

consumption of  $\text{IrCl}_6^{2-}$  in the presence of oxygen probably occurs because sulfur(V) intermediates are scavenged by oxygen instead of by  $\text{IrCl}_6^{2-}$ . The absence of strong catalysis by copper(II) suggests that sulfur(V) intermediates react very rapidly with  $\text{IrCl}_6^{2-}$ , however. The lack of rate dependence on buffer concentration confirms that the  $[\text{H}^+]$  dependence shown in eq II should not be replaced by acetate or acetic acid dependences.

The fact that the data do not show much evidence that a term second order in  $\text{HSO}_3^-$  should be added to eq II shows that reduction by  $\text{S}_2\text{O}_5^{2-}$  is not an important reaction under the conditions of this study. We present this fact as some evidence that the  $[\text{HSO}_3^-]^2$  term in the reduction of the very similar  $\text{FeL}_3^{3+}$  ion<sup>6</sup> does not arise from a reactive  $\text{S}_2\text{O}_5^{2-}$  species. Even though the evidence is not conclusive, we think it is significant because of the many similarities be-

tween  $\text{FeL}_3^{3+}$  and  $\text{IrCl}_6^{2-}$ ; both oxidants are substitution-inert low-spin  $d^5$  ions; they have one-electron reduction potentials of 1.06<sup>22</sup> and 1.02<sup>23</sup> V, respectively. The different charges on the two ions probably at least partially account for the different behavior with respect to second-order bisulfate dependences.

We conclude that net reaction 1 probably occurs by a sequence of two outer-sphere electron transfers and that net reaction 2 occurs by outer-sphere electron transfer followed by combination of S(V) radicals.

Registry No.  $\text{IrCl}_6^{2-}$ , 16918-91-5;  $\text{HSO}_3^-$ , 15181-46-1.

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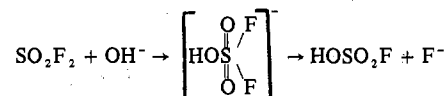
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## Hydrolysis of Sulfuryl Fluoride

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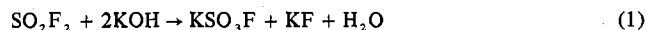
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Sulfuryl fluoride dissolves rapidly in water and may be quickly removed from solution by dynamic vacuum. The solubility of the gas has been measured at 0.0 and 23.3°. Hydrolysis of sulfuryl fluoride is slow in water but rapid in basic solutions, the net reaction being  $\text{SO}_2\text{F}_2 + 2\text{OH}^- \rightarrow \text{SO}_3\text{F}^- + \text{F}^- + \text{H}_2\text{O}$ . The rate law may be written as  $-\text{d}[\text{SO}_2\text{F}_2]/\text{d}t = [\text{SO}_2\text{F}_2] \cdot \{k_w + k[\text{OH}^-]\}$ . At pH values of 7.5 or greater,  $k_w$  is negligible when compared to  $k[\text{OH}^-]$ . Over the temperature range 0–25°,  $k = 1.67 \times 10^{12} e^{-13,100/RT}$ , when time is in seconds and concentrations are in moles per liter. The reaction is considered to be a nucleophilic displacement of fluorine in which the controlling process is

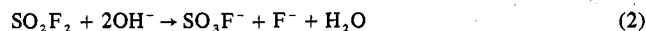


Sulfuryl fluoride reacts readily in aqueous solution with the nucleophiles  $\text{NH}_3$ ,  $\text{C}_6\text{H}_5\text{O}^-$ , and  $\text{CN}^-$ .

Previous studies of the hydrolysis of sulfuryl fluoride<sup>1–3</sup> have shown that the reaction with water is much slower than with a basic solution and that the rate increases as the concentration of KOH is increased. The reaction with alcoholic KOH has been reported<sup>2</sup> to be



and with water containing hydroxide ion<sup>4</sup> to be



If the resulting solution is allowed to stand, the fluorosulfate ion hydrolyzes to give sulfate and fluoride ions. However, studies by Ryss, Gribanova, and Drabkina<sup>5,6</sup> and by Jones and Lockhart<sup>7</sup> have shown that this reaction is very slow within the conditions of temperature and pH used in the

present research. Substantially none of the  $\text{SO}_3\text{F}^-$  ion reacted while the experiments now to be described were under way.

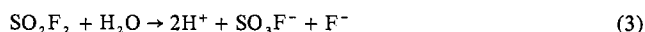
### Results

**Solubility of Sulfuryl Fluoride in Water.** By working rapidly one can measure the solubility of sulfuryl fluoride in water before a substantial fraction of the solute has hydrolyzed. By use of experimental measurements given below and by assuming Henry's law to be obeyed, it can be calculated that 100 ml of water dissolves 52.9 cm<sup>3</sup> (STP) of  $\text{SO}_2\text{F}_2$  at 0.0° or 21.5 cm<sup>3</sup> (STP) of  $\text{SO}_2\text{F}_2$  at 23.3°. Trautz and Ehrmann<sup>3</sup> have reported the solubility at 16.5° to be 0.4–0.5 cm<sup>3</sup> of  $\text{SO}_2\text{F}_2$  in 10 ml of water and Moissan and Lebeau<sup>1</sup> have reported 10 cm<sup>3</sup> of gas per 100 ml of water at 9°. These values are too low.

When an aqueous solution of sulfuryl fluoride is held under the dynamic vacuum of a water aspirator, the dissolved gas is rapidly removed from solution. When a 10-ml sample of solution is under vacuum and subjected to vigorous shaking, the removal of sulfuryl fluoride is substantially complete within 20 sec.

**Hydrolysis of Sulfuryl Fluoride.** Upon standing at 25°, a solution of sulfuryl fluoride in water becomes increasingly acidic and the concentration of fluoride ion increases, because of the slow reaction

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The approximate rate of this process is given in Table I. Since the rate in water or in 0.01 *M* HCl is much higher than would result from reaction of the OH<sup>-</sup> ion in these solutions, it may be concluded that water (and not just OH<sup>-</sup> ion) reacts with sulfuryl fluoride.

Basic hydrolysis follows eq 2. This was shown by an experiment in which a 0.1269-g (1.243-mmol) sample of sulfuryl fluoride just neutralized 24.30 ml of 0.1028 *N* NaOH (2.500 mmol) and produced 1.246 mmol of F<sup>-</sup> ion. In another experiment the corresponding numbers of millimoles were 1.228, 2.441, and 1.227, respectively. Addition of barium chloride to the solutions gave no precipitate of BaSO<sub>4</sub>. Because of the high rate of basic hydrolysis the reaction was studied in the present research at hydroxide ion concentrations up to only about  $2.5 \times 10^{-5}$  *M*. During each experimental run, the concentration of hydroxide ion was held nearly constant by using a suitable buffer and by adding only a small amount of sulfuryl fluoride. Various buffer solutions were tried, and the ones which were considered best were those containing borax. In some cases either HCl or NaOH was added to give the desired pH. Basic hydrolysis in borax buffers, as in NaOH solution, failed to give SO<sub>4</sub><sup>2-</sup> ion. Attempts were made to learn whether species in the borax buffers other than hydroxide ion had an influence upon the rate. In two cases a change from 0.01335 to 0.00667 *M* borax appeared to increase the rate of hydrolysis and in two cases appeared to decrease the rate. It therefore is concluded that the influence of doubling the concentration of borax upon the rate was smaller than the experimental error in measuring the rate. It is unlikely that species other than OH<sup>-</sup> ion in the buffer had much influence upon the rate.

At the beginning of a run, sulfuryl fluoride was added to the buffer. The reaction was then followed by measuring the activity of fluoride ion at known time intervals. At any time, *t*, during a run, the molarity of SO<sub>2</sub>F<sub>2</sub> was considered to be related to the activity of fluoride ion according to the equation  $[\text{SO}_2\text{F}_2] = Q(\text{final activity of F}^- - \text{activity of F}^- \text{ at time } t)$ . *Q* is a constant.

For each run, a graph was made in which  $\ln(\text{final activity of F}^- - \text{activity of F}^- \text{ at time } t)$  was plotted against *t*, in seconds. The data gave a straight line having a slope equal to  $d \ln [\text{SO}_2\text{F}_2]/dt$ . At constant pH the reaction was pseudo first order and the slope of the line was taken to be equal to the first-order rate constant, *k'*. Data for the runs are given in Table I. The first three columns give the composition of the buffer solution. Column 9 gives *k'*. Column 7 gives the initial and final pH values for the solutions as judged from the tables of Bates and Bower<sup>8</sup> for borax buffers. For the three solutions involving addition of NaOH and use at 0°, the pH was measured in this research. When estimating the decrease in pH during a run, it was considered that each mole of SO<sub>2</sub>F<sub>2</sub> consumed would have the same effect as adding 2 mol of HCl. From the range of pH and from the dissociation constant of water at each of the four temperatures, it was possible to calculate the activity of hydroxide ion at the beginning and at the end of each run. To obtain the corresponding concentrations (molarities) of OH<sup>-</sup> the activities were divided by the activity coefficient,  $\gamma_{\text{OH}^-}$ , given in column 6 of Table I. The coefficient was found from the ionic strength (column 5) and information given by Kielland.<sup>9</sup>

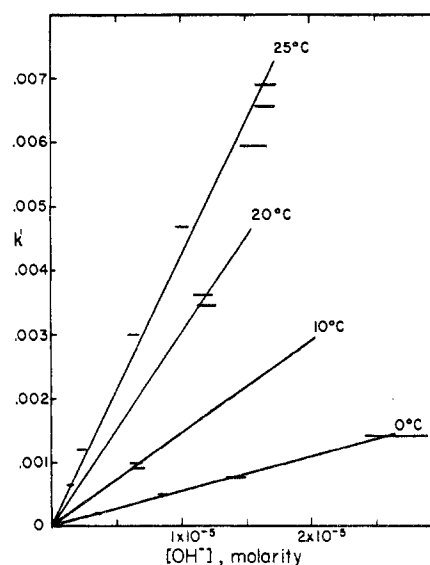
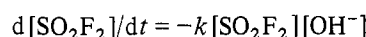


Figure 1. Relationship between the pseudo-first-order rate constant, *k'*, and the molarity of OH<sup>-</sup> at certain temperatures.

Figure 1 represents the relationship between the pseudo-first-order rate constant and molarity of OH<sup>-</sup> ion. In the graph, the length of the line for each value of *k'* corresponds to the range of [OH<sup>-</sup>]. Data for the runs at 0 and 25° correspond to the relationship that *k'* is proportional to the molarity of hydroxide ion. It follows that the rate obeys the equation

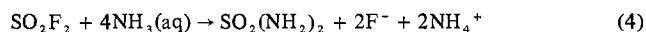


For a run at constant pH, the value of *k* is equal to *k'*/[OH<sup>-</sup>]. Column 10 in Table I gives the ratio of *k'* to the average value of [OH<sup>-</sup>] given by the run.

In Figure 2, the points represent values of *k* corresponding to the straight lines drawn in Figure 1. The slope of the line in Figure 2 corresponds to an activation energy of 13.1 kcal/mol.

The equation  $k = 1.67 \times 10^{12} e^{-13,100/RT}$  summarizes the rate information in Table I and gives the following calculated values of *k* at the indicated temperatures: 55.6, 0.0°; 131, 10.0°; 289, 20.0°; 418, 25.0°.

**Reaction of Sulfuryl Fluoride with Nucleophiles.** Buffers other than those listed in Table I were tried but found to be unsatisfactory for studies of basic hydrolysis, because they contained nucleophilic species, other than OH<sup>-</sup> ion, which reacted with sulfuryl fluoride. In each case the sulfuryl fluoride was consumed more rapidly than would be true if only the hydroxide ion in the buffer were reacting. The stoichiometry of reaction of sulfuryl fluoride with an NH<sub>3</sub>-(aq)-NH<sub>4</sub><sup>+</sup> buffer indicated that 1 mol of SO<sub>2</sub>F<sub>2</sub> consumed nearly 4 mol of ammonia as required by the equation



(It has long been known that sulfamide is produced by the reaction of sulfuryl fluoride with ammonium hydroxide.<sup>2,10</sup>) In another experiment sulfuryl fluoride was absorbed in an excess of ammonium hydroxide which contained no ammonium chloride. The stoichiometry indicated that about 70% of the SO<sub>2</sub>F<sub>2</sub> reacted by eq 4 and that about 30% reacted with OH<sup>-</sup> by eq 2.

The phenolate ion, formed by neutralizing phenol with a

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Table I. Rate of Hydrolysis of  $\text{SO}_2\text{F}_2$  in Alkaline Solutions

Soln molarities			Temp, °C	Ionic strength, $\mu$	Assumed $\gamma_{\text{OH}^-}$	pH range during run	Calcd range of molarity of $\text{OH}^-$ , $\times 10^6$	$-\ln [\text{SO}_2\text{F}_2] / dt$ or $k^a$	$k'/[\text{OH}^-]$ or $k^a$
Borax	HCl	NaOH							
0.01335	0	0	0.0	0.0267	0.888	9.46-9.44	3.74-3.54	$2.02 \times 10^{-4}$	55.5
0.00667	0	0	0.0	0.0133	0.916	9.46-9.44	3.63-3.43	$1.92 \times 10^{-4}$	54.4
0.01335	0	0.01542	0.0	0.0421	0.866	10.05-10.01	14.9-13.5	$7.56 \times 10^{-4}$	53.2
0.01335	0	0.01028	0.0	0.0370	0.873	9.83-9.80	8.82-8.24	$4.95 \times 10^{-4}$	58.1
0.01335	0	0.02056	0.0	0.0473	0.858	10.34-10.26	29.0-24.1	$1.40 \times 10^{-3}$	52.7
0.01335	0	0	10.0	0.0267	0.888	9.33-9.28	7.06-6.26	$9.1 \times 10^{-4}$	137
0.00667	0	0	10.0	0.0133	0.916	9.33-9.28	6.84-6.07	$9.9 \times 10^{-4}$	153
0.01335	0	0	20.0	0.0267	0.888	9.22-9.16	12.8-11.2	$3.45 \times 10^{-3}$	287
0.00667	0	0	20.0	0.0133	0.916	9.22-9.16	12.5-10.9	$3.61 \times 10^{-3}$	308
0.01335	0	0	25.0	0.0267	0.888	9.18-9.14	17.2-15.6	$6.91 \times 10^{-3}$	421
0.01335	0	0	25.0	0.0267	0.888	9.18-9.14	17.2-15.6	$6.56 \times 10^{-3}$	400
0.00667	0	0	25.0	0.0133	0.916	9.18-9.12	16.7-14.5	$5.95 \times 10^{-3}$	381
0.01335	0.00536	0	25.0	0.0267	0.888	8.97-8.92	10.5-9.44	$4.68 \times 10^{-3}$	469
0.01335	0.01072	0	25.0	0.0267	0.888	8.78-8.71	6.75-5.82	$3.00 \times 10^{-3}$	477
0.01335	0.01822	0	25.0	0.0267	0.888	8.36-8.27	2.60-2.11	$1.20 \times 10^{-3}$	510
0.01335	0.02144	0	25.0	0.0267	0.888	8.13-8.00	1.53-1.13	$6.52 \times 10^{-4}$	491
0	0.01072	0	25.0			Near 2.0	Near $1 \times 10^{-12}$	$1.5 \times 10^{-6}$	
	Water only		25.0			Near 5.9	Near $8 \times 10^{-9}$	$2.6 \times 10^{-6}$	

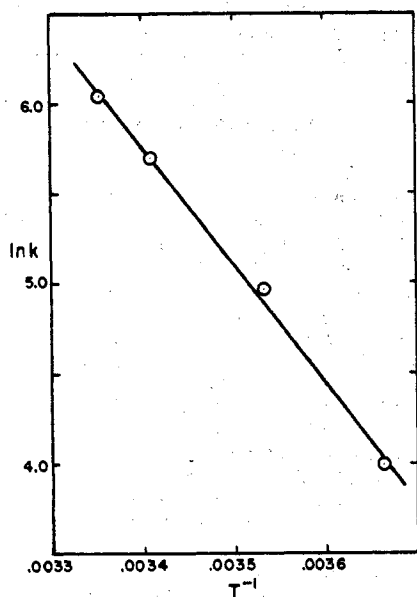
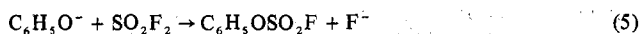
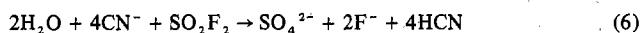
<sup>a</sup> Time in seconds.

Figure 2. Relationship between  $T^{-1}$  and values of the rate constant,  $k$ , corresponding to the straight lines in Figure 1. The slope of the line corresponds to an activation energy of 13.1 kcal.

solution of sodium hydroxide, gave phenyl fluorosulfate



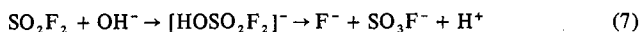
while a solution containing cyanide ion gave sulfate ion



In these reactions, the species  $\text{NH}_3(\text{aq})$ ,  $\text{C}_6\text{H}_5\text{O}^-$ , and  $\text{CN}^-$  are thought to attack the sulfur atom of  $\text{SO}_2\text{F}_2$  and displace  $\text{F}^-$  ion. If  $\text{SO}_2(\text{CN})_2$  is formed as an intermediate, it hydrolyzes promptly to give  $\text{SO}_4^{2-}$ . Fluorosulfate ion was shown not to be an intermediate in these reactions.

## Discussion

Since the rate of basic hydrolysis of sulfuryl fluoride is proportional to the molarities of  $\text{SO}_2\text{F}_2$  and  $\text{OH}^-$ , it is probable that the rate-controlling step is the nucleophilic displacement



which is followed by neutralization of  $\text{H}^+$  or  $\text{HSO}_3\text{F}$ . Basic

hydrolysis of fluorosulfate ion also is considered to be a displacement of fluoride ion by hydroxide ion;<sup>7</sup> however, the reaction is much slower than that for sulfuryl fluoride.

It would be desirable to have more definite information about the influence of species, other than  $\text{OH}^-$ , in the borax buffers upon the rate of disappearance of  $\text{SO}_2\text{F}_2$ . Knowing that the influence is smaller than the experimental error in measurements does not answer the question, but it does point to a need for a better experimental method. Great accuracy is not claimed for the rate measurements reported here. It can be said, however, that much effort went into attempts to obtain more accurate data and that numerous procedures were tried. The best method tried is described below.

## Experimental Section

**Materials.** Sulfuryl fluoride was obtained in a cylinder from a commercial source. It was found to contain a gas, probably air, not absorbed by sodium hydroxide solution. Most of this impurity was removed by cooling the cylinder to  $-78^\circ$  and removing gas by dynamic vacuum. After this treatment, over 99% by volume of the gas removed from the cylinder could be dissolved in a deaerated solution of sodium hydroxide. A sample of sulfuryl fluoride was condensed in a trap, and successive portions were evaporated and used for gas density determinations until all of the sample had been used. Calculated values for molecular weights for the successive portions were 101.3, 101.6, 101.6, 102.0, and 100.9 (theory 102.0). This gives evidence that the material was substantially pure.

Other chemicals were commercial items of good quality.

**Solubility of  $\text{SO}_2\text{F}_2$  in Water.** Gas from the cylinder of  $\text{SO}_2\text{F}_2$  was allowed to flow out, when desired, through a slender hollow needle of the type used for a hypodermic syringe. Dead space from the seat of the valve to the needle was only about 0.5 ml. When not in use, the needle was kept closed by a tight rubber cap. The needle was used as a duct for transferring about 20-40  $\text{cm}^3$  of gas from the cylinder through a thin rubber stopper into a polyethylene bottle containing deaerated water but no air above the liquid. The lower part of the bottle (originally of 50-ml capacity) had previously been expanded by heat and blowing to make a thin flexible bulb of about 200-ml volume. This gave a readily handled supply of sulfuryl fluoride saturated with water vapor. The vessel was not used to store sulfuryl fluoride for a long time. Within about 1 min a measured sample was removed into a hypodermic syringe in which the walls were wet with water. The needle of this syringe containing the gas at atmospheric pressure was then inserted into the needle of another similar syringe which was filled with a known volume of deaerated water. The region of connection of the two needles was sealed with a tight rubber sleeve. The two syringes, one with gas and one with water, were attached to a small board by rubber bands. The assembly was then held in a vertical position, with gas in the top syringe, so that the volume of gas could be measured under atmospheric pressure plus the pressure due to the mass of the plunger of the syringe. Gas and water were then caused to mix by operating the plungers of the sy-

Table II. Solubility of  $\text{SO}_2\text{F}_2$  in Water

Vol of water, ml	Vol of gas, $\text{cm}^3$		Dis-solved	Room temp, $^\circ\text{C}$	$\text{cm}^3$ dissolved/100 ml of water
	At start	At end			
Gas Measured over Water at Room Temp; Water Also at Room Temp; Total $P = 763$ mm					
10.0	6.25	3.83	2.42	22.0	24.2
10.0	4.90	2.57	2.33	23.5	23.3
15.7	5.03	1.44	3.59	23.6	22.9
10.9	9.20	6.68	2.52	23.1	23.1
					Av 23.3
Water at $0.0^\circ$ ; Gas Measured at Room Temp; Total $P = 762$ mm					
11.12	8.85	2.37	6.48	21.7	58.5
10.00	9.83	4.03	5.80	22.7	58.0
10.00	9.90	4.04	5.86	22.0	58.6
					Av 58.4

ringes. The whole assembly was shaken vigorously (about 2 min) by hand until the total volume within the syringes became constant. The final shaking and the final measurement of volume were made with the syringes held vertically. This required taking into account the pressure resulting from the weight of the upper plunger. One series of measurements was made with the whole system at room temperature. A second series was made with the lower syringe containing water at  $0.0^\circ$  (surrounded by ice). The syringe containing gas was originally at room temperature. At the end of each experiment the liquid was still at  $0.0^\circ$  and all of the remaining gas, for measurement, was in the upper syringe. Data for the runs are given in Table II. Since the syringe containing gas was graduated in 0.2-ml units, an error of 0.02 ml in measuring the volume was possible. If the final series had involved measuring the gas at  $0^\circ$ , the solubility would have been  $52.9 \text{ cm}^3$  of gas/100 ml of water.

**Hydrolysis of Sulfuryl Fluoride.** The reaction vessel was a tall 200-ml glass beaker. Buffer solutions described in Table I were prepared by mixing appropriate measured volumes of 0.0534  $M$  borax with water and in some cases with 0.1072  $N$  HCl or 0.1028  $N$  NaOH. In most of the runs, the solution had a volume of 90 ml. It was held in a constant-temperature bath and was stirred with a magnetically driven stirring bar. A solution of sulfuryl fluoride in water was prepared in much the same manner as that described above for the measurement of solubility. Usually the solution contained about  $2 \text{ cm}^3$  of gas ( $8 \times 10^{-5}$  mol) dissolved in 10 ml of water. Usually 10 ml of the solution was used in a run. Both solutions were brought to within  $0.1^\circ$  of the temperature of the constant-temperature bath, and this temperature was maintained while rate measurements were in progress. Concentrations given in columns 1-3 in Table I are those existing immediately upon mixing the reactants. For runs made with 0.00667  $M$  borax, the amount of  $\text{SO}_2\text{F}_2$  used was about  $4 \times 10^{-5}$  mol.

Before mixing the solutions, the buffer was covered with a disk of plastic foam which floated on the solution and fitted closely to the wall of the beaker. When liquid was added or removed, the disk moved up or down, respectively, and continued to cover the surface of the liquid. All air bubbles were removed from under the plastic. (Suitable tests showed that the loss of  $\text{SO}_2\text{F}_2$  by evaporation from a stirred solution in this reactor was so small that the loss could be neglected when measuring rate of hydrolysis.) The foamed plastic disk had a small notch at one side to allow the needle of a syringe to be inserted into the body of the solution.

At time zero in a run, the measured portion of sulfuryl fluoride solution was added to the buffer from a syringe. During the course of a run, samples of about 8-ml volume were quickly removed at known time intervals using a syringe. After removal, each sample was immediately injected through a thin rubber stopper into a flask under the dynamic vacuum of a water aspirator. The flask was shaken vigorously for about 25 sec to aid in removal of dissolved  $\text{SO}_2\text{F}_2$ . The sample was then poured into a flask for storage and the aspirator assembly was prepared for the next sample. This procedure permitted samples to be taken at intervals as short as 1 min. A run gave about eight samples and left enough of the reacting mixture for storage until all  $\text{SO}_2\text{F}_2$  had reacted.

The fluoride ion concentration of the various samples and the final solution were now measured using an Orion Research specific ion electrode for fluoride and a Leeds and Northrup 7400-A2 series pH meter. This meter had 0.1 pH unit graduations and with experience could be read with confidence to 0.01 unit. The meter was calibrated against solutions of sodium fluoride of known concentration and was set to read pH 7.00 when  $[\text{F}^-] = 10^{-3} M$ . The meter reading

was very close to 6.00 when  $[\text{F}^-] = 10^{-4} M$ . For the runs, nearly all measured values of  $\text{F}^-$  activity fell within the range  $2 \times 10^{-5}$  to  $8 \times 10^{-4}$ .

Because of the long response time to change in  $\text{F}^-$  activity, it was not found possible to follow the hydrolysis reaction, when fast, with the fluoride ion sensitive electrode placed in the reacting mixture.

Each sample from a run was treated as follows. (1) A drop of Bromothymol Blue indicator was added. (2) Small pieces of Dry Ice were added with shaking until the solution changed from blue to yellow. (3) The solution was placed in a 50-ml beaker and was brought into contact with the fluoride specific ion electrode assembly. (4) While the solution was stirred with a stirring bar and a slow stream of gaseous carbon dioxide entered the beaker (to maintain constant pH at about 6), readings of the  $\text{F}^-$  activity were taken by use of the pH meter until they became constant. Some samples required as much as 30 min, but most of the final readings could be taken within 10 min or less. When the successive samples had about the same concentration of  $\text{F}^-$ , the waiting time was rather short, but for these, high precision was required, because very small error in the reading caused a large error in the calculated amount of dissolved  $\text{SO}_2\text{F}_2$ .

Table I reports rates of hydrolysis of  $\text{SO}_2\text{F}_2$  in water and in 0.01072  $N$  HCl. These reactions were followed for somewhat over 2 hr and during this time only a small fraction of the dissolved  $\text{SO}_2\text{F}_2$  reacted.

**Reaction of Sulfuryl Fluoride with Nucleophiles.**  $\text{NH}_3(\text{aq})$ . Sulfuryl fluoride ( $4.017 \times 10^{-4}$  mol) was absorbed by 20.00 ml of 0.08163  $M$   $\text{NH}_3(\text{aq})$  at  $21^\circ$ . Part of the resulting solution was used for a determination of fluoride ion by titration with thorium nitrate and part for titration of the remaining  $\text{NH}_3(\text{aq})$  by HCl to the Bromothymol Blue end point. The observed stoichiometry, in moles, was  $\text{SO}_2\text{F}_2$  ( $4.017 \times 10^{-4}$ ) +  $\text{NH}_3$  ( $13.79 \times 10^{-4}$ )  $\rightarrow$   $\text{F}^-$  ( $6.73 \times 10^{-4}$ ). These data indicate that about 70% of the  $\text{SO}_2\text{F}_2$  reacted by eq 4 and about 30% by eq 2.

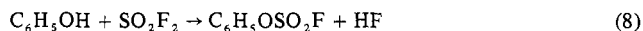
$\text{NH}_3(\text{aq}) + \text{NH}_4^+$  Buffer. Sulfuryl fluoride ( $4.033 \times 10^{-4}$  mol) was absorbed rapidly by 20.74 ml of a solution containing 0.08163  $M$   $\text{NH}_3(\text{aq})$  and 0.08163  $M$   $\text{NH}_4\text{Cl}$ . The resulting solution was titrated to the Bromothymol Blue end point with 0.1072  $N$  HCl (volume of acid 0.955 ml). The observed consumption of  $\text{NH}_3$  ( $15.91 \times 10^{-4}$  mol) corresponded closely to the requirement of eq 4.

$\text{C}_6\text{H}_5\text{O}^- - \text{C}_6\text{H}_5\text{OH}$  Buffer. A 10.00-ml solution made by mixing equal volumes of 0.20  $M$  phenol and 0.1028  $N$  NaOH was added slowly, with shaking, to  $3.99 \times 10^{-5}$  mol of  $\text{SO}_2\text{F}_2$  at  $22^\circ$ . The gas reacted rapidly with the solution. A portion of the resulting solution was titrated to the Bromothymol Blue end point using 0.1072  $N$  HCl. The remainder was used for a fluoride determination by titration with thorium nitrate solution. The observed stoichiometry in moles (assuming the base to be  $\text{C}_6\text{H}_5\text{O}^-$ ) was  $\text{SO}_2\text{F}_2$  ( $3.99 \times 10^{-4}$ ) +  $\text{C}_6\text{H}_5\text{O}^-$  ( $4.18 \times 10^{-4}$ )  $\rightarrow$   $\text{F}^-$  ( $4.01 \times 10^{-4}$ ). This corresponds well to eq 5.

In another experiment the gas was added to the buffer at  $21^\circ$ . Under this condition, the concentration of  $\text{OH}^-$  ion was higher than in the run described above. The observed stoichiometry was  $\text{SO}_2\text{F}_2$  ( $3.96 \times 10^{-4}$ ) + ( $\text{C}_6\text{H}_5\text{O}^- + \text{OH}^-$ ) ( $4.33 \times 10^{-4}$ )  $\rightarrow$   $\text{F}^-$  ( $3.85 \times 10^{-4}$ ). The ratio of base to  $\text{SO}_2\text{F}_2$  indicates that about 90% of the  $\text{SO}_2\text{F}_2$  reacted by eq 5 and 10% by eq 2.

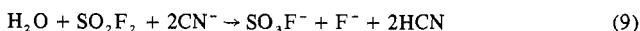
As reaction occurred, a white turbidity developed in the solution. This must have been caused by precipitated  $\text{C}_6\text{H}_5\text{OSO}_2\text{F}$ .

Cramer and Coffman<sup>11</sup> produced  $\text{C}_6\text{H}_5\text{OSO}_2\text{F}$  by the reaction of  $\text{SO}_2\text{ClF}$  with phenol in pyridine at  $0^\circ$ . They also obtained the compound as one of the products of the reaction of  $\text{SOF}_4$  with phenol at  $150^\circ$  and considered the compound to be formed by the reaction



$\text{CN}^-$ . Sulfuryl fluoride ( $4.01 \times 10^{-4}$  mol) was rapidly absorbed by 20.16 ml of 0.100  $M$  NaCN solution at about  $22^\circ$ . The resulting solution was then titrated to the Bromothymol Blue end point and required 7.20 ml of 0.1072  $N$  HCl. The amount of fluoride ion in the solution was found by titration with thorium nitrate to be  $6.10 \times 10^{-4}$  mol. The amount of  $\text{CN}^-$  consumed was  $12.45 \times 10^{-4}$  mol.

In another similar experiment  $4.01 \times 10^{-4}$  mol of  $\text{SO}_2\text{F}_2$  consumed  $12.99 \times 10^{-4}$  mol of  $\text{CN}^-$  and produced enough sulfate ion to form 0.0536 g of  $\text{BaSO}_4$  ( $2.295 \times 10^{-4}$  mol). While the quantities measured in these experiments are not completely self-consistent, they correspond rather well to the relationship that about 55% of the  $\text{SO}_2\text{F}_2$  reacted by eq 6 and about 45% by eq 9. Equations 6 and



(11) R. Cramer and D. D. Coffman, *J. Org. Chem.*, **26**, 4164 (1961).

9 do not reveal mechanisms. It seems likely that (9) involves hydrolysis of  $\text{CN}^-$  to give  $\text{OH}^-$  which then reacts with  $\text{SO}_2\text{F}_2$  to form  $\text{SO}_3\text{F}^-$  and  $\text{F}^-$  ions. Equation 6 may involve the formation of  $\text{SO}_2\text{-(CN)}_2$  or some other intermediate with cyanide attached to sulfur.

**Fluorosulfate Ion Not an Intermediate in Reactions 4-6.** Solution S was prepared by shaking 20 ml of 0.1028 *N* NaOH with an excess of  $\text{SO}_2\text{F}_2$ . This gave a solution containing 0.0514 *M*  $\text{F}^-$  and 0.0514 *M*  $\text{SO}_3\text{F}^-$ . The fluoride specific ion electrode gave a reading for this solution corresponding to  $[\text{F}^-] = 0.052$  *M* (a good check). The solution was found to be free from  $\text{SO}_4^{2-}$  ion.

Five milliliters of solution S was mixed with an equal volume of 0.08163 *M*  $\text{NH}_3\text{OH}$  and was then tested with the fluoride specific ion electrode after it had been seasoned in a similar solution. The emf remained constant while observed for a 13-min period and indicated  $[\text{F}^-]$  to be 0.028 *M*. This is higher than 0.0259 (half of 0.0519) and can be in error, because of interference by hydroxide ion. It can be concluded, however, that not over 10% of the  $\text{SO}_3\text{F}^-$  ion reacted to give  $\text{F}^-$ . If the reaction of  $\text{NH}_3(\text{aq})$  with  $\text{SO}_2\text{F}_2$  involved  $\text{SO}_3\text{F}^-$  as an intermediate, it would be necessary for  $\text{SO}_3\text{F}^-$  to react rapidly with  $\text{NH}_3(\text{aq})$ , because ammonia quickly displaces both fluorine atoms from sulfuryl fluoride.

Five milliliters of solution S was mixed with 2.00 ml of 0.200 *M* phenol. The fluoride specific ion electrode indicated  $[\text{F}^-]$  to be 0.038 *M*, in good agreement with 0.0368 *M* corresponding to no reaction of  $\text{SO}_3\text{F}^-$  with phenol. Two milliliters of 0.1028 *N* NaOH

was then added to neutralize part of the phenol and give  $\text{C}_6\text{H}_5\text{O}^-$ . The fluoride sensitive electrode then indicated  $[\text{F}^-]$  to be 0.029 *M*, in good agreement with 0.0286 *M*, corresponding to no reaction of  $\text{SO}_3\text{F}^-$  with either phenol or  $\text{C}_6\text{H}_5\text{O}^-$  ion.

Five milliliters of solution S was mixed with 5 ml of 0.100 *M* NaCN. The fluoride specific ion electrode then indicated a constant value of  $[\text{F}^-]$  of 0.028 *M*, a value close to that expected (0.0257 *M*) for no reaction. The solution was then titrated to the Bromothymol Blue end point with 0.1072 *N* HCl (volume used 4.50 ml) (theoretical volume for no reaction of  $\text{SO}_3\text{F}^-$  with  $\text{CN}^-$  is 4.66 ml). It can be concluded that not over 10% of the  $\text{SO}_3\text{F}^-$  reacted with  $\text{CN}^-$  and that fluorosulfate ion is not an intermediate in the rapid reaction of cyanide ion with aqueous  $\text{SO}_2\text{F}_2$  to give  $\text{SO}_4^{2-}$  ion.

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**Registry No.**  $\text{SO}_2\text{F}_2$ , 2699-79-8;  $\text{NH}_3$ , 7664-41-7;  $\text{C}_6\text{H}_5\text{OH}$ , 108-95-2; NaCN, 143-33-9.

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## Kinetics and Mechanism of the Reaction between Formate and Peroxodisulfate in Aqueous Solution

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A kinetic study is made of the reaction of formate with peroxodisulfate in aqueous solution. In the three ranges of concentrations of formate, the rate law approaches three different forms. The rate law for this reaction in a solution of pH 4.5 to 7 in the absence of oxygen, at concentrations of formate smaller than 0.01 *M*, is  $-\text{d}[\text{S}_2\text{O}_8^{2-}]/\text{d}t = k_a[\text{HCOO}^-]^{1/2}[\text{S}_2\text{O}_8^{2-}]$  with an activation energy of  $23 \pm 1$  kcal/mol. At concentrations of formate 0.01 to 0.2 *M*, the rate law is  $-\text{d}[\text{S}_2\text{O}_8^{2-}]/\text{d}t = (k_b + k_c[\text{HCOO}^-]^{1/2})[\text{S}_2\text{O}_8^{2-}]$ , and at the formate concentrations greater than 0.2 *M*, the rate is independent of the formate and described as  $-\text{d}[\text{S}_2\text{O}_8^{2-}]/\text{d}t = k_d[\text{S}_2\text{O}_8^{2-}]^{3/2}$  with an activation energy of  $21 \pm 1$  kcal/mol. The proposed mechanism is a chain reaction with  $\text{SO}_4^{\cdot-}$ ,  $\text{OH}^{\cdot}$ , and  $\text{CO}_2^{\cdot-}$  radicals. Therefore, the reaction rate is greatly inhibited by the presence of radical scavengers like acrylonitrile and oxygen and also by iron(III). The effect of pH on the reaction rate is examined at the pH range 0.7 to 12.6. In the pH range from 4.5 to about 7, the reaction rate reaches a maximum constant value.

### Introduction

Recently, the oxidation of oxalate and oxalic acid by peroxodisulfate<sup>1</sup> and by several other oxidants<sup>2</sup> has been studied. Both formate and oxalate molecules are subject to formation of the same radical  $\text{CO}_2^{\cdot-}$  upon their oxidation. Therefore, the mechanism of the oxidation of the two molecules is anticipated to be analogous. However, the rate of oxidation of formate and oxalate is very different. Oxidation of oxalate by peroxodisulfate hardly occurs at room temperature without catalyst.<sup>1</sup> In contrast, oxidation of formate by the same oxidant under the same conditions occurs considerably faster. When peroxodisulfate, hereafter referred to as persulfate, reacts with formate under the conditions studied here, the stoichiometry of the reaction does not deviate appreciably from the reaction equation of  $\text{S}_2\text{O}_8^{2-} + \text{HCOO}^- \rightarrow 2\text{SO}_4^{2-} + \text{H}^+ + \text{CO}_2$  to agree with the reports by

the earlier researchers. However, there are a number of contradictory reports on the reaction between formate and persulfate, especially on the reaction order and the reaction mechanism. The reaction of persulfate with formate has been investigated by many researchers and reviewed by House<sup>3</sup> and by Wilmarth and Haim<sup>4</sup> in 1962. Kappanna<sup>5</sup> obtained markedly different results from those of an earlier study by Srivastava and Ghosh.<sup>6</sup> The latter found that the rate of reaction was independent of the formate concentration, but Kappanna concluded that the reaction was second order. Hart<sup>7</sup> has investigated the yield of  $\text{CO}_2$  from the formate-persulfate reaction induced by the  $\gamma$ -ray and found that  $G(\text{CO}_2)$  is a function of  $[\text{HCOOH}]^{1/2}$ , indicating the half-order in formate. Thus, in 1969 O'Flynn and House<sup>8</sup> reinvestigated the same reaction with a view to establishing (a) the reaction order and (b) pH dependence upon the rate,

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