

Gas-Phase Reactions of Weak Brønsted Bases I^- , PO_3^- , HSO_4^- , FSO_3^- , and $CF_3SO_3^-$ with Strong Brønsted Acids H_2SO_4 , FSO_3H , and CF_3SO_3H . A Quantitative Intrinsic Superacidity Scale for the Sulfonic Acids XSO_3H ($X = HO, F, \text{ and } CF_3$)

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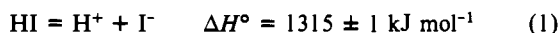
Abstract: Using a selected ion flow tube at 368 K, we have measured rate constants for ion-molecule reactions between I^- , PO_3^- , HSO_4^- , FSO_3^- , $CF_3SO_3^-$, $NO_3^- \cdot HNO_3$, $FSO_3^- \cdot FSO_3H$, and H_2SO_4 , FSO_3H , CF_3SO_3H . Channels observed include proton transfer and clustering. These results allow free energies (enthalpies) of deprotonation (kJ/mol) to be estimated (within ± 10 kJ/mol) as follows: HPO_3 , 1270 (1300); H_2SO_4 , 1265 (1295); FSO_3H , 1255 (1285); CF_3SO_3H , 1250 (1280). In two cases, electron affinities are estimated as follows: HSO_4^- , 4.7 ± 0.2 eV; FSO_3^- , 4.8 ± 0.2 eV. For the title acids, the gas-phase acidity order is discussed and is used to explain the differing acidity orders found for these acids in different solvents. The same data measure basicities for the conjugate bases, and these are related to nucleophilicity and leaving group ability. This study explores a region of the acidity scale where no acidities are established that would calibrate the scale. The scale is calibrated here using cluster ions whose free energy of protonation can be reliably estimated.

Introduction

Which is the strongest acid? There is no unambiguous answer to this question for the strongest Brønsted acids in solution.¹ The answer depends upon the solvent. In acetic acid, CF_3SO_3H is the strongest acid,² yet in sulfuric acid, the strongest acid is FSO_3H .³ Unambiguous answers to such questions come from measurements in the gas phase that establish *intrinsic* Brønsted acidity for strong acids and superacids.⁴ Measurement of intrinsic acidity (without solvent in the gas phase) reveals why an acidity scale in solution can be ambiguous.⁵

We have studied proton-transfer reactions between strong and superacids and their respective conjugate bases (which are therefore the weakest bases). This ranks the acids in order of increasing Brønsted acid strength. The experiments were not routine, using highly corrosive acids at elevated temperatures in both the ion source and the flow tube of a SIFT (selected ion flow tube). This extends previous studies of sulfuric acid⁶ and nitric acid⁷ (exploring their role as trace components of the atmosphere) and complements studies of triflic anhydride⁸ and of dissociative electron attachment to some strong and superacids.⁹

The present study extends our previous investigation of PO_3^- and HPO_3 .^{10,11} By comparing the acidity of HPO_3 with those of trifluoromethylsulfonic (triflic) acid (CF_3SO_3H), fluorosulfonic acid (FSO_3H), sulfuric acid (H_2SO_4), and hydrogen iodide (HI), we establish if HPO_3 is a superacid. The benchmark for superacidity is set by sulfuric acid, whereby stronger acids are called superacids.¹² The superacids CF_3SO_3H and FSO_3H are included because they are the strongest found in solution.¹³ Hydrogen iodide is included to provide a quantitative calibration of the acidity scale, it being the strongest acid for which an enthalpy of deprotonation has been accurately established in the gas phase.¹⁴



Necessarily, by studying the strongest acids we also study the weakest bases, and this extends our previous investigations of weak bases NO_3^- ⁷ and PO_3^- .^{10,11} (The latter is postulated as a reactive intermediate for biochemical phosphorylation and phosphate ester hydrolysis.¹⁵) Proton transfer to PO_3^- has inadvertently "synthesized" metaphosphoric acid HPO_3 , which is unstable in the condensed phase in a monomeric form. The acidity order established for the acids establishes a basicity order for the conjugate bases; these basicities may be related to nucleophilicity

and leaving group ability, important quantities for the sulfonic acids studied here, because of their synthetic applications.¹⁶ Finally, we have probed the differing action of different solvents, comparing intrinsic, solvent-free chemistry in the gas phase with that observed in solution.¹⁷

Experimental Section

The experiments were performed in a selected-ion flow tube. This technique has recently been reviewed extensively.^{18,19} The apparatus used here has been described in detail previously,^{20,21} and only details

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(4) For preliminary summaries, see: (a) Paulson, J. F.; Viggiano, A. A.; Henchman, M.; Dale, F. In *Symposium on Atomic and Surface Physics '86*; Howorka, F., Lindinger, W., Märk, T. D., Eds.; Studia Studienförderungsgesellschaft m.b.H.: Innsbruck, 1986; pp 7-11. (b) Henchman, M.; Viggiano, A. A.; Paulson, J. F.; Dale, F.; Deakne, C. *Faraday Discuss. Chem. Soc.* **1988**, *85*, 87. (c) Lias, S. G.; Bartmess, J.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1, 658. (d) Kebarle, P.; Dillow, G. W.; Paul, G. J. C. *Adv. Mass Spectrom.* **1989**, *11*, 506.

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particular to the present measurements are discussed. Ions were made in a high-pressure ion source, operating at pressures of up to a few tenths of a Torr and with primary electron energies of ~ 150 eV. Ions were produced by dissociative attachment of primary and secondary electrons and could react further in the source. Six different ions were used and were prepared in the ion source as follows: O^- from N_2O , $CF_3SO_3^-$ from triflic acid anhydride, FSO_3^- from fluorosulfonic acid, HSO_4^- from sulfuric acid, PO_3^- from dimethyl phosphite, and NO_3^- (HNO_3) from nitric acid. For all of the ions except HSO_4^- , the source gas was taken directly from the liquid or gas. The procedure for introducing H_2SO_4 has been described previously.⁶

Three neutral reactants were used in the flow tube: CF_3SO_3H , FSO_3H , and H_2SO_4 . All measurements were made with the flow tube maintained at 95 ± 5 °C. Two different techniques were used to introduce the reactants into the flow tube. For CF_3SO_3H and FSO_3H , the vapor pressures were high enough to introduce them directly, and liquid samples were maintained in a reservoir at 55 °C to give a vapor pressure of ~ 10 Torr. Inlet lines were maintained at a temperature of over 100 °C to prevent sticking of these acids to the walls. The flow rates were measured and controlled by an MKS 550 flow controller (designed to handle highly corrosive materials), maintained at 121 °C and calibrated by the manufacturer for H_2O . Because the controller operates in the molecular flow region, the correction for other gases depends only on the molecular weight, and a temperature correction has also to be applied. Two complications may affect determinations of the reactant gas concentrations in the flow tube. First, both gases are sticky and are therefore difficult to handle and measure. Second, the flow controller is operated just at the limit of the molecular flow region, and the flow may not be strictly molecular. We estimate that the absolute values of the flow rates may be uncertain by a factor of 2. Relative flow rates are not affected by these uncertainties and should be accurate to within 20%.

The experimental sequence was as follows, the measurements with FSO_3H as reactant in the flow tube being made immediately after the completion of those with CF_3SO_3H . It took half an hour to establish a steady flow of FSO_3H in the flow tube, it behaving as a "sticky" vapor. As discussed below, this observation may have some bearing on the magnitude of the rate constants observed for the reactions with FSO_3H .

A different technique was used for sulfuric acid, which has too low a vapor pressure to sustain an adequate flow into the flow tube. Following the procedure described previously,^{6,9} helium carrier gas was bubbled through a heated stainless steel vessel containing glass wool coated with sulfuric acid. With the temperature of the heater held constant, the flow rate of the sulfuric acid is proportional to the square root of the carrier gas flow rate. The relative concentration of H_2SO_4 in the flow tube may thus be controlled by adjusting the flow rate of the helium carrier gas. This concentration is put on an absolute scale by studying a calibration reaction for which the rate constant has been determined.

The inlet system was designed to handle highly corrosive reagents. Stainless steel was used throughout in tubing, gaskets, and Nupro bellows valves. The MKS flow controllers were constructed of stainless steel and were fitted with Teflon and Kalrez gaskets. At the conclusion of these experiments, the system and flow controllers were cleaned, and the only items which had to be replaced were parts of the tubing and gaskets on some of the pumps. Such experiments on some of the most corrosive substances known were performed with only minor effects on the apparatus.

Results

Table I lists experimental rate constants and branching ratios measured for 19 reactions of weak Brønsted bases with strong Brønsted acids. Of these, 18 are new measurements from this laboratory,²⁶ and the result for eq 20, measured previously at a

different temperature,¹⁰ is included to complete the set. For the 18 new reactions, three acids were used (H_2SO_4 , FSO_3H , and CF_3SO_3H) and five bases (I^- , PO_3^- , HSO_4^- , FSO_3^- , and $CF_3SO_3^-$). Only $HSO_4^- + H_2SO_4$ of the 15 possible combinations was not studied. (Only one inlet system was constructed for H_2SO_4 .) The four additional reactions utilized cluster ions, namely, $NO_3^-(HNO_3)$, reacting with all three superacids, and $FSO_3^-(FSO_3H)$, reacting only with triflic acid.

In addition to the experimental rate constants k_{expt} , Table I lists theoretical collisional rate constants k_{coll} (which are upper bounds on k_{expt}) and the ratios $k_{\text{expt}}/k_{\text{coll}}$. The calculations of k_{coll} require numerical values for the dipole moments and polarizabilities of H_2SO_4 , FSO_3H , and CF_3SO_3H , as indicated in footnote a of Table I. The dipole moments of FSO_3H and CF_3SO_3H , which are unknown, are assigned the value measured for H_2SO_4 . We emphasize that any uncertainty in this procedure has no bearing whatsoever on the conclusions of the paper. Values of $k_{\text{expt}}/k_{\text{coll}}$ are considered solely to assess the self-consistency of the data, particularly where they fail to meet the condition $k_{\text{expt}}/k_{\text{coll}} \leq 1.0$.

Measurement of the rate constants requires that the concentration of the neutral reactant in the flow tube be determined. For two of the three reactants, FSO_3H and CF_3SO_3H , the concentrations were determined from measurements using a flow meter. Because the gases are corrosive, these measurements may be subject to systematic error, but in that case, all the rate constants for reaction with FSO_3H (and/or all of those for CF_3SO_3H) should be either systematically high or low. Table I shows that the rate constants for CF_3SO_3H (eq 2–7) are too high, while those for FSO_3H (eq 10–14) may be low, as discussed below.

In contrast, when H_2SO_4 was used as the neutral reactant, its concentration in the flow tube could not be measured directly with a flow meter. Only relative concentrations of H_2SO_4 were measured in the flow tube, and therefore relative rate constants were measured. These were put on an absolute scale by assuming that reaction occurs on every collision for a chosen calibration reaction. Exothermic proton-transfer reactions are good choices as calibration reactions since they frequently occur with unit collision efficiency,²⁸ but the reactions in Table I are uncertain candidates, because their exothermicity is uncertain. Instead, because additional data were available in the present study for the proton-transfer reaction $O^- + HX = OH + X^-$, these data were used as a calibration check. (It would have been preferable to use a closed-shell proton acceptor such as F^- for which proton transfer routinely occurs with unit collision efficiency. This reservation, however, is offset by the high reaction exothermicity in each case (>400 kJ/mol), virtually assuring unit reaction efficiency for the reactants $HX = H_2SO_4$, FSO_3H , and CF_3SO_3H .) The results for this calibration test are shown in Table II. The assumption that $k_{\text{expt}} = 3.6 \times 10^{-9}$ cm³/(molecule s) (the collisional value²⁷) for the $O^- + H_2SO_4$ reaction allows rate constants to be assigned to the reactions with H_2SO_4 (eq 15–19) in Table I. The calibration procedure is validated by the result that all proton transfers from H_2SO_4 are observed to occur with unit collision efficiency.

Because the experiments were not routine measurements, their reliability needs to be assessed. Runs were made as quickly as possible to minimize any damage to the equipment. Each reaction was run only once. The primary aim was to establish whether or not proton transfer was facile, and to establish thereby the relative acidity order. These data also allowed us to derive rate constants. Given the nature of the chemicals, the need for speed, and the absence of replicate runs, the rate constant data appear to be surprisingly good. For example, as a check, previous measurements of the rate constants for eq 15 and eq 17, relative to eq 23, yielded 0.50 in both cases,^{6a} which may be compared with the values here of 0.44 and 0.56, respectively.

The collision efficiencies $k_{\text{expt}}/k_{\text{coll}}$ for most (but not all) of the reactions with CF_3SO_3H are greater than unity ($1 \leq k_{\text{expt}}/k_{\text{coll}} \leq 1.6$), whereas most (but not all) of those with FSO_3H are less

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Table I. Branching Ratios and Rate Constants for the Reactions of the Brønsted Bases I^- , PO_3^- , HSO_4^- , FSO_3^- , and CF_3SO_3^- with the Brønsted Acids $\text{CF}_3\text{SO}_3\text{H}$, FSO_3H , and H_2SO_4 (flow tube pressure, 0.8 Torr helium; temp, 368 ± 5 K)

eq	Reaction	Rate constant (10^{-9} cm ³ /molec s)		
		k_{expt}	k_{coll}^a	$k_{\text{expt}}/k_{\text{coll}}$
2.	$\text{I}^- + \text{CF}_3\text{SO}_3\text{H} \longrightarrow \text{CF}_3\text{SO}_3^- + \text{HI}$	2.4	1.7	1.4
3.	$\text{PO}_3^- + \text{CF}_3\text{SO}_3\text{H} \longrightarrow \text{CF}_3\text{SO}_3^- + \text{HPO}_3$	3.2	2.0	1.6
4.	$\text{HSO}_4^- + \text{CF}_3\text{SO}_3\text{H} \longrightarrow \text{CF}_3\text{SO}_3^- + \text{H}_2\text{SO}_4$	2.8	1.9	1.5
5.	$\text{NO}_3^-(\text{HNO}_3) + \text{CF}_3\text{SO}_3\text{H}$	2.6	1.7	1.5
	$-50\% \longrightarrow \text{CF}_3\text{SO}_3^- + [\text{2HNO}_3]^b$			
	$-50\% \longrightarrow \text{CF}_3\text{SO}_3^-(\text{HNO}_3) + \text{HNO}_3$			
6.	$\text{FSO}_3^- + \text{CF}_3\text{SO}_3\text{H}$	2.5	1.9	1.3
	$-30\% \longrightarrow \text{CF}_3\text{SO}_3^-(\text{FSO}_3\text{H})$			
7.	$\text{CF}_3\text{SO}_3^- + \text{CF}_3\text{SO}_3\text{H} \longrightarrow \text{CF}_3\text{SO}_3^-(\text{CF}_3\text{SO}_3\text{H})$	2.0	1.7	1.2
8.	$\text{FSO}_3^-(\text{FSO}_3\text{H}) + \text{CF}_3\text{SO}_3\text{H} \longrightarrow \text{CF}_3\text{SO}_3^-(\text{FSO}_3\text{H}) + \text{FSO}_3\text{H}$	1.1	1.6	0.7
9.	$\text{I}^- + \text{FSO}_3\text{H} \longrightarrow \text{FSO}_3^- + \text{HI}$	2.0	1.8	1.1
10.	$\text{PO}_3^- + \text{FSO}_3\text{H} \longrightarrow \text{FSO}_3^- + \text{HPO}_3$	1.5	2.1	0.7
11.	$\text{HSO}_4^- + \text{FSO}_3\text{H} \longrightarrow \text{FSO}_3^- + \text{H}_2\text{SO}_4$	1.3	2.0	0.7
	$-15\% \longrightarrow \text{FSO}_3^- + [\text{2HNO}_3]^b$			
12.	$\text{NO}_3^-(\text{HNO}_3) + \text{FSO}_3\text{H}$	1.3	1.8	0.7
	$-85\% \longrightarrow \text{FSO}_3^-(\text{HNO}_3) + \text{HNO}_3$			
13.	$\text{FSO}_3^- + \text{FSO}_3\text{H} \longrightarrow \text{FSO}_3^-(\text{FSO}_3\text{H})$	1.3	1.9	0.7
14.	$\text{CF}_3\text{SO}_3^- + \text{FSO}_3\text{H} \longrightarrow \text{CF}_3\text{SO}_3^-(\text{FSO}_3\text{H})$	1.2	1.8	0.6
15.	$\text{I}^- + \text{H}_2\text{SO}_4 \longrightarrow \text{HSO}_4^- + \text{HI}$	1.6 ^d	1.7	0.9
16.	$\text{PO}_3^- + \text{H}_2\text{SO}_4 \longrightarrow \text{HSO}_4^- + \text{HPO}_3$	2.0 ^d	2.0	1.0
	$<-15\% \longrightarrow \text{HSO}_4^- + [\text{2HNO}_3]^b$			
17.	$\text{NO}_3^-(\text{HNO}_3) + \text{H}_2\text{SO}_4$	2.0 ^d	1.8	1.1
	$\longrightarrow 85\% \longrightarrow \text{HSO}_4^-(\text{HNO}_3) + \text{HNO}_3$			
18.	$\text{FSO}_3^- + \text{H}_2\text{SO}_4 \longrightarrow \text{FSO}_3^-(\text{H}_2\text{SO}_4)$	2.0 ^d	1.9	1.1
19.	$\text{CF}_3\text{SO}_3^- + \text{H}_2\text{SO}_4 \longrightarrow \text{CF}_3\text{SO}_3^-(\text{H}_2\text{SO}_4)$	1.3 ^d	1.7	0.7
20.	$\text{PO}_3^- + \text{HI} \longrightarrow \text{PO}_3^-(\text{HI})$	0.007 ^e	0.9	0.008

^a Calculated according to the procedure of Su and Chesnavich (ref 22) using dipole moments and polarizabilities as follows: $\mu_{\text{D}}(\text{H}_2\text{SO}_4) = 2.725$ D (ref 23); $\mu_{\text{D}}(\text{CF}_3\text{SO}_3\text{H}) \sim \mu_{\text{D}}(\text{FSO}_3\text{H}) \sim 3$ D, supported by calculations at the HF 321-G* level showing comparable values of μ_{D} for $\text{CF}_3\text{SO}_3\text{H}$, FSO_3H , and H_2SO_4 ; $\alpha(\text{H}_2\text{SO}_4) = 5.6 \text{ \AA}^3$ (ref 24), compared to a value of 5.2 \AA^3 , derived from the refractive index (ref 62); $\alpha(\text{CF}_3\text{SO}_3\text{H}) = 6.9 \text{ \AA}^3$ derived using group additivity (ref 63) and the value for $\alpha(\text{H}_2\text{SO}_4)$, as compared to the value of 7.1 \AA^3 derived from the refractive index (ref 62); $\alpha(\text{CF}_3\text{SO}_3\text{H}) = 5.0 \text{ \AA}^3$ derived using group additivity (ref 63) and the value for $\alpha(\text{H}_2\text{SO}_4)$; $\mu_{\text{D}}(\text{HI}) = 0.45$ D; $\alpha(\text{HI}) = 5.5 \text{ \AA}^3$ (ref 25). ^b Neutral products not identified. ^c When the pressure in the flow tube is decreased from 0.8 to 0.4 Torr, the branching ratio changes from 70%:30% to 75%:25%. ^d Rate constants for the reactions with H_2SO_4 (eqs 15–19) are measured as relative rate constants and are assigned absolute values assuming the rate constant quoted for eq 15 (see text). ^e Not measured in this study but taken from ref 10 where the temperature of measurement was 300 K.

Table II. Calibration Reactions for Determining Absolute Values for the Rate Constants of Reactions with the Brønsted Acids $\text{CF}_3\text{SO}_3\text{H}$, FSO_3H , and H_2SO_4 (flow tube pressure, 0.8 Torr helium; temp, 368 ± 5 K)

eq	reaction	rate constant (10^{-9} cm ³ /molecule s)		
		k_{expt}	k_{coll}^a	$k_{\text{expt}}/k_{\text{coll}}$
21	$\text{O}^- + \text{CF}_3\text{SO}_3\text{H} \longrightarrow \text{CF}_3\text{SO}_3^- + \text{OH}$	5.3 ^b	3.8	1.4
22	$\text{O}^- + \text{FSO}_3\text{H} \longrightarrow \text{FSO}_3^- + \text{OH}$	2.6 ^b	3.9	0.7
23	$\text{O}^- + \text{H}_2\text{SO}_4 \longrightarrow \text{HSO}_4^- + \text{OH}$	3.6 ^c	3.6	1.0

^a Calculated using the procedure and data given in Table I, footnote a. ^b Reference 26, pp 193–4. ^c k_{expt} is assumed to be equal to k_{coll} .

than unity ($k_{\text{expt}}/k_{\text{coll}} \leq 0.7$). The data in Table II, which we have used as a calibration test, eq 21 and eq 22, are consistent with this. In summary, the data are self-consistent but seem subject to a systematic error. One explanation could be a faulty flow measurement using the MKS 550 flowmeter, $\sim 50\%$ too large for

$\text{CF}_3\text{SO}_3\text{H}$ and $\sim 30\%$ too low for FSO_3H . Given our experience that FSO_3H stuck to the walls of the flow tube, this possibility seems plausible for FSO_3H (but fails to explain the data for eq 9). A second explanation, uncertainty in estimating k_{coll} , seems inadequate. Values of k_{coll} are insensitive to the value chosen for the polarizability, and, to account for the reaction efficiencies observed, the dipole moment of H_2SO_4 would have to be half that for $\text{CF}_3\text{SO}_3\text{H}$ and twice that for FSO_3H . It seems unlikely that the dipole moment of $\text{CF}_3\text{SO}_3\text{H}$ could exceed that for FSO_3H by a factor of 4.

In summary, the measured rate constants are self-consistent and the relative values reliable. The absolute values of the rate constants seem 50% too high for $\text{CF}_3\text{SO}_3\text{H}$ and 30% too low for FSO_3H , on the basis of the expectation that, for these systems as for others, protons are expected to transfer on every collision. Given the difficulty and uncertainty of the measurements, the absolute accuracy is certainly no better than $\pm 50\%$. The measurements support the conclusion that proton-transfer reactions, where observed, are very efficient.

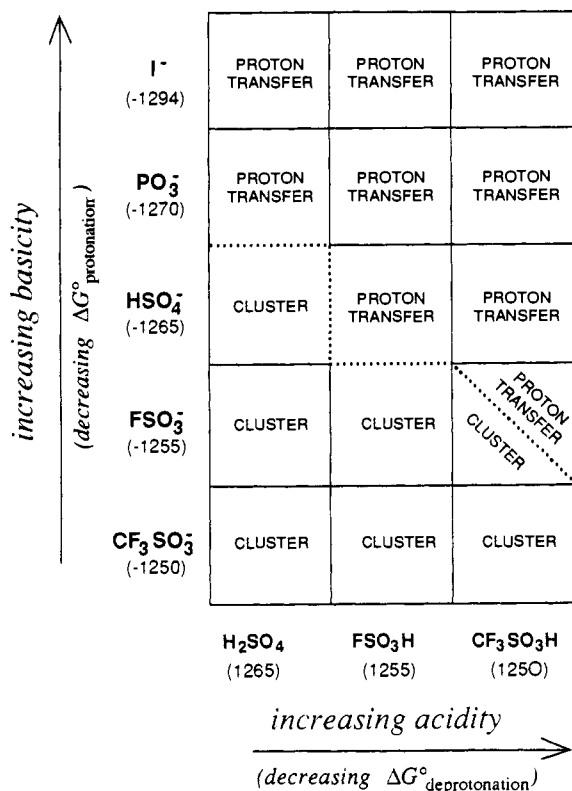
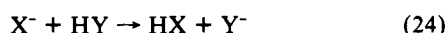


Figure 1. Reaction matrix for the reactions of the bases I^- , PO_3^- , HSO_4^- , FSO_3^- , and $CF_3SO_3^-$ with the sulfonic acids H_2SO_4 , FSO_3H , and CF_3SO_3H to indicate the reaction channels observed (Table I): proton transfer or clustering. The matrix is shown as a function of increasing basicity of the bases (decreasing free energy of protonation) and increasing acidity of the acids (decreasing free energy of deprotonation). The numbers shown are the appropriate free energies: protonation for the bases and deprotonation for the acids (Table V). (The reaction between HSO_4^- and H_2SO_4 was not studied here, but clustering is a reasonable inference⁶).

Acidity Order. Acidity and basicity orders are now derived from the kinetic data. If eq 24 proceeds with unit efficiency, HY is



a stronger Brønsted acid than HX, and X^- is a stronger Brønsted base than Y^- . The eight reactions in Table I, eqs 2–4, 9–11, 15, 16, therefore, establish the acidity order



Clustering reactions are next used to establish relative acidity and basicity orders. Where polyatomic reactants cannot react, they may cluster, usually with less than unit collision efficiency. Clustering is also rarely seen where exothermic proton transfer is possible. For the present experiments clustering can occur in two situations: (i) for the reactants $Y^- + HX$, where HY is a stronger acid than HX; and (ii) for $Y^- + HY$ where “symmetric” proton transfer is possible but not identifiable. In the absence of competing reaction, cluster ions of the sort $Y^- \cdots HX$ and $Y^- \cdots HY$ are to be expected for (i) and (ii), respectively. Applying these criteria to the clustering reactions, listed in Table I, eqs 14 and 18–20 fall in category i and eqs 7 and 13 fall in category ii. The former therefore establish the acidity order



which, with eq 25, determine the final acidity order



This acidity order is deduced from kinetic data, from observing which reactions do occur and which do not. Increasing acidity is therefore an order of decreasing free energy of deprotonation.

Table III. Estimates^a of the Enthalpies and Free Energies of Protonation of $NO_3^-(HNO_3)$ To Form Either HNO_3 or $(HNO_3)_2$

eq	reaction channel	ΔH°	ΔG°
28	$NO_3^-(HNO_3) + H^+ \rightarrow 2HNO_3$	-1250	-1250
29	$NO_3^-(HNO_3) + H^+ \rightarrow (HNO_3)_2$	-1290	-1260

^aIn kJ/mol, accurate to the nearest 10 kJ/mol.

Table IV. Percentage Product Distributions for the Reaction of $NO_3^-(HNO_3)$ with the Acid HX (HX = CF_3SO_3H , FSO_3H , H_2SO_4)

eq	reaction channel	neutral reactant HX, % increasing acidity →		
		H_2SO_4	FSO_3H	CF_3SO_3H
30	$NO_3^-(HNO_3) + HX \rightarrow X^- + 2HNO_3$	<15	15	50
31	$NO_3^-(HNO_3) + HX \rightarrow X^-(HNO_3) + HNO_3$	>85	85	50

Figure 1 summarizes the data and the conclusions in the form of a reaction matrix.

Free Energies and Enthalpies of Deprotonation. The remaining data in Table I may be used to estimate free energies and enthalpies of deprotonation. Consider the reaction of FSO_3^- (with and without solvation) with CF_3SO_3H (eqs 6 and 8). The major reaction of eq 6 is proton transfer, consistent with the acidity order assigned in eq 27, but clustering does compete. (The competition behaves as expected, clustering decreasing and proton transfer increasing as the pressure is reduced (Table I, footnote c)). This competition implies that the proton-transfer reaction is only slightly exothermic. The results for eq 8 are consistent with those for eq 6. Equation 8 may be viewed as repeating eq 6, with a FSO_3H molecule clustered initially to the reactant ion and ultimately to the product ion.²⁹

Equations 5, 12, and 17 provide further insight, using the cluster ion $NO_3^-(HNO_3)$ as a reactant. Nitric acid, for which $\Delta H^\circ_{\text{deprotonation}} = 1358$ kJ/mol,³⁰ is weaker than the acids investigated here, for which $\Delta H^\circ_{\text{deprotonation}} < 1315$ kJ/mol, as shown by eq 1. When NO_3^- is solvated by HNO_3 as $NO_3^-(HNO_3)$, it acts as a weaker base, to an extent determined by the solvation energy. Since the dissociation enthalpy of $NO_3^-(HNO_3)$ is ~ 110 kJ/mol,³¹ an effective $\Delta H^\circ_{\text{protonation}}$ of -1250 kJ/mol can be assigned to $NO_3^-(HNO_3)$ when it reacts according to eq 28 (Table III). In effect, $NO_3^-(HNO_3)$ may be considered as the conjugate base of a pseudo-superacid, for which $\Delta H^\circ_{\text{deprotonation}} = 1250$ kJ/mol.

However, another channel (eq 29 in Table III) could compete with eq 28. In eq 29 the two nitric acid molecules in the product form a dimer. Since the $O \cdots H \cdots O$ hydrogen bond energy in the water dimer is ~ 20 kJ/mol³² and since $(HNO_3)_2$ could have a ring structure bound by two hydrogen bonds, the effective $\Delta H^\circ_{\text{protonation}}$ of $NO_3^-(HNO_3)$, reacting according to eq 29, could be increased (made more negative) by ~ 40 kJ/mol to -1290 kJ/mol. Table III also lists the corresponding free energies of protonation for eq 28 and 29.³³

(29) In Table I cluster ions are represented as $X^-(HY)$ if HX is a stronger acid than HY, but as the acidities become comparable, the cluster should be represented as $X \cdots H \cdots Y^-$. Thus, in eq 8 the product ion is not $CF_3SO_3^-(F-SO_3H)$, as listed in Table I, but rather $CF_3SO_3 \cdots H \cdots O_3SF^-$. Because “symmetric” cluster ions $X \cdots H \cdots X^-$ are more strongly bound than “asymmetric” ones $X \cdots H \cdots Y^-$, eq 8 will be slightly less exothermic than eq 6 [Caldwell, G.; Rozeboom, M. D.; Kiplinger, J. P.; Bartmess, J. E. *J. Am. Chem. Soc.* 1984, 106, 4660]. The observation of (8) is consistent again with CF_3SO_3H being a slightly stronger acid than FSO_3H . The observation of clustering as a competing channel in eq 6 but not in eq 8 is consistent with a reduced energy for binding the second molecule: $D[X \cdots H \cdots Y^-] > D[X \cdots H \cdots X \cdots H \cdots Y^-]$.

(30) The value is 1358 ± 1 kJ/mol from ref 4c. Because the thermodynamic values in the following discussion are not accurately known, values are quoted to three significant figures, this value as 1360.

(31) Davidson, J. A.; Fehsenfeld, F. C.; Howard, C. J. *Int. J. Chem. Kinet.* 1977, 9, 17.

(32) See footnote 6 of: Ng, C. Y.; Trevor, D. J.; Tiedemann, P. W.; Ceyer, S. T.; Kronebusch, P. L.; Mahan, B. H.; Lee, Y. T. *J. Chem. Phys.* 1977, 67, 4235.

Table V. Free Energies and Enthalpies of Deprotonation of the Acids H, HI, HPO₃, H₂SO₄, FSO₃H, and CF₃SO₃H (kJ/mol)^a

acid	$\Delta G^\circ_{\text{deprotonation}}$	$\Delta H^\circ_{\text{deprotonation}}$
H	1311 ^b	1318 ^c
HI	1294 ± 1 ^d	1315 ^d
HPO ₃	1270 ^e	1300 ⁺¹⁵ / ₉ (1311) ^g
H ₂ SO ₄	1265 ^h	1295 ^e
FSO ₃ H	1255 ^h	1285 ^e
CF ₃ SO ₃ H	1250 ^h (1248) ⁱ	1280 ^e

^aAll data in kJ/mol. The accuracy of the present determinations is ±10 kJ/mol. Measurements were made at 368 ± 5 K. The corrections necessary to correct these values to 298 K (~2 kJ/mol) are ignored, being smaller than the uncertainty of the measurement. ^bAt 298 K (ref 36). ^cAt 298 K (ref 37). ^dAt 298 K (ref 14). ^eDerived using $\Delta H^\circ - \Delta G^\circ \approx 30$ kJ/mol (footnote 33). ^fReference 11. A thermodynamic temperature cannot strictly be assigned to this value, which comes from a drift-tube measurement in the effective temperature range 1000–3000 K. Our previous estimate was 1314⁺⁴/₋₆₄ kJ/mol (ref 10). ^gReference 38. The value given as ΔE°_0 is adjusted to a value for ΔH°_{298} . ^hPresent measurements. ⁱReference 39.

It is not possible to decide between the two channels (eq 28 and 29) by identifying the neutral product in our study. Although indirect evidence suggests that eq 29 does not compete effectively with eq 28,³⁴ a choice between eqs 28 and 29 is actually irrelevant to the assignment of free energies and enthalpies.

Data for the reactions of NO₃⁻(HNO₃) with CF₃SO₃H, FSO₃H, and H₂SO₄ (eqs 5, 12, and 17) are summarized in Table IV. Two channels are identified: proton transfer with and without solvation transfer (eqs 31 and 30, respectively).³⁵ Proton transfer is not observed for H₂SO₄, is a minor channel for FSO₃H, and is the major channel for CF₃SO₃H. This is consistent with the acidity order already assigned (eq 27). The second channel, proton and solvation transfer (eq 31), can always occur for the reactions considered here and does so. Where there is insufficient energy to drive the simple proton transfer (eq 30), the binding energy of X⁻ to HNO₃ is large enough to make up the difference and drive the proton transfer (eq 31). (A reasonable estimate of this binding energy is 100 kJ/mol⁷).

A free energy/enthalpy of deprotonation is now assigned to triflic acid. The crucial observation is that NO₃⁻(HNO₃) reacts with CF₃SO₃H at the collision limit, with both channels equally weighted. The free-energy change for the proton-transfer reaction has to be approximately zero. Because the free-energy change of protonating NO₃⁻(HNO₃) is approximately independent of the reaction products (eq 28 and 29 in Table III), the free energy of deprotonation of triflic acid is set at 1250–1260 kJ/mol. (In view of the argument already given against forming the dimer, the smaller value is given in Table V, although the difference is less than the uncertainty of our estimate). Our result is consistent with an unpublished value of 1248 kJ/mol, due to Taft and Kahfel.³⁹ The deprotonation enthalpy is derived as before.³³ The agreement within independent measurement supports our method for deriving thermodynamic quantities by the method described above.

(33) Tabulated acidity data (ref 4c) reveal a constant value $\Delta H^\circ - \Delta G^\circ \approx 30$ kJ/mol for the difference between the enthalpy and free energy of deprotonation for HA = H⁺ + A⁻, corresponding to an entropy increase of $\Delta S^\circ \approx 80$ J/(mol K). This will apply to eq 29 but not to eq 28, for which $\Delta S^\circ \approx 0$ giving $\Delta G^\circ \approx \Delta H^\circ$.

(34) Reactions such as H⁺(H₂O)₃ + M = MH⁺(H₂O) + 2H₂O may be used in bracketing experiments to estimate proton affinity differences (here M and H₂O). If (H₂O)₂ were formed rather than 2H₂O, then the thermochemistry would differ by 17 kJ/mol. To date no such results have been found that would require dimer formation.

(35) An alternative description of eq 31 (that it involves a switching reaction to form the product NO₃⁻(HX)) can be eliminated. The HX acids under discussion are stronger acids than HNO₃ by nearly 100 kJ/mol.

(36) Henchman, M. In *Fundamentals of Gas Phase Ion Chemistry*; Jennings, K. R., Ed.; Kluwer: Dordrecht, 1991; p 285.

(37) Henchman, M. In *Symposium on Atomic and Surface Physics*, '90; Märk, T. D., Howorka, F., Eds.; Studia Studienförderungsgesellschaft m.b.H: Innsbruck, 1990; pp 217–220.

(38) Lohr, L. L.; Boehm, R. C. *J. Phys. Chem.* **1987**, *91*, 3203.

(39) Taft, R. W.; Kahfel, I. Private communication.

Table VI. Systematic Trends in Bond Energies $D(\text{H}-\text{A})$ and Electron Affinities EA(A) in Determining Enthalpies of Deprotonation, $\Delta H^\circ_{\text{deprotonation}}(\text{HA})$, of the Strongest Acids (kJ/mol, 298 K)^a

acid	$\Delta H^\circ_{\text{deprotonation}}(\text{HA})^b$	$D(\text{H}-\text{A})$	EA(A)
H	1318 ^c		
HI	1315	298 ^d	301 ^d
HPO ₃	1300 (1311) ^e	(496) ^e	(504) ^e
H ₂ SO ₄	1295	435 ^f	~460 ^g
FSO ₃ H	1285	440 ^f	~470 ^g
CF ₃ SO ₃ H	1280		>470 ⁱ
HCo(PF ₃) ₄	<1280 ^j	~250 ^k	>288 ^l

^aThe quantities $\Delta H^\circ_{\text{deprotonation}}(\text{HA})$, $I(\text{H})$, $D(\text{H}-\text{A})$, and EA(A) are related by eq 32 and are all *enthalpy differences*. For H = H⁺ + e⁻, $\Delta H^\circ = I(\text{H})$, where $I(\text{H})$ is an enthalpy of ionization. For A + e⁻ = A⁻, $\Delta H^\circ = -\text{EA}(\text{A})$, the electron affinity is strictly an enthalpy decrease for electron attachment. All values in the table supersede previous values^{4d} but in general are rather similar. ^bValues are taken from Table V (±10 kJ/mol) except where specified. ^cThis table is based not on the zero-energy electron convention (ref 4c) but the thermal-energy electron convention (see refs 36 and 37). Thermodynamic values for processes which do not involve free electrons, such as $\Delta H^\circ_{\text{deprotonation}}(\text{HA})$ and $D(\text{H}-\text{A})$, are unchanged, but thermodynamic values for processes which do involve free electrons, such as $I(\text{H})$ and EA(A), are changed. Thus $I_{298}(\text{H}) = I_0(\text{H}) + 6.2$ kJ/mol and $\text{EA}_{298}(\text{A}) = \text{EA}_0(\text{A}) + 6.2$ kJ/mol. ^dReference 37. ^eValues from a theoretical study,³⁸ adjusted to 298 K. ^fReference 46 (±10 kJ/mol). ^gThe enthalpy decrease for electron attachment, calculated from eq 32, is 458 ± 15 kJ/mol, reported in the table to two significant figures as 460. The value at 0 K is 452 ± 15 kJ/mol, which is reported as an electron affinity of 4.7 ± 0.2 eV. ^hThe enthalpy decrease for electron attachment, calculated from eq 32, is 473 ± 15 kJ/mol, reported in the table to two significant figures as 470. The value at 0 K is 467 ± 15 kJ/mol, which is reported as an electron affinity of 4.8 ± 0.2 eV. ⁱReference 8. ^jReference 44. ^kReference 47. ^lDerived using eq 32.

A free energy/enthalpy of deprotonation is next assigned to fluorosulfonic acid. Several results reveal FSO₃H to be only slightly weaker than CF₃SO₃H. (i) CF₃SO₃H transfers a proton to FSO₃⁻ (70%) and also clusters to it (30%) (eq 6), so the deprotonation enthalpy of FSO₃H cannot exceed that of CF₃SO₃H by more than ~5 kJ/mol. (ii) FSO₃H clusters without transferring a proton to CF₃SO₃⁻ (eq 14). (iii) FSO₃H transfers a proton to NO₃⁻(HNO₃) with a 15% yield (eq 12), whereas CF₃SO₃H does the same with a 50% yield (eq 5). (iv) NO₃⁻(HNO₃) and CF₃SO₃⁻ are bases of comparable strength (eq 5). The free energy of deprotonation of FSO₃H is therefore assigned as 1255 kJ/mol in Table V, with a corresponding enthalpy of deprotonation derived as before.³³ The enthalpy value 1285 ± 10 kJ/mol is compatible with an independent estimate of 1310 ± 40 kJ/mol.⁴⁰

As an acid, sulfuric acid stands between FSO₃H and HPO₃, and to determine the free energy of deprotonation for H₂SO₄, we consider first HPO₃. A drift-tube measurement gives for HPO₃ $\Delta H^\circ_{\text{deprotonation}} = 1300^{+15}$ /₉ kJ/mol.¹¹ (This value agrees with a high-level theoretical study, performed before the experiment,³⁸ but because the drift-tube result is not strictly a thermodynamic measurement, the theoretical and experimental values are not strictly comparable). The corresponding free energy of deprotonation for HPO₃, $\Delta G^\circ_{\text{deprotonation}} = 1270$ kJ/mol, is derived as before.^{33,41}

Sulfuric acid is stronger than HPO₃ and weaker than FSO₃H (eq 27) ($\Delta G^\circ_{\text{deprotonation}} = 1270$ and 1255 kJ/mol, respectively). We assign a value for H₂SO₄, 1265 kJ/mol, in the middle of that range. For it to be lower, clustering would compete with proton transfer in the reaction of HSO₄⁻ with FSO₃H (eq 11), by analogy with eq 6. For it to be higher, clustering would compete with

(40) Based on $\Delta H^\circ[\text{FSO}_3^-] = -971 \pm 45$ kJ/mol (ref 4c, p 769) and $\Delta H^\circ[\text{FSO}_3\text{H}] = -180$ kJ/mol; Benson, S. W. *Chem. Rev.* **1978**, *78*, 30, Table X.

(41) A convincing test of this procedure for HPO₃ is provided by the data for HNO₃: $\Delta G^\circ_{\text{deprotonation}} = 1330$ kJ/mol and $\Delta H^\circ_{\text{deprotonation}} = 1358$ kJ/mol (ref 14).

proton transfer in the reaction of PO_3^- with H_2SO_4 (eq 16). A deprotonation enthalpy for H_2SO_4 is assigned as before.³³

Electron affinities may be derived from the data in Table V. (This is done below for HSO_4 and FSO_3 in Table VI).

Discussion

Study of acids and bases in the gas phase yields new insights for the comparable studies in solution, which are as old as chemistry itself.⁴² It is ironic that unanswered questions about acid/base solution chemistry can be resolved by corresponding studies in the gas phase. Two such questions are addressed in the present study (i) identifying which acid is the strongest acid and (ii) explaining how acidity orders can be reversed in different solvents. New information is provided in both cases.

Systematic Trends. Table V demonstrates that, of the conventional strong and superacids, triflic acid shows the lowest free energy of deprotonation and is therefore intrinsically the strongest acid. There are omissions from the table, most notably perchloric acid, which is unstable to the point of being explosive.⁴³ But we already know from the work of Stevens Miller and colleagues⁴⁴ that triflic acid is not the strongest acid; indeed, a whole family of compounds may be expected to show intrinsic acidities stronger than triflic acid. These are the hydrides of certain transition metals coordinated with ligands which withdraw electrons strongly from the transition metal; $\text{HCo}(\text{PF}_3)_4$ is an example.⁴⁴

To consider why $\text{HCo}(\text{PF}_3)_4$ is a stronger acid than H_2SO_4 , recall how the enthalpy of deprotonation of an acid HA is related to the ionization energy of the hydrogen atom, $I(\text{H})$, the electron affinity of A, $\text{EA}(\text{A})$, and the bond dissociation energy of HA, $D(\text{HA})$:⁴⁵

$$\Delta H^\circ_{\text{deprotonation}} = I(\text{H}) + D(\text{HA}) - \text{EA}(\text{A}) \quad (32)$$

Values of $\Delta H^\circ_{\text{deprotonation}}$, $D(\text{HA})$, and $\text{EA}(\text{A})$ are tabulated in Table VI for the acids under discussion. From top to bottom, there is a monotonic decrease in the enthalpy of deprotonation reflecting the increase in acidity. Is this reflected in corresponding monotonic trends in the bond energies $D(\text{HA})$ and electron affinities $\text{EA}(\text{A})$? The data in the Table VI do not support this conclusion. Thus from HI to HPO_3 , $\Delta H^\circ_{\text{deprotonation}}$ decreases by 15 kJ/mol, but both $D(\text{HA})$ and $\text{EA}(\text{A})$ increase by increments of 200 kJ/mol. The decrease in $\Delta H^\circ_{\text{deprotonation}}$ represents a subtle difference between very much larger changes.

Systematic trends are found within a chemically similar family, and the sulfonic acids $\text{X-SO}_3\text{H}$ ($\text{X} = \text{HO}, \text{F}, \text{CF}_3$) provide an example. Down this series, $\Delta H^\circ_{\text{deprotonation}}$ falls in steps of 10–15 kJ/mol, with corresponding increases in the bond energy of ~ 5 kJ/mol and in the electron affinity of perhaps 10–15 kJ/mol. The acidity increases because the electron affinity increases more markedly than the bond energy.

Now compare $\text{CF}_3\text{SO}_3\text{H}$ with $\text{HCo}(\text{PF}_3)_4$, which are chemically dissimilar. In this case, the parameters $D(\text{HA})$ (the values for $\text{CF}_3\text{SO}_3\text{H}$ and FSO_3H will be similar) and $\text{EA}(\text{A})$ jump, as they do from HI to HPO_3 . However, the effect is in the opposite direction. In the HI/ HPO_3 case, decreasing $\Delta H^\circ_{\text{deprotonation}}$ by 15 kJ/mol increases both $D(\text{HA})$ and $\text{EA}(\text{A})$ by ~ 200 kJ/mol. In contrast, for the $\text{CF}_3\text{SO}_3\text{H}/\text{HCo}(\text{PF}_3)_4$ case, $D(\text{HA})$ and $\text{EA}(\text{A})$ are decreased by ~ 200 kJ/mol.

This non-monotonic behavior is not surprising. Acidity is not simply correlated with either $D(\text{HA})$ or $\text{EA}(\text{A})$ but with their

difference. For the strong acids considered here, there does appear to be some correlation between the two of them, $D(\text{HA})$ with $\text{EA}(\text{A})$: when one is large so is the other. In short, acidity cannot be expressed as a simple function of any one atomic or molecular property.⁴⁸

Acidity Order in Solution. Frequently, the acidity order measured in the gas phase mirrors the acidity order found in solution, although important exceptions due to ion solvation have been extensively discussed.⁴⁹ These exceptions are largely due to the differences in solvation of the anionic base. Such differences are often due to size, larger anions being more poorly solvated and hence the conjugate acid being a weaker acid in solution than predicted from relative gas-phase data. Other factors influencing the anion solvation are solvent specific, e.g., hydrogen bonding effects. Triflic acid, the strongest intrinsic acid investigated here, is the strongest Brønsted acid found in certain solvents. In contrast, we predict that $\text{HCo}(\text{PF}_3)_4$, a stronger intrinsic acid than triflic, will *not* be the stronger acid in solution. Its conjugate base $\text{Co}(\text{PF}_3)_4^-$ will show a comparatively low solvation energy in dipolar, protic solvents since it acts as a poor proton acceptor. We therefore understand, for the case of $\text{HCo}(\text{PF}_3)_4$ and $\text{CF}_3\text{SO}_3\text{H}$, how the acidity order in the gas phase is reversed in solution.

Why is $\text{CF}_3\text{SO}_3\text{H}$ a weaker acid than FSO_3H in sulfuric acid solution? A naive argument provides a simple way of rationalizing the results. Protic solvents are characterized by a three-dimensional array of solvent molecules linked by an array of hydrogen bonds, which is determined in turn by the geometry of the individual solvent molecules. Dissolving any solute in the solvent will destroy the hydrogen bond array to some extent, and this will cost energy. In energetic terms, solute molecules of similar structure will be the easiest to accommodate. In actuality, the anionic chemistry can be quite complex in superacid solutions, but our simple-minded picture ignores that. Consider FSO_3^- and HOSO_3^- , the major anions formed when FSO_3H and H_2SO_4 , respectively, are dissolved. Fluorine is substituted for hydroxyl. From consideration of space filling and of hydrogen bonding, FSO_3^- and HOSO_3^- are rather similar ions. In hydrogen bonding, F can act as a proton acceptor. Thus, the substitution of F for OH may disrupt the hydrogen bond array minimally. In terms of free energy, the solvation of FSO_3^- into H_2SO_4 should be favorable.

Replacing F with CF_3 is different. The CF_3 is larger, and it is neither a proton donor nor a proton acceptor. It must break the hydrogen bond array. In terms of free energy, dissolving $\text{CF}_3\text{SO}_3\text{H}$ in H_2SO_4 solution (forming CF_3SO_3^-) would be less favorable. Solvent/solute interactions favor FSO_3^- (from FSO_3H) and are sufficient to overcome the slightly greater intrinsic acidity of $\text{CF}_3\text{SO}_3\text{H}$. Thus, there is a simple, plausible rationalization of the experimental finding that, in H_2SO_4 , FSO_3H is a stronger acid than $\text{CF}_3\text{SO}_3\text{H}$.

The argument is readily extended to the behavior observed in acetic acid solution, in which the order found is the intrinsic acidity order, so solvent/solute interactions cannot be overriding factors. In CH_3COOH , the methyl group shows no capacity for hydrogen bonding. Fitting $\text{CF}_3\text{SO}_3\text{H}$ into this solvent would not alter significantly the array of solvent hydrogen bonds. In acetic acid, solvent/solute interactions should not reverse the acidity order. Such orders are subtle; the gas-phase acidities of FSO_3H and $\text{CF}_3\text{SO}_3\text{H}$ differ by only 5 (± 10) kJ/mol, and extremely small differences in solvation enthalpies may act to reverse acidity order in solution.

Electron Affinities. The data in Table VI yield values for the electron affinities of HSO_4 and FSO_3 . Previous information has been limited to the single value $\text{EA}(\text{FSO}_3) = 4.6 \pm 0.6$ eV.⁵⁰ The

(42) See, for example: Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1968**, *90*, 6561.

(43) Evidence that HClO_4 may be a stronger acid than $\text{CF}_3\text{SO}_3\text{H}$, for which $\Delta H^\circ_{\text{deprotonation}}[\text{HClO}_4] < 1280$ kJ/mol, comes from the sequence of acids: H_3PO_4 , H_2SO_4 , HClO_4 formed from elements in the third period of the periodic table. As the acid strengths increase with increasing electronegativity along the period, so the $\Delta H^\circ_{\text{deprotonation}}$ values decrease: H_3PO_4 , 1350 kJ/mol (J. E. Bartmess, private communication); H_2SO_4 , 1295 kJ/mol (Table V), with HClO_4 unknown. The implication that HClO_4 is a stronger intrinsic acid than H_2SO_4 suggests it may also be stronger than $\text{CF}_3\text{SO}_3\text{H}$.

(44) Stevens Miller, A. E.; Kawamura, A. R.; Miller, T. M. *J. Am. Chem. Soc.* **1990**, *112*, 457.

(45) See, for example: Moylan, C. R.; Brauman, J. I. *Annu. Rev. Phys. Chem.* **1983**, *34*, 187.

(46) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23.

(47) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629.

(48) Strictly physical arguments identify positronium as the strongest intrinsic superacid ($\Delta H^\circ_{\text{deprotonation}} \sim 650$ kJ/mol).

(49) See, for example, ref 17, Chapter 4.

(50) Reference 4c, p 769.

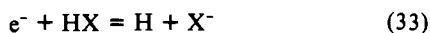
(51) Smith, D.; Adams, N. G. *J. Phys. B: At. Mol. Phys.* **1987**, *20*, 4903.

(52) Fehsenfeld, F. C. *J. Chem. Phys.* **1975**, *63*, 1686.

(53) Alajajian, S. H.; Man, K.-F.; Chutjian, A. *J. Chem. Phys.* **1991**, *94*, 3629.

procedure is indicated in footnotes *g* and *h* of Table VI. Note that the values for the "electron affinities" given in Table VI are for 300 K. The results are as follows: EA(HSO₄) = 4.7 ± 0.2 eV and EA(FSO₃) = 4.8 ± 0.2 eV. The error limit is based on the uncertainty of ±10 kJ/mol in our values for Δ*H*^o_{deprotonation} (HA) and the uncertainty of ±10 kJ/mol in the bond energies *D*(H-A).⁴⁶ These values, which lie in the range of 4.7–4.8 eV, are of interest, being among the largest yet known.

Dissociative Attachment and Associative Detachment. The data in Table V show that the dissociative attachment reaction



is exothermic for all acids stronger than H. We have indeed shown that the acids HI, H₂SO₄, FSO₃H, and CF₃SO₃H attach electrons in the temperature range 300–500 K with rate constants ranging from 10⁻⁷ to 10⁻⁸ cm³/(molecule s).⁹ This too is consistent with the present study. As we noted previously, the physical description of dissociative attachment is equivalent here to the chemical description of proton transfer. The electron acts as though the weak conjugate base of the hydrogen atom, which acts as though a strong Brønsted acid. Viewed thus, the large rate constants found for eq 33 are consistent with expectations for exothermic proton-transfer reactions. However, the rate constants show a range of values and, in certain cases, a positive temperature dependence.

We have studied the reverse of eq 33, whereby hydrogen atoms react with the bases X⁻ = PO₃⁻, HSO₄⁻, FSO₃⁻, CF₃SO₃⁻, and NO₃⁻·HNO₃. In no case was reaction detected. The results are shown in Table VII along with the previously measured dissociative attachment rate constants.⁹ These results are also consistent with the conclusions reached in Table V.

Table VII. Rate Constants for Reactions As Indicated: in the Reverse Direction, Dissociative Electron Attachment to Acids, and in the Forward Direction, Associative Detachment of Hydrogen Atoms to the Conjugate Bases of the Acids

eq	reaction	rate constant	
		forward ^a (10 ⁻¹¹ cm ³ / (molecule s)) 368 K	reverse ^b (10 ⁻⁷ cm ³ / (molecule s)) 300 K
34	NO ₃ ⁻ (HNO ₃) _{0,1} + H = (HNO ₃) _{1,2} + e ⁻	<1	<i>c</i>
35	PO ₃ ⁻ + H = HPO ₃ + e ⁻	<1	
36	FSO ₃ ⁻ + H = FSO ₃ H + e ⁻	<1	0.6
37	HSO ₄ ⁻ + H = H ₂ SO ₄ + e ⁻	<1	≥0.5 ^d
38	CF ₃ SO ₃ ⁻ + H = CF ₃ SO ₃ H + e ⁻	<1	1.0 ^e

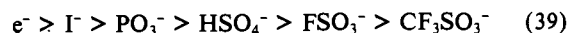
^aNo reaction was observed. The experimental procedure (ref 51) used a dilute mixture of H₂ in He passed through a microwave discharge into the flow tube. Hydrogen atom concentrations in the flow tube were determined from the decay of O₂⁻ as a function of hydrogen flow through the discharge, using the rate constant previously measured for the reaction O₂⁻ + H = O₂H + e⁻ (ref 52). The hydrogen atom concentration was measured before and after each rate determination to ensure the absence of drift. The rate constants are estimated to be accurate to within a factor of 2. ^bTaken from ref 9. ^cFor the reaction e⁻ + HNO₃ = NO₂⁻ + OH, *k* = 0.5 × 10⁻⁷ cm³/(molecule s) is determined. ^d510 K. ^eThreshold electron attachment data are consistent with a large rate constant (ref 53).

Table VIII. Comparison of the Basicities (Enthalpies of Protonation) of the Bases e⁻, I⁻, PO₃⁻, HSO₄⁻, FSO₃⁻, and CF₃SO₃⁻ with Their Nucleophilic Power Measured in Solution

base	Δ <i>H</i> ^o _{protonation} (kJ/mol) ^a	nucleophilic power (in sulfolane at 308 K) ^b
e ⁻	-1318	
I ⁻	-1315	+1.3
PO ₃ ⁻	-1300	
HSO ₄ ⁻	-1295	
FSO ₃ ⁻	-1285	-4.1
CF ₃ SO ₃ ⁻	-1280	-4.2

^aValues from Table V. ^bReference 54.

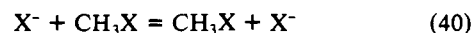
Basicity and Nucleophilicity. While the discussion so far has focused on the acidity order and its applications (Tables V and VI), the same results may be presented as the intrinsic basicity order for the conjugate Brønsted bases



for which the appropriate quantitative measure is the enthalpy of protonation (Table VIII). This parameter expresses quantitatively the strength of these very weak bases. For example, this provides hard data to inform the continuing 40-year-old debate as to the reactive intermediacy of PO₃⁻ in phosphate ester hydrolysis and phosphorylation.^{55,56} Table VIII shows PO₃⁻ to be one of the least reactive bases to have been characterized thermodynamically.

Important properties of these bases include nucleophilicity and leaving-group ability. Debate continues as to how these properties may be measured quantitatively and hence related to the basicity.¹⁶ Yet qualitative correlations are obvious. For example, the triflate moiety is the great facilitator in organic synthesis, the leaving group *par excellence*,⁵⁷ and our identification of triflic as a very strong acid and of triflate as a very weak base is consistent with triflate's behavior as a leaving group. Some limited quantitative comparison is possible. Through a particularly felicitous choice of systems, combined with critical analysis, Lewis et al. have been able to derive quantitative measures of the "nucleophilic power" of several nucleophiles.⁵⁴ Where available, these are listed for comparison in Table VIII. Triflate has the lowest nucleophilic power which has been measured in solution, and this correlates with our finding that it has the lowest basicity in the gas phase. Of greater significance, fluorosulfonate has only a slightly greater nucleophilic power than triflate in solution; this correlates with our finding in the gas phase that fluorosulfonate is only a slightly stronger base than triflate. The comparison in Table VIII is between gas-phase basicity and nucleophilic power in solution. For the solution studies, Lewis⁵⁴ used sulfolane as the solvent, and this might be expected to mirror the results in the gas phase. Sulfolane is a dipolar, aprotic solvent, with a high dielectric constant and without capacity for forming hydrogen bonds.¹⁷ Sulfolane differs from sulfuric acid as a solvent. As already explained, sulfuric acid solvent can reverse an intrinsic acidity order; by the same criteria, sulfolane should not.

Another comparison is possible. Using numerical basicity values measured for bases, Brauman has derived a quantitative measure of nucleophilic character.^{58,59} Use is first made of an empirical correlation found between enthalpies of protonation and methyl cation affinities.⁶⁰ (Quantitatively, this is uncertain for the bases in Table VIII because the values lie outside the range for which the correlation has been established). This transforms basicities of -1315 to -1280 kJ/mol (I⁻ to CF₃SO₃⁻ in Table VIII) to methyl cation affinities in the approximate range -820 to -850 kJ/mol. Second, the methyl cation affinity is transformed through another empirical correlation to an "intrinsic nucleophilicity", which is the height of the central energy barrier for the "identity" reaction



The interesting result which is obtained for the bases in Table VIII is that the bases are so weak that *there is no central energy barrier for the identity reaction* (eq 40). Thus, for example, our results suggest that triflate makes no contribution to the energy barrier for a displacement reaction. This is the "kinetic" aspect of triflate's ability as a leaving group.⁵⁸

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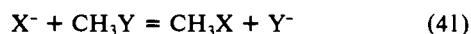
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(58) Pellerite, M. J.; Brauman, J. I. *ACS Symp. Ser.* **1982**, *No. 198*, 81.

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(60) Brauman, J. I.; Han, C.-C. *J. Am. Chem. Soc.* **1988**, *110*, 5611; **1989**, *111*, 3485.

In the Marcus analysis that Brauman^{58,59} has applied to eq 41,



an "intrinsic barrier" is first computed, this being the barrier which eq 41 would have if it were thermoneutral. The "intrinsic barrier" is taken as the mean of the barriers for the two identity reactions, $X^- + CH_3X \rightarrow CH_3X + X^-$ and $Y^- + CH_3Y \rightarrow CH_3Y + Y^-$. The "intrinsic barrier", which would be appropriate if eq 41 had zero exothermicity, is then scaled according to the true exothermicity, and interpreted as the "thermodynamic" contribution to the final barrier.⁵⁸

This analysis may be applied to triflate as a leaving group in eq 42. The "intrinsic barrier" will consist of half the barrier for



eq 40 with no "kinetic" contribution from triflate. Because the exothermicity of eq 42 will, in general, be large, the thermodynamic scaling will reduce the barrier for eq 42 and will further facilitate the displacement.⁶¹ This is the "thermodynamic" aspect of triflate's ability as a leaving group. With respect to both "kinetic" and "thermodynamic" components, the present results on superacids can provide some quantitative basis for extreme leaving-group ability.

If the Marcus-type analysis of the barriers to these reactions has a general validity, the present analysis yields an unexpected prediction. For the identity reaction eq 40, the height of the central barrier for the methyl transfer and inversion decreases as the strength of the base X^- decreases. For the three extreme cases here, XSO_3^- ($X = HO, F, CF_3$), the three "identity" displacement reactions



are predicted to undergo Walden inversion via a pathway that shows no energy barrier.

Conclusions

(1) Bracketing techniques (identifying which reactions are facile and which are not) have been used to derive free energies and enthalpies of deprotonation for the acids HPO_3 , H_2SO_4 , FSO_3H , and CF_3SO_3H . At this extreme end of the acidity scale, there

(61) The exothermicity is $MCA(X^-) - MCA(CF_3SO_3^-)$ where MCA is the methyl cation affinity. Because the basicity (enthalpy of protonation) of triflate is so low, its methyl cation affinity will be low and, in general, the exothermicity of eq 36 will be large.

(62) Aldrich 1990-1991 Catalog/Handbook, Aldrich Chemical Co., Milwaukee, WI.

(63) Miller, K. J.; Savchik, J. A. *J. Am. Chem. Soc.* 1979, 101, 7206.

are, as yet, few acids and no "markers" with established acidities. To calibrate the scale, we have used cluster ions such as NO_3^- , HNO_3 which behave like the conjugate base of a *pseudo*-superacid. Where competition between proton transfer and clustering has been observed, limits have been set on the free energy change for the proton-transfer reaction. In this way, qualitative kinetic data have been used to derive quantitative thermodynamic data of limited accuracy. This same approach would seem applicable to future efforts to extend the acidity scale.

(2) This study extends the acidity scale from its previous limit of 1294 kJ/mol for HI to a new limit of 1250 kJ/mol for CF_3SO_3H . (These numbers are free energies of deprotonation).

(3) In two cases, the derived enthalpies of deprotonation have been used to estimate the electron affinities where no previous values have been available, i.e., $EA(HSO_4) = 4.7 \pm 0.2$ eV and $EA(FSO_3) = 4.8 \pm 0.2$ eV, which are among the largest yet known.

(4) The acidities of the strong and superacids derived here are surprisingly close, the three sulfonic acids lying within a range of 15 kJ/mol. This may imply that, as far as the conventional superacids are concerned, the end of the scale has essentially been reached. In contrast, no quantitative information is available yet on the acidities of the transition metal hydrides.

(5) The gas-phase studies offer insight into acidity orders observed in solution. The confusing situation with respect to FSO_3H and CF_3SO_3H in solution is seen to be the consequence of the two having very similar intrinsic acidities. Using very simple arguments, it is possible to predict which solvents will reverse the intrinsic acidity order and which will not.

(6) The extreme leaving group ability of triflate reflects the extreme acidity of triflic acid. The intrinsic acidity order, reported here, necessarily establishes an intrinsic basicity order for the conjugate bases and, from this, an intrinsic order of nucleophilicity and leaving-group ability. A correlation is found with the few measurements available of "nucleophilic power" in solution.

(7) All the acids investigated here undergo dissociative electron attachment with large rate constants ($\sim 10^{-7}$ cm³/(molecule s)). In chemical terms, the reactions may be considered formally as proton-transfer reactions. The thermodynamic results establish the exothermicities of these reactions and a lack of correlation between the rate constant and the exothermicity.

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