Fluorosulphonic Acid. Part I. Some Properties of the Aqueous Solution.

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Aqueous solutions of the practically unhydrolysed acid can be prepared by passage of alkali fluorosulphonates through cation-exchange resins. The acid is shown to be a strong acid, by comparison with sulphuric acid in alkalimetric titrations. Conductivity measurements indicate a simple ionization to H_3O^+ and SO_3F^- in dilute solutions. The mobility of the latter ion is close to that of the perchlorate ion. The heat of ionization, 1·1 kcal. for 0·04M-solutions, indicates other species in more concentrated solutions.

The only two solvents of any general application for the preparation of simple and complex fluorides are hydrogen fluoride and bromine trifluoride. Since both have limitations, additional solvents are required to extend the range of preparations. Fluorosulphonic acid, first prepared by Thorpe and Kirman (*J.*, 1892, **61**, 921), may combine some of the desirable properties of hydrogen fluoride and sulphuric acid, and the present work aims at the elucidation of its solvent and general acid properties.

The only evidence previously advanced that fluorosulphonic acid was a strong monobasic acid was the existence of metal fluorosulphonates stable in the solid state and in solution. The lack of any quantitative measurements on the acid presumably arises from the difficulty in interpreting results on the hydrolysis mixture. The hydrolysis of the anhydrous acid according to the scheme $H{\cdot}SO_3F + H_2O = HF + H_2SO_4$ (Traube and Reubke, *Ber.*, 1921, **54**, 1618) has been confirmed by a complete analysis (it has also been shown that the anhydrous acid is a true compound and not a constant boiling-point mixture). In concentrated solutions an equilibrium is attained, the constant of which—calculated from concentrations—varies widely on dilution. Lange (*Z. anorg. Chem.*, 1933, **215**, 321), by examination of the effect of added acids and salts on the equilibrium, concluded that the equilibrium constant was not made up of two superimposed constants due to different forms of fluorosulphonic acid. The kinetics of the hydrolysis, however, are not incompatible with two hydrolysis mechanisms. The extent of the initial hydrolysis depends both on the method by which the water is added, and the quantity added; the slower the rate of addition and the lower the temperature, the less the hydrolysis. The hydrolysis subsequent to the initial instantaneous reaction is slow and it seems that the rate of fission of the sulphur–fluorine bond in the predominantly covalent structure of the anhydrous acid $HO{-}SO_2{-}F$ is more rapid than in the fluorosulphonate ion, $(O_3S{-}F)^-$. Thus part of the anhydrous acid could hydrolyse directly and the remainder be converted into a hydroxonium acid, which hydrolyses slowly even at high temperatures. There are practical limits to the velocity of addition of the anhydrous acid to water, and hence solutions free from appreciable sulphate and fluoride cannot be prepared in this way. It is possible to form solutions of the almost unhydrolysed acid by a displacement reaction of the alkali ions of the fluorosulphonates with the hydrogen ions on strongly acidic ion-exchange resins. The aqueous acid so formed is of the same order of stability as aqueous tetrafluoroboric acid (Wamser, *J. Amer. Chem. Soc.*, 1948, **70**, 1209; 1951, **73**, 409). It is more stable than the complex fluoro-acids of Group VA. The stability of the latter, when prepared on exchange resins, increase from hexafluoroantimonic to hexafluorophosphoric acid.

The pH values of the aqueous acid show that a 1 : 1 electrolyte is present in dilute solutions, because the values calculated for a complete ionization, with allowance for interionic attraction, agree with the experimental values. The well-known similarity in solubilities and crystallographic properties between perchlorates and fluorosulphonates means that these ions have similar radii in the solid state and are similarly solvated in solution. Hence the ionic mobility should be similar. The mobility of the fluorosulphonate ion was found from the equivalent conductivity at infinite dilution of potassium fluorosulphonate, there being no reason to suppose that it ionizes differently in solution from the solid. The value obtained (71) is close to that of the perchlorate ion (69). By deducting this mobility from the equivalent conductivity of aqueous fluorosulphonic acid, the mobility of the hydroxonium ion should result if the species present in dilute solutions are indeed H_3O^+ and SO_3F^-. The value obtained was in satisfactory agreement with this ionization when the hydrolysis of the fluorosulphonate ion was considered. (Even potassium fluorosulphonate solutions have an acid reaction, and will precipitate insoluble sulphates when left in contact with barium or benzidine salt solutions.)

The species present in concentrated solutions may differ from those in dilute solutions. The heat of neutralization is 14·4(6) kcal. for 0·04M-solutions, so the heat of ionization, *viz.*, 1·1 kcal., although less than that of hydrofluoric or sulphuric acid at the same concentration (2·7 and 2·0 kcal., respectively), may indicate ions other than H_3O^+ and SO_3F^- in solution. One possibility is an ionization to H_3O^+ and $HS_2O_6F_2^-$. The latter ion can retain the preferred four-fold co-ordination of the sulphur oxy-acid anions if it has the structure $O_3S{-}SO_3(FHF)$. Concentrated solutions of fluorosulphonic acid can be prepared by freeze-drying and it is hoped to examine their properties.

EXPERIMENTAL

Analysis of Fluorosulphonic Acid and its Hydrolysate.—The problem is essentially that of analysing a F^-, $SO_4^{=}$, SO_3F^- mixture. Previous incomplete analyses are reported by Thorpe and Kirman (*loc. cit.*), Ruff and Braun (*Ber.*, 1914, **47**, 654), and Goddard, Hughes, and Ingold (*J.*, 1950, 2575).

0·5—1 Ml. of freshly distilled anhydrous acid were weighed in an all-glass syringe whose end was closed with a Polythene capillary and cap. The acid was slowly expelled under 200—500 ml. of carbon dioxide–free water in a Polythene bottle. Aliquot parts of 20—25 ml. were weighed in waxed beakers for analysis.

Analysis of hydrolysate. (i) Sulphate. Benzidine hydrochloride was shown to be specific for sulphate in the presence of fluoride and fluorosulphonate. Quantitative analyses of potassium sulphate solutions in the presence and absence of potassium and hydrogen fluorides agreed to 0·3%. The following volumetric procedure was adopted after trial experiments. 50 Ml. of reagent (9·35 g. of benzidine hydrochloride and 20 ml. of concentrated hydrochloric acid per l.) were added to 50 ml. of sulphate solution (*ca.* N/20 with respect to sulphuric acid). After 12 min. at 0° the precipitate was filtered on a pulp-pad (about ¼ of a No. 41, 12·5-cm. Whatman paper) supported by a Witt plate, and washed with 20 ml. of water at 0°. The pad and precipitate were suspended in hot water and titrated with N/10-alkali to the phenolphthalein end-point (Belcher, Nutten, and Stephen's 4-amino-4′-chlorobenzidine reagent could be used; *J.*, 1953, 1334).

(ii) Fluorosulphonate. Nitron acetate is specific for the fluorosulphonate ion in the mixture. 10 Ml. of 10% nitron in 20% acetic acid were added to the aliquot, and the whole kept at 0° for a few hours. The precipitate, washed with 20 ml. water at 0°, was dried at 120°.

(iii) Fluoride. The aliquot, neutralized to alizarin-red and buffered to pH 3 with chloroacetic acid–sodium chloroacetate, was titrated with a thorium nitrate solution standardized against fluoride solutions which had approximately the same sulphate content as the unknown.

(iv) Alkalimetric titration. This titration, which is possible because of the increase in acidity from 1 to 3 equivs. on hydrolysis, is the most accurate and is taken as the standard for comparison. The carbon dioxide-free aliquot portion in a platinum dish was titrated quickly in the cold with carbonate-free alkali with phenolphthalein as indicator. If x is the fraction of acid hydrolysed, the hydrolysis mixture contains $(1 - x)$ equiv. of HSO_3F, x of HF, and $2x$ of H_2SO_4. When $x = 1$, the total acid formed is 3 equiv., whence

$$\text{Titre obtained/titre for complete hydrolysis} = (1 + 2x)/3 = R \text{ and } x = (3R - 1)/2.$$

Comparison of the degree of hydrolysis calculated from the alkalimetric and other titrations will agree if the assumption that the hydrolysis is $H_2O + H{\cdot}SO_3F = HF + H_2SO_4$ is correct. The results are expressed as percentage degree of hydrolysis, the alkalimetric result being given first in each instance: $SO_4^{=}$, 51·6, 51·9; 53·3, 53·9; SO_3F^-, 55·2, 55·2; 53·3, 54·2; F^-, 53·3, 54·5; 58·1, 59·3. (The values for fluoride are high because about 1—2% of the fluorosulphonate ion is titratable with thorium nitrate.)

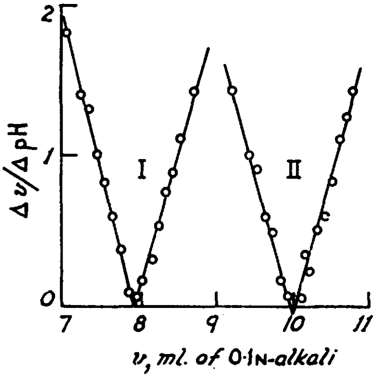
Analysis of the acid. (i) Total fluoride. This was found by Willard and Winter's method after addition of perchloric acid and steam-distillation. The thorium nitrate in this instance was standardized against a sodium fluoride solution treated in the above manner.

(ii) Total sulphate. The fluoride was removed by evaporation in glass at 133° in a slow stream of air. (A chlorobenzene constant-temperature jacket was used.) The residual sulphate was determined as barium sulphate.

$H{\cdot}SO_3F$ (g./100 g. H_2O)	% of total found F	SO_4	HF/SO_3
(1) 0·561	100·0	99·5	1·005
(2) 0·361	99·3	99·4	0·999
(3) 0·488	99·6	99·9	0·997
(4) 0·395	99·8	99·9	0·999

The results were as shown in the above table: (1) and (2) were hydrolysates of the acid distilled at atmospheric pressure, (3) and (4) at approx. 10^{-4} mm.

Preparation of Aqueous Fluorosulphonic Acid.—Potassium fluorosulphonate, prepared from analytical-grade potassium persulphate and bromine trifluoride (Emeléus and Woolf, *J.*, 1950, 164), was powdered and heated at 150° *in vacuo* to remove all traces of solvent. The resultant salt was free from bromide, sulphate, and fluoride. When recrystallised from water the product was contaminated with sulphate. Solutions of up to 0·5 g. were passed through 5 g. (dry weight) of Amberlite IR 120(H) resin in a Polythene column at the rate of 200 ml./hr. Blank runs with potassium sulphate solutions showed that the resin was unaffected by the fluorosulphonic acid formed. Larger quantities (up to 4 g. of KSO_3F) were passed through 20 g. of resin in a waxed glass column. The acid formed was estimated alkalimetrically, with the following results:



Curve I. 0·1084 g. of $K{\cdot}SO_3F$ passed through column: end-point found, 7·90 ml. of N/10-alkali (Calc.: 7·84 ml.); original normality of acid 0·0079; pH found, 2·15 (Calc.: 2·15). (The pH is calculated from the activity of the solution by use of the activity coefficient f derived from $-\log f = 0{\cdot}5\sqrt{I}$, where I is the ionic strength.)

Curve II. Titration of 10 ml. of 0·0998N-H_2SO_4 diluted to 100·05 ml.: end-point found, 10·00; pH found, 2·10 (Calc.: 2·09).

	KSO_3F added, g.	HSO_3F formed Found	Calc.
Small column	0·2287	0·1146	0·1143
	0·1019	0·0740	0·0738
Large column	1·369	0·992	0·991
	3·675	2·665	2·660

Properties of Aqueous Fluorosulphonic Acid.—The strength of the acid was shown by comparison of the neutralization curve with that of equivalent concentrations of sulphuric acid. The results of one such pair of titrations are illustrated on the derived $\Delta v/\Delta pH$–v curves (Gran, *Acta Chem. Scand.*, 1950, 559) shown here.

Comparison with Group V Fluoro-acids.—Potassium hexafluorophosphate (Emeléus and Woolf, *loc. cit.*) solution, after passage through an exchange column, gave a steady but higher titre than that required for HPF_6 (0·2034 g. required 12·05 ml. of N/10-alkali. Calc.: 11·04). This is due presumably to the rapid equilibration between HPF_6, HPO_2F_2, H_2PO_3F, and H_3PO_4. Direct passage of the eluant into excess of alkali still gave high results. The eluant from silver hexafluoroantimonate (Woolf and Emeléus, *J.*, 1949, 2865) solution hydrolysed on titration, but an approximate end-point was reached with 2·1 equiv. of alkali. The solution hydrolysed further to 3·2 equiv. in 20 days. By heating it at 100° in the presence of excess of alkali the hydrolysis was completed in a matter of minutes [Found: 7·10 equiv., *i.e.*, $HSbF_6 + 6H_2O \longrightarrow HSb(OH)_6 + 6HF$]. Fluorosulphonic acid solutions can be boiled for the same time with little change in titre.

Conductivity of Solutions.—The dilute solutions examined (less than 0·01M) were without action on Pyrex glass, the same conductivity values being found in a Polythene cell. The values obtained in the latter were of no great accuracy because of small air bubbles on the surfaces and lack of absolute rigidity. De-ionized water of specific conductivity 0·48 × 10^{-6} mho was used. The Pyrex-glass cell had a constant of 5·985. The values in dilute solutions were difficult to reproduce, especially at lower concentrations, presumably because of hydrolysis (high values were obtained). The procedure was to prepare a concentrated solution (*ca.* 0·01M) and dilute this by weight in Polythene bottles immediately before measurement. The stock solution was rejected after 2 hr. Results were as shown below, concentration (C) being given in moles per 1000 g. of water, and conductivity (κ) in ohm^{-1}; $\Lambda = \kappa/C$.

Fluorosulphonic acid solutions at 25°.

10^3C	$10^4\kappa$	Λ	10^3C	$10^4\kappa$	Λ
0·6055	2·496	412	1·876	7·638	407
0·884	3·635	411	3·623	14·66	405
1·025	4·195	409	6·465	25·91	401

Potassium fluorosulphonate solutions at 25°.

10^3C	$10^5\kappa$	Λ	10^3C	$10^5\kappa$	Λ
0·491	6·89	140·4	1·069	14·79	138·3
0·586	8·23	140·5	1·898	25·95	136·7
0·924	12·85	139·1	3·772	50·35	133·4

No solvent correction was applied in calculating the equivalent conductivities since all solutions were acidic. For fluorosulphonic acid solutions, the linear plot of Λ against $C^{\frac{1}{2}}$ leads to a Λ_0 value of 415·5, and for the salt solutions, a value of 144·5. The slopes calculated from Onsager's equation are in approximate agreement with the experimental values and it is considered that closer agreement would be fortuitous in view of the hydrolysis which occurs in dilute solutions.

Heat of Neutralization of the Aqueous Acid.—A Dewar-flask calorimeter was used. The alkali was added by piercing an ampoule suspended in the liquid. The values obtained were the same within experimental error in waxed and unwaxed vessels. The hydrolysis which occurred in the course of an experiment was not greater than 1%, and the results are significant to this accuracy. The solutions were handled, as a precaution, in waxed flasks before addition to the calorimeter. The results were :

Moles of H_2O per mole of $H{\cdot}SO_3F$	1,332	1,715	1,448	1,119
Heat of neutralization/mole (kcal.)	14·40	14·43	14·47	14·55

A mean value for a 0·039M-solution of 14·4(6) ± 0·1 is deduced (at 25°).

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