Stable Carbonium Ions. CXVI.[1] Sulfonyl Halide–Antimony Pentafluoride Complexes and Study of Protonation and Cleavage of Sulfonyl Halides in Fluorosulfuric Acid–Antimony Pentafluoride–Sulfuryl Chloride Fluoride Solution

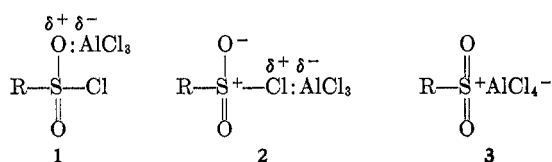GEORGE A. OLAH,* ALICE T. KU,[2] AND JUDITH A. OLAH

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Sulfonyl chlorides and fluorides form oxygen coordinated complexes with antimony pentafluoride. In "magic acid," FSO_3H-SbF_5 solution, diluted with SO_2ClF, sulfonyl halides are protonated on sulfonyl oxygen. Two isomeric forms were observed for protonated methanesulfonyl chloride and fluoride. For higher protonated homologs, only one isomer was found. No long-lived sulfonyl cations could be observed in any of the systems studied.

The reaction of acyl halides with aromatic compounds or olefins in the presence of Friedel–Crafts catalysts is one of the most commonly used reaction in organic chemistry. The mechanism of Friedel–Crafts acylation[3] was extensively studied and many intermediate acyl cations (oxocarbonium ions) were isolated and investigated by various methods, ir, nmr, etc.

The sulfonylation reaction can be regarded as a modification of the acylation reaction in which a sulfonyl group is substituted for a carbonyl group and the product is a sulfone instead of a ketone.[4] Olivier[5] was the first to study the mechanism of the sulfonylation reaction and the structure of addition complex between aluminum chloride and benzenesulfonyl chloride in the acid chloride as solvent. The existence of 1:1 addition complex was demonstrated. There has been no determination of the structure of the complex, but according to Jensen and Goldman[4] the following structures **1**, **2**, and **3** are possible. Brown and Jensen studied in detail the mechanism of the sulfonylation reaction[4] and based primarily on kinetic evidence, considered **1** and **3** to be present in equilibrium, with **3** being the effective sulfonylating agent.

Burton and Hopkins[6] claimed the use of sulfonylium perchlorates as reagents in sulfonylation reactions. It should be pointed out, however, that in the metathetic reactions of chlorides with silver perchlorate the elimination of silver chloride does not necessarily prove the formation of an ionic complex, as covalent perchlorates can also be formed.

$$RSO_2Cl + AgClO_4 = AgCl + RSO_2^+ClO_4^- \text{ or } RSO_2OClO_3$$
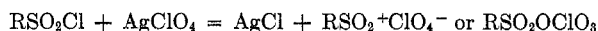
Klages and Malecki[7] subsequently studied "tosyl perchlorate" in the interaction of p-toluenesulfonyl chloride (bromide) with silver perchlorate in nitromethane solution. They concluded that sulfonyl cations in contrast to acyl cations are very electrophilic and react even with weakly nucleophilic anions to give sulfonyl halides. Thus, p-toluenesulfonyl bromide with anhydrous silver tetrafluoroborate gave only the sulfonyl fluoride and no aryl sulfone was formed. Toluene with p-toluenesulfonyl chloride and silver perchlorate, on the other hand, gave 4,4'-dimethyldiphenyl sulfone. As no direct physical observation of tosyl perchlorate was made, no conclusion can be reached whether it should be considered as the covalent ester $p\text{-}CH_3C_6H_4SO_2OClO_3$ or the ionic complex $p\text{-}CH_3C_6H_4SO_2^+ClO_4^-$.

Lindner and Weber claimed[8] the formation of the p-N,N-dimethylaminobenzenesulfonylium ion by the reaction of p-N,N-dimethylaminobenzenesulfonyl chloride with silver hexafluoroantimonate in sulfur dioxide solution.

$$p\text{-}(CH_3)_2N-C_6H_4SO_2Cl + Ag[MF_6] \xrightarrow[SO_2]{-25°}$$
$$[p\text{-}(CH_3)_2N-C_6H_4SO_2][MF_6] + AgCl$$
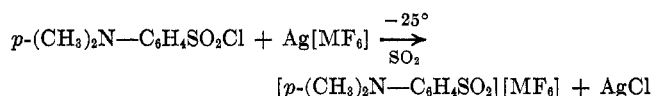
With the exception of Lindner and Weber's study,[8] no direct observation of the intermediate complexes was reported.[9] We wish now to report the antimony pentafluoride complexes of sulfonyl halides and the behavior of sulfonyl halides in the superacid system, FSO_3H-SbF_5.

Results and Discussion

We have extended our previous investigations of acyl halide–antimony pentafluoride complexes[10] to the study of sulfonyl halide complexes and also studied the behavior of sulfonyl halides in the superacid system, $FSO_3H-SbF_5-SO_2ClF$.

Preparation of the sulfonyl halide–antimony pentafluoride complexes was carried out according to our previously reported method for obtaining acyl halide complexes using excess antimony pentafluoride.[10]

The antimony pentafluoride complexes of sulfonyl halides and protonated sulfonyl halides were studied by nmr spectroscopy. Table I summarizes the pmr data obtained.

The following sulfonyl fluorides and chlorides were studied in both SbF_5-SO_2ClF and $FSO_3H-SbF_5-SO_2ClF$

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(1) Part CXV: G. Olah and R. D. Porter, *J. Amer. Chem. Soc.*, in press.

(2) National Institutes of Health Predoctoral Research Investigator, 1970.

(3) For summary, see F. R. Jensen and G. Goldman, in "Friedel–Crafts and Related Reactions," Vol. III, G. A. Olah, Ed., Wiley–Interscience, New York, N. Y., 1963–1964, p 1003.

(4) F. R. Jensen and G. Goldman, ref 3, p 1319.

(5) M. S. C. J. Olivier, *Recl. Trav. Chim. Pays-Bas*, **35**, 166 (1915).

(6) H. Burton and H. B. Hopkins, *J. Chem. Soc.*, 4457 (1952).

(7) F. Klages and F. E. Malecki, *Justus Liebigs Ann. Chem.*, **691**, 15 (1966); *Chem. Ber.*, **96**, 2054 (1963).

(8) E. Lindner and H. Weber, *ibid.*, **101**, 2832 (1968).

(9) After conclusion of our work, P. A. W. Dean and R. J. Gillespie, [*J. Amer. Chem. Soc.*, **91**, 7260 (1969)] reported the ¹⁹F nmr spectrum of a single donor:acceptor complex:the methanesulfonyl fluoride–antimony pentafluoride complex.

(10) (a) G. A. Olah, S. J. Kuhn, W. S. Tolgyesi, and E. B. Baker, *ibid.*, **84**, 2733 (1962); (b) G. A. Olah, *Rev. Chim. Acad. Raumain*, **7**, 1139 (1962); (c) G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, **88**, 3313 (1966).

TABLE I

PMR SPECTRAL PARAMETERS[a] OF THE PARENT AND PROTONATED SULFONYL
HALIDES AND SULFONYL HALIDE–ANTIMONY PENTAFLUORIDE COMPLEXES AT −60°

Compd	Registry no.	Solvent[b]	H₁	H₂	H₃	H₄	C₆H₅
$CH_3-S(=O)_2-F$ (1)	558-25-8	A	3.35 (d, 6.0)				
		B	4.40 (d, 7.0) / 4.26 (d, 7.0)				
		C	4.36 (d, 6.8)				
$CH_3-S(=O)_2-Cl$ (1)	124-63-0	A	3.70				
		B	4.73 / 4.60				
		C	4.70				
$CH_3CH_2-S(=O)_2-F$ (2,1)	754-03-0	D	3.71 (m)	1.70 (t, 7.0)			
		B	4.66 (m)	2.20 (t, 7.0)			
		C	4.65 (m)	2.20 (t, 7.2)			
$CH_3CH_2-S(=O)_2-Cl$ (2,1)	594-44-5	A	3.63 (q, 7.0)	1.63 (t, 7.0)			
		B	4.71 (q, 7.0)	2.23 (t, 7.0)			
		C	4.63 (q, 7.0)	2.10 (t, 7.0)			
$CH_3CH_2CH_2-S(=O)_2-F$ (3,2,1)	762-69-6	A	3.50 (m)	2.10 (m)	1.26 (t, 7.5)		
		B	4.50 (m)	2.65 (m)	1.70 (t, 7.0)		
		C	4.61 (m)	2.66 (m)	1.70 (t, 7.5)		
$CH_3CH_2CH_2-S(=O)_2-Cl$ (3,2,1)	10147-36-1	A −30°	3.81 (t, 7.5)	2.23 (m)	1.30 (t, 7.5)		
		B −40°	4.71 (t, 7.0)	2.63 (m)	1.63 (t, 7.0)		
		C	4.63 (m)	2.55 (m)	1.57 (t, 7.0)		
$CH_3CH_2CH_2CH_2-S(=O)_2-F$ (4,3,2,1)	660-12-8	A	3.60	1.96 (m)	1.63 (m)	1.15 (t, 7.2)	
		B	4.50 (m)	2.53 (m)	2.03 (m)	1.46 (t, 6.5)	
		C	4.56 (m)	2.47 (m)	2.00 (m)	1.45 (t, 6.5)	
$CH_3CH_2CH_2CH_2-S(=O)_2-Cl$ (4,3,2,1)	2386-60-9	A	3.81 (m)	2.10 (m)	1.66 (m)	1.20 (t, 6.0)	
		B	4.73 (m)	2.53 (m)	2.00 (m)	1.65 (t, 7.0)	
		C	4.66 (m)	2.50 (m)	2.00 (m)	1.46 (t, 6.0)	
$C_6H_5-S(=O)_2-F$	368-43-4	A					7.78
		B					8.42
		C					8.60
$C_6H_5-S(=O)_2-Cl$	98-09-9	A					7.90
		B					8.56
		C					8.50
$p\text{-}CH_3C_6H_4-S(=O)_2-F$ (1)	455-16-3	A	2.57				7.76
		B	2.93				8.25
		C	3.05				8.36
$p\text{-}CH_3C_6H_4-S(=O)_2-Cl$ (1)	98-59-9	A	2.57				7.73
		B	2.93				8.23
		C	3.12				8.40

[a] Chemical shifts are in parts per million from external TMS. Coupling constants in hertz are given in parenthesis following the multiplicities: d = doublet; t = triplet; q = quartet; m = multiplet. [b] A = SO_2ClF; B = $FSO_3H\text{-}SbF_5\text{-}SO_2ClF$; C = $SbF_5\text{-}SO_2ClF$; D = SO_2.

solutions: methanesulfonyl, ethanesulfonyl, propanesulfonyl, butanesulfonyl, benzenesulfonyl fluoride and chloride and toluenesulfonyl fluoride and chloride.

Sulfonyl Halide–Antimony Pentafluoride Complexes.—The pmr spectrum of **methanesulfonyl fluoride,** CH_3SO_2F, in SO_2ClF solution at $-60°$, showed a doublet at δ 3.35 with a coupling constant of 6.0 Hz. The ^{19}F spectrum consisted of a quartet at ϕ 59.0 (from external CCl_3F). Attempted ionization of methanesulfonyl fluoride in SbF_5–SO_2ClF solution to obtain the corresponding sulfonylium ion was unsuccessful. The pmr spectrum recorded at $-80°$ showed a methyl doublet at δ 4.41 with a H–^{19}F coupling of 6.8 Hz. The ^{19}F nmr spectrum showed the corresponding quartet at ϕ 58.6, further indicating that the fluorine atom is still bonded to sulfur and is further shielded by complex formation on sulfonyl oxygen atom with SbF_5. Thus, we conclude, as also indicated by Dean and Gillespie's ^{19}F study,[9] that the oxygen bonded donor:acceptor complex 1 is formed.
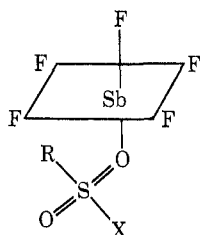
1, R = CH_3; X = F or Cl

Methanesulfonyl chloride in excess SbF_5 diluted with SO_2ClF at $-80°$ showed a singlet at δ 4.56 deshielded about 0.86 ppm from that of the parent compound, indicating again the oxygen coordinated complex 1.

Ethanesulfonyl fluoride in antimony pentafluoride–SO_2ClF solution showed the deshielded CH_2 multiplets at δ 4.77 and the methyl triplet at δ 2.23. The CH_2–F coupling (7.0 Hz) observed indicates that the oxygen coordinated donor:acceptor complex is formed.

The nmr spectrum of **ethanesulfonyl chloride** in antimony pentafluoride diluted with SO_2ClF similarly showed the methylene quartet at δ 4.63 and the methyl triplet at δ 2.10.

n-Propanesulfonyl chloride, n-propanesulfonyl fluoride, n-butanesulfonyl chloride and **n-butanesulfonyl fluoride** in SbF_5–SO_2ClF solution also gave the sulfonyl oxygen coordinated donor:acceptor complexes. The pmr chemicals shifts and coupling constants are summarized in Table I, together with those of the parent sulfonyl halides. The H–^{19}F coupling observed in the complexes of propanesulfonyl fluoride and butanesulfonyl fluoride indicates that fluoride atoms are still bonded to sulfur and no sulfonylium ions are formed.

Benzenesulfonyl chloride and **fluoride** in SbF_5–SO_2ClF also form the donor:acceptor complexes with the aromatic protons centered at δ 8.50 and 8.60, respectively (about 0.6 ppm deshielded from the parent compounds in SO_2ClF).

The nmr spectrum of *p*-**toluenesulfonyl fluoride** and **chloride** in SbF_5–SO_2ClF showed the aromatic AB quartets at δ 8.36 and 8.40 (about 0.6 ppm deshielded from those of the parent compounds) and the methyl protons at δ 3.05 and 3.12, respectively, indicating that the donor:acceptor complexes are again formed. Furthermore, a ^{19}F spectrum of *p*-toluenesulfonyl fluoride–

antimony pentafluoride complex showed a fluorine resonance in the –SO_2F region at ϕ 64.8, implying that the fluoride atom is still bonded to the sulfur atom.

Cleavage Reactions of the Sulfonyl Halide–Antimony Pentafluoride Complexes.—The **methanesulfonyl fluoride–antimony pentafluoride** complex is thermally stable; the nmr spectrum showed no significant change from -80 to $+65°$. **Methanesulfonyl chloride–antimony pentafluoride** complex at $+20°$ undergoes chlorine–fluorine exchange to give the methanesulfonyl fluoride–antimony pentafluoride complex, but it is not cleaved or decomposed.

Ethanesulfonyl chloride–antimony pentafluoride complex at $+20°$ undergoes both chlorine–fluorine exchange and alkyl–sulfur cleavage, to give ethyl cation which rearranges to the more stable *tert*-butyl and *tert*-hexyl cations.[11] The same behavior was also observed in the case of the **ethanesulfonyl fluoride–antimony pentafluoride** complex.[12]

Both **propanesulfonyl fluoride–antimony pentafluoride** complex and **propanesulfonyl chloride–antimony pentafluoride** complex at $+15°$ undergo alkyl–sulfur cleavage to give the (propyl cation) which is not observed as such and is immediately rearranged to the more stable *tert*-hexyl cations.

X = Cl, F
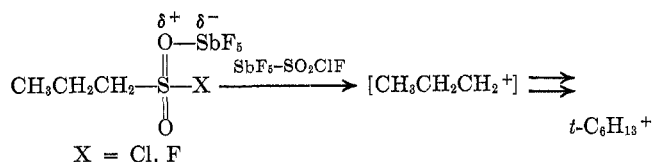
The **butanesulfonyl fluoride–antimony pentafluoride** and **butanesulfonyl chloride–antimony pentafluoride** complexes are stable up to $-10°$. At higher temperatures, alkyl–sulfur cleavage occurs to give the *tert*-butyl cation, as shown by a sharp singlet in the pmr spectra of the system at δ 4.10.

The donor:acceptor complex of **benzenesulfonyl fluoride** and **chloride** and **toluenesulfonyl fluoride** and **chloride** are stable. The nmr spectra showed no significant change from $-60°$ to room temperature.

Our system is not well adaptable to study *p-N,N*-dimethylaminobenzenesulfonyl halides, as complexing on nitrogen cannot be avoided. We therefore have no data on the claimed highly stabilized *p*-$(CH_3)_2NC_6H_4SO_2^+$ ion.[8] As metathetic reactions with silver salts frequently run into serious difficulties, we await with interest further data, including nmr studies, on this reported system which presently seems to be the only claimed example of a stable sulfonylium ion.

Prontonated Sulfonyl Halides.—All the alkylsulfonyl halides studied are protonated in FSO_3H–SbF_5–SO_2 superacid system on sulfonyl oxygen. Although the proton on oxygen is not directly observed, yet the protonation is evident by the deshielding of the alkyl pro-

X = F, Cl; R = CH_3–, CH_3CH_2–, $CH_3CH_2CH_2$–, $CH_3CH_2CH_2CH_2$–, C_6H_5–, *p*-$CH_3C_6H_4$–
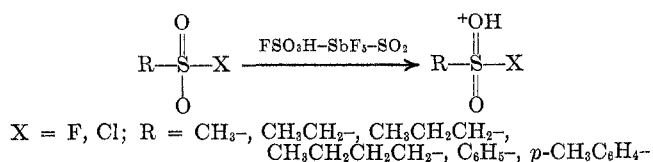
(11) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2227 (1967).

(12) The reversibility of the reaction was recently observed in the reaction of the ethyl fluoride–antimony pentafluoride complex with sulfur dioxide: G. A. Olah and J. R. DeMember, unpublished work.

ton nmr chemical shifts and the proton–fluorine coupling observable in protonated sulfonyl fluorides (see Table I).

The pmr spectrum of **protonated methanesulfonyl fluoride** in FSO_3H–SbF_5–SO_2ClF solution at $-60°$ showed two doublets at δ 4.40 and 4.26 (J_{HF} = 7.0 Hz) with a relative area ratio of 30:70. This indicates, as in the case of the previously observed protonated methyl sulfone,[13] that two isomeric species (**2a** and **2b**, where X = F) are present.

X = Cl, F

The coupling (7.0 Hz) between CH_3 and F indicates that the fluorine atom is still bonded to the sulfur atom and is not rapidly exchanging. It is interesting to note that only one isomeric form was observed for the methanesulfonyl fluoride–antimony pentafluoride complex. This is believed to be due to the steric effect of antimony pentafluoride which is much larger than the proton and sterically favors one form.

For **protonated methanesulfonyl chloride**, two forms (**2a** and **2b**, where X = Cl) are again observed. The pmr spectrum recorded at $-60°$ showed the two methyl singlets at δ 4.75 and 4.60 with a relative area ratio of 60:40.

For protonated higher homologs of sulfonyl halides only one isomeric form is observed. No observable coupling was found between the proton on oxygen and the α-alkyl protons; hence no structural assignments could be made. Chemical shifts and coupling constants are summarized in Table I.

Cleavage Reactions of Protonated Sulfonyl Halides.—Protonated alkylsulfonyl chlorides in FSO_3H–SbF_5–SO_2ClF solution undergo chlorine–fluorine exchange at $-10°$ to give the corresponding protonated sulfonyl fluoride. **Protonated methanesulfonyl fluo-**

(13) G. A. Olah, A. T. Ku, and J. A. Olah, *J. Org. Chem.*, in press.

ride is stable with no indication of cleavage even when the solution was heated up to $+65°$. **Protonated ethanesulfonyl fluoride** is also stable. The pmr spectrum showed no significant change from $-60°$ to room temperature. On further heating to $+40°$, the solution

R = CH_3–, CH_3CH_2–, $CH_3CH_2CH_2$–, $CH_3CH_2CH_2CH_2$–

turned dark and solidified. **Protonated propanesulfonyl fluoride** at $+10°$ undergoes alkyl–sulfur cleavage to give, through alkylative dimerization of the propyl cation, *tert*-hexyl cations. **Protonated *n*-butanesulfonyl fluoride** also undergoes alkyl–sulfur cleavage to give the *tert*-butyl cation at $-10°$. **Protonated benzenesulfonyl fluoride** and **chloride** and **p-toluenesulfonylfluoride** and **chloride** are stable. The nmr spectrum showed no significant change from $-60°$ to room temperature.

Experimental Section

Materials.—All the alkylsulfonyl chlorides and methanesulfonyl fluoride were commercially available materials. Ethane-, propane-, and butanesulfonyl fluoride were prepared by the method of Davis and Dick[14] by heating the corresponding sulfonyl chloride with 70% KF solution on a water bath for 20 min followed by distillation and extraction with ether.

Nmr Spectra.—Varian Associates Model A-56/60A spectrometer, equipped with a variable temperature probe, was used for all spectra. Chemical shifts are reported in ppm (δ) from external (capillary) tetramethylsilane or ppm (ϕ) from capillary $CFCl_3$.

Preparation of Solutions.—The procedures used for the preparation of solutions of the protonated sulfonyl halides and the sulfonyl halide–antimony pentafluoride complexes were identical with those described previously.[15,16]

(14) W. Davis and J. H. Dick, *J. Chem. Soc.*, 483 (1932).
(15) G. A. Olah, D. H. O'Brien, and A. M. White, *J. Amer. Chem. Soc.*, **89**, 5694 (1967).
(16) G. A. Olah and A. T. Ku, *J. Org. Chem.*, **35**, 331, 2159 (1970).