Dynamic Nuclear Magnetic Resonance Measurements of the Basicity of Weak Organic Bases in Super-acid Media

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Solutions of a number of weak organic bases (such as nitro-compounds, ketones, aldehydes, ethers, and alcohols) in mixtures of fluorosulphuric acid and antimony pentafluoride have been examined by dynamic n.m.r. measurements. The rate of proton loss from the conjugate acids of these bases affords an inverse measure of their relative basic strengths, and amplifies the acidity measurements on the solvent system. N.m.r. spectral parameters are listed for the protonated bases.

It has been shown that kinetic studies of rapid proton-transfer reactions by n.m.r. line-shape analysis can be used to derive a thermodynamic measure of the acidity of super-acidic media.[1,2] The acidity of a range of media of widely differing acid strength, and the acidity function through which it is expressed, has to be measured with respect to several solute bases. The quantitative establishment of such a scale of acidity for media of widely differing composition is therefore complemented by the assignment of relative basicities to the various bases used. This paper is concerned with the behaviour of several solute bases in mixtures of antimony pentafluoride and fluorosulphuric acid. Because all the solutions used contained some water, the measurements usually involved the line-shape analysis of three-site systems.[3]

The features of solutions of different bases are discussed in the Results and Discussion sections. The paper reports not only the results for bases for which quantitative conclusions concerning pK and H_0 could be deduced from the measurements, but also contains qualitative information on bases whose behaviour did not lend itself to detailed kinetic analysis. In particular, results are given for a number of compounds that were briefly studied only in 50% SbF_5 ('magic acid').

Experimental

The preparation of acid mixtures has been described before.[2] Weighed amounts of solute were generally introduced directly. In cases where this appeared to lead to considerable decomposition, the solvent acid (*ca.* 1 cm^3) and the solute base were separately diluted with liquid sulphur dioxide (*ca.* 1 cm^3) and the two solutions were mixed at −78 °C. The mixture was then taken out of the cooling bath, and sulphur dioxide was removed by a stream of dry nitrogen. Alternatively, the base was slowly added to a layer of n-hexane (1—2 cm^3) from which it was gradually extracted into the acid layer below. In all cases the final stoicheiometric composition of the solution was either checked or established by integration of n.m.r. signals. All samples whose spectra were subjected to quantitative line-shape analysis were handled under nitrogen.

Organic bases of the highest commercially available purity were generally used without further treatment.

Rate constants were evaluated by the methods previously described.[3] Except where this is explicitly indicated, the results relate to three-site complete line-shape analysis with independently estimated natural line widths.[4] When deuteriated solute bases were employed, the solute itself served as lock and reference, and the use of an external standard was unnecessary. In such cases the sample was contained in a standard 5 mm n.m.r. tube; in others, except where noted, the arrangement of sample and reference in concentric tubes was used.[2] The spectra illustrated were taken at 90 MHz and are superpositions of experimental and computed spectra.

In the following section the subscript 1 (in relation to rate constants and populations) refers to the solvent acid, 2 to the H_3O^+ ion, and 3 to the proton accepted by the solute base. The symbols p_1, p_2, and p_3 designate the respective proton atom fractions. The term % SbF_5 signifies the mole percentage, *i.e.*, as shown in equation (1), $[HSO_3F]_{st}$ being the stoicheiometric concentration.

$$\%\,SbF_5 = 100[SbF_5]/([HSO_3F]_{st} + [SbF_5]) \quad (1)$$

Results

[$^2H_6$]*Acetone.*—This is a slightly stronger base than water. Depending on the concentration and temperature, the resonance of the protonated carbonyl group appears in the region δ 7—8, which is upfield of the proton resonances of both the acid (which is furthest downfield) and the H_3O^+ ion. The signal due to the latter is distinct at 272 K or lower temperatures, and a three-site line-shape analysis was performed on the system.

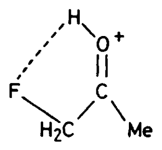
Because of the dependence of the solvent acid peak on temperature, there is overlap between the two downfield signals at higher temperatures, and the spectrum analysis was then treated as a two-site problem. The acid sample used contained 50.74% SbF_5. The two solutions studied over the temperature range 240—355 K had the following compositions: (*i*) $[HSO_3F]$ = 5.2M, $[SO_3F^-]$ = 2.02M; (*ii*) $[HSO_3F]$ = 3.74M, $[SO_3F^-]$ = 3.45M. The symbol $[SO_3F^-]$ refers to the sum of all solvent anions.

Fluoroacetone.—Details concerning the line-shape analysis[3] and measurement of spin–spin and spin–lattice relaxation times[4] for this base have been published. At temperatures between 234 and 308 K five separate proton resonances appear (those due to the CH_3 and CFH_2 groups remaining distinct at all temperatures). At 259 K the extreme downfield peak due to $C{=}O^+H$ (δ 15.35) is a doublet (J_{HOCCF} = 8.2 Hz), and because of viscosity broadening, the peaks due to CH_3 (δ 3.86, s) and CH_2F (δ 6.63, d, J_{HCF} 44.2 Hz) do not show the full fine structure. At higher temperatures the additional spin–spin splitting is observed. The CH_2 resonance becomes a doublet of quartets (J_{HCCCH} 1.8 Hz); the quartet splitting is due to the methyl group protons and collapses upon irradiation of the methyl resonance. The methyl resonance is correspondingly a doublet (J_{FCCCH} 2.5 Hz) of triplets (J_{HCCCH} 1.8 Hz, as above). Table 1 compares the spectral parameters for the protonated and unprotonated chemical species. The evident reduction in the value of J_{HCCCF} and increase in J_{HCCCH} upon protonation may be due to an increase in the barrier to rotation of the CH_2F

Table 1. Spectral parameters of acetone, fluoroketones, and their corresponding conjugate acids

	δ/p.p.m.			*J*/Hz			
Species	C=O*H*$^+$	C*H*$_3$	C*H*$_i$F$_{3-i}$	HCCCF	HCF	HCCCH	*T*/K
$CD_3COH^+CD_3$	14.40						298
CH_2FCOMe[a]		2.21	4.82	4.1	47.8	*b*	298
CH_2FCOH^+Me	15.35	3.86	6.63	2.5	44.2	1.8	377
CF_3COMe[c]		1.92		1.1			213
CF_3COH^+Me[d]	18.03	4.34		1.6[e]			228
CF_2HCOCF_2H[f]			5.85	6.2	55		296
$CF_2HCOH^+CF_2H$	16.9						
$CF_3CF_2COH^+Et$	17.19	2.39					

[a] In $CDCl_3$, chemical shifts relative to internal Me_4Si. [b] Too small for observation at this viscosity. [c] Ref. 5*a*. [d] 50.4 mol % SbF_5; for 82 mol % SbF_5 (at 253 K), δ(C=O$^+$H) 17.4. [e] Fine structure resolved only above 250 K. [f] In [$^2H_6$]DMSO.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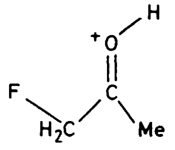
(2)

group caused by hydrogen bonding between fluorine and the protonated carbonyl group (**1**).

The proton-decoupled ^{13}C n.m.r. spectrum of protonated fluoroacetone at 300 K gave signals at δ 223.8 (d, J_{CCF} 13.2 Hz), ascribed to the carbonyl carbon, at δ 75.4 (d, J_{CF} 193 Hz), and at δ 14.72 (s). The sample was in the inner compartment (5 mm diameter) of a coaxial 10 mm sample tube, the outer compartment of which contained D_2O as lock and a trace of [$^2H_6$]acetone, the carbonyl frequency of which (taken to be at δ 206.0) served as reference.

The appearance of the C=O$^+$*H* signal and of the C*H*$_3$ and C*H*$_2$F signals gave no evidence for the presence of (long-lived) *E,Z*-isomers (**1**) and (**2**).

1,1,1-*Trifluoroacetone*.—The formation of the conjugate acid of this ketone in the equimolar mixture of fluorosulphuric acid and antimony pentafluoride with a viscosity-lowering diluent was established by n.m.r. chemical shift measurements.[5a] In the absence of such diluents we have found it possible to observe this ion as a long-lived species, and have already reported the measurement of relaxation times for it.[4] Solutions had a faint yellow colour, which deepened on standing or on being heated to 400 K, but without perceptible change in the appearance of the n.m.r. spectrum. This suggests that the coloration is due to a trace impurity rather than to decomposition of the substrate.

In acid of 50.4% SbF_5 and at temperatures below 228 K the proton n.m.r. spectrum shows a broad peak at δ 18.03, attributed to C=O$^+$*H*, and a peak due to the methyl group at δ 4.34, in addition to the usual signals of solvent acid (δ 12.26) and H_3O^+ (δ 10.3). The broadening below the coalescence temperature of 228 K is due to both exchange (between H_3O^+ and C=O$^+$*H*) and viscosity.

In media containing a higher percentage of SbF_5 the corresponding signals are sharper, and in 80% SbF_5 separate signals are observed at temperatures as high as 253 K (Figure 1). The sharpness of the C=O$^+$*H* resonance indicates grossly reduced coupling to fluorine compared with the case of fluoroacetone.

In all solutions only a single C=O$^+$*H* proton signal is observed, *i.e.*, there is no evidence for the presence of long-lived *E,Z*-isomers in the system, such as are found for some other unsymmetrical carbonyl compounds upon protonation.[5b]

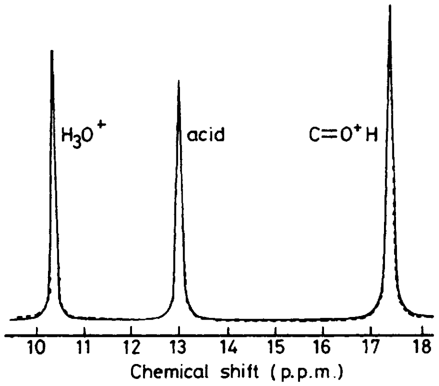

Figure 1. Proton n.m.r. spectrum of 1,1,1-trifluoroacetone in fluorosulphuric acid with 82 mol % antimony pentafluoride at 253 K

1,1,3,3-*Tetrafluoroacetone*.—There is no evidence of protonation in 'magic acid,' but in acid containing 90 and 96 mol % antimony pentafluoride a broad peak at δ 16.9 (ascribed to C=O$^+$*H*) was observed. It broadened further as the temperature was raised over the range 240—297 K. Line-shape analysis was possible in these solutions on the assumption that the line widths of all three proton resonances in the absence of exchange were the same and equal to the observed line width of the H_3O^+ peak, which showed no exchange broadening over this temperature range.

The main results from the rate measurements on solutions of acetone and its fluoro-derivatives are summarised in Table 2.

[$^2H_3$]*Nitromethane*.—Solutions in acids containing between 47.8 and 82.1 mol % antimony pentafluoride were stable and colourless. They showed a low-field peak attributed to –NO$_2$*H*$^+$. At 228 K this appeared at δ 16.7. Results for line-shape analysis of the three-site system, with line widths evaluated from detailed measurements of spin–lattice relaxation times, are illustrated in Figure 2 and summarised in Table 3. As can be seen from Figure 2, exchange between solvent acid and H_3O^+ is slow by comparison and satisfactory rate data are also obtainable by two-site analysis.

Nitroethane and 2-*Nitropropane*.—These bases were studied with [$^2H_6$]tetrahydrofuran as internal deuterium lock. Two-site analysis of line broadening of the low-field (NO$_2$*H*$^+$) and solvent acid resonances is possible, since exchanges involving protonated tetrahydrofuran and H_3O^+ are relatively slow. A comparative result for nitroethane is included in Table 3.

Table 2. Rate parameters for acetone and fluoroketones

Base	SbF_5 (mol %)	p_1	p_2	p_3[a]	$k_{HB.A}(T/K)$[b]	$[A^-]$/mol dm^{-3}	E_a/kJ mol^{-1}
CD_3COCD_3	50.7	0.589	0.212	0.199	133 (333)	2.022	37.2
	50.7	0.477	0.124	0.399	97 (333)	3.451	37.2
CH_2FCOMe	50.4	0.712	0.080	0.208	84 (298)	2.045	41.7
CF_3COMe	50.4	0.658	0.184	0.158	155 000 (298)	1.888	46.2
	50.4	0.540	0.290	0.169	677 000 (298)	2.461	45.2
	82.6	0.279	0.317	0.404	89 (298)	1.516	60.0
	82.6	0.635	*c*	0.365	119 (298)	0.943	61.4
	89.7	0.437	*c*	0.563	51 (298)	0.770	61.8
CF_2HCOCF_2H	89.8	0.271	0.423	0.306	60 300 (298)	0.769	39.6
	95.0	0.498	0.300	0.202	69 100 (298)	0.251	33.5
C_2F_5COEt	82.0	0.860	*c*	0.140	395 (298)	0.858	74.7

[a] Site 3 is the protonated carbonyl group. [b] Values in column 6 are mutiples of dm^3 mol^{-1} s^{-1} (at a temperature *T*) and refer to the base indicated. [c] For the purposes of the line-shape analysis these were treated as two-site systems.

Table 3. Rate parameters for nitroalkanes

Nitroalkane	SbF_5 (mol %)	p_1	p_2	p_3	$k_{HB.A}(T/K)$	$[A^-]$/mol dm^{-3}	E_a/kJ mol^{-1}
CD_3NO_2	47.8	0.552	0.285	0.163	5 680 (298)	2.449	45.0
	47.8	0.708	0.026	0.266	5 310 (298)	2.126	42.9
	50.0	0.653	0.019	0.327	5 690 (298)	2.415[a]	45.9
	56.0	0.493	0.035	0.472	2 910 (298)	3.417	45.9
	65.7	0.489	0.053	0.458	336 (298)	2.454	41.4
	69.4	0.559	0.031	0.410	142 (289)	2.393	46.6
	82.0	0.708	0.023	0.269	163 (298)	0.724	48.3
	82.1	0.413	0.048	0.539	33 (298)	1.396	51.2
$EtNO_2$	50.0	0.659	0.056	0.285	2 192 (298)	2.587[a]	43.7
$PrNO_2$	50.0	0.702	0.061	0.237	4 450 (298)	2.182[a]	50.2

[a] System also includes [$^2H_8$]THF as internal lock.

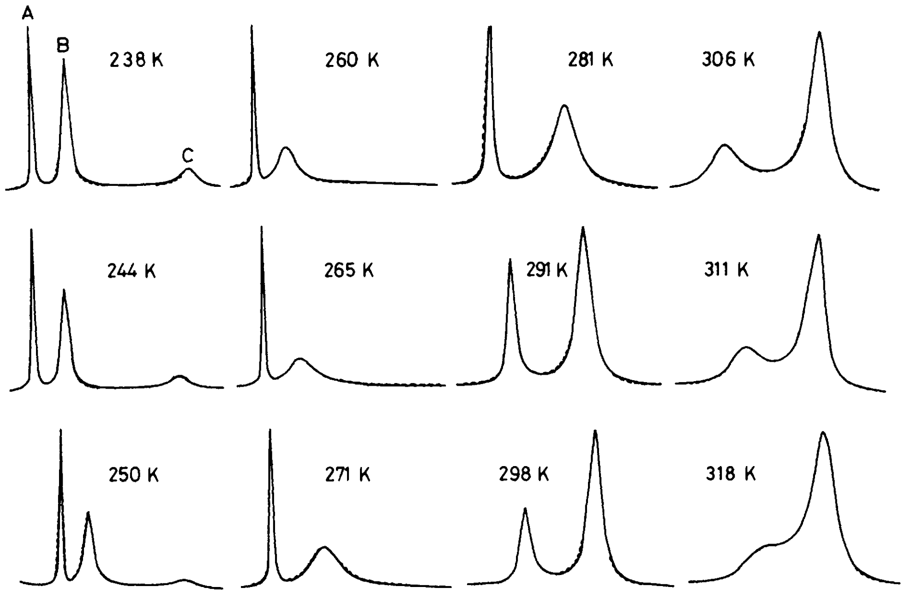

Figure 2. Proton n.m.r. spectra (90 MHz) illustrating proton exchange in solutions of CD_3NO_2 (47.8 mol % SbF_5). The three peaks shown in the spectrum for 238 K are, from left (upfield) to right, A H_3O^+, B solvent acid, and C $-NO_2H$

Table 4. Summary of rate data (average values[a]) for bases in HSO_3F–SbF_5 system at 298 K

Base	SbF_5 (mol %)	$k_{HB.A}$/dm^3 mol^{-1} s^{-1}	E_a[b]/kJ mol^{-1}
CD_3COCD_3	50.7	23	37.2
CH_2FCOMe	50.4	84	41.7
CF_3COMe	50.4	324 000	45.7
	82.6	103	60.7
	89.7	51	61.8
CF_2HCOCF_2H	89.8	60 300	39.6
	95.0	69 100	33.5
CD_3NO_2	47.8	5 490	44.0
	50.0	5 690	45.2
	56.0	2 910	45.9
	65.7	336	41.4
	69.4	142	46.6
	82	73	49.8
$EtNO_2$	50	2 190	43.7
$PrNO_2$	50	4 450	50.2
CD_3SOCD_3	50.2	481	24.2
C_5F_5N	0.0	7.3×10^7	45[c]
	0.0	2.2×10^9	58[c]
	50	2.1	58
HCHO	57.6	3 160	
MeCHO	50	*ca.* 10 000	
	57.6	40	
EtCHO	57.6	200	
PrCHO	57.6	< 100	
Me_2CHCHO	57.6	250	
EtCOMe	50	2.6	41
EtCOFt	50	0.16	63
Cyclopentanone	50	*ca.* 110	*ca.* 25
Cyclohexanone	50	*ca.* 210	*ca.* 12
$CF_3CF_2COCH_2Me$	82.0	395	74.7
p-MeC_6H_4COMe	0.0	10 000	
	2.5	8 317	
	3.8	6 310	
	4.1	7 586	
	6.5	63	
	9.0	50	
	14.7	1.86	64.7

[a] When several measurements have been averaged the geometric mean is used. [b] Arithmetic mean. [c] These values have been estimated in order to extrapolate to 298 K.

Methanol.—Although other reactions supervene when solutions are kept in the cold or, more rapidly, at high temperatures, protonated methanol is sufficiently stable for relaxation times to be recorded over a short range of temperatures. The value of the previously defined parameter[4] ξ for the methyl protons at 297.5 K was found to be 3.54. On the assumption that the same value applies to the other positions, the natural line widths W of H_3O^+, $-O^+H_2$, and solvent acid protons in a decoupled (irradiation of CH_3) spectrum were taken to be 1.82 Hz at that temperature. Values of rate constants were then calculated from the observed line widths (W),[3] (Table 4).

Olah *et al.*[6] showed that a solution of methanol in 'magic acid,' diluted with sulphur dioxide, is chemically stable at low temperatures and that it can be heated up to 323 K without noticeable change in the n.m.r. spectrum. Above this temperature, Olah *et al.* report, the spectrum broadens, the solution becomes viscous and then solid. Our experience with solutions not containing sulphur dioxide is somewhat different. Even in the cold (*ca.* 260 K) the solution changes into a chemically different system. The resulting sharp spectrum (which is stable for at least a week) shows also some very weak signals, corresponding to those given by a freshly prepared solution of dimethyl ether in the same acid system (septet centred at δ 9.12; doublet at δ 5.00; J_{HOCH} 3.3 Hz). However, the most intense peak of the spectrum is a singlet at δ 5.10, close to the triplet of $CH_3OH_2^+$ centred at δ 5.06 (J 3.4 Hz), but well resolved from it. The intensity of this signal corresponds to 60% of the original methyl resonance. Its origin is uncertain and the problem has not been investigated further. The most probable species responsible is methyl fluorosulphate, the formation of which (as well as that of dimethyl ether) has parallels in sulphuric acid as solvent. Other possibilities are $MeSbF_5(OSO_3F)$ (an analogue of methyl hexafluoroantimonate) and the trimethyloxonium ion. All these species are either known to or expected to show proton resonances near the observed position of the new signal.

Pentafluoropyridine.—A peak at δ 13.5 in 'magic acid' at 243 K is attributed to nitrogen-protonated base. The line broadening (line width at half height 4.9 Hz) is predominantly quadrupolar broadening. Exchange broadening becomes noticeable only above *ca.* 300 K. Measurements at higher temperatures suggest that the line width in the absence of exchange is more or less constant at around 5 Hz. This gives rise to spectra at room temperature in which this peak appears as broad as that arising from dissolved water at δ 10.4 (at first sight suggesting equal basicity). However, the peak due to protonated pentafluoropyridine does not coalesce with the solvent peak until the solution is warmed to 378 K, indicating that it is a stronger base than water in 'magic acid.' Furthermore, although the H_3O^+ peak is always fully coalesced with the solvent acid peak in FSO_3H without added SbF_5, it is possible to observe protonated pentafluoropyridine as a separate, though exchange-broadened, resonance, at 180 K in FSO_3H. As the temperature is raised this peak soon coalesces with the solvent. Assuming typical activation parameters observed in FSO_3H–SbF_5 media, one can deduce a value of $k_{HB.A}$ in the range 7×10^7—2×10^9 dm^3 mol^{-1} s^{-1} for this base in FSO_3H at 298 K (Table 4).

1,1,1,2,2-*Pentafluoropentan*-3-*one*.—This base appears to be less basic than trifluoroacetone, and a stronger acid than 'magic acid' is required for observation of the long-lived conjugate acid. In 82 mol % SbF_5 at 253 K the proton on the carbonyl oxygen is observed at δ 17.19 ($t_{\frac{1}{2}}$ = 0.05 s) in a solution containing $CD_3C(OH)^+CD_3$ (δ 14.22) as internal deuterium lock. Correspondingly, δ(CH_2) is 4.77 (q) and δ(CH_3) is 2.39 (t, J_{HCCH} 5.9 Hz). These resonances were referenced with respect to internal H_3O^+, assumed to have δ 10.4. Fluorine–proton coupling constants were too small to be observed.

[$^2H_6$]*Dimethyl Ether.*—The spectrum of the protonated base in 'magic acid' (J_{HOCH} 3.3 Hz, septet, δ 9.12) is similar to that observed in 'magic acid' solution diluted with sulphur dioxide.[7] No significant exchange broadening was observed even at a temperature as high as 353 K where discoloration and decomposition of the sample is evident. This behaviour suggests that the compound is a much stronger base than water.

Butanone.—Because of the possibility of the existence of two interconverting *E,Z*-isomers in asymmetrical protonated ketones, line-shape analysis referring to intermolecular proton exchange was attempted only in 50 mol % SbF_5 and at temperatures where this complication was unimportant. [$^2H_3$]Nitromethane was used as internal lock solute, since the signal from $-NO_2{}^+H$ coalesces with that due to solvent acid at much lower temperatures.

Cyclohexanone and Cyclopentanone.—[$^2H_6$]Dimethyl ether was used as internal lock solute in 50 mol % SbF_5, as it is a much stronger base than the ketones and does not exchange under the conditions used.

Pentan-3-*one*.—Line-shape analysis was again performed with [$^2H_3$]nitromethane as internal lock solute in 50 mol % SbF_5.

[$^2H_{10}$]*Diethyl Ether*.—In 50% SbF_5 and at 254 K the signal due to the protonated ether appeared at δ 8.6, *i.e.*, upfield from the signals from solvent acid (δ 11.7) and H_3O^+ (δ 10.4). As the temperature was raised, coalescence between the latter two signals occurred but there was no significant exchange broadening of the upfield signal up to 353 K. Above 373 K several new peaks, due to irreversible decomposition, became evident.

[$^2H_8$]*Tetrahydrofuran*.—In 50 mol % SbF_5 the resonance due to protonation of the ether oxygen again appeared upfield of the H_3O^+ signal (by 1.4 p.p.m.) and only slight broadening was perceptible at 353 K. Irreversible decomposition became evident at 363 K and above.

Dimethyl Sulphide.—Spectra in 'magic acid' in the temperature range 297—383 K showed a new (methyl-coupled) peak downfield from that of the acid, which was slightly broadened at the highest temperature.

Discussion

Whilst not all of the systems studied could be analysed in detail, the results for a number of the compounds allowed the evaluation of rate constants. As explained in the preceding paper,[2] the parameter of chief interest for the purpose of comparing p*K* values of bases or the acidities of super-acid media is the second-order rate constant $k_{HB.A}$, expressing the rate of proton transfer from the conjugate acid (HB^+) of the solute base B to the conjugate base (A^-) of the solvent acid HA. Relative values of $k_{HB.A}$ (or differences in lg $k_{HB.A}$ for different solute bases) can be derived in two ways. First, the line-shape analysis can be performed for solutions of different bases in separate samples of the same solvent system. Alternatively, three-site line-shape analysis can be carried out on the signals arising from two simultaneously present solutes and the solvent acid. Although it is of limited applicability, the second procedure is completely free from uncertainties of solvent composition. Since most specimens examined contained at least a trace amount of water (and hence of the species H_3O^+), it was thus possible to make a number of comparisons between H_3O^+ and another protonated solute base, but only when that other solute base was of similar basic strength to water. Where the basicities differ too widely, two out of the three peaks may be coalesced into a single sharp one under all conditions, or else one of the peaks may remain sharp over the whole range of temperatures in which two of the other peaks begin to broaden, coalesce, and ultimately sharpen into a single peak.

Differences in values of lg $k_{HB.A}$ at 298 K calculated by either of these methods are given in Table 5. Bold numbers refer to the second procedure outlined above. The reference base throughout is H_2O [*i.e.*, Δ lg $k_{HB.A}$ = lg $(k_{HB.A})_B$ − lg $(k_{HB.A})_{H_2O}$]. According to the analysis and assumptions previously presented[2] we obtain equation (2).

$$\Delta \lg k_{HB.A} = (pK_a)_{H_3O} - (pK_a)_{HB} \qquad (2)$$

Table 5. Comparison of the basicities of various bases

Base	$\Delta pk_{HB.A}$[a]	δ_H/p.p.m.[b]	pK_{HB}
Cyclohexanone	0.9		−6.8[c]
Cyclopentanone	0.7		−7.5[c]
CD_3COCD_3	**−0.32**	14.40	−2.85[d]
EtCOMe	−1.0	14.1	−7.2[c]
EtCOEt	−2.2	14.06	
CH_2FCOMe	**0.53**	15.35	
CF_3COMe	**3.94 ± 0.27**	17.75	
CF_2HCOCF_2H	**7.0**	16.9	
C_2F_5COEt	4.5	17.2	
CD_3NO_2	**1.94 ± 0.12**	16.7	−11.9[c]
$EtNO_2$	2.0		
$PrNO_2$	2.3		
CD_3SOCD_3	4.76 − (*T*/80)[e]	5.9[f]	−1.54[d]
MeOH	**−1.03**	9.6	−2.2[c]
C_5F_5N	−1.1	13.5	
HCHO	2.1	16.9	
MeCHO	2.6 to 0.5	15.25	
EtCHO	1.5	15.5	
PrCHO	0.7	15.2	
Me_2CHCHO	1.1	15.5	
MeOMe	< −1	9.12	
EtOEt	< −2	8.6	−2.4[d]
[$^2H_6$]Tetrahydrofuran	< −2	9.0	−2.3[d]
MeSMe	< −2		−5.3[c]
p-MeC_6H_4COMe	**−2.9**	12.8	−5.7[g]

[a] $\Delta pk_{HB.A}$ = lg $k_{HB.A}$(base) − lg $k_{HB.A}$(water); more positive values indicate weaker bases. Bold entries refer to three-site analysis; $\Delta pk_{HB.A}$ from measurements on same sample. [b] δ_H is the chemical shift of the proton accepted by the base to form the conjugate acid, relative to internal H_3O^+ (δ = 10.4). [c] Ref. 8. [d] From the review in ref. 9. [e] *T* represents the temperature, $\Delta pk_{HB.A}$ = 1.04 at 298 K. [f] Relative to external CD_3COCD_2H (δ 2.04). [g] Ref. 2*a*.

The p*K* values for some of the bases have previously been determined by indicator measurements in less strongly acidic media, and the corresponding literature values are included in Table 5. For these bases there is no convincing correlation between $\Delta pk_{HB.A}$ and the indicator pK_{HB} value. It would be premature to speculate about the absence of such a relationship, or to discuss the relative merits of these two quantities as measures of basicity, particularly since the ionization of ketones in sulphuric acid–water mixtures is now thought to be complicated by hydration of the protonated carbonyl group.

The notion of a connection between pK_a values and proton n.m.r. line widths in fluorosulphuric acid had previously been entertained by Birchall and Gillespie.[10] From measurements on acetophenone and five *p*-substituted derivatives they concluded that there was no such correlation. A reconsideration of these results in the light of our experience suggests that an (imperfect) correlation does exist for these compounds. In particular, the results appear in a different light if one accepts that their most deviant point (for *p*-nitroacetophenone) may have been affected by a suspect extrapolation to a common temperature. If it is assumed that the appropriate activation energy of proton transfer for this base has a value more in line with those for the other acetophenones, then the result for *p*-nitroacetophenone ceases to be anomalous, and Birchall and Gillespie's measurements even give a certain amount of support for our analysis.

Birchall and Gillespie suggest that there is a more valid connection between the chemical shift of the proton added to the base (measured in the absence of exchange) and the pK_a value. In agreement with this proposal, our results exhibit a correlation between the downfield shift of that proton and the lg $k_{HB.A}$ value derived by line-shape analysis, thus suggesting that both lg $k_{HB.A}$ and δ are related measures of basicity. However, over a wide range of basicities the precise nature of the connection is not clear, and we do not expect that δ values for unrelated structures should fall on the same curve, as indicated in Figure 3.

For two of the bases that are weaker than water (nitromethane and 1,1,1-trifluoroacetone), measurements of $k_{HB.A}$

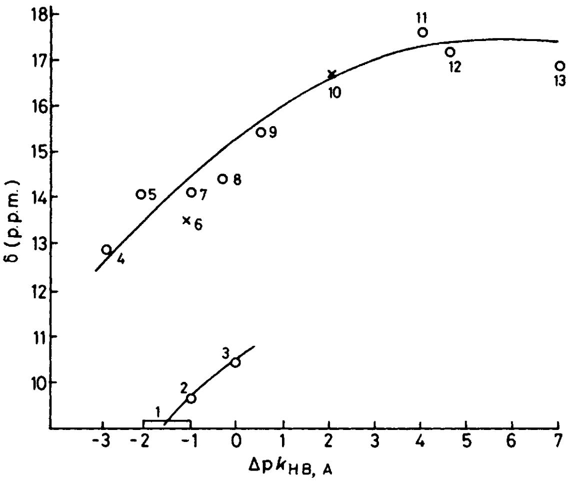

Figure 3. Correlation between $\Delta pk_{HB.A}$ and chemical shift of proton added to solute base: upper curve, ketones (○), nitromethane and pentafluoropyridine (×); lower curve, saturated oxygen bases. 1, Ethers; 2, methanol; 3, water; 4, *p*-methylacetophenone; 5, pentan-3-one; 6, pentafluoropyridine; 7, acetophenone; 8, acetone; 9, fluoroacetone; 10, nitromethane; 11, 1,1,1-trifluoroacetone; 12, 1,1,1,2,2-pentafluoropentan-3-one; 13, 1,1,3,3-tetrafluoroacetone

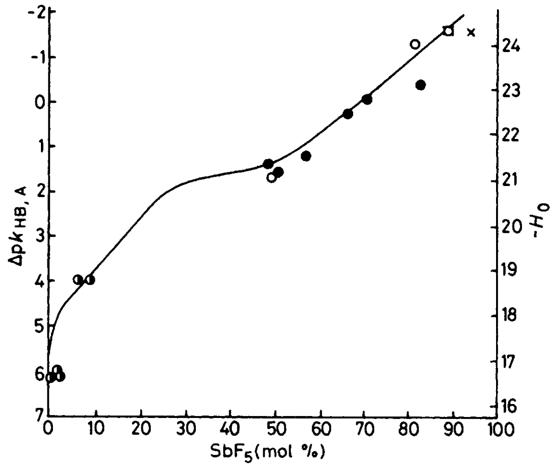

Figure 4. H_0 function for HSO_3F–SbF_5 mixtures. The course of the curve up to 50 mol % SbF_5 is taken from the preceding paper. Marked data points refer to organic solutes (◑, *p*-methylacetophenone; ●, nitromethane; ○, 1,1,1-trifluoroacetone; and ×, 1,1,3,3-tetrafluoroacetone

over a range of stoicheiometric compositions $HSO_3F:SbF_5$ were used to extend the acidity function towards higher concentrations of antimony pentafluoride. In neither case was the range of overlapping compositions for measurements on different indicators sufficiently extensive for us to have proved that a common acidity function is applicable to all the indicators. On the assumption that there is such a continuous function we have used the overlapping measurements to extend the scale of H_0 values previously derived by use of water as solute base (Figure 4). The reservations concerning differences in behaviour between indicators of different structure, taken in conjunction with our observations concerning the long-term stability of the media, are emphasised lest the precision of the primary measurements be thought also to apply to the precision of the derived acidity function.

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