Table IV. Trisilane Pyrolyses at 330°

Time, hr	$(SiH_4/Si_3H_6)10^4$	$(Si_2H_6/Si_3H_8)10^4$	SiH_4/Si_2H_6
0.5	10	4.2	2.4
1.0	21	7.5	2.8
1.5	21	10	2.1

was pyrolyzed at 330° with the low-temperature trap set at −63° for 5.5 hr consuming 0.53 mmol of Si_3H_8. The products which passed the −57° trap and condensed at −78° were identified as a mixture of *n*- and *i*-S_4H_{10} (0.10 mmol) by its infrared spectrum and retention times.[37] Similarly the fraction which passed the −23° trap and condensed at −57° was a mixture of *n*- and *i*-Si_5H_{12} (0.07 mmol).[37] The ratio, *n*-Si_4H_{10}/*i*-Si_4H_{10}, was 2.2. In a similar experiment the ratios were 3.5 and 2.0.

C. Copyrolysis of Si_3H_8 and $(CH_3)_3SiD$. Trimethylsilane-*d* (1.42 mmol) and Si_3H_8 (0.45 mmol) were pyrolyzed at 370° for 5 hr with a −57° trapping bath. A mass spectrum of the fraction condensed at −78° (0.05 mmol) consisted of fragment ion envelopes of *m/e* = 101–105, 112–122, 129–137, and 147–152 which is consistent with the products $(CH_3)_3Si_2H_2D$, Si_4H_{10}, $(CH_3)_3Si_3H_4D$, and Si_5H_{12}, respectively.

D. Copyrolysis of Si_3H_6 with CH_3SiD_3. A mixture of Si_3H_8 (0.47 mmol) and CH_3SiD_3 (1.25 mmol) was pyrolyzed at 340° for 6 hr with a −63° trapping bath. The infrared spectrum of the fraction passing a −160° trap demonstrated that the SiH_4 produced was free from any SiH_3D as well as other deuteriosilanes.

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[37] The identification of the normal and iso isomers was based on the fact that the iso isomers have shorter retention times than the normal isomers. Further, the normal isomers were removable from the system by 5 Å molecular sieves.[28]

The Hammett Acidity Function for Some Superacid Systems. II.[1] The Systems H_2SO_4–HSO_3F, KSO_3F–HSO_3F, HSO_3F–SO_3, HSO_3F–AsF_5, HSO_3F–SbF_5, and HSO_3F–SbF_5–SO_3

R. J. Gillespie* and T. E. Peel

Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada. *Received February 22, 1973*

Abstract: Using a set of aromatic nitro compound indicators, the Hammett acidity function, H_0, has been determined for the systems H_2SO_4–HSO_3F, KSO_3F–HSO_3F, HSO_3F–SO_3, HSO_3F–AsF_5, HSO_3F–SbF_5, and HSO_3F–SbF_5–SO_3.

In part I[1] of this series we presented the results of our measurements of the Hammett acidity function, H_0, for the systems H_2SO_4–$H_2S_2O_7$, H_2SO_4–HSO_3F, H_2SO_4–HSO_3Cl, and H_2SO_4–$HB(HSO_4)_4$. This work provided for the first time quantitative, or at least semiquantitative, information on the relative acidities of these superacid systems. In recent years fluorosulfuric acid has become a widely used superacid solvent, and systems such as HSO_3F–SbF_5 and HSO_3F–SbF_5–SO_3 have become recognized as the most highly acidic media available. A 1:1 mixture of HSO_3F and SbF_5 has proved to be so useful as a medium for obtaining stable solutions of otherwise very unstable carbonium ions that it has been called "magic acid." The object of the work reported in this paper was to extend our earlier studies to these still more acidic superacid media based on fluorosulfuric acid and to obtain values for the Hammett acidity function for the systems HSO_3F–SO_3, HSO_3F–AsF_5, HSO_3F–SbF_5, and HSO_3F–SbF_5–SO_3. During the course of the work it was necessary to make some measurements on the system HSO_3F–KSO_3F and to further study the HSO_3F–H_2SO_4 system in the region of excess HSO_3F; these results are also reported here.

Results and Discussion

Determination of H_0 Values. The indicators used in the present study were *p*-nitrochlorobenzene, *m*-nitrochlorobenzene, 2,4-dinitrotoluene, 2,4-dinitrofluorobenzene, 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene, and 2,4,6-trinitrochlorobenzene. The ionization ratios, $I = [BH^+]/[B]$, of the indicators were determined by the spectroscopic method previously described[1] making use of the equation $[BH^+]/[B] = (\xi_B - \xi)/(\xi - \xi_{BH^+})$, where ξ is the measured extinction coefficient and ξ_B and ξ_{BH^+} are the extinction coefficients, at the same wavelengths (usually the wavelength of maximum absorption of BH^+) of the neutral, B, and protonated, BH^+, forms of the indicator, respectively. During the course of the work it became apparent that the polynitro indicators could undergo a second protonation at very high acidities. Use was made of this second protonation in the determination of the acidities for which no sufficiently weak neutral base was available.

As a result of his earlier studies of the protonation of nitro compounds in acid media Brand, *et al.*,[2] had concluded that the absorptions due to separate nitro groups are essentially independent and the diprotona-

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[1] Part I: R. J. Gillespie, T. E. Peel, and E. A. Robinson, *J. Amer. Chem. Soc.*, **93**, 5083 (1971).

[2] J. C. D. Brand, W. E. Horning, and M. B. Thornley, *J. Chem. Soc.*, 1374 (1952).

Table I. ξ_B, ξ_{BH^+}, and pK_{BH^+} Values for the Aromatic Nitro Indicators[a]

	H_2O–H_2SO_4–SO_3 system			H_2SO_4–HSO_3F–SO_3 and HSO_3F–MF_5 systems			Av
Indicator	ξ_B	ξ_{BH^+}	$-pK_{BH^+}$	ξ_B	ξ_{BH^+}	$-pK_{BH^+}$	$-pK_{BH^+}$
p-Nitrotoluene	2100	19,200	11.35				11.35
m-Nitrotoluene	1200	16,100	11.99				11.99
Nitrobenzene	900	15,150	12.14				12.14
p-Fluoronitrobenzene	600	16,500	12.44				12.44
p-Chloronitrobenzene	400	21,800	12.70	400	24,350	12.70	12.70
m-Chloronitrobenzene	400	12,850	13.20	440	14,380	13.13	13.16
2,4-Dinitrotoluene	1700	13,900	13.74	1700	13,900	13.76	13.75
2,4-Dinitrofluorobenzene	920	12,100	(14.03)	920	12,100	14.52	14.52
2,4,6-Trinitrotoluene				960	10,600	15.60	15.60
1,3,5-Trinitrobenzene				800	10,700	16.04	16.04
2,4,6-Trichlorochlorobenzene				700	11,600	16.12	16.12
(2,4-Dinitrofluorobenzene)H$^+$				900	20,450	17.35	17.35
(2,4,6-Trinitrotoluene)H$^+$				0	14,500	18.36	18.36

[a] Table taken in part from ref 1.

tion of aromatic nitro compounds would be accompanied by the appearance in the spectrum of a peak resulting from this second protonated nitro group in addition to the peaks of the first protonated nitro group and the unprotonated nitro groups. We indeed found this to be the case and although the three peaks overlapped each other to a greater or lesser extent we were always able to resolve them using a "Dupont 510 Curve Resolver." Thus in determining the extent of the second protonation the overlapping absorption of the first protonated nitro group could be subtracted from the absorption spectrum allowing the ionization ratio, $[BH^{2+}]/[BH^+]$, to be calculated in the normal manner.

Values of ξ_B, ξ_{BH^+}, and $\xi_{BH^{2+}}$ were either those previously determined or they were determined at sufficiently low or high acidities that in each case the indicator was present entirely in either the unprotonated or protonated form. Although the diprotonation of the indicators 1,3,5-trinitrobenzene and 2,4,6-trinitrochlorobenzene were observed, $\xi_{BH^{2+}}$ values could not be obtained for this second protonation because these indicators were not completely diprotonated even in the most highly acidic medium that we prepared, namely 50 mol % $SbF_5 \cdot 3SO_3$ in HSO_3F. Values of ξ_B, ξ_{BH^+}, and $\xi_{BH^{2+}}$ for all the indicators that we have used are given in Table I. Values of $-\log I$ for all the systems studied are listed in Tables II–VI.

Table II. Ionization Ratios for the H_2SO_4–HSO_3F–SO_3 System

Mol % H_2SO_4	Log *I*	Mol % SO_3	Log *I*
2,4-Dinitrotoluene		2,4,6-Trinitrotoluene	
2.00	0.46	0.00	0.52
1.50	0.40	0.10	0.46
1.00	0.31	0.25	0.39
0.50	0.17	0.50	0.30
0.25	0.03	1.00	0.19
0.10	−0.15	1.50	0.12
0.00	−0.54	2.00	0.10
		3.00	0.08
Mol % SO_3		4.00	0.08
0.10	−0.61	5.00	0.08
0.25	−0.66	7.50	0.08
0.50	−0.75	10.00	0.08
1.00	−0.90		
1.50	−1.00		

Table III. Ionization Ratios for the KSO_3F–HSO_3F System

Mol % KSO_3F	Log *I*	Mol % KSO_3F	Log *I*
p-Chloronitrobenzene[a]		2,4-Dinitrotoluene[a]	
0.393	−0.61	0.393	0.56
0.145	−0.70	0.145	0.24
0.079	−0.92	0.079	0.09
m-Chloronitrobenzene[a]		2,4-Dinitrofluorobenzene[b]	
0.145	−0.43	0.156	0.76
0.079	−0.51	0.047	0.33
		0.022	0.32

[a] Absorption spectra taken from J. Barr, Ph.D. Thesis, University of London, 1959. [b] Absorption spectra taken from T. Birchall, Ph.D. Thesis, McMaster University, 1963.

Table IV. Ionization Ratios for the HSO_3F–AsF_5 System

	Log *I*	
Mol % AsF_5	2,4,6-Trinitrotoluene	1,3,5-Trinitrobenzene
0.10	0.25	0.62
0.20	0.06	0.47
0.30	−0.09	0.35
0.40	−0.21	0.26
0.50	−0.31	0.18
0.75	−0.48	0.04
1.00	−0.58	−0.04
1.25	−0.67	−0.09
1.50	−0.75	−0.14
2.00	−0.93	−0.23
2.50		−0.31
3.00		−0.37
3.50		−0.42
4.00		−0.49
4.50		−0.54
5.00		−0.57

Values for the ionization constant, pK_{BH^+} (and $pk_{BH^{2+}}$) were determined by the overlap technique used originally by Hammett and Deyrup[3] and are based upon the value of $pK_{BH^+} = -10.10$ for 2,4,6-trinitroaniline given by Jorgenson and Hartter.[4] The average ΔpK_{BH^+} between two consecutive indicators was determined from their ionization curves within the range $\log I = \pm 1$.

Because we did not have available any sufficiently weak neutral bases we had to resort to the use of the second protonation of some of the indicators that were available in order to study the most highly acidic media. Strictly speaking the acidity function obtained in this

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(3) T. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, **54**, 2721 (1932).

(4) M. J. Jorgenson and D. R. Hartter, *ibid.*, **85**, 876 (1963).

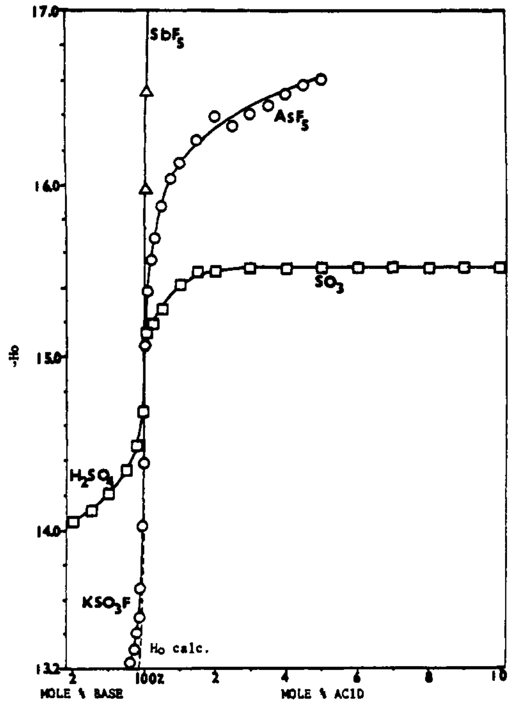

Figure 1. $-H_0$ function near 100% HSO_3F.

Table V. Ionization Ratios for the HSO_3F–SbF_5 System

Mol % SbF_5	Log I	Mol % SbF_5	Log I	Mol % SbF_5	Log I
2,4,6-Trinitrotoluene		1,3,5-Trinitrobenzene			
0.010	0.31	0.030	0.50	1.00	0.03
0.020	0.11	0.040	0.26	1.20	−0.04
0.030	−0.06	0.050	0.07	1.40	−0.11
0.040	−0.21	0.060	−0.08	1.60	−0.17
0.050	−0.35	0.070	−0.22	1.80	−0.21
0.075	−0.67	0.080	−0.33	2.00	−0.26
0.100	−0.94	0.090	−0.42	2.50	−0.38
0.125	−1.36	0.100	−0.51	3.00	−0.50
		0.125	−0.65	3.50	−0.61
2,4,6-Trinitrochlorobenzene		0.150	−0.77	4.00	−0.72
		0.175	−0.89	4.50	−0.82
0.030	0.50	0.200	−1.02	5.00	−0.95
0.040	0.27			5.50	−1.03
0.060	−0.07				
0.080	−0.31	[2,4-Dinitrofluorobenzene]H^+		[2,4,6-Trinitrotoluene]H^+	
0.100	−0.47				
0.120	−0.56	0.10	0.80	2.50	0.67
0.140	−0.62	0.20	0.55	3.00	0.52
0.160	−0.66	0.30	0.42	4.00	0.28
0.180	−0.70	0.40	0.33	5.00	0.08
0.200	−0.73	0.50	0.26	6.00	−0.12
0.224	−0.76	0.60	0.20	7.00	−0.31
0.249	−0.78	0.80	0.11	8.00	−0.43
0.274	−0.80			9.00	−0.52
0.299	−0.81			10.00	−0.58
0.349	−0.84			11.00	−0.63
0.497	−0.94				
0.563	−1.00				

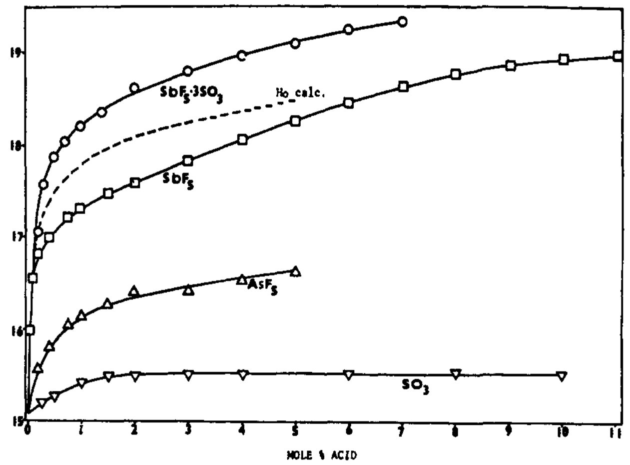

Figure 2. $-H_0$ values for acids of the fluorosulfuric acid solvent system.

Table VI. Ionization Ratios for the HSO_3F–$SbF_5 \cdot 3SO_3$ System

Mol % $SbF_5 \cdot 3SO_3$	Log I	Mol % $SbF_5 \cdot 3SO_3$	Log I
[2,4-Dinitrofluorobenzene]H^+		1.70	0.17
0.20	0.29	0.80	0.10
0.30	−0.15	0.90	0.05
0.40	−0.32	1.00	0.01
0.50	−0.42	1.20	−0.07
0.60	−0.48	1.40	−0.12
0.70	−0.56	1.60	−0.17
0.80	−0.61	1.80	−0.23
0.90	−0.68	2.00	−0.26
1.00	−0.72	2.50	−0.36
1.20	−0.80	3.00	−0.45
1.40	−0.89	3.50	−0.52
1.60	−0.97	4.00	−0.60
1.80	−1.05	4.50	−0.67
		5.00	−0.75
[2,4,6-Trinitrotoluene]H^+		5.50	−0.83
0.30	0.70	6.00	−0.90
0.40	0.51	6.50	−0.95
0.50	0.37	7.00	−0.99
0.60	0.25		

manner is $H_+ = pK_{BH^{2+}} - \log I$ but the behavior of 2,4-dinitrofluorobenzene and 2,4,6-trinitrotoluene upon diprotonation was sufficiently similar to that of the other indicators undergoing monoprotonation to justify the approximation of describing it as an H_0 function. From the plots of log I against solution composition values of $pK_{BH^+} - \log I$, within the range log $I = \pm 1$, were obtained at integral acid concentrations, and the average of each of these values for all the indicators used was taken as the H_0 value. These values are given in Tables VII, VIII, and IX and in Figures 1 and 2.

Table VII. H_0 Values for the HSO_3F–H_2SO_4 and HSO_3F–SO_3 Systems

Mol %	H_0	
	H_2SO_4	SO_3
0.00	15.07	15.07
0.10	14.68	15.14
0.25	14.49	15.19
0.50	14.35	15.28
1.00	14.21	15.42
1.50	14.12	15.50
2.00	14.06	15.50
4.00	13.98	15.52
6.00	13.90	15.52
8.00	13.81	15.52
10.00	13.73	15.52

As discussed previously[1] it is important to show that the indicators form a consistent set in that they give plots of log I *vs.* H_0 that are parallel and of unit slope. As before this was tested by the method of Johnson,

Table VIII. H_0 Values for the HSO_3F–KSO_3F System

Mol % KSO_3F	$-H_0$	Mol % KSO_3F	$-H_0$
0.000	15.07	0.200	13.40
0.025	14.35	0.250	13.35
0.050	14.11	0.300	13.31
0.075	13.75	0.350	13.28
0.100	13.66	0.400	13.24
0.150	13.56		

Table IX. H_0 Values for the HSO_3F–AsF_5, HSO_3F–SbF_5, and HSO_3F–$SbF_5 \cdot 3SO_3$ Systems

	$-H_0$		
Mol %	AsF_5	SbF_5	$SbF_5 \cdot 3SO_3$
0.00	15.07	15.07	15.07
0.02	15.14	15.49	15.49
0.04	15.20	15.81	15.81
0.06	15.26	16.13	16.13
0.08	15.33	16.37	16.37
0.10	15.38	16.55	16.55
0.15	15.48	16.74	16.85
0.20	15.56	16.82	17.08
0.40	15.80	17.01	17.71
0.60	15.96	17.14	17.97
0.80	16.06	17.24	18.11
1.00	16.13	17.32	18.21
2.00	16.40	17.61	18.62
3.00	16.41	17.84	18.81
4.00	16.53	18.08	18.96
5.00	16.61	18.28	19.10
6.00		18.48	19.26
7.00		18.66	19.35
8.00		18.79	
9.00		18.88	
10.00		18.94	
11.00		18.99	

Table X. Evaluation of Overlap of Aromatic Nitro Indicators in the Fluorosulfuric Acid Systems

Indicator	$a_{i,i-1}$ = log (I_i/I_{i-1})	$\Pi a_{i,i-1}$
2,4-Dinitrofluorobenzene[a]	0.91	0.95
2,4,6-Trinitrotoluene	1.08	1.03
1,3,5-Trinitrobenzene	0.87	0.90
2,4,6-Trinitrochlorobenzene	1.09	0.98
Protonated 2,4-dinitrofluorobenzene	0.89	0.87
Protonated 2,4,6-trinitrotoluene	0.97	0.84

[a] Indicator is compared to behavior of 2,4-dinitrotoluene.[1]

et al.[5] The results are given in Table X where $a_{i,i-1}$ is a constant that measures the degree of parallelism of the log I *vs.* H_0 plots for the indicators i and $i - 1$ and should be unity for a pair of well behaved indicators. The product $\pi a_{i,i-1}$ indicates how the ith indicator behaves with respect to the acidity function H_1 defined by the first indicator. The results given here are a continuation of those given in Table IV of ref 1; the values of $a_{i,i-1}$ are comparable to those previously reported.[1,5] The indicators that are diprotonated appear to give slightly smaller $a_{i,i-1}$ values, but we consider that these smaller values are still within the acceptable range for a series of consistent indicators although the values of $-H_0$ above 17 must be regarded as less accurate than the lower values.

The H_2SO_4–HSO_3F System. The H_0 values for the H_2SO_4–HSO_3F system which are given in Table VII are a detailed extension, in the region of 100% HSO_3F, of the results previously reported.[1] In solutions in fluorosulfuric acid sulfuric acid behaves as a weak base and is partially protonated according to eq 1.

$$HSO_3F + H_2SO_4 \rightleftharpoons SO_3F^- + H_3SO_4^+ \qquad (1)$$

The fluorosulfate ion produced shifts, the equilibrium of the autoprotolysis reaction (K_{AP} = 3.8 × 10^{-8} mol^2 kg^{-2})[6] decreasing the $H_2SO_3F^+$ concentration and thus decreasing the acidity. It was not found possible to directly measure the acidity of 100% HSO_3F because the concentration of the basic indicator required for acidity measurements was of the same magnitude as that of the autoprotolysis ions. The SO_3F^- ion arising from the ionization of the indicator represses the autoprotolysis equilibrium (2), thus

$$2HSO_3F \rightleftharpoons H_2SO_3F^+ + SO_3F^- \qquad (2)$$

reducing the $H_2SO_3F^+$ concentration and lowering the acidity below that of pure 100% HSO_3F. It was, however, possible to extrapolate the H_0 curve for the H_2SO_4–HSO_3F system to 100% HSO_3F and this gave an H_0 value of −15.07. The same value was obtained by similar extrapolations of the data obtained for the HSO_3F–SO_3 and KSO_3F–HSO_3F systems.

The KSO_3F–HSO_3F System. The experimental results of Barr[7] and Birchall[8] on the absorption spectra of solutions of aromatic nitro indicators in the KSO_3F–HSO_3F system were used in calculating H_0 values for this system. These values are given in Table VIII and Figure 1 and as would be expected, because KSO_3F is a strong base in HSO_3F, the H_0 value decreases rapidly as the KSO_3F concentration is increased.

The HSO_3F–SO_3, AsF_5, and SbF_5 Systems. The H_0 values for solutions of solutes which behave as acids in solution in fluorosulfuric acid are given in Tables VII and IX and Figures 1 and 2. The ability of the solutes to increase the acidity increases in the order $SO_3 < AsF_5 < SbF_5 > SbF_53 \cdot SO_3$. This is consistent with conductivity studies[9,10] which have shown that $SbF_5 \cdot 3SO_3$ is a strong acid, fully ionized in HSO_3F, that SbF_5 is a weak acid with K_a = 3.7 × 10^{-3} mol kg^{-1}, that AsF_5 is weaker still, and that SO_3 causes no measurable increase in the conductivity of HSO_3F solutions and thus must be an exceedingly weak acid.

The very small initial rise in the H_0 curve for the HSO_3F–SO_3 system near 100% HSO_3F is consistent with SO_3 behaving as an extremely weak acid in HSO_3F. The formation of HS_2O_6F and higher polymeric acids ($HS_nO_{3n}F$) in solutions of SO_3 in HSO_3F has been demonstrated[11,12] by Raman and nmr spectroscopy. The very slight initial increase in acidity may presumably be attributed to a very slight ionization of fluorodisulfuric acid and the resulting repression of the solvent

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(5) C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, **91**, 6654 (1969).

(6) J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.*, **3**, 1149 (1964).

(7) J. Barr, Ph.D. Thesis, University of London, 1959.

(8) T. Birchall, Ph.D. Thesis, McMaster University, 1963.

(9) R. C. Thompson, J. Barr, R. J. Gillespie, J. B. Milne, and R. A. Rothenbury, *Inorg. Chem.*, **4**, 1641 (1965).

(10) R. J. Gillespie, K. Ouchi, and G. P. Pez, *ibid.*, **8**, 63 (1969).

(11) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **40**, 675 (1962).

(12) F. A. W. Dean and R. J. Gillespie, *J. Amer. Chem. Soc.*, **92**, 2362 (1970).

$$HS_2O_6F + HSO_3F \rightleftharpoons H_2SO_3F^+ + S_2O_6F^- \quad (3)$$

autoprotolysis. At higher SO_3 concentrations the plot of H_0 against SO_3 concentration becomes essentially horizontal and one must conclude that the very limited ionization of HS_2O_6F and the higher polymeric acids ($HS_nO_{3n}F$) are insufficient to perceptibly increase the acidity of the solution. It may be noted that the behavior of SO_3F is markedly different from its behavior in H_2SO_4[1] where it acts as a reasonably strong acid *via* the formation of $H_2S_2O_7$.

The initial increase in H_0 upon the addition of AsF_5 to 100% HSO_3F is considerably greater than that produced by SO_3 which is consistent with our earlier conductivity measurements which indicated that AsF_5 is a stronger acid.[10] Both AsF_5 and SbF_5 are Lewis acids and ionize in HSO_3F according to eq 4.

$$MF_5 + 2HSO_3F \rightleftharpoons MF_5SO_3F^- + H_2SO_3F^+ \quad M = As, Sb \quad (4)$$

Except in very dilute solutions the ionization of SbF_5 or AsF_5 is in fact more complicated because of the formation of polymeric anions such as $(MF_5)_2SO_3F^-$ which have been shown[9] to be somewhat stronger acids than the monomeric species $MF_5SO_3F^-$. The formation of these polymeric anions at high MF_5 concentrations accounts for the fact that the plot of H_0 against acid concentration has a slightly steeper slope at higher acid concentrations than would have been predicted by the single ionization equilibrium (4). The range of the H_0 measurements for the HSO_3F–AsF_5 system was limited by the high vapor pressure of AsF_5 above solutions containing more than 5 mol % AsF_5.

The very rapid initial rise of the H_0 curve for the HSO_3F–SbF_5 system is consistent with the relatively large ionization constant for the ionization of SbF_5 according to eq 4; moreover, the dimeric species, $H[(SbF_5)_2SO_3F]$, has a still larger ionization constant.[9,10] The limiting concentration of SbF_5 for which we could obtain a reliable H_0 value was 11 mol %. Solutions of higher SbF_5 concentrations were in fact studied, in order to obtain the spectra of the fully diprotonated forms of the indicators 2,4-dinitrofluorobenzene and 2,4,6-trinitrotoluene, but, since we consider that H_0 values based on log I values outside the range ±1 are not sufficiently reliable, we are only able to quote H_0 values for solutions containing up to 11 mol % SbF_5. In order to extend these measurements to still higher acidities it will be necessary to find a medium that is sufficiently acidic to fully diprotonate the indicators 1,3,5-trinitrobenzene and 2,4,6-trinitrochlorobenzene or other suitably very weak bases. By extrapolation of the data in Figure 2 and Table IX it is estimated that the H_0 of "magic acid," *i.e.*, 50 mol % SbF_5 in HSO_3F, is approximately −19.5.

When SO_3 is added to solutions of SbF_5 in HSO_3F it reacts according to the eq 5–7. These compounds

$$SbF_5 + SO_3 \rightleftharpoons SbF_4(SO_3F) \quad (5)$$

$$SbF_5 + 2SO_3 \rightleftharpoons SbF_3(SO_5F)_2 \quad (6)$$

$$SbF_5 + 3SO_3 \rightleftharpoons SbF_2(SO_3F)_3 \quad (7)$$

appear to increase in acid strength with increasing number of fluorosulfate groups and indeed $SbF_2(SO_3F)_3$ has been shown[9] to be virtually fully ionized according to eq 8.

$$SbF_2(SO_3F)_3 + 2HSO_3F \rightleftharpoons SbF_2(SO_3F)_4^- + H_2SO_3F^+ \quad (8)$$

We have accordingly measured the acidities of solutions of $SbF_5 \cdot 3SO_3$ in fluorosulfuric acid and we have found that indeed the solutions are more acidic than those of SbF_5 (Figure 2). This solute in fact gives solutions of the highest acidities that have been measured. Again the range of concentrations for which H_0 values could be obtained was limited, to 7 mol %, because we were unable to obtain $\xi_{BH^{2+}}$ values for the very weak bases needed to study more concentrated solutions.

Conclusions

It has been known for sometime that HSO_3F is a stronger acid than H_2SO_4. The measurements described in the present paper and in the first paper of this series provide the basis for a quantitative comparison. The H_0 values for various acids are compared in Table XI from which it appears that HSO_3F is a stronger acid than $H_2S_2O_7$ although the opposite conclusion has been reached previously[13] on the basis of conductivity and cryoscopic studies of solutions of various weak bases in the two acids. The apparent discrepancy may be explained by the extensive autoprotolysis and other self-dissociation reactions of disulfuric acid compared with HSO_3F. As a result of this extensive self-dissociation[13,14] $H_2S_2O_7$ ($K_{AP} = 3.6 \times 10^{-3}$ mol² kg⁻²) may be said to be highly buffered and the addition of the relatively large amount of base, needed for cryoscopic or conductometric measurements, does not produce a very significant change in the total concentration of the basic anion, which is believed to be $HS_3O_{10}^-$, and hence does not cause an appreciable change in the acidity of the medium. Fluorosulfuric acid is, however, much less extensively self-ionized ($K_{AP} = 3.8 \times 10^{-8}$ mol² kg⁻²)[15] and the same amount of base added to fluorosulfuric acid markedly represses the autoprotolysis reaction correspondingly diminishing the acidity. This difference in behavior is clearly evident from the different form of the acidity function curves in the region of the 100% acid; whereas for $H_2S_2O_7$ the curve is very flat in this region, it is very steep in the region of 100% HSO_3F (Figure 2) showing clearly that even a very small amount of added base causes a marked decrease in the acidity of HSO_3F. It was for this reason that it was not possible to obtain the H_0 of 100% HSO_3F directly as even the very small amount of basic indicator needed in the spectroscopic measurements has a considerable effect on the acidity. The relatively large amount of base needed for the cryoscopic and conductometric measurements is sufficient to reduce the acidity of HSO_3F to a value below that of $H_2S_2O_7$.

Table XI. H_0 Values for Some Acids

Acid	$-H_0$
H_2SO_4	11.93
$H_2S_2O_7$	14.14
HSO_3F	15.07
HSO_3F (10% SbF_5)	18.94
HSO_3F (7% $SbF_5 \cdot 3SO_3$)	19.35

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(13) R. J. Gillespie and K. C. Malhotra, *J. Chem. Soc. A*, 1933 (1968).

(14) R. J. Gillespie and K. C. Malhotra, *ibid.*, 1994 (1967).

Thus it is important to realize that although the acidity of 100% HSO_3F is greater than that of 100% $H_2S_2O_7$ in many practical cases when a small amount of base is present, the opposite will generally be true.

The values in Table XI also serve to illustrate the enormous effect of SbF_5 on the acidity of HSO_3F. The rather slow increase in $-H_0$ in the more concentrated solutions of SbF_5 and $SbF_5 \cdot 3SO_3$ shows that these solutions are also highly buffered like $H_2S_2O_7$ and resist changes in acidity on addition of small amounts of acid or base.

It is reasonable to assume that the acidity of solutions in HSO_3F is determined primarily by the concentration of $H_2SO_3F^+$ just as the acidity of dilute aqueous solutions is determined by the concentration of H_3O^+. From the concentration of $H_2SO_3F^+$ in 100% HSO_3F, which has been found to be 1.9×10^{-4} m,[15] and the H_0 of 100% HSO_3F, one may obtain the following relation[16]

$$H_0 = -\log [H_2SO_3F^+] - 18.79 \qquad (9)$$

Assuming strong acid or strong base behavior theoretical H_0 values may be calculated; these calculated H_0 curves are shown in Figures 1 and 2 where it may be seen that they agree well with the observed curves obtained for a strong base (KSO_3F) and a strong acid ($SbF_5 \cdot 3SO_3$) except in concentrated solutions. The differences observed at higher concentrations may presumably be attributed to activity effects.

For the weak acids SO_3, AsF_5, and SbF_5 eq 9 can be used to calculate a value for their ionization constants; from the measured H_0 the concentration of $H_2SO_3F^+$ can be calculated and then since the concentrations of $MF_5SO_3F^-$ and $H_2SO_3F^+$ in eq 4 are to a very good approximation equal and

$$K_a = [H_2SO_3F^+][MF_5SO_3F^-]/[MF_5] \qquad (10)$$

K_a may be calculated. It has been found that the apparent K_a for SbF_5 decreased with decreasing concentration, and on extrapolation to infinite dilution the value of 2.2×10^{-3} mol kg^{-1} was obtained which is in reasonable agreement with the value of 3.7×10^{-3} mol kg^{-1} determined by a conductometric method.[9] The increase in the apparent K_a with increasing concentration is consistent with the previously demonstrated formation of the stronger polymeric acids such as $H[(SbF_5)_2SO_3F]$ at higher concentrations. In a similar manner values of $K_a = 3.7 \times 10^{-6}$ and 4.6×10^{-7} were obtained for the very weak acids AsF_5 and SO_3. The K_a for AsF_5 increased as the concentration increased indicating the presence of stronger polymeric acids. No values have been given previously for these two dissociation constants.

Experimental Section

Materials. All aromatic nitro compounds were recrystallized from appropriate solvents and dried over standard desiccants. 2,4-Dinitrofluorobenzene was further purified by fractional freezing of the melt. All indicators had melting points consistent with the literature values.

Commercial grade fluorosulfuric acid was purified by simple fractional distillation in an all-glass still at atmospheric pressure. The resulting colorless liquid was found to contain a slight excess of SO_3 presumably arising from the very slight dissociation of HSO_3F in the gas phase followed by the subsequent loss of HF.

$$HSO_3F \rightleftharpoons HF + SO_3 \qquad (11)$$

The 100% HSO_3F was prepared by the addition of the appropriate amount of HF as computed from the conductivity or the freezing point of the initial acid.

Reagent grade H_2SO_4 was adjusted to 100% by the addition of 30% oleum until the minimum conductivity or maximum freezing point was reached. Solutions of H_2SO_4 in HSO_3F were prepared by weight in a drybox.

Potassium fluorosulfate was prepared by the action of HSO_3F on an ice-cold KOH solution. The resulting precipitate was recrystallized from water and dried in a vacuum desiccator. KSO_3F–HSO_3F solutions were prepared by weight in a drybox.

HSO_3F–SO_3 mixtures were prepared by weight by the distillation of Sulfan (stabilized SO_3; Allied Chemicals) into 100% HSO_3F. HSO_3F–AsF_5 mixtures were prepared by weight by distillation in a grease-free Pyrex and Teflon vacuum line. AsF_5, which was found by means of its gas-phase infrared spectrum to be free of impurities, was condensed directly onto frozen HSO_3F.

Antimony pentafluoride was purified by double distillation in a Pyrex glass still in an atmosphere of dry nitrogen. The fraction boiling between 141 and 142° was collected. HSO_3F–SbF_5 solutions were prepared by weight by vacuum disillation of SbF_5 in a vacuum line onto frozen 100% HSO_3F. HSO_3F–SbF_5–SO_3 solutions were prepared by weight by mixing stock solutions of HSO_3F–SbF_5 and HSO_3F–SO_3 in a drybox. These mixtures were then diluted as required by the weighed addition of 100% HSO_3F.

Preparation of solutions and spectrophotometric measurements were carried out as previously outlined.[1]

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(15) R. C. Thomoson, Ph.D. Thesis, McMaster University, 1962.

(16) T. E. Peel, Ph.D. Thesis, McMaster University, 1971.