

Fluorosulfuric Acid and Related Superacid Media

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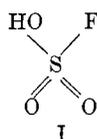
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Fluorosulfuric acid is one of the most highly acidic media that have been investigated in any detail. Its physical and chemical properties are described. It has proved to be a very useful solvent for studying the protonation of very weak bases, particularly as its low freezing point, -88.98° , has enabled the nmr spectra of the protonated forms of many weak bases to be observed. The acidity of fluorosulfuric acid may be further increased by the addition of SbF_5 and of both SbF_5 and SO_3 . Acids such as $\text{H}[\text{SbF}_5(\text{SO}_3\text{F})]$ and $\text{H}[\text{SbF}_2(\text{SO}_3\text{F})_4]$ are formed in these systems. These still more acidic media have also proved very useful in the study of protonation reactions and for the formation of carbonium ions and related species. By oxidizing iodine with $\text{S}_2\text{O}_8\text{F}_2$ the cations I_2^+ , I_3^+ , I_5^+ , and I_8^{2+} have been obtained in solution in fluorosulfuric acid, and by the oxidation of selenium with $\text{S}_2\text{O}_8\text{F}_2$ in HSO_3F the cations Se_4^{2+} and Se_8^{2+} have been obtained. From a solution of Se_4^{2+} in HSO_3F the compound $\text{Se}_4(\text{SO}_3\text{F})_2$ has been obtained. Fluorosulfuric acid is a useful reagent for preparing oxyfluorides from oxides and oxy acid salts, e.g., KMnO_4 gives MnO_3F , BaSeO_4 gives SeO_2F_2 , and KClO_4 gives ClO_3F .

I. Properties of Fluorosulfuric Acid

Fluorosulfuric acid (I) is one of the strongest of the simple protonic acids. Of all the acids studied, only



disulfuric acid ($\text{H}_2\text{S}_2\text{O}_7$) appears to be a more highly acidic,¹ i.e., a more strongly proton-donating, medium, than 100% fluorosulfuric acid. Moreover, the acidity of fluorosulfuric acid can be considerably increased by the addition of SbF_5 and $\text{SbF}_5\text{-SO}_3$, and the resulting solutions are the most highly acidic media known at the present time. These systems may therefore be justifiably called superacid media. In particular they are considerably more acidic than 100% sulfuric acid, which is a much better known acidic solvent.²

In addition to its higher acidity fluorosulfuric acid has a number of other properties that give it advantages over sulfuric acid as a highly acidic medium. Some of the physical properties of fluorosulfuric acid are summarized in Table I. The freezing point (-88.98°)³ is considerably lower than that of sulfuric acid (10.371°), and although this is something of a disadvantage for cryoscopic measurements it has enabled nmr spectra to be obtained at temperatures low enough for proton-transfer reactions to be slowed up sufficiently that signals have been obtained for the first time from the acidic proton of the conjugate acids of a large number of weak bases.

The electrical conductivity of the pure acid ($\kappa =$

$1.085 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$)⁴ is lower than that of sulfuric acid ($1.043 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$), and it has been shown that this conductivity is largely, if not entirely, due to the ions resulting from the autoprotolysis of the solvent. The concentration of each ion in



the solvent is approximately $2 \times 10^{-4} \text{ mole kg}^{-1}$. As this is quite small, the autoprotolysis is essentially completely repressed even in quite dilute solutions, and in contrast to the situation in sulfuric acid the

Table I
Physical Properties of Fluorosulfuric Acid

Measurement	Value	Ref
Boiling point, $^\circ\text{C}$	162.7	5
Freezing point, $^\circ\text{C}$	-88.98	3
Density (d_{25}^{25})	1.726	4
Viscosity at 25° , cP	1.56	4
Specific conductance at 25° , $\text{ohm}^{-1} \text{ cm}^{-1}$	1.085×10^{-4}	4

autoprotolysis does not give rise to any problems in the interpretation of conductometric and cryoscopic measurements.

Fluorosulfuric acid has a boiling point of 162.7° ,^{4,5} which is considerably lower than that of sulfuric acid. Thus fluorosulfuric acid is readily removed from a reaction mixture by distillation, if necessary under reduced pressure, and it is also easily purified by distillation, although the last traces of sulfur trioxide are difficult to remove completely. When free from HF, fluorosulfuric acid does not attack glass even at its boiling point. Thus fluorosulfuric acid can be easily and conveniently handled in conventional glass apparatus.

(1) R. J. Gillespie and K. C. Malhotra, *J. Chem. Soc.*, 1994 (1967).

(2) R. J. Gillespie and E. A. Robinson in "Non-Aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press Inc., New York, N. Y., 1965.

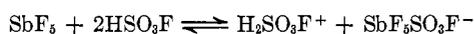
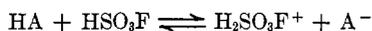
(3) R. J. Gillespie, J. B. Milne, and R. C. Thompson, *Inorg. Chem.*, **5**, 468 (1966).

(4) J. Barr, R. J. Gillespie, and R. C. Thompson, *ibid.*, **3**, 1149 (1964).

(5) T. E. Thorpe and W. Kirman, *J. Chem. Soc.*, 921 (1892).

The viscosity of fluorosulfuric acid (1.56 cP at 25°)⁴ is much lower than that of sulfuric acid, which gives it some advantage as a reaction medium as it is much easier to obtain solid products free from solvent by filtration than is the case for sulfuric acid. Presumably this lower viscosity is a consequence of the fact that fluorosulfuric acid has only one, rather than two, hydroxyl groups and thus can form only two, rather than four, hydrogen bonds per molecule, which in turn leads to its being less extensively associated than sulfuric acid. That it is nevertheless considerably associated is easily seen by comparing its boiling point with that of sulfonyl fluoride, SO₂F₂ (bp -52°), a nonassociated liquid of very similar molecular weight.

Acids and bases may be defined in terms of the two characteristic solvent ions produced in the autoprotolysis reaction. Acids of the fluorosulfuric acid solvent system ionize to give the H₂SO₃F⁺ ion, *e.g.*



Bases ionize to give the SO₃F⁻ ion, *e.g.*



II. Electrical Conductivity and Cryoscopic Measurements

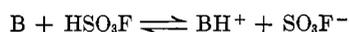
These two methods have been extensively used for the investigation of solutions in fluorosulfuric acid in addition to various spectroscopic techniques such as visible and uv absorption spectroscopy and nmr spectroscopy. Electrical conductivity of solutions of acids and bases in fluorosulfuric acid occurs very largely by proton-transfer conduction involving the ions H₂SO₃F⁺ and SO₃F⁻, respectively.⁴ This mechanism gives considerably greater ionic mobilities in this solvent than the ordinary diffusion mechanism, and this means that these two ions have considerably greater mobilities than all other ions. One consequence of the abnormally

Molar Ionic Conductivities at Infinite Dilution and 25°

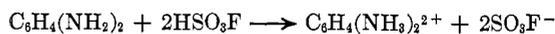
SO ₃ F ⁻	H ₂ SO ₃ F ⁺	K ⁺	NH ₄ ⁺
135	185	17	21

high mobility of SO₃F⁻ is that the conductivities of identical concentrations of the alkali metal fluorosulfates are all very similar. In fact, in a solution of any base the conductivity is very largely due to the SO₃F⁻ ion and the conductivity may to a good approximation be considered to be proportional to the concentration of this ion.

It is convenient to define γ as the number of moles of SO₃F⁻ ions produced by the ionization of 1 mole of solute. Thus for a simple strong base such as KSO₃F $\gamma = 1$, for a weak base with a degree of dissociation α , *i.e.*



$\gamma = \alpha$, and for the strong base *o*-phenylenediamine



$\gamma = 2$. Since the conductivity is due predominantly to the fluorosulfate ion, the value of γ for any solute is given, to a good approximation, by the ratio of the concentration c_s of a solution of a standard electrolyte for which $\gamma = 1$, *e.g.*, KSO₃F, to the concentration c of the solution of the solute having the same concentration; *i.e.*, for $\kappa = \kappa_s$, $\gamma = c_s/c$. Figure 1 shows the conductivities of solutions of the strong bases *o*-phenylenediamine, potassium fluorosulfate, and nitrobenzene, together with some weak bases.

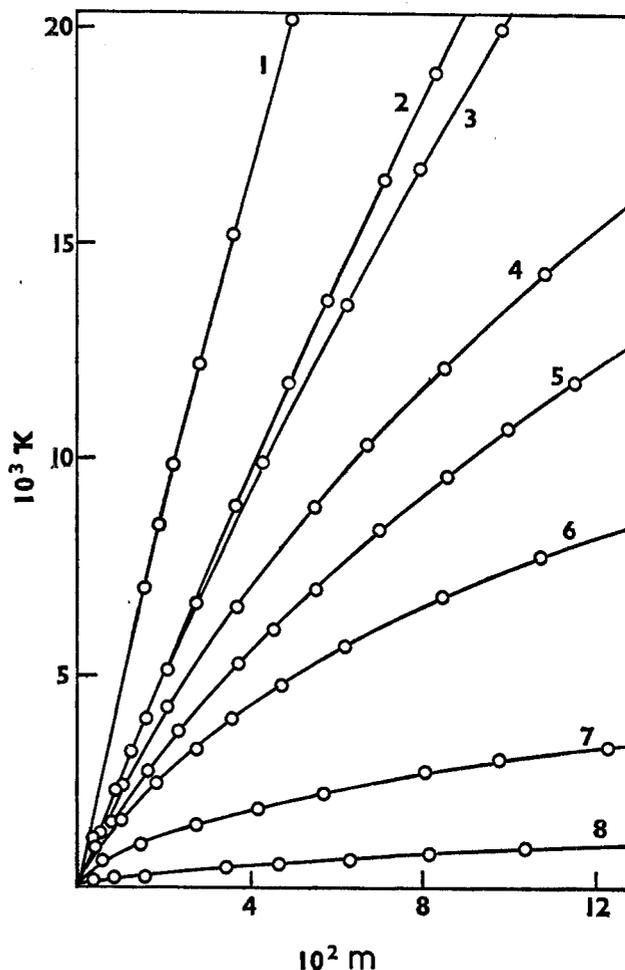


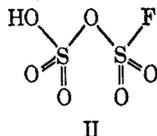
Figure 1. Conductivities of some bases: (1) *o*-phenylenediamine; (2) potassium fluorosulfate; (3) nitrobenzene; (4) *m*-nitrochlorobenzene; (5) nitromethane; (6) 2,4-dinitrotoluene; (7) 2,4-dinitrochlorobenzene; (8) sulfuric acid.

Although the freezing point of fluorosulfuric acid is rather low, freezing-point depression measurements present no special problem in this solvent and suitable apparatus and methods have been described.³ If it is assumed that the freezing-point depression is strictly proportional to the number of molecules and ions in solution, *i.e.*, that the solution is ideal, then a value for ν , which is the total number of moles of molecules and ions produced in the solution by 1 mole of the solute, is easily determined if the cryoscopic constant is known. The cryoscopic constant ($k_f = 3.93$) was found by measuring the freezing-point depression produced by

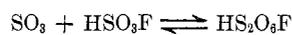
a number of solutes that were shown by conductivity measurements to be nonelectrolytes, *e.g.*, $S_2O_6F_2$, $S_2O_5F_2$, and CH_3SO_2F .³

III. Sulfur Trioxide and Hydrogen Fluoride

Sulfur trioxide and hydrogen fluoride are two solutes of fundamental importance in the fluorosulfuric acid system. Freezing-point-depression measurements³ have shown that both these solutes behave as nonelectrolytes, giving $\nu = 1$ and $\gamma = 0$. The two freezing-point curves meet in a very sharp maximum, showing that the self-dissociation of fluorosulfuric acid into SO_3 and HF is extremely small and corresponds to a self-dissociation constant ($K = [SO_3][HF]$) of less than 3×10^{-7} . The Raman spectrum of a solution of sulfur trioxide in fluorosulfuric acid, however, shows a number of new lines that are not due to monomeric or trimeric SO_3 and which can only be reasonably attributed to the species HS_2O_6F (II).⁶ New lines at 300, 460, and 730 cm^{-1} , for example, have very similar frequencies to lines that have been observed in the spectra of $H_2S_2O_7$ and



$S_2O_5F_2$. Thus SO_3 reacts with HSO_3F according to



but HS_2O_6F is not a sufficiently strong acid to ionize as such in solution in HSO_3F , in contrast to the analogous acid $H_2S_2O_7$ which is a moderately strong acid of the sulfuric acid solvent system.²

IV. Weak Bases

Cryoscopic and conductometric studies of the ionization of a number of weak bases, *e.g.*, nitro compounds, in fluorosulfuric acid have shown that they are more extensively ionized than in sulfuric acid (Table II).^{3,4} It may be concluded therefore that fluorosulfuric acid is a more highly acidic medium than sulfuric acid. The same conclusion has been reached from a spectroscopic study of the ionization of the same weak bases from which it has been shown that the Hammett acidity

Table II

Comparison of Ionization Constants of Some Nitro Compounds in Fluorosulfuric Acid and in Sulfuric Acid

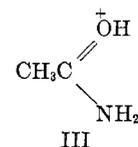
Base	$10^2 K_b^a$	$10^2 K_b^b$
Nitrobenzene	Fully ionized	1.0
<i>m</i> -Nitrotoluene	Fully ionized	2.3
<i>p</i> -Nitrochlorobenzene	76	0.4
<i>m</i> -Nitrochlorobenzene	7.9	c
Nitromethane	2.7	0.25
2,4-Dinitrotoluene	1.4	c
2,4-Dinitrochlorobenzene	0.16	c
2,4-Dinitrofluorobenzene	0.16	c
1,3,5-Trinitrobenzene	0.004	c

^a In HSO_3F . ^b In H_2SO_4 . ^c Too weak to be measured.

(6) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **40**, 675 (1962).

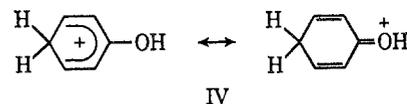
function, H_0 , has a value of -13.9 for fluorosulfuric acid compared with -12.1 for sulfuric acid.⁷

The high acidity of fluorosulfuric acid and its low freezing point have been utilized in nmr studies of the protonation of weak bases in which it has been possible to determine the site of protonation of many bases for the first time. For example, acetamide in fluorosulfuric acid gives a proton magnetic resonance spectrum at room temperature which consists of two peaks due to the methyl group and to protons on nitrogen.⁸ On cooling the solution to -92° a third peak appears in the spectrum at low field, and as the three peaks have relative areas of 1:2:3 they can be unambiguously assigned to OH, NH_2 , and CH_3 , showing that the conjugate acid of acetamide has the structure III and that



protonation therefore occurs on oxygen rather than on nitrogen.

A solution of phenol in fluorosulfuric acid gives a low-temperature proton magnetic resonance spectrum which can only be explained on the basis of protonation at the *para* position of the aromatic ring (IV) and not on the oxygen atom.⁹ Many other protonation studies



have been carried out, many of them in the still more highly acidic and less basic media obtained by adding a Lewis acid such as SbF_5 to fluorosulfuric acid. Some of these are discussed in section VI.

V. Acids

Although HSO_3F is a very acidic solvent it was of interest to see if a still more acidic medium could be produced by the addition of suitable solutes, *i.e.*, acids of the fluorosulfuric acid solvent system. Previous experience with the sulfuric acid solvent system would lead one to expect that there might be very few such acids. We have already seen that neither HF nor HS_2O_6F behaves as an acid in solution in HSO_3F . Measurements on solutions of H_2SO_4 show that it is not ionized as an acid but is probably very slightly ionized as a base.⁴ Similarly, $KClO_4$ undergoes complete solvolysis and there is no evidence for any acid ioniza-



tion of $HClO_4$.⁴ In order to find substances capable of exhibiting acid behavior in the very weakly basic HSO_3F it is necessary to turn to the strong Lewis acids and in

(7) J. Barr, R. J. Gillespie, and E. A. Robinson, unpublished results.

(8) R. J. Gillespie and T. Birchall, *Can. J. Chem.*, **41**, 148 (1963).

(9) T. Birchall, A. N. Bourns, R. J. Gillespie, and P. J. Smith, *ibid.*, **42**, 1433 (1964).

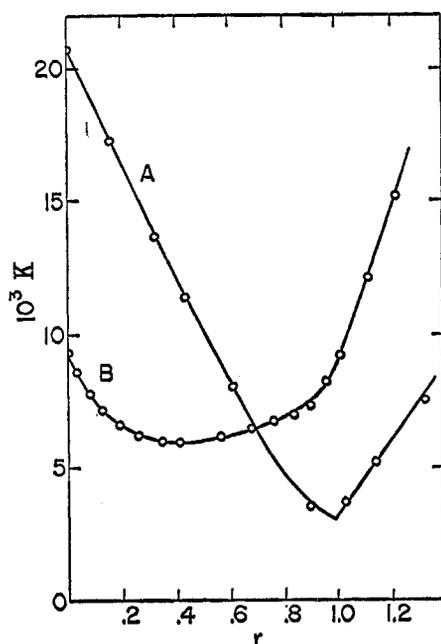
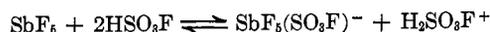


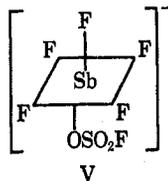
Figure 2. Conductometric titrations of acids with KSO_3F : (A) $\text{H}[\text{SbF}_2(\text{SO}_3\text{F})_4]$; (B) $\text{H}[\text{SbF}_5(\text{SO}_3\text{F})]$. r = moles of KSO_3F /mole of acid.

particular to antimony pentafluoride. This gives a conducting solution in HSO_3F , but the shape of the conductivity-concentration curve indicates that ionization is not complete.¹⁰

Conductometric titrations of solutions of SbF_5 with KSO_3F showed that SbF_5 does indeed behave as a weak acid. On addition of KSO_3F the conductivity of the solution decreases, passes through a minimum at $\text{KSO}_3\text{F}:\text{SbF}_5 \sim 0.4$, and then increases slowly until $\text{KSO}_3\text{F}:\text{SbF}_5 = 1.0$. At that point, there is a reasonably sharp break in the conductivity curve followed by a rather rapid increase in conductivity due to the excess KSO_3F (curve B, Figure 2). Presumably the ionization of SbF_5 may be described by

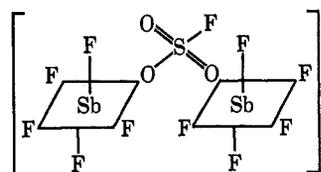


The $\text{SbF}_5(\text{SO}_3\text{F})^-$ ion would be expected to have the structure V in which the antimony is octahedrally coordinated.

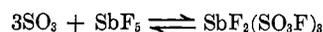
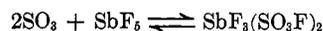
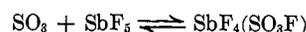


The ^{19}F nmr spectrum of this ion would consist of a doublet-quintet pattern for the fluorine on antimony and a single line for fluorine on sulfur, in addition to the single line for the solvent. In fact the observed spectrum was somewhat more complicated and could only be explained by assuming that, in addition to V, the dimeric species VI, in which there is a fluorosulfate

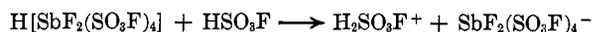
bridge between two square-pyramid SbF_5 groups, is also formed.



A still stronger acid can be prepared by adding SO_3 to a solution of SbF_5 in HSO_3F .¹⁰ The addition of SO_3 causes a marked increase in the conductivity which continues up to a mole ratio $\text{SO}_3:\text{SbF}_5$ of ~ 3 . In conductometric titrations with KSO_3F of solutions containing SO_3 , having the mole ratio $\text{SO}_3:\text{SbF}_5 \geq 3.0$, a minimum conductivity is obtained at $\text{KSO}_3\text{F}:\text{SbF}_5 = 1.0$ (curve A, Figure 2), showing that the solutions contain a strong acid. It was concluded that SO_3 reacts with SbF_5 in solution as follows.



Some excess SO_3 appears to be necessary to ensure complete conversion of SbF_5 to $\text{SbF}_2(\text{SO}_3\text{F})_3$. Antimony difluoride trifluorosulfate ($\text{SbF}_2(\text{SO}_3\text{F})_3$) is a strong acid of the fluorosulfuric acid solvent system, *i.e.*



The formation of the acids $\text{H}[\text{SbF}_4(\text{SO}_3\text{F})_2]$, $\text{H}[\text{SbF}_3(\text{SO}_3\text{F})_3]$, and $\text{H}[\text{SbF}_2(\text{SO}_3\text{F})_4]$ has also been confirmed by ^{19}F nmr measurements.¹⁰

VI. Formation of Carbonium Ions, Oxocarbonium Ions, and the Conjugate Acids of Very Weak Bases in $\text{HSO}_3\text{F}-\text{SbF}_5$ and $\text{HSO}_3\text{F}-\text{SbF}_5-\text{SO}_2$

Considerable use has been made of the highly acidic solutions of SbF_5 in fluorosulfuric acid for the preparation and identification of many new conjugate acid and carbonium ion species. Many previously unobserved species have been found to be stable in this medium, particularly at low temperatures, and they have generally been identified by their proton magnetic resonance spectra. The ternary system $\text{HSO}_3\text{F}-\text{SbF}_5-\text{SO}_2$ has also often been used as a solvent in such studies.¹¹ Although sulfur dioxide is completely miscible with $\text{HSO}_3\text{F}-\text{SbF}_5$ mixtures, it is not protonated to any measurable extent and it does not appear to cause any appreciable reduction of the very high acidity of $\text{HSO}_3\text{F}-\text{SbF}_5$.¹² Sulfur dioxide considerably reduces the rather high viscosity of $\text{SbF}_5-\text{HSO}_3\text{F}$ solutions. This has the advantage of making it easier to obtain homogeneous solutions. Also, it helps to avoid local overheating when a solute is added to the solvent and possible resulting undesirable side reactions. The decreased viscosity

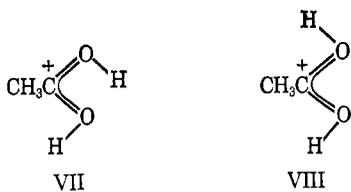
(10) R. C. Thompson, J. Barr, R. J. Gillespie, J. B. Milne, and R. A. Rothenbury, *Inorg. Chem.*, **4**, 1641 (1965).

(11) G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, *J. Am. Chem. Soc.*, **87**, 2997 (1965).

(12) R. J. Gillespie and G. Pez, unpublished results.

of the medium also appears to give rise to somewhat sharper and better resolved nmr spectra.

One of the first applications of the $\text{HSO}_3\text{F}-\text{SbF}_5$ medium was the observation for the first time of the proton magnetic resonance spectra of the conjugate acids of acetic, propionic, and benzoic acids at temperatures of -70° and lower.¹³ For acetic and propionic acids these spectra showed, in addition to the expected peaks for the alkyl groups, two equally intense signals at very low field due to protons on oxygen. It was concluded that these arise from the conjugate acid having structure VII. More recent work^{14,15} using an $\text{HSO}_3\text{F}-\text{SbF}_5-\text{SO}_2$ solvent has shown that there are other weak signals in the spectrum which may be attributed to the other isomeric form of the conjugate acid VIII in which both protons on oxygen are equivalent. Isomer VIII is present to the extent of only 3% in the case of acetic acid, but the corresponding forms of protonated formic acid are present in approximately equal amounts in $\text{HSO}_3\text{F}-\text{SbF}_5-\text{SO}_2$ at -60° .¹⁵ At temperatures of -40° and above the nmr spectrum shows that protonated acetic acid undergoes a slow first-order cleavage to give the oxomethylcarbonium (acetyl) ion CH_3CO^+ .¹⁵



The spectrum of the conjugate acid of acetone was similarly observed for the first time in $\text{SbF}_5-\text{HSO}_3\text{F}$, the $=\text{OH}^+$ proton giving a signal at very low field, 14.5 ppm downfield from tetramethylsilane.¹³ Protonated methyl ethyl ketone shows two resonances for the proton on oxygen, at -14.3 and -13.9 ppm in $\text{SbF}_5-\text{HSO}_3\text{F}-\text{SO}_2$ at temperatures below -20° . It was shown that under these conditions there is 81% of isomer IX and 19% of isomer X.¹⁶ Both isomers were also found for the conjugate acids of several other unsymmetrical ketones. The nmr spectra of the conjugate acids of aldehydes can similarly be observed in $\text{HSO}_3\text{F}-\text{SbF}_5-\text{SO}_2$ at temperatures of -60° .¹⁷ The nmr spectrum of protonated acetaldehyde is somewhat complex. The proton on oxygen gives rise to a doublet centered at -15.11 ppm and a doublet of quartets centered at -15.47 ppm. This clearly indicated the presence of two forms of protonated acetaldehyde in which the proton is either *cis* (XI) or *trans* (XII) to the hydrogen on the carbonyl groups. The isomer ratio was found to be approximately *cis:trans* 80:20 at -60° .

In $\text{HSO}_3\text{F}-\text{SbF}_5-\text{SO}_2$ solution many normal and secondary aliphatic alcohols have been observed as stable O-protonated species at -60° .¹⁸ At some higher

(13) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **43**, 1045 (1965).

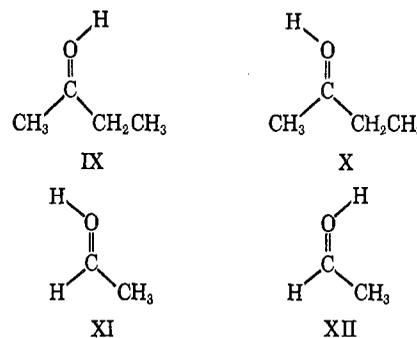
(14) M. Brookhart, G. C. Levy, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1735 (1967).

(15) G. A. Olah and A. M. White, *ibid.*, **89**, 3591 (1967).

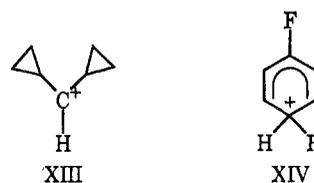
(16) G. A. Olah, M. Calin, and D. H. O'Brien, *ibid.*, **89**, 3586 (1967).

(17) G. A. Olah, D. H. O'Brien, and M. Calin, *ibid.*, **89**, 3582 (1967).

(18) G. A. Olah, J. Sommer, and E. Namanworth, *ibid.*, **89**, 3576 (1967).



temperature cleavage occurs to give a carbonium ion, although this is not generally stable but rearranges to give a more stable carbonium ion, *e.g.*, the trimethylcarbonium ion, or reacts to give other products. Cleavage of protonated tertiary alcohols is generally extremely rapid even at low temperatures, and the spectrum of the protonated alcohol cannot be observed. Thus a solution of *t*-butyl alcohol in $\text{HSO}_3\text{F}-\text{SbF}_5-\text{SO}_2$ at -60° gave only the single-line nmr spectrum of the trimethylcarbonium ion. Many other carbonium ions have been obtained in the same way from their corresponding alcohols,¹⁹ *e.g.*, the diphenylethylcarbonium ion, the methylethylphenylcarbonium ion, the norbornyl cation, and various cyclopropylcarbonium ions, *e.g.*, XIII. Of related interest is the protonation of



several mono-, di-, and trifluorobenzenes to give benzenonium ions, *e.g.*, XIV, in $\text{HSO}_3\text{F}-\text{SbF}_5$, as shown by the nmr spectra at low temperatures.²⁰ Evidence has also been obtained in the same way for other interesting carbonium ions such as alkynylcarbonium ions, *e.g.*, $(\text{C}_6\text{H}_5)_2\text{C}^+\text{C}\equiv\text{CCH}_3$,²¹ and various fluorocarbonium ions, *e.g.*, $\text{C}_6\text{H}_5\text{CF}_2^+$.²²

The stability of carbonium ions in HSO_3F and $\text{HSO}_3\text{F}-\text{SbF}_5$ can be attributed to the very weak basicity of these media in which the strongest base is the SO_3F^- ion or the HSO_3F molecule. Carbonium ions and many other cations are strong Lewis acids and are readily attacked by even weakly basic species. Thus carbonium ions are in general not stable in aqueous media, and the nitronium ion, although stable in the weakly basic sulfuric acid, is immediately converted to nitric acid in water.

VII. Iodine Cations

In addition to its importance in the study of new organic cations, fluorosulfuric acid has proved to be a

(19) C. U. Pittman and G. A. Olah, *ibid.*, **87**, 2998 (1965).

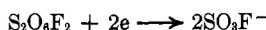
(20) G. A. Olah and T. E. Klovsky, *ibid.*, **89**, 5692 (1967).

(21) C. U. Pittman and G. A. Olah, *ibid.*, **87**, 5632 (1965).

(22) G. A. Olah, M. B. Comisarow, and C. A. Cupas, *ibid.*, **88**, 362 (1966).

very useful solvent for the preparation and investigation of new cationic inorganic species.

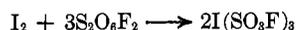
It has been known for some time that iodine gives a deep blue solution in 65% oleum.²³ It had been claimed that this blue color is due to the iodine cation I^+ .²⁴ However 65% oleum is a difficult solvent to work with, and the interpretation of physical measurements, *e.g.*, electrical conductivity, is not simple because of the complexity of the solvent which contains a number of polysulfuric acids in addition to free sulfur trioxide.²⁵ The same blue species can be obtained, however, by oxidizing iodine in solution in fluorosulfuric acid with sulfur trioxide or more conveniently with peroxydisulfuryl difluoride which is reduced to fluorosulfate ion.



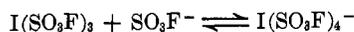
Using this oxidizing agent it was possible to carry out a quantitative investigation of the possible oxidation states of iodine in fluorosulfuric acid²⁶ and in particular to determine the nature of the blue species which had been supposed to be I^+ and which might be formed according to



Iodine was oxidized with various amounts of $S_2O_8F_2$ and cryoscopic and conductometric measurements were made on the resulting solutions. For $S_2O_8F_2:I_2 \geq 3$, $I(SO_3F)_3$ is formed, the excess $S_2O_8F_2$ remaining unchanged. In these solutions $I(SO_3F)_3$ is essentially a

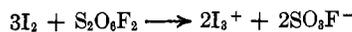


nonelectrolyte, although there is evidence from experiments in which excess SO_3F^- was added to a solution of $I(SO_3F)_3$ that it is a weak acid.²⁷ Iodine tri(fluoro-



sulfate) is a pale yellow solid that can be prepared from iodine and excess $S_2O_8F_2$ in the absence of any solvent,²⁸ and salts of the type $MI(SO_3F)_4$ have been prepared.²⁹

Leaving aside for the moment the interesting 1:1 case we consider the results on solutions containing excess iodine. The cryoscopic and conductometric results on the 3:1 solution ($\nu = 0.69$ and $\gamma = 1.26$)²⁶ show that I_3^+ is formed quantitatively according to



The I_3^+ cation has been known for some time. It was first prepared from iodine and iodosyl sulfate in solution in sulfuric acid,³⁰ and it may also be prepared by allow-

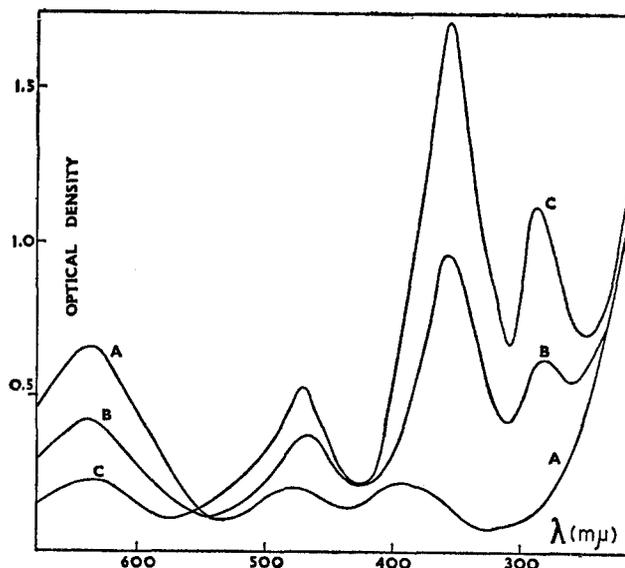
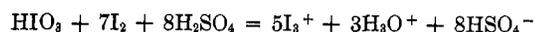


Figure 3. Temperature dependence of the absorption spectrum of a solution of I_2^+ in sulfuric acid: (A) -23° ; (B) -70° ; (C) -86.5° .

ing iodic acid and iodine to react in solution in sulfuric acid³¹ according to



More iodine can be dissolved in a solution of I_3^+ in HSO_3F or H_2SO_4 without causing any change in the freezing point or conductivity of the solution up to at least the 5:1 ratio.^{26,32} There is an accompanying marked change in the absorption spectrum,^{26,32} and it appears that a new iodine cation that is probably I_5^+ is formed. The structures of these ions are not known, but I_3^+ presumably has an angular structure like ICl_2^+ .³³

The 1:1 $I_2:S_2O_8F_2$ solutions have the characteristic blue color and absorption spectrum (curve A, Figure 3) that had previously been attributed to I^+ . However the ν and γ values of 1.2 and 0.8 (at low concentration), respectively, are not in agreement with the formation of I^+ , which requires $\nu = 4$ and $\gamma = 2$. Moreover it was



found that addition of more iodine causes an increase in the intensity of the three characteristic peaks in the spectrum at 640, 490, and 410 $m\mu$ until the $I_2:S_2O_8F_2$ ratio 2:1 is reached. This suggested that the blue species is not I^+ but is I_2^+ which is formed according to



The conductivity results for $I_2:S_2O_8F_2 = 2:1$ solutions which gave $\gamma = 1.0$ at low concentrations are in agreement with this interpretation. Magnetic susceptibility measurements gave a limiting value for the magnetic moment of 2.0 BM at low concentrations, as

(23) M. C. R. Symons, *J. Chem. Soc.*, 387 (1957).

(24) J. Arotzky and M. C. R. Symons, *Quart. Rev.* (London), 282 (1962).

(25) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, 40, 658 (1961).

(26) R. J. Gillespie and J. B. Milne, *Inorg. Chem.*, 5, 1577 (1966).

(27) R. J. Gillespie and J. B. Milne, *ibid.*, 5, 1236 (1966).

(28) J. E. Roberts and G. H. Cady, *J. Am. Chem. Soc.*, 82, 352 (1960).

(29) M. Lustig and G. H. Cady, *Inorg. Chem.*, 1, 714 (1962).

(30) I. Masson, *J. Chem. Soc.*, 1708 (1938).

(31) R. A. Garrett, R. J. Gillespie, and J. B. Senior, *Inorg. Chem.*, 4, 563 (1965).

(32) J. Arotzky, H. C. Mishra, and M. C. R. Symons, *J. Chem. Soc.*, 2582 (1962).

(33) C. G. Vonk and E. H. Wiebenga, *Acta Cryst.*, 12, 859 (1959).

expected for a ${}^2\Pi_{1/2}$ ground state for the I_2^+ molecule. The I_2^+ ion is not completely stable but disproportionates to an increasing extent with increasing concentration according to

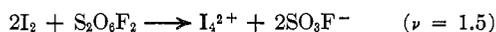


which accounts for the decrease in the apparent magnetic moment and in γ with increasing concentration. Determination of the concentration of the I_2^+ ion with increasing concentration of I_2 - $S_2O_6F_2$ at various I_2 : $S_2O_6F_2$ ratios by means of magnetic susceptibility, absorption spectra, and conductivity gave results in good agreement and enabled a value of $K = 2.0$ to be determined for the above equilibrium. In a 0.1 *m* I_2 + SO_3F^- solution approximately one-third of the I_2^+ is disproportionated at 25°.

Cryoscopic measurements on the 2:1 and 1:1 solutions were, however, not in good agreement with the formation of I_2^+ as they gave $\nu = 1.5$ for the 2:1 solution and $\nu = 1.2$ for the 1:1 solution. Moreover the magnetic susceptibility of the solutions decreases with decreasing temperature, and at -90° the solutions become diamagnetic.³⁴ The absorption spectrum also changes drastically with decreasing temperature (Figure 3). The concentration dependence of the 640- $m\mu$ peak of I_2^+ and the 300- $m\mu$ peak characteristic of the new species at any given temperature indicates that there is an equilibrium between $2I_2^+$ and a dimeric ion, presumably I_4^{2+} , which lies almost completely on the right-



hand side at low temperatures. The cryoscopic results on the $2I_2$ - $S_2O_6F_2$ solutions are also in good agreement with the formation of this ion, *e.g.*



Thus studies of solutions in fluorosulfuric acid have provided further evidence for the ions I_3^+ and I_5^+ and have also shown the existence of the new species I_2^+ and I_4^{2+} . Studies of the structures and properties of these new species will be of great interest.

VIII. Selenium Cations

Recently some new cations of selenium have been discovered, mainly as a result of studies of solutions in fluorosulfuric acid.³⁵ Selenium can be oxidized with $S_2O_6F_2$ in solution in fluorosulfuric acid to give first a green species and then a yellow species. The green species is formed at ratios of Se: $S_2O_6F_2$ of 8 or more. The solutions are, however, not completely stable, and further oxidation of the green species occurs slowly. The green species could not be identified with complete certainty from measurements on the fluorosulfuric acid solutions, but studies of the very stable solutions in sulfuric acid showed that the species is Se_3^{2+} . In solution in HSO_3F this is formed by $S_2O_6F_2$ according to



On addition of further $S_2O_6F_2$ the green species is replaced by a yellow species which has an intense absorption peak at 410 $m\mu$. The intensity of this peak passes through a maximum at the mole ratio Se: $S_2O_6F_2 = 4$. This yellow species is the Se_4^{2+} ion, formed according to



Cryoscopic and conductometric measurements on solutions having Se: $S_2O_6F_2 = 4$ gave $\nu = 0.75$ and $\gamma = 0.5$, in excellent agreement with the above equation. Removal of the solvent from the yellow 4:1 solution gave an orange solid which had the composition $Se_2(SO_3F)$ and which appears to be the simple ionic compound $Se_4^{2+}(SO_3F^-)_2$. A red species is formed by oxidation of tellurium with $S_2O_6F_2$ in solution in HSO_3F . This has been shown by similar methods to be the Te_4^{2+} ion.

Similar new cations are also formed by the oxidation of sulfur with $S_2O_6F_2$ in HSO_3F solvent, but these have not yet been studied in sufficient detail to warrant their discussion here.

IX. Preparation of Fluorides and Fluorosulfates

Fluorosulfuric acid is an excellent fluorinating agent and reacts with many oxides and oxy acids and their salts.³⁶ Oxyfluorides are the usual products of these reactions, but occasionally a fully fluorinated product is obtained. These reactions, which are summarized in Table III, in some cases proceed at room temperature,

Table III
Preparation of Fluorides and Fluorosulfates
with HSO_3F

Reactant	Product
B(OH) ₃	BF ₃
SiO ₂ · xH ₂ O	SiF ₄
As ₂ O ₅	AsF ₅ , AsF ₂ (SO ₃ F) ₃ , AsF ₃ (SO ₃ F) ₂
As ₂ O ₃	AsF ₃
KMnO ₄	MnO ₂ F
K ₂ CrO ₄ , CrO ₃ , K ₂ Cr ₂ O ₇	CrO ₂ F ₂
P ₄ O ₁₀	POF ₃
BaSeO ₄	SeO ₂ F ₂
BaTeO ₄	Te(OH)F ₅
BaH ₄ TeO ₆	TeF ₅ (SO ₃ F)
KClO ₄	ClO ₃ F
KCl, KF	KSO ₃ F

but in other cases reaction is not appreciable unless the mixture is heated. Thus no perchloryl fluoride can be detected by ¹⁹F nmr spectra in a cold solution of potassium perchlorate in fluorosulfuric acid, and cryoscopic and conductometric measurements indicate complete solvolysis to give HClO₄,⁴ but on heating to 50-85° ClO₃F distills in good yield. It is thought that these reactions proceed by a fluorosulfate intermediate,³⁶ *e.g.*



(34) R. J. Gillespie and M. J. Morton, unpublished observations.

(35) J. Barr, R. J. Gillespie, R. Kapoor, and K. C. Malhotra, *Can. J. Chem.*, **46**, 149 (1968).

(36) A. Engelbrecht, *Angew. Chem. Intern. Ed. Engl.*, **4**, 641 (1965).

but there is no experimental evidence for this mechanism. In contrast the analogous reactions which lead to MnO_3F and CrO_2F_2 are very rapid at room temperature and strongly exothermic.

Occasionally the fluorosulfate is stable enough to distil from the reaction mixture without decomposition. Thus in the reaction of As_2O_5 with HSO_3F , in addition to AsF_5 , and probably also AsOF_3 , varying amounts of $\text{AsF}_2(\text{SO}_3\text{F})_3$ and $\text{AsF}_3(\text{SO}_3\text{F})_2$ are obtained.³⁷ From BaH_4TeO_6 the fluorosulfate $\text{F}_6\text{TeOSO}_2\text{F}$ is obtained in very good yield.³⁸ Alkali and alkaline earth chlorides

(37) E. Hayek, A. Aigensberger, and A. Engelbrecht, *Monatsh. Chem.*, **86**, 735 (1955).

(38) A. Engelbrecht and F. Sladky, *ibid.*, **96**, 159 (1965).

and fluorides are converted to the corresponding fluorosulfates when dissolved in fluorosulfuric acid, and the pure salts can be obtained by removal of HCl or HF and excess HSO_3F .^{39,40} Dinitrogen trioxide and dinitrogen pentoxide yield nitronium fluorosulfate and nitrosyl fluorosulfate, respectively, on reaction with fluorosulfuric acid.^{41,42} Nitrosyl fluorosulfate has also been prepared by allowing fluorosulfuric acid to react with nitrosyl chloride.⁴³

(39) O. Ruff, *Ber.*, **47**, 656 (1914).

(40) W. Traube, J. Hoerenz, and F. Wunderlich, *ibid.*, **52B**, 1272 (1919).

(41) W. Lange, *ibid.*, **60B**, 967 (1927).

(42) D. R. Goddard, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2559 (1950).

(43) A. A. Woolf, *J. Chem. Soc.*, 1053 (1950).

The Base-Induced Rearrangement of α -Halo Sulfones

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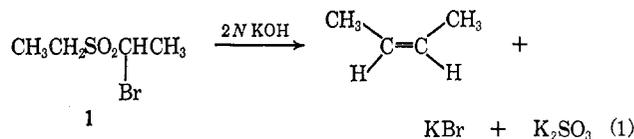
The hydroxide ion promoted rearrangements of α -chloro, α,α -dichloro, and α,α,α -trichloro sulfones are discussed. The reactions are shown to proceed by means of initial α' -sulfonyl carbanion formation and 1,3 elimination of chloride ion, most probably *via* semi-W transition states. The mechanism by which α -chloro sulfones are converted predominantly to the less stable *cis*-alkenes is discussed in some detail. Episulfones are formed in each instance, and such three-membered heterocycles (whether of *cis* or *trans* stereochemistry) decompose stereospecifically to olefins under the customary reaction conditions unless endowed with particularly acidic protons; the rates of formation of the isomeric episulfones are considered to be controlled by the relative rates of various preequilibria as well as by those of intramolecular displacement. The rearrangement of related dichloro sulfones proceeds to a substantial extent by way of thiirene dioxide intermediates, unless structural considerations disallow elimination of a second molecule of HCl . α,α,α -Trichloro sulfones behave similarly and give rise in certain instances to chlorothiirene dioxide derivatives. Such strained and reactive tetravalent sulfur-containing molecules are not stable to the reaction conditions and yield a variety of products. Application of the electrocyclic selection rules to the decomposition of episulfones and thiirene dioxides predicts a nonconcerted thermal expulsion of SO_2 . A tentative explanation is advanced to reconcile such apparent nonconcertedness with the specificity of alkene formation from episulfones.

The marked resistance of α -halo sulfones to *intermolecular* nucleophilic substitution reactions has been well documented over the years¹ and has been the subject of considerable speculation. In 1940, however, Ramberg and Bäcklund^{2a} reported on their discovery that α -bromoethyl ethyl sulfone (**1**) and several related α -halo sulfones readily released halide ion when treated with 2 N KOH and were converted in good yield to alkenes, the *cis* isomers of which predominated.

(1) (a) F. Raschig and W. Prahl, *Ann.*, **448**, 307 (1926); (b) T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 69 (1932); (c) W. M. Ziegler and R. Connor, *J. Am. Chem. Soc.*, **62**, 2596 (1940); (d) T. B. Johnson and I. B. Douglass, *ibid.*, **63**, 1571 (1941); (e) F. G. Bordwell and G. D. Cooper, *ibid.*, **73**, 5184 (1951); (f) note however, the recent report of F. G. Bordwell and B. B. Jarvis, *J. Org. Chem.*, **33**, 1182 (1968).

(2) (a) L. Ramberg and B. Bäcklund, *Arkiv. Kemi Mineral. Geol.*, **13A**, No. 27 (1940); *Chem. Abstr.*, **34**, 4725 (1940); (b) F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5187 (1951).

Although such contrasting facile displacements of halide ion are of obvious mechanistic interest, further work



on this rearrangement did not appear again until 1951. At this time, Bordwell and Cooper^{2b} set forth data that permitted them to propose a mechanism for alkene formation. On the basis of the fact that the rate of release of halide ion from an α -halo sulfone is first order in both hydroxide ion and sulfone, these workers proposed the reaction scheme given by eq 2-4.

Albeit this mechanism did explain in a qualitative