Validation of Gas-Phase Acidity Measurements of Superacids

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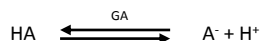
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INTRODUCTION

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

$$HA \xrightarrow{\text{GA}} A^- + H^+$$

GA values are independent of solvent effects and represent the intrinsic acidity of the compound. Superacids (acids more acidic than sulphuric acid) and their anions are used e.g. as reactants and catalysts in organic synthesis and industrial processes,[1] energy storing devices and ionic liquids.[2]

It is increasingly evident that the reported experimental GA values of several superacids differ significantly from the corresponding computational values.[3] There is thus a necessity to validate or revise the previously reported GA values.

EXPERIMENTAL METHODS

An FT-ICR mass spectrometer with a 7T superconducting magnet was used. The basic principle of the measurement method is described in detail by Leito et al.[3] Two gaseous acids were leaked into the ICR cell region and their anions were generated by low energy electron impact. The formed ions were trapped in the ICR cell, allowed to react with the neutrals in the gas-phase ("reaction time") and then detected. Partial pressures of the compounds (estimated from mass spectra), denoted below as $p(A_1H)$ and $p(A_2H)$, as well as the equilibrium-state intensities of the anions, $I(A_1^-)$ and $I(A_2^-)$, were used to calculate the equilibrium constant value (K) and ΔGA of the proton transfer reaction between acids A_1H and A_2H, using the following equations:
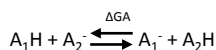
$$A_1H + A_2^- \xrightarrow{\Delta GA} A_1^- + A_2H \qquad K = \frac{I(A_1^-)p(A_2H)}{I(A_2^-)p(A_1H)}$$

$$\Delta GA = -RT \ln K$$

We introduced some changes to the previous method:[3]

1. **Negative ion mass spectra were used to estimate $p(A_1H)/p(A_2H)$**. The reading of the pressure gauge, the most common way of estimating partial pressures used in the studies previously published, provided inconsistent results. We approximated $p(A_1H)/p(A_2H)$ by extrapolating the ratios of conjugate bases of the acids to zero reaction time, this approach gave consistent results.

2. **Data acquisition was performed also in "double resonance mode".** All the ions except the conjugate base of one the acids were removed from the ICR cell shortly after the ionization. Equilibrium constant value must be similar to one measured without the removal of ions to ensure that true equilibrium state was indeed reached.

3. **The GA ladder is anchored to theoretical GA values.** Previously, the experimental GA value of HBr (317.3 kcal mol⁻¹) has been used as a reference for anchoring the scale. Although very reliable, it is approximately 40 kcal mol⁻¹ higher than the GA of the strongest acids in this work. Such range involves a lot of ΔGA measurements, leading to a serious extrapolation and decrease in reliability of the results. We have anchored the results to the computational values of acids **4** and **15** (Scheme 1), calculated using the W1BD method. Based on evaluation, this method provides results with standard uncertainty of roughly 1 kcal⁻¹.

RESULTS

Fig. 1: Self-consistent gas-phase acidity scale compiled in this work with previously reported GA values (GA lit.). Each arrow denotes one ΔGA measurement series.

	Acid	ΔGA	GA exp.	GA lit.
1	(CF₃SO₂)₂CH₂		295.3	300.6[d]
2	3-NO₂-4Cl-C₆H₃SO₂NH-Tos[c]		295.2	
3	4-Cl-C₆H₄SO₂NHSO₂C₆H₄-4-NO₂		292.7	297.0[d]
4	**CF₃SO₃H[b]**		292.2	299.5[e]
5	C₆F₅SO₂NHSO₂C₆H₄-4-Cl		291.5	296.0[d]
6	3,5-(NO₂)₂-C₆H₃SO₂NH-Tos[c]		290.7	
7	(C₃F₇SO₂)₂CH₂		290.5	
8	(C₄F₉SO₂)₂CH₂		289.5	282.8[h]
9	(3-NO₂-C₆H₄SO₂)₂NH		289.4	293.3[d]
10	2,4-(NO₂)₂-C₆H₃SO₃H		289.2	
11	(C₈F₁₇SO₂)₂CH₂		288.0	
12	3-NO₂-C₆H₄SO₂NHSO₂C₆H₃-4-NO₂-3-Cl		287.5	291.1[d]
13	C₆F₅SO₂NHSO₂C₆H₄-4-NO₂		286.5	289.2[d]
14	C₆F₅SO₂NHSO₂C₆H₃-3-NO₂-4-Cl		285.4	287.8[d]
15	**(FSO₂)₂NH[b]**		285.3	283.1[f]
16	(C₆F₅SO₂)₂NH		285.3	287.5[d]
17	(CF₃SO₂)₂NH		282.9	286.5[d]
18	(C₂F₅SO₂)₂NH		280.0	283.9[f]
19	(C₃F₇SO₂)₂NH		278.8	281.1[f]
20	(C₄F₉SO₂)₂NH		278.0	278.7[f]
21	C₄F₉SO₂NHSO₂C₈F₁₇		277.1	

[a] All values at 373K and in kcal mol⁻¹. [b] Results have been anchored to the computational *GA* values of acids **4** and **15** (W1BD, 291.3 and 286.2 kcal mol⁻¹, respectively). [c] Tos denotes the 4-CH₃-C₆H₄SO₂- group. [d] Ref [3]. [e] Ref [4]. [f] Ref [5].

VALIDATION

The obtained values are presented on Fig 1. As we can see, there are disagreements with the previous results. The potential reasons for these discrepancies, as well as the improvements, are explained above.

Validation is rather inherent when it comes to the relative measurement methods as it is necessary to have as many independent pathways between different parts of the scale as possible in order to ensure the quality of the results. To represent this, we have chosen the section of the scale which spans from acid **4** to acid **9** because:

- it involves compounds rather different in terms of size,
- it includes –NH, –OH and –CH acid(s),
- all of the introduction methods are involved.

Due to all of these factors, this part of the scale is the most scrutinized by us. There are 4 independent pathways on Fig. 1 which connect acids **4** and **9**, the (combined) ΔGA values (in kcal mol⁻¹) of those are as following: 2.4; 3.0; 3.3 and 2.6. For comparison, acids **17-21** are all rather similar in terms of most of the considerations described above and all three independent pathways spanning this part of the scale yield a ΔGA value of 5.8 kcal mol⁻¹. The consistency standard deviation[3] for the whole GA scale is 0.2 kcal mol⁻¹, indicating very good consistency.

CONCLUSION

The gas-phase acidities measured in this work are in good agreement with each other and also with the reported computational values. There is strong evidence presented that the current GA values are more reliable than the previously published ones.

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