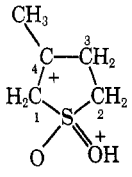
at −30° showed two triplets at δ 4.50 and 3.68, indicating two adjacent methylene groups formed. In addition to these two methylene groups, the nmr spectrum showed two singlets at δ 2.70 and 7.30. Diprotonation on the sulfonyl oxygen and the carbon–carbon double bond would presumably lead to the dication **4**. However, upon comparison of the pmr chemical shifts with that of 1-methylcyclopentyl cation **5**[18] ($CH_3-\overset{+}{C}<$) at δ 3.98) it appears that the methyl and methylene chem-

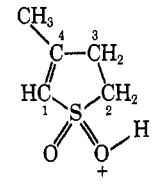


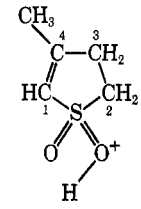
4

5

ical shifts, except that of the methylene protons between the two positive centers, are at too high field to be considered as species **4**. Noteworthy is also that the long-range coupling (J_{HH} = 4.0 cps) of the methylene and methyl protons through the sp^2 hybridized center of ion **5** is absent. Furthermore, integration showed the relative area ratio of the resonances at δ 2.70, 3.68, 4.50, and 7.30 is 3:2:2:1 indicating that there is only one proton on carbon 1. This indicates that structure **6** is in accord with the nmr data. Thus as soon as ion **4** is

(18) G. A. Olah, J. M. Bollinger, C. A. Cupas, and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2692 (1967).





6

formed, it undergoes deprotonation to form a double bond conjugated to the protonated sulfonyl group. At −60° the nmr spectrum shows a small singlet at δ 2.83, broad multiplets at δ 3.86, 4.90, and a weak resonance at δ 7.50 in addition to the major resonances. This probably indicates as in the case of protonated dimethyl sulfone, that two isomeric species of **6** are present.

Experimental Section

Materials.—All sulfoxides and sulfones were commercially available materials.

Nmr Spectra.—Varian Associates Model A-56/60A spectrometer with variable-temperature probe was used for all spectra.

Preparation of Protonated Sulfoxides and Sulfones.—The procedure used for the preparation of solutions of protonated sulfoxides and sulfones was identical with that described previously.[19]

Acknowledgment.—Support of this work by a grant from the National Institutes of Health is gratefully acknowledged.

(19) G. A. Olah, D. H. O'Brien, and A. M. White, *ibid.*, **89**, 5694 (1967).

Stable Carbonium Ions. CVI.[1] Protonation and Cleavage Reactions of Alkyl- and Arylsulfonic Acids and -sulfinic Acids and Alkyl Sulfonates and Sulfinates in Fluorosulfuric Acid–Antimony Pentafluoride Solution

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Received April 9, 1970

A series of sulfonic acids, sulfinic acids, and sulfonates were protonated in fluorosulfuric acid–antimony pentafluoride–sulfuryl chloride fluoride solution at low temperature (−60°). Two isomers were found for both protonated methanesulfonic acid and methyl methanesulfonate. At higher temperatures, protonated methane-, benzene-, and toluenesulfonic acid underwent dehydration to give the suggested sulfonylium ion which is not observed as it quickly picks up a fluoride ion from the acid system to form the corresponding sulfonyl fluoride. For protonated higher alkyl homologs, carbonium ions are the cleavage products. Protonated methyl methanesulfonate and methyl benzenesulfonate underwent alkoxy–sulfur cleavage whereas alkyl–oxygen cleavage was found for protonated ethyl and propyl methanesulfonate. Protonated sulfinic acids and methyl methanesulfinate are very stable; no cleavage reaction was observed.

Our recent investigations of protonated thiocarboxylic acids, *S*-alkyl esters,[3] dithiocarboxylic acids, thion esters, and dithio esters[4] lead us to study the protonation of a series of sulfonic acids, sulfinic acids, sulfonates, and sulfinates in the strong acid system, FSO_3H–SbF_5–SO_2ClF. No systematic studies relating to these systems in superacid solutions was previously reported.

Hantzsch[5] in 1908 studied the cryoscopic behavior of the sodium salts of benzene-, *m*-nitrobenzene-, and *p*-toluenesulfonic acids in sulfuric acid, and concluded that benzene- and *p*-nitrobenzenesulfonic acids behave as nonelectolytes in sulfuric acid while *p*-toluenesulfonic acid behaves as a weak base. Gillespie[6] carried out similar measurements on solutions of sodium benzenesulfonate and sodium *p*-toluenesulfonate in slightly aqueous sulfuric acid and concluded that these acids behave as weak bases. The conductimetric behavior of methanesulfonic acid in sulfuric acid studied by Gillespie and

* To whom correspondence should be addressed.

(1) Part CV: G. A. Olah, A. T. Ku, and J. A. Olah, *J. Org. Chem.*, **35**, 3904 (1970).

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

(3) G. A. Olah, A. T. Ku, and A. M. White, *J. Org. Chem.*, **34**, 1827 (1969).

(4) G. A. Olah and A. T. Ku, *ibid.*, **35**, 331 (1970).

(5) R. Hantzsch, *Z. Phys. Chem.*, **65**, 41 (1908).

(6) R. J. Gillespie, *J. Chem. Soc.*, 2542 (1950).

TABLE I

PMR CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS[b] OF THE PARENT AND PROTONATED SULFONIC ACIDS

Compd	Registry no.	Solvent	Temp, °C	OH	CH_3	α-CH_2	β-CH_2	γ-CH_2
CH_3SO_3H	75-75-2	SO_2[c]	−60	10.9 (s)	3.1 (s)			
	26428-16-0[d]	FSO_3H–SbF_5 SO_2ClF	−60		4.07 (s) 4.15 (s)			
$CH_3CH_2SO_3H$	594-45-6	SO_2ClF	−40	12.2 (s)	1.58 (t, 7.0)[b]	3.43 (q, 7.0)		
	26428-17-1[d]	FSO_3H–SbF_5 SO_2ClF	−60		2.18 (t, 7.0)	4.50 (q, 7.0)		
$CH_3CH_2CH_2SO_3H$	5284-66-2	SO_2ClF	−10	11.8	1.27 (t, 7.5)	3.51 (t, 7.5)	2.13 (m)	
	26428-18-2[d]	FSO_3H–SbF_5 SO_2ClF	−60		1.58 (t, 7.0)	4.26	2.53 (m)	
$CH_3CH_2CH_2CH_2SO_3H$	2386-47-2	SO_2ClF	−40	12.7	1.17 (t, 7.0)	3.43	1.85 (m)	1.60 (m)
	26428-19-3[d]	FSO_3H–SbF_5 SO_2ClF	−60		1.53 (t, 7.0)	4.46	2.50 (m)	2.10 (m)

[a] In parts per million from external TMS. [b] The coupling constants are indicated in hertz next to the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. [c] Methanesulfonic acid does not dissolve in SO_2ClF. [d] Protonated.

coworkers[7] was interpreted in terms of its behavior as either a nonelectrolyte or as a very weakly ionized base. Hall and Robinson[8] studied the cryoscopic behavior of sodium *p*-toluenesulfonate and sodium 2,4-dinitrobenzenesulfonate in sulfuric acid and found that the ionization goes according to the following example.

$$p\text{-}CH_3C_6H_4SO_3Na + H_2SO_4 = CH_3C_6H_4SO_3H + Na^+ + HSO_4^-$$

Thus they concluded that these arylsulfonates behave as nonelectrolytes in sulfuric acid.

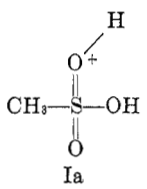
Results and Discussion

Sulfonic Acids.—In the superacid system, FSO_3H–SbF_5, all the sulfonic acids studied were protonated.

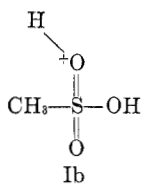
$$RSO_3H \xrightarrow[-60°]{FSO_3H\text{–}SbF_5\text{–}SO_2ClF} R\overset{+}{S}O_3H_2$$

The protonation is evident by the deshielded nmr chemical shifts of the alkyl protons of the protonated species as compared to those of the parent compounds in SO_2ClF (see Table I). It is presumed that the protonation occurred on sulfonyl oxygen. The S–OH protons of protonated sulfonic acids could not be seen in the nmr spectra but their chemical shift might be expected to be similar to that of the acid solvent system (δ 11–12.8). Assignments of derived chemical shifts and coupling constants of the parent and protonated sulfonic acids studied: methane-, ethane-, propane-, and butanesulfonic acid are summarized in Table I.

Protonated methanesulfonic acid at −60° shows two sharp singlets at δ 4.15 and 4.07 with a relative area ratio of 60:40 for the methyl protons. This indicates the existence of two isomeric species possibly Ia and Ib due to hindered rotation about the S—O bond and further indicates that the initial protonation is on sulfonyl oxygen. No coupling was observed between the methyl protons and the protons on oxygen. Therefore,



Ia



Ib

no structural assignments of protonated methanesulfonic acid could be made based on the present data.

The nmr spectrum of **protonated ethanesulfonic acid** showed only one set of triplet and quartet at δ 2.18 and 4.50, respectively, indicating that only one isomer exists, or at least the concentration of the other is so low that it is not observed under the experimental condition.

In the protonation of higher homologs, again only one isomer is observed (presumably there is one sterically favored isomer, although based on available data no assignment of structure can be made).

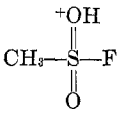
Cleavage Reactions of Protonated Sulfonic Acids.—Protonated methanesulfonic acid is stable up to +10°. At higher temperature, cleavage reactions occurred. At +20°, the pmr spectrum shows a doublet at δ 4.50 (J = 7.0 Hz) similar to that found in the methanesulfonyl fluoride–antimony pentafluoride complex in SbF_5–SO_2ClF solution and also similar to that of protonated methanesulfonyl fluoride in FSO_3H–SbF_5–SO_2ClF solution. The ^{19}F nmr spectrum of this cleavage product shows the fluorine resonance as a quartet at ϕ 58.6 downfield from $CFCl_3$ with a coupling constant of 7.0 Hz. These data indicate that methanesulfonyl fluoride indeed is formed in the cleavage reaction. In addition, the pmr spectrum of the solution also displays a very strong intense H_3O^+ peak indicating that dehydration had occurred.

It is evident that, if the methylsulfonylium ion is formed by dehydration during the cleavage reaction, it appears to react immediately with fluoride ion (from its gegenion or the solvent system) to form methanesulfonyl fluoride which in turn gives the methanesulfonyl fluoride–antimony pentafluoride donor:acceptor complex. In "magic acid," FSO_3H–SbF_5 solution, the

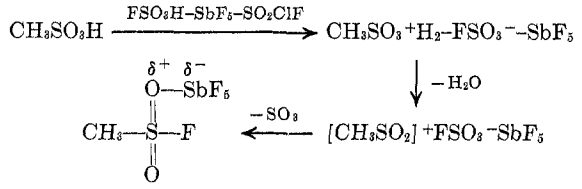
(7) J. Barr, R. J. Gillespie, and E. A. Robinson, *Can. J. Chem.*, **39**, 1266 (1961).

(8) S. K. Hall and E. A. Robinson, *ibid.*, **42**, 1113 (1964).

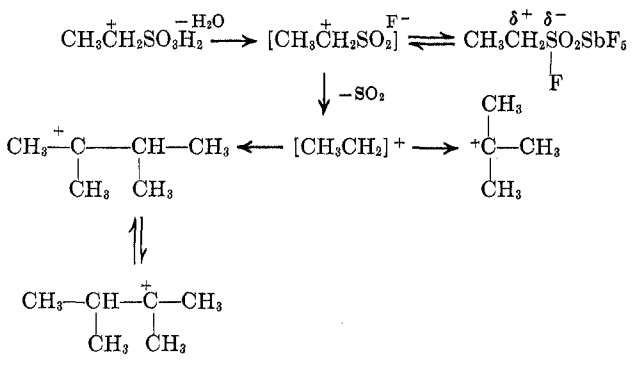
methanesulfonyl fluoride formed could also possibly be in the protonated form



We have found, however, that methanesulfonyl fluoride in FSO_3H–SbF_5 solution diluted with SO_2ClF, gave two protonated species, whereas only one isomer of the donor:acceptor complex[9] was found for methanesulfonyl fluoride in SbF_5–SO_2ClF solution. The obvious explanation can be a steric effect, due to the bulkiness of SbF_5. In the cleavage reaction of protonated methanesulfonic acid thus obviously the donor:acceptor complex of the sulfonyl fluoride–antimony pentafluoride is formed.



Protonated ethanesulfonic acid at room temperature also undergoes dehydration. After the solution of protonated ethanesulfonic acid in FSO_3H–SbF_5–SO_2ClF has stood at room temperature for about 15 min, the nmr spectrum shows in addition to the resonances of protonated ethanesulfonic acid, a methyl triplet at δ 2.23 and a methylene quartet at δ 4.60 assignable to the donor:acceptor complex, $CH_3CH_2\overset{\delta+}{S}O_2F\overset{\delta-}{S}bF_5$. When the solution was allowed to stand at room temperature for a longer period of time, alkyl–sulfur cleavage occurs to give the ethyl cation[10] which is not stable in the medium and immediately reacts further to the stable *tert*-butyl and *tert*-hexyl cations.



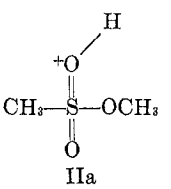
Protonated *n*-propane- and isopropanesulfonic acid at room temperature undergo cleavage reaction to give *tert*-hexyl cations. Similarly, **protonated butanesulfonic acid** at room temperature gives the *tert*-butyl cation. The protonated acids first are assumed to undergo dehydration (indicated by the intense H_3O^+ peak at δ 10.2) to give the corresponding alkyl sulfonyl cations which undergo alkyl–sulfur cleavage to give the related alkyl cations (*n*-propyl, isopropyl and *n*-butyl cation). The primary and secondary cations are not observed, since they are not stable under the reaction conditions and immediately rearrange to the stable *tert*-hexyl and *tert*-butyl cations, respectively.

Protonated **benzenesulfonic acid** could not be observed in FSO_3H–SbF_5–SO_2ClF solution even at $-60°$. The nmr spectrum of benzenesulfonic acid in FSO_3H–SbF_5–SO_2ClF at $-60°$ showed a strong H_3O^+ peak indicating that dehydration occurred. The aromatic protons centered at δ 8.43, similar to that of benzenesulfonyl fluoride–antimony pentafluoride complex (δ 8.49). It, therefore, is indicated that benzenesulfonic acid is first protonated in FSO_3H–SbF_5–SO_2ClF solution, followed by dehydration to give the benzenesulfonylium ion which then quickly abstracts fluoride ion from the gegenion or solvent to form the benzenesulfonyl fluoride–antimony pentafluoride complex.

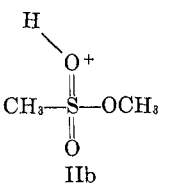
Protonated *p*-toluenesulfonic acid could not be observed either. *p*-Toluenesulfonic acid in FSO_3H–SbF_5–SO_2ClF solution, just as in the case of benzenesulfonic acid, gave the donor:acceptor complex of p-$CH_3C_6H_4\overset{\delta+}{S}O_2(F)\overset{\delta+}{S}bF_5$ (ArH, δ 8.33; CH_3, δ 3.00).

Alkyl Sulfonates.—Alkyl sulfonates in FSO_3H–SbF_5–SO_2ClF solution are protonated on the sulfonyl oxygen. Again, as in the case of protonated sulfonic acids, the S–OH protons of the protonated sulfonates cannot be directly observed. The protonation is evident by the deshielding of the alkyl proton chemical shifts of the protonated sulfonates as compared to those of the corresponding parent sulfonates in SO_2ClF (see summary of data in Table II).

The nmr spectrum of **methyl methanesulfonate** in FSO_3H–SbF_5–SO_2ClF solution at $-60°$ shows two singlets at δ 4.80 and 4.03 for the OCH_3 and $-CH_3$ protons, respectively. Two shoulders at δ 4.70 and 3.93 are also observed indicating, as in the case of protonated methanesulfonic acid, that two isomeric species (IIa and IIb) are present.



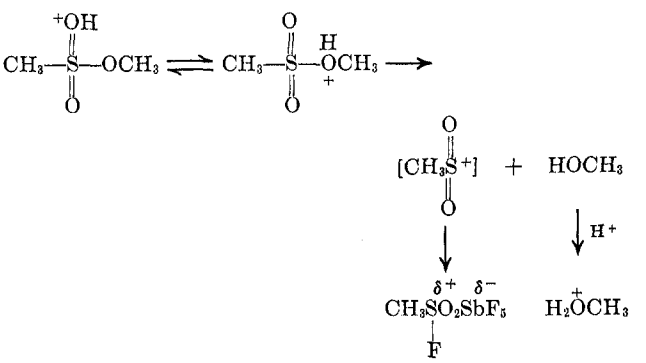
IIa



IIb

No coupling was observed between the proton on oxygen and the methyl protons. Therefore, no differentiation and assignment of the structures could be made. At $-30°$, only the singlets at δ 4.80 and 4.03 for the major isomer were observed. (The observation of the lower temperature spectrum is, however, reversible.)

Protonated methyl methanesulfonate is stable up to $+20°$. At room temperature it undergoes alkoxy–sulfur cleavage and reacts with the acid solvent system to



(9) G. A. Olah, A. T. Ku, and J. A. Olah, *J. Org. Chem.*, **35**, 3925 (1970).

(10) The reversibility of this cleavage was found by reacting the C_2H_5F → SbF_5 complex with SO_2 to give ethanesulfonyl fluoride (G. A. Olah, J. R. DeMember, and R. H. Schlosberg, unpublished work).

TABLE II

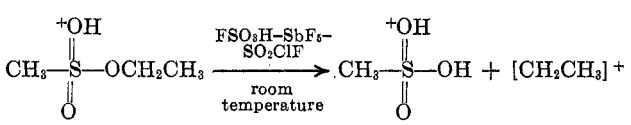
PMR CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS (IN HERTZ)[b] OF THE PARENT AND PROTONATED SULFONATES

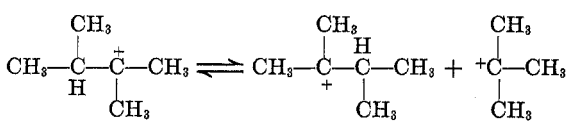
Compd	Registry no.	Solvent	Temp, °C	CH_3–S	α-CH_2	β-CH_2	–CH_3	Aromatic H
$CH_3SO_2OCH_3$	66-27-3	SO_2ClF	−60	3.03 (s)			3.96 (s)	
	26428-20-6[b]	FSO_3H–SbF_5 SO_2ClF	−60	4.03 (s) 3.93 (s)			4.80 (s) 4.70 (s)	
$CH_3SO_2OCH_2CH_3$	62-50-0	SO_2ClF	−60	3.11 (s)	4.47 (q, 7.5)		1.55 (t, 7.5)	
	26428-21-7[b]	FSO_3H–SbF_5 SO_2ClF	−60	4.21 (s)	5.80 (q, 7.0)		2.18 (t, 7.0)	
$C_6H_5SO_2OCH_3$	80-18-2	SO_2ClF	−60				3.80 (s)	7.90
	26428-22-8[b]	FSO_3H–SbF_5 SO_2ClF	−60				4.80 (s)	8.36

[a] Same as that of Table I. [b] Protonated.

give the methanesulfonyl fluoride–antimony pentafluoride complex.

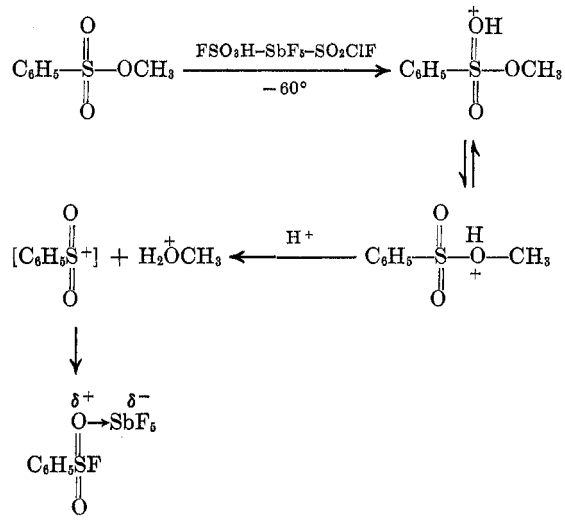
Ethyl methanesulfonate is protonated in FSO_3H–SbF_5–SO_2 solution (chemical shifts and coupling constants are given in Table II). The protonated species is stable up to +10°. After the sample stood at room temperature for about 10 min, the nmr spectrum shows resonances characteristic for the *tert*-butyl cation, the *tert*-hexyl cations, and protonated methanesulfonic acid in addition to those of protonated ethyl methanesulfonate. This indicates as shown in the following equation that alkyl oxygen cleavage occurred to give ethyl cation which then forms the stable *tert*-butyl and *tert*-hexyl cations.





Protonated propyl methanesulfonate in FSO_3H–SbF_5–SO_2ClF solution could not be observed even at a temperature as low as −80°. The nmr spectrum showed only the *tert*-hexyl cations and protonated methanesulfonic acid, indicating complete cleavage by the time spectra were obtained. **Butyl methanesulfonate** under similar conditions gave the *tert*-butyl cation and protonated methanesulfonic acid.

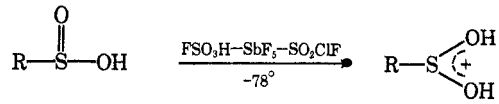
The nmr spectrum of protonated **methyl benzenesulfonate** recorded at −80° showed the methyl singlet at δ 4.86 and the ring protons centered at δ 8.43. At room temperature protonated methyl benzenesulfonate undergoes alkoxy–sulfur cleavage to give protonated methanol (CH_3 at δ 4.80 and $\overset{+}{O}H_2$ at 9.42 at −60°) and the benzenesulfonyl fluoride–antimony pentafluoride complex with a chemical shift of δ 8.46 for the aromatic protons. The cleavage reaction again can be represented as in the following reactions.



Sulfinic Acids and Sulfinates.—No direct investigation relating to the protonation of alkyl- or arylsulfinic acids and sulfinates in superacid system have been reported so far in the literature. Sulfination of aromatics by sulfur dioxide[11] and the reactions of benzenonium ions with sulfur dioxide is known[12,13] and was studied also in strong acid media to yield protonated arylsulfinic acids.[14]

In continuation of our study of the protonation of sulfonic acids, we considered it of interest to extend our investigation to the protonation of sulfinic acids and sulfinates in the extremely strong acid system.

Methane-, benzene-, and toluenesulfinic acid studied were all protonated on the sulfinyl oxygen at low temperature. The nmr spectrum showed the S–OH protons as a singlet at δ 9.12 to 9.40. The pmr chemical



(11) G. A. Olah, "Friedel-Crafts and Related Reactions," Vol. I, Wiley-Interscience, New York, N. Y., 1963, Chapter 2.

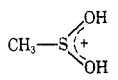
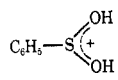
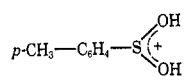
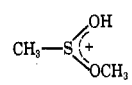
(12) G. A. Olah, C. U. Pittman, Jr., E. Namanworth, and M. B. Comisarow, *J. Amer. Chem. Soc.*, **88**, 5571 (1966).

(13) M. Brookhart, F. A. L. Anet, and S. Winstein, *ibid.*, **88**, 5657 (1966).

(14) G. A. Olah, R. H. Schlosberg, D. P. Kelly, and Gh. D. Mateescu, *ibid.*, **92**, 2546 (1970).

TABLE III

PMR CHEMICAL SHIFTS[a] OF PROTONATED SULFINIC ACIDS AND METHYL METHANESULFONATE IN FSO_3H–SbF_5–SO_2ClF SOLUTION

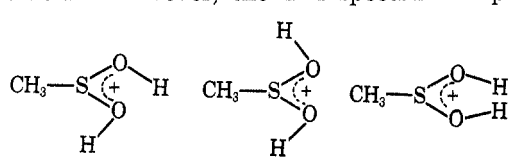
Compd	Registry no.	Temp, °C	S–OH	CH_3	OCH_3	Aromatic H
	26428-23-9	−60	9.40 (s)	3.93 (s)		
	26428-24-0	−80	9.30 (s)			8.05 to 8.56
	26428-25-1	−80	9.12 (s)	2.78		8.00
	26428-26-2		8.93 (s)	3.70 (s)	4.66 (s)	

[a] Same as that of Table I.

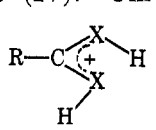
shifts and coupling constants of protonated sulfinic acids are summarized in Table III.

Protonated **methanesulfinic acid,** at −60° gave an nmr spectrum having a methyl singlet at δ 3.93 and one S–OH singlet at δ 9.40 with a relative area ratio of 2:3. These resonances, although broad, showed no couplings.

As in the case of protonated simple carboxylic acids,[10] thiocarboxylic acids,[3] and dithiocarboxylic acids,[4] one would expect that two or even three possible isomers (IIIa, IIIb, IIIc) would exist for protonated methanesulfinic acid. However, the nmr spectrum of protonated methanesulfinic acid at −80° indicated that only one isomer exists. An attempt was made in order to see if the S–OH resonances could be resolved into two singlets, as in the case of the predominant isomers of protonated carboxylic acids[10] (IV) and protonated dithiocarboxylic acids[4] (IV). Unfortunately, at temperatures lower than −80°, the solution became very viscous and the resonance became broad. Therefore, the structure of the protonated sulfinic acid could not be assigned.



IIIa IIIb IIIc



IV

X = O, S

Benzene- and *p*-toluenesulfinic acid in FSO_3H–SbF_5–SO_2ClF solution are also protonated on the sulfinyl oxygen. The pmr chemical shifts are summarized in Table III.

The protonated sulfinic acids studied are extremely stable. No cleavage reactions could be observed even when the solutions were heated up to +65°.

The only sulfinate we studied in the present work was **methyl methanesulfinate.** The nmr spectrum of methyl methanesulfinate in FSO_3H–SbF_5 solution diluted with SO_2ClF showed a singlet in the S–OH region at δ 8.93 indicating that it is also protonated on the sulfinyl oxygen. The pmr chemical shifts of the parent and protonated methyl methanesulfinate are given in Table III.

No couplings were observed between the S–OH protons and the two methyl protons. Hence, the structure of protonated methyl methanesulfinate could not be assigned.

Protonated methyl methanesulfinate is very stable. No cleavage reaction occurred even when the solution was standing at room temperature for days.

Experimental Section

Materials.—All the compounds used in this study were commercial available reagents except methanesulfinic acid and methyl methanesulfinate.

Methanesulfinic acid were prepared by the method described by Cram and coworkers[15] by the reaction of distilled water and methanesulfinyl chloride at −30° under dry nitrogen. The methanesulfinyl chloride was prepared following the method of Douglass and coworkers[16] by the reaction of chlorine and methyl disulfide in glacial acetic acid at low temperature. Methyl methanesulfinate was also prepared by the method described by Douglass[17] by the reaction of methanesulfinyl chloride and methanol at −30°.

Nmr Spectra.—Varian Associates Model A-56/60A with variable-temperature probes was used for all spectra.

Preparation of Solutions.—The procedure used for the preparation of solutions of the protonated sulfonic acids, sulfonates, sulfinic acid, and methyl methanesulfinate was identical with that described previously.[18]

Acknowledgment.—Support of our work by a grant from the National Institutes of Health is gratefully acknowledged.

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