

SOME ASPECTS OF CHEMISTRY IN STRONGLY ACIDIC SOLVENT MEDIA

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ABSTRACT

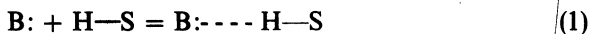
An account is given of some recent developments in the chemistry of solutions in highly associated strong protonic acid solvents, including sulphuric acid and oleums, fluorosulphuric acid and hydrogen fluoride. Topics discussed include solvent-solute interactions, super-acid systems, Hammett acidity functions and polyatomic cations of the elements of Groups VI and VII.

INTRODUCTION

This paper reviews certain aspects of chemistry in the solvents sulphuric acid, disulphuric acid and oleums, fluorosulphuric acid, and anhydrous hydrogen fluoride.

SOLVENT CHARACTERISTICS

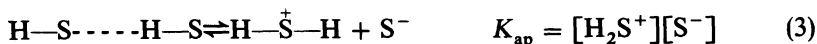
All of the solvents mentioned above have certain characteristics in common, which significantly affect their behaviour as solvents. They are all of course very strong protonic acids, or, otherwise expressed, electron-pair acceptors. Their most characteristic interaction with another molecule is the formation of a strong hydrogen bond, followed in most cases by transfer of a proton to the basic species (electron pair donor) involved:



Despite their strong acid character, all of these solvents have in addition a by no means negligible basicity, arising from lone pairs of electrons on their oxygen atoms (or fluorine atom in the case of hydrogen fluoride). They can therefore accept hydrogen bonds from other molecules of the same kind, and are extensively associated in the liquid state. While details of the liquid structures are not known, it seems reasonable that units of the solid structures, chains, sheets or three-dimensional networks, persist as transient entities, constantly breaking down and reforming, in the liquid phase. As a consequence of their high degree of association, the acids have higher melting points and much higher boiling points than non-associated liquids of the same molecular weight, and wide and convenient liquid ranges. Their dielectric constants are relatively high, due to the cooperative orientation

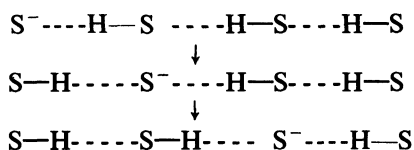
of the molecules in an electric field. This is in contrast to the behaviour of other strongly acidic solvents, such as the higher hydrogen halides, which are only very weakly basic, and are much less associated, more volatile, and have low dielectric constants.

Transfer of a proton along a hydrogen bond, from one neutral solvent molecule, HS, acting as an acid, to its neighbour, acting as a base, followed by separation of the resulting ions, leads to self-ionization, or autoprotolysis:



The autoprotolytic cation and anion are, respectively, the strongest acid and base that can exist as such in a given solvent. The extent of autoprotolysis, as measured by the magnitude of the autoprotolysis constant, $K_{\text{ap}} = [\text{H}_2\text{S}^+][\text{S}^-]$, clearly depends upon the base strength as well as the acid strength of the solvent molecules.

The autoprotolysis ions differ from solvent molecules only by the presence or absence of a proton, and can thus fit with minimum distortion into the solvent structure, being linked by hydrogen bonds to neighbouring solvent molecules. Proton transfers along hydrogen bonds occur very readily, permitting excess or defect proton sites to move rapidly through the solution without the necessity of the actual physical migration of ions. The application of an external electric field distorts the potential well in which the protons move in such a way as to favour proton transfers in the field direction, resulting in a net transfer of charge. This is shown diagrammatically below for the ion S^- in the hypothetical solvent HS.



Only the autoprotolysis ions can conduct electricity by this proton transfer mechanism, in a given solvent, and these ions tend to have much higher mobilities than all other ions, which can conduct only by migration through the solution. In some cases, when the solvent is very viscous, the mobilities of normally conducting ions are very low, and the autoprotolysis ions conduct almost all of the current.

Recently, Zundel and co-workers¹ have suggested that proton transfer conduction in aqueous solutions is associated with the presence of the species H_5O_2^+ and H_3O_2^- in acidic and basic solutions, respectively. These species have the structures I and II, in which the bridging proton moves in a double potential well with a low energy barrier or in a very broad single minimum potential well.



Such hydrogen bonds are highly polarizable and give rise to infra-red absorption continua. The participation of analogous entities in proton

STRONGLY ACIDIC SOLVENT MEDIA

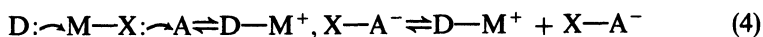
transfer conduction in the strong acid solvents with which we are concerned seems highly plausible.

The completion of a proton transfer step leaves the solvent molecule in an unsuitable orientation to participate in a further transfer in the same direction. There are thus two possible rate-determining steps for this conduction mechanism: (1) proton transfer along a hydrogen bond, and (2) reorientation of a solvent molecule following proton transfer. Conway² argued very convincingly some years ago, on the basis of deuterium isotope effects on ion mobilities, that in aqueous solutions the reorientation step is rate-determining. It has been argued that a molecular reorientation process is rate-determining in sulphuric acid also³, and this would be expected to be the case in other strong acid solvents.

A related mechanism of conduction, the asymmetric autoprotolysis mechanism, was proposed by Wyatt⁴. In the absence of an external electric field, proton transfers between pairs of neutral solvent molecules leading to self-ionization (equation 3) occur with equal frequency in all directions. Application of an external electric field causes a slight preponderance of such proton transfers to occur in the field direction. Since proton transfer in the reverse sense, i.e. from cation to anion to re-form two neutral molecules, occurs whenever a pair of ions approaches within a certain critical distance, under diffusion control, there is no preferred direction for this process, and the asymmetry of the ionization process results in a net transfer of charge. The contribution of this mechanism to the specific conductivity was shown to be directly proportional to the autoprotolysis constant of the solvent, $K_{ap} = [H_2S^+][S^-]$. Thus the mechanism will only be important for extensively dissociated solvents. There is evidence that this mechanism makes a constant contribution to the conductivity of solutions in sulphuric acid equal to about 36 per cent of the conductivity of the pure solvent. It appears from the magnitude of their specific conductivities that both selenic⁵ and phosphoric⁶ acids are even more extensively dissociated than sulphuric acid, and it is to be expected that the asymmetric autoprotolysis mechanism of conduction will play a significant role in these two solvents also.

SOLVENT-SOLUTE INTERACTIONS

The importance of specific solvent-solute interactions, i.e. electron pair donor-acceptor interactions, in determining solute behaviour in a given solvent has been strongly emphasized in recent years, most notably, and from somewhat different points of view, by Drago⁷ and by Gutmann^{8,9}. It has been shown that the ionization (as opposed to dissociation) of a covalent solute is determined relatively little by the dielectric constant of the solvent, but rather by the ability of the solvent to stabilize the ionic fragments formed, by the formation of coordinate covalent bonds. Thus for example the ionization of a covalent metal halide MX_n depends critically upon the ability of a solvent molecule to coordinate to the metal ion and so to displace a halide ion X^- from its inner coordination sphere. The tendency towards ionization will be further enhanced if either the solvent molecule or some other molecule present is capable of behaving as an electron pair acceptor towards the displaced anion:



Here D and A represent, respectively, electron pair donor and acceptor functions, which may both belong to the same kind of molecule, e.g. a solvent molecule, or to different molecules. Dissociation of the initial ionized species shown into free ions will occur to an extent determined mainly by the dielectric constant of the solvent.

The coordination approach has been most successfully applied to solution chemistry in electron pair donor solvents, in which cation stabilization through coordination by solvent molecules is of prime importance. It has been relatively little used in the discussion of chemistry in strong protonic acid solvents.

The reason for this is perhaps not far to seek. Although not devoid of basic properties, as has already been mentioned, these solvents are nonetheless, by normal standards, very weak bases. Cation solvation in these solvents will therefore tend to be of a non-specific nature, based primarily on ion-dipole interactions, with very little transfer of electron density from the solvent molecules to the cation. Probably because of the poor coordinating ability of the solvent molecules, most transition metal salts are of low solubility in strong acid solvents and relatively little transition metal chemistry has been studied in such media. It is in fact just because they are such poor electron pair donors that these solvents are so useful as media for the preparation of highly electrophilic cations, such as carbonium ions R_3C^+ , NO^+ and polyatomic cations of the non-metallic elements, e.g. I_3^+ , S_{16}^{2+} and Se_8^{2+} , which could not exist in more basic media.

I do not mean to imply that cation solvation is unimportant in strong acid solvents; only that it does not involve significant electron transfer to the cation. Reasonable solvation numbers have been obtained, for example, for a number of cations in sulphuric acid, based on osmotic coefficients derived from very accurate freezing point depression data¹⁰, and from apparent molar volumes¹¹ (Table 1). It should be noted that the numbers cited are for

Table 1. Cation solvation numbers in sulphuric acid solutions of hydrogensulphates

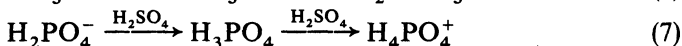
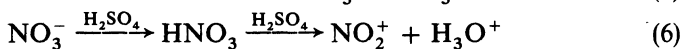
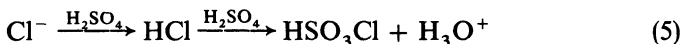
Cation	Li	Na	K	Rb	Cs	Ca	Sr	Ba
Solvation number from cryoscopy	2.3	3.0	2.1	—	—	—	—	6.5
Solvation number from molar volume	2	3	2	1	0	8	8	5

the solute $MHSO_4$ or $M(HSO_4)_2$, and were assigned as cation solvation numbers on the basis of the assumption, now recognized to be incorrect, that the HSO_4^- ion is not solvated. Furthermore the order of increasing specific conductivities of alkali metal hydrogensulphates in sulphuric acid at higher concentrations, $Li < Na < K < Rb < Cs$, is most satisfactorily explained by assuming that the smaller ions are most strongly solvated, and thus by hindering the reorientation of solvent molecules, interfere most with proton transfer conduction by the HSO_4^- anion^{3b}. Similar results in other strong

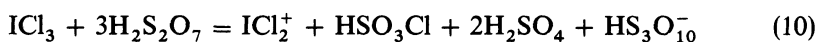
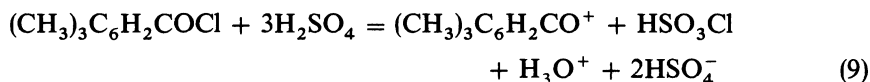
acid solvents (e.g. $\text{HSO}_3\text{F}^{1,2}$, $\text{HSO}_3\text{Cl}^{1,3}$) have been explained in the same way.

In contrast to their relatively weak interactions with cations, strong acid solvents interact strongly, by hydrogen bond formation, possibly followed by proton transfer, with even very weakly basic solutes. Soluble non-electrolytes are substances such as poly-nitrocompounds and sulphuryl halides, which although too feebly basic to undergo protonation, are basic enough to act as hydrogen bond acceptors toward the solvent, and so compensate for the breaking of hydrogen bonds between solvent molecules caused by the dissolution of the solute.

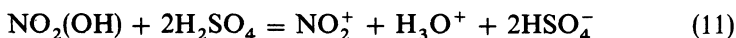
Anions of course interact very strongly with the solvent, and are usually completely solvolyzed to their parent acids, which may then undergo some further reaction. Some examples, all for sulphuric acid as solvent, are given below:



Interaction of the solvent with the anionic species released plays an important role in the ionization of certain covalent species in strong acid solvents, e.g.:



The many instances in which cationic species are formed from hydroxy-compounds may, at least formally, be regarded as examples of the abstraction of a hydroxide ion in the same way, e.g.:

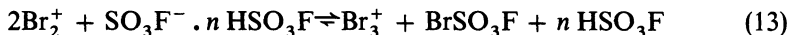


Many of the highly electrophilic cations which have been studied in strong acid solvents are in practice generated in solution, not by the ionization of pre-existing covalent compounds, but by the oxidation of the element concerned to the appropriate formal oxidation state in the acid medium. In these cases, too, the ability of the solvent to solvate or solvolyse anions is of importance for the stability of the cations in solution. Decomposition of the cation involves reaction with a base, usually an anion or water, to form a covalent species, often accompanied by disproportionation. Thus in fluoro-sulphuric acid the cation Br_2^+ reacts with fluorosulphate ion, with disproportionation:¹⁴



Anions which are stronger bases than the solvent anion are of course fully solvolyzed and are thus prevented from reacting with the electrophilic species. The basicity of the solvent anion itself is also reduced by solvation, as its charge is partly delocalized onto the solvent molecules to which it is

hydrogen bonded. We may think of a reaction such as the above as involving competition between two acids, namely the electrophile, e.g. Br_2^+ , and the bulk solvent, for the strongest available base, the solvent anion:



In this particular instance the bulk solvent is not a sufficiently strong acid to compete effectively, and the disproportionation is effectively complete in fluorosulphuric acid solution.

It was at one time believed that an anion such as SO_3F^- or HSO_4^- would not be solvated in its parent solvent, because of its large size. This assumption, based on a purely electrostatic view of solvation, is now recognized to be incorrect. In order to conduct by the proton transfer mechanism, the anion must of necessity form strong hydrogen bonds to neighbouring solvent molecules. Studies of ^1H chemical shifts in solutions of metal hydrogen sulphates in sulphuric acid showed that the average signal, for the rapidly exchanging H_2SO_4 and HSO_4^- protons, was strongly shifted to lower field from that of the solvent alone^{15, 16}. Since the proton of an isolated HSO_4^- ion would be more shielded than those of H_2SO_4 , a shift to higher field would have been anticipated, if the anion were indeed not solvated. The results could only be explained by assuming that the HSO_4^- ion is strongly hydrogen bonded to solvent molecules, leading to deshielding of the protons. Similar results have recently been reported for solutions of fluorides in anhydrous hydrogen fluoride¹⁷, and perchlorates in anhydrous perchloric acid¹⁸.

To summarize: whereas in donor solvents, cationic species are stabilized in solution by strong coordination to solvent molecules, the stability of highly electrophilic cations in strong acid media depends rather upon the absence of any strong specific interaction between solvent molecules and cations and upon the strong interaction of the solvent with basic species, such as anions, with which the cation might otherwise react.

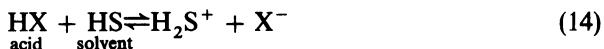
SUPER-ACID SYSTEMS

As was stated above, the Br_2^+ cation is unstable towards disproportionation in fluorosulphuric acid, because the solvent is not a strong enough acid to compete effectively with the cation for the fluorosulphate anion. The Br_2^+ cation can, however, be stabilized by the addition to the solution of the still stronger acid, $\text{SbF}_2(\text{SO}_3\text{F})_3$, which combines with fluorosulphate ion to form the anion, $\text{SbF}_2(\text{SO}_3\text{F})_4^-$, and so shifts the equilibrium in equation 12 to the left. Extremely acidic media, such as a solution of $\text{SbF}_2(\text{SO}_3\text{F})_3$ in fluorosulphuric acid, can be used to protonate exceedingly weak bases, and to stabilize highly electrophilic cations, and are often referred to as super-acids. This term has tended to be used rather loosely; perhaps the concept does not permit a very precise definition. A recent suggestion by Gillespie¹⁹ that the term 'super-acid' be used to refer to any medium which is more acidic than 100% sulphuric acid, seems to be finding favour among other workers in the field. This definition would include a number of pure solvents, such as fluorosulphuric, chlorosulphuric and trifluoromethanesulphonic

STRONGLY ACIDIC SOLVENT MEDIA

acids, and probably anhydrous perchloric acid, as well as the systems containing complex acids which have usually been referred to by this term.

According to the Brønsted concept, an acid in a given solvent is a species which can donate a proton to a solvent molecule, to form the autoprotolysis cation of the solvent:



The formation of H_2S^+ will of course shift the autoprotolysis equilibrium so as to reduce the concentration of the solvent anion, S^- .

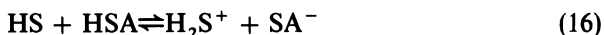
The acid species may be a complex between a strong electron pair acceptor, A, (e.g. $\text{SbF}_2(\text{SO}_3\text{F})_3$ in the above example) and a solvent molecule, in which the latter acts as a weak electron pair donor:



Since the formation of such a complex involves a shift of electron density away from the proton site, the complex will be a stronger acid than HS itself:



It will therefore ionize in solution in HS:

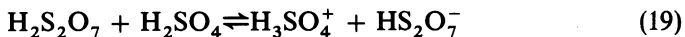
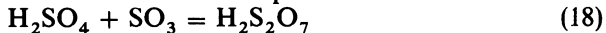


In only a few cases is there definite evidence for the existence of the neutral complex acid HSA. Where such evidence is lacking it may be more correct to think of the un-ionized form of the acid as the electron pair acceptor A itself, which combines with a solvent anion:

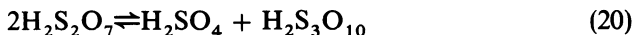


Removal of S^- then shifts the autoprotolysis equilibrium so that the concentration of H_2S^+ is increased.

Among the first super-acid systems to be studied were dilute oleums, solutions of excess sulphur trioxide in sulphuric acid. These solutions contain disulphuric acid, $\text{H}_2\text{S}_2\text{O}_7$, which may be regarded as a complex between the electron pair acceptor SO_3 and a solvent molecule H_2SO_4 . Disulphuric acid behaves as a weak acid in sulphuric acid:



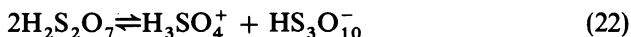
More concentrated oleums contain higher polysulphuric acids, $\text{H}_2\text{S}_3\text{O}_{10}$, $\text{H}_2\text{S}_4\text{O}_{13}$, etc., which are somewhat stronger acids than disulphuric acid. Oleum containing 50 mole % SO_3 , corresponding to the stoichiometric composition $\text{H}_2\text{S}_2\text{O}_7$, is very extensively self-dissociated²⁰:



and

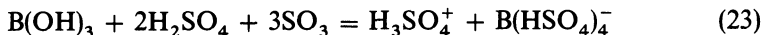


Self-ionization in this system is best represented by:



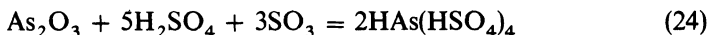
Still more concentrated oleums contain appreciable concentrations of free sulphur trioxide, in addition to polysulphuric acids.

Solutions prepared by dissolving the correct stoichiometric amounts of boric acid and sulphur trioxide in sulphuric acid contain the ions of the rather strong acid, $\text{HB}(\text{HSO}_4)_4$, tetrahydrogensulphatoboric acid²¹:

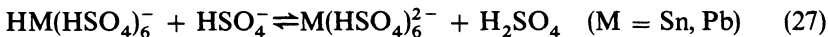


Attempts to isolate the parent acid $\text{HB}(\text{HSO}_4)_4$ or its salts from concentrated solutions have been unsuccessful. Elimination of sulphuric acid and sulphur trioxide occurs, and polymeric products are obtained.

A complex acid of similar stoichiometry, $\text{HAs}(\text{HSO}_4)_4$ is formed in the reaction:



This is, however, a much weaker acid²². Sulphuric acid solutions of lead and tin tetraacetates contain the diprotic acids $\text{H}_2\text{Pb}(\text{HSO}_4)_6$ and $\text{H}_2\text{Sn}(\text{HSO}_4)_6$, respectively^{23, 24}, along with their singly and doubly charged anions:



Super-acidic solutions of these acids have not been obtained, as they are formed in the above reactions in the presence of an excess of acetic acid, which behaves as a strong base in sulphuric acid.

The only simple acids of the sulphuric acid system are fluorosulphuric acid, chlorosulphuric acid and trifluoromethanesulphonic acid, all of which are very weak. Dissociation constants for acids in sulphuric acid are shown in *Table 2*.

Table 2. Dissociation constants of acids in sulphuric acid at 25°C

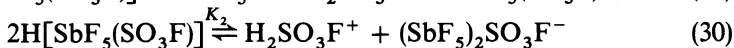
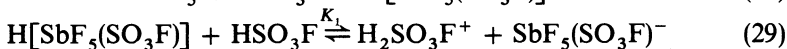
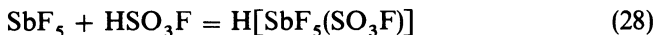
Acid	K_a (mol kg ⁻¹)	Reference
$\text{HB}(\text{HSO}_4)_4$	2×10^{-1}	22
$\text{H}_2\text{S}_2\text{O}_7$	1.4×10^{-2}	22
$\text{H}_2\text{Pb}(\text{HSO}_4)_6$	1.2×10^{-2} (K_1)	24
	1.8×10^{-3} (K_2)	
HSO_3F	2.3×10^{-3}	22
$\text{HAs}(\text{HSO}_4)_4$	1.5×10^{-3}	22
HSO_3Cl	9×10^{-4}	22
$\text{CF}_3\text{SO}_3\text{H}$	8×10^{-4}	25
HClO_4	very weak	22

No simple acids are known in the fluorosulphuric acid system. Solutions of sulphur trioxide in fluorosulphuric acid have been shown by Raman spectroscopy to contain fluorodisulphuric acid, $\text{HS}_2\text{O}_6\text{F}$, but this substance shows barely detectable acidic properties in this solvent²⁶.

Antimony pentafluoride gives solutions in fluorosulphuric acid which are considerably more acidic than the pure solvent²⁷. Conductivity data have been interpreted in terms of the formation of the weak acid, $\text{H}[\text{SbF}_5(\text{SO}_3\text{F})]$.

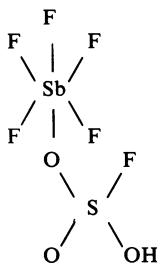
STRONGLY ACIDIC SOLVENT MEDIA

At higher concentrations, however, the conductivity is higher than can be accounted for assuming only this single acid species, and it is necessary to postulate the formation of a dimeric anion, $(\text{SbF}_5)_2\text{SO}_3\text{F}^-$, which behaves as the anion of a strong acid. The situation at 25°C can be represented by the following equations:

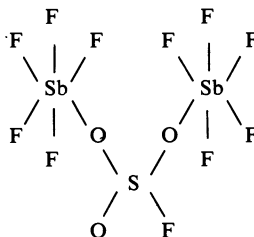


$$K_1 = 3.7 \times 10^{-3} \text{ mol kg}^{-1}; K_2 = 7 \times 10^{-3}$$

^{19}F n.m.r. studies led to the structure III, containing octahedrally coordinated antimony, for the monomeric acid. This is one instance where the existence of the neutral complex acid may be regarded as well-established. The monomeric anion differs from III only by the loss of the proton. The dimeric anion has the structure IV, also containing octahedral antimony, with a bridging fluorosulphate group.



III



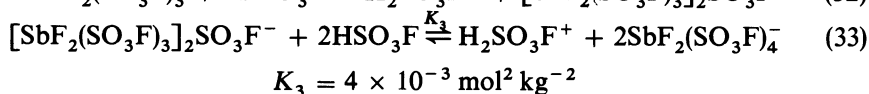
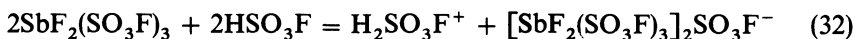
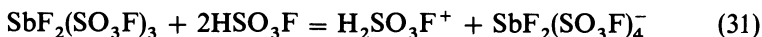
IV

The fluorosulphate group in the monomeric anion is more weakly basic than a free fluorosulphate ion, because it donates electron density to the SbF_5 group, but still retains some basic character, as shown by its ability to coordinate to a proton, to form the un-ionized acid, or to a second SbF_5 molecule, to form the dimeric anion. The bridging fluorosulphate group in the dimeric anion, coordinated to two strongly acidic SbF_5 groups, retains almost no basic character. A similar situation has long been familiar in aqueous solutions of hydrogen fluoride, in which the polymers, $(\text{HF})_n$, present at higher concentrations, are stronger acids than the monomer HF . In this case the basicity of the fluoride ion is reduced by coordination to one or more HF molecules in the anions $\text{H}_{n-1}\text{F}_n^-$.

Solutions of antimony pentafluoride in fluorosulphuric acid have found very wide use for the protonation of very weak bases, and for the preparation of unstable carbonium ions, especially in the work of Olah and his co-workers²⁸. The name 'magic acid' has been given to the solution containing 50 mol % SbF_5 .

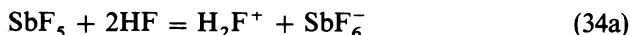
The addition of sulphur trioxide to solutions of antimony pentafluoride in fluorosulphuric acid, up to the mole ratio $\text{SO}_3/\text{SbF}_5 = 3.0$, results in increased acid strength³⁷. Sulphur trioxide is inserted into up to three $\text{Sb}-\text{F}$ bonds, resulting in the substitution of fluorosulphate for fluoride, with

formation of the compounds $\text{SbF}_{5-n}(\text{SO}_3\text{F})_n$, where $n = 1, 2$ or 3 . Fluorosulphate ion is much less basic than fluoride, since its charge is more delocalized, so that the substituted compounds are more acidic than SbF_5 itself. ^{19}F n.m.r. studies have shown the presence of the acids $\text{H}[\text{SbF}_{5-n}(\text{SO}_3\text{F})_{n+1}]$ and/or their monomeric anions. Dimeric, fluorosulphate-bridged anions with structures analogous to IV are also believed to be present, although only for the ion $[\text{SbF}_4(\text{SO}_3\text{F})]_2\text{SO}_3\text{F}^-$ could a separate n.m.r. spectrum be observed. The detailed interpretation of the conductimetric titration curve of $\text{SbF}_5 \cdot 3\text{SO}_3$ with the strong base, potassium fluorosulphate, was only possible on the assumption that both monomeric and dimeric anions were formed, and that both were anions of strong acids²⁷. The situation in solutions of this solute can be summed up in the equations:

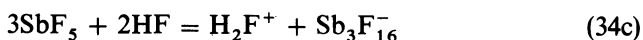
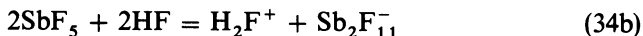


A number of other covalent fluorides have been shown to behave as acids in fluorosulphuric acid, but all are much weaker than antimony pentafluoride²⁹. The addition of sulphur trioxide, up to the mole ratio $\text{SO}_3/\text{AsF}_5 = 3.0$ considerably enhanced the acidity of solutions of arsenic pentafluoride, but had no effect on acidity in the other cases studied. In this case also, insertion of sulphur trioxide into up to three As—F bonds can occur, and substitution of fluorosulphate for fluoride increases the acid strength. The order of acid strengths was found, from conductivity measurements, to be: $\text{PF}_5 \sim \text{NbF}_5 < \text{TiF}_4 \sim \text{AsF}_5 < \text{BiF}_5 < \text{AsF}_4\text{SO}_3\text{F} < \text{SbF}_4 < \text{AsF}_2(\text{SO}_3\text{F})_3 < \text{SbF}_2(\text{SO}_3\text{F})_3$. Phosphorus and niobium pentafluorides showed no acidic behaviour detectable by conductivity measurements, although recent acidity function measurements have shown niobium pentafluoride to be an extremely weak acid³⁰.

Several covalent fluorides behave as acids, i.e. fluoride ion acceptors, in anhydrous hydrogen fluoride. The same general order of acid strengths prevails as in fluorosulphuric acid, namely: $\text{TiF}_4 \sim \text{SnF}_4 < \text{BF}_3 < \text{PF}_5 < \text{NbF}_5 < \text{TaF}_5 < \text{AsF}_5 < \text{SbF}_5$ ^{19,31}, but since hydrogen fluoride is a more basic solvent than fluorosulphuric acid, the extent of ionization of any given fluoride tends to be greater. Thus, antimony pentafluoride, which is rather a weak acid in fluorosulphuric acid, has been shown to be fully ionized as an acid in hydrogen fluoride³²:



In dilute solutions only a single ^{19}F n.m.r. signal is observed, assigned to the SbF_6^- ion, while in more concentrated solutions, the low-temperature spectrum can be interpreted in terms of SbF_6^- and the fluorine-bridged dimer, $\text{Sb}_2\text{F}_{11}^-$. In still more concentrated solutions higher polymers, such as $\text{Sb}_3\text{F}_{16}^-$, occur:



STRONGLY ACIDIC SOLVENT MEDIA

ACIDITY FUNCTIONS

The Hammett acidity function, H_0 , is defined operationally by the equation:

$$H_0 = pK_a - \log \frac{[\text{BH}^+]}{[\text{B}]}$$

where BH^+ and B are the protonated and unprotonated forms of an indicator base, and pK_a for the indicator is referred to the standard state in water. It is now recognized that the protonation of different types of base is described by different acidity functions³, but the H_0 function, defined by the use of primary anilines as indicators, continues to be the most widely used measure of the acidity of strongly acidic media.

Although much use has been made of the ability of super-acid media to protonate very weak bases, the only acidity function data available for such systems, until very recently, were those of Brand *et al.*³⁴ for oleums, and of Palm for the system $\text{H}_2\text{SO}_4\text{-HSO}_3\text{Cl}$ ³⁵. Gillespie *et al.* have recently published H_0 data for a number of systems, in sulphuric and fluorosulphuric acids as solvents^{36, 37}. Although the H_0 function proper is based on primary anilines as indicators, it is difficult to find primary anilines which are weak enough bases for use in very acidic media, and a series of aromatic nitro-compounds were used to extend the scale into the super-acid region. In the most acidic solutions studied, no sufficiently weak neutral base was available, and the second protonations of some polynitro-compounds were used to establish the scale. Strictly speaking the acidity function thus obtained is an H_+ function, and values of $-H_0$ greater than 17 are regarded as less reliable than lower values. Figures 1 and 2 show the results obtained. Table 3 shows H_0 values for some acids.

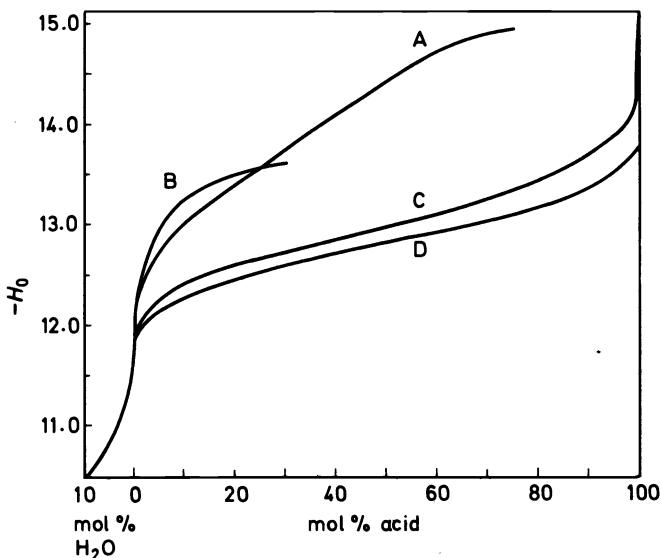


Figure 1. H_0 values for the systems: $\text{H}_2\text{O-H}_2\text{SO}_4\text{-SO}_3$ (A), $\text{H}_2\text{SO}_4\text{-HB(HSO}_4)_4$ (B), $\text{H}_2\text{SO}_4\text{-HSO}_3\text{F}$ (C), $\text{H}_2\text{SO}_4\text{-HSO}_3\text{Cl}$ (D)

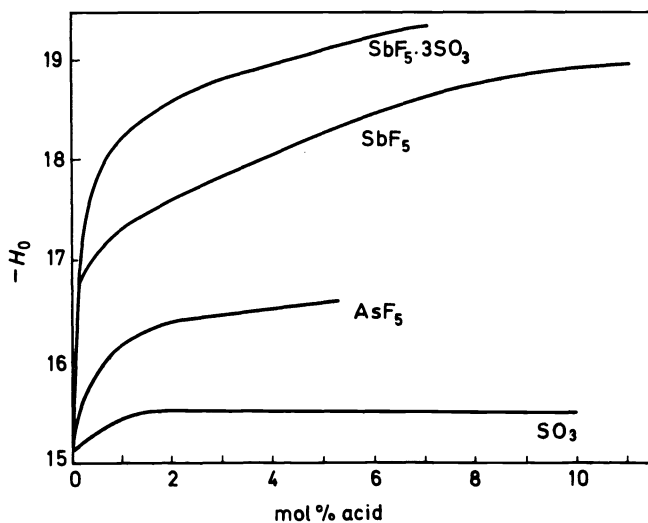


Figure 2. H_0 values for acids in fluorosulphuric acid

Table 3. H_0 values for some acids

Acid	$-H_0$	Reference
HF	11	31
H_2SO_4	11.93	36
HSO_3Cl	13.80	36
$H_2S_2O_7$	14.44	36
HSO_3F	15.07	37
HSO_3F (10% SbF_5)	18.94	37
HSO_3F (7% $SbF_5 \cdot 3SO_3$)	19.35	37

The rapid increase in acidity in the immediate vicinity of the compositions 100% H_2SO_4 and 100% HSO_3F , arising from rapid changes in concentrations of the solvent autoprotolysis ions, should be noted. At higher concentrations of base or acid the solutions are buffered, and H_0 changes more slowly with concentration. The curves are analogous to the familiar pH titration curves for acids and bases in aqueous solution. No rapid change in acidity occurs at the composition $H_2S_2O_7$, where extensive self-dissociation leads to a highly buffered system. The value of H_0 for fluorosulphuric acid could not be measured directly, because even the very low concentration of indicator base required produced sufficient fluorosulphate ion to disturb the autoprotolysis equilibrium and reduce the concentration of the $H_2SO_3F^+$ ion to a value appreciably below that in the pure solvent. The H_0 value of -15.07 for pure fluorosulphuric acid was derived by extrapolation of the data for the H_2SO_4 - HSO_3F system. From their respective H_0 values it appears that fluorosulphuric acid ($-H_0 = 15.07$) is a stronger acid than disulphuric acid ($-H_0 = 14.44$). However, at the higher solute concentrations used in cryoscopic and conductimetric studies, weak bases are found to be more

STRONGLY ACIDIC SOLVENT MEDIA

extensively ionized in disulphuric acid than in fluorosulphuric acid, because while the acidity of the latter solvent is greatly reduced by the added base, that of the highly buffered disulphuric acid is hardly affected.

It can be seen from the H_0 -composition curves that fluorodisulphuric acid, formed in solutions of sulphur trioxide in fluorosulphuric acid, does in fact behave as an extremely weak acid, although its ionization could not be detected by conductimetric means. Arsenic pentafluoride is a somewhat stronger acid, in agreement with conductimetric data, and antimony pentafluoride is stronger still. In both these cases the acidity increases more than might have been expected at higher concentrations, owing to the formation of the dimeric anions, $(MF_5)_2SO_3F^-$, whose parent acids are stronger than the monomers.

The strong acid, $SbF_2(SO_3F)_3$, gives, as expected, still more acidic solutions. The value of $-H_0$ for a 7 mol% solution of this acid is 19.3, the highest value so far measured.

Just as, by definition, in very dilute aqueous solution, $H_0 \approx -\log[H_3O^+]$, so it might be anticipated that in the immediate vicinity of the compositions of pure sulphuric acid or fluorosulphuric acid, H_0 would be a log function of the concentration of $H_3SO_4^+$ or $H_2SO_3F^+$, respectively. The relation:

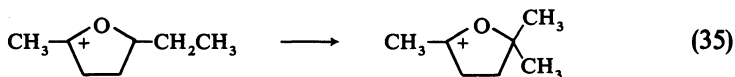
$$H_0 = -\log[H_3SO_4^+] - 13.95$$

was in agreement with experimental data for very dilute solutions of water or sulphur trioxide in sulphuric acid³⁸, and the relation:

$$H_0 = -\log[H_2SO_3F^+] - 18.79$$

has been proposed for dilute solutions of acids or bases in fluorosulphuric acid³⁷. By the use of the latter expression, approximate K_a values for the weak acids in fluorosulphuric acid have been derived from acidity function data, as follows: SbF_5 , 2.2×10^{-3} (cf. 3.7×10^{-3} from conductivity); AsF_5 , 3.7×10^{-6} ; HS_2O_6F , 4.6×10^{-7} mol kg⁻¹. Very recent acidity function measurements show that niobium pentafluoride behaves as an extremely weak acid in fluorosulphuric acid, while tantalum pentafluoride is a slightly weaker acid than arsenic pentafluoride³⁰.

Recent, unpublished measurements³⁰ of the H_0 function for dilute solutions of antimony pentafluoride in hydrogen fluoride (up to 0.4 mol% SbF_5) show that, at very low concentrations, the acidity increases very rapidly with increasing concentration, because of the very small extent of self-dissociation of hydrogen fluoride. The H_0 -concentration curve then runs approximately parallel to the curve for antimony pentafluoride in fluorosulphuric acid, but at H_0 values about two units less negative. It seems reasonable that antimony pentafluoride should, as found, give more acidic solutions in fluorosulphuric acid, in which it is only partly ionized, than in hydrogen fluoride, in which it is fully ionized and its acid strength is levelled to that of the H_2F^+ ion. Furthermore, since substitution of fluorosulphate for fluoride has been shown to enhance acid strength, the un-ionized $H[SbF_5(SO_3F)]$ should be inherently a stronger acid than $HSbF_6$. It is therefore all the more surprising that in a series of recent studies by Brouwer *et al.*³⁹ it has been found that rearrangement reactions such as:



which proceed via doubly protonated intermediates, and occur only in super-acid media, are very much faster in HF-SbF₅ media than in HSO₃F-SbF₅. From the rates of the above and related reactions, the following order of relative acidities has been derived:

1: 1HF-SbF ₅	> 500
9: 1HF-SbF ₅	1
1: 1HSO ₃ F-SbF ₅	10 ⁻¹
5: 1HSO ₃ F-SbF ₅	10 ⁻⁵

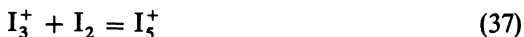
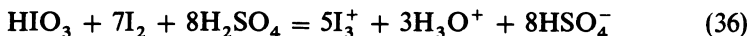
It would probably not be profitable at present to speculate on the reasons for this apparently discrepant behaviour. These results do, however, serve as a warning that estimates of acidity based on the *H*₀ function may prove to be very misleading in other applications. Clearly it will be important to extend acidity function measurements to still higher acid concentrations, and to study the protonation behaviour of different types of bases in these super-acid media.

NOVEL POLYATOMIC CATIONS IN STRONG ACID MEDIA

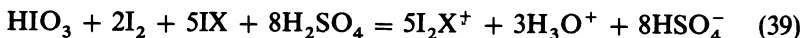
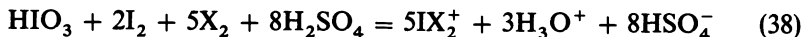
Strong acid solvents have been extensively used in recent years in studies of polyatomic cations, especially those of the elements of Groups VI and VII, many of which are stable in solution only in super-acid media.

HALOGEN CATIONS⁴⁰

The brown solutions formed by the oxidation of iodine with iodic acid or iodine pentoxide in concentrated sulphuric acid were long believed on chemical grounds to contain the cations I₃⁺ and I₅⁺. This has been confirmed by cryoscopic⁴¹ and conductimetric^{41, 42} studies in 100% sulphuric acid:



These cations have also been characterized in fluorosulphuric acid⁴³. The preparation and n.q.r. spectra of the solid compounds I₃⁺AlCl₄⁻ and I₅⁺AlCl₄⁻ have recently been reported⁴⁴. Cryoscopic and conductimetric evidence has also been presented for the formation of the interhalogen cations, ICl₂⁺ and IBr₂⁺⁴⁵, and of the unsymmetrical species, I₂Cl⁺ and I₂Br⁺⁴¹, in 100% sulphuric acid:



(X = Cl, Br)

STRONGLY ACIDIC SOLVENT MEDIA

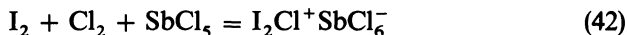
The ICl_2^+ cation is known in the solid compounds $\text{ICl}_2^+\text{AlCl}_4^-$ and $\text{ICl}_2^+\text{SbCl}_6^-$ in which it has been shown to have an angular structure⁴⁶, and has also been obtained in solutions of iodine trichloride in disulphuric acid⁴⁷:



It has been suggested that the unsymmetrical cations might undergo disproportionation in solution to give the symmetrical cations^{40, 41}:



Very recently the solid compounds $\text{I}_2\text{Cl}^+\text{SbCl}_6^-$ and $\text{IBrCl}^+\text{SbCl}_6^-$ have been prepared in the reactions^{48, 49}:



Their Raman spectra support the ionic formulations, and the structures $\text{I}-\overset{+}{\text{I}}-\text{Cl}$ and $\text{Br}-\overset{+}{\text{I}}-\text{Cl}$ (probably bent, by analogy with ICl_2^+) for the cations. NQR studies of the $\text{ICl}-\text{AlCl}_3$ system have shown the existence of the compound $\text{I}_2\text{Cl}^+\text{AlCl}_4^-$ ⁴⁴. The fluorosulphates of a series of triatomic halogen cations have also recently been prepared⁵⁰:



Conductimetric studies showed that these compounds were all fully ionized in fluorosulphuric acid, e.g.:



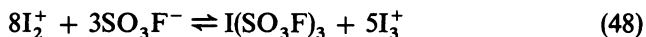
Vibrational spectra of the solids showed the presence of essentially ionic fluorosulphate groups, and supported the unsymmetrical structures, $\text{I}-\text{I}-\text{X}$, for the I_2X^+ cations. The existence of the unsymmetrical cations in the solid state may thus be regarded as established. Detailed studies of u.v.-visible absorption spectra indicate further that these ions are by no means fully disproportionated in solution⁵⁰.

While the species so far mentioned are stable even in relatively basic media such as 97% sulphuric acid, other halogen cations can be obtained in solution only in super-acid media.

Solutions of iodine in concentrated oleums contain a blue paramagnetic species which was for a long time believed to be the cation I^+ ⁵¹. It was first shown conclusively by Gillespie and Milne in 1966⁵², by spectrophotometric, conductimetric and magnetic susceptibility measurements, that this species is in fact the diatomic cation, I_2^+ . When iodine was oxidized with peroxodisulphuryl difluoride in fluorosulphuric acid, the concentration of the iodine cation reached its maximum at the mole ratio $\text{I}_2/\text{S}_2\text{O}_6\text{F}_2 = 2.0$, corresponding to the reaction:

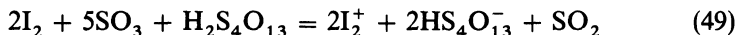


The diiodine cation is in fact partly disproportionated in this medium:



Disproportionation can be prevented by the addition of antimony pentafluoride, which reduces the basicity of the medium by combining with fluoro-sulphate ion. In 100% sulphuric acid the disproportionation of I_2^+ to I_3^+ and an iodine(III) species is essentially complete.

A reinvestigation of the blue solutions of iodine in oleums⁴⁷ has confirmed the formation of I_2^+ , which in 65% oleum may be represented by:

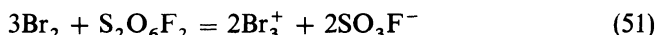


Crystalline solids, formulated as $I_2^+Sb_2F_{11}^-$ and $I_2^+Ta_2F_{11}^-$ have been obtained by Kemmitt *et al.*⁵³, who have also studied blue solutions of the diiodine cation in antimony pentafluoride and in iodine pentafluoride.

At temperatures close to the freezing point of fluorosulphuric acid ($-90^\circ C$), I_2^+ dimerizes to the intensely red-brown coloured, diamagnetic cation, I_4^{2+} ⁵⁴:



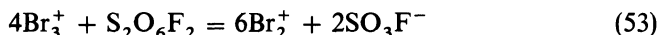
A much more weakly basic medium is required in order to stabilize bromine cations. The red-brown Br_3^+ can be produced by the oxidation of bromine with peroxodisulphuryl difluoride in fluorosulphuric acid¹⁴:



It is, however, not completely stable in this medium, and exists in equilibrium with bromine and bromine(i)fluorosulphate:



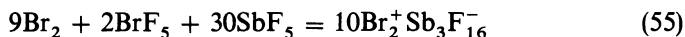
In a solution of $SbF_2(SO_3F)_3$ in fluorosulphuric acid, Br_3^+ is not disproportionated, and can be oxidized further to the cherry-red Br_2^+ :



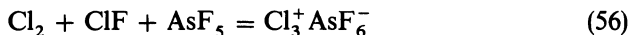
Both bromine cations have been obtained in solid compounds. The compound $Br_3^+AsF_6^-$ was prepared by the oxidation of bromine with $O_2^+AsF_6^-$ ⁵⁵:



At the same time that the dibromine cation was first characterized in solution, Edwards *et al.*⁵⁶ reported the preparation of the compound $Br_2^+Sb_3F_{16}^-$, and determined its crystal structure.



The corresponding chlorine cations are even more unstable, and neither Cl_3^+ nor Cl_2^+ could be obtained even in solutions of chlorine and chlorine(i)fluorosulphate in the most acidic medium available, namely $SbF_2(SO_3F)_3$ in fluorosulphuric acid⁵⁷. Earlier claims to have obtained the Cl_2^+ cation in less acidic media⁵⁸ seem to have been in error⁴⁰. The solid $Cl_3^+AsF_6^-$ has, however, been prepared at $-76^\circ C$ by the reaction⁵⁹:



It is completely decomposed at room temperature. An analysis of the vibrational spectrum of this compound suggests a bent structure for Cl_3^+ , with a bond angle of about 100° .

CATIONS OF GROUP VI ELEMENTS⁶⁰

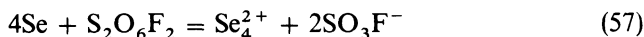
The long-standing controversy over the nature of the species present in the coloured solutions formed by sulphur, selenium and tellurium in sulphuric acid and oleums has been largely settled within the last few years by the characterization of a number of polyatomic cations of these elements, in solution in strong acids and in the solid state. In general, it has proved more convenient to study these ions in solution in fluorosulphuric acid rather than in the more complex and more strongly oxidizing oleums.

Tellurium dissolves in fluorosulphuric acid to give red solutions, shown by conductivity measurements to contain tellurium in the formal oxidation state $+ \frac{1}{2}$ ⁶¹. Solutions with the same spectrum were obtained by the reaction of tellurium and tellurium tetrachloride in molten NaCl-AlCl₃⁶². A number of solids containing the red species have been obtained, e.g. Te₄(Sb₂F₁₁)₂, Te₄(AsF₆)₂, Te₄(SO₃F)₂ and Te₄S₃O₁₀^{63, 64, 65} and the crystal structures of two of them, Te₄(AlCl₄)₂ and Te₄(Al₂Cl₇)₂, have been determined⁶⁶. They contain the square planar Te₄²⁺ cation, with a Te—Te bond distance of 2.76 Å. This confirmed previous identification of this species based on similarities of its u.v.-visible, and Raman spectra and magnetic circular dichroism⁶⁷ to those of the Se₄²⁺ ion.

Further oxidation of tellurium in fluorosulphuric acid with peroxodisulphuryl difluoride gives yellow solutions containing tellurium in the +1 oxidation state^{63, 64}. The species present may be formulated as Te_n⁺, where *n* remains uncertain. Solids of empirical formula TeSbF₆, TeSO₃F and Te₂S₃O₁₀, containing this species have been obtained^{63, 64, 65}. They are diamagnetic, so that *n* must be even. Cryoscopic measurements in fluorosulphuric acid are said to rule out Te₂⁺, while not distinguishing with certainty between *n* = 4, 6 or 8^{63, 64}. On the other hand, cryoscopic studies of yellow solutions of tellurium in disulphuric acid have been claimed⁶⁵ to support the formulation Te₂²⁺, and a tellurium(i) species present in solutions formed by the reduction of tellurium tetrachloride (in large excess) with tellurium in molten KAlCl₄ buffered with KCl-ZnCl₂ at 300°C, has also been claimed⁶⁸ to be Te₂⁺.

Black solids, (Te₃AsF₆)_n and (Te₃AlCl₄)_n have been obtained^{64, 69}. The latter is diamagnetic and since the size of its unit cell shows that *n* cannot be greater than two, it is formulated⁶⁹ as Te₆²⁺ (AlCl₄⁻)₂. No evidence for the structure of the Te₆²⁺ cation is yet available.

When selenium is oxidized with peroxodisulphuryl difluoride in fluorosulphuric acid, the solutions are first green, then yellow, and finally colourless⁷⁰. By photometric titration and conductimetric and cryoscopic measurements, the yellow species was shown to be Se₄²⁺, formed in the reaction:



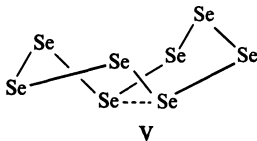
Addition of selenium to these solutions, up to the mole ratio Se/S₂O₆F₂ = 8.0, gives the green species Se₈²⁺:



Selenium can also be oxidized in fluorosulphuric acid alone at room temperature, and in sulphuric acid at 50–60°C to give Se₈²⁺. In disulphuric

acid, selenium undergoes successive oxidation by the solvent, first to Se_8^{2+} and then to Se_4^{2+} .

A number of solid compounds containing selenium cations have been isolated, e.g. $\text{Se}_4(\text{HS}_2\text{O}_7)_2$, $\text{Se}_4\text{S}_4\text{O}_{13}$, $\text{Se}_4(\text{SO}_3\text{F})_2$, $\text{Se}_4(\text{Sb}_2\text{F}_{11})_2$ ⁷¹, $\text{Se}_4(\text{AsF}_6)_2$ ⁶⁰, $\text{Se}_4(\text{AlCl}_4)_2$ ⁷⁴, $\text{Se}_8(\text{Sb}_2\text{F}_{11})_2$, $\text{Se}_8(\text{AsF}_6)_2$ and $\text{Se}_8(\text{AlCl}_4)_2$ ⁷³. X-ray crystallographic studies of $\text{Se}_4(\text{HS}_2\text{O}_7)_2$ have shown that Se_4^{2+} is square planar, with an Se—Se bond distance of 2.28 Å. The crystal structure of $\text{Se}_8(\text{AlCl}_4)_2$ has also been determined⁷³ and it has been shown that the Se_8^{2+} cation has the *endo, exo* bridged ring structure V.

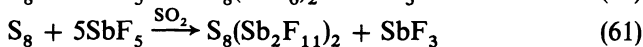
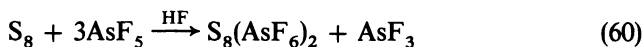


Oxidation of sulphur in fluorosulphuric acid with peroxodisulphuryl difluoride gives successive red, blue and pale yellow solutions⁷⁵. Conductimetric and cryoscopic studies show that the red solutions contain the cation S_{16}^{2+} :

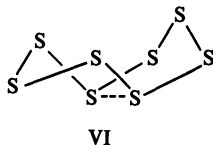


This cation is also produced in solutions of sulphur in 5% oleum⁷⁶. These solutions give an e.s.r. signal at $g = 2.027$, which has been assigned to the radical cation S_8^+ present in small concentrations in equilibrium with S_{16}^{2+} . The solid compounds $\text{S}_{16}(\text{AsF}_6)_2$ and $\text{S}_{16}(\text{SbF}_6)_2$ have been prepared⁷⁵, but unfortunately their crystal structures have not yet been reported.

At the mole ratio $\text{S}_8/\text{S}_2\text{O}_6\text{F}_2 = 1.0$ in fluorosulphuric acid, blue solutions are formed, containing the S_8^{2+} cation⁷⁵. The solutions are unstable and deposit sulphur on standing. Compounds containing the S_8^{2+} ion have been prepared by the reactions⁷⁵:



The crystal structure of $\text{S}_8(\text{AsF}_6)_2$ has been determined⁷⁷. The S_8^{2+} cation has the folded ring structure VI with an *endo, exo* conformation, and a rather long bond across the middle of the ring.

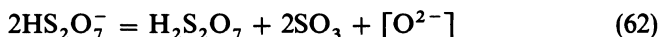


A paramagnetic species, giving an e.s.r. signal at $g = 2.014$ is associated with S_8^{2+} both in the solid state and in solution⁷⁶. It is believed to be the ion S_4^+ , present at low concentrations in equilibrium.

STRONGLY ACIDIC SOLVENT MEDIA

The slow oxidation of sulphur with peroxodisulphuryl difluoride in sulphur dioxide at low temperature gives eventually a white product, $S_4(SO_3F)_2$ ⁷⁸. On the basis of similarities between its Raman spectrum (solid state) and ultra-violet spectrum (in SbF_5-HSO_3F solution) and those of Se_4^{2+} , the solid is believed to contain the square-planar S_4^{2+} ion⁷⁵. The compound $S_4(SbF_6)_2$ has also been obtained^{75, 78}.

The effect of solvent basicity on the stability of the cations of a given element is well illustrated by the behaviour of sulphur in sulphuric acid and oleums⁷⁶. On prolonged heating at 75°C in 95–100% sulphuric acid, sulphur dissolves in the form of S_8 molecules. In 5% oleum, oxidation to S_{16}^{2+} occurs. In 5–15% oleum S_8^{2+} is formed, and above 15% SO_3 , S_4^{2+} is the predominant species. Thus, as expected, the ions with the higher charge per atom are stable in the more acidic media. In oleum containing less than 15% SO_3 , S_8^{2+} tends to disproportionate to S_{16}^{2+} and SO_2 , and in oleum containing less than 30% SO_3 , S_4^{2+} is partly disproportionated to S_8^{2+} and SO_2 . The higher oxidation state, S(IV), is stabilized by coordination of O^{2-} , which is derived from the solvent anion according to some such scheme as:

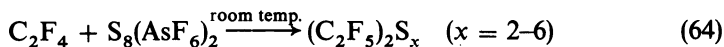


so that, for example, the disproportionation of S_4^{2+} may be written as:

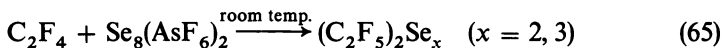


The tendency of a given cation to disproportionate in a sufficiently basic medium to a lower and a higher oxidation state, the latter being stabilized by coordination, has already been illustrated for Br_2^+ (equation 12), Br_3^+ (equation 52) and I_2^+ (equation 48) in fluorosulphuric acid.

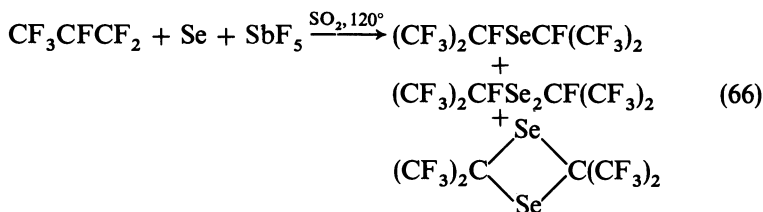
As highly electrophilic species, the polyatomic Group VI cations and their compounds are of great interest as potential synthetic reagents. Paige and Passmore⁷⁹ have recently studied the reaction of perfluoroethylene with the compound $S_8(AsF_6)_2$:



The corresponding selenium compound reacts similarly⁸⁰:



The compound $Se_8(Sb_2F_{11})_2$, containing the less basic anion, reacts similarly at 100°. In solution in liquid sulphur dioxide, the reaction with $Se_8(AsF_6)_2$ gave, in addition to $(C_2F_5)_2Se_2$, the novel compound, perfluoroethyldiselenylperfluoroacetyl fluoride, $C_2F_5Se_2CF_2COF$. The reaction of perfluoropropylene with selenium and antimony pentafluoride in sulphur dioxide gave a number of selenium-containing products⁸¹:



The Se_4^{2+} cation was postulated as an intermediate in this reaction. It is clear that the reactions of these novel electrophiles have scarcely begun to be explored, and many further interesting developments are to be expected.

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