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Protonation and Site of Protonation of Anilines. Hydration and Site of Protonation after Hydration

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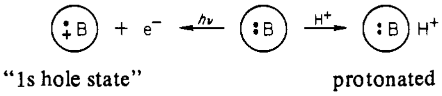
Abstract: The gas-phase basicities (proton affinities) of 15 substituted anilines were determined by measuring proton-transfer equilibria with a pulsed electron beam high-pressure mass spectrometer. The gas-phase basicities are compared with experimentally measured ionization energies of the nitrogen 1s electron. A straight-line relationship is observed for the substituted anilines that are nitrogen protonated. This line includes aniline. *m*-NH_2-, *m*-MeO-, *m*-MeS-, *m*-OH-, and *m*-C_2H_5-aniline were found to have higher gas-phase basicities than those prediced by the linear relationship. These compounds are ring protonated. The energies for proton transfer from ring to nitrogen for these compounds can be estimated from the straight-line correlation. Hydration equilibria $BH^+ + OH_2 = BHOH_2^+$ were measured for several protonated anilines BH^+. The BH^+ which are normally nitrogen protonated have hydrogen bonding energies to water which increase approximately linearly with the acidity of BH^+. The ring-protonated BH^+ do not fit this relationship; they have lower hydration energies. Hydration induces proton transfer from ring to nitrogen for *m*-MeS, *m*-OH, and *m*-C_2H_5. The hydrated *m*-MeO and *m*-NH_2 remain ring protonated. The water molecule is expected to hydrogen bond to the neutral NH_2 group of these two ions. The two hydrogens of the amino group carry fractional positive charges which make this a relatively strong hydrogen bond. The gas-phase basicities are also compared with the aqueous basicities. An approximate linear dependence is obtained for the nitrogen-protonated ions. The gas-phase-substituent effect is attenuated by a factor of 4 in liquid water.

The gas-phase basicity (proton affinity) of ammonia is some 20 kcal/mol higher than that of benzene. Therefore one might have expected that aniline, a well-known nitrogen base in aqueous solution, should have a considerably larger proton affinity for N protonation than for ring protonation. It was a surprise when an examination of experimentally determined gas-phase basicities showed that aniline may be ring protonated in the gas phase.[1] Protonation of benzene represents a prototype of electrophilic attack of the benzene ring. The proton affinities of monosubstituted benzenes which protonate on the ring may be expected to obey a linear relationship when plotted vs. the σ_p^+ constants of the substituents. A plot of this type showed[1] that Cl, F. Me, Et, OH, OMe, and NH_2 do give a linear plot while CHO, CN, and NO_2 lead to proton affinities which are considerably higher, i.e., fall considerably above the line. It was concluded that the first group protonates on the ring while the second protonates on the substituent.[1] The first group consists of σ- or π-electron-donating substituents which stabilize the benzenium ions, while the opposite is true for the electron-withdrawing second group. The stabilization of the benzenium ion by the electron-donating substituent can be very large, for example, the proton affinity of aniline for ring protonation is some 27 kcal/mol higher than that of benzene.[1] Other qualitative arguments indicated that the stabilities of the ring and nitrogen-protonated aniline must be very similar,[1] i.e., within a couple of kilocalories/mole.

A later analysis by Hehre, Taft, and co-workers,[2] using a combination of STO-3G calculated energy changes for isodesmic proton-transfer reactions and experimentally determined proton affinities of substituted anilines, identified the nitrogen-protonated aniline as being some 1–3 kcal/mol lower in energy than the ring-protonated compound. While this work provided valuable new insights, some of the arguments were based on energy differences of a few kilocalories/mole. The prediction of such small differences with STO-3G and not fully optimized geometries may not be reliable, even when isodesmic processes are used. Therefore information on the site of protonation in aniline and substituted anilines, based on some experimental method, is of interest.

Recently we have examined correlations between gas-phase basicity and core binding energies ($\Delta G°$ and E_B) (see eq 1) and in particular the circumstances under which these correlations fail.[3] These studies[3a] provided examples which confirmed earlier suggestions[4] that failure to correlate is observed when (a) the sites of photoionization and protonation are different and (b) a significant molecular geometry change accompanies protonation which cannot be monitored by the fast photoionization process. Herein we present an application of the method correlating N_{1s} E_B and experimental gas-phase $\Delta G°$ values for a series of anilines.



(1)

The correlation of N_{1s} E_B and gas-phase basicity values given in Results and Discussion shows that some of the substituted anilines are N protonated while others are ring protonated. In aqueous solution all these anilines are N protonated. The change of site of protonation from ring to nitrogen in aqueous solution is an expected result since strong hydrogen bonds are formed between water molecules and an anilinium ion, while the interaction of water with the ring-protonated ions should be very weak because of the extensive charge delocalization present in these ions. If only one water molecule is available for hydration, the difference in bonding to the water molecule may or may not be large enough to change the site of protonation. To examine for the operation of this effect, we have measured monohydration equilibria in the gas phase as shown in eq 2 for several protonated substituted anilines. The hydration energies obtained allow one

$$BH^+ + OH_2 = (BHOH_2)^+ \qquad (2)$$

to determine whether a change of the protonation site has occurred or not and provide examples of hydration energies of both nitrogen- and ring-protonated anilines.

Experimental Section

The gas-phase basicities were determined by measuring the equilibrium constants for the proton-transfer reaction (eq 3), with a pulsed

$$B' + BH^+ = B'H^+ + B \qquad (3)$$

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Table I. Gas-Phase Basicities of Anilines

X	$\Delta G°_{PT}(600)^a$	$\Delta G°_{PT}(300)^b$	$\Delta H_{PT}{}^c$	$\sigma_B/\sigma_{BH^+}{}^d$	$\Delta E_{STO\text{-}3G}$	$\Delta G°_{PT}(N)^f$	$\Delta E_B(N_{1s})^g$
m-NH$_2$	-12.2^g	-11.2	-10.1^h	2^h $(2/3)^i$	-18.2^h	-3.5	-3.5
m-MeO	-7.3^h	-6.7 $(-5.2)^j$	-6.0^h	1^h $(1/3)^i$		-2.0	-1.8
o-NH$_2$	-5.6^i	-5.2^i	-4.8^i	$2/3^i$			
m-MeS	-4.7^h	-4.1^h	-3.4^h	1^h $(1/3)^i$		-1.5	-1.4
o-NH$_2$	-3.9^i	-3.5^i	-3.1^i	$2/3^i$			
m-OH	-3.9^h	-3.3^h	-2.6^h	1^h $(1/3)^i$		-2.5	-2.5
m-Et	-3.7^h	-3.1^h	-2.4^h	1^h $(1/3)^i$		-3.0	-2.7
m-Me	-3.0^h	-2.4^h $(-2.8)^j$	-1.7^h	1^h $(1/3)^i$	-1.3^h	-2.6	-2.5
d	0.0^i	0.0^i	0.0^i	$1/3^i$			0.0
m-I	0.9^i	0.9^i	0.9^i	$1/3^i$			$+2.3$
m-Br	2.2^i	2.2^i	2.2^i	$1/3^i$			$+3.0$
m-Cl	3.1^i	3.1^i $(2.9)^j$	3.1^i	$1/3^i$			$+4.8$
m-F	3.2^i	3.2^i $(3.4)^j$	3.2^i	$1/3^i$	$+3.8^i$		$+3.7$
m-CF$_3$	6.1^i	6.1^i	6.1^i	$1/3^i$	$+5.0^i$		$+7.6$
m-CN	9.6^i	9.6^i	9.6^i	$1/3^i$	$+9.0^i$		$+11.8$

[a] $\Delta G°_{PT}(600)$ in kcal/mol corresponds to standard free energy change at 600 K for reaction $B_0H^+ + B = B_0 + BH^+$ where B_0 is aniline and B is substituted aniline. Basicity increases from botton to top of table. From experimental measurements in Figure 1. [b] Same reaction as in *a* but at 300 K. Estimated value based on $\Delta G°_{PT}(600)$ and $\Delta S \approx R \ln [\sigma(B_0H^+)\sigma(B)/\sigma(B_0)\sigma(BH^+)]$. [c] Same reaction as in *a*. Estimated value based on entropy change, see footnote *b*. [d] Symmetry numbers for external and internal rotations used for estimate of entropy change (see footnote *b*). [e] STO-3G calculated energy change for proton transfer reaction $B_0H^+ + B = B_0 + BH^+$ (Hehre and Taft).[2] [f] Free energy change for proton transfer $B_0H^+ + B = B_0 + BH^+$ where BH^+ is *nitrogen* protonated. The N-protonated BH^+ is less stable than the ring-protonated isomer. Obtained from correlation in Figure 2. [g] Experimental N_{1s} electron binding energies. $\Delta E_B = E_B - E_{B_0}$ (kcal/mol). Additional ΔE_B used in Figure 2 were taken from Brown.[3a] [h] BH^+ is ring protonated. [i] BH^+ is nitrogen protonated. [j] Taft,[2] ICR equilibria measurements at 300 K.

electron beam high ion source pressure mass spectrometer. The apparatus and method have been described previously.[5,6] Most of the measurements were made at 600 K where there is no interference from proton held dimers BHB^+ which dominate at low temperatures. The $\Delta G°_3$ values shown in Figure 1 were obtained from the equilibrium constants K_3 with use of the equation $\Delta G° = -RT \ln K$. The pressure ratio B/B′ was generally varied by a factor of 5 in order to ascertain that K_3 is independent of the B and B′ pressures used.

The measurement of the *p*-NH$_2$- and *o*-NH$_2$-aniline basicities had been attempted earlier in connection with work on the diaminonaphthalenes.[6] at that time the measurements (at 600 K) were not successful. The protonated bases were not reaching equilibrium and the formation of an ion of molecular weight lower by two mass units was observed. This time we tried a lower temperature, 433 K. The unwanted ion was not observed for the *o*-NH$_2$ compound but was still present for the para isomer. However, at this temperature both of the protonated isomers were reaching equilibrium in the respective proton-transfer measurements with other bases.

The equilibrium constants for monohydration reaction 2 of the protonated bases were determined with the same apparatus as the proton-transfer equilibria. The measurements were in all respects similar to those performed in previous work involving hydration of protonated pyridines.[7] Only traces of the anilines ($\sim 10^{-2}$ mtorr) were used in $\sim$4 torr CH_4 and 10–20 mtorr H_2O. Under these conditions, the methane-produced CH_5^+ and $C_2H_5^+$ react rapidly with water leading to H_3O^+. This ion attaches other water molecules such that the clustering equilibria $H^+(H_2O)_{n-1} + H_2O = H^+(H_2O)_n$ establish rapidly, i.e., within some 50 μs. The proton hydrates then proton transfer to the aniline. Generally the initial protonated aniline observed was the monohydrate BH^+OH_2, which then produced BH^+ and OH_2 until the BH^+ and BH^+OH_2 reached equilibrium.

Neat water vapor at pressures 1–3 torr was used with the *m*-NH$_2$-, *m*-MeO-, and *m*-MeS-aniline, since the hydration interaction for these protonated bases was very weak and could not be measured at lower water pressures.

The N_{1s} E_B energies were obtained as previously described[3] and are referenced to the Ne Auger line of KE = 804.56 eV. Values reported are the average of at least three repetitive runs and have a precision of ±0.03 eV, i.e., ±0.7 kcal/mol.

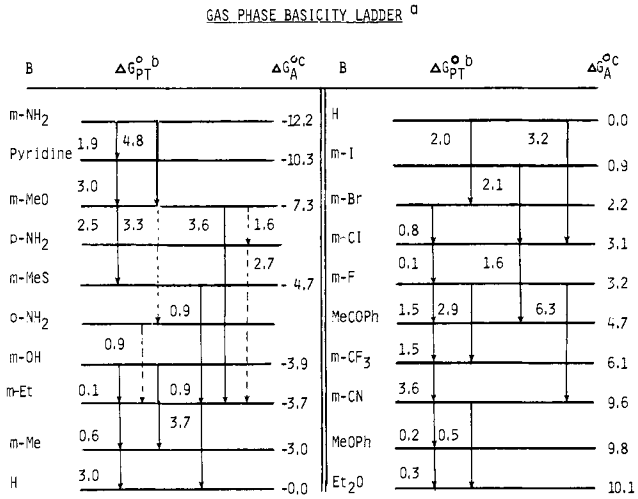

Figure 1. Gas phase basicity ladder: (a) B are substituted anilines unless otherwise indicated. All values in kcal/mol. (b) Standard free energy change for reaction $B'H^+ + B = B' + BH^+$ where B is base at the tip of the arrow, i.e., basicity decreases from top to bottom of figure. Measurements at 600 K (—); measurements at 433 K (---). ΔG values placed close to base of arrow. (c) ΔG_A is the standard free energy change for proton-transfer reactions B + aniline $H^+ = BH^+$ + aniline, i.e., ΔG_A is the gas-phase basicity of bases B relative to aniline at 600 K. The $\Delta G°$(600 K) for aniline + NH_4^+ = aniline $H^+ + NH_3$ is −6.9 kcal/mol,[6] therefore the gas-phase basicities relative to NH_3 at 600 K are given by: ΔG_A − 6.9 kcal/mol.

Results and Dicussion

a. Gas-Phase Basicities and N_{1s} Electron-Binding Energies. The gas-phase-basicity ladder based on the $\Delta G°_3$ values obtained from the measured proton-transfer equilibria is shown in Figure 1. A few of the compounds incorporated in the ladder are not anilines. These compounds were used as convenient stepping rungs or standards by means of which the present determinations were connnected to previous basicity ladders. An inspection of the multiple cycles available shows that in general the data are self-consistent to within 0.2 kcal/mol. Table I summarizes the data for the substituted anilines. $\Delta G°_{300}$ and $\Delta H°$ values based on the present results are also given. These values were calculated from the $\Delta G°_{600}$ and the equation $\Delta G = \Delta H - T\Delta S$, using calculated ΔS values based on rotational symmetry number changes only. These ΔS values are only estimates since they neglect any internal changes on protonation. The neglect of freezing or unfreezing of internal rotations on protonation is probably the most serious fault of this approach. Table I includes also experimental values obtained earlier by Taft and co-workers.[2] The agreement

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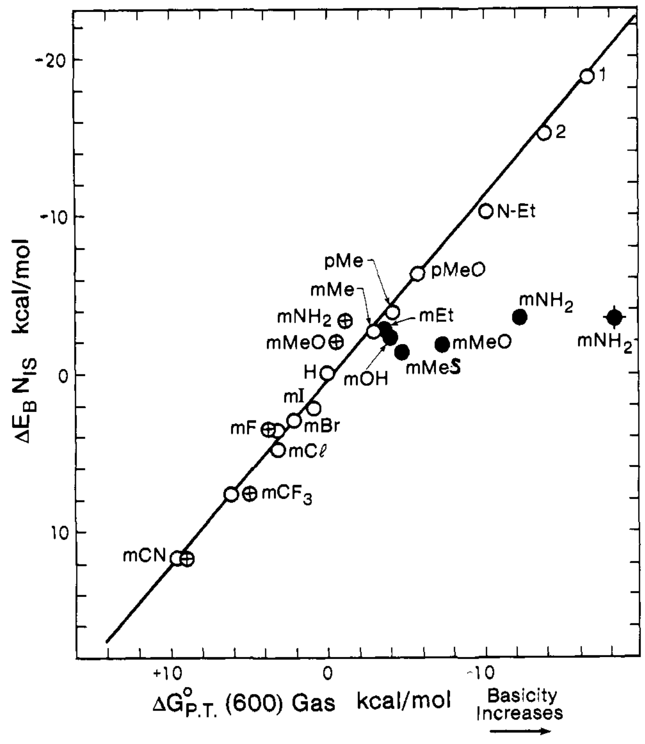
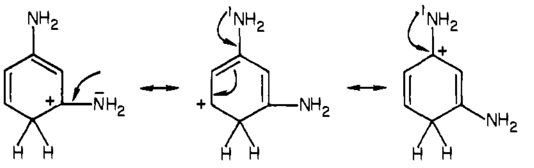


Figure 2. Correlation of experimental nitrogen 1s core electron ionization energies $E_B(N_{1s})$ with free energies for proton transfer of substituted anilines. $\Delta E_B = E(B) - E(B_0)$ where B is substituted aniline and B_0 is aniline. $\Delta G°_{PT}$ corresponds to standard free energy for the proton-transfer reaction $B_0H^+ + B = B_0 + BH^+$: (○) experimental values which fall close to straight line (these anilines must be nitrogen protonated); (⊕) basicity difference for nitrogen-protonated anilines from ΔE(STO-3G) of Hehre and Taft;[2] (●) experimental values which deviate toward higher gas-phase basicity (these compound must be ring protonated); (✚) same as above but from ΔE(STO-3G) of Hehre and Taft.[2] Compounds **1** and **2** are N-phenylpiperidine and N-phenylpyrrolidine, respectively. The gas-phase basicities for these N-cycloalkylated anilines are from Taft.[2c]

is generaly within 0.3 kcal/mol except for m-MeO-aniline where a difference of 1.5 kcal/mol occurs.

A comparison of the gas-phase basicities and the core nitrogen-electron binding energies is shown in Figure 2. A good linear correlation is observed for the compounds which can be expected to be nitrogen protonated. Strongly electron-withdrawing substituents like m-CF_3 and m-CN lead to nitrogen protonation because they destabilize the ring-protonated base more than the nitrogen-protonated base. σ- and π-donating substituents in the p position and electron-donating substituents on the nitrogen (p-CH_3O-aniline, N-C_2H_5-aniline, N-phenylpiperdine, and N-phenylpyrrolidine) stabilize the nitrogen base more and this leads to nitrogen protonation. On the other hand, as pointed out earlier by Taft,[2] π-donating substituents in the meta position favor ring protonation since they stabilize the ring-protonated base by π donation as shown below for the m-NH_2-aniline. Thus, m-SCH_3-, m-OCH_3-, and m-NH_2-aniline are seen not to fall on the line in Figure 2. They have gas-phase basicities which are higher than those predicted by the line. The deviation increases in the order SCH_3, OCH_3, NH_2, i.e., in the same order as the π donation ability of the substituent.



The m-F and m-Cl substituents which are π donating and σ withdrawing are seen to lead to nitrogen protonation (Figure 2). These substituents had only a very small effect on the basicity of benzene,[1] an indication that for benzene their π and σ effects cancelled. Evidently in the ring-protonated meta-substituted aniline, the π-electron demand is lower than that in benzene because of strong π donation from the amino group. Therefore σ withdrawal by the m-F and m-Cl dominates and enhances nitrogen protonation.

Aniline itself is seen to fit on the line of nitrogen protonation. This is in agreement with the predictions of Hehre and Taft.[2] Electron donation from the m-CH_3 and m-C_2H_5 substituents in aniline should favor ring protonation. Hehre and Taft[2] predicted that m-CH_3 favors ring protonation by about 1 kcal/mol. In the present correlation m-CH_3 falls very close to the line such that it could be nitrogen or ring protonated. The m-C_2H_5 is also quite close to the line. It deviates slightly toward higher gas-phase basicity, which indicates that ring protonation might be somewhat more favorable. The basicities for nitrogen protonation predicted by the straight-line correlation in Figure 2 for m-NH_2, m-MeO, m-MeS, m-OH, and m-Et are summarized in Table I.

The present results, Table I and Figure 2, provide the first experimental gas-phase basicities for N and C protonation for a number of substituted anilines (o-, m-, p-NH_2, m-MeO, m-MeS, m-CN, m-CF_3, etc.). These data should be useful to workers engaged in the elucidation of substituent effects and the separation of these effects into resonance and field contributions.[8]

Also given in Table I are the ΔE(STO-3G) values calculated by Hehre and Taft.[2] These results should be compared with the corresponding ΔH values. In general, the agreement is within 1 kcal/mol except for m-aminoaniline for which the calculation predicts a value which is 8 kcal/mol higher.

b. Hydration of the Anilinium Ions. The results from the gas-phase measurements of hydration reactions 2, where BH^+ are

$$BH^+ + OH_2 = (BHOH_2)^+ \qquad (2)$$

various protonated anilines, are summarized in Table II. The equilibrium constants K_2 were measured only at one temperature, 433 K. Selection of this temperature made possible the experimental determination of the equilibrium constants for a number of anilinium ions of interest. The free energies $\Delta G°_2$ are plotted in Figure 3 vs. the gas-phase basicities of the respective anilines.

Table II. Hydration Energies of Protonated Anilines BH^+ from Gas-Phase Equilibria: $BH^+ + H_2O = BH^+ \cdot H_2O$

substituent on aniline	K_{433}, torr^{-1}	$-\Delta G°_{433}$,[a] kcal/mol	$-\Delta H$,[g] kcal/mol
m-CN	11.5	7.8[b]	17.3[b]
m-CF_3	2.9	6.6[b]	16.1[b]
H	0.9	5.6[b]	15.1[b]
m-Cl	0.64	5.3[b]	14.8[b]
m-F	0.62	5.3[b]	14.8[b]
p-NH_2	0.55	5.2[b]	14.7[b]
o-NH_2	0.23	4.4[b]	13.9[b]
m-Me	0.135	4.0;[c] 4.5[e]	13.5;[c] 14[e]
m-Et	0.1	3.7;[c] 4.5[e]	13.2;[c] 14[e]
m-OH	4.5×10^{-2}	3.0;[c] 4.6[e]	12.5;[c] 14.1[e]
m-MeS	4.7×10^{-3}	1.1;[c] 4.6[e]	10.6;[c] 14.1[e]
m-MeO	3.5×10^{-3}	0.8;[d] 5.0[f]	10.4;[d] 14.5[f]
m-NH_2	2.1×10^{-3}	0.4;[d] 4.8[f]	9.9;[d] 14.3[f]

[a] Experimental value from $RT \ln K = -\Delta G°_2$. Standard state 1 atm. [b] Experimental $\Delta G°_2$ corresponds to free energy of hydration of the nitrogen-protonated aniline. [c] Proton transfer ring to nitrogen occurs on hydration. [d] Experimental $\Delta G°_2$ corresponds to free energy of hydration of the ring-protonated compound. [e] Estimated $\Delta G°_2$ for hydration of N-protonated aniline by adding $\Delta G°$ proton transfer ring to nitrogen to experimental $\Delta G°_2$. [f] Estimated $\Delta G°_2$ for hydration of N-protonated species from straight line in Figure 3. [g] Rough estimate of ΔH for reaction 2 obtained from corresponding $\Delta G°_2$ and assumed $\Delta S°_2 = -22$ cal/deg. The assumed entropy change represents an average of experimental values for similar reactions.[7,9]

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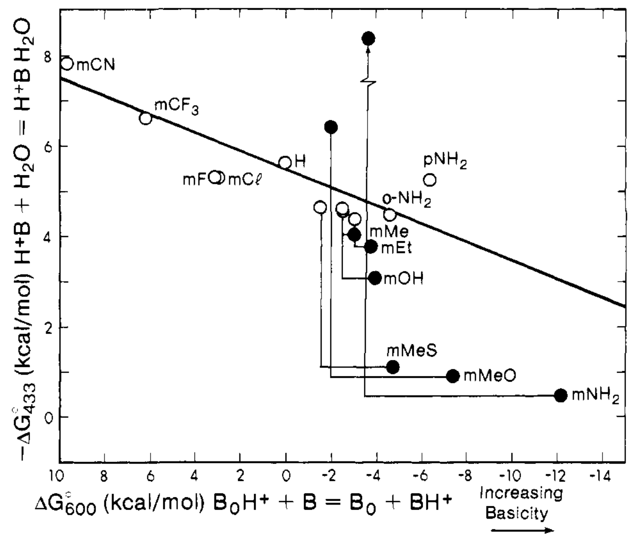


Figure 3. Correlation of gas-phase hydration energies of protonated anilines BH^+ with gas-phase basicities of B. $\Delta G^\circ(433\ K)$ for reaction $BH^+ + OH_2 = BH^+OH_2$ from Table II. Gas-phase basicities from Table I. (○) Hydration energies of nitrogen-protonated anilines. (●) Experimental hydration energies of anilines known to be ring protonated. Horizontal and vertical line length represents energy for internal proton transfer from ring to nitrogen. Shifted points ending close to straight line indicate that proton transfer occurs on hydration (*m*-MeS, *m*-OH, *m*-Et, *m*-Me). Points ending up above straight line indicate that anilines remain ring protonated after hydration (*m*-NH_2 and *m*-MeO), with the water molecule hydrogen bonding to the neutral amino group.

Addition of a water molecule to the nitrogen-protonated anilines leads to formation of a strong hydrogen bond. We have shown in earlier work[7,9] that the strength of the hydrogen bond to water increases with the acidity of the onium ions. For example, an approximately linear relationship was observed[7] between the binding energies of water to substituted pyridinium ions and the gas-phase acidities of the pyridinium ions.

Examining the data shown in Figure 3, one finds that the strength of the bond to water ($-\Delta G^\circ_2$) increases with the acidity of the protonated anilines. Only the anilines which according to the correlation in Figure 2 are nitrogen protonated fit the straight-line relationship. Large deviations occur for the ions known to be ring protonated (*m*-NH_2, *m*-MeO, *m*-MeS, *m*-OH). For these ions lower hydration energies are observed.

The ability of the nitrogen-protonated anilines to form strong hydrogen bonds to water may serve as an inducement for proton transfer from the ring to nitrogen, on monohydration of the ring-protonated ions. It is possible to determine whether this process has occurred for some or all of the ring-protonated ions in Figure 3. The free energies for ring protonation and nitrogen protonation were given in Table I. From these data we can calculate the free-energy change for the internal proton transfer from ring to nitrogen, ΔG°_{IPT}. A ring-protonated base which

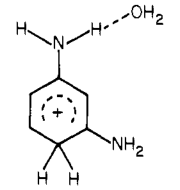
$$(XC_6H_5NH_2)^+ = (XC_6H_4NH_3)^+ \qquad \Delta G^\circ_{IPT}$$

on hydration becomes nitrogen protonated must provide the energy ΔG°_{IPT} for the internal proton transfer. Therefore the experimentally observed hydration energy of that species, $\Delta G^\circ_2(XC_6H_5NH_2^+, \text{exptl})$ will be equal to:

$$\Delta G^\circ_2(XC_6H_5NH_2,\text{exptl}) = \Delta G^\circ_2(XC_6H_4NH_3^+) - \Delta G^\circ_{IPT}$$

where $\Delta G^\circ_2(XC_6H_4NH_3^+)$ is the hydration energy of the nitrogen-protonated base. In order to check whether the internal proton transfer occurs on hydration we can add ΔG°_{IPT} to the expermentially determined ΔG°_2. In this manner we obtain a predicted hydration energy for the nitrogen-protonated base. If that predicted energy fits on the correlation in Figure 3 then proton transfer on hydration has occurred. The results from this procedure are shown in Figure 3 where the experimental points for the ring-protonated bases are shown shifted upward by ΔG°_{IPT}. They are also shifted to the left by the same amount, in order to position them at the basicity corresponding to nitrogen protonation. The shifted points for *m*-MeS, *m*-OH, *m*-Et, and *m*-Me fall approximately on the line. Therefore these initially ring-protonated bases have shifted the proton on hydration. For *m*-MeO and particularly *m*-NH_2, the shifted points fall considerably above the line. This means that these ring-protonated bases have remained ring protonated after hydration. Evidently for these compounds the proton-transfer price is too high.

The hydration energies for the N-protonated *m*-MeO- and *m*-NH_2-anilines can be estimated from the straight-line relationship betweem the hydration energies and the nitrogen basicities (Figure 3). These values are given in Table II. Now, we can compare the energies of hydration of the nitrogen-protonated *m*-NH_2 and *m*-MeO and the ring-protonated isomers. This is better done on the basis of the estimated $-\Delta H^\circ_2$ (see Table II) since the $-\Delta G^\circ_2$ values depend on the choice of standard state. We find that the hydration enthalpies for the nitrogen-protonated species of *m*-NH_2 and *m*-MeO are about 14 kcal/mol while the ring-protonated isomers have hydration energies around 10 kcal/mol. As expected, the anilinium ions have higher hydration enthalpies than the charge delocalized benzenium isomers. This difference would have been much larger had the benzenium ion been unsubstituted, i.e., protonated benzene. Studies of the hydration equilibria of protonated benzene have shown[10] that the monohydration of $C_6H_7^+$ is a very weak interaction. The situation is different for the *m*-MeO- and *m*-NH_2-benzenium ions. Although there will be charge delocalization, a considerable portion of the charge may be expected to be on the amino substituent(s) which have been so effective in stabilizing the ion. This means that also a significant amount of positive charge will be located on the hydrogens of the amino group(s). Therefore efficient hydrogen bonding of the H_2O can occur to this group as shown below for the *m*-NH_2-aniline. The net atomic charges on the amino hydrogens in ring- and nitrogen-protonated aniline were determined by Hehre and Taft[2] from STO-3G Mulliken electron populations. The amino hydrogens in the nitrogen-protonated compound carry +0.33 charges each while for the ring-protonated compound that charge is +0.27, which leads to a ratio between the charges of 1.2. It has been found that the strength of the hydrogen bond increases with the positive net atomic charge of the hydrogen[7,11] participating in the bond. Therefore, for the protonated anilines one might expect the hydrogen-bond energy to follow approximately the above net atomic charges. The ratio of the hydrogen-bond energies for the nitrogen- and ring-protonated *m*-NH_2-aniline is 14/10 = 1.4. This is somewhat larger than the STO-3G net atomic charge ratio 1.2 for the ***unsubstituted*** protonated anilines. The net atomic charge ratio in the nitrogen- and ring-protonated *m*-NH_2-aniline is also expected to be larger. The nitrogen-protonated isomer receives only small stabilization from the *m*-NH_2 substituent. This is reflected in the small differences between the basicities of aniline and *m*-NH_2-aniline for N protonation (see Table I). Therefore the net atomic charge on the hydrogens of the anilinium group should be quite similar to that in unsubstituted aniline. For the ring-protonated aniline and *m*-NH_2-aniline the basicity difference is very large. This



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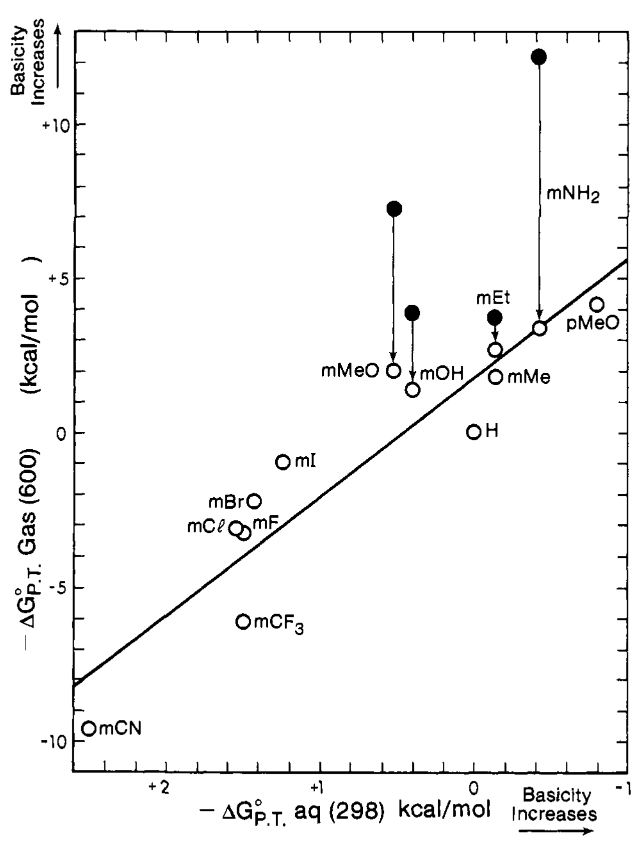

Figure 4. Relationship between basicities of anilines in the gas phase and in aqueous solution. Abscissa: ΔG° for proton transfer in water $B_0H^+ + B = B_0 + BH^+$ where B_0 is aniline and B are substituted anilines. Ordinate, same reaction but in gas phase. (○) Gas-phase basicity for nitrogen protonation. (●) Gas-phase basicity for ring protonation. Only gas-phase basicities of nitrogen-protonated anilines fit approximate linear correlation between gas-phase and aqueous basicities. Slope of line gives an attenuation factor ~4 for substituent effect in gas phase vs. solution.

means that considerable positive charge is delocalized on to the m-NH_2 group, i.e., the net atomic charge on the four amino hydrogens will be correspondingly small.

The observation that ring-protonated anilines give lower hydration energies may have an analytical application in chemical ionization (CI) mass spectrometry. For example, it is clear from Figure 3 that it would be easy to distinguish the m-NH_2 substituent in aniline from the ortho and para substituents. Ammonia is used much more often than water as reagent gas in CI work. It is reasonable to expect that similar binding energy differences will occur also for the ammoniates. Samples run with the chemical ionization source of an analytical mass spectrometer (AEI-MS12) of the Alberta Chemistry Department gave the following intensity for the BH^+NH_3 ion per 100 units of BH^+; 0.14 (m-NH_2); 38.0 (o-NH_2); 17.3 (p-NH_2) (ion source temperature 225 °C, ion source NH_3 pressure ~0.3 torr). These results show that it is very easy to distinguish between m-NH_2-aniline and the ortho and para isomers on the basis of the $BHNH_3^+/BH^+$ ratio.

Additional hydration of a ring-protonated aniline hydrate will cause ultimately a proton transfer from ring to nitrogen. In liquid water both m-OMe- and m-NH_2-aniline are known to be nitrogen protonated. It is interesting to note that one more amino group in the meta position, as in 1,3,5-triaminobenzene, leads to a stable ring-protonated species also in the condensed medium.[12]

A correlation of the gas-phase basicities with the aqueous basicities is shown in Figure 4. As expected only the basicities for nitrogen protonation fit the approximate straight-line relationship. A similar plot was given earlier by Taft,[2] but the present data cover a wider basicity range. The attenuation of the substituent effect, from the gas phase to solution obtained from the slope of the straight line in Figure 4 is ~4. Linear correlations between gas phase and aqueous basicities and acidities have been observed previously for the pyridines[13] (attenuation 3.5), phenols, and benzoic acids[14] (attenuation 7 and 10, respectively). The scatter in the correlation for these systems has been considerably smaller than that observed in Figure 4 for the anilines.

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