TABLE I

VAPOR PRESSURE OF $C_4F_9(SO_3F)$

P, mm.	T, °K.	P, mm.	T, °K.	P, mm.	T, °K.
26.2	266.0	283.6	316.3	515.6	332.3
55.5	280.0	338.5	320.8	582.4	335.7
106.8	294.5	408.8	325.8	678.8	340.2
155.4	301.1	446.5	328.1	714.9	341.7
198.6	307.9	454.0	328.7	803.5	354.4
231.2	311.1				

The compound is a clear, colorless liquid, which is inert toward mercury and which slowly dissolves fluorocarbon stopcock grease. Experimental measurements gave a molecular weight of 317 compared to a calculated value of 318 for $C_4F_9(SO_3F)$. The liquid density is 1.738 g./cc. at 22.2°; 1.805 at 0.1°; 1.780 at 7.8°; 1.756 at 16.0°; and 1.698 at 35.1°. A plot of the data gives the expression d (g./cc.) = 1.8056 − 0.0031t (°C.). The compound forms a cracked glass when cooled to −183°. A melting point could not be determined but the temperature at which the cracked appearance vanished was about −130°. The vapor pressure values, measured over the temperature range from 266.0 to 354.4°K., are given in Table I. A boiling point of 342.5°K. and a molar heat of vaporization of 7.7 kcal. are indicated by the data. The Trouton constant is 22.3. The infrared spectrum was obtained at 20 mm. pressure with a 5-cm. path length. Strong bands at 1500 cm.$^{-1}$ may be attributed to S–O stretch; at 1300–1225 cm.$^{-1}$ (complex) to S–O and C–F; at 1172 and 1130 cm.$^{-1}$ to C–F; and at 870–840 cm.$^{-1}$ (broad) to S–F. Other bands at 1085, 1060, 958, 900, and 738 cm.$^{-1}$ were not assigned. *Anal.* Calcd. for $C_4F_9(SO_3F)$: S, 10.1; F, 59.8. Found: S, 10.0; F, 59.6. The mass spectrum at an ionization potential of 70 v. had peaks attributed to the following species with the respective mass numbers and relative abundances shown: SO_2^+, 64, 5.3; SOF^+, 67, 13.8; CF_3^+ and $^{34}SOF^+$, 69, 100.0; SO_2F^+, 83, 89.9; $C_2F_3O^+$, 97, 31.4; $C_2F_4^+$, 100, 7.4; $C_2F_5^+$, 119, 29.8; $C_3F_5^+$, 131, 6.4; $C_2F_5SO_3^+$, 199, 6.4; $C_4F_9^+$, 219, 0.02; $C_3F_7SO_3^+$, 249, 3.2; and $C_4F_9SO_3^+$, 299, 0.5. The nuclear magnetic resonance spectrum of $C_4F_9(SO_3F)$ was run at 40 Mc. with $CFCl_3$ as the internal standard. Resonances were found at −51.3 p.p.m. due to the fluorine of the SO_3F group; +78.3 and +80.8 p.p.m. due to the two CF_3 groups; +124.5 p.p.m. due to the CF_2 of the CF_3CF_2 group; and +139.1 p.p.m. due to the CF of the CF_3CF group.

Reaction of Ennea-2-(fluorosulfato)butane with Cesium or Potassium Fluorides.—In the presence of either excess cesium or potassium fluoride at 70° for 16 hr., a 6.48-mmole sample of enneafluoro-2-(fluorosulfato)butane was partially converted to octafluoro-2-butanone, $CF_3CF_2COCF_3$, and SO_2F_2. The yield was about 31%. Separation and purification of C_4F_8O was accomplished by extended pumping for 48 hr. at −126°. The observed molecular weight was found to be 215 compared to a calculated value of 216. An infrared spectrum of this compound was taken at 20 mm. pressure. The following bands were identified: 1800 cm.$^{-1}$ (m), C═O stretch; 1310 (s), 1260–1185 (br, s), and 1075 cm.$^{-1}$ (m), C—F stretch. Other bands at 909 (ms), 885 (ms), and 720 cm.$^{-1}$ (s) were not assigned. Octafluoro-2-butanone was first synthesized in 15% yield by the fluorination of methyl ethyl ketone at 135° in the presence of copper.[13]

Preparation of Trifluoroacetyl Fluorosulfate.—Trifluoroacetyl bromide and dry nitrogen in a 1:3 mixture were introduced into a 1-l. Pyrex reaction vessel which was held at 3°. Peroxodisulfuryl difluoride was added slowly until the molar ratio of trifluoroacetyl bromide to $S_2O_6F_2$ was 2.5:2. After 20 min., a red-brown vapor began to appear. The cold bath was removed after 12 hr., and the contents of the vessel were separated by fractional codistillation. Each component was identified from its infrared spectrum. Since bromine and trifluoroacetyl fluorosulfate, $CF_3CO(SO_3F)$, were not separable by codistillation, the former was removed by contact of the gaseous mixture with mercury, which permitted the recovery of the pure $CF_3CO(SO_3F)$ in approximately 65% yield based on the CF_3COBr present initially. The equation for the reaction can be written as

TABLE II

VAPOR PRESSURE OF $CF_3CO(SO_3F)$

P, mm.	T, °K.	P, mm.	T, °K.	P, mm.	T, °K.
24.6	249.8	171.9	286.1	505.7	308.8
49.2	262.5	184.0	286.5	632.8	314.4
68.3	268.7	208.3	288.6	675.6	316.2
116.0	277.2	280.3	295.4	721.5	318.0
133.4	280.4	356.9	301.7	770.0	319.6
160.6	283.8	439.3	305.9	785.8	320.5
167.4	284.6				

$$2CF_3COBr + 2S_2O_6F_2 \xrightarrow{3°} CF_3CO(SO_3F) + CF_3SO_3F + CO_2 + S_2O_5F_2 + Br_2$$

Trifluoroacetyl fluorosulfate is a clear, colorless liquid which hydrolyzes slowly with 0.1 N sodium hydroxide at 100° and which is inert toward mercury, at least for short periods of time. Experimental measurements resulted in a molecular weight of 195 compared to a calculated value of 196 for $CF_3CO(SO_3F)$. A liquid density of 1.618 g./cc. was found at 23.5°; other values obtained include: 1.672 at 6.7°, 1.654 at 12.6, 1.599 at 29.3°, and 1.595 at 31.5°. These data yield the expression d (g./cc.) = 1.6916 − 0.0031t (°C.). A melting point was not obtained. The point at which the compound loses the cracked glass appearance taken on when cooled to −183° was estimated to be −134 ± 2°. A boiling point of 319.5°K. is obtained from the vapor pressure data given in Table II. The molar heat of vaporization is 8.0 kcal., and the Trouton constant is 25.1. The infrared spectrum of $CF_3CO(SO_3F)$ is as follows: A band at 1850 cm.$^{-1}$ (s) corresponds to C═O stretch; at 1487 (vs) and 1250 cm.$^{-1}$ (s) to S—O; at 1303 (m) and 1200 cm.$^{-1}$ (s) to C—F; and at 862 and 830 cm.$^{-1}$ (s) to S—F stretch. Bands at 1040 (s) and 778 cm.$^{-1}$ (m) were not assigned. *Anal.* Calcd. for $CF_3CO(SO_3F)$: C, 12.2; S, 16.3; F, 38.8. Found: C, 15.1; S, 14.7; F, 37.5. The n.m.r. spectrum consisted of two resonances. The sulfur–fluorine and carbon–fluorine resonances occurred at shifts of −47.8 and +73.1 p.p.m., respectively, relative to $CFCl_3$, and had an area ratio of 1:3.

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Stepwise Hydrolysis of Hexafluoroantimonate(V)

BY WILLIAM A. MAZEIKA[1] AND H. M. NEUMANN

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To explain the acidity of solutions resulting from the dissolving of hexafluoroantimonate(V) salts Lange and

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(13) F. F. Holub and L. A. Bigelow, *J. Am. Chem. Soc.*, **72**, 4879 (1950).

(1) *Taken from a thesis submitted by William A. Mazeika in partial fulfillment of the requirements for the M.S. degree, Dec. 1961.*

Askitopoulos[2] postulated a stepwise hydrolysis through ions of the type $[SbF_{6-n}(OH)_n]^-$. By adding stoichiometric amounts of base to $KSbF_6$ in water, Kolditz and Sarrach[3] were able to form, and then identify by a paper chromatographic technique, ions of this type in which $n = 1, 2, 3,$ and 4.

In principle the extent of the hydrolysis reaction of SbF_6^- can be followed as a function of time by titration of either the fluoride ion or the hydrogen ion formed in the reaction

$$SbF_6^- + nH_2O \longrightarrow [SbF_{6-n}(OH)_n]^- + nF^- + nH^+$$

The present paper reports a kinetic investigation of the steps in the hydrolysis reaction.

Experimental Section

Preparation and Analysis of $KSbF_6$.—Solid Sb_2O_3 and KOH were mixed in a 1 : 2.2 mole ratio and oxidized by slow addition of a 30% H_2O_2 solution over a period of hours. After decantation of the supernatent the remaining solid was treated with 48% HF and heated on a steam bath. After filtering off a slight residue a clear solution remained. Evaporation and cooling led to the appearance of a white crystalline substance. This was recrystallized twice from 48% HF and dried in a desiccator containing solid NaOH. Initially the salt still retained the odor of HF, but the salt no longer possessed this odor after 3 days in the desiccator.

Anal. Calcd. for $KSbF_6$: Sb, 44.30; F, 41.50. Found: Sb, 44.05; F, 40.87.

At this stage the salt dissolved rapidly in water, HCl, or NaOH solutions. In about 3 weeks the $KSbF_6$ became difficult to dissolve in water. However, recrystallization from HF produced salt with the earlier characteristics. The salt is not strongly deliquescent, but gains weight on prolonged exposure to the atmosphere.

Analysis for fluoride was accomplished by volatilization as fluorosilicic acid,[4] followed by titration with standard thorium nitrate solution.[5]

The method for the determination of Sb(V) in $KSbF_6$ is worth noting. The method was basically that described by Willard and Diehl[6] in which Sb(V) oxidizes iodide ion in about 3 *M* hydrochloric acid and the liberated iodine is titrated with standard thiosulfate solution. In preliminary experiments to test the validity of the method it was observed that the presence of fluoride caused a low value for antimony (sometimes by as much as 50%). The addition of boric acid, followed by heating for several minutes, proved a satisfactory method of eliminating the complication due to the fluoride ion. In tests on samples containing a known amount of antimony the method was found to be accurate within 2%.

Kinetic Runs.—The reaction was begun by dissolving a weighed portion of $KSbF_6$ in a solution of the desired composition, which was thermostated at 25°. The time required for dissolution varied with the age of the salt and the nature of the solution and was of the order of several minutes. The recorded starting time for hydrolysis was the time of the first addition of solution to the salt in a volumetric flask. Aliquots were removed at appropriate intervals for analysis. A titration for fluoride was made as soon as possible after solution of $KSbF_6$ and was followed by a titration for hydrogen ion when this was appropriate. The time intervals for subsequent titrations varied depending on the speed of reaction; at least five additional titrations were performed on the first day, three on the second day, and one or two on the following days.

The titration for fluoride followed known procedures,[5] using 0.011 *N* $Th(NO_3)_4$ solution as titrant and sodium alizarin sulfonate as indicator. In the early stages of the reaction titrations were performed by transferring a 5-ml. aliquot (4 ml. for a solution that contained more than 0.6 *M* $HClO_4$) to a 125-ml. erlenmeyer flask, adding 20 ml. of 95% ethyl alcohol, indicator, buffer, and enough distilled water to maintain a volume of 50 ml. at the end of the titration, and then titrating with $Th(NO_3)_4$. For titration in the later stages, where the amount of fluoride was greater, the alcohol was omitted. In either case sufficient amount of a buffer solution prepared from sodium hydroxide and chloroacetic acid was added to make the final pH of the solution fall in the range 2.9 to 3.1.

When the free fluoride ion concentration is plotted *vs.* time, fairly distinct breaks are observed for the replacement of one, two, and four fluoride ions. In a more detailed treatment the assumption is made that the system consists of several consecutive first-order or pseudo-first-order reactions. A plot of log (fluoride retained) *vs.* time is then made, and the resulting curve is resolved into its straight-line components. Although the rate of hydrolysis is dependent on the pH, in most runs the solutions were sufficiently acidic or basic so that the hydrogen ion generated in the reaction did not cause a markedly changing pH during the reaction. When this condition was satisfied, each step appeared pseudo-first order within experimental error. Taking into account the difficulties of the fluoride titration and the limitations of the graphical resolution of the data, we consider the half-times to be accurate to ±10%.

Results

Rates were measured by titration of fluoride ion in solutions ranging from 1 *M* $HClO_4$ to 1 *M* NaOH (Table I). In a few solutions the rate was also measured by titration of hydrogen ion.

TABLE I

RATES OF HYDROLYSIS OF $[SbF_5(OH)]^-$ AND $[SbF_4(OH)_2]^-$ AT 25°

Original soln.	$KSbF_6$, *M*	Half-time, hr.	$k_2 \times 10^4$, sec.$^{-1}$	Half-time, days	$k_3 \times 10^5$, sec.$^{-1}$
1.08 *M* $HClO_4$[a]	0.0108	1.00	1.9	0.70	1.1
0.83 *M* $HClO_4$[a]	0.0108	1.10	1.7	0.77	1.0
0.62 *M* $HClO_4$[a]	0.0108	1.08	1.8	1.21	0.66
0.40 *M* $HClO_4$[a]	0.0108	1.22	1.6	2.3	0.35
0.21 *M* $HClO_4$[a]	0.0108	3.20	0.60	3.0	0.27
0.08 *M* $HClO_4$[a]	0.0108	9.2	0.21	5.2	0.15
0.012 *M* $HClO_4$[b]	0.0108	13.2	0.15	5.9	0.14
Water[b]	0.0108	15.8	0.12	6.7	0.12
0.011 *M* NaOH[b]	0.0100	...[c]	...	5.8	0.14
0.10 *M* NaOH[a]	0.0108	0.35[d]	5.5	...[d]	...
1.0 *M* NaOH[a]	0.113	<0.05	>39	...	>390

[a] Titration of fluoride only. [b] Titration of both fluoride and hydrogen ion. [c] The pH varied sufficiently during this step so that the reaction does not appear first order. [d] First-order plot gave a single straight line.

Both titration methods indicate that the first fluoride is lost within the time necessary for the dissolution of the solid and the titration of an aliquot. That this fluoride is not lost during the titration procedures is indicated by the fact that the expected drop in pH (calculated for a solution of HF) can be observed with a pH meter on dissolving the solid in water. This is also in agreement with the work of Kolditz and Sarrach,[3] who find $[SbF_5OH]^-$, but not SbF_6^-, when $KSbF_6$ is dissolved in water.

In acidic solution the rate of fluoride release becomes

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(2) W. Lange and K. Askitopoulos, *Z. anorg. allgem. Chem.*, **223**, 369 (1935).

(3) L. Kolditz and D. Sarrach, *ibid.*, **293**, 132 (1957).

(4) W. D. Armstrong, *J. Am. Chem. Soc.*, **55**, 1741 (1933); H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933).

(5) W. D. Armstrong, *ibid.*, **8**, 384 (1936); R. J. Rowley and H. V. Churchill, *ibid.*, **9**, 551 (1937).

(6) H. H. Willard and H. Diehl, "Advanced Quantitative Analysis," D. Van Nostrand Co., Inc., Princeton, N. J., 1960, p. 352.

extremely slow after about 60% of the fluoride has been released. Some of the runs were followed for as long as 4 months; others were heated to speed up the reaction in order to obtain an effective infinite time reading. Values obtained at different acidities were 64.45, 65.11, 64.35, 65.60, and 64.92% of fluoride released. Although these values are within experimental error equal to 66.67, which would correspond to a final product containing F and Sb in a ratio of 2:1, the resolution of each kinetic curve was begun by subtracting a value of 35.0% fluoride remaining.

The residual curves resulting from this subtraction could be resolved satisfactorily into two linear components. The intercepts indicate that these linear portions correspond to the hydrolysis of $[SbF_5(OH)]^-$ and $[SbF_4(OH)_2]^-$. According to this interpretation the following steps of hydrolysis have been measured

$$SbF_6^- + H_2O \xrightarrow{\text{fast}} SbF_5(OH)^- + H^+ + F^-$$

$$SbF_5(OH)^- + H_2O \xrightarrow{k_2} SbF_4(OH)_2^- + H^+ + F^-$$

$$SbF_4(OH)_2^- + H_2O \xrightarrow{k_3} \text{final product}$$

The pseudo-first-order rate constants, k_2 and k_3, and the corresponding half-times are given in Table I. The success of the resolution is due to the marked difference in rates for these steps; $[SbF_5(OH)]^-$ disappears over the period of hours, while $[SbF_4(OH)_2]^-$ disappears over the period of days.

Attempts to resolve the residual first-order plots into three linear components, corresponding to the hydrolysis of $[SbF_5(OH)]^-$, $[SbF_4(OH)_2]^-$, and $[SbF_3(OH)_3]^-$, provided a much less satisfactory fit of the data than did the resolution into two components. More positive support for the proposed three-step hydrolysis has been provided by experiments in which the antimony species present in the reaction mixture are separated by chromatography on cellulose columns.[7] Only three species (corresponding to $[SbF_5(OH)]^-$, $[SbF_4(OH)_2]^-$, and the final product), rather than four, are observed.

The rate of release of hydrogen ion is equal to the rate of release of fluoride ion during the first two stages of hydrolysis, but during the third stage the ratio of hydrogen ion released to fluoride ion released is 1.17:2. A small amount of a fine solid was also observed at this stage in some of the reactions. These observations suggest that the final product is not an anion as simple as $[SbF_2(OH)_4]^-$, but is instead a polymeric anion which contains F and Sb in a ratio very close to, but not necessarily equal to, 2:1. There is considerable evidence that antimony(V) forms polymeric anions in acid solution, with most of the evidence suggesting a hexaantimonate.[8]

In solutions more basic than pH 12 the hydrolysis was complete and all six fluorides were lost quite rapidly. The reaction in 1 *M* NaOH was so rapid that a fine white precipitate, probably $NaSb(OH)_6$, formed before the first aliquot could be taken. In 0.1 *M* NaOH the rate was measurable and could be followed both by the fluoride titration and by titration with HCl. In aqueous ammonia at pH 10.2 after 1 month of reaction 17% of the fluoride still remained complexed.

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[7] These experiments were performed by Mr. Jesse H. Hall.

[8] P. Souchay and D. Peschanski, *Bull. soc. chim. France*, **15**, 439 (1948); B. Ricca, G. D'Amore, and A. Bellomo, *Ann. chim.* (Rome), **46**, 491 (1956); G. Jander and H. J. Ostmann, *Z. anorg. allgem. Chem.*, **315**, 241, 250 (1962).

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Polycyclic Borazines[1]

BY J. L. BOONE AND G. W. WILLCOCKSON

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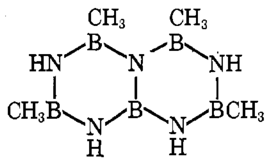
The yield of B-trimethylborazine from B-trichloroborazine and methylmagnesium bromide has never exceeded 34% in this laboratory. In every case, large amounts of residue remained which had infrared spectra that strongly resembled the spectrum of B-trimethylborazine. Some trimethylborane and methane were also formed. It appears from the present work that ring opening occurs followed by condensation which gives as the second principal product a B-methylborazine (I) analogous to naphthalene. Elemental analyses checked closely for this compound but were also consistent with a structure analogous to biphenyl. However, cryoscopic determination of the molecular weight in benzene gave values which were consistently within 0.5–1.5% of the value calculated for structure I.



I

A similar reaction using butylmagnesium halides has been reported by Harris to yield the B-butyl derivative analogous to biphenyl.[2] Laubengayer and co-workers have reported both the naphthalene and biphenyl analogs of the borazine system from the pyrolysis of borazine,[3,4] and Wagner and Bradford have reported the biphenyl analogs of hexamethylborazine from the condensation of N-lithioborazines and B-chloroborazines.[5]

Further workup of the products of the B-trichloroborazine–methylmagnesium bromide reaction gave two more boron–nitrogen compounds which were appar-

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[1] Presented in part to the Inorganic Division, 142nd National Meeting of the American Chemical Society, Sept. 11, 1962, paper No. 16.

[2] J. J. Harris, *J. Org. Chem.*, **26**, 2155 (1961).

[3] A. W. Laubengayer, P. C. Moews, Jr., and R. F. Porter, *J. Am. Chem. Soc.*, **83**, 1337 (1961).

[4] A. W. Laubengayer and O. T. Beachley, Jr., Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, pp. 281–289.

[5] R. I. Wagner and J. L. Bradford, *Inorg. Chem.*, **1**, 99 (1962).