

INFORMATION ON ION-SOLVENT INTERACTIONS OBTAINED FROM THE STUDY OF ISOLATED  
COMPLEXES CONTAINING THE ION AND A SMALL NUMBER OF SOLVENT MOLECULES

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**Abstract** - The measurement of gas phase ion-molecule equilibria by special mass spectrometric techniques (high pressure mass spec., ICR, Flowing Afterglow) provides for the first time abundant and accurate thermochemical data for organic and inorganic ions of interest. The energies of formation so obtained used in Born cycles lead to energies of solvation of ions from gas phase to a particular solvent. Ion-solvent molecule equilibria  $\text{Ion}^\pm(\text{S}\ell)_{n-1} + \text{S}\ell = \text{Ion}^\pm(\text{S}\ell)_n$  measured in the gas phase with the above techniques lead to  $\Delta H^\circ_{n-1,n}$  and  $\Delta G^\circ_{n-1,n}$ . These data show that the essential features of the energies of solvation of the ions in a given liquid solvent  $\text{S}\ell$  are contained in the energetics of the ion solvent molecule clusters  $\text{Ion}^\pm(\text{S}\ell)_n$  where  $n$  can be as low as 4 or 5. The substituent effects on the solvation of pyridinium cations and phenoxide anions in protic solvents are examined. Substituents that stabilize the ions in the gas phase (because of charge delocalization) reduce the hydrogen bonding interactions of the solvent with the ion. This can be directly observed by measuring the  $\Delta G^\circ_{n-1,n}$  and  $\Delta H^\circ_{n-1,n}$  values for water clustering to the substituted ions.

INTRODUCTION

Measurements of ion-molecule reaction equilibria in the gas phase, initiated first in the authors' laboratory some thirteen years ago (Ref. 1,2), provide thermochemical data for positive and negative ions, which are of importance to the solution chemist dealing with ions. The gas phase data fall into two categories. In the first are equilibria which provide enthalpies and free energies of formation of the isolated ions in the dilute gas phase. In the second category are ion-molecule equilibria involving the ion and a controlled small number of solvent molecules forming an ion solvent molecule cluster.

Several reaction types provide the required data of the first category. Reactions 1-2 are examples of the thermochemically most useful reactions. Reaction 1 represents proton transfer reactions involving neutral bases  $B$  which may be  $\sigma$ ,  $\pi$  or  $n$  donors. Particularly important examples are the  $n$  donor oxygen and nitrogen bases like alcohols, ethers, amines,



pyridines etc. The molecular basicities of a very large number of such bases has been determined by the ion equilibrium method with high pressure mass spectrometers, ion cyclotron resonance spectrometers (ICR) and flowing afterglow apparatus, (for a review of methods and a data compilation see ref. 3 and 4).

Reaction 2 represents proton transfer involving negative ions.  $AH$  are neutral acids like  $HCl$ , carboxylic acids, alcohols, phenols, carbon acids etc. Measurements of these proton transfer equilibria by high pressure mass spectrometry and ICR have provided relative acidities for hundreds of acids as well as heats and free energies of formation of the corresponding anions  $A^-$ , (ref. 3 and 5). Process 3 is a hydride transfer reaction. Typically  $R_1^+$  is a carbocation like iso-propyl and  $RH$  a hydrocarbon like cyclohexane. Measurements of hydride transfer equilibria have provided heats of formation for a number of carbocations (ref. 3 and 6). In many cases the heats of formation of carbocations can be obtained also by proton transfer equilibria 1 involving the corresponding  $\pi$  bases i.e. olefins (ref. 3 and 4). For example the heat of formation of the 2-norbornyl cation can be obtained either by hydride transfer from norbornane (ref.6) or by proton transfer to 2-norbornene (ref.7 and 8). The

results from ion equilibria like (1) - (3) mark the beginning of a new era in ion thermochemistry in which abundant and accurate data for organic and inorganic positive and negative ions are available. Previously information on ion energetics was based on mass spectrometric measurements of appearance potentials. This earlier method had severe drawbacks. Data for many positive ions of interest like the protonated bases  $BH^+$  could not be obtained. Appearance potentials for most negative ions of interest could also not be measured and what was worse, the data for the ions whose appearance potentials could be measured were often unreliable because of presence of internal excitation in the ionic and neutral fragments.

Once the energies of formation of the ions in the gas phase are known, the relevant information, concerning the ion in solution, is the enthalpy and free energy of solvation of the given ion in the given solvent i.e., the energy of transfer of the ion from the gas phase to the solvent:  $\Delta H_{g \rightarrow S}^{\pm}(\text{Ion}^{\pm})$  and  $\Delta G_{g \rightarrow S}^{\pm}(\text{Ion}^{\pm})$ . Often one is interested only in changes of solvation of different ions in the same solvent. For such cases one can obtain the relative ionic solvation energies by Born type cycles. Arnett has made outstanding use of the gas phase equilibrium data for the elucidation of the relative energies of solvation of a number of organic anions and cations in water, fluorosulfonic acids and some aprotic solvents (ref. 9-13).

If one wants to compare the solvation energies of positive and negative ions in the same solvent or the solvation of ions in two different solvents, then of course, one needs to know the energy of solvation of one ion in the given solvent. Unfortunately only very limited data are available. The most reliable results are probably the volta potential measurements of Randles for water (ref. 14) and Parsons for acetonitrile (ref. 15). Data of lesser reliability are also available from extrathermodynamic assumptions.

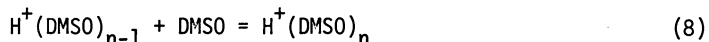
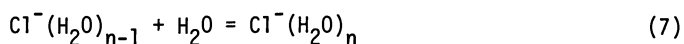
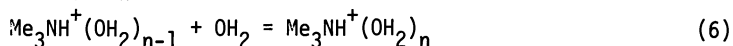
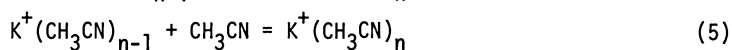
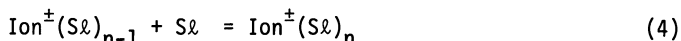
Once the energies of ion transfer from the gas phase to the solvent are known one has reached the stage of interpretation, i.e. of efforts to understand the reasons for solvation differences of different ions in a given solvent or of the same ion in different solvents. Early attempts to explain ion solvation energies were most often based on the Born equation. Considering the intricate chemical differences between solvents like water, ethanol, dimethylformamide, dimethylsulfoxide etc. it is clear that representing their interactions with the ion, through one number, - the dielectric constant, as is done in the Born equation, cannot be an adequate or realistic approach.

Results from gas phase ion solvent molecule interactions can provide information vital to understanding of ion solvation.

The data come from the second class of reactions mentioned earlier in this introduction namely gas phase ion equilibria involving the ion and a small number of solvent molecules. These are discussed in the next section.

#### ION SOLVENT MOLECULE EQUILIBRIA

Reactions 4-8 illustrate the types of equilibria that can be measured in the gas phase.



Reaction 4 gives the general type of equilibrium considered.  $\text{Ion}^{\pm}$  is a positive or negative ion and  $\text{S}l$  is a solvent molecule. Equations (5) - (8) give specific examples of measured equilibria. van't Hoff plots of the equilibrium constants  $K_{n-1,n}$  obtained at different temperatures lead to the stepwise solvation data:  $\Delta H_{n-1,n}^{\circ}$ ,  $\Delta S_{n-1,n}^{\circ}$  and  $\Delta G_{n-1,n}^{\circ}$ .

The stepwise solvation energies often lead to very direct answers of ion solvation problems. For example we may consider the results in Fig. 1 showing measured solvation enthalpies  $\Delta H_{n-1,n}^{\circ}$  for the isoelectronic ions  $K^+$  and  $\text{Cl}^-$  which are of similar size and the two solvent molecules, the protic water and the aprotic acetonitrile (ref. 16). The results show clearly that the solvation of the negative ion  $\text{Cl}^-$  with the aprotic  $\text{CH}_3\text{CN}$  is much weaker than that for the positive  $K^+$ . Furthermore this difference is present for the first solvent molecule and persists with the addition of further acetonitrile molecules. A weak solvation of the negative ion by liquid acetonitrile is directly indicated. With water, the initial interaction with  $\text{Cl}^-$  is weaker, but the addition of further water molecules leads to a cross over between  $K^+(\text{H}_2\text{O})_n$  and  $\text{Cl}^-(\text{H}_2\text{O})_n$ . Therefore a much weaker overall solvation of the negative ion is not indicated for water. Since already the first acetonitrile molecule solvates the negative ion very much less well than the positive ion, and the bonding should be governed

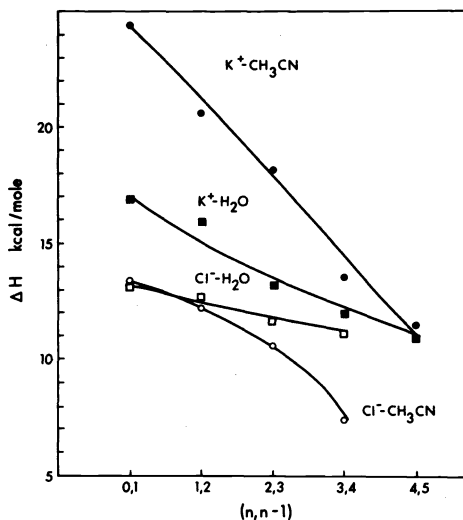


Fig. 1. Enthalpy changes for reactions:  $\text{Ion}^{\pm}(\text{S}l)_n = \text{Ion}^{\pm}(\text{S}l)_{n-1} + \text{S}l$  where the ions are the isoelectronic pair  $\text{K}^+$  and  $\text{Cl}^-$  and  $\text{S}l$  are  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{CN}$ .

largely by electrostatic forces, the specific distribution of the dipole in acetonitrile can be invoked to explain the solvation differences between the positive and the negative ion. The net atomic charges for the three aprotic solvent molecules acetonitrile, acetone and DMSO are shown in fig. 2. These charges are based on Mulliken electron populations obtained

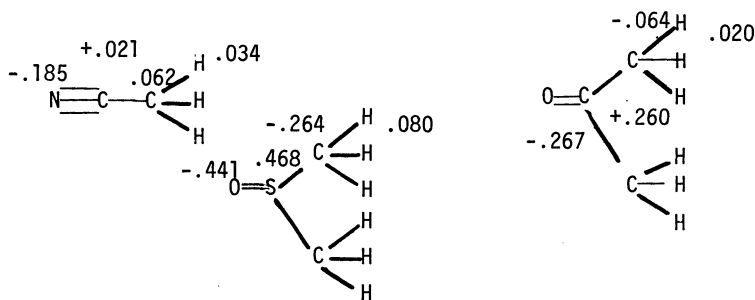
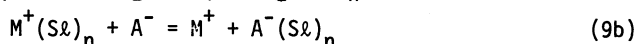
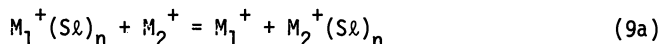


Fig. 2. Net atomic charges from ab initio MO calculations (STO-3G). Acetonitrile and acetone (ref. 17), DMSO present work. Large part of the dipole is concentrated on the functional group CN, CO and SO. The bulky methyl groups hinder close approach of this dipole to negative ions.

from ab initio STO-3G calculations, (acetonitrile, acetone ref. 17, DMSO present work). As will be noticed a large fraction of the dipole is located on the CN, CO and SO group respectively. This means that the bulky methyl groups sterically interfere with a close approach of the solvent molecule dipole to the negative ion, while such steric hindrance does not occur for the positive ion. The situation worsens for the negative ion when more solvent molecules are added since the steric interference for approach to the ion becomes more serious due to methyl group interference also from neighboring molecules. This should be particularly true for two methyl molecules like acetone and DMSO.

A rather direct proof that the  $\Delta G^{\circ}_{0,n}$  and  $\Delta H^{\circ}_{0,n}$  results provide pertinent information on the solvation energies of the ions in liquid solvents is obtained from a comparison of the  $n$  molecule transfer energies, defined in equation 9 and the solvation energies of the ions in the given solvent,  $\Delta H^{\circ}_{g \rightarrow S}l$  and  $\Delta G^{\circ}_{g \rightarrow S}l$ . The  $\Delta H^{\circ}_g$  (or  $\Delta G^{\circ}_g$ ) is obtained from the  $\Delta H_{0,n}$



defined in equation 10. Evidently, for high  $n$  equation (11) should hold.

$$\Delta H_{0,n} = \Delta H_{0,1} + \Delta H_{1,2} + \dots + \Delta H_{n-1,n} \quad (10)$$

$$\Delta H_{0,n}(M_1^+) - \Delta H_{0,n}(M_2^+) = \Delta H^{g \rightarrow S\ell}(M_1^+) - \Delta H^{g \rightarrow S\ell}(M_2^+) \quad (11)$$

Expressions analogous to that shown in 11 can be written for the free energies and for a positive and a negative ion interacting with the same solvent as in reaction 9b. Four examples of such treatment of the data are shown in Fig. 3 and Fig. 4. It is interesting to

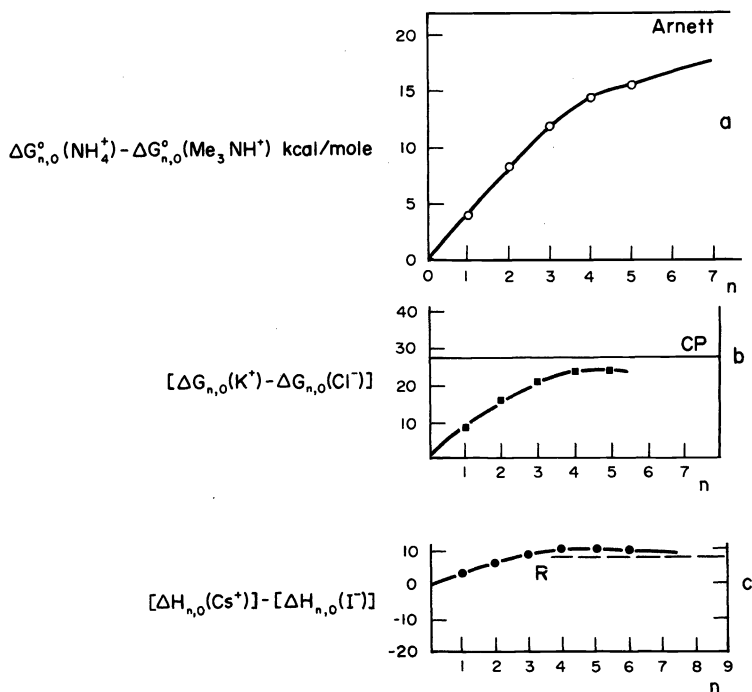


Fig. 3 a. Plot of  $\Delta G^\circ$  for reaction:  $NH_4^+(OH_2)_n + Me_3NH^+ = NH_4^+ + Me_3NH^+(OH_2)_n$  versus  $n$ . Difference between total single ion energies of solvation in water is shown as straight line above figure.

b. Plot of  $\Delta G^\circ$  for reaction:  $K^+(CH_3CN)_n + Cl^- = K^+ + Cl^-(CH_3CN)_n$  versus  $n$ . Difference of total single ion free energies of solvation due to Case and Parsons (ref. 15).

c. Plot of  $\Delta H^\circ$  for reaction:  $Cs^+(OH_2)_n + I^- = Cs^+ + I^-(OH_2)_n$  versus  $n$ . Dashed line represents difference between total single ion enthalpies of hydration due to Randles (ref. 14).

note that the  $n$  molecule transfer energies approach the differences of the ionic solvation energies in the liquid solvent for  $n$  as low as 6 or 7. These results show that ionic solvation energies can be understood and modelled, at least qualitatively but realistically, on basis of the interactions of the ion with only a few solvent molecules. This is of course a very important simplification. Furthermore, the results show that the Born equation can not have relevance since the Born equation is not applicable to the first shell of solvent molecules where there is "dielectric saturation" i.e. the solvent molecules are fairly frozen in their positions.

In Figure 4 an example is given for the solvation of one given ion, the proton, in two different solvents, water and DMSO. Equation 11 cannot be applied directly to systems where two different solvents are involved. The appropriate expression, correcting for the different enthalpies of evaporation of the two solvents is given in equation 12.

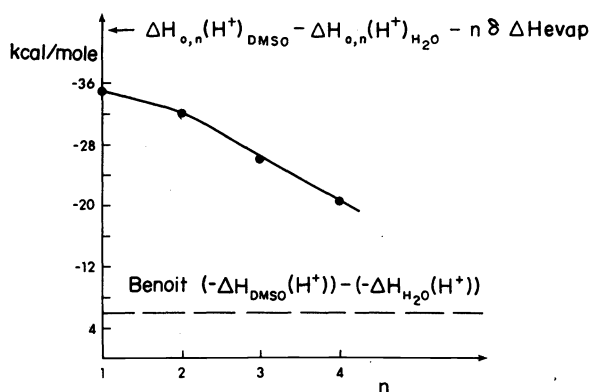


Fig. 4. Plot of  $\Delta H$  for reaction:  $H^+(H_2O) + nDMSO = H^+(DMSO)_n + nH_2O$  minus difference of enthalpies of evaporation for  $n$  moles DMSO and  $n$  moles  $H_2O$ . Straight line gives Benoit's estimate (ref. 18) of the enthalpy of transfer of the proton from liquid water to liquid DMSO.

$$\Delta H_{0,n}^{DMSO}(H^+) - \Delta H_{0,n}^{H_2O}(H^+) - n(\Delta H_{\text{evap}}^{DMSO} - \Delta H_{\text{evap}}^{H_2O}) = \Delta H^{g \rightarrow DMSO}(H^+) - \Delta H^{g \rightarrow H_2O}(H^+) \quad (12)$$

It is interesting to note that  $\Delta H_{1,0}^{DMSO}(H^+) = PA(DMSO)$  is a whole 36 kcal/mole higher than  $\Delta H_{1,0}^{H_2O}(H^+) = PA(H_2O)$  (this corresponds to a difference of 39 pK units). As  $n$  is increased this difference decreases quite rapidly. The limiting value i.e. the difference in the two liquid solvents is only 6 kcal/mole. This value is due to Benoit (ref. 18).

#### CHANGES OF SOLVATION IN PROTIC SOLVENTS UPON IONIC CHARGE DISPERSAL

When comparing different ions interacting with the same solvent one may consider two general types of changes. The first one is change of ionic radius, a parameter significant when more or less spherical ions with fairly uniform charge distribution are involved. The second type of change is charge dispersion. In this case the shape of the molecular ion remains essentially the same but the charge initially concentrated on a functional group may be more or less dispersed by the introduction of suitable electron withdrawing or releasing substituents. Examples in this class are anions derived by deprotonation of substituted benzoic acids or phenols or cations derived by protonating substituted pyridines or anilines. In the subsequent discussion we shall consider the response of protic solvents to such charge dispersal.

The substituent effect on the acidities of phenols in the gas phase and in aqueous solution is shown in Fig. 5 (from ref. 19). A fair linear correlation is observed. The slope of the line is

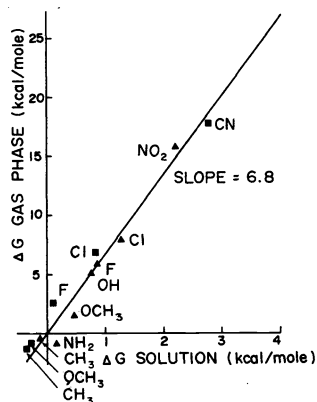


Fig. 5. Acidities of substituted phenols in the gas phase and in aqueous solution (from ref. 19).

6.8 which means that the substituent effect in solution is 6.8 smaller than that in the gas phase. An even bigger attenuation of substituent effect in aqueous solution is observed for the benzoic acids (ref. 19) where the slope found was 10. The acidities of pyridinium ions also show attenuation in aqueous solution with a slope of ~3 (ref. 13). The attenuation of the substituent effect for the above cases must be directly connected with a substituent effect on the solvation of the ions. Evidently the substituent effect on the solvation must be in opposition to the effect of the substituent on the molecular ((intrinsic) acidity. Furthermore because of the linear relationships observed (see Fig. 5), the adverse change of solvation must be proportional to the favorable change of molecular acidity. The obvious mechanism responsible for a proportionate change of the ion solvation is the hydrogen bonding interaction of the ion with the solvent. For example for the phenols an electron withdrawing substituent like  $\text{NO}_2$  or  $\text{CN}$  which increases the molecular acidity by definition decreases the Arrhenius basicity of the resulting phenoxide ion and may be expected to decrease the hydrogen bonding interaction of this ion with a protic solvent molecule like water. A near linear correlation between the basicity of  $\text{A}^-$  and the hydrogen bond strength in  $\text{A}^-\text{-HOH}$  was reported from this laboratory some time ago (ref. 21 and 22). The hydrogen bond energies were obtained by determining the temperature dependence of the gas phase equilibria:  $(\text{AHOH})^- = \text{A}^- + \text{HOH}$ . A similar relationship between the acidity of  $\text{BH}^+$  and the hydrogen bond in  $\text{BH}^+\text{-OH}_2$  was reported also (ref. 20-22). A graph illustrating the relationship between the acidity of  $\text{BH}^+$  and the strength of the hydrogen bond in  $\text{BH}^+\text{-OH}_2$  is shown in Fig. 6. Included in this figure are more recent results on the hydration of the pyridinium ions (ref. 23). The other data were taken from ref. 3. Fig. 6 shows clearly that the higher the acidity of  $\text{BH}^+$  (i.e. the lower the basicity of B) the stronger is the hydrogen bond in  $\text{BH}^+\text{-OH}_2$ . This, and the other similar relationships mentioned above, are easily rationalized if one considers the hydrogen bond in these systems as resulting from partial proton transfer from the acid  $\text{BH}^+$  to the base  $\text{OH}_2$ . It is interesting to note that the slope of the curve in Fig. 6 changes from 0.12 for the very weakly acidic pyridinium ions to about 0.75

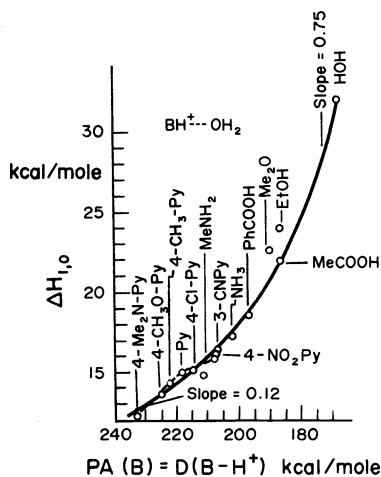
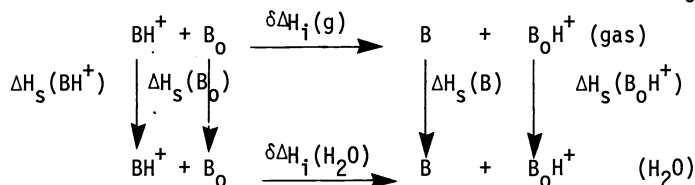


Fig. 6. Relationship between hydrogen bond energy in  $\text{BH}^+\text{-OH}_2$  versus basicity of B.  $\Delta H_{1,0}$  corresponds to enthalpy for reaction  $\text{BH}^+ = \text{B} + \text{H}^+$ . Note monotonic increase of H bond energy with increasing acidity of  $\text{BH}^+$ , i.e. decreasing  $\text{PA}(\text{B})$ .

for the strong acids i.e. acids of strength comparable to  $\text{H}_3\text{O}^+$ . In  $\text{H}_2\text{OHOH}_2^+$  one has maximum proton transfer and proton sharing and this corresponds to maximum stabilization for this series. (A more detailed exploration of hydrogen bond and acidity relationships in  $\text{B}_1\text{H}^+\text{-B}_2$  can be found in ref. 23).

The results in Figure 6 represent data for one molecule solvation of the onium ions  $\text{BH}^+$ , thus they show the first step in the hydrogen bonding attenuation mechanism which modifies the basicities of the substituted pyridines in aqueous solution. Before we examine the effect of additional water molecules we must consider some recent results by Arnett, Taft and coworkers (ref. 13) which deal with the gas phase and aqueous basicities of the substituted pyridines. The Born cycle used by these authors is shown below.  $\text{B}_0$  is pyridine



and B is a substituted pyridine. The  $\Delta H_i(g)$  were obtained from gas phase proton transfer measurements (ref. 13). The  $\Delta H_s(B_0)$  and  $\Delta H_s(B)$  were evaluated from measured heats of vaporization and solution of the pyridines. The  $\delta\Delta H_i(H_2O)$  were taken from basicity determinations of the pyridines available in the literature. With these data and the cycle, the  $\delta\Delta H_s(BH^+) = \Delta H_{g \rightarrow H_2O}(BH^+) - \Delta H_{g \rightarrow H_2O}(B, H^+)$  could be evaluated. A representative sample of the results are reproduced in Table I. The authors were able, by making

Table I. Basicities and Solvation of Pyridines:  $Py + XPyH^+ = PyH^+ + XPy^a$

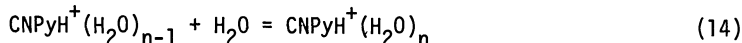
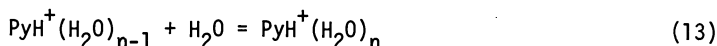
	$\delta\Delta H_i(g)$ $\approx \delta\Delta G_i(g)$	$\delta\Delta G_i(H_2O)$	$\delta\Delta H_i(H_2O)$	$\delta\Delta H_s^{g \rightarrow H_2O}(B)$	$\delta\Delta H_s^{g \rightarrow H_2O}(BH^+)$
4-NMe <sub>2</sub>	14.6	5.9	6.9	(-1.7) <sup>b</sup>	(6.5) <sup>b</sup>
3-OMe	6.7	1.9	2.5	-2.2 (-0.8) <sup>b</sup>	2.0 (3.9) <sup>b</sup>
3,5-diMe	5.5	1.1	1.6	-2.5 (-0.7) <sup>b</sup>	1.4 (3.3) <sup>b</sup>
4-Me	4.0	1.1	1.3	-1.3 (-0.5) <sup>b</sup>	1.4 (2.3) <sup>b</sup>
H	0	0	0	0 (0)	0 (0) <sup>b</sup>
4-Cl	-3.1	-1.9	-1.2	(0.8) <sup>b</sup>	
4-CF <sub>3</sub>	-7.8	-3.5	-2.6	0.3 (1.0) <sup>b</sup>	-4.9 (-4.0) <sup>b</sup>
4-CN	-10.5	-4.6	-3.8	1.9 (1.4) <sup>b</sup>	-4.8 (-5.0) <sup>b</sup>

(a) All values from Arnett, Chavla, Bell, Taagepera, Taft, J. Am. Chem. Soc. 99, 5729 (1977). All numerical values correspond to kcal/mole.

(b) Values given in brackets correspond to the hydrogen bonding contribution to  $\delta\Delta H_s^{g \rightarrow H_2O}$  (see text).

some extrathermodynamic assumptions to separate the hydrogen bonding contributions to  $\delta\Delta H_s^{g \rightarrow H_2O}$  from the other factors affecting the ionic heat of solvation, (cavity formation in solvent, and structure modifying term in solvent). Examining the data in the table we find that the hydrogen bonding terms for  $\delta\Delta H_s^{g \rightarrow H_2O}(BH^+)$  are the major factor in the attenuation of the substituent effect in aqueous solution. Some additional and regular attenuation is provided also by the hydrogen bonding of H<sub>2</sub>O to the neutral bases B which is strong for strong bases B i.e. the strong H bonding of water to strong bases B and the weak H bonding of water to the weak conjugate acids BH<sup>+</sup> combine to produce the full attenuation.

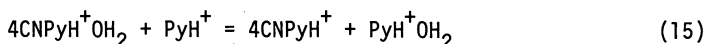
The  $\delta\Delta H_s^{g \rightarrow H_2O}(BH^+)$  is compared in Fig. 7 with the stepwise gas phase hydration energies for the pyridinium and 4-CN pyridinium ion. The data for the hydrated pyridinium were obtained from determinations of the temperature dependence of the hydration equilibria (13) and (14). Unfortunately, measurements could not be carried out beyond n=4 since at temperatures



low enough for these equilibria to establish, condensation of liquid water on the walls of the reaction chamber occurred. Evidently the equilibrium partial pressure of dissociating water vapor from  $PyH^+(H_2O)_n$  (for n > 4) is larger than the equilibrium vapor pressure of liquid water. It is interesting to note that the  $\delta\Delta H_{0,n}$  for n = 3 is still very much smaller than the  $\delta\Delta H_s^{g \rightarrow H_2O}(BH^+)$ . We must conclude that for this system it takes a large cluster of water molecules (H<sub>2</sub>O)<sub>n</sub>, where n is at least 10, to mimic the differences of the hydrogen bonding ability of liquid water towards the pyridinium ions. This means also that pyridinium ions in liquid water, while directly hydrogen bonded to only one water molecule, interact much more strongly with it since the basicity of this first molecule is greatly increased by the cluster of water molecule hydrogen bonded to it.

In Figure 3a, where the behavior of water towards NH<sub>4</sub><sup>+</sup> and Me<sub>3</sub>NH<sup>+</sup> was examined in a plot analogous to Fig. 7, we found that the approach of  $\delta\Delta G_{0,n}^{\circ}(BH^+)$  to  $\delta\Delta G_{0,n}^{g \rightarrow H_2O}$  was faster than that in Fig. 7. One obvious difference in the ammonium systems is the blocking of hydrogen bonding positions by the methyl groups in Me<sub>3</sub>NH<sup>+</sup>. Thus, while  $\delta\Delta H_{0,1}$  covers a similar fraction of the  $\delta\Delta H_s^{g \rightarrow H_2O}(BH^+)$  for both ammonium and pyridinium systems, the decrease of H bonding in the n = 2,3,4 steps for the Me<sub>3</sub>NH<sup>+</sup> is much faster and leads to a more rapid approach to  $\delta\Delta H_s^{g \rightarrow H_2O}(BH^+)$  than for the pyridinium system.

One single point shown in Figure 7 corresponds to the electronic energy difference  $\Delta E$  for reaction 15. This  $\Delta E_{15}$  was obtained from STO-3G calculations of the electronic energies  $E$



of the reactants and products of reaction 15 by Hehre (Arnett, Taft, Hehre ref. 13). The calculated  $\Delta E$  predicts the right trend, but is almost twice as large as the experimentally observed  $\delta\Delta H_{0,1}$ . Considering that the difference between the two values is only 1 kcal/mole one can hardly expect anything better from the calculation. Apart from problems connected with the limited basis set used in STO-3G and correlation errors, geometry optimization to within 1 kcal/mole represents a serious difficulty because of high computational cost.

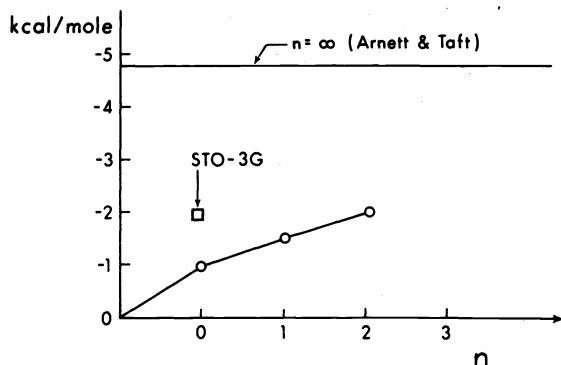


Fig. 7. Plot of enthalpy of reaction  $4\text{-CNPyH}^+(\text{OH}_2)_n + \text{PyH}^+ = 4\text{-CNPyH}^+ + \text{PyH}^+(\text{OH}_2)_n$  versus  $n$ . Note stronger hydrogen bonds to stronger acid. Horizontal line represents difference of hydration energies of the two ions evaluated by Arnett and Taft (ref. 13).

The gaseous and aqueous acidities of phenols, incorporated in Born cycles like those for the pyridines, provide the relative hydration energies of the phenoxide ions (ref. 24). These results have shown that a substituent that decreases the gas phase deprotonation energy (i.e. increases the acidity) decreases the hydration enthalpy of the corresponding phenoxide ion by nearly the same amount. This decrease of hydration energy must be caused by the weaker hydrogen bonding of water to the weaker phenoxide ion base. Unfortunately, we have not yet been able to measure the gas phase hydration energies of the phenoxide ions. However the hydrogen bonding of HCl to the phenoxide ions has been measured (ref. 25). The results are shown in Fig. 8. A near linear relation is observed between the hydrogen bond  $\text{A}^-\cdots\text{HCl}$  and the basicities of  $\text{A}^-$ . The slope is approximately 0.5. Since in the gas phase hydrochloric acid and the phenols are of similar acidity, considerable proton sharing should be

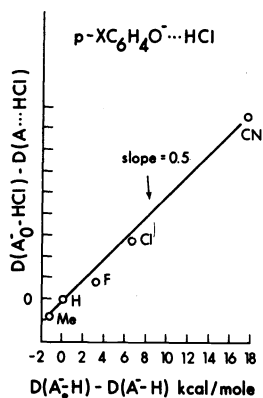


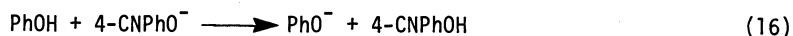
Fig. 8. Plot of enthalpy for reaction  $(\text{PhOHCl})^- + \text{p-XPhO}^- = \text{PhO}^- + (\text{p-XPhOHCl})^-$  versus relative acidities of substituted phenols. Note increasing strength of hydrogen bond  $\text{p-XPhO}^-\cdots\text{HCl}$  with increasing basicity of  $\text{p-XPhO}^-$ .

occurring in  $\text{A}^-\cdots\text{HCl}$ , so that the large slope is expected.

We have obtained  $\Delta E_{17}$  for reaction 17 from STO-3G (ref. 26) calculations of the energies of the reactants. The hydration difference between phenoxide and 4-cyanophenoxide ion  $\Delta E_{17}$  was found to be 3 kcal/mole.

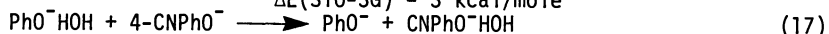


$$\Delta E(\text{STO-3G}) = 21.6 \text{ kcal/mole}$$



$$\Delta H(\text{exp}) = 17.9 \text{ kcal/mole (ref. 19)}$$

$$\Delta E(\text{STO-3G}) = 3 \text{ kcal/mole}$$



Reaction 16 gives the molecular acidity difference between phenol and 4-CN-phenol. For this reaction experimental measurements  $\Delta H_{\text{exp}}$  are also available (ref. 19). From (16) and (17) it is evident that the hydrogen bonding trend follows the expected change with change of basicity of  $A^-$  i.e. the anion of the stronger acid, CN-phenol, hydrogen bonds more weakly to water than the unsubstituted phenoxide. The  $\Delta E_{17}/\Delta E_{16} = 0.14$  represents the slope of a relationship analogous to that shown in Fig. 6 and 8. Since water is a much weaker acid i.e. a much poorer proton donor the slope is only 0.14 as compared with 0.5 in Fig. 6 where the much stronger HCl was the proton donor.

The difference between the solvation enthalpies of  $\text{PhO}^-$  and  $\text{CNPhO}^-$   $\delta\Delta H_{\text{g} \rightarrow \text{H}_2\text{O}}(\text{A}^-)$ , may be estimated from results of Arnett (ref. 24) to be about 80% of the gas phase acidity difference, which means  $\delta\Delta H_{\text{g} \rightarrow \text{H}_2\text{O}}(\text{A}^-) \approx 15.5 \text{ kcal/mole}$  (for  $\text{CNPhO}^-$ ). The difference in hydrogen bonding energies, for one water molecule predicted by STO-3G eqn. 17 is 3 kcal/mole. We see that the first hydration step provides only some ~20% of the total solvation energy difference of 15.5 kcal/mole observed in liquid water. Therefore, as in the case of the pyridinium ions, we find that the cooperative effect of a rather large cluster of water molecules interacting with the  $\text{O}^-$  group on the phenoxide ion is required to achieve the total difference  $\delta\Delta H_{\text{g} \rightarrow \text{H}_2\text{O}}(\text{A}^-)$  in liquid water. In this case the agglomerate of water molecules acts as a much stronger H-bond proton donor, while in the pyridinium case the water cluster was acting as a stronger proton acceptor.

We hope that the above examples have illustrated the two fold utility of gas phase ion equilibria measurements to the ion in solution chemist. The first important result was the provision of thermochemical information on the isolated ions. This information combined with other data in Born cycles provides the relative solvation energies of the ions in the liquid solvents. Much information regarding the chemical causes for different solvation of the ions can be obtained from the gas phase ion-solvent molecule equilibria. Probably the most important result of this work is the realization that relative solvation energies can be obtained by considering the interactions of the ion and a few solvent molecules only.

Unfortunately, the gas phase ion-solvent cluster equilibria do not provide structural information. Clearly here is a real challenge for quantum chemists. Fortunately several quantum chemists have become aware of the possibilities. Work by Kraemer and Dierksen (ref. 27), Clementi (ref. 28), Pullman (ref. 29), and others (30) (Note, the references given are only representative work) has dealt with systems involving an ion and one or more solvent molecules. These have generally been in good agreement with the gas phase clustering equilibria data. Fortunately, in ion molecule binding energy calculations, considerable cancellation of the electron correlation error occurs, which makes the results quite reliable (ref. 28). Theoretical extensions to one ion and many solvent molecules have been made on basis of pair potential functions involving the pairs: ion-molecule and molecule-molecule. The pair potential functions are based on ab initio calculations of the binding energies in function of distance and orientation for the two given partners in the given pair (ref. 28). The availability of such pair potential functions permits the calculation of approximate binding energies of large ion-solvent molecule clusters (ref. 28, 31, 32). Furthermore with the aid of Monte Carlo calculations, the enthalpies (equivalent to  $\Delta H_{0,n}$ ) and free energies can be obtained (ref. 31,32). While most of this work has been restricted to water and simple ions, its extension to other solvents and more complex ions is only a question of time. Probably such work will at long last lead to a good, realistic understanding of the solvation of different ions in different solvent systems.

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