Methyl and Ethyl Hexafluoroantimonate and Related Compounds

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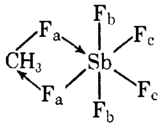
Abstract: Low-temperature proton and fluorine nuclear magnetic resonance spectra have been obtained for the ethyl fluoride–SbF_5–SO_2, methyl fluoride–SbF_5–SO_2, and ethyl fluoride–SbF_5–SO_2ClF systems. These spectra can best be interpreted in terms of rapidly exchanging 1:1 and 1:2 fluorine-bridged complexes between the alkyl fluoride and SbF_5 in SO_2 and 1:1, 1:2, and 1:3 complexes in SO_2ClF solution. The complexes have the structures $RSbF_6$, RSb_2F_{11}, and RSb_3F_{21} with a fluorine bridge between the alkyl group and antimony, and even at −120° there is rapid inter- or intramolecular exchange of the alkyl group. These molecules appear to be a new type of "fluxional" molecule.

It has recently been reported that methyl fluoride forms a strong methylating agent when dissolved at low temperature in a sulfur dioxide solution of SbF_5.[1] It would appear that the methyl cation is not formed under these conditions, since only small deshieldings of the proton and ^{13}C nuclear magnetic resonances were observed. From this and some Raman data, Olah, *et al.*,[1] concluded that methyl fluoride forms a donor–acceptor complex with SbF_5. Excess methyl fluoride in solution was present as the free molecule. The proton resonance assigned to the complex showed no splitting due to proton–fluorine coupling, in marked contrast with methyl fluoride itself, where $J_{HF} = 46$ Hz. The authors suggested a rapid exchange of the methyl group to account for this and they proposed that the donor–acceptor complex has the structure **1**. No fluorine spectra were reported for the system



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Such spectra should give considerable information on the nature of the complex and on any exchange mechanism. Moreover, it is of considerable importance to determine if the fluorine spectrum of a rapidly exchanging donor–acceptor complex can be distinguished from that of the anion formed when ionization occurs. The anions $Sb_2F_{11}^-$ and *cis*-$Sb_3F_{16}^-$ have been shown to occur when alkyl fluorides, such as *tert*-butyl fluoride, ionize to carbonium ions in SO_2 or SO_2ClF.[2,3] In the present work we report proton and fluorine spectra for solutions of methyl fluoride and ethyl fluoride in SbF_5–SO_2 and SbF_5–SO_2ClF and show that these spectra can best be interpreted in terms of rapidly exchanging 1:1 and 1:2 complexes between the alkyl fluoride and SbF_5 in SO_2 and 1:1, 1:2, and 1:3 complexes in SO_2ClF solutions, although these complexes do not have structure **1** or analogous structures.

Solutions in SO_2. The −80° proton spectrum of a solution in SO_2 (~1.4 *M* in SbF_5) having the composition EtF/SbF_5 = 1/5 was found to be an ethyl group spectrum consisting of a methylene quartet at 6.53 and a methyl triplet at 2.29 ppm below external TMS.[4] The fluorine couplings ($^3J_{HF} = 25.8$, $^2J_{HF} = 47.3$ Hz) to the methyl and methylene protons seen in the proton and fluorine spectra of neat ethyl fluoride do not appear in this spectrum. The proton–proton coupling constant is 7.0 Hz, the same as in ethyl fluoride. The proton spectrum of ethyl fluoride gives chemical-shift values of 4.17 and 1.03 ppm for the methylene and methyl resonances, respectively. Thus, in the EtF–SbF_5 system there is a 2.36-ppm deshielding of the methylene resonance and a 1.26-ppm deshielding of the methyl resonance as well as elimination of proton–fluorine coupling.

The fluorine spectrum of the EtF–5.0SbF_5–SO_2 sample at −85° is shown in Figure 1. It consists of four resonances, and would appear at first sight to be that of a mixture of $Sb_2F_{11}^-$ and SbF_5–SO_2, by comparison with the spectra of ref 2, for example. The chemical shifts, $a = 92.3$, $b = 111.5$, $c = 134.4$, and $d = 102.4$, are only ~1.5 ppm to high field of those found for *tert*-butyl halides in SbF_5–SO_2.[2] The areas are in the ratio $a/b/c/d$ = 1.3/8/4.6/10.9 which agrees quite well with the areas expected for $Sb_2F_{11}^-/SbF_5 \cdot SO_2$ = 1/2.7 which would be 1/8/4.7/10.8. If $Sb_2F_{11}^-$ were produced by ionization of the ethyl fluoride to the ethyl ion then, since EtF/SbF_5 = 1/5, we would

$$CH_3CH_2F + 2SbF_5 \xrightarrow{SO_2} CH_3CH_2^+ + Sb_2F_{11}^-$$

expect $Sb_2F_{11}^-/SbF_5 \cdot SO_2$ = 1/3, since $Sb_2F_{11}^-$ is the largest polyanion which can exist in SO_2 and any SbF_5 in excess of the amount necessary to produce $Sb_2F_{11}^-$ will combine with the solvent, giving $SbF_5 \cdot SO_2$.[2] Thus, it might appear that ionization to the ethyl ion does occur except for the fact that we should expect a methylene resonance at ≈14 ppm and a methyl resonance at ≈4 ppm, by comparison with the isopropyl ion.[5] The observed shifts, given above, are 6.53 and 2.29 ppm. Some other explanation for the fluorine spectrum must therefore be found. Another possible ionization reaction is that to the ethylfluoronium ion.

$$2CH_3CH_2F + 2SbF_5 \longrightarrow (CH_3CH_2)_2F^+ + Sb_2F_{11}^-$$

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(1) G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **91**, 2112 (1969).

(2) J. Bacon, P. A. W. Dean, and R. J. Gillespie, *Can. J. Chem.*, **47**, 1655 (1969).

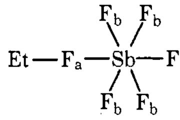
(3) J. Bacon, P. A. W. Dean, and R. J. Gillespie, *ibid.*, **48**, 3413 (1970).

(4) All proton chemical shifts in this paper are given in parts per million to low field of TMS.

(5) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Amer. Chem. Soc.*, **86**, 1360 (1964).

The analogous ions $(CH_3CH_2)_2Cl^+$, $(CH_3CH_2)_2Br^+$, and $(CH_3CH_2)_2I^+$ have been reported by Olah and DeMember.[6] In this reaction, 1 mol of SbF_5/mol of ethyl fluoride is ionized to 0.5 mol of $Sb_2F_{11}^-$, leading to $Sb_2F_{11}^-/SbF_5 \cdot SO_2 = 1/8.0$ when $EtF/SbF_5 = 1/5$ initially. This is not in accord with the spectral areas, which would indicate $Sb_2F_{11}^-/SbF_5 \cdot SO_2 = 1/2.7$, as discussed above. The discrepancy could be accounted for only if large amounts of $SbF_5 \cdot SO_2$ were precipitated at −85°. When the nmr sample was kept at −85° for 1 hr, only a very small amount of precipitate was observed. It appears, therefore, that ionization to the ethylfluoronium ion can also be ruled out.

The only plausible explanation for the experimental spectrum would appear to be that a donor–acceptor complex is formed, as already suggested by Olah, *et al.*, for methyl fluoride in $SbF_5 \cdot SO_2$.[1] Two possible structures for a 1:1 donor–acceptor complex are **1** and **2**. Structure **1** would give rise to three resonances of equal intensity. If we recall that in other species containing an SbF_6 unit, $J_{cis} \approx$ 50–100 Hz when one of the fluorines involved is in a bridging position and 100–150 Hz otherwise, we see that the resonances of F_a and F_c should each be split into triplets, while that of F_b should be a triplet of triplets. Clearly this structure can be ruled out immediately, by comparison with the experimental spectrum. Structure **2** would give rise to three resonances of relative areas 1/4/1, split into two quintets (F_a, F_c) and a doublet of doublets (F_b). This is superficially similar to the spectrum of the $Sb_2F_{11}^-$ ion, assuming similar chemical shifts, except that the bridging fluorine resonance would be a quintet and would have twice the relative area that the bridging fluorine resonance has in the $Sb_2F_{11}^-$ ion. Moreover, the relative areas observed, already given above, would correspond to $EtFSbF_5/SbF_5 \cdot SO_2 = 1/1.35$, for which $a/b/c/d$ = 2/8/4.7/10.8. However, the stoichiometry of the solution would imply $EtFSbF_5/SbF_5 \cdot SO_2 = 1/4$. Structure **2** is also unsatisfactory in that it does not explain the disappearance of proton–fluorine coupling.



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Let us now consider the 1:2 complex, **3**. If we assume that the ethyl group undergoes rapid exchange between fluorines, we account for both the lack of proton–fluorine coupling and the fact that only three fluorine resonances are observed. Presumably the C–F bond in the C–F–Sb linkage is considerably weaker than the F–Sb bond. As far as the effects on the proton and fluorine spectra are concerned, the exchange can be intramolecular or intermolecular, and may involve only the F_2 fluorines or the F_3 fluorines or both. Since fluorine bridges are generally cis to one another, the exchange of the ethyl group between F_2 fluorines alone would seem to be the most likely situation. If a 1:2 complex is formed, we expect $EtSb_2F_{11}/SbF_5 \cdot SO_2 = 1/3$. The observed areas give 1/2.7 for this ratio. The small discrepancy can be explained by the small amount of white solid in the sample at low temperatures. Of all the possibilities considered, the exchanging 1:2 complex appears to be the only satisfactory one. An exchanging 1:1 complex would, of course, give a single fluorine resonance.

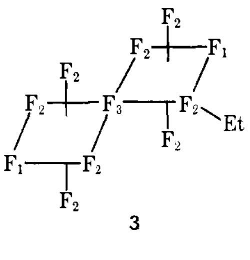

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Figure 1. Fluorine (56.4 MHz) spectrum of ethyl fluoride–5.0SbF_5–SO_2 at −85° (top). Fluorine spectrum of ethyl fluoride–1.3·SbF_5–SO_2 at −90° (bottom).

The −80° proton spectrum showed the presence of very small amounts of *tert*-butyl, *tert*-amyl, and *tert*-hexyl ions corresponding to not more than 4% reaction of the ethyl fluoride. There were also two small singlet resonances. One, at 5.76 ppm below external TMS, is probably that of the methyl fluoride–SbF_5 donor–acceptor complex as the neat ethyl fluoride sample appeared to contain a small amount (1%) of methyl fluoride as an impurity. The other singlet in the −80° proton spectrum of $EtSb_2F_{11}$ occurred at 1.23 ppm and is not identified, although it is probably an alkane. In any case, at −80° over 95% of the area of the proton spectrum corresponds to $EtSb_2F_{11}$. When the sample was warmed to −60°, a very slow reaction giving *tert*-butyl ion occurred, presumably as follows: $CH_3CH_2Sb_2F_{11} \rightarrow CH_3CH_2^+ + Sb_2F_{11}^-$; $2CH_3CH_2^+ \rightarrow (CH_3)_3C^+ + H^+$. After 75 min at −35°, this reaction was 60% complete. The signal from the acid proton, presumably present as H_2F^+, $HSbF_6$, or HSb_2F_{11}, was seen at 10.6 ppm below external TMS. Clearly the ethyl ion is not stable even at −60°.

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(6) G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **91**, 2113 (1969).

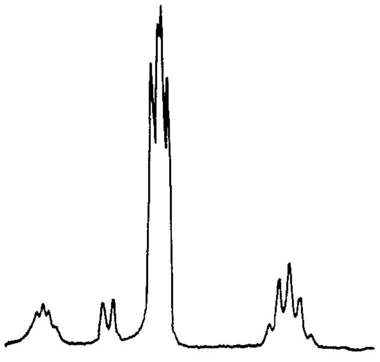

Figure 2. Fluorine (56.4 MHz) spectrum of methyl fluoride–2.0·SbF_5–SO_2 at −90°.

After a total of 150 min at −35° the proton spectrum indicated essentially complete reaction to give the *tert*-butyl ion, but the fluorine spectrum was essentially unchanged. The chemical shifts after ionization were a = 90.8, b = 111.1, c = 133.0, and d = 101.6. Although this represents a slight shift, ≈ 1 ppm, to low field from the resonance positions found before ionization, this change in chemical shift is much less than the concentration and cation effects for $Sb_2F_{11}^-$ we have previously found.[3] Thus we are forced to the, at first sight, somewhat surprising conclusion that the fluorine spectrum of $Sb_2F_{11}^-$ is essentially the same when it is present as a free ion together with the *tert*-butyl ion or in a complex with the ethyl ion.

The low-temperature proton spectra of solutions in SO_2 (1.5 M in SbF_5) having EtF/SbF_5 = 1/1.3 and 1/0.78 were found to consist of the ethyl group resonance shifted to low field and exhibiting no coupling to fluorine as already discussed above. The fluorine spectrum of the EtF–1.3SbF_5–SO_2 sample at −90° is shown at the bottom of Figure 1. It is similar to the spectrum for EtF–5.0SbF_5–SO_2 already discussed above, except that the resolution is better and little or no $SbF_5 \cdot SO_2$ is present. The spectrum would appear to be that of the 1:2 complex, $EtSb_2F_{11}$, this time uncomplicated by the presence of $SbF_5 \cdot SO_2$. The composition of the solution would suggest that considerable amounts of either the 1:1 complex, $EtSbF_6$, or free ethyl fluoride should be present. Free ethyl fluoride is not seen in the proton spectrum of this sample and only one deshielded ethyl resonance appears in the proton spectrum, so if both $EtSbF_6$ and $EtSb_2F_{11}$ are present, either there must be intermolecular exchange and/or the proton chemical shifts are the same in the 1:1 and 1:2 complexes. We may note that the fluorine resonance of $EtSbF_6$ might well be a broad partially collapsed multiplet due to relatively slow quadrupole relaxation of antimony. Such a broad line might be difficult to observe at all but the highest concentrations of $EtSbF_6$. When the spectrum of the EtF–0.78SbF_5–SO_2 sample was obtained at −90°, it was in fact found to consist of just such a broad resonance, 2000 Hz wide, in the fluorine on antimony region of the spectrum, which has superimposed on it the spectrum found for the EtF–1.3·SbF_5–SO_2 sample, already discussed. The width of the broad resonance decreases as the temperature is lowered (which is to be expected if this resonance is a partially collapsed multiplet), the rate of quadrupole relaxation, and hence the degree of collapse toward a sharp line, increasing as the temperature is lowered.[7] The broad resonance makes up about 90% of the total area. In this case the solution appears to contain mainly $EtSbF_6$ with some $EtSb_2F_{11}$ although the stoichiometry implies $EtSbF_6$ with some free ethyl fluoride. As no free ethyl fluoride is seen in the proton spectrum, it appears that some ethyl fluoride must be consumed by a reaction other than donor–acceptor complex formation. Formation of a small amount of yellow solid which was partially soluble in SO_2 was in fact observed, particularly in the samples which were more concentrated in ethyl fluoride. The majority of the ethyl fluoride, however, appeared to be present as the donor–acceptor complexes $EtSbF_6$ and $EtSb_2F_{11}$.

It should be noted that the observation of a partially collapsed multiplet due to residual fluorine–antimony coupling for fluorine containing species of antimony has previously been noted only for SbF_6^-, all other species giving essentially complete collapse of the multiplet due to Sb–F coupling to a relatively narrow line. Very rapid exchange of the weakly bonded ethyl group in the postulated $EtSbF_6$ complex would appear to give rise to an averaging effect which can be regarded as providing an effectively octahedral symmetry about the antimony.

The proton spectrum of a methyl fluoride–SbF_5 solution in SO_2 approximately 1.5 M in SbF_5 and having the mole ratio MeF/SbF_5 = 1/2.0 had only a single peak at 5.33 ppm below external TMS. A second sample, having the same concentration of SbF_5 but a mole ratio of 1/0.91, had the same single peak at 5.29 ppm and also the methyl fluoride doublet which had an area of approximately 15% of that of the single peak indicating that the ratio of free methyl fluoride to complexed methyl fluoride was 0.15. The fluorine spectrum for the MeF–2.0SbF_5–SO_2 sample obtained at −90° (Figure 2) consists of the resonance of a small amount of SbF_5–SO_2 and the same $Sb_2F_{11}^-$-like spectrum found for the EtF–1.3SbF_5–SO_2 sample and identified as that of a 1:2 donor–acceptor complex. Since the proton resonance of the CH_3 group is only slightly deshielded, we can assign the Sb_2F_{11}-like spectrum to $MeSb_2F_{11}$. The spectrum is quite well resolved. The fluorine spectrum of the MeF–0.91·SbF_5–SO_2 sample at −90° shows a broad single resonance having the spectrum of a 1:2 complex superimposed upon it. The broad peak is presumably the resonance of a 1:1 complex, as in the case of the EtF–0.78SbF_5–SO_2 sample. From the areas in the spectrum, we obtain $MeSb_2F_{11}/MeSbF_6$ = 0.08. We note that some $MeSb_2F_{11}$ is formed even though methyl fluoride is present in slight excess. It would appear that, in the presence of 1 mol of methyl fluoride, 0.91 mol of SbF_5 forms about 0.79 mol of $MeSbF_6$ and 0.06 mol of $MeSb_2F_{11}$, leaving 0.15 mol of free methyl fluoride. These amounts give $MeSb_2F_{11}/MeSbF_6$ = 0.08, already found from the fluorine spectrum, and free methyl fluoride/complexed methyl fluoride = 0.18, compared with the value of 0.15 already deduced

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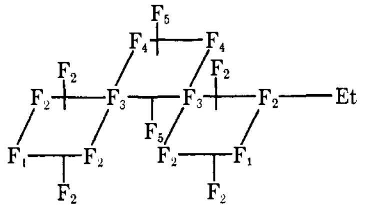
(7) J. Bacon, R. J. Gillespie, and J. W. Quall, *Can. J. Chem.*, **41**, 3063 (1963).

for this ratio from the proton spectrum. Virtually all of the methyl fluoride in solution is therefore accounted for, and the stoichiometry would appear to confirm the spectral assignments. Solutions of methyl fluoride are colorless, as reported by Olah, *et al.*,[1] in contrast to the ethyl fluoride solutions. As only one singlet peak appears in the proton spectrum, even when both 1:1 and 1:2 complexes are present, at least some of the exchange of the methyl groups is taking place by an intermolecular mechanism or the proton chemical shifts for the 1:1 and 1:2 complexes are the same.

Solutions in SO_2FCl. A solution in SO_2FCl (7.4 *M* in SbF_5) having the mole ratio $EtF/SbF_5 = 1/2.0$ gave the fluorine spectrum shown in Figure 3 at −85°. The spectrum appears to arise from at least four distinct species. At 121.1 ppm there is a single line which appears to be the resonance of $EtSbF_6$. The strong, complex resonance in the middle of the spectrum could be made up of two overlapping double doublets, one centered on 114.9 ppm and the other on 113.2 ppm. The less intense of these, centered on 114.9 ppm, can be assigned to the eight equivalent fluorines in $EtSb_2F_{11}$, the remaining fluorines in this species giving rise to the quintet at 137.4 and part of the broad resonance in the bridging region at 90.4. The doublet centered on 106.0 ppm would appear to be the resonance of the four equivalent fluorines of $SbF_5 \cdot SO_2ClF$, the weak quintet resonance of this species lying under the large quintet at 141.9 ppm. Dean and Gillespie[8] report chemical values of 105.1 and 141.8 for this species in SO_2ClF solution. The remaining resonances in the spectrum, that is, part of the broad resonance at 90.4 ppm, a small multiplet at 108.9, a double doublet centered at 113.2, the triplet at 128.6 having doublet splittings on two of its lines, and the strong quintet at 141.9 are similar to those previously found for the *cis*-$Sb_3F_{16}^-$ anion.[3] We therefore assign them to the species $EtSb_3F_{16}$ (**4**), assuming as before that the ethyl group is undergoing rapid exchange.



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In samples containing a greater proportion of SbF_5, the doublet assigned to SbF_5SO_2ClF increased in size, while the resonances of $EtSbF_6$ and $EtSb_2F_{11}$ decreased in size. No resonances attributable to $EtSb_4F_{21}$ were found in the samples, in contrast to the behavior of the SbF_6^-–SbF_5–SO_2ClF system where small but significant amounts of the *cis,cis*-$Sb_4F_{21}^-$ anion were found at high concentrations of SbF_5.[3] It would appear therefore that the donor–acceptor complexes are more readily solvolyzed than the corresponding anions.

The resonance at 121.1 ppm, assigned to $EtSbF_6$, is relatively narrow, whereas the resonance assigned to $EtSbF_6$ in the SO_2 solutions is 2000 Hz wide (see above). Similar behavior has been observed for the SbF_6^- anion. In SO_2ClF solution the SbF_6^- resonance is relatively narrow, having a width of approximately 90 Hz,[3] while in SO_2 solution it is several thousand hertz wide,[9] making small amounts of the anion difficult to observe by the nmr method.[10] Apparently this difference in line width results from a much faster rate of quadrupole relaxation of the antimony spins in SO_2ClF solution, brought about by an electric field gradient induced by the dipole moment of the solvent, or by a slower rate of molecular reorientation due to the higher viscosity of the SO_2ClF solution. A change in the rate of nuclear quadrupole relaxation with change in solvent has been observed previously for the AsF_6^- anion.[11]

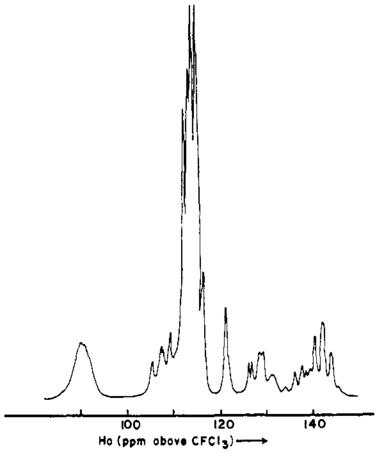

Figure 3. Fluorine (56.4 MHz) spectrum of ethyl fluoride–2.0·SbF_5–SO_2ClF at −85°.

The freezing point of SO_2ClF is much lower than that of SO_2, permitting nmr studies at very low temperatures. At no temperature, down to −120°, was it possible to stop the exchange of the ethyl group in $EtSbF_6$, $EtSb_2F_{11}$, or $EtSb_3F_{16}$. This would suggest a very fast exchange on the nmr time scale.

Discussion

The results reported above indicate that methyl and ethyl fluoride form donor–acceptor complexes with SbF_5 in solution in SO_2 or SO_2ClF which may be written for convenience as $RSbF_6$, RSb_2F_{11}, and RSb_3F_{16}. The observed rapid exchange of the ethyl and methyl group implies that the C–F bond is much weaker than the F–Sb bonds. This exchange occurs down to the lowest temperature that could be obtained in the spectrometer probe, −120°. The rate of exchange may be very rapid indeed, as the effective symmetry about the antimony nucleus in both $MeSbF_6$ and $EtSbF_6$ appears to approach that in the SbF_6^- ion itself, since the very broad lines in the fluorine resonances of these two complexes in SO_2 solution can reasonably be attributed to a partially collapsed multiplet arising from fluorine–antimony coupling which is not completely averaged out. Since the chemical shift of the nonequivalent fluorines in a 1:1 complex in which exchange was not occurring would, by analogy with other base–SbF_5

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(8) P. A. W. Dean and R. J. Gillespie, *J. Amer. Chem. Soc.*, **91**, 7260 (1969).

(9) R. J. Gillespie and P. K. Ummat, unpublished work.

(10) We have noted this many times in the course of work done in this laboratory. Examples of other solvents in which the fluorine resonance of SbF_6^- is so broad as to make the detection of the ion difficult are ethanol, water, and hydrogen fluoride.

(11) M. St. J. Arnold and K. J. Packer, *Mol. Phys.*, 10, 141 (1966).

complexes,[8] be expected to be as large as 2500 Hz, the rate of the exchange which leads to the apparent equivalence of the fluorines must be of the order of 10^6 sec^{-1}. All the proton spectra recorded show no change in chemical shift (to 0.03 ppm) with changing alkyl fluoride concentration if the SbF_5 concentration is constant. Since the relative amounts of $EtSbF_6$ and $EtSb_2F_{11}$ (or $MeSbF_6$ and $MeSb_2F_{11}$) change with alkyl fluoride concentration, this implies $RSbF_6$ and RSb_2F_{11} have the same proton chemical shift. Separate proton resonances for $RSbF_6$ and RSb_2F_{11} will not be observed, therefore, regardless of the exchange mechanism. It is not satisfactory to regard the complexes as tight ion pairs because the protons of the alkyl groups do not show the large downfield shifts expected for carbonium ions. We should then perhaps consider the alkyl fluoride–SbF_5 complexes formed in SbF_5–SO_2 and SbF_5–SO_2ClF solutions as members of a new class of what Cotton[12] has called "fluxional molecules." The apparent absence of proton–fluorine coupling may then be attributed to its having been reduced to a very small value by the weakening of the C–F bond and by rapid intramolecular exchange of the alkyl group. In the case of $MeSbF_6$, for example, if it is assumed that the coupling of a proton to a fluorine which is more than two bonds distant is zero then the methyl resonance would be expected to be a septet, with a splitting equal to one-sixth of the coupling between the methyl protons and a fluorine in the bridging position. In free methyl fluoride itself the two-bond H–F coupling constant is 46 Hz, but in the complex this coupling might be expected to be considerably smaller, since the rapid alkyl group exchange indicates the C–F bond is considerably weakened. By summing Lorentzian line shapes of the appropriate intensities we find that the individual lines in a septet overlap in a single broad resonance when the width of an individual line is 1.5 times the coupling constant. The width of the resulting resonance is approximately 3.8 times the coupling constant. The line width of 1.5–2.0 Hz observed in the proton spectrum therefore corresponds to an upper limit of 0.5 Hz for the average H–F coupling, or 3.0 Hz for the coupling of the methyl protons with a fluorine in the bridge position. Similar reasoning applies to the H–F coupling in the other compounds, $MeSb_2F_{11}$, $EtSbF_6$, $EtSb_2F_{11}$, and $EtSb_3F_{16}$. MacLean and Mackor[13–15] have noted an effect similar to this in the spectrum of protonated hexamethylbenzene where a rapid intramolecular exchange gives one methyl resonance and an average H–H coupling of 2.1 Hz, although the individual H–H couplings are 6.8, 3.5, 1, and 0 Hz.

Although most of the features of the experimental results can be explained by either inter- or intramolecular exchange the observation of a broad SbF_6^- resonance resulting from incompletely collapsed fluorine–antimony coupling in $EtSbF_6$ suggests that an intramolecular mechanism predominates. Several workers have found that the rapid intramolecular exchange of the fluorine atoms in VOF_4^- [16,17] and VF_5[18] appears to give a higher symmetry about the vanadium nucleus than would otherwise be expected, resulting in the observation of vanadium–fluorine coupling. The essentially octahedral symmetry about the antimony nucleus in $EtSbF_6$ would therefore seem to require an exchange process as rapid as the intramolecular exchange ("pseudorotation") in VOF_4^- and VF_5. If the exchange is predominately intermolecular, it must be unusually rapid. There may in fact be both a very rapid intramolecular exchange and a somewhat slower intermolecular exchange.

Although the methyl and ethyl group exchange is rapid, each half of the complex appears to retain a stereochemically rigid structure similar to that found in more conventional environments. The fluorine spectrum of RSb_2F_{11} is so similar to that of $Sb_2F_{11}^-$ that it would be extremely difficult to distinguish the two structures on the basis of fluorine spectra alone. Also, the proton–proton coupling constant in the ethyl group of the ethyl fluoride–SbF_5 complexes is 7.0 Hz, which is quite normal for an ethyl group, suggesting that no gross change has occurred in the structure of the ethyl group. We should note that in RSb_2F_{11} and RSb_3F_{16} the exchange must involve both ends of the Sb_2F_{11} or Sb_3F_{16} group, since both ends are chemically equivalent.

Olah, *et al.*,[1] postulated that a 1:1 complex is formed between methyl or ethyl fluoride and antimony pentafluoride. Our work shows conclusively that both 1:1 and 1:2 complexes are formed in both SO_2 and SO_2ClF and a 1:3 complex is also formed in SO_2ClF. The ^{19}F spectra provide important information on the structures of these complexes and clearly indicate that they may be formulated as $RSbF_6$, RSb_2F_{11}, and RSb_3F_{16}, respectively. Moreover, these spectra taken in conjunction with the proton spectra show that the complexes are not ionic but have the alkyl group bonded to the remainder of the molecule by an essentially covalent fluorine bridge. The similarity of the ^{19}F spectra to those of the anions SbF_6^-, $Sb_2F_{11}^-$, and $Sb_3F_{16}^-$ can be best explained by postulating rapid exchange of the alkyl group among all the available fluorines. Although an intramolecular exchange was previously postulated by Olah, *et al.*,[1] our fluorine spectra require that the exchange process be several orders of magnitude more rapid than could be inferred from the proton spectra since ^{19}F chemical-shift differences of up to 2500 Hz must be averaged to a mean value, whereas in the proton spectrum it is an H–F coupling constant of only 46 Hz that is reduced to zero.

Experimental Section

Fluorine spectra were recorded at 56.4 MHz on a Varian DA-60 spectrometer. Proton spectra were obtained at 60.0 MHz using a Varian A-60 spectrometer. Both spectrometers were equipped with Varian variable-temperature analytical probes and temperature controllers. Fluorine spectra were calibrated by generating side bands with an audiooscillator and referenced relative to $CFCl_3$ by sample interchange. Proton spectra were referenced relative to tetramethylsilane (TMS) by sample interchange. Fluorine chemical shifts and coupling constants were reproducible to better than 1 ppm and about 1 Hz, respectively, while proton chemical shifts and coupling constants were reproducible to 0.05 ppm and 0.1 Hz, respectively.

Antimony pentafluoride was obtained from Ozark Mahoning

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Co. and distilled twice in glass apparatus in an atmosphere of dry air before use. Ethyl fluoride (Air Products and Chemicals, Inc.) and methyl fluoride (Peninsular Chemresearch, Ltd.) were purified by vacuum fractionation. Sulfuryl chlorofluoride, SO_2ClF, was prepared by the method of Seel and Riehl[18] and purified as previously described.[3] Sulfur dioxide was obtained from Matheson of Canada, Ltd. Both solvents were stored as a gas over anhydrous phosphorus pentoxide before use.

Nmr samples were prepared on a vacuum line using a small flask with a detachable tap and nmr tubes sealed to the flask. A small weighed quantity of SbF_5 (about 0.01 mol) was distilled into the flask. Enough solvent (SO_2 or SO_2ClF) to dissolve the SbF_5 was then distilled into the flask. The resulting solution was approximately 1.5 *M* in SbF_5 in the case of SbF_5–SO_2 and 7.5 *M* in the case of SbF_5–SO_2ClF. The solution was held at Dry Ice temperature and stirred while a known volume of alkyl fluoride was allowed to evaporate into the reaction flask, giving a solution of known alkyl fluoride–SbF_5 ratio. The flask was then removed from the vacuum line and tilted so that a suitable amount of solution entered the nmr tube and the tube sealed off, all at low temperature.

Reactions of Phosphinates in Sulfuric Acid and Oleum[1,2]

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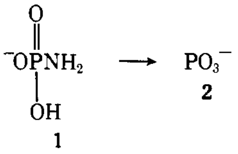
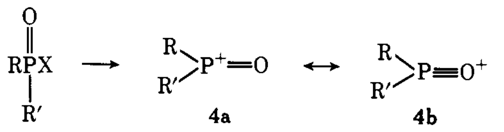
Abstract: In order to understand the fundamental tendency of pentavalent, tetracoordinate phosphorus to react by dissociative mechanisms and the nature of transformations in strong acids, phosphinic acids, R_2PO_2H, and derivatives, $R_2P(O)X$, have been studied by nmr and cryoscopy in sulfuric acid and oleum. Phosphinylium ions, R_2PO^+, do not appear to be formed. Instead, sulfonation occurs after protonation: $R_2PO_2H + 50\%\ H_2SO_4 \rightarrow R_2P^+(OH)_2$; $R_2P^+(OH)_2 + 10\%\text{ oleum} \rightarrow R_2P^+(OH)OSO_3H$; $R_2P^+(OH)OSO_3H + 55\%\text{ oleum} \rightarrow R_2P^+(OSO_3H)_2$. This is a distinct contrast to carboxylic acids which have been shown to protonate and then form acylium ions in about 10% oleum. An amide, $(C_6H_5)_2P(O)N(CH_3)_2$, forms three–four species on solution in 100% H_2SO_4 but all other phosphinates act as simple bases giving two species—protonated substrate and bisulfate ion.

There have been a number of proposals for the occurrence of dissociative mechanisms of displacement at phosphorus.[4-6] These have mainly concerned the reactions of phosphate derivatives, such as phosphoramidate (**1**), where the substituents might participate in the stabilization of the intermediate with reduced coordination number (*e.g.*, **2**). It is therefore important to establish the fundamental facts on the tendency of phosphorus to react by dissociative mechanisms. In this paper we examine the reactions of phosphinic acid derivatives (**3**) in the spectrum of acidities provided by the water–sulfuric acid–oleum system. Spectroscopy of solutions in this system and cryoscopy in 100% sulfuric acid have provided some of the clearest evidence for the existence of carbonium ions.[7] The first studies of acylium ions involved the abnormal freezing point depression of mesitoic acid in sulfuric acid.[8] In this paper, we examine spectral and cryoscopic data on solutions of **3** for evidence of formation of phosphinylium ions, **4** (orbital considerations may make **4b** a minor contributor unlike acylium ions). We have previously observed phosphinylium ions as important fragments in the mass spectra of phosphinates.[9,10] This and the subsequent paper evaluate their stability and occurrence in solution chemistry.



$$^{-}O\overset{O}{\underset{OH}{P}}NH_2 \longrightarrow PO_3^{-} \quad (1)$$



$$R\overset{O}{\underset{R'}{P}}X \longrightarrow \begin{matrix}R\\R'\end{matrix}\!\!>P^{+}{=}O \longleftrightarrow \begin{matrix}R\\R'\end{matrix}\!\!>P{\equiv}O^{+} \quad (2)$$

Results

Cryoscopy. Cryoscopic measurements on solutions of phosphinates were carried out using the apparatus devised by Gillespie, *et al.*[11] The average number, ν, of dissolved species produced from a given substrate was calculated by eq 3, where θ is the freezing point depression from 10.625°, m^s is the molality of added

$$\nu = \frac{\theta(1 - 0.098m^{s}s)}{6.12m^{s}} - \frac{m^{d}}{m^{s}} \quad (3)$$

substrate, s is the number of H_2SO_4 molecules reacting

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