The Methyl Fluoride–Antimony Pentafluoride and Arsenic Pentafluoride Systems: the Formation of $CH_3F{\cdot}SbF_5$ and $CH_3F{\cdot}AsF_5$ and the Methylation of SOF_2 and SO_2FCl

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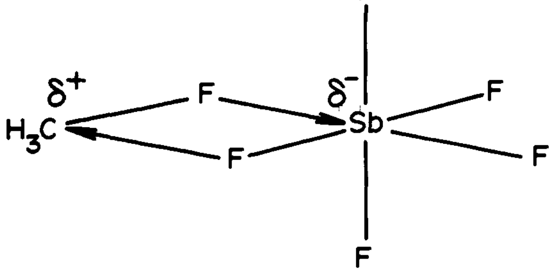
Abstract: The proton and fluorine NMR spectra of the following systems have been studied at low temperature: $CH_3F/SbF_5/SOF_2$, $CH_3F/AsF_5/SOF_2$, $CH_3F/SbF_5/SO_2FCl$, $CH_3F/AsF_5/SO_2FCl$, $CH_3F/SbF_5/SO_2F_2$, $CH_3F/AsF_5/SO_2F_2$. It was found that SOF_2 is methylated by SbF_5, giving the cation $CH_3OSF_2^+$, the accompanying anion being $Sb_2F_{11}^-$. Arsenic pentafluoride also methylates SOF_2 but the reaction is incomplete as the complex $CH_3F{\cdot}AsF_5$ is also present in the solution. In SO_2FCl both $CH_3F{\cdot}SbF_5$ and $CH_3OSOFCl^+$ are formed by a mixture of SbF_5 and CH_3F. In the similar reaction with AsF_5 in SO_2ClF only the labile adduct $CH_3F{\cdot}AsF_5$ is formed and the solvent is not methylated. When SO_2F_2 is used as solvent it is not methylated by the mixture of CH_3F with either AsF_5 or SbF_5 and only the complexes $CH_3F{\cdot}SbF_5$ and $CH_3F{\cdot}AsF_5$ are formed. The former is a stable species that does not undergo either inter- or intramolecular exchange at temperatures below −60 °C, whereas the $CH_3F{\cdot}AsF_5$ complex undergoes intermolecular exchange which is rapid on the NMR time scale even at −160 °C. It is concluded that $CH_3F{\cdot}AsF_5$ is a somewhat more labile species and a weaker methylating agent than $CH_3F{\cdot}SbF_5$. Comparison of the different solvents leads to the conclusion that SOF_2 and SO_2FCl are too basic to allow the existence of the carbenium ion CH_3^+ as a stable entity while in SO_2F_2 it is the basicity of SbF_6^- and AsF_6^- which prevents the existence of the free methyl ion.

The nature of Friedel–Crafts alkylation systems has long been of interest, and these systems have received considerable investigation. In recent years Olah and his collaborators have carried out extensive studies of new alkylating reagents prepared by the reactions of alkyl halides with antimony pentafluoride.[2,3] In particular, mixtures of methyl fluoride and antimony pentafluoride in sulfur dioxide or sulfuryl chlorofluoride have been recognized as the strongest known methylating systems.[4,5] Accordingly it is somewhat surprising that the nature of the species in these solutions has not, until now, been clearly established.

Since a Friedel–Crafts alkylation can arise from a displacement reaction of the alkyl halide–Lewis acid complex $RX{\cdot}MX_n$ or from a direct alkylation by the free carbenium ion R^+,[6] the nature of the alkylating agent in CH_3F/SbF_5 solutions has been explained on the basis of both of these two limiting hypotheses. Although the carbenium ion Me_3C^+ is formed in solutions of Me_3CF in SbF_5, the existence of the Me^+ ion is much less likely. Nevertheless, the −80 °C proton NMR spectrum of a $CH_3F/SbF_5/SO_2$ solution shows only one deshielded singlet due to reacted methyl fluoride. This disappearance of proton–fluorine coupling has been explained by postulating the formation of some type of CH_3F–SbF_5 complex undergoing intramolecular exchange. On the basis of proton NMR and Raman data Olah et al.[4] proposed the structure I



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undergoing rapid intramolecular fluorine exchange. This suggestion was later slightly modified by the same authors[5] who concluded that in SO_2 or SO_2FCl solutions, a small amount of a $CH_3^+SbF_6^-$ ion-pair was present in rapid equilibrium with the $CH_3F{\cdot}SbF_5$ complex. Bacon and Gillespie[7] examined the proton and fluorine spectra of these systems and proposed the existence of the fluxional molecules CH_3SbF_6 and $CH_3Sb_2F_{11}$ in SO_2 and CH_3SbF_6, $CH_3Sb_2F_{11}$, and $CH_3Sb_3F_{16}$ in SO_2FCl in order to account for the lack of proton–fluorine coupling. As neither of the above explanations for the absence of the proton–fluorine coupling seemed entirely satisfactory and as the actual structure of the proposed $CH_3F{\cdot}SbF_5$ (or CH_3SbF_6) complex remained uncertain, the study of these systems has been continued in our laboratory.

From a $CH_3F/SbF_5/SO_2$ mixture white crystals have been obtained which have been shown, by x-ray diffraction, to be $CH_3OSO^+Sb_2F_{11}^-$.[8] Some evidence for this species in SO_2 solution has been very recently reported by Peterson et al.[9] who have shown that the reaction of $CH_3F/SbF_5/SO_2$ with alcohols produces sulfite esters and not ethers as had been previously proposed.[5] In view of these results, a thorough reinvestigation of the reactions of methyl fluoride with antimony and arsenic pentafluorides, in different solvents, was undertaken and some of our results were reported in a preliminary communication.[10] Dean and Gillespie[11] and Brownstein and Gillespie[12] have investigated the formation of adducts between SbF_5 and AsF_5 and a number of weak bases and have established the following order of basicity: $SO_2 > SOF_2 > SO_2FCl > SO_2F_2$, the latter being apparently too weak a base to form any complex with either SbF_5 or AsF_5. Since the structure of CH_3OSO^+ resembles closely that of F_5SbOSO, it seems reasonable to consider the CH_3OSO^+ ion as a donor–acceptor complex between SO_2 and the methyl ion CH_3^+. Thus, with a view to obtaining evidence for the free methyl ion CH_3^+ and/or further information on the nature of the $CH_3F{\cdot}SbF_5$ and $CH_3F{\cdot}AsF_5$ complex, the proton and fluorine NMR spectra of solutions of CH_3F/SbF_5 and CH_3F/AsF_5 in SOF_2, SO_2FCl, and SO_2F_2 have been studied.

Independently from our work, Olah et al. have also reinvestigated the CH_3F/SbF_5 system and have reported preliminary results.[13] From the similarity of the ^1H spectra of solutions in SO_2 and in SO_2FCl they suggested that both solvents are methylated. From ^1H and ^{13}C NMR data of solutions in SO_2F_2 they concluded that in this case the solvent is not methylated but that a complex of CH_3F and antimony pentafluoride is formed.

Table I

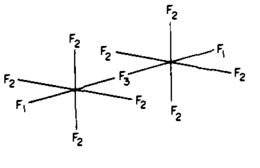
Species	Solvents	T (°C)	F-on-S	Chemical shifts ϕ (ppm)[a] F-on-Sb (As) F_1	F_2	F_3	Coupling constants J (Hz) $J_{F_1F_2}$	$J_{F_2F_3}$	$J_{F_1F_3}$
$CH_3OSF_2^+Sb_2F_{11}^-$	SOF_2	−147	−22	134	112	89	100	60	0
$CH_3OSOFCl^+Sb_2F_{11}^-$	SO_2FCl	−150	−92	136	113	90	100	60	0
$(CH_3)_3C^+Sb_2F_{11}^-$ [b]	SO_2FCl	−95	—	136	113	90	101	60	0
$CH_3OSF_2^+As_2F_{11}^-$	SOF_2	−168	−21	83	46	17	125	50	0
$Bu_4N^+As_2F_{11}^-$ [c]	SO_2FCl	−140	—	85	48	21	127	51	0
				F_a	F_e	F_b	$J_{F_aF_e}$	$J_{F_eF_b}$	$J_{F_aF_b}$
$CH_3F{\cdot}SbF_5$	SO_2FCl	−150	—	140	115	197	94	48	0
$CH_3F{\cdot}SbF_5$	SO_2F_2	−145	—	141	115	196	94	48	0
$CH_3F{\cdot}AsF_5$	SOF_2	−168	—	93	47	175	124	30	0
$CH_3F{\cdot}AsF_5$	SO_2FCl	−165	—	94	47	176	124	30	0
				F_A	F_X		$J_{F_AF_X}$		
$SbF_5{\cdot}SOF_2$ [d]	SOF_2	−100	−47	138	102		92		
$SbF_5{\cdot}SO_2FCl$ [d]	SO_2FCl	−115	−95	142	105		96		
$AsF_5{\cdot}SOF_2$	SOF_2	−168	−43	88	32		130		

[a] Measured from the solvent peak and converted to the ϕ scale (with respect to $CFCl_3$) by using $\delta(SOF_2) = \phi + 73.5$ ppm, $\delta(SO_2FCl) = \phi + 99$ ppm, and $\delta(SO_2F_2) = \phi + 31$ ppm. [b] Reference 15. [c] Reference 16. [d] Reference 11.

We now report definite ^{19}F and ^1H NMR evidence for the structures of the species present in mixtures of SbF_5 or AsF_5 with CH_3F in the solvents SOF_2, SO_2ClF, and SO_2F_2.

Results and Discussion

The ^{19}F NMR parameters for the systems $CH_3F/SbF_5/SOF_2$, $CH_3F/SbF_5/SO_2FCl$, $CH_3F/SbF_5/SO_2F_2$, $CH_3F/AsF_5/SO_2FCl$, and $CH_3F/AsF_5/SOF_2$ are summarized in Table I. The assignments are based on structures II, III, and IV and compared to some related complexes. Very low temperatures are necessary to reduce the quadrupole broadening of the spectra, due to the antimony and arsenic nuclei and to slow down the exchange in the AsF_5 solutions.



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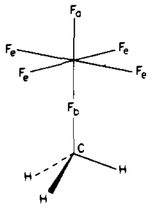

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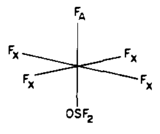

IV

The $CH_3F/SbF_5/SOF_2$ System. The ^{19}F NMR spectrum of a supercooled solution containing an excess of methylfluoride at −147 °C is reproduced in Figure 1. The quartet (ϕ = 265 ppm) due to the excess methyl fluoride and the solvent line (ϕ = −73.5 ppm) have been omitted. In the F-on-Sb region, this spectrum shows three very well-resolved multiplets F_1, F_2, and F_3, characteristic of $Sb_2F_{11}^-$.[14] There is one other sharp singlet at ϕ = −22 ppm which has an intensity relative to the F-on-Sb multiplets of 2:11 and this must be assigned to reacted SOF_2. Since the F-on-Sb multiplets are unambiguously assigned to $Sb_2F_{11}^-$ there is no evidence for the presence of any adducts such as $SbF_5{\cdot}SOF_2$ or $(SbF_5)_2{\cdot}SOF_2$.

The −90 °C proton spectrum shows only a deshielded sharp singlet at δ 5.27 ppm and the doublet (J = 46 Hz) of free methyl fluoride at δ 4.50 ppm. In previous studies, in which SO_2 or SO_2FCl was used as solvent, a similar singlet was observed and attributed to a methyl cation or a methyl group in a $CH_3F{\cdot}SbF_5$ complex undergoing rapid exchange.[4,5,7] We now postulate the formation of the cation $CH_3OSF_2^+$ which accounts for both ^{19}F and ^1H NMR spectra and is consistent with recent evidence for CH_3OSO^+ in SO_2 solutions.[8,9,13] Thionyl fluoride, which is a weaker base than SO_2, would appear therefore to be methylated by a mixture of CH_3F and SbF_5 just as SO_2 is methylated. It is not surprising that the long-range coupling constant J_{FSOCH} is not observed in $CH_3OSF_2^+$ since it is expected to be very small by comparison to J_{FSCH} which is only 5.3 Hz in methylsulfuryl fluoride.

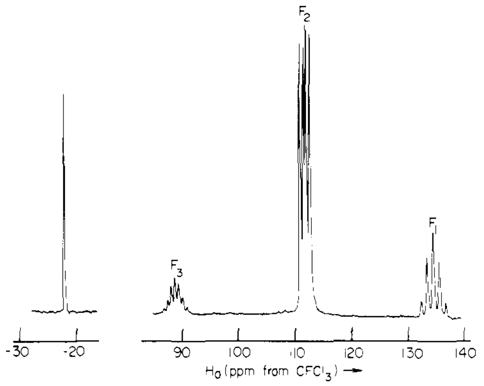

Figure 1. The 94.1-MHz ^{19}F spectrum (CH_3F and solvent line omitted) of a solution with $CH_3F/SbF_5/SOF_2$ = 5/1/10, at −147 °C.

When these solutions are allowed to warm to approximately −70 °C the cation slowly decomposes although the fluorine spectrum in the F-on-Sb region remains unchanged. The resulting products, which give rise to a second singlet (ϕ = −16 ppm) in the ^{19}F NMR spectrum and two signals in the ^1H NMR spectrum (δ 4.60 ppm and δ 5.35 ppm), have so far not been identified.

The $CH_3F/SbF_5/SO_2FCl$ System. These solutions must be supercooled to −150 °C in order to observe the fine structure of all the ^{19}F NMR multiplets. This requires that an excess of methyl fluoride be used. The 94.1-MHz spectrum shown in Figure 2 is more useful than the 56.4-MHz spectrum, since the overlap of adjacent resonances is reduced. Despite the relative complexity in the F-on-Sb region, the thee multiplets F_1, F_2, and F_3 can be assigned to $Sb_2F_{11}^-$. Although the resonances of the terminal (F_1) and equatorial (F_2) fluorines in this anion overlap with other signals (F_a and F_e, respectively), the multiplet at ϕ = 90 ppm arises only from the bridging fluorine (F_3). Thus, integration of the adjacent multiplets F_2 and F_e and subtraction of the area due to F_2, which is eight times F_3, yields the intensity of F_e. In this way it was found that the relative areas of F_e, F_a, and F_b are 4:1:1. The −95 °C ^1H spectrum,

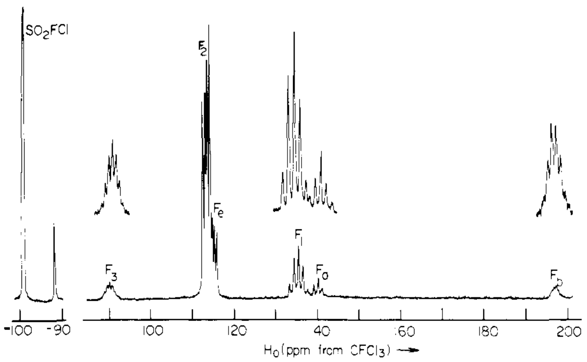

Figure 2. The 94.1-MHz ^{19}F spectrum (excess CH_3F omitted) of a solution with $CH_3F/SbF_5/SO_2FCl = 5/1/6$, at −150 °C. Expanded spectra have been recorded at different amplitudes.

shown in Figure 3, consists of a doublet at δ 4.50 ppm ($J = 46$ Hz) due to free methyl fluoride, a singlet at δ 5.48 ppm and another doublet at δ 5.85 (J = 40 Hz), which was not reported by Olah et al.[13]

The additional lines F_a and F_c could possibly be due to the $SbF_5{\cdot}SO_2FCl$ complex which would have a spectrum consisting of a doublet–quintet pattern due to F-on-Sb and a singlet due to coordinated SO_2FCl. The signal F_a could be the expected quintet and the doublet could be overlapping the double-doublet of $Sb_2F_{11}^-$. However, there are in fact more than two additional lines overlapped with the double-doublet F_2. Moreover, as can be seen from Table I, the doublet resulting from the equatorial fluorines of the $SbF_5{\cdot}SO_2FCl$ complex is expected at $\phi = 105$ ppm and it should, therefore, not overlap with F_2. Thus we conclude that $SbF_5{\cdot}SO_2FCl$ cannot be responsible for F_a or F_e. A 2:1 complex $(SbF_5)_2SO_2FCl$ can also be eliminated since the chemical shifts of the six different types of fluorine range from $\phi = 85$ to $\phi = 141$ ppm[11] and these are not observed.

The doublet at δ 5.85 ppm in the proton spectrum has a splitting of 40 Hz. This suggests a proton–fluorine coupling and we assign this doublet to a donor–acceptor complex of CH_3F with SbF_5 which has structure III. Although the integration is not precise near the solvent line, the singlet at $\phi = -92$ ppm has an area of approximately one-half that of one of the lines of the F_2 double-doublet of $Sb_2F_{11}^-$. Thus, as in the $CH_3F/SbF_5/SOF_2$ system, we propose that methylation of the solvent occurs. The cation $CH_3OSOFCl^+$ gives rise to the singlet at $\phi = -92$ ppm in the ^{19}F NMR spectrum and to the singlet at δ 5.48 ppm in the ^1H NMR spectrum.

It remains, therefore, to assign the fluorine multiplets F_c, F_a, and F_b of relative intensities 4:1:1. The F_e equatorial fluorines coupled to both F_a and F_b give rise to a doublet of doublets, one of these peaks being under one F_2 line of $Sb_2F_{11}^-$. The signal due to F_a is a quintet due to coupling with the four equivalent F_c nuclei. Since this latter does not show any additional splitting, the coupling constant between F_a and F_b must be very small. Accordingly the signal arising from the bridging fluorine F_b is a quartet of quintets because of coupling with the three methyl protons ($J_{HF} = 40$ Hz) and the four F_e equatorial fluorines ($J_{F_bF_c} = 48$ Hz). Since these two coupling constants are very similar, the resulting complex multiplet is not well resolved. Table I shows that $J_{F_aF_c}$ is of the same magnitude as in other Lewis acid–base complexes. It is also of the same magnitude as $J_{F_1F_2}$ in $Sb_2F_{11}^-$, which may be considered as an adduct between SbF_5 and SbF_6^-. Similarly, $J_{F_bF_c}$ is close to $J_{F_2F_3}$, and $J_{F_aF_b}$ like $J_{F_1F_3}$ is close to zero.

The ^{19}F NMR quartet of free methyl fluoride remains well resolved through the temperature range from −80 to −150 °C. This clearly indicates that there is no interaction, within the NMR time scale, between free and complexed methyl fluoride.

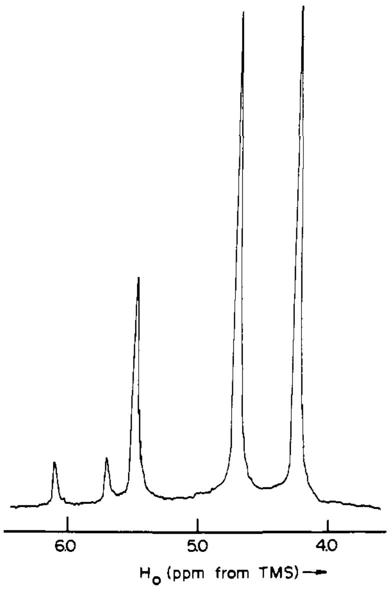

Figure 3. The 100-MHz ^1H spectrum of a solution with $CH_3F/SbF_5/SO_2FCl = 2.5/1/8$, at −95 °C.

The $CH_3F/SbF_5/SO_2F_2$ System. A typical ^{19}F NMR spectrum at −145 °C is shown in Figure 4. In contrast to the preceding case there is no evidence for reacted solvent since there is only one line ($\phi = -31$ ppm) in the F-on-S region and the anion $Sb_2F_{11}^-$ is not present in significant concentration. The proton spectrum shows a deshielded doublet (δ 5.80 ppm, $J = 41$ Hz) due to reacted methyl fluoride in addition to the doublet due to excess CH_3F. By comparison with the above discussion, all the lines in the ^{19}F NMR spectrum doublet of doublets (F_e, $\phi = 115$ ppm, quintet F_a, $\phi = 141$ ppm, and multiplet F_b $\phi = 196$ ppm) may be unambiguously assigned to the $CH_3F{\cdot}SbF_5$ complex (Table I). The ^{19}F NMR data reported by Olah et al.[13] for this system do not agree with our data. They reported only two broad signals at −80 °C, one at $\phi = 100$ ppm is claimed to be characteristic of the fluoroantimonate system and the other ($\phi = 162.2$ ppm) was assigned to the fluorine of the complexed methyl fluoride. We found on warming our samples to −80 °C that there was a broadening of the peaks and a loss of fine structure but there was no change in the chemical shift of the three peaks due to the complex while the quartet due to excess methyl fluoride remained sharp. The line broadening may presumably be attributed to increased quadrupole relaxation of the antimony nucleus. On raising the temperature further to −50 °C (56.4 MHz) a further broadening of all the signals was observed including that of the free methyl fluoride together with some changes in the chemical shifts as the peaks began to collapse. However, even at this temperature three peaks due to the complex were still observed. These further spectral changes may be attributed to the onset of intermolecular exchange between the complex and excess methyl fluoride.

Dean and Gillespie[11] concluded that SO_2F_2 acts as an inert diluent for SbF_5. It also appears that SO_2F_2 is not methylated by a mixture of CH_3F and SbF_5.

Reactions in Mixed Solvents: Relative Base Strengths of Solvents. From the above discussion it is concluded that CH_3F/SbF_5 methylates SOF_2 just as it does SO_2 and there is no evidence for the existence of a $CH_3F{\cdot}SbF_5$ complex in this solvent. In SO_2FCl there is some methylation of the solvent but the $CH_3F{\cdot}SbF_5$ complex is also observed while in SO_2F_2 there is no methylation of the solvent and only the $CH_3F{\cdot}SbF_5$ complex is observed. Thus it appears that SOF_2 like SO_2 is a strong base toward the methyl ion, that SO_2FCl is weaker, and that SO_2F_2 has no basic properties toward the methyl ion. In

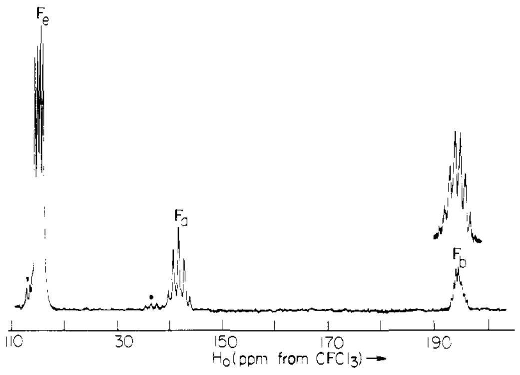

Figure 4. The 94.1-MHz ^{19}F spectrum (excess CH_3F and solvent line omitted) with $CH_3F/SbF_5/SO_2F_2 = 5/1/10$, at −145 °C. *lines due to $Sb_2F_{11}^-$.

order to further compare the base strengths of these solvents with respect to CH_3^+ some additional reactions using mixtures of solvents were carried out. When CH_3F was added to an SbF_5 solution in SO_2/SOF_2 or SO_2/SO_2FCl or $SO_2/SOF_2/SO_2FCl$ the only lines arising in the F-on-S region of the ^{19}F NMR spectrum were the lines of the solvents themselves but in all cases the proton spectrum showed only a deshielded singlet due to reacted CH_3F. This indicates that the only cation present was CH_3OSO^+ and shows that SO_2 is a stronger base toward CH_3^+ than SOF_2 or SO_2FCl. The order of base strengths toward CH_3^+, i.e., $SO_2 > SOF_2 > SO_2FCl > SO_2F_2$ is the same as that previously found toward SbF_5.[11]

The $CH_3F/AsF_5/SO_2FCl$ System. The −100 °C ^{19}F spectra of a solution of composition $CH_3F{:}AsF_5{:}SO_2FCl = 0.5{:}1{:}3$ showed, in addition to the solvent line, a sharp singlet ($w_{1/2}$ = 40 Hz) in the F-on-As region (ϕ = 54 ppm) and a quartet due to methyl fluoride (ϕ = 188 ppm). When additional MeF was added to this solution the quartet moved upfield and even when a very large excess of MeF was added no additional line appeared at this temperature. These data suggest a very fast intermolecular exchange reaction between free and complexed MeF. This is also in agreement with the proton spectrum which shows only a doublet whatever the excess of MeF. The sharpness of the F-on-As peak indicates a greater rate of quadrupole relaxation than in AsF_5 alone. This is expected as the electric field gradient about arsenic is greater in the complexed molecule than in uncomplexed AsF_5.[12]

The solutions containing a large excess of MeF can be supercooled and studied at very low temperature. As the temperature is lowered the quartet, due to CH_3F, slowly collapses and broadens to a single line and the F-on-As peak broadens (Figure 5, −135 °C), then the CH_3F line becomes unsymmetrical and splits into two broad lines at about −140 °C (in the case of a mixture of composition $CH_3F{:}AsF_5{:}SO_2FCl = 5{:}1{:}3$) as the F-on-As peak also divides. At −147 °C, the spectrum shows four broad signals at ϕ = 47, ϕ = 93, ϕ = 176, and ϕ = 267 ppm. At −160 °C the signals at ϕ = 47 and ϕ = 94 ppm evolve into a doublet-quintet pattern (J = 124 Hz) which can be assigned to fluorines F_e and F_a of the $CH_3F{\cdot}AsF_5$ complex, while that at ϕ = 267 ppm is developing into a quartet, which can be attributed to free CH_3F. At −165 °C the doublet further evolves into a double-doublet although no fine structure can be observed on the peak at ϕ = 176 ppm.

These data clearly indicate the formation of the very labile $CH_3F{\cdot}AsF_5$ complex, and establish its structure as the donor-acceptor complex III analogous to that found with SbF_5 in the same solvent. However, in this case, there is no metylation of the solvent. The fact that the signal due to the bridging fluorine is not resolved is not surprising since this nucleus is coupled to the four F_e fluorines and also the the three methyl protons.

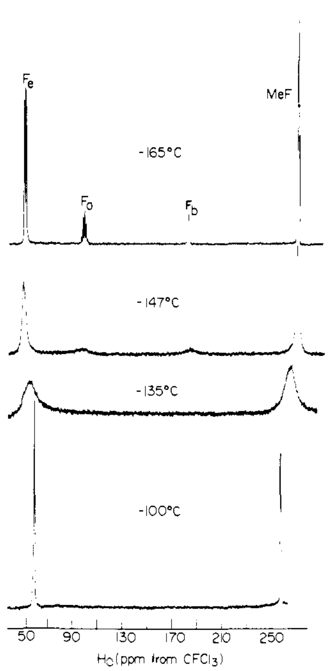

Figure 5. The 94.1-MHz ^{19}F spectrum of a solution with $CH_3F/AsF_5/SO_2FCl = 5/1/3$ at various temperatures.

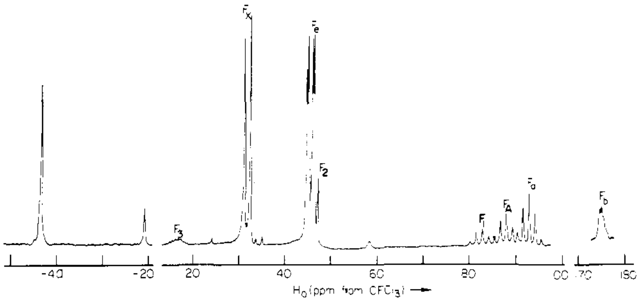

Figure 6. The 94.1-MHz ^{19}F spectrum (excess CH_3F and solvent line omitted) with $CH_3F/AsF_5/SOF_2 = 5/1/4$, at −168 °C.

The same reaction was also carried out in SO_2F_2, but as the mixture crystallized on cooling it was not possible to reach a low enough temperature to achieve the slow exchange limit.

The $CH_3F/AsF_5/SOF_2$ System. At −100 °C, the ^{19}F spectrum of a solution of composition $CH_3F{:}AsF_5{:}SOF_2 = 5{:}1{:}4$ shows, in addition to the solvent peak, a very sharp singlet at ϕ = −21 ppm, another singlet (ϕ = 55 ppm) in the F-on-As region, and a quartet (ϕ = 250 ppm) due to methyl fluoride. The chemical shift of this quartet varied with the relative amount of CH_3F, and this again indicates that a very rapid intermolecular exchange process is occurring at this temperature. The −100 °C ^1H spectrum displays a doublet (J = 45 Hz) and a deshielded singlet at 0.6 ppm from the center of the doublet. As the temperature is lowered, the peak due to F-on-As broadens and the MeF quartet collapses, whereas the singlet at ϕ = −21 ppm does not seem to be affected, as it remains very sharp. Upon continuing to decrease the temperature, there slowly appears a series of broad signals between ϕ = 20 and ϕ = 90 ppm. A second singlet also appears at ϕ = −43 ppm and another broad signal at about ϕ = +177 ppm. Then, all these broad signals sharpen at slightly different rates and finally evolve into very well-resolved multiplets (Figure 6). The same spectral changes are observed in reverse on raising the temperature.

By comparison with the solutions in SO_2FCl, the double-doublet F_e, the quintet F_a, and the signal F_b, which just starts

Table II.

Reactants	Solvents	Products	
$CH_3F + SbF_5$	SO_2	$CH_3OSO^+Sb_2F_{11}^-$	↑ donor ability of the solvent
	SOF_2	$CH_3OSF_2^+Sb_2Sb_2F_{11}^-$	
	SO_2FCl	$CH_3OSOFCl^+Sb_2F_{11}^-$ $CH_3F \cdot SbF_5$	
	SO_2F_2	$CH_3F \cdot SbF_5$	
$CH_3F + AsF_5$	SOF_2	$CH_3OSF_2^+As_2F_{11}^-$ $CH_3F \cdot AsF_5$ $AsF_5 \cdot SOF_2$	
	SO_2FCl	$CH_3F \cdot AsF_5$	

to display a fine structure at −168 °C, are assigned to the complex $CH_3F \cdot AsF_5$ (structure III). The multiplets F_1, F_2, and F_3 are attributed to $As_2F_{11}^-$ (structure II). These are resolved at a slightly higher temperature than those due to $CH_3F \cdot AsF_5$. The signal due to the eight equivalent fluorines of $As_2F_{11}^-$ is expected to be a double-doublet, this partially overlaps with the double-doublet due to the equatorial fluorines of $CH_3F \cdot AsF_5$. The singlet at $\phi = -21$ ppm, which has an intensity of approximately that of one of the F_2 lines of $As_2F_{11}^-$, is attributed to methylated SOF_2. This $MeOSF_2^+$ cation gives rise to a deshielded singlet in the ^1H NMR spectrum. The signal at $\phi = 59$ ppm may be due to a small amount of AsF_6^-. It remains, therefore, to assign the singlet at $\phi = -43$ ppm, the doublet F_x and the quintet F_A. The singlet has an area equal to that of one of the FX lines. This indicates the presence of the complex $AsF_5 \cdot SOF_2$, with the structure IV. Some ^{19}F NMR evidence for this complex has already been obtained[12] but no fine structure was observed in the spectrum.

Conclusions

The reactions in the various solvents are summarized in Table II where they are arranged in order of decreasing solvent basicity. These results indicate also that SbF_6^- is a base of comparable strength to that of SO_2FCl and that it is a stronger base than SO_2F_2. Thus in SO_2F_2 as solvent CH_3^+ coordinates preferentially with SbF_6^- to form the $CH_3F \cdot SbF_5$ complex. With AsF_5, there is no methylation of SO_2FCl and the only complex formed in solution is $CH_3F \cdot AsF_5$. This shows that AsF_6^- is a stronger base than SO_2FCl. In the SOF_2 solution, both $CH_3F \cdot AsF_5$ and $MeOSF_2^+$ are formed and this indicates that SOF_2 is a base of comparable strength to that of AsF_6^-. Moreover, since both $AsF_5 \cdot SOF_2$ and $MeOSF_2^+$ are present, it is reasonable to assume that AsF_5 is an acid of comparable strength to CH_3^+. Accordingly, CH_3^+ should be a less strong acid than SbF_5, as the $SbF_5 \cdot SO_2FCl$ adduct does not exist in these solutions, even in the presence of an excess of CH_3F. It is clear that a free CH_3^+ cation could only exist in the presence of an anion less basic than SbF_6^- or AsF_6^- and our studies are continuing in this direction.

The ^{19}F NMR spectrum of the complex $CH_3F \cdot SbF_5$, which has been observed for the first time, shows coupling of the bridging fluorine to both the protons on carbon and the fluorines on antimony and this, together with the double-doublet quintet fine structures of the F-on-Sb spectrum, clearly establishes its structure as the simple donor–acceptor complex III analogous to that of many other $SbF_5 \cdot$base complexes including $Sb_2F_{11}^-$ which can be regarded as a complex of SbF_6^- and which is the only other example of a fluorine-donor:SbF_5 complex. The rapid intramolecular fluorine exchange that was previously postulated,[3-7] to occur in the $CH_3F \cdot SbF_5$ complex even at low temperature, was not observed. For the similar complex with AsF_5, a very low temperature was necessary to achieve the slow exchange limit. As $CH_3F \cdot SbF_5$ methylates SO_2FCl whereas $CH_3F \cdot AsF_5$ does not it seems reasonable to conclude that $CH_3F \cdot SbF_5$ is a stronger methylating agent than $CH_3F \cdot AsF_5$.

Experimental Section

Nuclear Magnetic Resonance Spectra. These were obtained as described in earlier papers.[7,15]

Materials. These were purified and stored as previously described[7,11,12,15] In particular, sulfur dioxide, present as an impurity in sulfuryl chlorofluoride was removed by distilling the product onto SbF_5 on a vacuum line and distilling the SO_2ClF back out from this solution. The SO_2 forms a much stronger complex with SbF_5, than does SO_2FCl,[11] and remains behind. The resulting material was stored over anhydrous sodium fluoride before use.

Sample Preparation. All manipulations were carried out on a calibrated glass, grease-free vacuum line outfitted with Teflon stopcocks. An all-glass syringe was used to transfer a weighed amount of SbF_5 to a glass flask with an NMR tube sealed to a side arm, this operation being performed in a drybox. The vessel was closed with a detachable tap and connected to the vacuum line. In the case of AsF_5, a known volume of the gas was introduced into the tube through the vacuum line. Then, a known amount of solvent was condensed into the flask. Homogenization of samples was achieved by stirring at −78 °C. A known amount of MeF was allowed to condense into the reaction flask, giving a solution of known composition. These mixtures were stirred at −78 °C for 0.5 h. The required amount was quickly tipped into the NMR tube, both the main vessel and the NMR side arm were cooled in liquid nitrogen, and the NMR tube was sealed off. Samples were kept in liquid nitrogen until used.

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