A Dynamic N.M.R. Study of the Acidity of Super-acid Media (Mixtures of HSO_3F and SbF_5 from 0 to 90 mol % of SbF_5)

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Summary Rates of proton exchange between fluorosulphuric acid and protonated solute bases were used to derive pK differences between the bases and the approximate course of an H_0 function between 0 and 90 mol % of SbF_5; the acidity increases monotonically over this range.

IONIZATION ratios of solute bases in the super-acid solvent system fluorosulphuric acid–antimony pentafluoride have been measured by the indicator method,[1] using aromatic nitro-compounds as bases, up to *ca.* 11 mol % of SbF_5 ($H_0 = -19$), and up to *ca.* 25 mol % ($H_0 = -21$ to -22) by use of an original dynamic n.m.r. method with aromatic aldehydes as bases.[2,3] Above *ca.* 10 mol % there is a slight disagreement between the values of the H_0 function derived from these sets of measurements, neither of which extends sufficiently far to settle the question whether the rise in acidity with SbF_5 attains a maximum value in the equimolecular mixture.

We have employed a novel experimental approach to the problem in which n.m.r. line-shape analysis methods are used to study the kinetics of hydrogen exchange reactions of the type $\overset{*}{H}A + HB^+ \rightleftharpoons HA + \overset{*}{H}B^+$ where HA represents the acid of the solvent system and HB^+ the protonated form of an added base. We consider that the hydrogen exchange observed (involving interchange of asterisked and un-asterisked positions), in solutions in which the degree of conversion of B into HB^+ is 'complete' in a practical sense, proceeds *via* the forward and reverse steps of reaction (1).

$$HA + B \underset{k_{HB,A}}{\overset{k_{HA,B}}{\rightleftharpoons}} HB^+ + A^- \qquad (1)$$

The equilibrium (1) implies equation (2). The first-order

$$K = k_{HA,B}/k_{HB,A} = [HB^+][A^-]/[B]\,[HA] \qquad (2)$$

rate coefficients obtainable from the line-shape analysis (k_a and k_b, respectively equal to the inverse of the mean residence times of protons on HA and HB^+) are related to the rate constants of equation (1) by equations (3) and (4).

$$k_{HA,B} = k_a/[B] \quad (3)$$

$$k_{HB,A} = k_b/[A^-] \quad (4)$$

Equations (2) and (4) then lead to equation (5) On the

$$k_{HA,B}[HA]/k_b = [HB^+]/[B] \quad (5)$$

assumption that it is valid to assume that equation (6)

$$H_0 = pK_{HB} - \lg([HB^+]/[B]) \quad (6)$$

defines a valid acidity function H_0 for the base B in our solvent system, substitution of equation (5) in equation (6) yields equation (7).

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

This analysis requires k_b to be proportional to the concentration of A^-, and to increase with temperature and with the value of K_{HB}. These requirements have been found to be obeyed.

The application of n.m.r. line-shape analysis to kinetic problems is well established.[4] Our procedure differs from earlier ones in the use of more effective computational techniques, in which the kinetic situation is treated as a three-site exchange, in order to allow for the additional presence of traces of water in mixtures of fluorosulphuric acid and antimony pentafluoride.

To assess the role of $k_{HA,B}$ in equation (7), we consider the case of *p*-methylacetophenone in neat fluorosulphuric acid. This is a typical solute used by us between 0 and 28·5 mol % of SbF_5. The H_0 value at which acetophenone is half-ionised[5] is $-6{\cdot}3$. The pK_a difference between acetophenone and its *p*-methyl derivative[6] is reported to be *ca.* 0·5 to 0·7 and hence the H_0 value for half-ionization of the latter is estimated to be *ca.* $-5{\cdot}7$. Gillespie and Peel[1] give a value of $-15{\cdot}1$ for H_0 of fluorosulphuric acid and, after allowing for the difference in the concentration of solute (and hence of fluorosulphate) between their study and ours, we estimate that the H_0 value for the solution of *p*-methylacetophenone in fluorosulphuric acid (with $[A^-]/[HA] = 0{\cdot}08$) was between -12 and -13. It follows that the ratio $[HB^+]/[B]$ for this solute base in neat fluorosulphuric acid lies between $10^{6\cdot3}$ and $10^{7\cdot3}$. The measured value of $k_{HB,A}$ in this solution was 10^4 dm^3 mol^{-1} s^{-1} at 293 K. The corresponding value of $k_{HA,B}$ can then be calculated from equation (7) as lying between 2×10^9 and 2×10^{10} dm^3 mol^{-1} s^{-1}, indicating that the reaction proceeds at a rate close to the limit set by the rate of encounters. Accordingly, $k_{HA,B}$ is likely to be insensitive to the chemical nature of B. It may be slightly dependent on the composition of the solution associated with changes in its structure, especially through association of SbF_5 with the fluorosulphate ion.[7]

Accordingly, we conclude that, on the assumption that $k_{HA,B}$ is nearly constant (and within the limits set by this assumption), equation (7) may be used to calculate (i) approximate differences in pK_{HB} between different bases in the same acid and (ii) relative H_0 values for acids of different composition by use of a common reference base B. A combination of (i) and (ii) then allows the tentative establishment of an acidity function over the entire composition range studied (0—90 mol % SbF_5), where H_0 values applicable at the lower end of the composition range are taken from Gillespie and Peel's spectrophotometric measurements[1] (Figure).

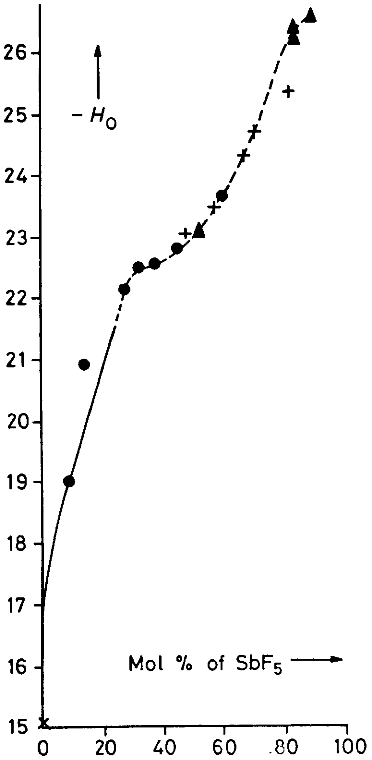

FIGURE. Acidity function for HSO_3F–SbF_5. [The continuous curve represents results due to Sommer *et al.* (refs. 2 and 3), the cross on the ordinate marks H_0 for HSO_3F (ref. 1). Results from the present work: ● = H_2O, + = CD_3NO_2, ▲ = CF_3COMe as base.]

Our n.m.r. measurements were made at various concentrations of solute base (and hence of fluorosulphate ion). To provide a common basis for comparison, the derived $k_{HB,A}$ (and hence H_0) values were recalculated by equation (2) so as to refer throughout to solutions in which the ratio of fluorosulphate to fluorosulphuric acid is 0·1. This also corresponds approximately to the ratio at the lowest concentration of adventitious water in commonly used samples of super-acid media and is accordingly of practical interest.

To the extent that $k_{HA,B}$ may not be completely independent of the SbF_5-content, the H_0 scale given in the Figure may slightly *underestimate* the acidity of the solutions. It must also be emphasized that it is now recognised that different bases define slightly different acidity functions, and that the range of measurements and reference bases used preclude us from specifying precisely to what other substances the acidity function formally defined by our data is applicable.

However, the results are sufficient to indicate that the acidity of HSO_3F–SbF_5 solutions increases monotonically at least up to 90 mol % SbF_5, despite the exceedingly low concentration of acidic protons in such solutions. The value of H_0 derived for 90 mol % SbF_5 (*ca.* $-26{\cdot}5$) makes this the most acidic liquid Brönsted acid measured so far. There are indications that mixtures of hydrofluoric acid with an excess of antimony pentafluoride may prove to be even stronger acids.[8]

$$\mathrm{p}K_\mathrm{a}(\mathrm{H_3O^+}) - \mathrm{p}K_\mathrm{a}(\mathrm{CD_3NO_2H^+}) = ca.\ 2{\cdot}5 \qquad (8)$$

$$\mathrm{p}K_\mathrm{a}(\mathrm{CD_3NO_2H^+}) - \mathrm{p}K_\mathrm{a}[\mathrm{CF_3C(\overset{+}{O}H)Me}] = ca.\ 1{\cdot}5 \qquad (9)$$

$$\mathrm{p}K_\mathrm{a}[\mathrm{(CF_2H)_2COH^+}] - \mathrm{p}K_\mathrm{a}[\mathrm{CF_3C(\overset{+}{O}H)Me}] = ca.\ 3{\cdot}0 \qquad (10)$$

The differences between $\mathrm{p}K_\mathrm{HB}$ values of the bases used, derived by use of equation (7), are given in equations (8)—(10). In these media water appears to be a slightly weaker base than acetone ($\Delta\mathrm{p}K_\mathrm{a} = ca.\ 0{\cdot}3$), confirming that the solute species produced is very different from the hydrated oxonium ion formed in aqueous media.

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