The Determination of the Acidity of Super-acid Media by Dynamic Nuclear Magnetic Resonance Measurements: the System Fluorosulphuric Acid–Antimony Pentafluoride

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N.m.r. measurements of the lifetime of the oxonium ion in mixtures of fluorosulphuric acid and antimony pentafluoride are used to derive relative acidities of media containing between 14 and 82 mol % of SbF_5. The acidity increases monotonically up to at least 80 mol % SbF_5. The assumptions underlying the method are critically examined.

The measurement of the acidity of strongly acidic and largely, or completely, non-aqueous media is generally based on Hammett's acidity function H_0 or on one of the modified acidity functions based on the general approach pioneered by Hammett and Deyrup.[1] The function H_0, defined in equation

$$H_0 = \mathrm{p}K_{\mathrm{HB}} - \lg([\mathrm{HB}^+]/[\mathrm{B}]) \qquad (1)$$

(1), requires the determination of the ionisation ratio $[HB^+]/[B]$ for an indicator base B which, in the case of the conventional H_0 scale, is an electrically uncharged primary aromatic amine. The ionisation ratio has generally been obtained by visible or ultraviolet spectrophotometry and also by measurement of the chemical shifts of (coalesced) n.m.r. signals. These 'conventional' methods suffer from the drawback that only a limited range of values of the ionisation ratio (typically bounded by a factor of *ca.* 100) is accessible for any one base and the range is generally centred on, or not far removed from, a value of unity. A dynamic n.m.r. technique described by Sommer *et al.*[2] greatly increases this range so that it covers ratios from 10 to 10^5. In the present work we describe a quite different dynamic n.m.r. method that provides an approach to the measurement of ratios of up to *ca.* 10^{11} and extending down to 10^7—10^4, depending on the field strength of the magnet used. It is based on measurement of the lifetimes of the protonated forms of added solute bases, *i.e.*, on their rates of proton loss to a solvent base.

The use of rates of deprotonation of conjugate acids of solute bases for the purpose of establishing p*K* differences was briefly considered by Birchall and Gillespie[3] in the context of n.m.r. line-broadening measurements in fluorosulphuric acid. However, they did not find the expected correlation between line broadening and spectrophotometrically determined p*K* values for *p*-substituted acetophenones. Some of the possible reasons for this lack of correlation were qualitatively diagnosed by them, but the approach was not taken up again.

The dynamic n.m.r. techniques for acidity measurement are particularly useful for, and have to date been used only in the context of, the study of super-acid solutions, particularly for mixtures of fluorosulphuric acid with antimony pentafluoride and related systems. The remarkable acidity of such media is indicated by a host of observations indicating the protonation of many chemical species that are not normally considered to be bases.[4] However, the quantitative measurement of the acidity in fluorosulphuric acid solution by conventional methods[5] has been confined to relatively low concentrations of antimony pentafluoride (*ca.* 11 mol %), and the general course of the acidity at concentrations above *ca.* 25 mol % had been uncharted until the present study.[6] The measurements reported here refer to a single solute base, water.

Experimental

Fluorosulphuric acid (B.D.H. Chemicals Ltd.) was distilled in an atmosphere of nitrogen, using apparatus that had been flamed out. Antimony pentafluoride (Aldrich, Spectrograde) was used without purification from new unopened bottles; older samples were distilled and then stored under nitrogen. Mixtures of these two components were made up by weight: fluorosulphuric acid was added to a weighed quantity of antimony pentafluoride and the mixture was weighed. Solutions containing different amounts of water were prepared by addition of a measured amount of solute to the acid mixture at −78 °C. In all cases the final composition of the solutions was checked by integration of n.m.r. signals.

Proton n.m.r. spectra (FT) were taken either at 90 MHz (Bruker HFX-90 with B-ST-100/700 temperature regulator and Nicolet 1080 computer) or at 250 MHz (Bruker WM 250 with BV1000 temperature regulator and Aspect computer, used in the quadrature detection mode). Depending on signal intensities, 32—4 K transients were accumulated in, typically, 8 K (HFX-90) or 16 K (WM 250) data channels. The sample was placed in the inside compartment and the deuteriated lock material (chloroform, acetone, methanol, nitromethane, dichloromethane, or dimethyl sulphoxide, depending on the temperature) in the outer annular space of a coaxial Wilmad sample tube. This unconventional use of the coaxial tube ensures good magnetic field homogeneity over the sample with negligible spinning bands in the sample spectrum.

The preliminary adjustment of the shim coils was performed by the usual optimisation of the ringing pattern of the deuterium lock. Once both the field and frequency were locked on the deuterium signal, further shimming was carried out to optimise the field homogeneity over the inner compartment by observation of the FID envelope.

Although the residual protium contained in the deuteriated lock material constitutes an external reference, the problem arising from the difference in bulk susceptibilities in the inner and outer compartments reduces its usefulness as a standard (although it might provide a basis for susceptibility measurements). For this reason, the frequencies of other signals were generally referenced with respect to the invariably present internal standard H_3O^+ (δ 10.40 at 298 K), since, with reference to an external standard, the position of this signal appeared relatively insensitive to temperature. The resonance for solvent acid (in the absence of exchange) appeared at *ca.* δ 12.6 in all spectra, but its position was more temperature-dependent.

The procedure for the evaluation of k_b by complete line-shape analysis has been described previously.[7] In that earlier paper this parameter is referred to as k_{21} (when the solute base is water in the presence of another solute base) or k_{31} (when it relates to that second solute base present in addition to water).

Table 1. Values of k_b for different concentrations of dissolved water in HSO_3F–SbF_5

SbF_5 (mol %)	T/K	k_b/s^{-1}	H_2O (mol %)[a]	Base (mol %)[a,b]	Base[b]	$[A^-]$/ mol dm^{-3}	$k_b/[A^-]$/ mol^{-1} dm^3 s^{-1}
5.17	298	707	4.20			0.680	1 039
5.17	298	2×10^7	5.94			0.96	2×10^7
8.42	298	377	6.34			0.989	381
8.42	298	1 570	7.68			1.198	1 310
8.42	298	8.68×10^6	8.74			1.364	6.36×10^6
49.5	333	138	2.55	4.41	$[^2H_8]$THF	0.618	224
49.5	333	153	4.33	4.68	$[^2H_8]$THF	0.848	180
49.5	333	203	7.55	4.96	$[^2H_8]$THF	1.054	192
49.5	333	283	10.87	4.87	$[^2H_8]$THF	1.353	209
49.5	333	305	14.18	5.75	CD_3COCD_3	1.730	176
50.4	333	318	18.8			1.486	214
50.7	333	569	8.23	23.19	CD_3COCD_3	2.022	281
50.4	333	349	6.99	19.01	CF_3COMe	1.888	185
50.4	333	330	2.8	22.0	CFH_2CMe	2.045	161
50.8	333	367	13.88			1.211	303
50.2	333	1 544	3.21	42.78	CD_3SOCD_3	3.565	378
50.0	333	1 101	1.55	51.3	CD_3SOCD_3	3.779	291
50.4	333	829	11.99	21.01	CF_3COMe	2.461	337

[a] This represents the number of moles of added base per 100 moles of stoicheiometric amount of HSO_3F initially present. [b] An additional base, always observed as the fully protonated conjugate acid, was added as internal deuterium lock or as the principal base of the rate study.

The effect of solute concentration on k_b was examined in detail for water as solute, with the results given in Table 1.

Table 2 lists results for k_b and $k_{HB.A}$ for a range of compositions at 298 K. Measurements were always carried out at a series of temperatures. The activation energies (for $k_{HB.A}$) were found to be independent of the antimony pentafluoride content (44 ± 4 kJ mol^{-1}). The Table includes, in addition to the results on the two-site system, also some values deduced by complete line-shape analysis of three-site systems (*i.e.*, for solutions also containing an organic base).

Spin–lattice relaxation times (T_1) were measured as previously described[7b] (Table 3).

Discussion

Our technique is based on consideration of the equilibrium of equation (2), where HA represents the solvent acid and B a particular solute base that is almost completely converted into HB^+ in the solution. Equation (2) implies the equilibrium condition expressed by equation (3a) or (3b). Experimental first-order rate coefficients (k_a and k_b, respectively equal to the inverse of the mean residence times of protons on HA and HB^+) are obtainable from line-shape analysis. If the two reactions of equation (2) are an adequate description of the processes controlling the mean lifetimes of HA and HB^+, k_a and k_b are simply related to the second-order rate constants in equations (2) and (3) by equations (4) and (5). Within limits, the implied proportionality of k_b and $[A^-]$ is confirmed experimentally for equimolar mixtures of fluorosulphuric acid and antimony pentafluoride (see Figure 1) and allows us to treat $k_{HB.A}$ as constant over a range of concentrations of added base in the same solvent acid.

$$HA + B \underset{k_{HB.A}}{\overset{k_{HA.B}}{\rightleftharpoons}} HB^+ + A^- \qquad (2)$$

$$K = k_{HA.B}/k_{HB.A} = [HB^+][A^-]/[B][HA] \qquad (3a)$$

$$[HB^+]/[B] = (k_{HA.B}/k_{HB.A})\cdot([HA]/[A^-]) \qquad (3b)$$

$$k_{HA.B} = k_a/[B] \qquad (4)$$

$$k_{HB.A} = k_b/[A^-] \qquad (5)$$

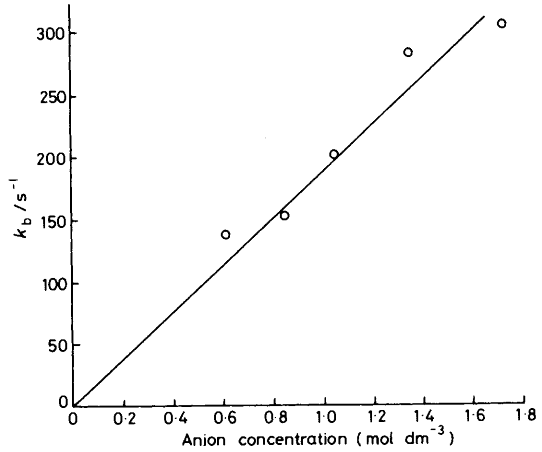

Figure 1. Dependence of k_b on concentration of solvent anion in fluorosulphuric acid containing 49.5 mol % antimony pentafluoride (at 333 K, for low concentrations of solute)

Combination of equations (1) and (3) gives equation (6). In

$$H_0 = pK_{HB} - \lg k_{HA.B} + \lg k_{HB.A} - \lg([HA]/[A^-]) \qquad (6)$$

this equation the ratio $[HA]/[A^-]$ is known from the stoicheiometric composition of the solution. This follows because $[A^-]$ must very closely approximate to the stoicheiometric concentration of the added base B if the latter is almost completely converted into its conjugate acid HB^+ (or to the sum of the stoicheiometric concentrations of all such bases present). The formation of A^- is accompanied by a corresponding reduction of the concentration of HA from its stoicheiometric value.

Table 2. Values of $k_{HB.A}$ (water) at 298 K for super-acids of different compositions

SbF_5 (mol %)	H_2O (mol %)	$[A^-]$/ mol dm^{-3}	[HA]/ mol dm^{-3}	lg ($k_{HB.A}$)[a]	Additional base (mol %)
1.80	2.97	0.500	16.35	6.30	
2.74	3.58	0.597	16.06	5.06	
4.06	4.73	0.779	15.68	4.59	
5.17	4.20	0.680	15.44	3.02	
5.17	5.94	0.960	15.16	7.3	
7.24	6.91	1.096	14.76	3.91	
8.42	6.34	0.989	14.66	2.58	
8.42	7.68	1.198	14.45	3.12	
8.42	8.74	1.364	14.29	6.8	
9.54	9.96	1.536	13.88	5.28	
12.86	5.48	0.769	13.27	2.08	
14.41	29.6	4.309	10.26	3.30	
14.67	1.69	1.578	11.83	3.21	p-MeC_6H_4COMe (10.1)
17.66	4.42	0.619	13.40	1.97	
27.12	11	1.968	10.34	2.08	$[^2H_8]THF$
28.5	19.4	2.34	9.73	1.79	
31.73	8	1.539	10.00	1.74	$[^2H_8]THF$
33.3	18.8	2.12	9.16	1.73	
36.19	11	1.682	9.06	1.65	$[^2H_8]THF$
37.5	20.8	2.21	8.45	1.63	
41.0	21.4	2.15	7.87	1.64	
43.79	10	1.408	8.03	1.46	$[^2H_8]THF$
44.4	18.2	1.71	7.70	1.46	
47.5	18.2	1.61	7.24	1.62	
47.8	11.75	2.449	5.310	1.68	CD_3NO_2 (20.2)
50.0	23.5	1.96	6.38	1.45	
50.0	1.55	3.779	2.234	1.60	CD_3SOCD_3 (51.3)
50.2	3.21	3.565	3.236	1.75	CD_3SOCD_3 (42.8)
50.4	2.8	2.045	5.764	1.39	CFH_2COMe (22.0)
50.4	6.99	1.888	5.663	1.44	CF_3COMe (18.0)
50.4	11.99	2.461	4.997	1.69	CF_3COMe (21.0)
50.4	18.18	1.486	6.687	1.44	
50.7	8.23	2.022	5.231	1.76	CD_3COCD_3 (23.2)
50.8	13.88	1.211	6.962	1.63	
52.3	24.2	1.91	5.99	0.95	
54.3	23.5	1.77	5.77	0.84	
56.0	1.21	3.417	3.661	1.46	CD_3NO_2 (48.3)
56.5	28.9	2.05	5.05	0.86	
57.0	13	1.310	5.67	0.78	$[^2H_8]THF$
58.3	30.6	2.08	4.70	0.63	
65.7	1.82	2.454	2.552	0.87	CD_3NO_2 (47.4)
82.1	1.63	1.396	1.051	−0.43	CD_3NO_2 (55.7)

[a] Expressed as multiples of dm^3 mol^{-1} s^{-1}.

By use of equation (5), equation (6) can be transformed into the equivalent expressions (7) which are more directly linked to the experimental data.

$$H_0 = pK_{HB} - \lg k_{HA.B} + \lg (k_b/[HA]) \qquad (7a)$$

$$H_0 = pK_{HB} - \lg k_{HA.B} - \lg ([HA]/[A^-]) + \lg (k_b/[A^-]) \qquad (7b)$$

The role of $k_{HA.B}$ in equation (7) has been assessed earlier,[6] with the conclusion that the value of this constant must be large and close to the limit set by the rate of encounters. It follows from this model that, even though there is spectroscopic evidence that the chemical nature of HA is changed as antimony pentafluoride is added,[8] an increase in the acidity of the medium (or the precise chemical identity of HA) cannot be accompanied by a *large* increase in $k_{HA.B}$, which would in effect take its value beyond the diffusion limit. For this reason, $k_{HA.B}$ is, in the first instance, assumed to have such a limiting value, which is taken to be the same for various solute bases. However, the viscosity

Table 3. Proton spin–lattice relaxation times in super-acid media

SbF_5 (mol %)	Added bases (mol %)	$\ln(T_1/ms)$ at 298 K
50.4	4% water	6.76
50.4	15.4% water	6.52
50.8	14.8% water	6.48
50.4	7% water, 18% CF_3COMe	6.77
50.4	12% water, 21% CF_3COMe	6.37
50.4	2.8% water, 22% CFH_2COMe	7.22
81.6	8% water	5.76

of the medium changes with composition and, since the rate of encounters depends on the viscosity of the medium,[9] $k_{HA.B}$ may not be absolutely constant. In fact, this assumption is unlikely to be seriously at fault for the media examined. The measured spin–lattice relaxation times for some HSO_3F–SbF_5 systems of different compositions are fairly constant (Table 3) in the absence of exchange effects. Since the value of T_1 is inversely related to the viscosity of the solution,[7b] it follows that the viscosities of these media must all be very similar. It is more questionable whether the concept of an encounter-limited reaction is strictly applicable at the high concentrations used, but our argument would not appear to depend on this.

With the above assumptions equation (6) [or (7)] can be applied to evaluate (*a*) differences between the H_0 values of two different media and (*b*) differences between the pK values of different indicator bases. If the same indicator is placed in two different HSO_3F–SbF_5 mixtures, it follows that the difference of the experimental function lg $k_{HB.A}$ − lg HA]/[A^-]) [or of its equivalent form lg (k_b/[HA])] measures the difference of the H_0 values of the two media. If two different bases, B and C, are dissolved in acid of the same composition (same H_0 and same [HA]/[A^-]) then the difference (lg $k_{HB.A}$ − lg $k_{HC.A}$) will equal the difference of pK values, (pK_{HC} − pK_{HB}). [It should incidentally be noted that $k_{HB.A}$ and K_{HB} contain the same symmetry factor[10] when there is more than one (equivalent) proton in the acid HB^+.]

It is an inherent limitation of the technique with currently available instruments that it requires the use of fairly high concentrations of solute and hence of the conjugate base of the solvent acid. For this reason, the values thus obtained refer not to the solvent system on its own but to a medium with an acidity that has been lowered by the presence of base. The effect is explicitly stated in equation (6) according to which a decrease in the ratio [HA]/[A^-], brought about by the addition of base, raises the value of H_0 (*i.e.*, reduces the acidity).

Equation (6) embodies the assumption that the equilibrium constant K of equation (3) is independent of the concentration of added base and depends only on the chemical composition of the solvent acid (in the present instance, the stoicheiometric proportions of fluorosulphuric acid and antimony pentafluoride). Equation (6) can also be written as equation (8) which was

$$H_0 = \text{constant} - \lg([\mathrm{HA}]/[\mathrm{A}^-]) \qquad (8)$$

shown by Brand[11] to be a good approximation for low concentrations of solute water even in the more weakly acidic solvent sulphuric acid. In principle, equation (6) provides a method for relating H_0 values obtained for different ratios [HA]/[A^-] and to bring measurements to a common basis, irrespective of the method of measurement. In applying it to our data we assume that $k_{HA.B}$ is independent of this ratio as the concentrations of HA and A^- are changed by the addition of base because it has a value close to the limit set by encounter rates. The experimental results in Figure 1 also show that $k_{HB.A}$ is constant under these conditions, but the data are restricted to low concentrations of A^-. Let us give the symbol $H_0(r_1)$ to the value of H_0 deduced according to equation (6) [or (7)] from measurements of $k_{HB.A}$ (or of k_b) at a particular ratio [HA]/[A^-] = r_1, *i.e.*, equation (9a).

$$H_0(r_1) = [\mathrm{p}K_{HB} - \lg k_{HA.B} + \lg k_{HB.A}] - \lg r_1 \qquad (9a)$$

The H_0 value of the acid containing the same stoicheiometric ratio of fluorosulphuric acid to antimony pentafluoride but a different value (*e.g.*, r_2) of the ratio [HA]/[A^-], called $H_0(r_2)$ for the purposes of this argument, will then similarly be given by equation (9b). The difference between these two H_0 values is thus evidently given by equation (10). If $H_0(r_2)$ and r_2 refer to an acid without any added base and $H_0(r_1)$ to the experimental system, then the value of H_0 for the limiting case of neat acid is obtainable from the measured value according to equation (11).

$$H_0(r_2) = [\mathrm{p}K_{HB} - \lg k_{HA.B} + \lg k_{HB.A}] - \lg r_2 \qquad (9b)$$

$$H_0(r_1) - H_0(r_2) = \lg r_2 - \lg r_1 \qquad (10)$$

$$H_0(r_2)(neat) = H_0(r_1)\,(\text{measured}) + \log r_1 - \lg r_2 \qquad (11)$$

In the case of fluorosulphuric acid without added SbF_5 the value of r_2 (for neat acid) can be calculated from the autoprotolysis constant for anhydrous fluorosulphuric acid, [5b] but this information is not available for mixtures containing antimony pentafluoride with which we are concerned. Alternatively, it is possible, on the same assumptions, to relate all measurements to an arbitrary common value of [HA]/[A^-]. If a common value of 10 is taken for r_2, the corresponding value of H_0 is called $H_0(10)$. It is related to a measured value $H_0(r)$, referring to [HA]/[A^-] = r, by equation (12) or, since according to equation (9), the value of $H_0(r)$ depends on r [equation (13)] we may also write equation (14).

$$H_0(10) = H_0(r) + \lg r - 1 \qquad (12)$$

$$H_0(r) = \mathrm{p}K_{HB} - \lg k_{HA.B} + \lg k_{HB.A} - \lg r \qquad (13)$$

$$H_0(10) = \mathrm{p}K_{HB} - \lg k_{HA.B} + \lg k_{HB.A} - 1 \qquad (14)$$

For the purpose of deducing a relative $H_0(10)$ scale [or any relative $H_0(r)$ scale] from measurements of $k_{HB.A}$, it is therefore unnecessary to introduce the values of r of the various solutions examined. All $H_0(r)$ scales follow a parallel course. Absolute values of H_0 for the solvent system without added bases cannot, however, be derived without additional information.

The importance of the concentration of added base in connection with the measured acidity function was also similarly recognised by Sommer *et al.*,[12] who used slightly different assumptions from ours concerning the underlying chemistry.

In principle it should be possible to refer our scale of measurements to spectrophotometric H_0 determinations on fluorosulphuric acid without or with only a low concentration of added antimony pentafluoride. In practice this overlap could not be achieved owing to the limited sensitivity of n.m.r. spectroscopy, which prevented observations on very dilute solutions containing less solute than antimony pentafluoride. However, concordant H_0 values covering the range up to 11 mol % antimony pentafluoride have been reported from the laboratories of Gillespie *et al.*[5] and Sommer *et al.*,[2] and Sommer *et al.* have extended the measurements up to 25 mol % antimony pentafluoride.[2,12] We find that over the range 7—25% these measurements[12] are reproduced by the equation (15).

$$-H_0 = 17.8 + 0.11 \times (\text{mol}\,\%\,\mathrm{SbF_5}) \qquad (15)$$

Our experimental values for log $k_{HB.A}$ are plotted in Figure 2 as a function of the composition of the solvent acid. The curve through the data points (covering a wide range of concentrations of added solute) has been superposed on a graph of equation (15) in the region of overlap by vertical translation of the separate graphs. The values on the H_0 axis required for equation (15) accordingly also represent the H_0 values corresponding to the log $k_{HB.A}$ values of the experimental points, within the limits of the data. These results all refer to H_2O as the solute base under consideration, so that there are no added complications arising from overlaps between different bases. The salient result is the continuing rise in acidity of the solutions as the proportion of antimony pentafluoride in the

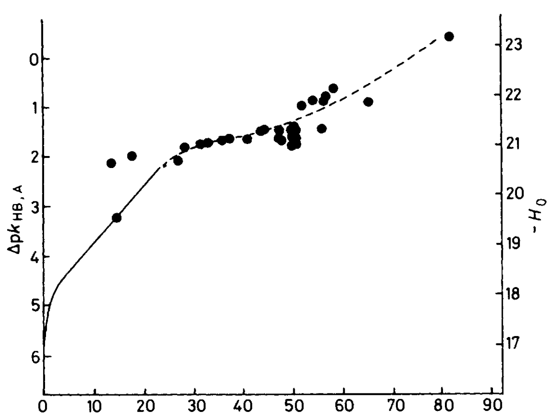

Figure 2. Values of log $k_{HB.A}$ (for water as solute, at 298 K) and corresponding H_0 values as a function of antimony pentafluoride concentration. (Solid line represents H_0 data from Sommer *et al.*, points relate to values of $k_{HB.A}$ for water as base)

solvent acid is raised even beyond 50 mol %. The increase in acidity appears less steep between 30 and 50 mol % than in the regions 10—30 and 50—70 mol %. Although there is considerable scatter of the points, the monotonic rise in acidity is supported by data on other bases (see following paper[13]).

The validity of the method and the interpretation of the results are subject to some further considerations.

The observed proton resonance signals always relate to bulk forms (or to rapidly equilibrating mixtures of bulk forms) of the chemical components of the systems. Accordingly, we may omit from our consideration low-concentration forms, such as $H_2SO_3F^+$, the concentrations of which must vary with the acidity of the medium. It is, however, clear that the remarkable increase in acidity that accompanies the addition of antimony pentafluoride to fluorosulphuric acid must also produce changes in the chemical nature of at least some of the bulk forms, which are here symbolically represented as HA,A$^-$, *etc.* In fact, we attribute the decrease in the value of $k_{HB.A}$ (which mirrors the increase in acidity of the medium) to the stabilisation (and hence decrease in base strength) of the fluorosulphate anion by its association with antimony pentafluoride. Equation (5) is accordingly expected to hold only over ranges of composition for which there is no profound change in the chemical nature and equilibrium proportions of the bulk forms of the chemical species making up solvent anions A$^-$. In particular, equation (5) cannot be valid if, over the composition range studied, the concentration of added solute base becomes comparable to or even exceeds the concentration of antimony pentafluoride. The resulting limitations on the practical use of the equations are essentially set by the sensitivity of the spectrometer. In principle, solutions containing sufficiently low concentrations of solute can always be prepared, but it depends on the sensitivity of the instrument (and available instrument time) whether the required line-width measurements or line-shape analysis can be performed with adequate precision.

A simple formulation of the role of antimony pentafluoride in enhancing the acidity (which differs from earlier analyses[2,5,12]) is represented by equation (16), implying that the bulk anion is

$$B + HSO_3F + SbF_5 \longrightarrow BH^+ + SbF_5(SO_3F)^- \quad (16)$$

$SbF_5(SO_3F)^-$. However, when the concentration of antimony pentafluoride is lower than that of the added base, the anion SO_3F^- must also be present in the system. In such circumstances, the chemical nature of the main form of A$^-$ gradually changes from $SbF_5(SO_3F)^-$ to SO_3F^- as the concentration of added base is increased. The range of validity of equation (5) is accordingly limited by the concentration of antimony pentafluoride in the system. The values of $k_b/[A^-]$ given in Table 1 are seen to have an approximately constant value of *ca.* 200 dm^3 mol^{-1} s^{-1} at 333 K for acids containing 49.5 mol % of antimony pentafluoride. In the light of the foregoing remarks this value relates to the base $SbF_5(SO_3F)^-$. There is a gradual drift to higher values for experiments in acids of similar content of antimony pentafluoride at high concentrations of added base (relative to antimony pentafluoride). More dramatically, the results for experiments at low concentrations of antimony pentafluoride show a very sharp increase in the ratio $k_b/[A^-]$ as the concentration of added base overtakes that of antimony pentafluoride, and this would be accompanied by the replacement of the base $SbF_5(SO_3F)^-$ by the stronger base SO_3F^-. For these reasons, our experimental points for solutions at SbF_5 concentrations below *ca.* 10—15 mol % are less reliable than those at higher concentrations.

The argument can also be put more explicitly as follows. The proton flux [in the reverse direction of equation (2)] characterised by the factor $k_{HB.A}[A^-]$ is a composite term, since the stoicheiometric concentration of the solvent base A$^-$ is a sum of concentrations, [equation (17)]. Correspondingly, the experimental rate constant k_b is a composite quantity, as given by equation (18).

$$[A^-] = \sum_{i=0}^{\infty}[SO_3F(SbF_5)_i^-] = \sum_{i=0}^{\infty}[A_i] \quad (17)$$

$$k_b = \sum_{i=0}^{\infty} k_{HB.A_i}[SO_3F(SbF_5)_i^-] \quad (18)$$

The very steep rise in the acidity of the solutions for small additions of antimony pentafluoride to fluorosulphuric acid suggests that of the (stepwise) association constants K_i [equation (19)] the constant corresponding to $i = 0$ has a large

$$K_i = [A_{i+1}]/[A_i][SbF_5] \quad (19)$$

value. In equation (18) the rate constant $k_{HB.A_i}$ would then have the largest value for $i = 0$ and it is conceivable that the corresponding term in the summation is the only important one at all compositions, with the concentration of the reactive uncomplexed fluorosulphate ion determined by the values of K_i. On this rather simple assumption, the sum in equation (18) would be dominated by a single term.

From equation (19) we can see that $[A_i]$ is as shown in equations (20a—c), so that we obtain equation (21), whence the dominant term in equation (18) becomes as given in equation (22).

$$[A_1] = K_0[SO_3F^-][SbF_5] \quad (20a)$$

$$[A_2] = K_0K_1[SO_3F^-][SbF_5]^2 \quad (20b)$$

$$[A_3] = K_0K_1K_2[SO_3F^-][SbF_5]^3 \ \textit{etc.} \quad (20c)$$

$$\Sigma[A_i] = [SO_3F^-](1 + K_0[SbF_5] + K_0K_1[SbF_5]^2 \ldots) \quad (21)$$

$$k_b = k_{HB.A_0}\Sigma[A_i]/(1 + K_0[SbF_5] + K_0K_1[SbF_5]^2 \ldots) \quad (22)$$

The concentration of SbF_5 in equation (22) is the actual concentration of *free* antimony pentafluoride which, on this model, is equal to the total concentration only in the absence of anions (*i.e.*, of added base). It also follows that k_b depends not only on the concentration of anions (added base) in the system but also on the *relative* concentrations of antimony pentafluoride and added base. For these various reasons, the acidity and basicity measurements are reliable only when the concentration of antimony pentafluoride greatly exceeds that of the added base.

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Received 2nd August 1984; *Paper* 4/1372