ions. The stabilities of the ring structures are due to the back CT or antisymmetric orbital interaction. The next step is the zigzag collapsing of the intermediates. This is an elementary process. The following nucleophilic attack leads to the double E,N-inversion. The proposed schemes are summarized in Figure 10.

The electrophilic edge attack has been believed to give the E-retention product. The most important finding here is that the edge attack may give the E-inversion product through the zigzag collapse of the edge attack intermediates.

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Registry No. CP, 75-19-4; H^+, 12408-02-5; Cl^+, 24203-47-2; Br^+, 22541-56-6.

Supplementary Material Available: Tables of exponents and coefficients of the MIDI-1 basis set given as the GAUSSIAN 80 or 82 input data and molecular Cartesian coordinates (12 pages). Ordering information is given on any current masthead page.

Superacid Solutions in Hydrogen Fluoride

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Abstract: The Hammett acidity function, H_0, has been determined for solutions of H_2O, KF, HSO_3F, PF_5, TaF_5, NbF_5, AsF_5, and SbF_5 in anhydrous HF, using a set of aromatic nitro compound indicators. The H_0 value for anhydrous HF was found to be −15.1 rather than −11 as previously believed. It was confirmed that water is not fully ionized as a base. The values of H_0 show that solutions of SbF_5 in HF are much more acidic than solutions of SbF_5 or $SbF_5{\cdot}3SO_3$ in HSO_3F.

It has long been recognized that solutions of antimony pentafluoride and some other pentafluorides in anhydrous HF are very highly acidic media. In this paper we present the results of some quantitative studies of the acidity of such media in terms of the Hammett acidity function, H_0, for solutions of KF, H_2O, SbF_5, AsF_5, NbF_5, TaF_5, and HSO_3F in anhydrous HF. We have used the same set of nitro aromatic weak-base indicators that we used for our earlier measurements[1,2] of the acidities of solutions in sulfuric acid and fluorosulfuric acid and some weaker bases of the same type.

On the basis of the ability of HF solutions of SbF_5, AsF_5, NbF_5, and PF_5 to dissolve CoF_3 and the metals Cr, Mg, and Mn, Clifford et al.[3-5] concluded that the acid strength of these pentafluorides decreased in the order $SbF_5 > AsF_5 > NbF_5 > PF_5$. McCaulay et al.[6] measured the ability of solutions of NbF_5, TaF_5, and PF_5 in HF to extract *m*- and *p*-xylene from *n*-heptane, and they concluded that the order of acid strengths was $TaF_5 > NbF_5 > PF_5$.

Kilpatrick and Lewis[7] made the first quantitative study of solutions of antimony pentafluoride in HF, and from their measurements of the electrical conductivity of dilute solutions of SbF_5 they concluded that SbF_5 is a strong acid ionizing according to the equation

$$SbF_5 + 2HF \rightarrow H_2F^+ + SbF_6^-{}_6$$

Further conductivity measurements by Hyman et al.[8] and by Gillespie and Moss[9] and cryoscopic measurements by Gillespie et al.[10] confirmed that SbF_5 is fully ionized in dilute solution in HF. But ^{19}F NMR studies[9] showed that, except in the most dilute solutions, increasing amounts of the polymeric ions $Sb_2F_{11}^-$, $Sb_3F_{16}^-$, etc., are formed with increasing concentration of SbF_5. Gillespie et al.[10] also showed that PF_5 is a nonelectrolyte and that at low temperatures AsF_5 is extensively ionized, although not fully, according to the equation

$$2AsF_5 + 2HF \rightleftharpoons H_2F^+ + As_2F_{11}^-$$

The Hammett acidity function for the H_2O–HF system has been studied by several groups of workers[11-13] and their results are shown in Figure 1. There is a sharp increase in $-H_0$ in the vicinity of 100% HF which is similar to that observed in the H_2SO_4–HSO_3F system in the vicinity of 100% HSO_3F.[2] This rapid increase in $-H_0$ is due to the rapidly increasing concentration of the solvated proton, H_2F^+ or $H_2SO_3F^+$, arising from the solvent autoprotolysis. This has meant that the value of H_0 for 100% HF has been very difficult to determine because very small concentrations of basic impurities such as water can drastically decrease the value of $-H_0$. We show later that, for this reason, the previously reported value[12,13] of $-H_0 = -11$ is too low.

There have been two previous studies of the acidity of solutions of SbF_5 in HF. Tremillion et al.[14] have measured the acidity of 1 M solutions of NaF and SbF_5 and some other pentafluorides in terms of the *R*(H) function using a chloranil electrode. They reported values of *R*(H) of 14.2 for 1 M NaF and 27.9 for 1 M SbF_5. Sommer and his collaborators[15] have obtained values of H_0 by studying the protonation of *p*-methoxybenzaldehyde by means of ^1H and ^{13}C NMR. The results of these earlier studies of SbF_5 solutions are discussed later together with our own.

Experimental Section

Hydrogen Fluoride. Anhydrous hydrogen fluoride (Harshaw Chemical Co.) was purified by fractional distillation with a column of the type described by Shamir and Netzer[16] in conjunction with a Monel and

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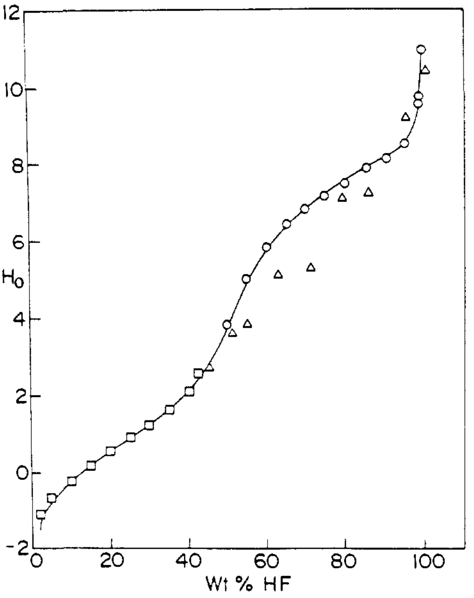

Figure 1. $-H_0$ for the HF-H_2O system: (□) Bell, Bascome, and McCoubrey; (○) Hyman, Kilpatrick, and Katz; and (△) Dallinga, Gaef, and Hackur.

Teflon vacuum line. After the mixture was refluxed for 12 h a fraction having a conductivity between 10^{-5} and 10^{-6} ohm^{-1} cm^{-1} was collected.

Hydrogen Fluoride–MF_5 Solutions. Solutions of the pentafluorides SbF_5, AsF_5, and PF_5 were prepared by distilling the pentafluoride onto a weighed amount of HF in a Kel-F trap equipped with a Teflon valve and then reweighing the trap. Solutions of NbF_5 and TaF_5 were prepared by distilling a weighed amount of HF onto a weighed amount of NbF_5 or TaF_5 in a Kel-F trap.

Pentafluorides. Antimony pentafluoride (Ozark-Mahoning Co.) was purified by double distillation in a Pyrex glass still in an atmosphere of dry nitrogen. The apparatus and procedure have been described previously.[17] The fraction boiling between 142 and 143 °C was collected. The distillate was placed in a Kel-F vessel and pumped at 60 °C until bubbling ceased.

Arsenic pentafluoride (Ozark-Mahoning Co.) was found to be free of impurities as shown by its gas-phase infrared spectrum and was distilled from the cylinder.

Tantalum pentafluoride (Ozark-Mahoning Co.) and niobium pentafluoride (Ozark-Mahoning Co.) were purified by vacuum sublimination in a Vycor apparatus.

Phosphorus pentafluoride (Ozark-Mahoning Co.) was distilled from the cylinder and used without further purification.

Indicators. The indicators *p*-nitrotoluene (mp 51.0 °C), 2,4,6-trinitrotoluene (mp 81.5 °C), 1,3,5-trinitrobenzene (mp 122 °C), 2,4,6-trinitrochlorobenzene (mp 82 °C), and 1,3-chloro-2,4,6-trinitrobenzene, obtained from Eastman Organic Chemicals, were recrystallized from anhydrous methanol. The indicator 2,4,6-trinitroaniline (mp 192 °C), obtained from Eastman Organic Chemicals, was purified by crystallization from glacial acetic acid. The indicators were air-dried and stored in desiccators over P_4O_{10} for 1 week before being sealed in air-tight containers.

Preparation of Solutions. Solutions of the indicators were prepared by using a vacuum drybox equipped with an analytical balance. A 0.020-g sample of an indicator was weighed into 10 g of acetone. A 0.0200-g aliquot of the resulting solution was weighed into a Kel-F trap fitted with a Teflon valve. The acetone was removed under vacuum and the HF solution under study was then poured onto the indicator through a Y-connector and Teflon valves. The volume of the solution was determined from a scale on the outside of the Kel-F tube that had been calibrated by weighing water in the tube. The solutions were then poured into the UV cell through Teflon valves. The UV cells had a Teflon body and sapphire windows. The windows were 1 in. in diameter and 1 mm thick and they were fitted into the Teflon body with Teflon gaskets and brass nuts. The cells had a path length of 1 cm and they were closed with a Teflon valve. The cells could be cleaned without dismantling them by placing them in an ultrasonic cleaner with acetone or water. They were then flushed with solvent in a spectrophotometer cell washer (Bel-Art Co.) and dried in an oven and evacuated on the vacuum line prior to use.

UV–Visible Spectra. UV–visible spectra were measured on a Cary 14 spectrophotometer.

Determination of H_0 Values. The indicators used in the present study were 2,4,6-trinitroaniline, *p*-nitrotoluene, 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene, 2,4,6-trinitrochlorobenzene, and 1,3-dichloro-2,4,6-trinitrobenzene. The Hammett acidity function H_0 is given by the expression $H_0 = \mathrm{p}K_{BH^+} - \log I$, where I is the ionization ratio $[BH^+]/[B]$ of a basic indicator B. The ionization ratios were determined by the spectroscopic method previously described[1,2] making use of the equation $[BH]^+/[B] = (\epsilon_B - \epsilon)/(\epsilon_{BH^+})$, where ϵ is the measured extinction coefficient and ϵ_B and ϵ_{BH^+} are the extinction coefficients at the same wavelength (usually the wavelength of maximum absorption of BH^+) of the neutral and protonated forms of the indicator. The experimentally determined extinction coefficients ϵ were plotted against the solution composition and values of ϵ read off at convenient concentrations of solute. Values of $\log I = \log [BH^+]/[B]$ were computed at these concentrations. The values are given in Table I. The values of H_0 given in Table II were then obtained from the expression $H_0 = \mathrm{p}K_{BH^+} - \log I$ for values of log I in the range +1 to −1. For the regions where two or more indicators covered the same range an average value is given.

Because of the very rapid change in H_0 in the vicinity of 100% HF it was not possible to use the usual overlap technique for the determination of $\mathrm{p}K_{BH^+}$ values over the whole acidity range studied. Values for indicators 1 to 5 (Table III) were those obtained in previous studies on solutions in H_2SO_4 and HSO_3F.[1,2] Although, strictly speaking, $\mathrm{p}K_{BH^+}$ values may not be transferable from one solvent to another we have shown previously that several indicators of the type we have used have very nearly the same $\mathrm{p}K_{BH^+}$ values in H_2SO_4 and HSO_3F solutions.[2] Therefore, it seems reasonable to assume that they also have approximately the same $\mathrm{p}K_{BH^+}$ values in HF. The $\mathrm{p}K_{BH^+}$ values for the second protonation of indicators 6, 7, and 8 which have not been used previously were obtained by the overlap method from the $\mathrm{p}K_{BH^+}$ value for the second protonation of indicator 5. Strictly speaking the acidity function that is obtained from these indicators should be described as H_+ rather than H_0. But we showed previously[2] that the behavior of polynitro compounds on diprotonation is sufficiently similar to that of similar polynitro compounds undergoing monoprotonation to justify the approximation of describing the acidity function as H_0.

We have shown previously that polynitro compounds form a consistent set of indicators in that they give plots of log I against H_0 that are parallel and of unit slope.[2] This was tested for the new indicators 5–8 by the method of Johnson et al.[18] These authors showed that in general one may write $\log I_2 = a_{2,1} (\log I_1) + a_{2,1}(\mathrm{p}K_1) - \mathrm{p}K_2$ and $H_2 = a_{2,1}H_1$, where $a_{2,1}$ is a constant that measures the degree of parallelism of indicators 1 and 2 and should be unity for a pair of well-behaved indicators. H_2 and H_1 are the acidity functions defined by indicators 2 and 1, respectively. The product $\prod a_{i,i-1}$ indicates how the ith indicator behaves with respect to the acidity function H_1 defined by the first indicator. Individual a_i, a_{i-1} values were obtained from plots of log I vs $\log_{i-1}$ and the results are given in Table IV. The values are not as close to unity as the values obtained previously for the monoprotonation of various nitroaromatic indicators in the H_2SO_4 and HSO_3F solvent systems but they are comparable to the values of approximately 0.9 obtained for indicators undergoing diprotonation in solution in HSO_3F.[2] It seems probable that the H_0 values determined in the present work are not as accurate as those measured previously for the H_2SO_4 and HSO_3F systems, although as the same type of indicator and the same method was used for all three systems the composition of their relative acidities should be valid.

Results and Discussion

The H_0 values that we obtained for solutions of H_2O are shown in Figure 2 together with the results of Hyman et al.[12] and of Dallinga et al.[13] Our H_0 values for KF solutions (Figure 3) are appreciably lower than those for H_2O. This result confirms that H_2O is not fully ionized in HF as has previously been concluded from conductimetric and cryoscopic measurements on solutions of water in HF.[19,20] Extrapolation of these two curves appears to give a value of approximately −11 for the H_0 value of anhydrous HF, as has been reported previously.[12,13] However, as we shall see, this value is much too low. H_0 values for solutions of HSO_3F and PF_5 are also given in Figure 3. The very small increase in

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Table I. Ionization Ratios

H_2O		KF		HSO_3F		AsF_5			
2,4,6-trinitroaniline		2,4,6-trinitroaniline		*p*-nitrotoluene		(2,4,6-trinitrotoluene)H^+		(1,3,5-trinitrobenzene)H^+	
mol %	log *I*	mol %	log *I*	mol %	log *I*	mol %	log *I*	mol %	log *I*
0.10	-0.56	0.10	0.20	0.10	0.48	0.05	0.09	0.05	0.64
0.20	-0.36	0.20	0.11	0.20	0.35	0.10	-0.17	0.10	0.39
0.30	-0.25	0.30	0.32	0.30	0.26	0.15	-0.36	0.15	0.22
0.40	-0.09	0.40	0.47	0.40	0.20	0.20	-0.49	0.20	0.05
0.60	0.08	0.60	0.66	0.50	0.16	0.25	-0.66	0.25	-0.07
0.80	0.18	0.70	0.82	0.60	0.11	0.30	-0.81	0.30	-0.18
1.00	0.36	0.80	0.91	1.00	-0.02	0.35	-1.09	0.40	-0.38
1.50	0.54	1.00	0.94	1.50	-0.13	0.40	-1.33	0.50	-0.56
2.00	0.82	1.00	0.94	2.00	-0.25			0.60	-0.79
				2.50	-0.42			0.70	-1.05

SbF_5				NbF_5			
(2,4,6-trinitrochlorobenzene)H^+		(1,3-dichloro-2,4,6-trinitrobenzene)H^+		2,4,6-trinitrotoluene		1,3,5-trinitrobenzene	
mol %	log *I*	mol %	log *I*	mol %	log *I*	mol %	log *I*
0.05	0.22	0.05	0.71	0.05	0.51	0.05	1.07
0.10	-0.02	0.10	0.51	0.20	-0.08	0.10	0.10
0.15	-0.22	0.15	0.25	0.15	-0.24	0.20	-0.14
0.20	-0.40	0.20	0.09	0.20	-0.45	0.25	-0.34
0.25	-0.58	0.25	-0.07	0.25	-0.65	0.30	-0.54
0.30	-0.69	0.30	-0.18			0.30	-0.54
		0.40	0.41			0.40	-0.81
		0.50	0.64				
		0.60	0.90				

TaF_5						PF_5	
(2,4,6-trinitrotoluene)H^+		(2,4,6-trinitrochlorobenzene)H^+		(1,3,5-trinitrobenzene)H^+		*p*-nitrotoluene	
mol %	log *I*	mol %	log *I*	mol %	log *I*	mol %	log *I*
0.05	0.52	0.40	1.13	0.20	0.29	0.02	0.01
0.10	0.32	0.50	0.97	0.25	0.62	0.06	-0.08
0.15	0.25	0.60	0.85	0.30	0.49	0.10	-0.23
0.20	0.15	0.70	0.72	0.40	0.31	0.20	-0.41
0.25	0.09	0.80	0.64	0.50	0.14	0.30	-0.57
0.30	-0.03	0.90	0.56	0.60	-0.03	0.40	-0.63
0.40	-0.18	1.00	0.49	0.70	-0.19	0.50	-0.67
0.50	-0.34			0.80	-0.35		
0.60	-0.54			0.90	-0.49		
0.70	-0.71						

Table II. $-H_0$ Values for Solutions in HF

H_2O		KF		HSO_3F		NbF_5	
mol %	$-H_0$	mol %	$-H_0$	mol %	$-H_0$	mol %	$-H_0$
0.10	10.66	0.02	10.79	0.10	10.87	0.05	15.09
0.20	10.46	0.04	10.63	0.15	10.95	0.10	15.65
0.30	10.35	0.06	10.53	0.20	11.00	0.15	15.92
0.40	10.19	0.08	10.39	0.25	11.05	0.20	16.13
0.60	10.07	0.10	10.30	0.30	11.09	0.25	16.35
0.80	9.92	0.15	10.13	0.40	11.15	0.30	16.65
1.00	9.80	0.20	9.94	0.50	11.19	0.40	16.98
1.50	9.56	0.30	9.78	0.60	11.24		
2.00	9.28	0.40	9.63	1.00	11.33		
		0.60	9.37	1.50	11.48		
		0.70	9.28	2.00	11.60		
		0.80	9.19	2.50	11.73		
		0.90	9.06				

PF_5		TaF_5		SbF_5		AsF_5	
mol %	$-H_0$	mol %	$-H_0$	mol %	$-H_0$	mol %	$-H_0$
0.02	11.34	0.05	17.83	0.05	19.53	0.05	18.28
0.06	11.43	0.10	18.04	0.10	19.75	0.10	18.54
0.10	11.58	0.15	18.13	0.15	19.98	0.15	18.72
0.20	11.76	0.20	18.18	0.20	20.15	0.20	18.87
0.30	11.92	0.25	18.31	0.25	20.32	0.25	19.04
0.40	11.98	0.30	18.42	0.30	20.43	0.30	19.14
0.50	12.02	0.40	18.60	0.40	20.64	0.40	19.31
		0.50	18.76	0.50	20.87	0.50	19.49
		0.70	19.08	0.60	21.13	0.60	19.72
		0.80	19.20			0.70	19.89
		0.90	19.32				

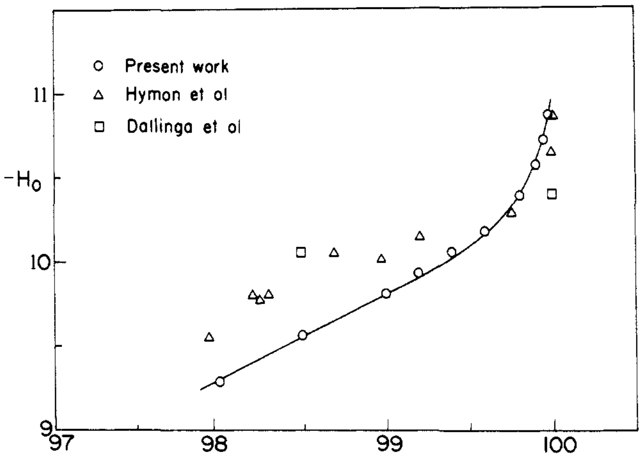

Figure 2. $-H_0$ for solutions of water in HF: (○) present work; (△) Hyman, Kilpatrick, and Katz; and (□) Dallinga, Gaef, and Mackor.

H_0 with increasing concentration of HSO_3F indicates that HSO_3F is an exceedingly weak acid in HF; indeed, it is essentially a nonelectrolyte. This is in agreement with previous cryoscopic and conductimetric measurements.[19,20] The H_0 values for PF_5 fall on a somewhat steeper curve but nevertheless the values indicate that PF_5 is a very weak acid; indeed, it is essentially a nonelectrolyte. It should be noted that the concentrations of the PF_5 solutions may in fact be somewhat lower than the values given because in

Table III. ϵ_B, ϵ_{BH^+}, λ_{max}, and pK_{BH^+} Values for the Indicators

indicator	ϵ_B	ϵ_{BH^+}	λ_{max}	pK_{BH^+}	ref
1. 2,4,6-trinitroaniline	8500	200	418	-10.10	1
2. *p*-nitrotoluene	2100	19,200	376	-11.35	2
3. 2,3,6-trinitrotoluene	2100	12,000	316	-15.60	3
4. 1,3,5-trinitrobenzene	2000	10,700	280	-16.04	3
5. (2,4,6-trinitrotoluene)H^+	2000	15,400	290	-18.36	3
6. (1,3,5-trinitrobenzene)H^+	2500	16,000	280	-18.93	this work
7. (2,4,6-trinitrochlorobenzene)H^+	1600	16,000	300	-19.76	this work
8. (1,3-dichloro-2,4,6-trinitrobenzene)H^+	4400	20,400	315	-20.23	this work

Table IV. Indicator Test

indicator	$a_{i,i-1}$	$\Pi a_{i},a_{i-1}$
5. (2,4,6-trinitrotoluene)H^+	0.97	0.97
6. (1,3,5-trinitrobenzene)H^+	0.88	0.85
7. (1,3-dichloro-2,4,6-trinitrobenzene)H^+	0.99	0.77

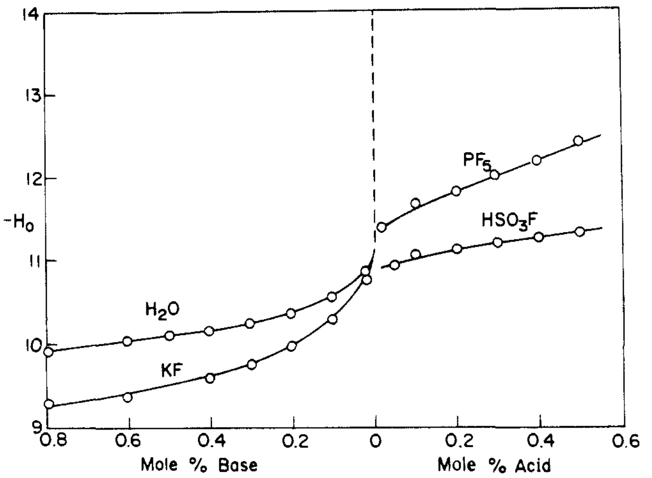

Figure 3. $-H_0$ for solutions of H_2O, KF, PF_5, and HSO_3F in HF.

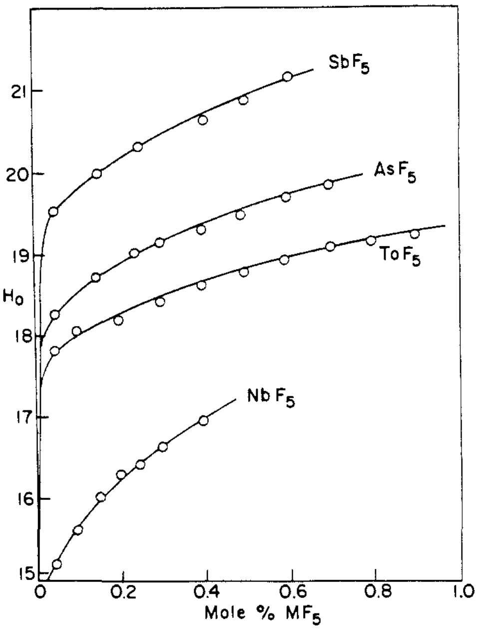

Figure 4. $-H_0$ for solutions of SbF_5, AsF_5, TaF_5, and NbF_5 in HF.

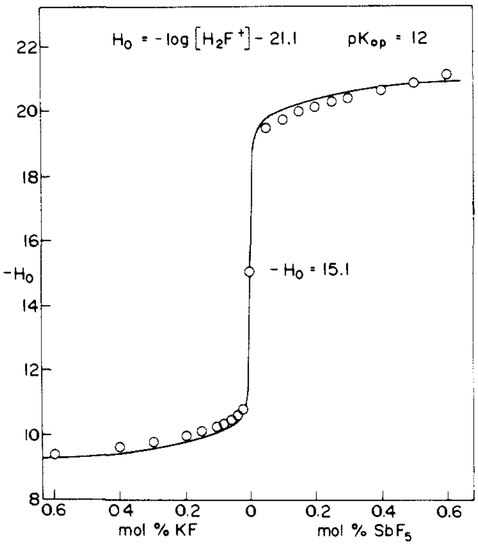

Figure 5. Comparison of calculated (full line) and experimental (circles) $-H_0$ values for the KF-HF-SbF_5 system.

previous cryoscopic measurements that also showed that PF_5 is a nonelectrolyte in HF we found that PF_5 solutions have an appreciable vapor pressure of PF_5 even at -80 °C.[10]

Niobium, tantalum, arsenic, and antimony pentafluorides have very much higher $-H_0$ values than PF_5 (Figure 4). The order of increasing acidity is $NbF_5 < TaF_5 < SbF_5$. The curves for these acids clearly do not extrapolate to a value of approximately 11.0 at zero concentration. There is an enormous increase in the acidity when any of these pentafluorides is dissolved in HF. Figure 5 shows that $-H_0$ increases from ~10 for a 0.1 mol % solution of KF to ~19 for a 0.1 mol % solution in SbF_5. The H_0 for 100% HF should be given by the point of inflection in this S-shaped curve. This point is difficult to determine accurately, but we estimate that the value of $-H_0$ for 100% HF is 15.1 ± 0.1. Very small amounts of water or other basic impurities are sufficient to decrease the $-H_0$ of even the purest HF that has been prepared to approximately 11. O'Donnell[21] has claimed that on storing HF in Kel-F containers small amounts of an unsaturated halocarbon are leached out and protonated, producing the base F^-. When acidic pentafluorides such as NbF_5, TaF_5, AsF_5, and SbF_5 are added to HF the small amount of basic impurity is completely removed and H_0 rises rapidly to the value for 100% HF and then to higher values as the concentration of H_2F^+ increases. Apparently HSO_3F and PF_5 are such weak acids that they do not completely remove even the very small amount of F^- arising from basic impurities.

The steep rise in H_0 in the vicinity of 100% HF is a consequence of the small autoprotolysis constant of HF. This has usually been taken to be in the region of 10^{-11} or 10^{-12} at 0 °C. Kilpatrick and Luborsky[22] gave a value of K_{ap} of 2×10^{-10} mol^2 kg^{-2} from their conductance measurements of solutions of BF_3 in HF. We have estimated a value of 1×10^{-11} at 0 °C and of 1×10^{-12} at 20 °C from the conductivity of carefully purified HF and the conductances of H_2F^+ and F^- at infinite dilution.[19] More recently Tremillon and co-workers[14] on the basis of acidity measurements using a chloranil electrode have proposed a value of K_{ap} of 2×10^{-14} at 0 °C. If we assume that the acidity of dilute solutions in HF is determined primarily by the concentration of H_2F^+ then

$$H_0 = -\log [H_2F^+] + \text{constant}$$

The value of the constant can be determined from the values of $-H_0 = 15.1$ for 100% HF and the concentration of H_2F^+ in the 100% acid. For an autoprotolysis constant of 10^{-12}, $[H_2F^+] =$

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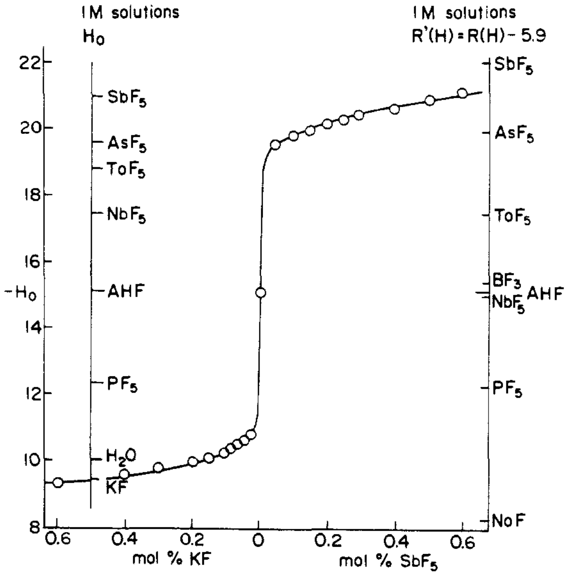

Figure 6. Comparison of $-H_0$ and R(H) values for 1 M solutions in HF.

10^{-6} and $\log [H_2F^+] = -6$ so the value of constant is 21.1 and therefore

$$-H_0 = \log [H_2F^+] - 21.1$$

Values of H_0 calculated from this equation for solution of KF and SbF_5 assuming that they are a strong base and a strong acid, respectively, have been plotted in Figure 6. The calculated curve agrees well with the measured values, indicating that KF and SbF_5 do behave as a strong base and as a strong acid, respectively, and that the autoprotolysis constant is of the order of 10^{-12} at 20 °C.

The order of acid strengths of the pentafluorides obtained in this work, namely $PF_5 < NbF_5 < TaF_5 < AsF_5 < SbF_5$, is identical with that obtained by Tremillon et al.[14] from their measurements of the R(H) function. There is no reason to think that the R(H) function differs from H_0 simply by a constant; nevertheless, if we adjust the R(H) scale by subtracting 5.9 to give $R'(H) = R(H) - 5.9$, then $R'(H) = H_0 = 15.1$ for 100% HF and there is remarkably good agreement between the H_0 and R'(H) values for the various pentafluorides (Figure 6). We note, however, that NbF_5 and TaF_5 have rather lower values on the R'(H) scale than on the H_0 scale. Also the R'(H) scale is a little more spread out than the H_0 scale which may well reflect the smaller value of K_{ap} at 0 °C than at 20 °C. Sommer et al.[15] obtained values of $-H_0$ of ~20 for a 0.5% solution and ~20.5 for a 1% solution of SbF_5 in HF. These values are slightly lower than ours but considering the different methods that were used and the difficulties associated with working with HF solutions the agreement is good.

Table V. $-H_0$ for Some Superacids

acid	$-H_0$	acid–SbF_5	$-H_0$
H_2SO_4	11.9		
CF_3SO_3H	13.8	CF_3SO_3H–2% SbF_5	16.4
$H_2S_2O_7$	14.1		
HSO_3F	15.1	HSO_3F–20% SbF_5	20
		HSO_3F–7% $SbF_5 \cdot 3SO_3$	19.4
HF	15.1	HF–0.5% SbF_5	21

It is interesting to note that the relative acid strengths of pentafluorides in HSO_3F which have been found to be $SbF_5 > AsF_5 > TaF_5 > NbF_5$[2] are essentially the same as in HF, and they also confirm earlier qualitative estimates of the Lewis strengths of these pentafluorides.

Within the rather large experimental error of the present measurements the H_0 value of anhydrous HF is the same as that of 100% HSO_3F. Thus, HF and HSO_3F are the strongest pure acids known (Table V). The acidity of both acids can be increased still further by the addition of several different pentafluorides, but the acidity increases more rapidly in HF than in HSO_3F on the addition of a pentafluoride, as has been found previously by Sommer et al.[15,23,24] Thus the acidity of a solution of SbF_5 in HF is greater than that of a solution of SbF_5 in HSO_3F at the same concentration. For example, a 0.5 mol % solution of SbF_5 in HSO_3F has a $-H_0$ value of 17 whereas a 0.5 mol % solution of SbF_5 in HF has a value of $-H_0$ of approximately 21 which is the highest value so far measured for any solution. Although SbF_5 is not fully ionized in HSO_3F we found in our earlier studies[2] that $SbF_5 \cdot 3SO_3$, i.e., $SbF_2(SO_3F)_3$, is a strong electrolyte in HSO_3F. Nevertheless, it produces smaller increases in $-H_0$ in HSO_3F than SbF_5 does in HF (Table V). Thus, it would appear that the H_2F^+ ion is an intrinsically stronger proton donor than the $H_2SO_3F^+$ ion.[15,24]

Registry No. HF, 7664-39-3; H_2O, 7732-18-5; KF, 7789-23-3; $FHSO_3$, 7789-21-1; PF_5, 7647-19-0; TaF_5, 7783-71-3; NbF_5, 7783-68-8; AsF_5, 7784-36-3; SbF_5, 7783-70-2; 1,3,5-trinitrobenzene, 99-35-4; 2,4,6-trinitrobenzene, 88-88-0; 1,3-dichloro-2,4,6-trinitrobenzene, 1630-09-7.

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