

RECHECKING OF THE EQUILIBRIUM GAS-PHASE BASICITY SCALE FOR LOW-BASICITY COMPOUNDS USING FOURIER TRANSFORM ION CYCLOTRON RESONANCE SPECTROMETRY

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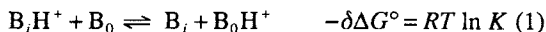
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Fourier transform ion cyclotron resonance (FT-ICR) spectrometry was used to study and recheck the proton transfer equilibria for a large number of low-basicity compounds, particularly those which are less basic than H_2O . The data obtained were used for the construction of a continuous scale of the relative gas-phase basicities between H_2S and SO_2F_2 . The present results are compared with the results obtained by McMahon and co-workers using ICR spectrometry and high-pressure mass spectrometric (HPMS) techniques. Satisfactory agreement is found with the existing ICR spectrometric data. The results, however, show unexplained variances with earlier and recent HPMS results that are also not internally self-consistent. The substituent effects for some families of low-basicity compounds (nitriles, carbonyl compounds, ethers and some others) are discussed.

INTRODUCTION

The gas-phase proton affinities for neutral bases have been determined for more than 800 compounds B_i over a wide interval between 41 kcal mol^{-1} (He atom) and $318.2 \text{ kcal mol}^{-1}$ (K_2O)¹⁻⁶ ($1 \text{ kcal} = 4.184 \text{ kJ}$). Most of the data were derived from the equilibrium constants by low-pressure ion cyclotron resonance (ICR), high pressure mass spectrometric (HPMS) or flowing after-glow techniques for the following gas-phase proton transfer equilibria:



where B_0 refers to the reference base (ammonia, isobutene, CO_2 , etc.).

Predominantly the attention of investigators has been centered on the measurement of the basicity of compounds which are usually significantly more basic than water [proton affinity ($PA = 166.5 \text{ kcal mol}^{-1}$)]^{2,7}. The basicity ladders¹⁻⁸ covering the basicity range from H_2O to ammonia^{9,10} and from the latter to diamines,^{1,2} substituted guanidines and amidines^{2,11} have been established, rechecked and sometimes critically re-evaluated.^{1,2,8} In particular, the value of the proton

affinity for ammonia has been intensively discussed.^{1,2,7-10} Values usually ranging from 202 to $208 \text{ kcal mol}^{-1}$ have been suggested. Mautner and Sieck^{8a} have recently proposed a 4 kcal mol^{-1} upward adjustment of the value of $PA(\text{NH}_3) = 204.0 \text{ kcal mol}^{-1}$ that has been accepted in the gas-phase thermochemistry database.² Their suggested value ($208.3 \text{ kcal mol}^{-1}$) was claimed to be supported by the HPMS experiments of Szuleijko and McMahon.^{8b} Later, however, the same authors^{8c} reversed their arguments in favor of the previously accepted value of $PA(\text{NH}_3) = 204 \text{ kcal mol}^{-1}$. In the same paper,^{8c} these authors voiced their belief that 'after two decades of equilibrium proton transfer measurements, it would appear that a reliable, absolute affinity scale is close at hand.'

However, based on the results of our present ICR spectrometric experiments and on a literature analysis, we can hardly agree with such an optimistic conclusion. Specifically, the doubts concern the basicity range for the compounds less basic than or comparable to water. Owing to the experimental difficulties, the study of this particular basicity region has so far received only very modest attention.

First, the basicity area between CO and CH_4 was

studied^{12,13} by the flowing afterglow technique. Later, in three separate papers by McMahon and co-workers,¹⁴⁻¹⁶ the basicity of some compounds, mostly less basic than water, was studied by the ICR technique at ambient temperature. In the overlapping region of basicities (from C_2H_4 to CF_3COF), the agreement between the results from the different studies can be considered reasonable.

HPMS was used by McMahon and Kebarle¹⁷ for the investigation at 400 K of the wide basicity range between H_2S , CF_3CH_2OH or H_2O and CH_4 . The latter study also involved the selection of compounds which mostly overlap with the collection of bases used in earlier ICR studies¹⁴⁻¹⁶ of relatively weak basicity (the range from H_2S and CF_3CH_2OH to CF_3COF and SO_2F_2). The comparison of the relative basicities $\delta\Delta G^\circ$ given in Refs 14-16 with those in Ref. 17 for CF_3CH_2OH and CF_3COCF_3 (8.2 and 15.9 kcal mol⁻¹, respectively) and for the transfer from CF_3CH_2OH to SO_2F_2 ($\delta\Delta G$ values derived by using ICR and HPMS techniques are 9.4 and 15.4 kcal mol⁻¹, respectively) shows that for the first pair the ratio $\delta\Delta G_{400}^{HPMS}/\delta\Delta G_{298}^{ICR} = 1.94$, whereas for the second pair of compounds this ratio is 1.80.

This means that a very significant inconsistency exists between all series of the ICR¹⁴⁻¹⁶ and the HPMS¹⁷ experiments. This disagreement does not vanish even after taking into account the actual ratio, i.e. $400/298 = 1.34$, of the experimental temperatures and reducing the $\delta\Delta G^\circ$ values to the same temperature. No explanation of these findings was suggested.¹⁷

Serious disagreements also exist in the low-basicity region for the 400 K HPMS basicity scale of McMahon and Kebarle¹⁷ and the new HPMS basicity scale of Szuleijko and McMahon.^{8c} Whereas the PA values for H_2S , H_2O , CS_2 and C_2H_4 are virtually identical in both studies, values for several other bases (CF_3CN , SO_2 , COS , SO_2F_2 , C_2H_6 , CO , N_2O and CH_4) are revised downward^{8c} by 4-5 kcal mol⁻¹. This has led to a significant expansion of the basicity scale from that in Ref. 17. Also, in Ref. 8c for some weak bases (CS_2 , CF_3CN , SO_2 , COS , $(CF_3)_2CO$) the relative basicity order has been found to be different from that given in Ref. 17. No explanation of the revision of the relative basicity order of those compounds was suggested.

The major goal of this work was to re-check the gas-phase basicity ladder spanning from CF_3CH_2OH to SO_2F_2 using an FT-ICR spectroscopic technique.

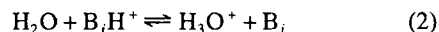
The equilibrium gas-phase basicity scale for compounds which are slightly or even moderately stronger than water is also not sufficiently abundant or well enough represented by the derivatives of bases belonging to the various families of compounds. Therefore, the second goal of this work was to investigate bases (mostly fluoro-organic compounds) whose basicity, as a rule, does not exceed that of water by more than 5-15 kcal mol⁻¹.

No attempt was made to tackle the problem of absolute values of gas-phase basicities or proton affinities of NH_3 , H_2O and some other frequently used reference compounds.

EXPERIMENTAL

Procedure. Gas-phase basicity measurements were performed at 373 K using a pulsed FT-ICR mass spectrometer from IonSpec (Irvine, CA, USA). The major details of the experimental technique used for the measurement of equilibrium constants K of the reversible proton transfer [reaction (1)] are mostly the same as described previously.^{18,19}

Only some specific features of the experiments performed will be given in this section. For a typical gas-phase basicity measurement, the pairs of comparable weak bases involved in the particular experiment were leaked into the FT-ICR instrument's vacuum system [the usual partial pressures of the components were in the range 10^{-7} - 10^{-8} Torr (1 Torr = 133.3 Pa)] through the Varian leakvalves. Temperatures in the spectrometer inlet system, analyzer cell and its compartment ('can') were measured separately using a thermocouple. Temperatures in the corresponding regions of the spectrometer were controlled to within 2-3°C. In cases where the bases themselves contained no hydrogen, ultra-high-purity methane (Matheson) was also leaked ($p = 10^{-7}$ Torr) into the ICR spectrometer system. Because of the presence of small but persistent water impurities in the samples of very weak bases and also in the methane gas, an adapter tube filled with high-quality anhydrous P_4O_{10} was installed in the region between the sample and CH_4 bulbs and the spectrometer's inlet system. In all cases the use of the P_4O_{10} filter eliminated completely the presence of hydroxonium ion (m/z 19) or its hydrates in the time plots of the mass spectrum due to switch-off of the channel of side-reactions between the 'strong' base H_2O and a much weaker base B_i :



With hydrogen-containing bases, parallel control experiments in the presence of the methane gas were always performed. As a rule, the equilibrium constants measured in this way coincided within their experimental uncertainties with those measured without the presence of the methane reagent gas.

The equilibrium constants K were calculated according to the equation

$$K_i = P(B_i)I(B_0H^+)/P(B_0)I(B_iH^+) \quad (3)$$

where $P(B_i)$ and $P(B_0)$ are the partial pressures of the given and the reference bases and $I(B_0H^+)$ and $I(B_iH^+)$ are the mass-spectral integrated peak intensities corresponding to the protonated forms of B_0 and B_i , respectively. A Bayard-Alpert-type ionization gauge

Table 1. Directly measured relative basicities $\delta\Delta G^\circ$ and the basicity relative to ammonia, $\delta\Delta G^\circ(\text{NH}_3)^{a,b}$

	Directly measured $\delta\Delta G^\circ$				$\delta\Delta G^\circ(\text{NH}_3)$
$(\text{CF}_3)_2\text{CHOCH}_3$					33.4
H_2S					33.9 ^c
CF_3COOH		0.9			33.8 ^c
CF_3SSCF_3		0.3			34.1
$\text{CF}_3\text{COOCH}_2\text{CF}_3$	1.5		2.0		34.2
$(\text{CF}_3\text{CH}_2)_2\text{O}$		0.7	1.2	3.7	34.8
$\text{CF}_3\text{CH}_2\text{OH}$		0.6			35.4 ^c
$(\text{F}_2\text{CH})_2\text{CO}$			0.7		36.1
$(\text{CN})_2\text{C}=\text{C}(\text{CN})_2$			2.1		37.4
H_2O		1.7			37.5 ^c
CF_3CN					39.1
$(\text{CF}_3)_2\text{CHOH}$	1.0	0.8			39.9
CF_3COCI		0.2	1.2		40.1
CF_3CHO	0.2			1.8	40.3
C_2H_4	0.2	0.2	2.4	1.3	40.5 ^c
$(\text{CN})_2$			1.7	1.5	40.5 ^c
FCN					41.2
$(\text{CF}_3)_3\text{COH}$		>1.3		1.8	41.7
$\text{CF}_3\text{C}\equiv\text{CH}$			0.5		42.2
FSO_2Cl			1.0		42.5
F_2NH		1.2		1.9	43.0
SO_2	1.2		1.4		43.0 ^c
COS		0.4		0.7	43.4
$(\text{CF}_3)_2\text{CO}$		0.5			43.7
F_2CO		1.3			45.0
$(\text{CF}_3)_2\text{O}$	0.2	1.0	1.5		45.2
SO_2F_2	0.9				46.0

^a All quantities are given in kcal mol⁻¹.^b $\delta\Delta G^\circ(\text{NH}_3) = \Delta G^\circ(\text{NH}_3) - \Delta G^\circ(\text{base})$.^c See also Ref. 2.

was used to measure the pressures of the reagents with the appropriate correction factors being applied to correct the gauge readings for the different ionization cross-sections of the various compounds.^{18,19}

Each equilibrium was examined several times with mixture ratios of B_0 and B_i which typically varied by a factor of 10.

Gibbs free energy changes $\delta\Delta G^\circ$ for each individual equilibrium are summarized in the ladder in Table 1. The uncertainty of the given values does not exceed 0.1–0.2 kcal mol⁻¹. Some additional proton transfer data are listed in Table 2. In both tables the $\delta\Delta G^\circ(\text{NH}_3)$

Table 2. Standard free energies (kcal mol⁻¹) of proton transfer reactions for some additional relatively weak bases

Base	Reference base	$\delta\Delta G^\circ$ ^a	$\delta\Delta G^\circ(\text{NH}_3)$ ^b
ClCN	AsH ₃	1.4	28.6 ^c
FCH ₂ CN	AsH ₃	0.5	26.1
BrCN	AsH ₃	-0.5	25.1
CF ₃ SO ₂ NH ₂	FCH ₂ CN	1.0	27.0
	CF ₃ COCH ₃	1.1	
CF ₃ COCH ₃	AsH ₃	0.6	26.1
HCOOCH ₂ CF ₃	AsH ₃	-0.5	25.1
CNCCH	FCH ₂ CN	-0.6	25.4
	CF ₃ COOCH ₃	1.5	
(CF ₃ CO) ₂ NH	FCH ₂ CN	-2.4	23.1
	CF ₃ CH ₂ CH ₃	0.8	
	(CF ₃ CO) ₂ CH ₂	1.5	
CF ₃ CH ₂ OCH ₃	ClCH ₂ CN	-0.2	21.8
(CF ₃ CO) ₂ CH ₂	CF ₃ CH ₂ OCH ₃	0.2	21.6
	CF ₃ COOC ₂ H ₅	1.5	
(CF ₃) ₃ CSC ₂ H ₅	CF ₃ COOC ₂ H ₅	-0.1	19.7
	(CF ₃) ₃ CCOOC ₂ H ₅	1.1	
(CF ₃) ₃ CCOOC ₂ H ₅	CF ₃ COOC ₂ H ₅	-1.6	18.4
	(CF ₃) ₃ CSC ₂ H ₅	1.1	
	CH ₃ CHO	0.6	
CF ₃ CH ₂ OC ₂ H ₅	CF ₃ COOC ₂ H ₅	-1.7	18.1
	CH ₃ CHO	0.1	
(CH ₃) ₃ SiCN	C ₂ H ₅ CHO	0.2	14.7
CF ₃ CONH ₂	C ₂ H ₅ CHO	-0.1	14.5
FCH ₂ COCH ₃	C ₃ H ₇ CHO	0.3	12.5
CF ₃ COCH ₂ COCH ₃	1,4-Dioxane	-1.5	8.9
	(CH ₃) ₂ CO	1.1	
CF ₃ CH ₂ OCH=CH ₂	(CH ₃) ₂ CO	-1.0	6.8
	AcOCH ₃	0.4	
(CH ₃) ₃ CCO ₂ C ₂ H ₅	(<i>i</i> -C ₃ H ₇) ₂ O	0.5	-1.5
	(CH ₃) ₂ NCN	-0.5	
(CH ₃) ₂ NCN	(<i>i</i> -C ₃ H ₇) ₂ O	1.3	-0.9
C ₂ H ₅ OCH=CH ₂	(C ₃ H ₇) ₂ S	-0.8	-4.8
	(C ₄ H ₉) ₂ S	0.1	
	CH ₃ OCON(CH ₃) ₂	0.6	
CH ₃ OSi(CH ₃) ₃	2-CH ₃ -THF	-0.5	0.8

^a Directly measured for the proton transfer equilibrium between a given and standard base. The positive sign of $\delta\Delta G^\circ$ means that the given base is weaker than the reference base.

^b See Table 1.

^c See also Ref. 2.

values of gas-phase basicities relative to the ammonia are also given. For water the $\delta\Delta G^\circ(\text{NH}_3)$ value of 37.5 kcal mol⁻² was used.

Chemicals. The following commercial samples of weak bases were used: CF₃CH₂OH, (CF₃)₂CHOH, (CN)₂C=C(CN)₂, CF₃CO₂H, (CF₃CH₂)₂O, CF₃CO₂C₂H₅, COS, SO₂, CF₃COCl and CF₃CO₂CH₃ were from Aldrich; CF₃CN, (CF₃)₃COH, CF₃COCl, F₂CO, (CF₃)₃CO, CF₃OCF₃, CF₃CCH, CF₃COF, SO₂Cl₂, SO₂F₂, CF₃SSCF₃ were from PCR; F₂NH was synthesized before each experiment from Ph₃CNF₂ (PCR) by treatment with concentrated H₂SO₄; CF₃CHO was liberated from its hydrate (PCR) by treatment with P₄O₁₀; (CF₃CO)₂CH₂ and (CF₃CO)₂NH were from Fluka; CF₃SO₂NH₂ was from Parish; CF₃COOCH₂CF₃ (b.p. 55.0 °C) was prepared from (CF₃CO)₂O and CF₃CH₂OH; HCOOCH₂CF₃ (b.p. 60 °C) was prepared from HCOOH and CF₃CH₂OH according to a reported procedure;²⁰ (CF₃)₃CCOOC₂H₅ and (CF₃)₃CSC₂H₅ were obtained from Professor L. German (Institute of Organoelement Compounds, Moscow); CF₃CH₂OCH₃ (b.p. 31.0 °C) and (CF₃)₂CHOCH₃ (b.p. 54–55 °C) were prepared by reacting CF₃CH₂ONa or (CF₃)₂CHONa with CH₃I according to a reported procedure;²¹ CF₃CH₂OC₂H₅ (b.p. 50.0 °C) was prepared by reacting CF₃CH₂ONa with C₂H₅Br; (CH₂F)₂CO was obtained from K & K; (F₂CH)₂CO was obtained from ICN Pharmaceuticals; ClCN was prepared by reaction²² of NaCN with Cl₂; FCH₂CN (b.p. 80 °C) was prepared from reacting a mixture of HCONH₂, KF, and ClCH₂CN as described in Ref. 23; CNCCH was donated by Dr S. Uejji; FCN was synthesized and donated by D. D. DesMarteau (Clemson University); and (CN)₂ was synthesized by reaction of a concentrated aqueous solution of KCN with a warm aqueous solution of CuSO₄. Ultra-high-quality methane (Matheson) was used.

RESULTS AND DISCUSSION

Comparison of the different low-pressure ICR basicity scales for compounds less basic than or comparable to water

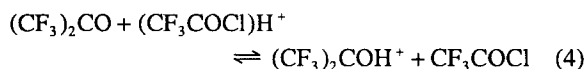
The FT-ICR gas-phase basicity scale for the weak bases constructed in the present work (see Table 1) could be compared with the combined ICR results of McMahon group. In order to compare the present results (at 373 K) with those in Refs 14–16 (at 298 K), a correction factor (1.26) for the ratio of the experimental temperatures was taken into account (i.e. the $\delta\Delta G$ values obtained in this work should roughly be 1.26 times larger than those of McMahon and co-workers^{14–16}). The straightforward comparison of these ICR basicity scales of different origins can be performed for either the basicity range from SO₂F₂ to CF₃CH₂OH or from SO₂F₂ to H₂S. From

Table 1, it is seen that in this work the overall span of the gas-phase basicity range between first two compounds is $11.6 \text{ kcal mol}^{-1}$, whereas McMahon and co-workers reported for the combined interval of $9.5 \text{ kcal mol}^{-1}$, which corresponds to a temperature ratio of 1.20, i.e. less than 4% or $0.5 \text{ kcal mol}^{-1}$ different from the expected value. Therefore, it could be concluded that despite the differences in the instrumentation, temperatures of the experiment and experimental techniques for the elimination of the effect of traces of water, etc., the results of our group and those of McMahon and co-workers¹⁴⁻¹⁶ are virtually identical. In even better agreement are the parallel basicity ladders between SO_2F_2 and $(\text{CF}_3)_3\text{COH}$ [$\delta\Delta G_{373}^\circ = 4.3 \text{ kcal mol}^{-1}$ and $\delta\Delta G_{298}^\circ = 3.5 \text{ kcal mol}^{-1}$ (ratio 1.23)] and between SO_2F_2 and CF_3CN [$\delta\Delta G_{373}^\circ = 6.9$ and $5.4 \text{ kcal mol}^{-1}$ (ratio 1.24)]. Finally, less strictly, the basicity gap between SO_2F_2 and H_2S as measured in this work ($12.1 \text{ kcal mol}^{-1}$) and by McMahon and co-workers ($10.2 \text{ kcal mol}^{-1}$) can also be compared. One can see that the ratio of these two estimates (1.19) is close to the ratio of the temperatures at which the ICR experiments were performed in our laboratories and those of McMahon and co-workers.

FT-ICR vs high-pressure mass spectrometric gas-phase proton transfer equilibria measurements for weak bases from H_2S to SO_2F_2

The HPMS gas-phase basicity (at 400 K) between H_2S and SO_2F_2 covers¹⁷ $19.7 \text{ kcal mol}^{-1}$, which exceeds significantly the above-mentioned difference in their basicities as determined by the ICR techniques¹⁴⁻¹⁶ (see above). Also, the expected ratios, as calculated from the differences in the corresponding experimental temperatures are, respectively, $400/373 = 1.07$ and $400/298 = 1.34$, i.e. roughly 1.4–1.5 times lower. This means that in that range of basicities the two parallel gas-phase basicity ladders between H_2S and SO_2F_2 differ from each other significantly even after taking into account the reported differences in the temperatures of the experiments. An even larger difference ($23.9 \text{ kcal mol}^{-1}$ or a *ca* 20% increase as compared with Ref. 17) was reported for this pair of bases in Ref. 8c. The major contributions to this discrepancy stem from the following proton transfer equilibria:

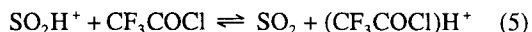
(a) From the direct (one-step) HPMS experiments, $\delta\Delta G^\circ = 7.4 \text{ kcal mol}^{-1}$ was reported¹⁷ for the equilibrium



whereas combining the $\delta\Delta G^\circ$ values for the ICR basicity ladder from the present work leads to $\delta\Delta G^\circ = 3.6 \text{ kcal mol}^{-1}$. In our low-pressure

experiments, extensive fragmentation occurred in the case of CF_3COCl . Along with the ions BH^+ and CF_3^+ (m/z 69), COCl^+ (m/z 63 and 65) ions are observed.

(b) The direct HPMS results give $\delta\Delta G^\circ = 5.5 \text{ kcal mol}^{-1}$ for the equilibrium



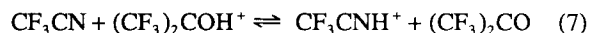
whereas our FT-ICR value obtained from summing $\delta\Delta G^\circ$ values is $2.9 \text{ kcal mol}^{-1}$. It should be mentioned that the formation of COCl^+ fragments with m/z 65, identical with the m/z for protonated SO_2 , might cause some complications in the direct measurements of that equilibrium.

(c) In a direct HPMS experiment, $\delta\Delta G^\circ = 5.2 \text{ kcal mol}^{-1}$ for the following proton transfer equilibrium:



was reported. The results of this work (combined $\delta\Delta G^\circ$ value = $2.6 \text{ kcal mol}^{-1}$) and the earlier ICR experiments of McMahon and co-workers¹⁴⁻¹⁶ (combined $\delta\Delta G^\circ = 1.5 \text{ kcal mol}^{-1}$) are at variance with those findings.

(d) For the equilibrium



based on the direct HPMS experiment $\delta\Delta G^\circ = 10.3 \text{ kcal mol}^{-1}$ was reported.¹⁷ In Ref. 8c this gap was revised upward by $0.9 \text{ kcal mol}^{-1}$. Combining the $\delta\Delta G^\circ$ values for stair-stepping overlaps measured by the ICR technique in this work and in earlier work by McMahon and co-workers¹⁴⁻¹⁶ leads correspondingly to $\delta\Delta G^\circ = 5.1$ and $5.0 \text{ kcal mol}^{-1}$ instead of expected values 9.6 and $7.7 \text{ kcal mol}^{-1}$ based on the differences in experimental temperatures.

We cannot provide any reasonable explanation for this disagreement between ICR and HPMS results. The origin of the discrepancy between the results of their earlier ICR work¹⁴⁻¹⁶ and those obtained by HPMS^{8c, 17} was never discussed by McMahon and co-workers. However, we note that the above-cited HPMS¹⁷ results would be in reasonable agreement with the ICR spectroscopic results from this work and from earlier works of McMahon and co-workers¹⁴⁻¹⁶ if the experimental temperature in the HPMS experiments¹⁷ was about 1.4–1.5 times higher than reported.

Evidently, future additional experiments will be needed to resolve this dilemma.

F-substituted carbonyl compounds (acetones, aldehydes, acid halides, esters, acids)

For the F-substituted acetones, there is reasonably good agreement between the results from this work and the ICR results of McMahon and co-workers¹⁴⁻¹⁶ (see Table 3). Usually the difference between the two series of measurements does not exceed 1 kcal mol^{-1} .

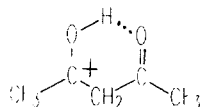
Table 3. Comparison of relative basicities $\delta\Delta G^\circ$ (kcal mol⁻¹, relative to acetone) of F-substituted acetones measured by the ICR technique in this work and literature values

Source	(CH ₃) ₂ CO	FCH ₂ COCH ₃	(FCH ₂) ₂ CO	CH ₃ COCF ₃	(F ₂ CH) ₂ CO	(CF ₃) ₂ CO
This work	0	4.6	11.5	19.0	27.6	35.2
Literature ¹⁴⁻¹⁶	0	3.9	10.4	16.8	28.0	34.6

The agreement between the results from those two independent series of ICR experiments for F₂CO, COS, CF₃CHO, and also for SO₂ and SO₂F₂, is also excellent. With exception of CF₃COOH, no more F-substituted carboxylic acids and/or their esters were involved in McMahon and co-workers' low-basicity scale.¹⁶ Therefore, no further direct comparisons with the present results are possible. Two features for the compounds in these classes should be mentioned. First, the findings that the substitution of F atom(s) in F₂CO by CF₃ groups results in a very modest increase in the basicity of the carbonyl compound (e.g. on going from F₂CO to (CF₃)₂CO $\delta\Delta G^\circ = 1.3$ kcal mol⁻¹, and between F₂CO and CF₃COF $\delta\Delta G^\circ = 0.2$ kcal mol⁻¹).¹⁶ This feature is also found for the corresponding esters: between FCOOC₂H₅ and CF₃COOC₂H₅ $\delta\Delta G^\circ = 0.4$ kcal mol⁻¹.

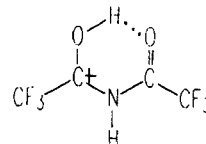
Also, a very slight increase of the basicity takes place ($\delta\Delta G^\circ = 1.6$ kcal mol⁻¹) when the CF₃ group in CF₃COOC₂H₅ is replaced by the more polar and more polarizable (CF₃)₃C group [$\sigma_F(\text{CF}_3) = 0.44$, $\sigma_F[(\text{CF}_3)_3\text{C}] = 0.61$, $\sigma_a(\text{CF}_3) = -0.25$, $\sigma_a[(\text{CF}_3)_3\text{C}] = -0.68$].²⁴ However, the present results show that a more significant basicity increase (ca 5 kcal mol⁻¹) accompanies the change of a CH₃ group for a (CH₃)₃C group (i.e. roughly the same increase in the polarizability of the substituent takes place²⁴ with fixed field/inductive effects) on going from CH₃COOC₂H₅ to (CH₃)₃CCOOC₂H₅ (Table 2).

The corresponding F-substituted derivatives of the acetylacetone family, owing to the extra stabilization of their protonated forms through an intramolecular H-bond, e.g.



are significantly more basic than the corresponding F-substituted monoketones. In a very rough approximation, one can assume that the basicity difference between a monoketone (e.g. acetone) and its acyl derivative (e.g. acetylacetone) can serve as a measure of the H-bonding chelation stabilization. For Me₂CO and acetylacetone the difference in their gas-phase basicities is 11.4 kcal mol⁻¹ and for CF₃COCF₃ and CF₃COCH₂COCF₃ 22.1 kcal mol⁻¹. Also, the same

effect must be characteristic of (CF₃CO)₂NH:



for which also intramolecular stabilization of the protonated form is possible. The gas-phase basicity of the diimide (CF₃CO)₂NH is only slightly weaker (by 1.5 kcal mol⁻¹) than (CF₃CO)₂CH₂ and their gas-phase acidities¹⁹ are also similar.

F-substituted methyl and ethyl ethers

The gas-phase basicity of these compounds was not studied earlier. As a literature² survey showed, the dialkyl ethers are usually by 1.5–4.0 kcal mol⁻¹ less basic than the corresponding dialkylketones. Thus, (CH₃)₂O is 4 kcal mol⁻¹ less basic than (CH₃)₂CO, (C₂H₅)₂O is 1.7 kcal mol⁻¹ less basic than (C₂H₅)₂CO, etc. The same rule seems to hold also for their perfluoromethyl analogs for which, according to the present results, CF₃COCF₃ is 1.5 kcal mol⁻¹ more basic than CF₃OCF₃. Unfortunately, the analogous comparison is not available for the other representatives of fluorine substituted ethers, (CF₃CH₂)₂O, CF₃CH₂OC₂H₅ and (CF₃)₂CHOCH₃. Rough additivity holds, however, for the consecutive substitution of ethyl group for CF₃CH₂ group(s) in (C₂H₅)₂O or in C₂H₅OCH₃ which decreases the basicity of the corresponding ethyl ether by approximately 15 kcal mol⁻¹ per one such substitution.

The substitution of a vinyl group for one of the ethyl groups in (C₂H₅)₂O (Table 2) results in a 9.1 kcal mol⁻¹ increase in basicity. The analogous substitution of the vinyl group for the ethyl group in C₂H₅OCH₂CF₃ also led to a very significant increase (11.3 kcal mol⁻¹) in the basicity.

Nitriles

The gas-phase basicity for a representative series of substituted nitriles XCN [X = CN²⁵, CF₃, (CN)₂C=C(CN), Cl, Br, F, C≡CH, FCH₂, (CH₃)₂N, (CH₃)₃Si] was measured or re-checked in this work.

The only common base with McMahon and co-workers' ICR basicity scale¹⁶ is CF_3CN , for which the agreement with the present work is excellent. The effect of substitution of the F atom in FCN by a CF_3 group is very similar to that for the substitution of the F atoms of fluorophosgene by CF_3 groups and leads also to a moderate increase ($2.1 \text{ kcal mol}^{-1}$) in basicity. On the other hand, the basicity of FCN is roughly equal to that of a cyanogen molecule $(\text{CN})_2$, whereas tetracyanoethylene is slightly more basic than CF_3CN but has virtually the same basicity as H_2O .

A three-parameter equation which includes the field/inductive, resonance and polarizability effects of the substituents attached to the CN group describes reasonably well the basicities of 25 different nitriles whose basicity relative to that of HCN covers more than 41 kcal mol^{-1} :

$$\delta_X \Delta G^\circ = (-3.0 \pm 1.0) + (38.1 \pm 1.6)\sigma_F + (25.0 \pm 1.5)\sigma_\alpha + (34.0 \pm 2.4)\sigma_R \quad (8)$$

$n = 25$; $R = 0.992$; $\text{s.d.} = 1.7 \text{ kcal mol}^{-1}$; $\delta \Delta G^\circ = 41.4 \text{ kcal mol}^{-1}$. Two major deviations were omitted in obtaining this regression equation, namely malononitrile ($-4.9 \text{ kcal mol}^{-1}$ deviation) and $(\text{CH}_3)_3\text{SiCN}$ ($-5.0 \text{ kcal mol}^{-1}$ deviation).

The relative contributions of F , P and R effects vary over a very wide range. As it was indicated earlier,^{5,6,26} for alkyl substituents the change of the $\delta_X \Delta G^\circ$ values is mostly due to the P effects. For electron acceptor groups, $\delta_X \Delta G^\circ$ values are determined by the interplay of F and P effects. For example, for CCl_3 group the P and F effects are roughly equal and have opposite signs, resulting in a negligible gross substituent effect (compared with the reference compound, HCN). For the $(\text{CH}_3)_3\text{C}$ group the net effect is mostly due to the P effects. In the case of Cl and Br substituents, all three contributions are important. For FCN, the field/inductive effect is dominant ($\text{ca } 16.4 \text{ kcal mol}^{-1}$) and the opposed ($-8.8 \text{ kcal mol}^{-1}$) resonance effect is significant. The R effects ($\text{ca } -18$ and $-23 \text{ kcal mol}^{-1}$, respectively) give major contributions to the increase in the basicity of H_2NCN and $(\text{CH}_3)_2\text{NCN}$.

Calculations

The basicity of difluoroammonia, F_2NH , appears to be close to those as for SO_2 and COS , i.e. roughly 43 kcal mol^{-1} weaker than that for ammonia. *Ab initio* quantum chemical calculations [Gaussian 92, HF/6-311G** basis set, fully optimized geometry, zero-point vibrational energy (ZPV) differences included] predict that $PA_{\text{calc}}(\text{NH}_3) = 208.3 \text{ kcal mol}^{-1}$ (see Refs 7 and 8 for discussion) and $PA_{\text{calc}}(\text{F}_2\text{NH}) = 159.4 \text{ kcal mol}^{-1}$. The difference, $\text{ca } 49 \text{ kcal mol}^{-1}$, is larger than the experimentally observed value [$\Delta PA(\text{NH}_3) = 43.0 \text{ kcal mol}^{-1}$].

Calculations on the same level of theory (ZPV corrections were introduced) predict $PA_{\text{calc}}(\text{FNH}_2) = 184.3 \text{ kcal mol}^{-1}$ (i.e. the decrease in basicity relative to ammonia is $\text{ca } 24 \text{ kcal mol}^{-1}$). Experimentally $(\text{CF}_3)_3\text{CNH}_2$ is less basic than NH_3 by $\text{ca } 17 \text{ kcal mol}^{-1}$ ($\text{ca } 7 \text{ kcal mol}^{-1}$ more basic than that predicted for FNH_2).² It appears that basicity in the XNH_2 series differs from that of carbonyl compounds (see above) where the replacement of an F atom for a $(\text{CF}_3)_3\text{C}$ group has little effect. The replacement of one hydrogen atom in NH_3 for a CF_3SO_2 group reduces its basicity much more significantly (by 27 kcal mol^{-1}).

As mentioned in the Experimental section, in this work the experimental proton affinity difference between water and ammonia was taken as equal to $37.5 \text{ kcal mol}^{-1}$.

At different times and different levels of MO theory, various calculated values of that gap have been suggested. Thus, Ref. 7 gives 'the best values' (large basis set, correlation and ZPV energy corrections) for the PA values of ammonia and water as 205.6 and 168.0 or $168.6 \text{ kcal mol}^{-1}$, respectively ($\Delta PA = 37.0$ or $37.6 \text{ kcal mol}^{-1}$). The calculations of Defrees and McLean²⁷ led to the similar results [$PA(\text{NH}_3) = 204.0$ and $PA(\text{H}_2\text{O}) = 165.1 \text{ kcal mol}^{-1}$; the difference is $38.9 \text{ kcal mol}^{-1}$], whereas Pople and co-workers'²⁸ G1 and G2 theory levels predict practically the same gap between basicities of ammonia and water, i.e. $39.4 \text{ kcal mol}^{-1}$.

Similar results could be obtained also by using a much lower (6-311G** basis set and ZPV energy corrections included) level of HF theory (this work). Thus, for the calculated gap between the PA s of ammonia ($208.3 \text{ kcal mol}^{-1}$) and water ($170.2 \text{ kcal mol}^{-1}$) a value of $38.1 \text{ kcal mol}^{-1}$ could be obtained. {Similar calculations (6-311G**, ZPVE included) show that the effect of successive introduction of fluorine atoms into H_2O [$PA_{\text{calc}}(\text{FOH}) = 135.0$, $PA_{\text{calc}}(\text{F}_2\text{O}) = 105.6 \text{ kcal mol}^{-1}$, oxygen protonation is favored] is predicted to deviate from additivity only by 8%.} Keeping in mind the significant uncertainties (up to $3\text{--}4 \text{ kcal mol}^{-1}$) of the experimental PA values of water and ammonia,^{1,2,6-10} and the still ongoing discussion on that matter, all these theoretical estimates of the basicity gap between these two compounds should be considered virtually indistinguishable from each other. Therefore, further refinements of experimental measurements and/or theoretical calculations are needed.

ACKNOWLEDGMENTS

We are indebted for the support in part of the Gaussian 92 calculations by the Office of Academic Computing at University of California, Irvine. Ilmar Koppel and Frederick Anvia would like to dedicate their

contribution to this paper to Professor Robert W. Taft on the occasion of his 70th birthday.

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