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Gas-Phase Basicities Around and Below Water Revisited

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This work employs Fourier transform ion cyclotron resonance (FT-ICR) and the Gaussian quantum chemistry composite methods W1 and G2 to experimentally and computationally analyze gas-phase basicities (GB) for a series of weak bases in the basicity region around and below water. The study aims to clarify the long-standing discrepancy between reported GB values for weak bases obtained via high-pressure mass spectrometry (HPMS) and ICR; the ICR scale is observed to be more than 2 times contracted compared to the HPMS scale. The computational results of this work support published HPMS data. This agreement improves with increasing sophistication of the computational method and is excellent at the W1 level. Several equilibria were also re-examined experimentally using FT-ICR. In the experiments with some polyfluorinated weak bases (hexafluoro-2-propanol and nonafluoro-2-methyl-2-propanol), it was found that two protonation processes compete in the gas phase: protonation on oxygen and protonation on fluorine. In these species, protonation on fluorine proceeds faster and is statistically favored over protonation on oxygen but leads to cations that are thermodynamically less stable than oxygen-protonated cations. The process may also lead to the irreversible loss of HF. The rearrangement of fluorine-protonated cations to oxygen-protonated cations is very slow and is further suppressed by the process of HF abstraction. These results at least partially explain the discrepancy between published HPMS data and earlier FT-ICR findings and call for the utmost care in using FT-ICR for gas-phase basicity measurements of heavily fluorinated compounds. The narrower dynamic range of ICR necessitates the measurement of several problematic bases and produces some differences between the ICR results in the present work and the published HPMS data; the wider dynamic range allows HPMS to overcome these difficulties in connecting the ladder.

Introduction

Gas-phase basicities (GB)¹ of molecules are of fundamental interest and allow useful information about molecular electronic structure to be derived. The GB and proton affinity (PA) of a base B refer to the following reaction:

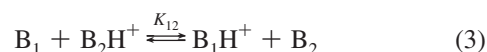


$$\Delta G = -RT \ln K \quad (2)$$

The GB of base B at temperature T is defined as the negative change in Gibbs free energy for eq 1: $GB \equiv -\Delta G$. The proton affinity (PA) of base B at temperature T is the negative change of the corresponding enthalpy.

GBs are most commonly measured by either the ion cyclotron resonance (ICR) method² or the high-pressure mass spectrometry (HPMS) method with flowing afterglow (FAG) and selected

ion flow tube (SIFT) enhancements.³ These techniques directly measure the relative GB ($\delta\Delta G$) of the two bases B_1 and B_2 in the equation



$$\delta\Delta G = -RT \ln K_{12} \quad (4)$$

The usual procedure is to construct a ladder of relative basicities using a set of compounds. To obtain absolute GB values for the compounds,⁴ the ladder must contain at least one base “anchor point” with an absolute GB value determined from other measurements or high-level computations.

Gas-phase measurements of intrinsic basicities and proton affinities of molecules have a long history dating back to the late 1960s. A large number of publications have appeared, and several compilations of GB and PA data have been published of which the NIST database⁴ is the most well-known. Although at present the gas-phase basicity scale in general is rather well established, certain regions of the scale continue to present noticeable inconsistencies. Very weak bases with basicity values near and immediately below water present a problematic region. Starting in the mid-1970s, the first basicity measurements near that region were carried out with the HPMS³ and ICR

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techniques.^{2,5–8} In 1993, Szulejko and McMahon⁹ published an extensive ladder of gas-phase basicities of weak bases obtained via HPMS measurements. Shortly thereafter, another paper devoted to ICR measurements of gas-phase basicities of weak bases⁵ was published. In general, ICR data from different studies^{5–8} agree well with each other as does HPMS data. There is, however, severe systematic disagreement between the ICR and HPMS data, and it is possible to correlate GBs of bases for which both ICR and HPMS data exist. For example, considering the bases H₂O, C₂H₄, CF₃CN, SO₂, COS, (CF₃)₂CO, and SO₂F₂ found with available HPMS data (ref 9) and ICR data (ref 5 and confirmed by ref 8), one obtains a slope of 2.27 for HPMS versus ICR results compared to a perfectly correlated slope of unity (see Table 2). The span of the HPMS scale is more than 2 times wider than that of the ICR scale. At the same time, no systematic disagreement between the ICR and HPMS methods has been found in regions of higher basicity.

Several computational studies on basicities of weak bases have also been carried out.^{10,11} Generally, these bases are small molecules, and their basicities can be calculated with a high level of computational rigor. The Gaussian-2 (G2) study by Smith and Radom¹⁰ is the most relevant of these studies, and its results tend to support the HPMS data. At present, computational studies have been performed for an insufficient number of compounds in this basicity region to draw solid conclusions.

Gas-phase basicity measurements with the ICR technique are demanding. There are numerous uncertainty sources including the following:

(1) To be meaningful, the measured ratios of ion responses and partial pressures (see ref 2 for details) must correspond to the equilibrium state. In earlier ICR measurements, instruments with electromagnets were used, and it was not possible to monitor the reactions for long periods of time because of the relatively weak magnetic fields (typically 1 T) that could be obtained. The possibility remains that true equilibrium was not always reached in the measurement of some bases^{5–8} with a very slow proton transfer reaction (e.g., fluorinated benzenes, see ref 12).

(2) Competing reactions may sometimes cause either consumption or formation of one of the ions participating in equilibrium. This can lead to a quasi-equilibrium state whereby the ratio of ion intensities is seemingly constant but equilibrium has not been attained.

(3) Because of ICR instrumental design constraints, the pressures of the neutrals cannot be measured directly in the cell. Often, the pressure sensor is located at a significant distance from the cell. While pressures measured this way are different from pressures in the cell region, the assumption is that the ratios of the pressures are approximately the same.

(4) The restricted dynamic range of ICR dictates that only bases with basicity difference preferably below 3 kcal mol^{–1} can be directly compared. Therefore, to cover a large basicity range, it is necessary to build a ladder using several bases and to carry out numerous measurements.

The above-described inconsistencies are still unresolved, and to help elucidate this issue, we have undertaken a computational (G2 and W1) and Fourier transform ion cyclotron resonance (FT-ICR) study of the gas-phase basicities of some weak bases.

Experimental Section

Computations. Computations were carried out at the ab initio G2 and W1 levels of theory using the Gaussian 98¹³ and Gaussian 03¹⁴ program packages. The G2 method is reported to compute thermochemical data with “chemical accuracy” (i.e.,

to within ± 2.5 kcal/mol of experimental quantities).¹⁵ To enhance reliability, additional calculations were performed for several small molecule bases with the highly accurate and computationally demanding W1 method.^{18,19} The W1 method is an incremental theoretical thermochemistry scheme based on extrapolation to an infinite basis set and has been demonstrated for simple molecules to reproduce proton affinities with experimental accuracy (i.e., mean absolute error 0.44 kcal/mol).

Full geometry optimizations and frequency analyses of the neutral and protonated forms of the bases were performed. All stationary points of the optimized geometries were found to be true minima (i.e., no imaginary frequencies). In addition, frequency analysis was applied to calculate the thermodynamic Gibbs free energies, which were temperature-corrected to 298.15 and 373 K. Gas-phase basicities were calculated as the Gibbs free energy changes for eq 1.

FT-ICR Measurements. Two FT-ICR instruments were used in the experiments. The Extrel FT-MS 2000 instrument with 3 T superconducting magnet (Kyushu University, Fukuoka, Japan) was used for most measurements. The temperature was measured by means of a thermocouple located near the cell. The electron-emitting filament was situated ca. 60 cm away from the cell and did not affect the cell temperature. Some of the measurements were performed using a modified Bruker CMS-47 FT-ICR mass spectrometer with 4.7 T superconducting magnet (Instituto “Rocasolano”, Madrid, Spain).

The equilibrium constant for eq 3 was measured at an ICR cell temperature of 373 K. The partial pressures of the two bases were controlled using leak-valves and were measured to be about 2×10^{-6} to 4×10^{-8} Torr. The partial pressures of the neutrals were monitored using a Bayard-Alpert gauge. The base pressure of the system was about 3×10^{-8} to 4×10^{-8} Torr. In measurements involving water as one of the bases, its partial pressure was ca. 1 order of magnitude higher than the base pressure. This is important because water vapor is one of the contributors to the base pressure in mass spectrometry systems. The partial pressures used in the calculations were corrected for differences in the ionization cross sections of the compounds. For that, the sensitivities of the Bayard-Alpert ion gauge relative to N₂ were estimated using the Bartmess–Giorgiadis method,¹⁶ and the molecular polarizabilities were determined by means of Miller’s $\alpha^*(\text{ahc})$ polarizability parameters¹⁷ for the appropriate elements. The estimated possible inaccuracy of this correction is up to 50% in the case of ratio measurement. This amounts to ca. ± 0.4 kcal mol^{–1} in terms of GB gap measurement. The ions were created using a short (3–10 ms) pulse of 20 eV electrons. When hydrogen-containing bases were used, they themselves served as proton sources. When neither of the bases contained hydrogen, then methane was also leaked into the system at a partial pressure of 1.3×10^{-7} Torr. Methane also served as the cooling gas. From the resulting K_{12} values, the $\delta\Delta G$ values were calculated according to eq 4. To ensure realization of true equilibrium, long reaction times, generally 15–25 s, were used, and well-defined plateaus (see Figure 1) could be monitored in the time plots of the relative abundances of the two protonated forms. In certain cases, the reaction times were up to 30–40 s. With several bases (CS₂, C₆F₆, C₆HF₅), very stable molecular ions were observed, which did not disappear even after several seconds. In such cases, the ¹³C peak of the molecular ion B^{•+} overlapped with the BH⁺ peak. This was corrected by subtracting the B^{•+} contribution from the BH⁺ peak. Nevertheless, this introduced additional uncertainty into the results.

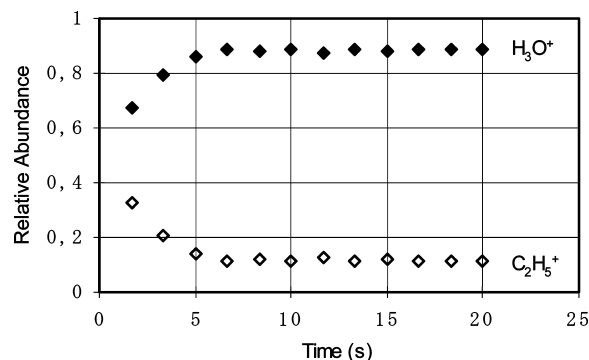


Figure 1. An example of a time plot obtained during the GB measurements.

Chemicals. Commercial samples of the following chemicals were used: Methane and ethylene (GL Sciences), CS₂ (Kishida Chemicals and Aldrich), (CF₃)₂CHOH (Aldrich), C₆F₆ (Lancaster), and (CF₃)₃COH (Aldrich). CH₃Cl (Aldrich) was dried through a tube containing P₄O₁₀. SO₂ was synthesized by reacting sulfuric acid (Kishida chemicals) with sodium sulfite (Hanawa). CF₃CN was synthesized by a dehydration reaction of CF₃CONH₂ (TCI) with P₄O₁₀ (Kishida Chemicals) at 140–150 °C. The nitrile CF₃CN formed by this method includes the amide CF₃CONH₂ as a byproduct because the latter is rather volatile. Presence of the amide impurity is undesirable because it is significantly more basic than the nitrile. The nitrile was therefore passed through a trap cooled to −44 °C with solid and liquid acetonitrile mixture (acetonitrile slush). This treatment completely eliminated CF₃CONH₂. CF₃CN was additionally purified using trap-to-trap distillation with a vacuum line. CF₃CHO and (CF₃)₂CO were prepared online from the corresponding hydrates (both from Aldrich). To efficiently convert the hydrate to its corresponding anhydrous compound, an evaporation–condensation treatment cycle was repeated four to six times in a P₄O₁₀-filled adapter tube between the sample tube and the ICR inlet system: first, the hydrate was allowed to evaporate into the apparatus inlet through the P₄O₁₀ tube; second, the compound was allowed to condense in the sample tube. Also, for some bases of significantly lower basicity than H₂O, a P₄O₁₀ adapter tube was used to remove traces of water (treatment similar to ref 5). As a result of these measures, we did not experience any problems due to H₂O as the competing base in our experiments.

Results

The results of our measurements and computations are presented in Table 1 and are compared with the most relevant literature data. The results of the direct FT-ICR measurements of $\delta\Delta G$ values are presented in Scheme 1. Multiple overlapping measurements were performed to confirm and increase the reliability of the results. Experimental gas-phase basicity values (relative to SO₂) were assigned to individual bases using a least-squares treatment. This procedure is described in ref 20 and serves to minimize the sum of squares of differences between the directly measured $\delta\Delta G$ values and the corresponding differences in ΔG values of the pairs of bases. The standard deviation of the ΔG values was calculated to be 0.4 kcal mol^{−1} according to the procedure described in ref 21. For the sake of consistency, all GB values are presented relative to SO₂.

In addition to the relative basicities (Table 1), we determined the absolute gas-phase basicity values by the W1 method for five bases: C₂H₄ (GB = 156.2 kcal·mol^{−1}), H₂O (GB = 157.5

kcal·mol^{−1}), SO₂ (GB = 144.8 kcal·mol^{−1}), CH₃Cl (GB = 148.3 kcal·mol^{−1}), and CS₂ (GB = 158.3 kcal·mol^{−1}). To the best of our knowledge, these are the most accurate computational GB values for these compounds yet published.

Discussion

Comparison of Experimental and Computational Data from Different Sources. Table 2 presents the pairwise correlation analysis of data from different sources. Although the span of our FT-ICR results is ca. 1.7 times wider than that of refs 5–8, it is still ca. 1.3 times contracted with respect to the HPMS scale of ref 9. Our computational results at the G2 and especially at the W1 level support previously reported HPMS results. The widely used density functional theory (DFT) method B3LYP/6-311+G** gave unsatisfactory results for our systems of interest: in several cases, the calculated GB values were in error by ≥ 7 kcal/mol and the predicted GB order was also incorrect (e.g., SO₂ vs (CF₃)₃COH or C₆F₅H vs CF₃CH₂OH). This poor performance of B3LYP was also observed in a recent study.²²

The basicities we calculated by W1 agree very well with HPMS literature results both in terms of the span of the scale and the strong correlation ($R^2 = 0.99$). Also, the slope (1.05 ± 0.04) of the regression line and the intercept (0.35 ± 0.37) are fairly close to the regression coefficients 1 and 0 corresponding to an ideal fit of experimental and calculated data. The agreement of our G2 values with the HPMS literature data is also good: $R^2 = 0.98$, slope 1.04 ± 0.06 , and intercept (-0.90 ± 0.45) kcal mol^{−1}. The mean unsigned differences in basicity values between the experimental HPMS and the computational G2 and W1 results are 1.1 and 0.8 kcal/mol, respectively. The G2 and W1 calculations exhibit a mean unsigned difference of approximately 0.04 kcal/mol and demonstrate very good correlation.

The span of our experimental ICR results is contracted compared to the G2, W1, and HPMS scales. Overall, there seems to be a systematic deviation in the basicity values between the ICR and the HPMS methods resulting in an expansion of the HPMS scale to lower basicity values of weak bases. For the weakly basic region, our measurements yield an 11.7 kcal/mol span of the basicity scale from CS₂ to (CF₃)₂CO. This corresponds to only 84% of the 13.8 kcal·mol^{−1} result obtained by HPMS measurements.

The possibility that the systematic contraction of the present GB ladder comes from the misassignment of the ICR cell temperature is highly unlikely. To agree with the HPMS results, the cell in our apparatus would have required a temperature of 275 °C, that is, an offset of 175 °C from the set point. This is very improbable.

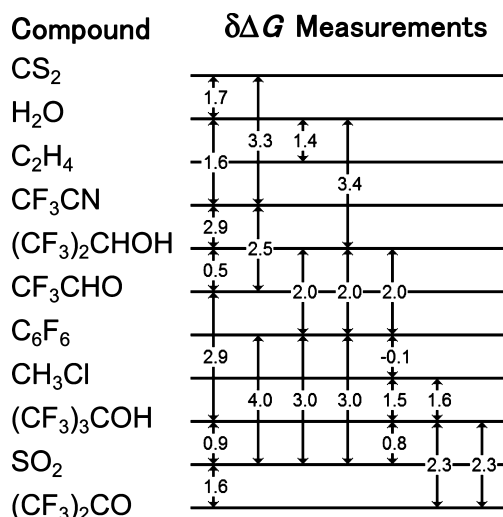
Closer comparison of our experimental ICR results with HPMS results of Szulejko and McMahon⁹ reveals, however, that measured $\delta\Delta G$ values are very close when direct comparison is possible (e.g., (CF₃)₂CO vs SO₂: 1.4 and 1.6 kcal/mol, SO₂ vs C₆F₆: 3.8 and 3.0 or 4.0 kcal/mol, CF₃CN vs CS₂: 3.2 and 3.3 kcal/mol, by HPMS and ICR, respectively). Thus, we conclude that the different absolute numbers stem from the capability of HPMS to measure much larger GB differences than ICR; therefore, compared to HPMS, the ICR scale requires more bases to cover the same GB range. Unfortunately, in the low basicity region, polyfluorinated compounds such as C₄F₉OH must be included to obtain a continuous ladder. For these compounds, measurements are less reliable. The possible reasons for this are explored in the next section.

Gas-Phase Chemistry of the Compounds Involved. H₂O is believed to be a problematic base to study in the gas phase.

TABLE 1: Results of the GB Measurements and Calculations along with the Most Relevant Data from the Literature^a

no	compound	this work ^b			lit. ^b		absolute ^c				
		ICR	G2	W1	HPMS ^d	ICR ^e	HPMS	W1	ref 4	recommended	
		373 K	373 K	373 K	373 K	373 K	373 K	373 K	298 K ^f	373 K	298 K
1	CS ₂	10.4	12.2	13.9	12.2		157.0	156.9	157.2	157.0	158.4
2	H ₂ O	8.6	11.2	12.6	12.4	5.5	157.2	155.6	157.7	156.4	158.3
3	FCN		11.4	12.9		1.8		155.9	143.7	155.9	157.8
4	C ₂ H ₄	7.2	9.6	11.4	10.8	2.5, -1.4 ^g	155.6	154.4	155.7	155.0	156.8
5	CF ₃ CN	7.2	8.6	9.8	8.7	3.9, 4.4 ^g	153.5	152.8	157.2	153.2	155.1
6	(CF ₃) ₂ CHOH	4.9	5.4			3.1			156.8	150.7	152.5
7	F ₂ NH		5.3	6.8		0.0		149.8		149.8	151.8
8	CF ₃ CHO	4.4	3.4	4.7		2.7		147.7	156.2	147.7	149.6
9	C ₆ F ₆	3.1	3.0		4.1		148.9		149.2	148.9	150.3
10	CH ₃ Cl	2.8	3.6	4.1				147.1	148.4	147.1	148.6
11	(CF ₃) ₃ COH	1.1	-0.5			1.3, 1.5 ^g			154.6	145.7	147.5
12	CF ₃ COCl		5.0			2.9			155.3	147.7	149.7
13	(CN) ₂		3.3	4.6		2.5		147.6	154.3	147.6	149.3
14	FSO ₂ Cl		1.5	2.5		0.5		145.5	155.3	145.5	147.3
15	SO ₂	0.0	0.0	0.0	0.0	0.0	144.8	143.0	153.8	144.8	146.6
16	(CF ₃) ₂ CO	-1.3	-3.3		-1.6	-0.7, -0.8 ^g	143.2		152.9	143.2	145.0
17	COS ^h		0.6	1.0	-0.4	-0.4	144.4	144.0	144.0	144.2	145.7
18	F ₂ CO		-3.8	-2.8		-2.0, -1.3 ^g		140.2	152.2	140.2	142.0
19	CF ₃ CCH ^h		4.7			0.8				145.6	146.3
20	(CF ₃) ₂ O ^h		-3.5			-2.2, -1.3 ^g				142.6	144.2
21	SO ₂ F ₂ ^h		-7.9	-6.0	-5.5	-3.0	139.3	137.0	138.7	138.1	139.9

^a All data are given in kcal/mol (1 cal = 4.184 J). ^b Values are given relative to SO₂. ^c Absolute values. HPMS from ref 9 and W1 from this work. ^d Reference 9. The GB values were recalculated from 600 K to 373 K using the Van't Hoff equation and the ΔH values given in ref 9. ^e Reference 5 if not specified otherwise. ^f Although the temperatures in ref 4 are quoted as 298 K, most of the measurements were made at other temperatures and were recalculated to 298 K. See ref 4 for details. ^g Reference 8. ^h Our G2 calculations indicate that CF₃CCH and (CF₃)₂O preferentially protonate on fluorine (more stable by 16.2 and 8.4 kcal/mol compared to protonation on the triple bond and oxygen, respectively), which yields complexes of HF and the remaining cation. These complexes can further dissociate depending on experimental conditions. In contrast, F₂SO₂ protonates on the oxygen (fluorine protonation is disfavored by 25 kcal/mol). COS protonates preferentially on sulfur (oxygen protonation is disfavored by 4.4 kcal/mol).

SCHEME 1: Results of Direct FT-ICR Measurements of $\delta\Delta G$ Values (in kcal·mol⁻¹)

At higher partial pressures, H₃O⁺ and water molecules tend to associate and complicate the measurement of the H₃O⁺ signal. Under normal ICR working conditions, H₃O⁺ binds to H₂O to give OH₃⁺...OH₂ at reaction times of several seconds. Thus, the concentration of H₃O⁺ continuously decreases, and it is difficult to guarantee a true equilibrium versus steady-state condition. There have been a limited number of measurements^{5,8} where equilibrium between H₂O and a base with GB below or near H₂O has been measured directly. One goal of this work has been to directly study as many proton transfer equilibria involving H₂O as possible. In this study, H₂O was used in altogether four relative basicity measurements with both stronger

TABLE 2: Correlations between GB Values from Different Sources^a

correlations	<i>a</i>	<i>b</i>	<i>R</i> ²	<i>S</i> ₀	<i>N</i>
HPMS vs ICR ¹	2.27 ± 0.29	0.95 ± 0.85	0.93	2.09	7
ICR vs ICR ¹	1.71 ± 0.25	0.11 ± 0.74	0.88	1.35	8
HPMS vs ICR	1.29 ± 0.1	0.19 ± 0.63	0.97	1.06	7
G2 vs ICR	1.36 ± 0.07	-1.25 ± 0.43	0.98	0.86	11
G2 vs ICR ¹	2.05 ± 0.32	0.64 ± 0.77	0.73	2.95	18
G2 vs HPMS	1.04 ± 0.06	-0.90 ± 0.45	0.98	1.09	9
W1 vs ICR	1.42 ± 0.10	-0.19 ± 0.65	0.97	0.86	7
W1 vs ICR ¹	2.15 ± 0.42	2.29 ± 1.09	0.73	3.4	12
W1 vs HPMS	1.05 ± 0.04	0.35 ± 0.37	0.99	0.76	7
W1 vs G2	1.07 ± 0.02	0.80 ± 0.16	0.996	0.39	14

^a ICR, ICR¹, HPMS: experimental basicities from this work, ref 5, and ref 9, respectively. G2 and W1: computational basicities from this work at the G2 and W1 level. *R*² is the squared correlation coefficient; *S*₀ is the standard deviation of the regression; *a*, slope of the regression; *b*, intercept of the regression; *N*, number of bases included in the regression model.

and weaker bases. The consistency of measurements in the “triangle” formed by H₂O, CS₂, and CF₃CN is very good. The consistency in the triangle formed by H₂O, CF₃CN, and (CF₃)₂CHOH is satisfactory at best. We did not succeed to build a third triangle involving C₂H₄ because of experimental difficulties; in some cases, the apparent equilibrium constants at different partial pressures did not agree, and in some cases, no well-defined plateau was formed. One might suggest that the discrepancy between ICR and HPMS data originates from the particular slice immediately below H₂O, the width of which has been possibly misassigned by several kcal mol⁻¹.

The outcome of the protonation of (CF₃)₂CHOH shows an interesting dependence on the acidity of the proton source. Using

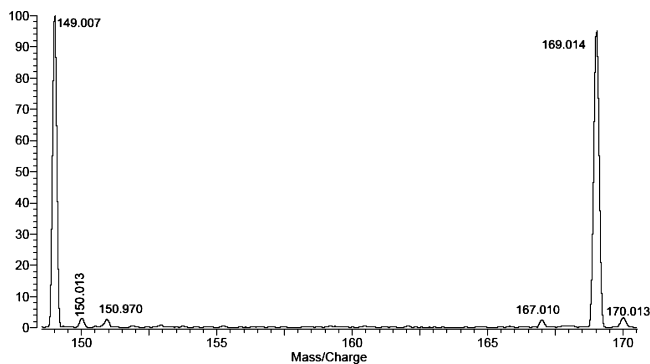


Figure 2. Protonation of $(\text{CF}_3)_2\text{CHOH}$ with CH_5^+ . $P_{(\text{CF}_3)_2\text{CHOH}} = 5.0 \times 10^{-8}$ mbar. $P_{\text{CH}_4} = 1.09 \times 10^{-7}$ mbar. Nominal ionization energy = 16 eV. Ion selected, $m/z = 17$. Reaction time = 6.50 s.

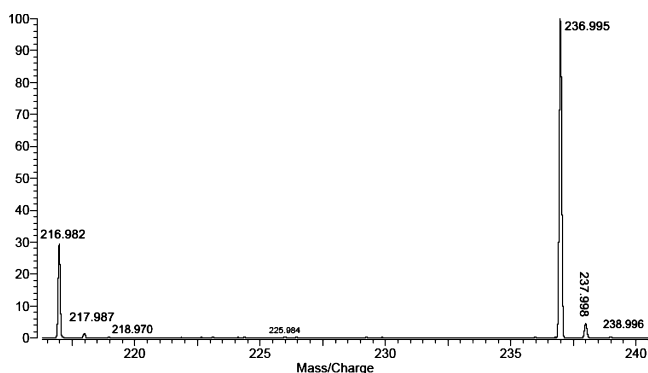


Figure 3. Self-protonation of $(\text{CF}_3)_3\text{COH}$. $P_{(\text{CF}_3)_3\text{COH}} = 3.63 \times 10^{-7}$ mbar. Nominal ionization energy = 14.5 eV. Reaction time = 6.50 s.

a strong acid such as CH_5^+ , the most abundant ion formed corresponds to $\text{C}_2\text{F}_5\text{CHOH}^+$ ($m/z = 149$) generated by F-protonation. This ion, however, is sufficiently acidic to protonate $(\text{CF}_3)_2\text{CHOH}$ on oxygen and, as the system evolves, $(\text{CF}_3)_2\text{CHOH}_2^+$ ($m/z = 169$) becomes the main ion present. Figure 2 shows such an evolution. The situation is quite simple in the case of a weaker acid such as CH_3CIH^+ , since the main ion directly formed is $(\text{CF}_3)_2\text{CHOH}_2^+$.

In the case of $(\text{CF}_3)_3\text{COH}$, the situation is more complex. The complexity originates again in the competition between the two protonation sites OH and F. Although OH is the thermodynamically preferred site (by as much as 14 kcal/mol according to G2), protonation on fluorine is significantly faster because of a larger negative partial charge. Furthermore, F-protonation leads to an irreversible HF loss.

We present in Figure 3 a spectrum obtained with pure $(\text{CF}_3)_3\text{COH}$. Here, the acidic species is the radical cation derived from the alcohol. It is important that the species $(\text{CF}_3)_3\text{COH}_2^+$ ($m/z = 237$) be perfectly characterized. The ion simultaneously formed by F-protonation followed by the irreversible loss of HF ($m/z = 217$) also appears quite cleanly. Very small amounts of the cation formed by the loss of H_2O from $(\text{CF}_3)_3\text{COH}_2^+$ are also likely formed.

Figure 4 shows a spectrum for the generation of $(\text{CF}_3)_3\text{COH}_2^+$ by protonation of the neutral alcohol by CH_3CIH^+ . The simultaneous presence of $\text{C}_3\text{F}_8\text{COH}^+$ ($m/z = 217$) is also observed. In fact, the decomposition of this ion can proceed further by abstraction of a second HF and the formation of $\text{C}_3\text{F}_7\text{CO}^+$ ($m/z = 197$). Furthermore, these ions are very prone to form hydrogen-bonded adducts. The complexity of the situation is depicted in Figure 5, which shows a spectrum pertaining to the system $\text{C}_6\text{F}_6/(\text{CF}_3)_3\text{COH}$ in which CH_4 was

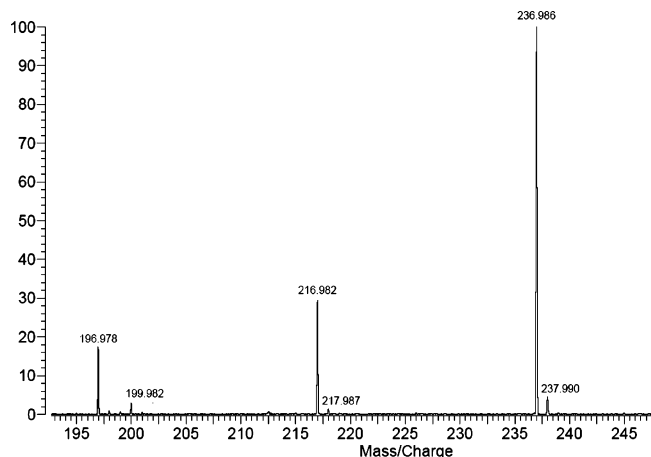


Figure 4. Protonation of $(\text{CF}_3)_3\text{COH}$ with MeCIH^+ . $P_{(\text{CF}_3)_3\text{COH}} = 4.55 \times 10^{-7}$ mbar. $P_{\text{CH}_4} = 3.23 \times 10^{-7}$ mbar. $P_{\text{MeCl}} = 3.50 \times 10^{-8}$ mbar. Ionization energy = 14.0 eV. Twenty-five acquisitions. Reaction time = 0.80 s.

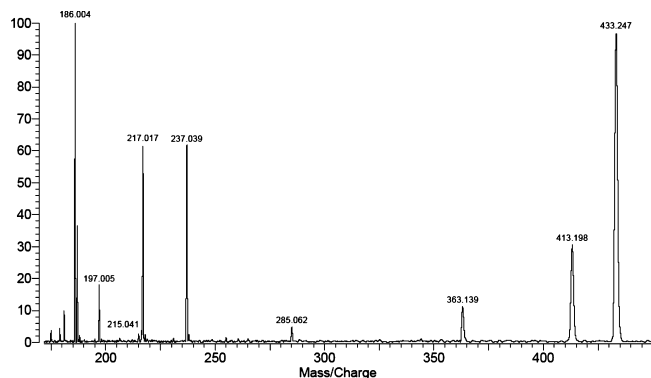


Figure 5. Proton exchange between $(\text{CF}_3)_3\text{COH}$ and C_6F_6 . $P_{(\text{CF}_3)_3\text{COH}} = 5.0 \times 10^{-7}$ mbar. $P_{\text{C}_6\text{F}_6} = 5.0 \times 10^{-8}$ mbar. $P_{\text{CH}_4} = 2.0 \times 10^{-7}$ mbar. Nominal ionization energy = 16 eV. Reaction time = 2.50 s.

used as both the initial proton source and the cooling gas. When allowing the reaction to proceed further, we observed a large peak at $m/z = 433$, which corresponds to $[\text{2}(\text{CF}_3)_3\text{COH} + \text{H}^+ - 2\text{HF}]$. There is also a fair amount of the ion $m/z = 413$ corresponding to $[\text{2}(\text{CF}_3)_3\text{COH} + \text{H}^+ - 3\text{HF}]$. These effects complicate achieving true equilibrium. Nevertheless, ion-selection experiments reveal the reversibility of the proton transfer between $(\text{CF}_3)_3\text{COH}$ and the reference.

In the case of C_6F_6 , similar competition is observed between C- and F-protonation. Furthermore, the low ionization energy of C_6F_6 leads to the formation of a large amount of its radical cation. Its ^{13}C satellite (with the relative intensity of ca. 6%) has the same nominal m/z ratio 187 as protonated C_6F_6 . During our measurements, the radical cation was either ejected or the ^{13}C satellite was accounted for in our calculations, but its presence increases the uncertainty of the result. On the other hand, it is a fortunate fact that F-protonation does not seem to lead to the irreversible loss of HF.

Revised Gas-Phase Basicity Values of the Compounds Involved. A reasonable outcome of the above experimental and computational results is a revision of the scale of gas-phase basicities in this region. The HPMS and W1 data are in good agreement. In Table 1, we provide “absolute” GB values anchored to the value of SO_2 , which is one of the few compounds for which data are available with all methods. We provide “recommended values” in the last two columns (for 373 and 298 K). The value at 373 K was generally taken as the

average of the absolute basicities obtained by HPMS experiments and the W1 computational method. If the HPMS data point is unavailable, only the W1 value is used (and vice versa). In several instances, neither HPMS nor W1 values are available; the absence of the latter is a consequence of the very large computational demand of this method. In these cases, we provide recommended values based on the FT-ICR data calculated in the following way. The directly measured $\delta\Delta G$ values from Scheme 1 are taken and added to the recommended GB values of the respective reaction partners from Table 1. The indicated recommended value is the average of the absolute GB values obtained in this manner. The recommended values at 298 K were calculated from the 373 K values using scaled (by a factor of 0.8929, see ref 23) HF/6-31G* frequencies.

We also provide a column with “reference values” given in the Hunter–Lias compilation.⁴ In a number of cases, our results nicely agree with these classical values.

As indicated above, while $t\text{-C}_4\text{F}_9\text{OH}$ reversibly exchanges protons with the reference bases, it also steadily decomposes. Therefore, the uncertainty of the revised GB value for this compound can be estimated at 2 kcal mol^{−1}.

Conclusions

The computational GB results of this work support published HPMS data. The agreement improves with increasing sophistication of the computational method used and is excellent at the W1 level. Experimental re-examination of several equilibria using FT-ICR revealed that for (CF₃)₃COH in the gas phase, two protonation processes compete: protonation on oxygen and protonation on fluorine. Protonation on fluorine proceeds faster than protonation on oxygen but leads to cations that are thermodynamically less stable than oxygen-protonated cations. The process of rearrangement of fluorine-protonated cations to oxygen-protonated cations is very slow and is further suppressed by the irreversible elimination of HF. These results at least partially explain the discrepancy between published HPMS data and earlier FT-ICR findings and call for the utmost care in using FT-ICR for gas-phase basicity measurements of heavily fluorinated compounds of weak basicity.

The different absolute GB values of the HPMS and ICR scales arise from the capability of HPMS to measure much larger GB differences than ICR. Also, the ICR measurements had to include several heavily fluorinated compounds of limited reliability as reference bases because of competing irreversible processes in the gas phase.

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