

ions is the spin distribution between the two equivalent π systems. Ample evidence now exists⁵ that such a distribution is governed by the association of the radical anion with its positively charged counterion. In the case of $1\cdot^-$ to $4\cdot^-$, the symmetry of an ion pair is reduced relative to that of the corresponding unassociated species, because the cation K^+ resides in an external position below or above the plane of either π system.^{5,6} Concomitantly, the spin population is shifted to that π system which is proximate to the counterion. Since the cation migrates between the two equivalent external positions, this effect will be averaged out when such a migration is rapid on the ESR time scale. Full symmetry of the radical anion will then be apparent, along with a time-averaged spin distribution between the two π systems.

Inspection of the data in Table I reveals that, with DME as solvent, such an equal spin distribution is found in all four radical anions. Changing to THF leads to an accumulation of spin population on one benzene ring in $1\cdot^-$, but it has no appreciable influence on the uniform spin distribution in $2\cdot^-$, $3\cdot^-$, and $4\cdot^-$. A shift of spin population to one naphthalene π system in $2\cdot^-$ and $3\cdot^-$ is effected only by the use of MTHF, whereas in $4\cdot^-$ even this solvent fails to bring about a measurable deviation from an equal spin distribution between the two anthracene π systems. Two factors thus determine the π -spin distribution in $1\cdot^-$ to $4\cdot^-$: (1) solvent, and (2) extension of the π systems. This result illustrates once more the relevance of the association between

the radical anion and its counterion, since the two factors are known to affect the stability and lifetime of such an ion pair. The spin population exhibits *more* tendency to accumulate on one π system when the association becomes *stronger*, i.e., with (1) the *decreasing* solvation of the cation in the order DME > THF > MTHF and (2) the *increasing* π -charge localization in the sequence $4\cdot^- < 2\cdot^- \approx 3\cdot^- < 1\cdot^-$.

Acknowledgment. We thank Professor H. H. Wasserman and Dr. P. M. Keehn, Yale University, for the samples of **2** and **3**, and Dr. G. Kaupp, University of Freiburg (Germany), for that of **4**. We are also obliged to Dr. B. Kowert, U.C.L.A., for carrying out some preliminary experiments. The work was supported by the Schweiz. Nationalfonds (Project No. 2.163.74).

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Gas-Phase Basicities and Proton Affinities of Compounds between Water and Ammonia and Substituted Benzenes from a Continuous Ladder of Proton Transfer Equilibria Measurements

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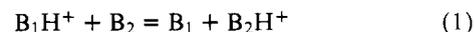
Abstract: The proton transfer equilibria $B_1H^+ + B_2 = B_1 + B_2H^+$ involving some 30 bases B with proton affinities between water and ammonia were measured with a pulsed electron beam high-pressure ion source mass spectrometer. A complete ladder of equilibria linking water to ammonia and often involving multiple cycles was obtained. Using the external standard PA(isobutene) = 193 kcal/mol (Lossing, Semeluk, and Tsang) one obtained absolute values for the proton affinities of the compounds. These include: water 169, hydrogen sulfide 172, CH_3OH 182.1, benzene 183.4, acetaldehyde 185.4, ethanol 186.8, dimethyl ether 190.1, acetone 194.6, diethyl ether 198.1, and ammonia 200.7 kcal/mol. The above values were obtained by assuming $\Delta G^\circ = \Delta H^\circ$. Corrections for ΔS changes due to rotational symmetry numbers are considered for some of the compounds. The basicities of benzene and some singly and multiply halo-substituted benzenes are briefly discussed.

A very large number of compounds have proton affinities which fall between those of water and ammonia. This includes organic oxygen compounds like alcohols, ethers, aldehydes, ketones, and acids as well as unsaturated and aromatic hydrocarbons.

Many previous determinations of proton affinities for compounds in this region and particularly of oxygenated compounds exist. The principal methods¹ used have been appearance potential measurements and the qualitative occurrence-nonoccurrence study of proton transfer reactions. The appearance potential method suffers from uncertainty regarding presence of excitation in the reaction products

and is therefore often not reliable. The occurrence-nonoccurrence technique provides only proton affinity orders and thus requires a large number of standards, i.e., proton affinities which have been determined by other methods. Since not many reliable standards exist, this often amounts to calibration to values obtained by appearance potentials.

Not long ago the gas-phase ion equilibrium method³ was applied to the study of proton transfer equilibria (eq 1) in ion cyclotron trapped ion sources,⁴ high-pressure mass spectrometers,⁵ and flowing afterglow



apparatus.⁶ Determination of K_1 leads to ΔG_1° via the equation: $\Delta G_1^\circ = -RT \ln K_1$. In general ΔS_1° is small ($\Delta S_1^\circ < 2$ eu) and largely due to changes of rotational symmetry numbers. Therefore ΔH_1° can be evaluated. The proton affinities of a large number of nitrogen compounds⁷ amines, pyridines, anilines, etc., were investigated with the equilibrium method. Since the equilibrium method gives only the proton affinity difference, viz., eq 2, again standard

$$\Delta H_1 = \text{PA}(\text{B}_1) - \text{PA}(\text{B}_2) \quad (2)$$

PA values obtained by other methods are required. However, since the equilibrium data give relative PA which are probably accurate to less than 0.2 kcal/mol only a few reliable standards are necessary.

As standard for the proton affinities of the nitrogen bases the $\text{PA}(\text{NH}_3) = 207$ kcal/mol⁸ was used. This value, which was the best available, had been obtained by an appearance potential technique in which the kinetic energy of the fragments was determined experimentally and used in a semi-empirical fashion to correct for the total energy of excitation. No extensive equilibria measurements have been made for compounds with proton affinities less than ammonia. The present work describes measurements which represent a complete chain of equilibria involving compounds between water and ammonia. In this manner, ammonia and all nitrogen bases with PA's higher than ammonia can be connected to other more reliable primary standards. But what is even more important, the whole range down to water becomes incorporated in a consistent set of equilibrium values.

Experimental Section

The measurements were made with a pulsed electron beam high-ion source pressure mass spectrometer of previously described design.⁹ A quadrupole mass analyzer was used in the present instrument.

Slowly flowing ultrahigh purity methane was used as carrier gas at 0.5–4 Torr. The two bases B_1 and B_2 were generally in the 10–200 mTorr range. The ratio B_1/B_2 was so selected as to make the ion ratio $\text{B}_1\text{H}^+/\text{B}_2\text{H}^+$ not deviate by more than two orders of magnitude from unity. The gas mixture methane, B_1 , and B_2 was prepared in 4-l. glass globe maintained at 150 °C by injecting the liquid bases B with calibrated syringes into 1 atm of methane. The flow from the globe to the ion source was regulated with an all metal valve. The ratio of B_1/B_2 was varied by the factor of 10 to ascertain that the equilibrium constant remains invariant. Nearly all measurements were made at 600 °K, since at lower temperatures often clusters BHB^+ become the dominant ions. Some measurements were also made at different temperatures to determine the entropy change of the reactions.

Results and Discussion

The ΔG_1° values obtained from the measured proton transfer equilibria (eq 1) are given in Table I. From the individual measurements a complete ladder of ΔG° values from water to ammonia was worked out which is also given in Table I. Assuming $\Delta G^\circ = \Delta H^\circ$ absolute proton affinities were obtained using the external standard $\text{PA}(\text{isobutane}) = 193$ kcal/mol. This value is based on the enthalpy of formation of $\Delta H_f(\text{tert-butyl}^+) = 169$ kcal/mol. This standard was selected because it is not too far off from ammonia whose proton affinity value we wished to establish with considerable accuracy. The enthalpy of formation of *tert*-butyl is based on the measurements of the ionization potential of the *tert*-butyl radical by Lossing and Semeluk¹⁰ and the heat of formation of the *tert*-butyl radical by Tsang.¹⁰

The two best heats of formation of the isopropyl ion, $\Delta H_f(i\text{-C}_3\text{H}_7^+) = 190$ kcal/mol¹¹ and 192 kcal/mol,¹⁰ lead to $\text{PA}(\text{propylene}) = 181$ and 179 kcal/mol. This is in as

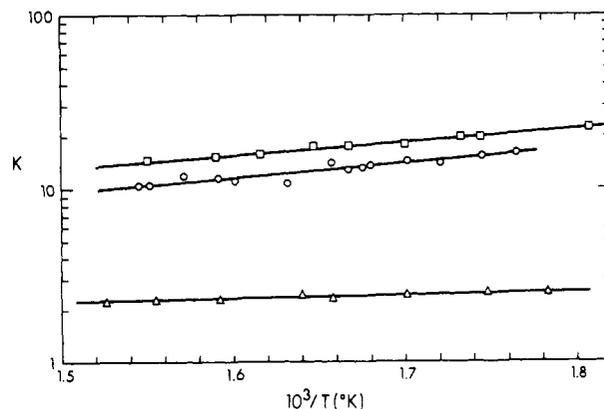


Figure 1. Temperature dependence of equilibrium constants for three proton transfer reactions. Acetone H^+ + ethyl acetate = acetone + ethyl acetate H^+ (\square); H_3O^+ + $\text{H}_2\text{S} = \text{H}_2\text{O} + \text{H}_3\text{S}^+$ (\circ); ethanol H^+ + methyl formate = ethanol + methyl formate H^+ (\triangle). Results from van't Hoff plots shown in Table II.

good an agreement as could be hoped for with the present value of 181 kcal/mol given in Table I.

Refaey and Chupka¹² have obtained a $\Delta H_f(\text{CH}_3\text{CHOH}^+) = 141.4$ kcal/mol from appearance potentials of the $\text{C}_2\text{H}_4\text{OH}^+$ ion from ethanol and from 2-propanol by photoionization. Since both processes correspond to a simple cleavage and are in agreement, it is likely that no excess energy was involved and that the heat of formation of the protonated acetaldehyde is reliable. This heat of formation leads to $\text{PA}(\text{acetaldehyde}) = 185$ kcal/mol which is in very good agreement with the present value of 185.4 kcal/mol.

On the basis of the above quoted good agreement with three good standards we believe that the absolute proton affinities given in Table I are generally accurate to ± 2 kcal/mol. The error in the relative values is probably much smaller, i.e., around 0.2–0.5 kcal/mol. Evidence for this is the generally good agreement in the multiple thermodynamic cycles (see Table I).

An examination of the proton affinities in Table II shows that many of them are in fair agreement with previous determination. Large discrepancies are found only in the region of ammonia and immediately below ammonia, i.e., down to ethyl formate. These literature data are due to Franklin^{2,8} and Long and Munson.¹³ The values for ammonia and acetone of Franklin^{2,8} are believed unreliable as pointed out in the introduction. Long and Munson's values obtained by the occurrence–nonoccurrence technique are basicity orders which were interpolated by Munson¹³ into Franklin's^{2,8} ammonia and acetone values.

It is interesting to note that the present $\text{PA}(\text{diethyl ether}) = 198.1$ kcal/mol is in agreement with an early value of 199 kcal/mol determined by Beauchamp.¹⁴

The temperature dependences of the equilibrium constants of three proton transfer reactions shown in Table II measured in the temperature range 550–670 °K are shown in Figure 1. A least-squares fit of the data gave the ΔS° and ΔH° values quoted in Table II.

The experimentally measured ΔS° are less than 1 eu. The resulting ΔH° values are within 0.3 kcal of the ΔG° . We believe these to be typical results, although in some cases the creation of restricted internal rotation, internal hydrogen bonding,¹⁵ or large changes of rotational symmetry numbers may produce larger entropy changes. Entropy changes due to change of rotational symmetry numbers are easiest to predict. For the above three reactions a change of symmetry number occurs for reaction 3. This $\Delta S_{\text{rot sym}} = R \ln \frac{1}{2} = -1.38$ eu. The experimental entropy, $\Delta S_{\text{exptl}} = 0.16$

Table I. Free Energies of Proton Transfer and Proton Affinities of Water, Ammonia, and Compounds in between^a

Compd	Directly measured ΔG°_{600}	ΔG°_{600} ^b NH ₄ ⁺ to B	Proton affinity	
			This work	Lit.
Ammonia		0	200.7	207 ⁸
<i>n</i> -Propyl acetate		2.2	198.5	207 ¹³
Diethyl ether		2.6	198.1	205, ¹³ 199 ¹⁴
Ethyl acetate		2.7	198.0	205 ¹³
Methyl acetate		5.3	195.4	202 ¹³
Acetone		6.1	194.6	188, ² 202, ¹³ 190 ¹⁴
Isobutene		7.7	(193.0)	193 ¹⁰
<i>n</i> -Propyl formate		9.0	191.7	198 ¹³
Ethyl formate		9.5	191.2	198 ¹³
Dimethyl ether		10.6	190.1	187, ² 190, ¹³ 186 ¹⁴
Propionic acid		11.2	189.5	187 ¹⁴
Propionaldehyde		12.8	187.9	187 ¹⁴
Methyl formate		12.9	187.8	188 ¹³
Acetonitrile		13.3	187.4	186, ² 186 ¹⁴
Acetic acid		13.3	187.4	188 ¹³
Ethanol		13.9	186.8	187, ¹³ 186 ¹⁴
Acetaldehyde		15.3	185.4	183, ¹⁴ 185 ¹²
Benzene		17.3	183.4	178, ^c 183 ⁸
Fluoroacetic acid		17.8	182.9	

Table I (Continued)

Compd	Directly measured ΔG°_{600}	ΔG°_{600} ^b NH ₄ ⁺ to B	Proton affinity	
			This work	Lit.
Fluorobenzene		18.2	182.5	
Chloroacetic acid		18.3	182.4	
Chlorobenzene		18.3	182.4	
Methanol		18.6	182.1	179, ^c 180 ¹⁴
<i>m</i> -Difluorobenzene		19.2	181.6	
Propylene		19.7	181.0	179, ¹⁰ 181 ¹¹
1,3,5-Trifluorobenzene		19.7	181.0	
Formic acid		22.6	178.1	178, ^c 175 ¹³
Hydrogen sulfide		28.7	172.0	170, ⁸ 170 ¹⁴
Trifluoroacetic acid		30.4	170.3	167 ¹³
Water		31.8	168.9	165, ⁸ 165, ¹³ 164 ^d

^a Values given in kcal/mol based on equilibria measurements $B_1H^+ + B_2 = B_1 + B_2H^+$ at 600 K. Assumption $\Delta H = \Delta G$. Absolute values obtained with PA(isobutene) = 193.0 kcal/mol based on $\Delta H_f/(CH_3)_3C^+ = 169$ kcal/mol (Lossing, Semeluk, and Tsang¹⁰). Vertical arrows indicate directly measured equilibria. Numbers between arrows give corresponding ΔG° at 600 K. ^b ΔG°_{600} NH₄⁺ to B relates to proton transfer reaction $NH_4^+ + B = NH_3 + BH^+$. ^c S. L. Chong and J. L. Franklin, *J. Am. Chem. Soc.*, **94**, 6347, 6630 (1972). ^d J. L. Beauchamp and S. K. Buttrill, *J. Chem. Phys.*, **48**, 1783 (1968).

Table II. Experimental Entropy Changes for Some Proton Transfer Reactions^a

Reaction	ΔG°_{600}	ΔG_{300} ^b	ΔH^c	ΔS_{exptl} ^d	$\Delta S_{\text{rot sym}}$ ^e
(3) $(CH_3)_2COH^+ + CH_3CO_2C_2H_5 = (CH_3)_2CO + CH_3CO_2HC_2H_5^+$	-3.4	-3.4	-3.3	+0.16	-1.38
(4) $H_3O^+ + H_2S = H_2O + H_3S^+$	-3.0	-3.4	-3.7	-1.0	0
(5) $C_2H_5OH_2^+ + HCO_2CH_3 = C_2H_5OH + H_2CO_2CH_3^+$	-1.0	-1.0	-1.0	0.1	0

^a Based on experimental data from Figure 1; ΔG and ΔH values in kcal/mol; ΔS values in eu. ^b From least-squares fit standard deviation ± 0.3 kcal/mol. ^c From least-squares standard deviation approximately ± 0.3 kcal/mol. ^d ΔS from least-squares fit standard deviation approximately ± 0.4 eu. ^e ΔS due to change of rotational symmetry numbers.

eu does not reflect this symmetry change. It is not clear whether the experimental measurement is caused by some other real effects or is in error. Such small entropy changes are difficult to measure particularly over the experimentally limited temperature range. The same holds true for reaction

Table III. Basicities of Substituted Benzenes

Compd B	$\Delta G,$ ^a	$\sigma_B/\sigma_{BH^+} + T\Delta S_{\text{rot sym}}$ ^c	$\Delta H,$ ^d
	kcal/mol		
<i>tert</i> -Butyl	-7.7 ^b	1	-1.5
<i>n</i> -Butyl	-7.5 ^b	1	-1.5
Isopropyl	-7.5 ^b	1	-1.5
<i>n</i> -Propylbenzene	-7.1 ^b	1	-1.5
Ethylbenzene	-6.2 ^b	1	-1.5
Toluene	-5.4 ^b	2	-1.1
Benzene	0	12	0
Fluorobenzene	+0.9 ^e	2	-2.1
Chlorobenzene	+1.0 ^e	2	-2.1
<i>m</i> -Difluorobenzene	+1.9 ^e	2	-2.1
1,3,5-Trifluorobenzene	+2.4 ^e	6	-0.8

^a Free energy change for reaction: benzene $H^+ + B = \text{benzene} + BH^+$. ^b Values correspond to McIver¹⁸ ΔG°_{300} . ^c Entropy change due to rotational symmetry numbers: $\Delta S = R \ln \sigma_B/(12\sigma_{BH^+})$. ^d Approximate value obtained from ΔG° and $T\Delta S_{\text{rot sym}}$. ^e From Table I, $T = 600$ K.

4 where the $\Delta S_{\text{exptl}} = -1$ eu suggest different symmetries of H_3O^+ and H_3S^+ . The ΔS_{exptl} could be explained by the assumption H_3S^+ planar, H_3O^+ nonplanar, but this is not

supported by what is known of the geometry¹⁶ of H₃O⁺. Therefore we think that the ΔS_{exptl} is not accurate enough.

The ΔG°_{600} data in Table I give a proton affinity difference between water and ammonia of 31.8 kcal/mol, with an estimated total error of 1 to 2 kcal/mol. This difference corrected for the ΔS change due to rotational symmetry numbers ($RT \ln (18/24) = -0.34$ kcal/mol (at 600 °K)) becomes 31.5 kcal/mol. Since the symmetry numbers involved in proton transfer from water to isobutene cancel, the symmetry correction should be applied to the difference between isobutene and ammonia. Thus the most probable proton affinities for these three compounds are: PA(H₂O) = 168.9 \approx 169, PA(isobutene) = 193, and PA(NH₃) = 200.4 kcal/mol.

Substituent effects on the basicities of oxygen compounds and most other compounds in Table I have been considered previously^{7,13} and need not be treated here. The only new compounds are the benzenes. Protonation of these compounds leads to the benzenium ions which have been studied quite extensively in solution.¹⁷ Recently McIver¹⁸ has determined the relative gas-phase basicities of alkyl-substituted benzenes by measuring proton transfer equilibria with an ICR spectrometer. Since his data involved methyl formate as a reference compound the present results for methyl formate, benzene, and the halobenzenes can be connected to his values. The resulting basicities are shown in Table III. Considering only the ΔG changes one finds that the halo substituents decrease the basicity of benzene. However, the deprotonation of benzene is connected with a large symmetry number change with a ratio of symmetry numbers equal to 12. The energy changes corrected for rotational symmetries are shown in the last column of Table III. These numbers show that single fluoro or chloro substitution enhances somewhat the basicity.¹⁹ Introduction of a second fluorine in the meta position reduces the basicity to almost that of benzene and the third fluorine makes 1,3,5-trifluorobenzene less basic than benzene. This reversal can be understood on the basis of the opposing tendencies of the fluorine substituent, which by π donation stabilizes while by σ withdrawal destabilizes the protonated base. Since the π donation effect decreases faster than the σ withdrawal with

multiple substitution, a reversal can be expected.

Unfortunately the above entropy correction includes only rotational symmetry numbers, yet other small entropy effects might also be involved. This underlines the desirability for good entropy corrections in all equilibria measurements. It is hoped that better experimental entropy measurements and theoretical considerations will lead to a further increase of the usefulness of the gas-phase equilibria data.

Acknowledgment. The present work was supported by funds from the Canadian National Research Council. Some of the ΔG_{600} measurements given in Table I were performed by Mr. Yan Lau.

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- (19) A measurement of the temperature dependence between 300 and 600 °K of the equilibrium constant for the reaction benzene H⁺ + fluorobenzene = benzene + fluorobenzene H⁺ which was just completed by Mr. Yan Lau in our laboratory gave a ΔS° value in close agreement with that predicted by symmetry number changes (see Table III).

Crossed Beam Studies of Ion-Molecule Reactions in Methane and Ammonia

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Abstract: The dynamics of the following ion-molecule reactions were studied by cross beam techniques at relative (CM) energies of 2–9 eV: CH₄⁺ + NH₃ → NH₄⁺ + CH₃ (1); CH₄⁺ + NH₃ → CNH₅⁺ + H₂ (2); NH₂⁺ + CH₄ → CNH₄⁺ + 2H (3) CH₃⁺ + NH₃ → CNH₄⁺ + 2H (4). Reaction 1 occurs by a rebound mechanism with two peaks in the forward direction. Labeling studies show proton transfer with no isotopic scrambling. Reaction 2 is direct with the H₂ expelled from the CH₄⁺. In (3) and (4), the product internal energy is sufficiently high that dissociation of the H₂ is likely. Labeling studies show limited isotopic scrambling.

Introduction

Using the crossed beam apparatus EVA, we have measured the product ion velocity and angular distributions for the following ion-molecule reactions in the relative (CM)

energy range of 2–9 eV:

