)$$

The calculated initial pressures  $p_c$  were obtained from a knowledge of the weight of sample added and the assumption that the undissociated molecules behave ideally.

Obviously the presence of a large excess of fluorine would repress the dissociation of fluorine fluorosulphonate. In these circumstances the observed initial pressure can be expected to agree with that theoretically required according to the ideal-gas laws. This

was found to be the case; hence in discussing the decomposition of fluorine fluorosulphonate in the presence of free fluorine, its degree of dissociation was regarded as negligible.

A plot of  $\alpha$  against  $(1/p)^{1/3}$ , the cube root of the reciprocal of various pressures at constant temperature, would then be expected to give a straight line passing through a point corresponding to zero dissociation at infinite pressure. Fig. 3 illustrates the experimental results.

The equilibrium constants  $K_p'$  at different temperatures were then calculated, and a plot of  $\log K_p'$  against the reciprocal of the temperature permitted evaluation of  $\Delta H$  for the

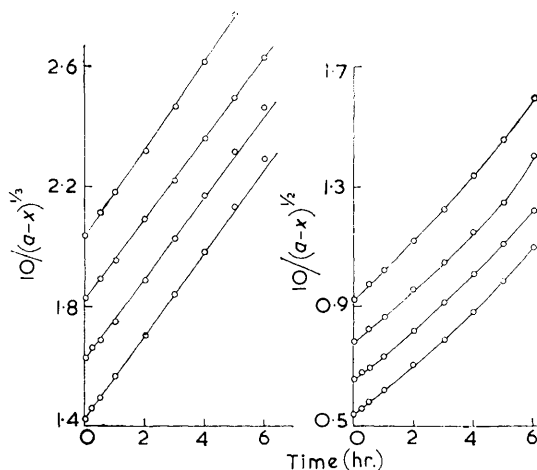


FIG. 2. The  $4/3$  order of the rate dependence is emphasised by the graphs for data on the homogeneous thermal decomposition of  $\text{SO}_3\text{F}_2$  at  $509^\circ\text{K}$ . The left-hand set are for  $4/3$  order (rate constant  $6.84 \times 10^{-4}$ ); the right-hand set are for the same data plotted for a  $3/2$  order.

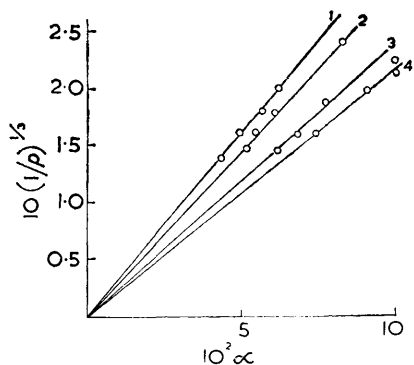


FIG. 3. Pressure and temperature dependence of the degree of dissociation of  $\text{SO}_3\text{F}_2$ . Curve 1,  $509^\circ$ ; curve 2,  $516^\circ$ ; curve 3,  $527^\circ$ ; curve 4,  $536^\circ\text{K}$ .

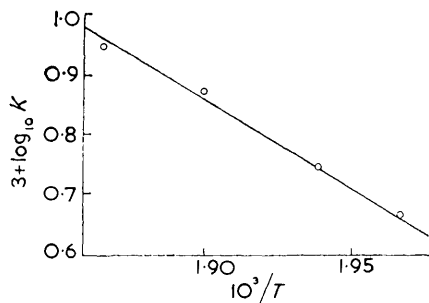


FIG. 4. Plot of  $\log_{10} K_p'$  against  $1/T$ , where  $K_p'$  is the dissociation constant for the equilibrium  $\text{SO}_3\text{F}_2 \rightleftharpoons \text{SO}_3\text{F} + \frac{1}{2}\text{F}_2$ .

thermodynamically reversible equilibrium as written above. The experimental results and the equilibrium constants  $K_p'$  calculated therefrom at different temperatures are shown in Fig. 4.

#### EXPERIMENTAL

**Materials.**—Fluorine was obtained in cylinders from Imperial Chemical Industries Limited, any relatively non-volatile impurities being removed by passage through a copper cold-trap cooled in solid carbon dioxide. Fluorine fluorosulphonate,<sup>8</sup> prepared by catalytic fluorination

<sup>8</sup> Dudley, Cady, and Eggers, *J. Amer. Chem. Soc.*, 1956, **78**, 290.

of sulphur trioxide at 200°C, was fractionally distilled at atmospheric pressure. The middle portion, b. p.  $-31.3^{\circ}$ , was stored in Pyrex glass tubes at liquid-air temperature. Oxygen was obtained by thermal decomposition of thoroughly dried "AnalaR" potassium chlorate. Sulphuryl fluoride, obtained as a product of thermal decomposition of fluorine fluorosulphonate, was retained after each run, and when a sufficient amount had accumulated it was purified by fractional distillation before use (the amount of impurity present was very small).

**Reaction Vessel.**—The reactor consisted of a cylindrical nickel vessel  $\sim 5''$  in diameter and 8' high, to which were connected two nickel tubes of  $\frac{3}{16}''$  internal diameter. One of these tubes was connected to a Booth-Cromer pressure-transmitter<sup>9</sup> and to a fluorine cylinder. The other tube was connected to the vacuum-line. Hoke needle-valves were inserted in both lines.

The temperature of the outside of the reaction vessel was determined at the top and the bottom, and at other places, by means of six chromel-alumel thermocouples taped to the surface of the vessel. Porcelain "fish-spine" insulators threaded on to resistance wire were used as spacers between the reaction vessel itself and the inside of the thermostat. The latter

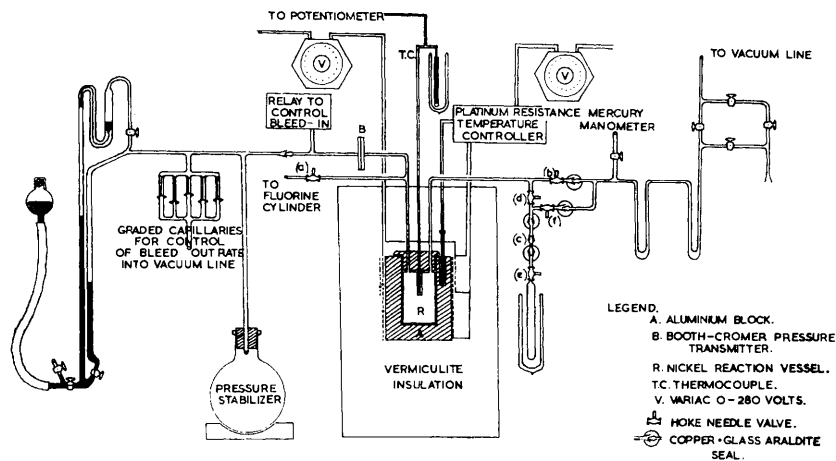


FIG. 5.

consisted of an 80-lb. block of aluminium, 9" in diameter, 12" high, having a well  $5\frac{1}{2}''$  in diameter and  $10\frac{1}{2}''$  deep. The lid for this well was  $2\frac{1}{2}''$  thick and was machined to form a  $2''$  plug of  $5\frac{1}{4}''$  diameter, with a flange  $\frac{1}{2}''$  deep and  $\frac{1}{2}''$  wide at the top. The reaction vessel, when inserted in the thermostat, was completely surrounded by a  $\frac{1}{4}''$  layer of air and a  $1\frac{3}{4}''$  thickness of aluminium.

The aluminium block was wrapped with a single layer of asbestos sheet ( $\frac{1}{8}''$  thick) on which was wound  $\frac{1}{16}''$  wide nichrome ribbon (40 ohms). Further nichrome ribbon (20 ohms) was wound on more asbestos insulation over the top 5" of the aluminium block. The heat input was controlled by means of a Variac resistance, constant temperatures being maintained by a Sunvic RT2 controller.

The nickel tubes and the Booth-Cromer transmitter were heated separately. Even though the volume of these tubes was negligible in comparison with the volume of the reaction vessel, it was necessary to keep both at approximately the same temperature in order to minimise heat losses by conduction and to prevent condensation of products in portions of the reaction system.

With this arrangement, depicted in Fig. 5, accurate temperature control over the whole surface of the reaction vessel was obtained, variations being less than  $\pm 0.2^{\circ}$  in spite of considerable fluctuations in the mains voltage.

**Fluorine-catalysed Decomposition.**—The reactor was "conditioned" by evacuating it at 650°K and admitting fluorine through the Hoke needle-valve (a). A fluorine pressure of more than 600 mm. was maintained at this temperature for a week, more fluorine being admitted when necessary. Uptake of fluorine never ceased completely, but it assumed a slow, steady

<sup>9</sup> Katz and Barr, *Analyt. Chem.*, 1953, 25, 619.

rate. It was observed later that after subsequent evacuation and readmission of fluorine the initial rate of uptake was increased, but that after  $\approx 2$  hr. the rate of pressure decrease resumed a slow, uniform rate.

In experiments where an excess of fluorine was present, the vessel was evacuated and fluorine then admitted in slight excess over that required for the reaction. After 2 hr. the fluorine pressure was adjusted to the required value by allowing the excess to expand through a Hoke valve (b) into a partial vacuum.

The sample of fluorine fluorosulphonate to be admitted was condensed in a prefluorinated copper tube fitted with a Hoke needle-valve and a B7 ground-glass cone. This was fitted to the vacuum line at (c), and the space between needle valves (d), (e), and (f) was evacuated through valve (f). Valve (f) was then closed, and valve (d) opened. This admittedly allowed some fluorine to escape from the reaction vessel, but the space between the valves (d), (e), and (f) had been reduced to a minimum, being less than 0.1% of the volume of the reaction vessel. In any case the bulk of this gas was carried back into the reaction vessel by the stream of fluorine fluorosulphonate produced when valve (e) was opened.

When sufficient fluorine fluorosulphonate had been admitted, valves (e) and (d) were closed in that order, (e) was reopened, and liquid air was poured into the flask around the sample tube. The latter step was only attended to after several pressure readings had been recorded. Admission of the sample could be completed within 30 sec., and zero time was taken as 15 sec. after the initial opening of valve (e). The weight of sample admitted was obtained by difference. Ideal-gas behaviour being assumed, the weight differences were found to give calculated pressures which agreed with the observed pressures to within 0.5%.

In view of the uncertainty arising from the correction to be applied for the uptake of fluorine by the reaction vessel, runs were made at different initial fluorine fluorosulphonate pressures but the same fluorine pressure. The initial rates were then measured graphically. In all cases the initial slopes of the  $\log p_{\text{SO}_2\text{F}_2}$ -time curves were practically identical. The departure of the complete graphs from straight lines was more pronounced for low initial pressures of fluorine fluorosulphonate. If the rate of uptake of fluorine is uniform the percentage error would be greatest under these conditions, but in general for the first  $\sim 30$  min. the rate was not appreciably affected by this complication.

Several runs were carried out in the presence of sulphuryl fluoride or oxygen, additional to fluorine. Neither of these reaction products appeared to affect the reaction rate. The results are recorded in Table 1.

TABLE 1.

Observed rate constants ( $\text{sec}^{-1}$ ) at (a) 509°, (b) 516°, (c) 527°, and (d) 536°K.

Initial pressures of fluorine fluorosulphonate and fluorine are represented by  $p_0$  and  $p_{\text{F}_2}$ , respectively. Experiments where  $\text{SO}_2\text{F}_2$  or  $\text{O}_2$  was added are marked \* or †, respectively.

Series (a)												
$p_0$ .....	63	106 *	193	49 †	102	183	61 *	151	214	31	63	98
$p_{\text{F}_2}$ ...	100	100	100	196	196	196	270	270	270	400	400	400
$10^4 k$ ...	1.07	1.09	1.07	1.56	1.50	1.52	1.72	1.84	1.85	2.17	2.16	2.12
Series (b)												
$p_0$ .....	52	92	185 *	56	98	188	46	109	156			
$p_{\text{F}_2}$ ...	100	100	100	289	289	289	400	400	400			
$10^4 k$ ...	1.64	1.65	1.68	2.73	2.60	2.57	3.25	3.14	3.2			
Series (c)												
$p_0$ .....	46 †	112	162	72	108	189	58	140	210	55	113	190
$p_{\text{F}_2}$ ...	100	100	100	144	144	144	289	289	289	400	400	400
$10^4 k$ ...	3.19	3.31	3.32	3.90	3.91	4.11	5.23	5.22	5.16	6.27	6.22	6.30
Series (d)												
$p_0$ .....	52	112	172	43	90	151	49	102	175	59	91	140
$p_{\text{F}_2}$ ...	100	100	100	169	169	169	289	289	289	400	400	400
$10^4 k$ ...	5.47	5.50	6.04	7.04	7.36	7.84	9.26	9.31	9.38	10.9	11.0	10.4

*Non-catalysed Decomposition.*—For decomposition of fluorine fluorosulphonate in the absence of fluorine, the reactor was kept filled with fluorine to a pressure of 100 mm. for 2 hr. as before, then evacuated for 15 min. before introduction of the sample in order to minimise the

possibility of fluorine uptake during the reaction. Dissociation apparently occurred in accordance with the equilibrium,  $\text{SO}_3\text{F}_2 \rightleftharpoons \text{SO}_3\text{F}\cdot + \frac{1}{2}\text{F}_2$ , but, owing to the much smaller concentrations of fluorine involved, uptake of fluorine by the reactor did not appear to become significant in spite of the longer reaction times involved. The samples were admitted as previously described, and the expected initial pressures were calculated from the weight of sample introduced into the reactor. The difference between the observed and the calculated pressures permitted calculation of the degree of dissociation into fluorosulphonate free radicals and fluorine molecules. It also provided a means of determining the pressure of undissociated fluorine fluorosulphonate at zero time. Very good agreement was invariably obtained with both the expected final pressure and the expected weight of sulphuryl fluoride. Decompositions were also effected in a packed reactor, the results again being in good agreement with those obtained previously. The packed and the unpacked reactors were of the same construction and dimensions (*ca.* 5" diameter and 7.75" in height). One reactor was packed with 128 nickel tubes (7.5" long; 0.200" i.d.; 0.375" o.d.). Relative to the unpacked reactor the surface area had been increased by a factor of *ca.* 12, whilst the surface to volume ratio had been increased by a factor of *ca.* 15. The experimental results are recorded in Table 2.

TABLE 2.

4/3 order rate constants  $k$  for the thermal decomposition of fluorine fluorosulphonate in the absence of added fluorine at (a) 509°, (b) 516°, (c) 527°, and (d) 536°K.  $p_c = p_{\text{SO}_3\text{F}_2}$  are calculated from the weight of sample admitted.  $p_e$  = the extrapolated initial  $p_{\text{SO}_3\text{F}_2}$ .  $p_d = 2(p_e - p_c)$  = a measure of the amount of dissociation into fluorosulphonate radicals and fluorine.  $p_\alpha = (p_c - p_d)$  = actual pressure of  $\text{SO}_3\text{F}_2$  at zero time, in equilibrium conditions for  $2\text{SO}_3\text{F}_2 \rightleftharpoons 2\text{SO}_3\text{F}\cdot + \text{F}_2$ . Experiments where  $\text{SO}_2\text{F}_2$  or  $\text{O}_2$  was added are marked \* and †, respectively. Data from a packed reactor is indicated by ‡.

	Series (a)				Series (c)					
$p_c$ .....	126	174.3	244	362	71.2 ‡	186.7 ‡	225.2 ‡	150.7	243.7	320.7
$p_e$ .....	129.9	179.2	250	369.8	73.8	191.8	230.8	156.5	252.0	330.5
$p_d$ .....	7.8	9.8	12	15.6	52	10.2	11.2	11.6	16.6	19.6
$p_\alpha$ .....	118.2	164.5	232	346.4	66	176.5	214	139.1	227.1	301.1
$10^4 k$ .....				6.84					23.7	
	Series (b)				Series (d)					
$p_c$ .....	71.5	188	238 †	316	89	106.5 *	130.2	150.7	243.7	320.7
$p_e$ .....	74.5	193.6	244.5	324.5	93.5	111.9	136.2	156.5	252.0	330.5
$p_d$ .....	6.0	11.2	13.0	16.6	9.0	10.8	12.0	11.6	16.6	19.6
$p_\alpha$ .....	65.5	176.8	225	299.4	80	95.7	118.2	139.1	227.1	301.1
$10^4 k$ .....		11.75				40.1				

*Stoichiometry of the Decomposition.*—The thermal decomposition of fluorine fluorosulphonate occurs in accordance with the reaction  $2\text{SO}_3\text{F}_2 \longrightarrow 2\text{SO}_2\text{F}_2 + \text{O}_2$ . The products were separated into condensable and non-condensable portions by slow expansion into a large evacuated flask after passage through a U-tube cooled in liquid air. The condensable portion was identified as sulphuryl fluoride by molecular-weight, b. p., and m. p. determinations and infrared and mass spectra. The non-condensable portion was identified by molecular-weight determinations and by quantitative absorption in alkaline pyrogallol. The weight of sulphuryl fluoride obtained on complete decomposition was always within 1% of theory. However, the pressure increases were 2–10% less than theory; this could be attributed to one or more of the following causes: reaction with the vessel walls forming non-volatile salts; formation of a product of higher molecular weight; presence of impurity in the fluorine fluorosulphonate; or uptake of fluorine by the reaction vessel. The first three were eliminated because the weight of sulphuryl fluoride agreed closely with theory, spectra of all the condensable products were essentially the same as those for sulphuryl fluoride, and m. p. curves of the reactant material, together with molecular-weight determinations, and oxidation with potassium iodide indicated high purity.

Very little has been reported on the corrosion of metals by fluorine, but observations similar to those observed in this study have been recorded by Brown *et al.*<sup>10</sup> for reaction of fluorine with copper. They found that vacuum-heating has a marked effect on the initial "uptake" rate,

<sup>10</sup> Brown, Crabtree, and Duncan, *J. Inorg. Nuclear Chem.*, 1955, **1**, 201.



and that the rate of fluorine uptake is independent of the fluorine pressure. They concluded that a simple diffusive process could not explain the observed facts, and that the most satisfactory interpretation was that the corrosion rate was due to random cracking of the corrosion film.

In connexion with this apparent "uptake" of fluorine by the reaction vessel, Winkelman<sup>11</sup> has shown that the rate of permeation of palladium, platinum, and iron by hydrogen is proportional to the square root of the hydrogen pressure, so that here the diffusion process involves hydrogen atoms and not molecules. The passage of oxygen through silver<sup>12</sup> is also proportional to the square root of the oxygen pressure; hence again the diffusion process involves atoms.

In view of the presence of both oxygen and fluorine atoms as transitory decomposition products it is highly probable that one or both contribute to the pressure discrepancy by diffusion into, and reaction with, the metal reaction vessel.

However, the effect of the higher initial uptake of fluorine after vacuum-pumping was minimised by allowing a uniform time interval of 2 hr. after addition of fluorine to the reaction vessel before the addition of fluorine fluorosulphonate. Several runs were conducted at fixed fluorine pressures but different fluorine fluorosulphonate pressures. First-order plots were then made and the rate constants determined graphically from the initial slopes. As expected, the larger the initial fluorine fluorosulphonate pressure, the smaller was the effect of fluorine uptake on the first-order rate graph.

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<sup>11</sup> Winkelman, *Ann. Phys.*, 1901, **6**, 104; 1902, **8**, 388; 1905, **16**, 773; 1905, **19**, 1045.

<sup>12</sup> Richardson, *Phil. Mag.*, 1904, **7**, 266; Richardson, Nicol, and Parnell, *ibid.*, 1904, **8**, 1.

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