on evidence from Raman spectroscopy that a relatively unperturbed methyl fluoride moiety is present in CH_3F-SbF_5-SO_2.[1b] We presume that the band at 1008 cm^{-1}, close to that of CH_3F (1010) arises from **1**. Although the close coincidence is unusual, it may be noted that in terms of **2a** or **2b** it is also remarkable that the Raman frequency is so slightly perturbed in the "complex" while NMR spectra are substantially different from those of CH_3F.

(3) **Carbon NMR.** The ^{13}C NMR spectrum of CH_3F-SbF_5-SO_2 (δ (CS_2) 119, J_{CH} = 149 Hz) appears to be equally compatible with structures **1** and **2a** or **2b**.

(4) **Fluorine NMR results.** An analogue of the structure **1** is formed from EtF-SbF_5.[1,2] In terms of the complex structure, the conversion of **7** (analogous to **2b**) to *tert*-butyl cation (eq 5) gave puzzling ^{19}F NMR results.

$$2CH_3CH_2F \rightarrow Sb_2F_{10} \longrightarrow H^+ + (CH_3)_3C^+ + 2Sb_2F_{11}^- \tag{5}$$

Bacon and Gillespie[2] noted: "We are forced to the, at first sight, somewhat surprising conclusions that the fluorine spectrum of $Sb_2F_{11}^-$ is essentially the same when it is present as the free ion together with the *tert*-butyl cation or in a complex with ethyl ion." The proposal that the reactant has the ethylated SO_2 structure $[CH_3CH_2O{=}S{=}O]^+$ resolves the problem, since $Sb_2F_{11}^-$ is present also in the reactant.

(5) **The Apparent Formation of 2a or 2b in Other Solvents.** According to our hypothesis the species formed from CH_3F-SbF_5 in SO_2ClF (δ 5.6), 1:1 HF-SbF_5 (δ 5.5), and neat SbF_5 (δ 5.5), previously assumed to be identical with that formed in SO_2 (δ 5.56), must have structures different from **1**. Anticipating that readers would be reluctant to accept this coincidence, we have reprepared solutions of CH_3F-SbF_5-SO_2ClF. The previously undetermined ^{13}C NMR chemical shift, 81.92 ppm from Me_4Si, is, in fact, 8.21 ppm from that found in CH_3F-$SbF_5 \cdot SO_2$ solutions (δ (Me_4Si) 73.71, our value, or 74.8[2b,7]). That solvent effects were not responsible for the difference is indicated by our finding that 16 ^{13}C chemical shifts in four nonequilibrating halonium ions in SO_2ClF were within the range −0.64 to +0.9 from their value in SO_2.[8] Accordingly, a species different from **1**, possibly methylated SO_2ClF or one of the originally proposed structures **2a** or **2b**, is present in the SO_2ClF system. The formation of a precipitate upon addition of SO_2 is readily interpreted as a reaction to form an insoluble salt of methylated SO_2, **1**, whereas **2a** or **2b** should not have given a precipitate, since, according to the previous interpretation, they are soluble in both solvents.

Our results suggest that other nucleophiles may be found to react with CH_3F-SbF_5-SO_2 at sulfur, followed by rearrangement to products of reaction at carbon. The results also indicate that methyl and primary cations cannot be formed in SO_2 solutions because they react with SO_2, not with SbF_6^- as previously thought. The possibility that cations of intermediate stability (between primary and *tert*-butyl) will exist in closely balanced, temperature dependent[9] equilibria with their SO_2 reaction products is suggested.

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(3) The yield of dimethyl sulfite was 44%, based on GC analysis of the methanol solution. The products of reaction with ethanol (30 s, −65°) were poured over ice-water and immediately extracted with CH_2Cl_2 to avoid complete transesterification, discussed later in this communication. Relative percent: dimethyl sulfite (**4,** 18%), methyl ethyl sulfite (**5,** 62%), and diethyl sulfite (**6,** 20%).

(4) Pure samples for quantitative gas chromatography were obtained by high-speed spinning-band distillation.

(5) For a similar result see E. Bourgeois and A. Vande Casteel, *Bull. Soc. Chim. Belg.*, **12,** 980 (1927); "Beilsteins Handbuch der Organischen Chemie", 4th ed, 2d Suppl., Vol I, p 326.

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Observation of the Methyl Fluoride–Antimony Pentafluoride Complex in Sulfuryl Fluoride Solution, an Exceedingly Low Nucleophilicity Solvent. Reinvestigation of the Complex in Sulfur Dioxide and Sulfuryl Chloride Fluoride Solution Showing O-Methylation[1]

Sir:

In our previous studies we have described the complex formed between methyl fluoride and antimony pentafluoride in sulfur dioxide and sulfuryl chloride fluoride solution, and reported its exceptional methylating ability.[2,3]

An unusual aspect of the CH_3F-SbF_5 complex in SO_2 and SO_2ClF solution was the absence of H–F coupling in the NMR spectra, showing a singlet ^1H NMR absorption at δ 5.56 and 5.63, respectively. As there was no exchange with excess uncomplexed methyl fluoride or antimony pentafluoride, we interpreted the results as a rapid intramolecular fluorine exchange in the complex. We have reported that O-methylation of sulfur dioxide by the complex can take place, but considered it to be a fast reversible process. We have, however, not suggested that this process, rather than the intramolecular fluorine exchange process, would be responsible for the absence of H–F coupling. This consideration was supported by the observation of a very similar spectrum of the complex in SO_2ClF solution, a system in which previously no alkylation by any carbocationic species was observed. Further, the methyl fluoride complex showed little deshielding in its ^{13}C NMR spectrum in SO_2 ($\delta_{^{13}C}$ 76.0) compared to methyl fluoride itself ($\delta_{^{13}C}$ 74.9, INDOR data) and the Raman spectra also indicated tetrahedral symmetry around carbon. Thus the suggestion at the time seemed reasonable.

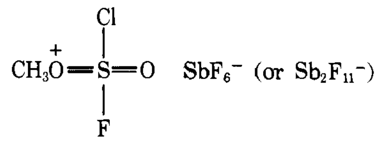
In our continued work, we have found that it was possible to isolate a relatively stable complex of methyl fluoride–antimony pentafluoride as a crystalline salt from the SO_2 solution. Elementary analysis, however, showed that the complex contained bonded SO_2, which was given off upon standing. When dissolved in SO_2 the complex gave identical properties with the original solution. This observation prompted us to reinvestigate the SO_2 and SO_2ClF solution of the CH_3F-SbF_5 system, including more complete ^{13}C and ^{19}F NMR, as well as chemical studies.

The CH_3F-SbF_5-SO_2 system showed the previously reported ^1H and ^{13}C NMR shifts of δ 5.50 (singlet) and δ_C 74.9 (quartet), with J_{CH} of 162.5 Hz. The CH_3F-SbF_5-SO_2ClF system also showed the previously observed ^1H NMR singlet at δ 5.63. The ^{13}C NMR shift, as now determined by FT method, is at δ 81.9 with J_{CH} = 165.9 Hz. In addition the ^{19}F spectrum shows, besides the characteristic broad absorption of the fluoroantimonate system ($\phi \sim 100$, studied in detail by Bacon and Gillespie,[4]) and that of SO_2ClF (ϕ −98.9), a singlet absorption at ϕ −90.8, which is different from that observed for the SO_2ClF-SbF_5 complex (ϕ −94.9).

The similarity of the methyl absorptions with those observed for O-methylated oxonium ions and the additional ^{19}F NMR absorption seems to indicate that both SO_2 and SO_2ClF are O-methylated by the CH_3F-SbF_5 system giving stable nonexchanging ions **1** and **2**.

$$CH_3\overset{+}{O}{=}S{=}O \quad SbF_6^- \text{ (or } Sb_2F_{11}^-\text{)}$$

1

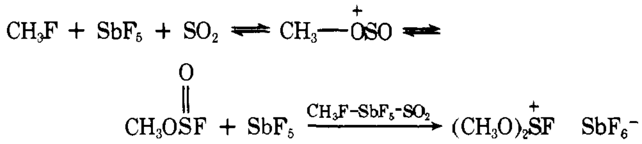


$$CH_3\overset{+}{O}{=}\overset{\overset{Cl}{|}}{\underset{\underset{F}{|}}{S}}{=}O \quad SbF_6^- \text{ (or } Sb_2F_{11}^-\text{)}$$

2

The SO_2 solution of CH_3F-SbF_5 seems to be stable, and shows no temperature dependence, except that upon standing $(CH_3O)_2S^+$-F is formed (due to further methylation of methyl fluorosulfite formed in the system).

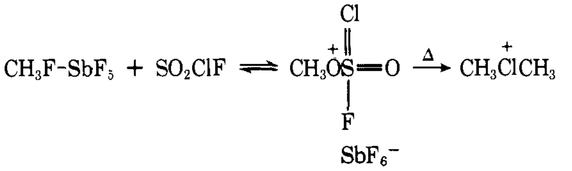
We have recently shown[5] that methyl fluorosulfite with SbF_5 and CH_3F-SbF_5-SO_2 forms the same complexes.



$$CH_3F + SbF_5 + SO_2 \rightleftharpoons CH_3{-}\overset{+}{O}SO \rightleftharpoons$$

$$CH_3O\overset{\overset{O}{\|}}{S}F + SbF_5 \xrightarrow{CH_3F\text{-}SbF_5\text{-}SO_2} (CH_3O)_2\overset{+}{S}F \quad SbF_6^-$$

When the SO_2ClF solution of CH_3F-SbF_5 was allowed to warm up to 0°, irreversible formation of the dimethylchloronium ion ($CH_3Cl^+CH_3$) was observed, showing the characteristic, ^1H NMR δ 4.59 (s) and ^{13}C NMR δ_C 49.8 (q), J_{CH} = 160 Hz, parameters of the previously reported ion.[6] Similar observations were made from the CH_3SO_2F-SbF_5 system in SO_2ClF solution.



$$CH_3F\text{-}SbF_5 + SO_2ClF \rightleftharpoons CH_3\overset{+}{O}\overset{\overset{Cl}{\|}}{\underset{\underset{F}{|}}{S}}{=}O \xrightarrow{\Delta} CH_3\overset{+}{Cl}CH_3$$

$$SbF_6^-$$

The initially formed CH_3F-SbF_5 complex must be, indeed, an exceedingly reactive methylating agent if it methylates not only SO_2 but also the considerable less nucleophilic SO_2ClF. Whereas SO_2 was observed previously to be alkylated by secondary alkyl cations such as the isopropyl cation and arenium ions, no previous observation of alkylation of SO_2ClF by either secondary or tertiary alkyl cations was ever made. In SO_2ClF, secondary ions such as the isopropyl and *sec*-butyl cations as well as arenium ions were found to be stable and not alkylated. The CH_3F-SbF_5 complex thus behaves as an incipient primary carbocation, showing extreme electron deficiency and reactivity.

If in SO_2 and SO_2ClF solutions of the CH_3F-SbF_5 system, O-methylation takes place, we were interested to see whether a noninteracting complex could be obtained in solvents having even lower nucleophilicity than SO_2ClF (or SO_2). We have found that sulfuryl fluoride, SO_2F_2, is indeed such a solvent. When methyl fluoride was added to a 10% solution of SbF_5 in SO_2F_2 at −80°, a CH_3F-SbF_5 donor:acceptor complex was obtained. The ^1H NMR spectrum of the SO_2F_2 solution showed a doublet at δ 5.68 with $J_{C\text{-}F}$ of 41.2 Hz (CH_3F in SO_2F_2 shown δ 4.17 with J_{CH} 47 Hz). The coupled ^{13}C NMR spectrum showed a doublet of quartets at $\delta_{^{13}C}$ 96.8 with J_{CH} = 164.4 Hz and $J_{C\text{-}F}$ of 126.0 Hz. The ^{19}F NMR spectrum showed two broad signals, one characteristic of the fluoroantimonate system ($\phi \sim 100$). The other one is assigned to the fluorine of the complexed methyl fluoride (ϕ 162.2). The aliphatic fluorine is deshielded by 108.4 ppm as compared to methyl fluoride (ϕ 270.6) in SO_2F_2.

That the addition of methyl fluoride to antimony pentafluoride in SO_2F_2 up to 1:1 molar ratio forms the same nonexchanging donor:acceptor complex as when excess methyl fluoride is present, is based on the observation of the characteristic doublet at δ 4.17 (J_{HF} = 47.0) in the ^1H NMR spectrum.

$$CH_3F + SbF_5 \xrightleftharpoons{SO_2F_2} CH_3F{\rightarrow}SbF_5 \text{ (or } {\rightarrow}Sb_2F_{10}\text{)}$$

No intramolecular fluorine exchange or exchange between the donor:acceptor complex and methyl fluoride occurs.

To obtain further direct proof for the methylation of SO_2 and SO_2ClF by the CH_3F-SbF_5 system we added SO_2 and SO_2ClF, respectively, to solutions of the complex in SO_2F_2 solution. We were able to observe the formation of **1** and **2** giving identical spectra with those observed in SO_2 or SO_2ClF solution of CH_3F-SbF_5.

The C_2H_5F-SbF_5 system in SO_2 solution was also found to be similar to the CH_3F-SbF_5 system, giving the $C_2H_5O^+SO$ ion which upon raising the temperature undergoes intermolecular equilibration with excess SO_2. In this process the ethyl cation $C_2H_5^+$ is an intermediate, as shown by the complete hydrogen and carbon scrambling observed, and further indicated by the reversible collapse of the ethyl group's triplet-quarter ^1H NMR absorption. In SO_2ClF solution the diethylchloronium ion is rapidly formed. There is, on occasion, even at −120° some formation of *tert*-butyl cation (or higher *tert*-alkyl cations). In SO_2F_2 solution the C_2H_5-F-SbF_5 complex is not observed, but readily forms the *tert*-butyl cation, and related other alkyl cations, showing the ease with which $C_2H_5^+$ is deprotonated and then further alkylated.

We consider the reported observations of substantial significance. They show that not only SO_2 but also SO_2ClF can display nucleophilic nature against exceedingly electron deficient, incipient primary carbocation systems. SO_2F_2, however, was found to be entirely nonnucleophilic and thus can be of significance as a noninteracting solvent for superacid-carbocation systems.

The alkylating ability of the CH_3F-SbF_5 (and C_2H_5F-SbF_5) systems reported previously are not affected by present observations, even if in SO_2 or SO_2ClF solution intermediate O-alkylated complexes are formed. The results of extensive studies of long-lived carbocations in superacidic systems using SO_2 or SO_2ClF as solvents are also not affected by present observations of the methyl (ethyl) fluoride systems. We have studied a wide range of tertiary and secondary carbocations under identical conditions in SO_2, SO_2ClF, and SO_2F_2 solutions and found no evidence of O-alkylation with tertiary carbocations (or if equilibria exist they are entirely on the carbocation side, with only small solvent effects observed). Secondary carbocations show an increased ability to O-alkylate sulfur dioxide, but not sulfuryl chloride fluoride. The isopropyl or *sec*-butyl cations, for example, are stable in SO_2ClF, but not in SO_2 solution where O-alkylation and subsequent cleavage-condensation reactions take place. SO_2F_2 has not affected any of the studied carbocationic systems. Results of these studies, including a comprehensive study of solvent effects, will be reported in full.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

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Inversion at Pyramidal Oxygen and Sulfur[1]

Sir:

Inversion about pyramidal nitrogen is a well-established phenomenon.[2] One way in which the rate of this inversion has been measured in solution is by proton magnetic resonance spectroscopy of tertiary benzyl amines.[3,4] Pyramidal geometry about tricoordinate oxygen has been established for $H_3O^+Cl^-$ in the solid,[5] and probably for $(CH_3)_2OBF_3$ in the gas phase.[6] Pyramidal geometry about oxygen in the liquid phase and the barrier to inversion have been determined for the oxonium salts of oxirane,[7] but not for a neutral species. Pyramidal configuration about trigonal sulfur was established many years ago by isolation of optically active trialkyl sulfonium salts.[8] The barrier to inversion in these salts is so high that racemization occurs by dissociation and recombination of the sulfonium ion.[9,10]

When a CH_2 group is bonded to a carbon atom bearing three different substituents the two methylene protons will be magnetically nonequivalent regardless of the rate of rotation about the carbon-carbon bond between the asymmetric center and the methylene group.[11] A similar situation prevails if the asymmetric center has only three groups but is held in a pyramidal configuration.[12] Upon inversion about the pyramidal center the nonequivalence of the methylene protons will be lost.

The BF_3 complex of benzyl ethyl ether was prepared by condensing equimolar quantities of the two reactants, separated by the sulfur dioxide solvent, into an NMR sample tube at liquid nitrogen temperature on a vacuum line. Upon thawing and mixing the complex is formed. The proton resonance spectrum of such a sample at 100 MHz and −65 °C is interpreted as having nonequivalent methylene protons. These results indicate slow inversion about pyramidal oxygen in the complex.

The ether alone, in sulfur dioxide as solvent, has sharp single lines from the aromatic protons at 7.26 ppm and the benzylic protons at 4.42 ppm, a quartet at 3.51 ppm from the methylene protons, and a triplet at 1.16 ppm from the methyl protons at both 25 and −65 °C. The para proton is shifted to 6.4 ppm and the ortho and meta protons to 7.0 ppm upon reaction with 1 equiv of BF_3. The three envelopes remain broad from 25 to −65 °C. The methyl triplet is shifted downfield to 1.46 ppm and the methylene quartet to 4.30 ppm at 25 °C. By −65 °C a complex but sharp pattern of lines is observed for the ethyl group and may be analyzed for the following parameters.

$$\delta CH_3 = 1.45 \text{ ppm} \qquad J_{CH_3\text{-}A} = 7.3 \text{ Hz}$$

$$\delta CH_A = 4.24 \text{ ppm} \qquad J_{CH_3\text{-}B} = 7.3 \text{ Hz}$$

$$\delta CH_B = 4.36 \text{ ppm} \qquad J_{A\text{-}B} = 14.4 \text{ Hz}$$

The broadening of the phenyl and benzyl proton signals in the complex may be explained by chemical shifts which would give a multiplicity of unresolved lines in this complicated spin system.

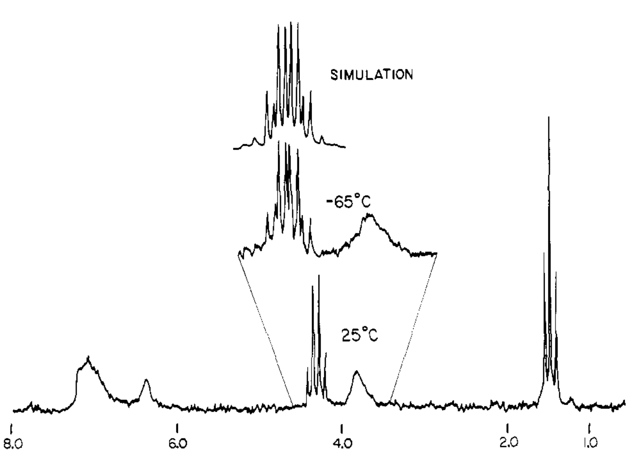

Figure 1. Experimental and theoretical proton resonance spectra of the benzyl ethyl ether boron trifluoride complex.

Experimental spectra at 25 and −65 °C are shown in Figure 1, along with a simulated spectrum of the methylene region in the slow exchange limit. The effects of temperature upon the spectrum are completely reversible. From a comparison of experimental spectra as a function of temperature and theoretical spectra as a function of exchange rate,[13] $\Delta H^{\ddagger}$ is calculated to be 4.1 ± 0.3 kcal/mol.

An unambiguous explanation of the spectral results in terms of hindered inversion about pyramidal oxygen requires refutation of the possible existence of two BF_3 complexes (with oxygen and the aromatic π electrons) and exchange between the two complexes. If there were two complexes one would expect different chemical shifts for the methyl as well as methylene protons, but the methyl lines remain narrow over the entire temperature range. The observed spectra were simulated by the spin system ABC_3. They cannot be simulated by exchange between two systems of type A_2B_3 even if the two groups of methyl protons are given the same chemical shift.

Nonequivalence of the methylene protons of benzyl ethyl ether complexes with tantalum pentafluoride has also been observed. However, complexes with niobium pentafluoride, boron trichloride, phosphorus pentafluoride, aluminum trichloride, and germanium tetrafluoride do not give nonequivalent methylene protons at low temperature. Phenetole, 2-ethoxynapthalene, diethyl ether, and diallyl ether complexes also gave no evidence of nonequivalent methylene protons.

Nonequivalence of the methylene protons in a complex of diethyl sulfide with BH_3 has been observed and attributed to hindered inversion about sulfur.[12] Hindered inversion has also been observed in platinum chloride complexes of dibenzyl sulfide and the barrier to inversion was found to be 18 kcal/mol.[14] In the present study nonequivalent methylene protons were observed in the complex between diethyl sulfide and boron trichloride, but not in complexes with boron trifluoride, tantalum pentafluoride, niobium pentafluoride, germanium tetrafluoride, titanium tetrafluoride, aluminum trichloride, and tungsten hexafluoride. Additional Lewis acids and other ethers and sulfides are being investigated to determine the factors which allow nonequivalent methylene protons to be ovserved in complexes of ethers and sulfides.

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