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Revision of the Gas-Phase Acidity Scale below 300 kcal mol^{-1}

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The gas-phase acidity (GA) scale from $(CF_3CO)_2NH$ to $(C_2F_5SO_2)_2NH$—about a 24 kcal mol^{-1} range of gas-phase acidities—was reexamined using the Fourier transform ion cyclotron resonance equilibrium measurement approach. Some additions and modifications to the standard methodology of GA measurements were introduced (estimation of partial pressures from mass spectra of the compounds, instead of the pressure gauge readings and use of long reaction times) to achieve higher reliability. Gas-phase acidities of 18 compounds were determined for the first time. The results reveal a contraction of the previously published values in this part of the scale. In particular, the GA values of $(CF_3SO_2)_2NH$ and $(C_2F_5SO_2)_2NH$ (important components of lithium ion battery electrolytes and ionic liquids) were revised toward stronger acidities from 291.8 kcal mol^{-1} to 286.5 kcal mol^{-1} and from 289.4 kcal mol^{-1} to 283.7 kcal mol^{-1} (i.e., by 5.3 and 5.7 kcal mol^{-1}), respectively. Experimental and computational evidence is presented in support of the current results.

Introduction

The gas-phase acidity (GA) of an acid HA is the Gibbs' free energy change on deprotonation of the acid according to the following equilibrium:

$$HA \overset{GA}{\rightleftharpoons} A^- + H^+ \qquad (1)$$

The currently available GA values of strong acids (GA values below ca. 310 kcal mol^{-1}) mainly originate from the large-scale study published by Koppel et al.[1] Those data have found intensive use during more than a decade in a variety of fields. An important use has been as a reference experimental data set for comparison with computational methods.[1−4] It has often been customary to apply linear scaling equations to the computational values to improve agreement with experimental data.[2−5] Different scaling equations are often necessary, depending on the compound classes and computational levels.[2−5] As the computational methodologies and hardware constantly advance, increasingly sophisticated methods with accuracies estimated as approaching experimental uncertainties can be applied for the calculation of structure and properties (including GA) of small- to medium-sized molecules.

Recently, a computational effort to verify the GA values of a set of strong acids obtained by the G3(MP2) method was undertaken.[6] It was observed that in the range of weak to medium strong acids (303 kcal mol^{-1} ≤ GA ≤ 342 kcal mol^{-1}) most of the calculated G3(MP2) GA values agreed with the experiment within 1.5 kcal mol^{-1}. In the GA range below 303 kcal mol^{-1}, five out of six G3(MP2) GA values were found to be more than 5 kcal mol^{-1} lower than the experimental values. This was interpreted by the authors as a possible problem with the experimental values.[6] These acids include two sulfonic acids (FSO_3H and CF_3SO_3H), three CH acids ($(CF_3SO_2)_3CH$, $(CF_3SO_2)_2CH_2$, and $(CF_3CO)_3CH$), and an NH acid ($(CF_3SO_2)_2NH$). Similar findings have been described also by other authors using G2[3] and G2(MP2)[3] as well as G3[7] computations.

The experimental GA values of FSO_3H and CF_3SO_3H are based on independent measurements using the Fourier transform ion cyclotron resonance (FT-ICR)[1] and high-pressure ion flow tube (SIFT) techniques,[8] and their verification would be a task for an independent study. At the same time, the CH and NH acids were measured in only one literature source, and examination of the GA ladder presented in ref 1 reveals that two regions—between $(CF_3SO_2)_2CH_2$ (GA = 301.5 kcal mol^{-1})[1] and $CF_3CONHSO_2CF_3$ (GA = 298.2 kcal mol^{-1})[1,9] as well as between $C_3F_7CONHSO_2CF_3$ (GA = 294.3 kcal mol^{-1})[1] and $(CF_3SO_2)_2NH$ (GA = 291.8)[1]—are bridged by only two sets of independent measurements of rather large ΔGA values (above 2 kcal mol^{-1}).

In this paper we report an experimental and computational reexamination of the lower part of the GA scale starting from a convenient and much-used reference acid $(CF_3CO)_2NH$ with the experimental GA value 307.5 kcal mol^{-1}. The strongest acid included in this study is $(C_2F_5SO_2)_2NH$.

Compounds. For building the ladder, we used some of the acids used previously,[1] but also some new compounds were introduced (see Scheme 1). In particular, an extensive set of substituted aromatic sulfonimides (compounds **5**, **7**, **11**, and **15−25**) was synthesized, and they proved to be key compounds for this work. Aromatic sulfonimides have been used earlier to set up the acidity scale of strong acids in acetonitrile (AN).[12] They are easily obtainable, and their acidity can be varied in small steps over a wide acidity range using different substituents,

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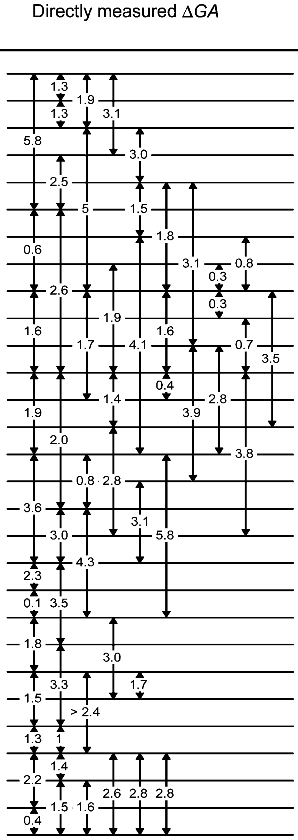
SCHEME 1: Experimental GA Ladder Together with Computational Data and AN pK_a Values[a–i]



No	Acid	*GA* exp	*GA*[b] calc	*PA* calc	pK_a Acetonitrile
1	$(CF_3CO)_2NH$	307.5	(303.4), 308.4, 308.5[c]	(311.2), 316.2	
2	$(CF_3CO)_2CHF$	306.6	(300.6), 308.2	(308.2), 315.5	
3	$(C_3F_7CO)_2CH_2$	305.6	(304.5)	(311.9)	
4	$(2\text{-}C_{10}F_7)_2CHCN$	304.2	(298.7)	(306.1)	
5	$(4\text{-}Cl\text{-}C_6H_4\text{-}SO_2)_2NH$	302.6	(304.2)	(311.6)	10.20[d]
6	$C_6(CN)_5CH_3$	301.6	(300.4), 304.7	(308.5), 311.2	20.14[e]
7	$Tos\text{-}NH\text{-}SO_2\text{-}C_6H_4\text{-}4\text{-}NO_2$[f]	301.2	(304.7)	(310.5)	10.04[d]
8	$C_6(CF_3)_5SH$	300.9	(288.2)	(294.7)	10.10
9	$(CF_3SO_2)_2CH_2$	300.6	(297.9), 297.9, 297.4[c]	(305.6), 305.3	
10	$C_6H_5\text{-}CH(Tf)_2$[g]	300.0	(300.3), 297.4	(307.7), 305.0	7.85[d]
11	$Tos\text{-}NH\text{-}SO_2\text{-}C_6H_3\text{-}4\text{-}Cl\text{-}3\text{-}NO_2$	299.8	(301.9)	(308.3)	9.71
12	$C_6(CF_3)_5OH$	299.0	(290.2)[h]	(297.8)	10.46[h]
13	$4\text{-}CH_3\text{-}C_6H_4\text{-}S(=NTf)_2NH_2$	298.8	(297.9)	(306.9)	
14	$2,4,6\text{-}Tf_3\text{-}C_6H_2\text{-}NHOH$	297.5	(298.3)	(305.5)	
15	$4\text{-}Cl\text{-}C_6H_4\text{-}SO_2\text{-}NH\text{-}SO_2\text{-}C_6H_4\text{-}4\text{-}NO_2$	297.0	(298.2)	(305.3)	9.17[e]
16	$4\text{-}Cl\text{-}C_6H_4\text{-}SO_2\text{-}NH\text{-}SO_2\text{-}C_6H_3\text{-}4\text{-}Cl\text{-}3\text{-}NO_2$	296.1	(297.8)	(304.5)	8.80
17	$C_6F_5\text{-}SO_2\text{-}NH\text{-}SO_2\text{-}C_6H_4\text{-}4\text{-}Cl$	296.0	(297.2)	(304.5)	7.57
18	$4\text{-}Cl\text{-}C_6H_4\text{-}SO_2\text{-}NH\text{-}Tf$	294.8	(296.1)	(303.4)	5.33[e]
19	$(3\text{-}NO_2\text{-}C_6H_4\text{-}SO_2)_2NH$	293.3	(293.8)	(301.2)	8.15
20	$3\text{-}NO_2\text{-}C_6H_4\text{-}SO_2\text{-}NH\text{-}SO_2\text{-}C_6H_3\text{-}4\text{-}Cl\text{-}3\text{-}NO_2$	291.1	(289.5)	(297.2)	7.88
21	$(4\text{-}NO_2\text{-}C_6H_4\text{-}SO_2)_2NH$	291.1	(290.9)	(298.7)	8.19[e]
22	$C_6F_5\text{-}SO_2\text{-}NH\text{-}SO_2\text{-}C_6H_4\text{-}3\text{-}NO_2$	290.3	(292.7)	(298.5)	6.73
23	$C_6F_5\text{-}SO_2\text{-}NH\text{-}SO_2\text{-}C_6H_4\text{-}4\text{-}NO_2$	289.2	(291.4)	(299.0)	6.60
24	$C_6F_5\text{-}SO_2\text{-}NH\text{-}SO_2\text{-}C_6H_3\text{-}4\text{-}Cl\text{-}3\text{-}NO_2$	287.8	(290.8)	(298.2)	6.20
25	$(C_6F_5SO_2)_2NH$	287.5	(289.4)	(296.5)	5.40
26	Tf_2NH	286.5	(286.4), 285.9, 283.3[i]	(294.0), 294.1	
27	$Tf\text{-}NH\text{-}SO_2C_2F_5$	285.2	(283.9), 285.3	(291.1), 293.1	
28	$CF_2(CF_2SO_2)_2NH$	284.2	(284.1), 283.3	(291.3), 290.5	
29	$(C_2F_5SO_2)_2NH$	283.7	(284.3), 284.2	(291.1), 291.0	

[a] All data from this work, unless indicated otherwise. See the Supporting Information for computational methods. [b] Without parentheses: G3(MP2). In parentheses: DFT B3LYP 6-311+G**. [c] Ref 6. [d] Ref 12. [e] Ref 13. [f] Tos denotes the $4\text{-}CH_3{-}C_6H_4{-}SO_2{-}$ group. [g] Tf denotes the $CF_3SO_2{-}$ group. [h] Ref 5. [i] Ref 14, DFT B3LYP 6-31+G*.

making this family very suitable for compiling acidity scales. The additivity of substituent effects in this compound family helps to spot possibly erroneous measurements.

The origin of all used compounds is presented in the Supporting Information.

GA Measurements. A pulsed FT-ICR mass spectrometer of Kyushu University with a 3 T superconducting magnet was used. The basic principle of the measurement method was the same as reported previously.[1,10,11] It consisted of leaking two gaseous acids into the ICR high-vacuum section (cell region), generating their anions by the impact of low-energy electrons, and letting the formed anions react with the neutrals in the gas phase until equilibrium is reached. The directly measured quantities are the equilibrium constant (K) values of the proton transfer reaction between two acids, A_1H and A_2H:

$$A_1H + A_2^- \overset{K}{\rightleftarrows} A_1^- + A_2H \tag{2}$$

$$K = \frac{I(A_1^-)\,p(A_2H)}{I(A_2^-)\,p(A_1H)} \qquad \Delta GA = -RT \ln K$$

where A_1^- and A_2^- are the anions of the acids. The partial pressures of the compounds were in the range of $(n \times 10^{-8})$–$(n \times 10^{-7})$ Torr.

However, a number of technical modifications were introduced to the earlier method to increase the reliability of the results:

1. Very long reaction times, up to 300 s, were used, when necessary. To ensure reaching the equilibrium, the actual maximum reaction time used for every equilibrium measurement was significantly longer than the time required to reach equilibrium (see Table S1 in the Supporting Information for details of the measurements).

2. The direct insertion probe was used for introducing compounds of low volatility. The probe allows the compound mounted into a small glass tube on the tip of the probe to be inserted (via a vacuum lock) into the immediate vicinity of the ICR cell and heated. This way, compounds of very low volatility can be introduced to obtain sufficient vapor pressure. A number of compounds used in this study (including all aromatic sulfonimides) can only be introduced via this approach. In some cases one of the reacting compounds was introduced from the oven and the other one from the probe, but in many cases (notably all measurements between aromatic sulfonimides) both of the compounds had to be introduced from the probe.

3. Besides the readings of the pressure gauge, mass spectra were also used to estimate the partial pressures of the compounds. Two approaches were used: (1) the ratio of the partial pressures is approximated by the ratio of overall ion intensities in the positive ion mass spectra (recorded with negligible reaction time) corrected by the ionization cross sections, and (2) the ratio of the partial pressures of the neutrals in the gas phase is approximated by the ratio of the signals of the anions in the negative ion spectra extrapolated to zero reaction time. The former approach was used in all cases when two aromatic sulfonimides were introduced simultaneously from the direct

insertion probe. The validity of the obtained pressure ratios was assessed from the consistency of the ΔGA measurements (see below).

Detailed description of the GA measurement method and the modifications are presented in the Supporting Information.

Results and Discussion

Revision of the GA Ladder. The obtained GA ladder and experimental and computational GA values together with pK_a values in AN for aromatic sulfonimides are presented in Scheme 1. The ladder has been anchored to the GA value of 307.5 kcal mol^{-1} of $(CF_3CO)_2NH$.[1] Detailed information on GA and pK_a measurements is given in the Supporting Information.

The whole range of gas-phase acidities from $(CF_3CO)_2NH$ to $(C_2F_5SO_2)_2NH$ can be covered by three independent "pathways" of ΔGA measurements. The relative acidity of any two acids can be obtained by at least two independent sets of ΔGA measurements. This is very important because uncertainty sources in GA measurements are often compound-specific. This also allows the assessment of the consistency of the results obtained with the different methods of estimating the partial pressure ratios of the compounds. Except for $(CF_3SO_2)_2NH$, any compound can be removed from the ladder without destroying the continuity of the ladder. The consistency standard deviation (see ref 12) is 0.3 kcal mol^{-1}. An indirect piece of evidence for the quality of these results is the observation of excellent additivity of the substituent effects observed in the aromatic sulfonimide family (see below).

There are five compounds that are common for this paper and ref 1: $(CF_3CO)_2NH$, $(CF_3SO_2)_2CH_2$, $(CF_3SO_2)_2CHC_6H_5$, $(CF_3SO_2)_2NH$, and $(C_2F_5SO_2)_2NH$. Their GA values in ref 1 are 307.5, 301.5, 301.3, 291.8, and 289.4 kcal mol^{-1}, respectively. The differences from the results of this study are 0.0 (anchor point of the scale), 0.9, 1.3, 5.3, and 5.7 kcal mol^{-1}, respectively.

We see the following possible reasons for the contraction of the lower part of the GA scale in ref 1. They probably operate in combination.

(1) The suboptimally bridged regions exist (see above).

(2) In ref 1, the partial pressures of the acids, including those of high polarity and low volatility, were estimated from the pressure gauge readings. The dangers of this are detailed in the Supporting Information.

(3) The FT-ICR machine used in this work is able to maintain ions in the cell for significantly longer reaction times (up to several hundred seconds) than that used in ref 1 (up to 10 s). We observed that with very few exceptions use of too short reaction times leads to a *smaller* (by absolute value) apparent acidity difference between the two measured acids than that corresponding to the true equilibrium situation. This effect is especially severe in the case of acidity differences above 2 kcal mol^{-1} and can lead to underestimating the acidity differences by 0.5−1.5 kcal mol^{-1}.

The experimental GA values presented here are supported by the computational data from this work and from ref 6 (see Scheme 1). The agreement between the data from experiments and both used computation levels is very good, except for $C_6(CF_3)_5OH$ and $C_6(CF_3)_5SH$. However, the $(CF_3)_5$-compounds have a very specific molecular structure,[5] and this deviation needs further examination.

On the basis of these considerations, we recommend that for the compounds $(CF_3SO_2)_2CH_2$, $(CF_3SO_2)_2CHC_6H_5$, $(CF_3SO_2)_2NH$, and $(C_2F_5SO_2)_2NH$ the experimental GA values reported in this paper should be used. Also our results suggest that the GA values of acids stronger than $(C_2F_5SO_2)_2NH$ need to be revised in the future because all of the acids that are more acidic than $(CF_3SO_2)_2NH$ are in ref 1 anchored to $(CF_3SO_2)_2NH$.

TABLE 1: Results of the Substituent Effect Analysis in the Gas Phase and in AN

X	ΔGA (X)	ΔpK_a (X)
$4\text{-}CH_3{-}C_6H_4{-}$	0.00	0.00
$4\text{-}Cl{-}C_6H_4{-}$	−4.02	−0.90
$3\text{-}NO_2{-}C_6H_4{-}$	−8.89	−1.88
$4\text{-}NO_2{-}C_6H_4{-}$	−10.01	−1.90
$4\text{-}Cl{-}3\text{-}NO_2{-}C_6H_3{-}$	−11.22	−2.25
$C_6F_5{-}$	−11.78	−3.46
$CF_3{-}$	−12.28	
$C_2F_5{-}$	−13.67	
intercept	311.09	11.97

Additivity of Substituent Effects in the Sulfonimide Family. The acidity data of the aromatic (and some aliphatic) sulfonimides $X_1{-}SO_2{-}NH{-}SO_2{-}X_2$ in the gas phase and in AN were treated using the following correlation equations:

$$\mathrm{GA} = \mathrm{GA}^0 + \Delta\mathrm{GA}(\mathrm{X}_1) + \Delta\mathrm{GA}(\mathrm{X}_2) \qquad (3)$$

$$\mathrm{p}K_\mathrm{a} = \mathrm{p}K_\mathrm{a}^0 + \Delta\mathrm{p}K_\mathrm{a}(\mathrm{X}_1) + \Delta\mathrm{p}K_\mathrm{a}(\mathrm{X}_2) \qquad (4)$$

The ΔGA and ΔpK_a values are the respective additive increments of the substituents. The increment of $4\text{-}CH_3{-}C_6H_4{-}$ is taken as zero. GA^0 and p$K_a{}^0$ are intercepts of the correlation, corresponding to the predicted acidities of $(4\text{-}CH_3{-}C_6H_4{-}SO_2)_2NH$. Table 1 presents the results. The additivity is excellent: the standard deviation of the analysis is 0.3 kcal mol^{-1} (16 GA values) in the gas phase and 0.05 pK_a units in AN (15 pK_a values). In the gas phase there are no outliers. Similar good additivity has been found earlier in different, other aromatic systems.[15] In AN $(C_6F_5SO_2)_2NH$ was handled as an outlier: its predicted pK_a value is 5.04 compared to the experimentally obtained value 5.40. We interpret the latter result as evidence of a contraction of the lower end of the AN acidity scale (see also ref 13), and this needs further experimental examination. Leaving $(C_6F_5SO_2)_2NH$ in the correlation leads to standard deviation 0.09 pK_a units, which is still good.

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Supporting Information Available: Details of the measurement and calculation methods. The origin of the compounds. Computational Cartesian coordinates of the acids and anions. This material is available free of charge via the Internet at http://pubs.acs.org.

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