$SbF_5 \cdot SO_2ClF \simeq SO_2ClF$, $SbF_5 \cdot OSF_2 > SO_2ClF$, and $SbF_5 \cdot SO_2 > SO_2ClF$. The basicity of an SO_n group might be expected to be closely related to the SO bond order, *i.e.*, to the relative contributions of S=O and $S^+—O^-$. Hall and Robinson[11] have shown that there is a linear relationship between the pK value for an X_2SO_n compound and the stretching frequency of the SO group and Gillespie and Robinson[5] have shown that the stretching frequency may be used as a measure of the bond order. Hence it is satisfactory to find that with the exception of CH_3SO_2F and SO_2 for which the order is reversed the base strengths of the donors that we have studied with SO_n groups are in the order that would be predicted from the bond orders given by Gillespie and Robinson.[5]

Experimental Section

Nmr Measurements. Fluorine nmr spectra were measured using a Varian DA-60IL spectrometer operating at 56.4 MHz. The 2497-Hz audio modulation side bands forming part of the base-line stabilization circuitry of the instrument usually overlapped part of the center-band spectrum, and the "lock box" was therefore modified to take an external manual oscillator frequency from a Muirhead D-890-A audiofrequency oscillator. Spectra were then measured using the first upper side band in the field sweep unlock mode.

For the homonuclear decoupling experiments, the irradiating frequency was produced by the Muirhead D-890-A oscillator and the swept frequency by a General Radio Co. 1164A frequency synthesizer.

Low-temperature spectra were obtained using a Varian V-4540 temperature controller with the variable temperature probe.

Materials. Antimony pentafluoride was obtained from Ozark Mahoning Co. and purified by double distillation in an atmosphere of dry air, using an all-glass apparatus. The purified material was stored in a Teflon bottle in a drybox.

Sulfuryl fluoride (Matheson of Canada Ltd.) and thionyl fluoride (Peninsular Chemresearch Inc.) showed only one line in the ^{19}F nmr spectrum and were used without further purification. Anhydrous grade sulfur dioxide (Matheson of Canada Ltd.) was stored in a gas bulb over P_2O_5, and methyl sulfuryl fluoride (Eastman Organic Chemicals) was distilled and stored over molecular sieves.

Sulfuryl chlorofluoride was prepared from potassium fluorosulfinate and chlorine according to Seel and Riehl.[12]

The preparation of tetraethylammonium hexafluoroantimonate was reported previously.[13]

Sample Preparation. In a drybox a weighed amount of antimony pentafluoride was transferred to an nmr tube using an all-glass syringe; for the competition reaction with Et_4NSbF_6, the tube already contained a known amount of the salt. The tubes were closed with detachable tops and attached to a calibrated glass vacuum line. Gases were condensed into the tube from storage bulbs using pressure difference (or, in the case of a single gas, weight) to determine the amount. If only gases were to be added the tubes were then sealed. When one of the components was to be $MeSO_2F$, the vacuum line and tube were filled with extra dry nitrogen over the frozen gas and the tube was removed from the line. The top was quickly removed, a flow of extra dry nitrogen led into the tube *via* a hypodermic needle, and a known weight of $MeSO_2F$ added from a hypodermic syringe. The top was then replaced and the sample reattached to the vacuum line, evacuated, and sealed.

Acknowledgments. We thank the United States Air Force Office of Scientific Research for financial support of this work. We are grateful to Mr. J. I. A. Thompson for technical assistance with the nmr spectrometer and to Mr. M. Brownstein, who undertook the study of the system $SbF_5–SOF_2$.

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(11) S. K. Hall and E. A. Robinson, *Can. J. Chem.*, **42**, 1113 (1964).

(12) F. Seel and L. Riehl, *Z. Anorg. Allg. Chem.*, **282**, 293 (1955).

(13) See Table I, footnote *e*.

Fluorine-19 Nuclear Magnetic Resonance Investigations of Complexes of Antimony Pentafluoride. II. The Reactions of Antimony Pentafluoride with Water, Sulfuric Acid, and Fluorosulfuric Acid

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Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada. *Received June 13, 1969*

Abstract: It is shown that water reacts with antimony pentafluoride in solution in SO_2 to form the complexes $SbF_5 \cdot OH_2$ and $SbF_5 \cdot OH_2 \cdot SbF_5$. These complexes undergo ligand redistribution reactions such as $2SbF_5 \cdot OH_2 \rightleftarrows SbF_4(OH_2)_2^+ + SbF_6^-$. Excess SbF_5 forms $Sb_2F_{11}^-$ and $SbF_5 \cdot SO_2$. With sulfuric acid, the complexes $SbF_5 \cdot OSO(OH)_2$ and $F_5Sb \cdot OS(OH)_2O \cdot SbF_5$ are formed. Ligand redistribution reactions similar to those proposed for the $SbF_5–H_2O$ system also occur in the $SbF_5–H_2SO_4$ and $SbF_5–FSO_3H$ systems.

In the preceding paper[1] it was shown that methyl sulfonyl fluoride and sulfuryl chlorofluoride form fluorine-bridged 2:1 SbF_5:donor complexes in which the donor occupies a terminal position. The complex $2SbF_5 \cdot FSO_3H$, however, has been shown to be bridged by two oxygens of the fluorosulfate group, and to be a strong acid of the fluorosulfuric acid solvent system.[2] Reaction of SbF_5 with SO_3 gives a fluorosulfate-bridged polymer $(SbF_4SO_3F)_n$ and not a simple adduct as SO_2 does.[3] It is possible that fluorosulfate bridges might possess some special stability in antimony fluoro complexes but it is more probable that the formation of such

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(1) P. A. W. Dean and R. J. Gillespie, **91**, 7260 (1969).

(2) R. C. Thompson, J. Barr, R. J. Gillespie, J. B. Milne, and R. A. Rothenbury, *Inorg. Chem.*, **4**, 1641 (1965).

(3) R. J. Gillespie and R. A. Rothenbury, *Can. J. Chem.*, **42**, 416 (1964).

Table I

Solution no.	Ligand B	Chemical shifts, ppm from $CFCl_3$, and coupling constants, J, Hz																
		$SbF_5 \cdot B$			$SbF_5 \cdot B \cdot SbF_5$			$Sb_2F_{11}^-$ [a]					$SbF_5 \cdot SO_2$			cis-SbF_4B_2 [b]		
		Doublet	Quintet	J	Doublet	Quintet	J	F_1	F_2	F_3	$J_{F_1-F_2}$	$J_{F_2-F_3}$	Doublet	Quintet	J	Triplet	Triplet	J
c											100	53						
d								131.2	109.1	89.4			100.9	133.7				
1	H_2O	110.5	128.2	103	107.9	125.2	104									93.6		~129
2	H_2O	108.9	127.6	~98	106.6	~123.5	~100	~132.9	110.9	~91.3	~93	~73	102.0	134.0	98	92.8	118.5	130
3	H_2O	~108.1		~95	~105.3		~92		110.3	91.5	101	65	100.7	133.4	99	92.3	118.1	129
4	H_2SO_4	105.9	128.6	105	106.7	126.3	103		110.7		~102	~65	101.6		100			
5	H_2SO_4	106.0	128.8	104	106.9	126.6	~103	133.3	111.0	~89.6	102	63	102.0	133.3	98			

[a] For assignments see ref 1. J_{1-3} is not observed and appears to have a near zero value. [b] When B = H_2O, may be either mono- or binuclear (see text). [c] In HF; R. J. Gillespie and K. Moss, *J. Chem. Soc., A*, 1170 (1966). [d] J. Bacon, P. A. W. Dean, and R. J. Gillespie, *Can. J. Chem.*, **47**, 1655 (1969). J. W. Moore, *et al., J. Amer. Chem. Soc.*, **90**, 1358 (1968), give chemical shifts of ϕ 105 and 137 for $SbF_5 \cdot SO_2$ and J = 100 Hz.

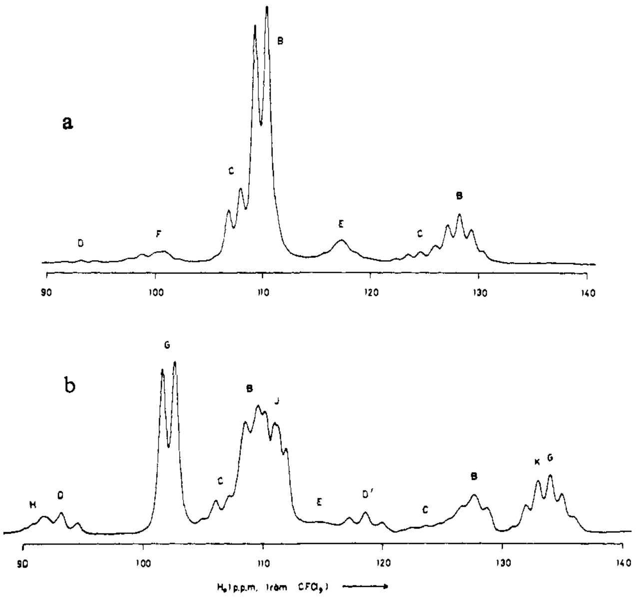
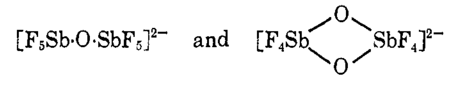


Figure 1. ^{19}F nmr spectra (94.1 MHz) of SbF_5–H_2O solutions in sulfur dioxide at −85°: (a) $SbF_5:H_2O:SO_2$ = 0.95:1.00:6.82; (b) $SbF_5:H_2O:SO_2$ = 1.84:1.00:9.48.

bridges is due to the basicity of the fluorosulfate group. It was therefore of interest to investigate the reactions of SbF_5 with other basic donors, in the present case water and sulfuric acid.

A compound $SbF_5 \cdot 2H_2O$ has been reported[4] which should probably be regarded as $H_3O^+SbF_5OH^-$. Kolditz and Nussbucker[5] postulate that thermal condensation of $NR_4^+SbF_5OH^-$ and $NR_4^+SbF_4(OH)_2^-$ give tetraalkylammonium salts of the anions



$$[F_5Sb{\cdot}O{\cdot}SbF_5]^{2-} \quad \text{and} \quad [F_4Sb\overset{O}{\underset{O}{\diamond}}SbF_4]^{2-}$$

respectively; by cation exchange they prepared aqueous solutions thought to contain the free acids $H_2[Sb_2F_{10}O]$ and $H_2[Sb_2F_8O_2]$. The titration curve of $H_2[Sb_2F_{10}O]$ showed the first acid ionization to occur extensively in aqueous solution.

Results and Discussion

SbF_5–H_2O Solutions in Sulfur Dioxide. The following solutions were examined: (1) $SbF_5:H_2O:SO_2$ = 0.95:1.00:6.82; (2) $SbF_5:H_2O:SO_2$ = 1.84:1.00:9.48; (3) $SbF_5:H_2O:SO_2$ = 4.49:1.00:21.3.

The ^{19}F nmr spectra of the solutions showed broad lines at room temperature but on cooling fine structure was observed. Figure 1 shows 94.1-MHz spectra obtained when the above solutions were cooled to −85°. The chemical shifts and spin–spin coupling constants are given in Table I. From the relative areas of the observed resonances for these solutions, the approximate relative amounts of the various species given in Table II were deduced.

Solution 1 (Figure 1a) shows two AX_4 patterns B and C, C being of lower intensity; the quintets of these spectra partly overlap. Also seen is a weak triplet, D, and two broadish lines with some fine structure, E and F.

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(4) O. Ruff, *Ber.*, **39**, 4310 (1906).

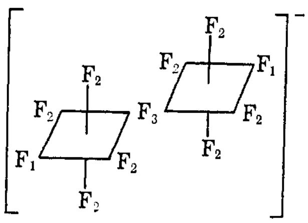
(5) L. Kolditz and B. Nussbucker, *Z. Anorg. Allg. Chem.*, **337**, 191 (1965).

Table II

Solution no.	Approximate relative amounts present in solution, mol % $SbF_5 \cdot OH_2$	$(SbF_5)_2 \cdot OH_2$	$Sb_2F_{11}^-$	$SbF_5 \cdot SO_2$	*cis*-$SbF_4(OH_2)_2^+$ [a]
1	81	11	~0	~0	2
2	36	7	20	31	5
3	9	3	8	77	8

[a] Or the binuclear species (see text).

When the $SbF_5:H_2O$ ratio is increased to 1.84 (Figure 1b) other features are present in the spectrum. The triplet D increases in relative intensity and another triplet D′ of equal intensity can be seen in a position previously obscured by E; the relative intensities and spin–spin coupling constants for these two triplets show them to be the two components of an A_2X_2 spectrum. E is now very broad and scarcely distinguishable from the base line. A new AX_4 spectrum G is seen, and a complex consisting of a small multiplet H (partly under D), a double doublet J (partly overlapping the B doublet), and a quintet K (overlapping the G quintet) appears. Comparison of the spectrum G with the previously observed spectrum of $SbF_5 \cdot SO_2$ shows it to be due to this complex. Similarly H, J, and K can be assigned to F_3, F_2, and F_1 of the $Sb_2F_{11}^-$ anion (I).



I.

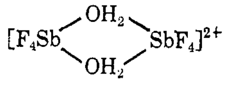
The spectrum of solution 3 is essentially the same as that of solution 2 (Figure 1b) except that the spectrum G of $SbF_5 \cdot SO_2$ is of much greater intensity.

The proton spectra of the solutions at 25° show one line in solution 1 (τ 1.1), two lines in solution 2 (τ 1.5 and 0.4, relative areas ~2 and 1, respectively), and two lines for solution 3 (τ 1.5 and 0.0, relative areas ~1 and 2, respectively). No additional resonances are observed on lowering the temperature of the solutions; at higher temperatures the two lines in 2 and 3 begin to merge. The low-field shift of the lines in these solutions suggests highly acidic protons, but assignments can only be tentative. Since the higher field line occurs in solution 1 where a large amount of $SbF_5 \cdot OH_2$ is present, it can probably be assigned to the protons in this complex, perhaps shifted slightly downfield by a relatively slow proton exchange with more acidic species. Both $(SbF_5)_2OH_2$ and $SbF_4(OH_2)_2^+$ can be expected to be more acidic than $SbF_5 \cdot OH_2$ and proton exchange between these two complexes may be facile. We tentatively assign the lower field line to the protons in $(SbF_5)_2OH_2$ and $SbF_4(OH_2)_2^+$ which must be undergoing fast exchange. As $(SbF_5)_2OH_2$ involves four-coordinated oxygen it is presumably fully ionized under all conditions to $(SbF_5)_2OH^-$.

The AX_4 spectrum B constitutes the major part of the intensity of solution 1, which is almost equimolar in SbF_5 and H_2O, and we assign this spectrum to the 1:1 complex $SbF_5 \cdot OH_2$ (and/or its conjugate base SbF_5OH^-). Since only one line is observed in the proton spectrum of solution 1, the ionized and un-ionized forms of this complex (if both are present) must be in labile equilibrium and hence they are not expected to give separate fluorine spectra. The spectrum C must therefore be assigned to the bridged complex $SbF_5 \cdot OH_2 \cdot SbF_5$ (and/or its conjugate base $[SbF_5 \cdot OH \cdot SbF_5]^-$). Since the spectra show that $Sb_2F_{11}^-$ anions are present in solutions 2 and 3, some corresponding cations must also be present, and some redistribution of fluorines must have occurred to give antimony complexes with fewer than five fluorines per antimony. Such complexes may be cations themselves, *e.g.*, $SbF_4(OH_2)_2^+$, or may be ionized to give their conjugate base and H_3O^+. This is consistent with the observation of an A_2X_2 pattern in the spectra which could be attributed to *cis*-$SbF_4(OH_2)_2^+$ (and/or its conjugate base). The value of J_{F-F} for the A_2X_2 spectrum, 130 Hz, is close to that observed for *cis*-$SbF_4(SO_3F)_2^-$, 122–126 Hz,[2] and the *cis*-bridged polymer $(SbF_4SO_3F)_n$, 125–128 Hz.[3] We suppose therefore that $SbF_5 \cdot OH_2$ undergoes a ligand redistribution reaction

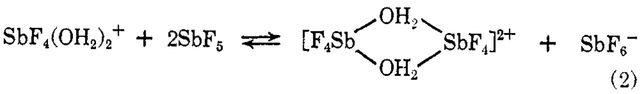
$$2SbF_5 \cdot OH_2 \rightleftarrows SbF_4(OH_2)_2^+ + SbF_6^- \tag{1}$$

and, in solutions 2 and 3, SbF_6^- combines with excess SbF_5 to give $Sb_2F_{11}^-$. The A_2X_2 spectrum could also possibly arise from the dimeric bridged ion



$$[F_4Sb(OH_2)_2SbF_4]^{2+}$$

or its conjugate base. This species might arise from the reaction of $SbF_4(OH_2)_2^+$ with excess SbF_5, *i.e.*



$$SbF_4(OH_2)_2^+ + 2SbF_5 \rightleftarrows [F_4Sb(OH_2)_2SbF_4]^{2+} + SbF_6^- \tag{2}$$

Estimation of the total amount of water from the areas of the peaks in the fluorine spectra of all the water-containing complexes does not account for quite all the water and it is reasonable to conclude that a small amount is present as H_3O^+ formed by the acid ionization of complexes such as $SbF_4(OH_2)_2^+$, *i.e.*, $SbF_4(OH_2)_2^+ + H_2O \rightleftarrows SbF_4(OH)(OH_2) + H_3O^+$.

Since water is a strong base, formation of $SbF_5 \cdot OH_2$ is expected to predominate in the presence of excess water, though the redistribution equilibrium 1 may occur to some extent. In the presence of excess SbF_5, the experimental results show that the amount of the binuclear complex $SbF_5 \cdot OH_2 \cdot SbF_5$ remains small relative to that of the 1:1 complex, so the formation of the dimer is not the most important consequence of adding an excess of the Lewis acid. The SbF_5 first preferentially takes up SbF_6^- produced in redistributions such as eq 1, forming $Sb_2F_{11}^-$.

A previous study[6] has shown the major product of the reaction of equimolar amounts of SbF_6^- and SbF_5 in SO_2 to be $Sb_2F_{11}^-$, and not $SbF_5 \cdot SO_2$. Therefore we do not expect formation of large amounts of $SbF_5 \cdot SO_2$ until the hexafluoroantimonate-producing equilibria are forced as far as possible to the right-hand side, and this is in agreement with observation; $SbF_5 \cdot SO_2$ only predominates in the presence of a large excess of SbF_5, *i.e.*, in solution 3.

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(6) See Table I, footnote *d*.

SbF_5–H_2SO_4 Solutions in Sulfur Dioxide. The solutions studied had the following compositions: (4) $SbF_5:H_2SO_4:SO_2 = 1.03:1.00:3.74$; (5) $SbF_5:H_2SO_4:SO_2 = 1.84:1.00:7.41$. Solubility problems were encountered in solutions with higher $SbF_5:H_2SO_4$ ratios.

When the solutions were prepared and measured at low temperatures, the ^{19}F nmr spectra showed no resonances attributable to fluorine-on-sulfur. Figure 2a shows the 56.4-MHz spectrum, measured at −90°, of solution 4. The nmr parameters are given in Table I. The spectrum consists of a low-intensity doublet G, two overlapping AX_4 spectra B and C (C being of lower intensity), a double doublet J, and a broad line E. When the $SbF_5:H_2SO_4$ ratio is increased to 1.84 (Figure 2b), the doublet G and the double doublet J increase in relative intensity, a low-intensity multiplet structure H can just be observed to low field, and two overlapping multiplets, K and G, can be seen to high field.

The chemical shifts and coupling constants of the AX_4 spectrum G, and the complex spectrum H, J, and K (Table I) show that they are due to $SbF_5 \cdot SO_2$ and F_3, F_2, and F_1 of $Sb_2F_{11}^-$ (I), respectively. By arguments similar to those used in assigning the spectra of the SbF_5–H_2O mixtures (see above), we assign the spectrum B to the 1:1 complex $SbF_5 \cdot OSO(OH)_2$ and C to the 2:1 complex bridged by a sulfate grouping, $F_5Sb \cdot OH(OH)_2OSbF_5$, both of which are probably ionized to some extent. These two complexes are analogous to the 1:1 and 2:1 $SbF_5:FSO_3H$ complexes formed in SbF_5–FSO_3H.[2]

The spectra therefore provide evidence for bridging by the sulfate group, but show that increase in the amount of the bridged complex is not the only result of adding an excess of SbF_5. Although our concentration range was limited and we did not observe the spectrum of any species with less than five fluorines per antimony, such species must be formed since $Sb_2F_{11}^-$ anions are present. Hence we conclude that redistribution equilibria of the type proposed for SbF_5–H_2O mixtures are also important in the SbF_5–H_2SO_4 mixtures.

The System SbF_5–FSO_3H. Very recently Commeyras and Olah[7a] have shown that the ^{19}F nmr spectrum of $Sb_2F_{11}^-$ is observed in solutions of SbF_5 in FSO_3H when the molecular ratio $SbF_5:FSO_3H$ is between 0.4 and 1.4. These authors suggest that the $Sb_2F_{11}^-$ ion, together with fluoropolysulfuric acids, is most probably formed by reaction with the solvent, *i.e.*

$$2SbF_5 + 2HSO_3F \rightleftharpoons Sb_2F_{11}^- + H_2SO_3F^+ + SO_3$$

$$SO_3 + HSO_3F \rightleftharpoons HS_2O_6F$$

$$SO_3 + HS_2O_6F \rightleftharpoons HS_3O_9F$$

but it seems unlikely that the major route to formation of the $Sb_2F_{11}^-$ is reaction with the solvent, since, as we have seen, the same anion is also formed with sulfuric acid and water. It is more probable that the $Sb_2F_{11}^-$ ion is formed largely by equilibria of the type outlined above for $SbF_5 \cdot H_2O$. In support of this hypothesis, the carefully measured ^{19}F nmr spectra of solutions with approximately equimolar amounts of SbF_5 and FSO_3H show details in both the region of fluorine-on-antimony and fluorine-on-sulfur which can only be interpreted as indicating the presence of fluorosulfate-containing complexes other than the two considered by Commeyras and Olah, *i.e.*, $SbF_5 \cdot SO_3F^-$ and $(SbF_5 \cdot SO_3F \cdot SbF_5)^-$.

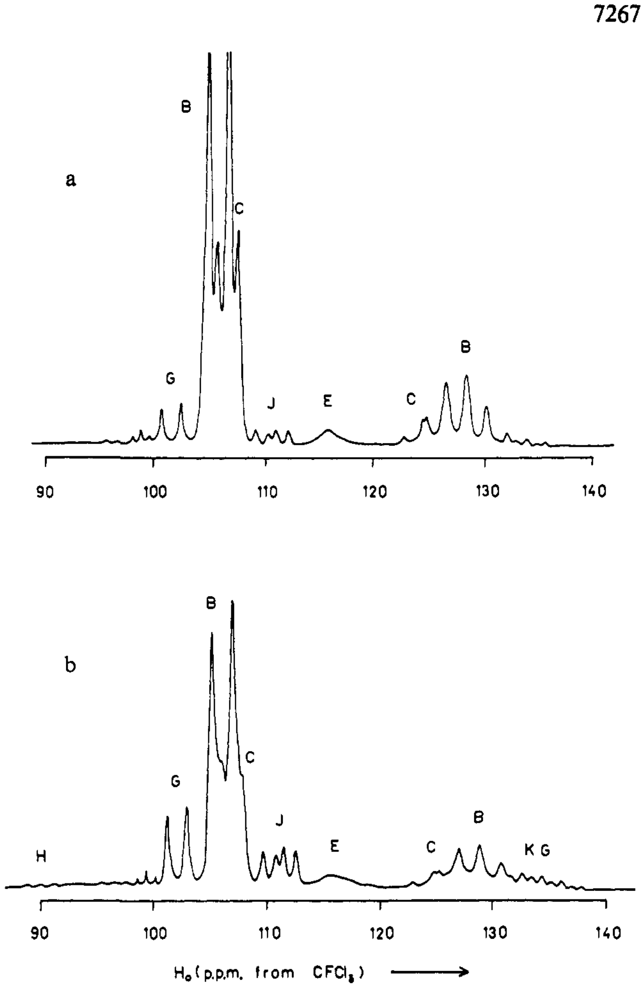

Figure 2. ^{19}F nmr spectra (56.4 MHz) of SbF_5–H_2SO_4 solutions in sulfur dioxide at −90°: (a) $SbF_5:H_2SO_4:SO_2 = 1.03:1.00:3.74$; (b) $SbF_5:H_2SO_4:SO_2 = 1.84:1.00:7.41$.

Figure 3 shows the spectrum, at −100°, of a sulfuryl chlorofluoride solution of an SbF_5–FSO_3H mixture with $SbF_5:FSO_3H = 0.92:1.00$; this spectrum is identical with that of the undiluted mixture except for its better resolution.[7b]

In the region of fluorine-on-antimony (Figure 3a) the two overlapping AX_4 spectra, B and C, of $SbF_5 \cdot SO_3F^-$ and $(SbF_5 \cdot SO_3F \cdot SbF_5)^-$, respectively, can be seen as well as the double doublet J previously assigned to F_2 of the $Sb_2F_{11}^-$ anion (I). In addition, in the two regions D where Commeyras and Olah were unable to make assignments, there are resonances made up of overlapping triplets which constitute the superimposed A_2X_2 spectra assigned by Thompson, *et al.*,[2] to *cis*-$SbF_4(SO_3F)_2^-$ and higher fluorosulfate-bridged polymers based on the *cis*-$SbF_4(SO_3F)_2$ grouping. Likewise, there are two single lines, L and M, which can be assigned to *trans*-$SbF_4(SO_3F)_2^-$ and other fluorosulfate-bridged polymers based on this unit. The line N was not observed either by Thompson, *et al.*, or by Commeyras and Olah; it is probably part of the doublet of an AX_4 spectrum expected for a terminal SbF_5 unit in a

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(7) (a) A. Commeyras and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2929 (1969). (b) We have found that SO_2ClF has no effect on the nmr spectra of SbF_5–FSO_3H mixtures other than to decrease viscosity and hence give better resolution, except when the $SbF_5:FSO_3H$ ratio is large. In the latter event there is evidence for formation of the $SbF_5 \cdot SO_2ClF$ complex which has been previously reported,[1] *e.g.*, in a solution with $SbF_5:FSO_3H:SO_2ClF = 1.69:1.00:1.44$, approximately 0.10 mol of SO_2ClF is complexed.

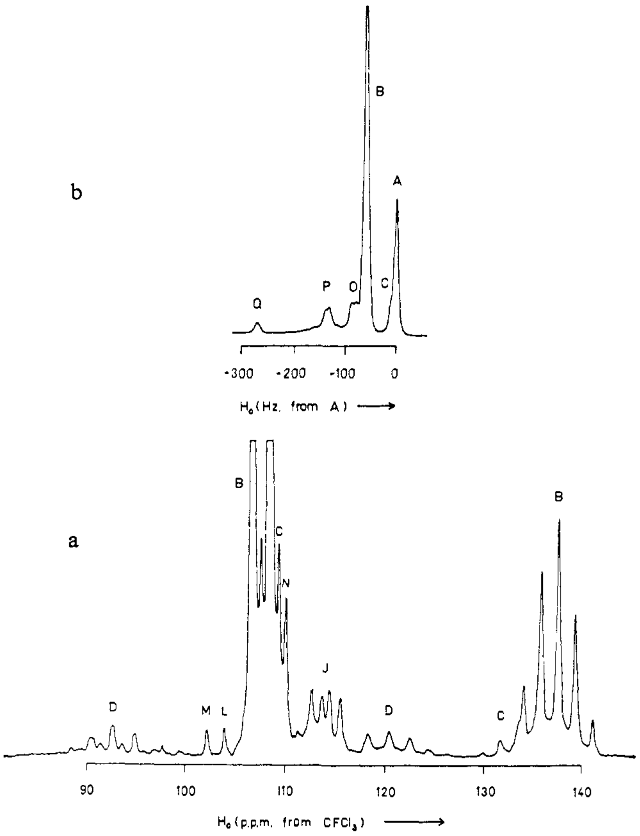

Figure 3. ^{19}F nmr spectrum (56.4 MHz) of a sulfuryl chlorofluoride solution of SbF_5:FSO_3H (0.92:1.00) at −100°: (a) fluorine-on-antimony region; (b) fluorine-on-fluorosulfate region.

fluorosulfate-bridged polymer such as $FSO_3 \cdot SbF_4 \cdot FSO_3 \cdot SbF_5$.

The fluorine-on-fluorosulfate region has several resonances (Figure 3b). The line B is that previously assigned[2] to the fluorine of the fluorosulfate group in $SbF_5 \cdot SO_3F^-$ while the signal C expected for this group in $[SbF_5 . SO_3F \cdot SbF_5]^-$ can just be observed as a shoulder on the resonance from uncomplexed fluorosulfuric acid, A. In SbF_5–SO_3–FSO_3H mixtures, the multiple resonances O and P have been tentatively assigned[2] to nonbridging and bridging fluorosulfate groupings, respectively, in the $SbF_4(SO_3F)_2^-$ monomers and polymers based on these. Since species such as these are shown by nmr spectrum of the fluorine-on-antimony region to occur in the present solution, we make the same assignments. It is concluded that the assignments of Commeyras and Olah, *i.e.*, that resonances O and P are due to FS_2O_6H and FS_3O_9H, respectively, are incorrect, and, as further evidence that this is so, we have observed the line from FS_2O_6H which, at −100°, occurs −182 Hz downfield from FSO_3H in the ^{19}F nmr spectrum of a mixture with SO_3:FSO_3H = 0.24. Therefore only the resonance Q, which constitutes less than 2% of the total intensity in this region, remains unassigned in our spectrum. This line is not present in the fluorosulfuric acid used but is observed in the undiluted SbF_5–FSO_3H mixture. It may be due to the fluorosulfate group in a complex not present in the relatively dilute mixtures of Thompson, *et al.*[2]

Our spectra thus provide convincing evidence for the formation of SbF_4X_2-type species in the concentrated SbF_5–FSO_3H solutions, and this is consistent with the proposed redistribution equilibrium being the main route to the observed formation of the $Sb_2F_{11}^-$ anion.

Conclusions

Evidence has been presented for the formation of 1:1 and 2:1 SbF_5:donor complexes when either water or sulfuric acid acts as a donor in sulfur dioxide solution. In the 2:1 complexes the donor is the bridging group which is also the case for $2SbF_5 \cdot FSO_3H$,[2] but not for $2SbF_5 \cdot SO_2ClF$ or $2SbF_5 \cdot MeSO_2F$.[1] In the presence of excess antimony pentafluoride over that required for the 1:1 complexes, both formation of the 2:1 complexes and redistribution equilibria are important, as well as reaction of the SbF_5 with the solvent. The redistributions produce the $Sb_2F_{11}^-$ anion as the best characterized species. It has also been shown that redistribution equilibria are important for SbF_5–FSO_3H mixtures.

The reaction of SbF_5 with ethanol has been shown by ^{121}Sb nmr to give SbF_6^-,[8] and Kolditz and Rehak[9] have suggested the redistribution $2SbF_5L \rightleftarrows SbF_6^- + SbF_4L_2^+$ to explain the conductivity of acetonitrile solutions of the complexes with L = acetonitrile or trimethylamine.

Experimental Section

Nmr Measurements. Fluorine nmr spectra were measured with either a Varian HA-100 spectrometer operating at 94.1 MHz, using the center-band mode, or a Varian DA-60IL spectrometer operating at 56.4 MHz and modified as described previously[1] to record spectra from the first upper side band in the field sweep unlock mode. Proton spectra were recorded using the Varian HA-100 machine.

Materials. Antimony pentafluoride (Ozark-Mahoning Co.) was purified by double distillation in an atmosphere of dry air using an all-glass apparatus, and was stored in Teflon bottles in a drybox.

Anhydrous grade sulfur dioxide was stored in a gas bulb over P_2O_5, and sulfuryl chlorofluoride was prepared from potassium fluorosulfonate and chlorine according to Seel and Riehl[10] and stored in a gas bulb.

Sulfuric acid and fluorosulfuric acid were purified by the standard literature methods.

Sample Preparation. For the experiments involving water, an all-glass syringe was used to transfer a weighed amount of antimony pentafluoride to a glass tube with an nmr tube sealed to a side arm, this operation being performed in a drybox. The vessel was closed with a detachable top and connected to a glass vacuum line of calibrated volume. A known amount of sulfur dioxide was condensed into the tube on top of the SbF_5. The vacuum line and vessel were filled with dry nitrogen and the apparatus was removed from the vacuum line. The top was quickly removed, a flow of extra dry nitrogen led into the vessel through a hypodermic needle, and a known weight of water added from a hypodermic syringe. The top was replaced and the sample reattached to the vacuum line, evacuated, and sealed off. On warming mixing occurred to give a homogeneous solution; the requisite amount was tipped into the nmr tube, both the main vessel and nmr side arm were cooled in liquid air, and the nmr tube was sealed off.

The procedure for preparing samples with sulfuric acid was similar to that described above except that samples were prepared directly in the nmr tubes and were kept at Dry Ice temperature while mixing and until spectra were measured.

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(8) J. V. Hatton, Y. Saito, and W. G. Schneider, *Can. J. Chem.*, **43**, 47 (1965).

(9) L. Kolditz and W. Rehak, *Z. Anorg. Allg. Chem.*, **342**, 32 (1966).

(10) F. Seel and L. Riehl, *ibid.*, **282**, 293 (1955).

SbF_5–FSO_3H samples were prepared in a drybox using weighed amounts of the constituents. When required, SO_2ClF was condensed into the nmr tubes on the vacuum line.

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Nuclear Magnetic Resonance Studies of Dimethylberyllium Adduct Species in Dimethyl Sulfide Solution

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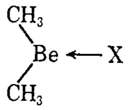
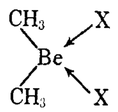
Abstract: Two equilibria are reported for dimethylberyllium in dimethyl sulfide: (A) $(CH_3)_2Be:S(CH_3)_2 + S(CH_3)_2 \rightleftharpoons (CH_3)_2Be:(S(CH_3)_2)_2$, and (B) $n(CH_3)_2Be:(S(CH_3)_2)_2 \rightleftharpoons ((CH_3)_2Be)_n:(S(CH_3)_2)_2 + (2n-2)S(CH_3)_2$, where n is as large as 9 in solution. Enthalpies for reactions A and B are found to be -3.23 and -9 kcal/mol, respectively. These data are compared with thermodynamic parameters for similar reactions. Methylberyllium chloride is shown to exist in dimethyl sulfide solution only as $(CH_3)BeCl:(S(CH_3)_2)_2$.

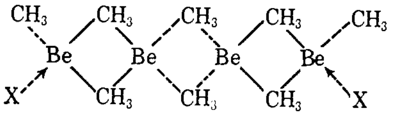
The reaction of Lewis bases with dimethylberyllium has been the subject of considerable interest. A tensimetric study of the reaction of solid dimethylberyllium with the bases trimethylamine, trimethylphosphine, trimethylarsine, dimethyl and diethyl ethers, and dimethyl sulfide has been reported.[1] In that investigation a measured quantity of an appropriate base was combined (in a bulb of known volume) with a quantitative sample of solid dimethylberyllium. The composition of the adduct was inferred from determination of the quantity of recoverable base at a given temperature. The bases trimethylamine,[2] trimethylphosphine, and dimethyl and diethyl ethers formed 1:1 (I) and 2:1 (II) adducts with dimethylberyllium, the 1:1 adducts being either monomeric or dimeric. At elevated temperatures the relatively weaker bases formed polymeric species (III) reminiscent of the structure of solid polymeric dimethylberyllium[3] with base molecules acting as chain ending groups. *There was no evidence for a reaction between dimethylberyllium and the bases dimethyl sulfide and trimethylarsine.*



I



II



III

$X = P(CH_3)_3, O(CH_3)_2, \text{ or } O(C_2H_5)_2$

The synthesis of beryllium alkyls by means of the Grignard reaction utilizing dimethyl sulfide as solvent[4] suggests that beryllium alkyls are soluble in this solvent. The Grignard method utilizing dimethyl sulfide as solvent in the synthesis of dimethylberyllium was performed successfully in this laboratory;[5] however, infrared analysis of the solid volatile product of this reaction indicated a complex with dimethyl sulfide. The infrared spectrum of this solid material matched the reported infrared spectrum of dimethylberyllium[6] only after about six sublimations indicating that dimethyl sulfide coordinates rather strongly to dimethylberyllium.

These preliminary observations suggest that dimethyl sulfide is able to rupture the electron-deficient bonds in solid polymeric dimethylberyllium resulting in the formation of adduct species. The nature of the adduct species present in dimethyl sulfide solution is an interesting question. Possible species include the 1:1 (I), 2:1 (II), and polymeric adduct (III) molecules. Proton magnetic resonance spectroscopy was invoked as the spectroscopic tool for analysis of these solutions, as each species is predicted to give rise to a different nmr resonance. Proton resonances of the methyl groups bonded to beryllium in II are expected at higher magnetic field than methyl groups bonded to beryllium in I. The species $(CH_3)_3B$ and $(CH_3)_3B:S(CH_3)_2$ exhibit proton resonance at 4.57 and 4.62 ppm relative to CH_2Cl_2 internal standard, respectively,[7] and bridging methyl groups involved in "electron-deficient" bonds are expected to resonate at lower field than methyl groups in terminal positions (bridging methyl groups in hexamethyldialuminum resonate at τ 9.93 while terminal methyl groups resonate at τ 10.50).[8]

It was decided to record the variable-temperature pmr spectra of these solutions, since fast chemical ex-

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(1) G. E. Coates and N. D. Huck, *J. Chem. Soc.*, 4501 (1952).

(2) N. A. Bell and G. E. Coates, *Can. J. Chem.*, **44**, 744 (1966).

(3) A. Snow and R. Rundle, *Acta Crystallogr.*, **4**, 348 (1951).

(4) G. Bahr and K. H. Thiele, *Ber.*, **90**, 1578 (1957).

(5) R. A. Kovar and G. L. Morgan, *Inorg. Chem.*, **8**, 1099 (1969).

(6) J. Goubeau and K. Walter, *Z. Anorg. Allg. Chem.*, **58**, 322 (1963).

(7) T. D. Coyle and F. G. A. Stone, *J. Amer. Chem. Soc.*, **83**, 4138 (1961).

(8) K. C. Williams and T. L. Brown, *ibid.*, **88**, 5460 (1966).