a prevalent one-center component arising from the p_yp_x transition density of the oxygen atom. In this respect, the transition is similar to the n → π^* transition in ketones. The high charge density around the oxygen in the σ molecular orbital also provides an explanation to the solvent shift of the transition (Table I) and to the fact that the protonation site of sulfoxides is at the oxygen atom.[6]

References and Notes

(1) (a) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy", Wiley, New York, N.Y., 1962, p 491; (b) J. N. Murrel "The Theory of the Electronic Spectra of Organic Molecules", Methuen, 1963, p 176.

(2) (a) G. L. Bendazzoli, G. Gottarelli, P. Palmieri, and G. Torre, *Mol. Phys.*, **25,** 473 (1973); (b) G. L. Bendazzoli, G. Gottarelli, and P. Palmieri, *J. Am. Chem. Soc.*, **96,** 11 (1974).

(3) T. Taunetsugu, J. Furukawa, and T. Fueno, *J. Polym. Sci.*, **3,** 3529 (1971).

(4) K. Kondo and A. Negishi, *Tetrahedron,* **27**, 4821 (1971).

(5) A. Moskowitz "Modern Quantum Chemistry", 3d ed, O. Sinanoglu, Ed., Academic Press, New York, N.Y., 1965, p 31.

(6) G. Gatti, A. Levi, V. Lucchini, G. Modena, and G. Scorrano, *J. Chem. Soc., Chem. Commun.*, 251 (1973).

G. L. Bendazzoli, P. Palmieri*
Istituto di Chimica Fisica e Spettroscopia
Facoltá di Chimica Industriale, Universitá di Bologna
Bologna, Italy

G. Gottarelli
Istituto di Chimica degli Intermedi
Facoltá di Chimica Industriale, Universitá di Bologna
Bologna, Italy

I. Moretti, G. Torre
Istituto di Chimica Organica, Universitá di Modena
Modena, Italy

Received December 9, 1975

Assignment of a Methylated Sulfur Dioxide Structure, $[CH_3O{=}S{=}O]^+$, to the Species Present in CH_3F-SbF_5-SO_2 Solutions and Precipitation of a Salt of $[CH_3O{=}S{=}O]^+$ upon Addition of SO_2 to CH_3F-SbF_5-SO_2ClF

Sir:

The question of the structure of methyl fluoride-antimony fluoride mixtures in SO_2 and other solvents has received detailed study in Olah's group[1] and Gillespie's.[2] We now report that reaction of SO_2 with CH_3F-SbF_5 in SO_2ClF at −78° gives a white, filterable precipitate which is inferred, from experiments to be described, to contain the cation **1**, the product of methylation of sulfur dioxide. The accompanying anion may be SbF_6^- (eq 1) or $Sb_2F_{11}^-$.

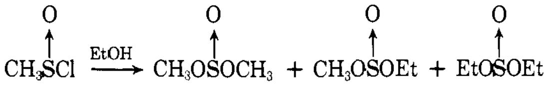
$$\underset{}{CH_3F\text{-}SbF_5 + SO_2 \xrightarrow{SO_2ClF} \underset{\textbf{1}}{[CH_3O{=}S{=}O]^+} + SbF_6^-} \quad (1)$$

We further propose that **1** is the principal[2] carbon-containing species present in SO_2 solutions of CH_3F-SbF_5. Presently, various Lewis complex structures, e.g., **2a** or **2b,** have been proposed to accomodate the rather extensive body of data pertaining to this system.[1,2] In **2a** or **2b,** but not in **1,** rapid exchange of carbon-fluorine bonds must be postulated to account for the absence of coupling to ^{19}F in the ^1H and ^{13}C NMR spectrum.

$$\underset{\textbf{2a}}{CH_3F \longrightarrow SbF_5} \qquad \underset{\textbf{2b}}{CH_3F \longrightarrow Sb_2F_{10}}$$

We have found that the solid formed from SbF_5 and CH_3F in SO_2ClF reacts with methanol or ethanol at −65° to give substantial amounts of dimethyl sulfite (**4**) or methyl ethyl sulfite (**5**).[3] Similarly, solutions of CH_3F-SbF_5 in SO_2 (1 M) appear to give sulfite esters in good yields upon reaction with methanol or ethanol. These products suggest that **1** is the reactant present in CH_3F-SbF_5-SO_2 and in the solid precipitated from SO_2ClF (eq. 1).

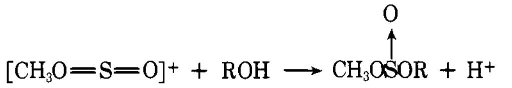
Two complicating circumstances must be mentioned. First, sulfite esters proved to undergo facile transesterification in acidic alcohol solutions. Our preparation of the reference sulfite **5** resulted in formation of **4** and **6** also (eq 2).[4,5] Accordingly, it is not surprising that the above mentioned reaction of 1 M CH_3F-SbF_5-SO_2 with EtOH (3 mol, −65°) gave a mixture of **4** (14%), **5** (41%), and **6** (36%), based on GC analysis of the ethanol solution.



$$CH_3\overset{\overset{O}{\uparrow}}{S}Cl \xrightarrow{EtOH} \underset{\textbf{4}}{CH_3O\overset{\overset{O}{\uparrow}}{S}OCH_3} + \underset{\textbf{5}}{CH_3O\overset{\overset{O}{\uparrow}}{S}OEt} + \underset{\textbf{6}}{EtO\overset{\overset{O}{\uparrow}}{S}OEt} \quad (2)$$

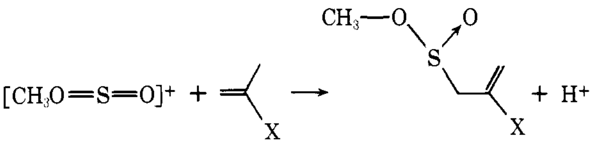
Second, SO_2 itself was shown to form some dimethyl sulfite (**4**) upon addition of 1 M SbF_5 in SO_2 to methanol, followed by workup with H_2O-CH_2Cl_2. However, the amount was only 18% of the amount of **4** (101% yield, GC; 82% distilled) formed by addition of 1 M CH_3F-SbF_5 to CH_3OH (3 mol, −65°).

Despite the complicating circumstances, the overall results appear to provide strong support for the hypothesis that most of the sulfite esters obtained from CH_3F-SbF_5-SO_2 arose from the initial reaction of cation **1** according to eq 3. The demonstration[3] that the solid material (eq 1) gives mainly methyl ethyl sulfite upon reaction with ethanol constitutes strong evidence that SO_2 is capable of forming a monomethylated derivative, strengthening the hypothesis that **1** may exist in SO_2 solutions. As expected, the ^1H NMR spectrum of the solid dissolved in SO_2 was identical with that of CH_3F-SbF_5 in SO_2.



$$\underset{\textbf{1}}{[CH_3O{=}S{=}O]^+} + ROH \longrightarrow CH_3O\overset{\overset{O}{\uparrow}}{S}OR + H^+ \quad (3)$$

That **1** (instead of **2a** or **2b**) is the *predominant* species present in CH_3F-SbF_5-SO_2 is indicated by the following argument. If **1** is present only in trace amounts in rapid equilibrium with **2a** or **2b**, the weak nucleophile SO_2 must be alkylated faster by **2a** or **2b** than the much more nucleophilic alcohols, in order to account for the formation of alkyl sulfites upon reaction of CH_3F-SbF_5-SO_2 with alcohols. A similar situation occurs in the case of the recently reported,[6] high yield "ene" reaction of CH_3F-SbF_5-SO_2 (eq 4), although in this instance the relative nucleophilicity of SO_2 and alkenes is not obvious.



(4)

Why has structure **2a** or **2b** been accepted while **1** was given only passing consideration? Below we reexamine five principal lines of evidence which provide insight into the situation. The evidence is shown to be compatible with structure **1.**

(1) Reactions with Alcohols. Alcohols previously were reported[1b] to give methyl ethers upon reaction with CH_3F-SbF_5-SO_2. The ethers (which may have been formed under different conditions, e.g., by reaction of moist SO_2 with CH_3F-SbF_5) provided no evidence for the incorporation of SO_2 in the reactant.

(2) Raman Spectra. Considerable reliance has been placed 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.

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

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·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.

References and Notes

(1) (a) G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *J. Am. Chem. Soc.*, **91**, 2112 (1969); (b) G. A. Olah, J. R. DeMember, R. H. Schlosberg, and Y. Halpern, *ibid.*, **94**, 156 (1972).

(2) J. Bacon and R. J. Gillespie, *J. Am. Chem. Soc.*, **93**, 6914 (1971).

(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.

(6) P. E. Peterson, R. Brockington, and M. Dunham, *J. Am. Chem. Soc.*, **97**, 3517 (1975).

(7) Converted from CS_2 reference by subtraction from 193.8 ppm.

(8) S. P. McManus and P. E. Peterson, unpublished values. Cf. S. P. McManus and P. E. Peterson, *Tetrahedron Lett.*, 2753 (1975).

(9) P. M. Henrichs and P. E. Peterson, *J. Am. Chem. Soc.*, **95**, 7449 (1973).

Paul E. Peterson,* Rhett Brockington, D. Warren Vidrine
Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

Received October 25, 1975

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).