Ions-gas phase and solution-dipolar aprotic solvents

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Abstract — Gas phase ion-molecule equilibria measurements provide thermochemical data with which the enthalpies and free energies of formation of ions in the gas phase can be obtained. These combined with the corresponding energies in solution provide ion solvation energies. The interpretation of solvation energies is aided by thermochemical results from gas phase ion-solvent molecule equilibria: $X^- + nL = X^-Ln_n$. This approach is applied to an elucidation of the factors causing faster kinetic rates of reactions: $X^- + B \rightarrow \text{products}$, in dipolar aprotic solvents and the smaller decrease of negative ion solvation in dipolar aprotic solvents with increase of ion size and charge delocalization in the ion.

I. INTRODUCTION

When one deals with ions in many different solvent environments it becomes particularly sensible to separate the intrinsic, molecular properties of the ion from the properties due to the interaction of the ion with the solvent. For example, the energy changes of a simple acid-base proton transfer reaction like (1) are strongly solvent dependent. While aqueous solution was and is often used as the normative solvent relative to which the energy changes in other solvents were compared, there are many advantages to comparison not with water but with the dilute gas phase. One obvious advantage is that one can compare the complex situation in solution with the simple state in the gas phase, while before one was comparing one complex and poorly understood situation with another. Another advantage is the possibility to determine the acidity of all acids in the gas phase, from the weakest like CH₄ to the strongest while in solution, due to the leveling effect of the solvent or solubility problems, only a given range of acids can be measured in a given solvent.

Until not too long ago, the use of the gas phase as a comparison state was not a practicable approach because there was great paucity of information on the energy changes of reactions like (1) in the gas phase. The development of ion-molecule equilibrium measurements in the gas phase, Kebarle (1), Bowers (2), has completely changed the situation of gas phase energetics. Abundant data are now available and the store continues to increase, Kebarle (3), Aue (4), McLver (4), Lias (5). While it has proven possible to measure ion molecule equilibria involving a large variety of reaction types and leading to the ion thermochemistry of many different classes of ions, for the present purposes we need consider only two types. One is the proton transfer reaction (1) already mentioned. Measurement of equilibria (1) leads via eq. 2 to the free energy change, while determinations of the equilibrium

$$K_1 = \frac{[A^-][BH]}{[B^-][AH]} \quad \Delta G_1^O = -RT\ln K_1$$

constants at different temperatures lead via a van't Hoff plot to the $\Delta H_1^O$.
change. One can then directly compare relative acidities in the gas phase with relative acidities in a given solvent, \( S \), where \( \Delta G^0_1(S) \) can be evaluated from (3) the acidity constants and eq. 3.

\[
\Delta G^0_1(S) = 2.3 \cdot R(pK_{BH} - pK_{AH}) \tag{3}
\]

It is also possible to obtain the (relative) solvation energies \( \Delta G^0_S \) of the anions \( A^- \) and \( B^- \) with use of the Born cycle 4 and resulting eq. 5. The

\[
\Delta G^0_S(A^-) - \Delta G^0_S(B^-) = \Delta G^0_{PT}(S) - \Delta G^0_{PT}(g) + \Delta G^0_S(AH) - \Delta G^0_S(BH) \tag{5}
\]

solvation energies of the ions (\( \Delta G^0_S \) or \( \Delta H^0_S \)) are in the fundamental units for the thermochemistry of ions in solution once one accepts the gas phase as the reference environment.

Even when the solvation energies of the ions are available, understanding of the effect of the solvent on a molecular level may be lacking. Very useful information towards this aspect is provided by the energy changes for sequential solvent molecule additions to the ion. These are obtained from the second type of equilibrium, which is shown in eq. 6 for the negative ion \( X^- \) and the solvent (ligand) molecule \( L \). The sequential equilibria (6) can be

\[
X^- L_{n-1} + L = X^- L_n \quad (n-1,n) \tag{6}
\]

\[
X^- + nL = X^- L_n \quad (o,n) \tag{7}
\]

experimentally measured, from the resulting \( \Delta G^0_{n-1,n} \) (or \( \Delta H^0_{n-1,n} \)) one can also evaluate \( \Delta G^0_{n,n} \) (or \( \Delta H^0_{n,n} \)) defined in eq. 7. Measurements for \( n \) up to 4–9 are generally possible, such that information on the strong initial interactions, for the inner shell and somewhat beyond it, are obtained. For reviews of this approach see Kebarle (3), (6). The results in Fig. 1, from Dzidic (7), demonstrate that the information is

![Fig. 1. Gas phase hydration enthalpies, \( \Delta H^0 \), for \( M^+ + nH_2O = M^+(H_2O)_n \) where \( M^+ = \bullet Li^+, \circ Na^+, \bigtriangleup K^+, \odot Rb^+ \). Hydration differences \( \delta \Delta H^0_n \) approach hydration differences in liquid \( H_2O \) (horizontal lines) at high \( n \).](image)
relevant to the situation in solution. The $\Delta H_{\text{O}}^\circ (\text{Cs}^+) - \Delta H_{\text{O}}^\circ (\text{M}^+)$ are plotted versus the corresponding hydration enthalpy difference in the liquid solvent. The gas phase data approach already, within the experimentally accessible $n$, the hydration energy in solution. Thus, at least for these simple spherical ions the magnitudes of relative solvation energies in solution are reflected to a large extent by the initial, strong ion solvent molecule interactions measured in the gas phase.

II. SOLVATION OF NEGATIVE IONS IN DIPOLAR APROTIC SOLVENTS

a. Effects of solvation on rates of reactions of the type $A^- + B \rightarrow \text{products}$. $S_{N2}$ reactions.

We shall consider specifically the $S_{N2}$ reaction (8) but much of the discussion will be equally applicable to the general reaction (9).

\[
\text{Cl}^- + \text{CH}_3\text{Br} \rightarrow (\text{ClCH}_3\text{Br}^-)^* \rightarrow \text{CH}_3\text{Cl} + \text{Br}^- \quad (8)
\]

\[
A^- + \text{B} \rightarrow (A\text{B}^-)^* \rightarrow \text{products} \quad (9)
\]

The reaction coordinate of (8) in the gas phase is shown in Fig. 2. It is based on measurements of the reaction kinetics of (8) in the gas phase, Brauman (8), Caldwell (9). It is important to note that the energy of the transition state is less than that of the reactants. The energy barrier for the formation of the transition state is smaller than the energy lowering due to the attraction between the ion with the dipole and polarizability of the molecule. The Born type cycle shown in Fig. 2 leads to eq. 10 for the $E_A$ i.e.

\[
E_A = \Delta E_{O(g)} + \Delta H_{S}^\circ(\text{Cl}^-\text{CH}_3\text{Br}^-)^* - \Delta H_{S}^\circ(\text{Cl}^-) - \Delta H_{S}^\circ(\text{CH}_3\text{Br}) \quad (10)
\]

the activation energy in solution. Since $\Delta E_{O(g)}$ and $\Delta H_{S}^\circ(\text{CH}_3\text{Br})$ are relatively small, $E_A$ is dominated by the difference of the solvation energy of the transition state and the reactant Cl$^-$ ion. This difference is positive because the transition state, being a larger ion is less exothermically solvated than the reactant ion.

$S_{N2}$ reactions like (8) are known to proceed much faster in dipolar aprotic solvents than in protic solvents. The rate differences may be as large as 107 and are due to a smaller $E_A$ in the aprotic solvents. Much effort has gone into the interpretation of the reasons for these differences and many useful insights have been obtained, Parker (10); however, we feel the present discussion, from Magnera (11), based on eq. 10 and data to be discussed provides an improved picture.

The solvation energies in the ligand solvents for the ions $X^-$ (I$^-$, Br$^-$) relative to Cl$^-$ are shown in Fig. 3. For references to these literature data
see Magnera (11). These results demonstrate that the solvation energies of $X^-$ in protic and aprotic solvents decrease with increase of the ion radius, however, the decrease is considerably smaller for the aprotic solvents. An accurate "radius" for the transition state can not be assigned. The radius chosen as indicated in Fig. 3 is arbitrary but falls within a reasonable range. The solvation energies obtained from Fig. 3 and this choice for the transition state, when substituted in eq. 10 lead to the activation energies for $H_2O$ and $DMF$ shown in Table 1. Both values are in good agreement with the experimental $E_A$.

**TABLE 1. Activation Energy $E_A$ in solution for reaction**

$$Cl^- + CH_3Br = ClCH_3 + Br^-$$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$E_A$ predicted</th>
<th>$E_A$ experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$</td>
<td>26</td>
<td>25</td>
</tr>
<tr>
<td>$DMF$</td>
<td>17</td>
<td>18</td>
</tr>
</tbody>
</table>

a. Units kcal/mol. b. eq. 10. c. Parker (10).

Considering the general reaction: $A^- + B ÷ (AB^-)^*_+$, since the transition state will always be larger than the reactant ion $A^-$, it follows that the lesser decrease of solvation with increasing ion size in dipolar aprotic solvents will generally provide very much higher rates in these solvents - a very important advantage in synthetic work.

**b. Solvation and ion size in protic and aprotic solvents**

We now will address the question: what are the causes for the smaller decrease of solvation exothermicity with increase of ion radius (ion size) in aprotic solvents? (See Fig. 3). Results from the gas phase clustering equilibria of $X^-$ (and $M^+$) with aprotic and protic solvents provide direct insights. The enthalpy changes $\Delta H_{0}^{\circ} - n$ for $Cl^-$, $Br^-$, $I^-$ and $K^+$ and DMSO are shown in Fig. 4. Much stronger interactions, particularly at low solvent number $n$ are observed for the positive ion. Similarly stronger interactions for the positive ion have been observed also for acetonitrile, Davidson (12) and acetone, Magnera (11). A plot of $\Delta G_{0}^{\circ,n} (Cl^-) - \Delta G_{0}^{\circ,n} (K^+)$ for acetonitrile versus $n$ is shown in Fig. 5. The $\Delta G_{0}^{\circ,n}$ is seen to approach at high $n$ the corresponding solvation energy difference in the liquid solvent. Unfortunately, the latter value is not accurately known, Davidson (12). The enthalpy changes for $K^+$ and $X^-$ associating with protic and aprotic solvent molecules are shown in Table 2. For the protic water the exothermicity for

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![Fig. 4. Enthalpies $\Delta H_{0}^{\circ} - n$ for gas phase reactions: $X(DMSO)_n^- + DMSO = X(DMSO)_n$, and same reactions for $K^+$.](image)

![Fig. 5. Plot of $\Delta G_{0}^{\circ,n} (Cl^-) - \Delta G_{0}^{\circ,n} (K^+)$ for acetonitrile versus $n$. Gas phase result approaches result in solution (horizontal line) already at low $n$.](image)
Ions-gas phase and solution-dipolar aprotic solvents

TABLE 2. Energy changes for reactions: $K^+ + nL = K^+L_n$ and $X^- + nL = XL_n$ (kcal/mol)

<table>
<thead>
<tr>
<th>L</th>
<th>$\mu^d$</th>
<th>$-\Delta H_{O,1}^\circ$</th>
<th>$\delta \Delta H_{O,4}^\circ$</th>
<th>$-\Delta H_{O,4}^\circ$</th>
<th>$\delta \Delta H_{O,4}^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$</td>
<td>1.8</td>
<td>16.9</td>
<td>14.6</td>
<td>10.3</td>
<td>4.3</td>
</tr>
<tr>
<td>MeCN</td>
<td>3.9</td>
<td>24.4</td>
<td>13.4</td>
<td>11.9</td>
<td>1.5</td>
</tr>
<tr>
<td>Me2CO</td>
<td>2.9</td>
<td>26.0</td>
<td>14.0</td>
<td>12.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Me2SO</td>
<td>4.1</td>
<td>34.5</td>
<td>18.6</td>
<td>15.7</td>
<td>3.1</td>
</tr>
</tbody>
</table>

a. Kebarle (3); b. Magniera (11); c. Caldwell, Kebarle recent unpublished result; d. dipole moment in Debye units.

$K^+$ is only slightly larger than that for $Cl^-$, while aprotic solvents have exothermicities with $K^+$ that are nearly twice as large as for $Cl^-$. The reasons for this difference are easily understood. The different orientation of the dipolar aprotic molecules towards the positive and negative ion (see Fig. 6) place the major site of the molecular dipole and polarizability, i.e. the S=O in DMSO and CN for acetonitrile, much further away from the negative ion. The structures in Fig. 6 are based on molecular orbital calculations with 4-31G basis set and an improved basis set for $K^+$. The data for DMSO are from Magnera (11) while those for acetonitrile are from Hirao (13,14). The calculated binding energies are in good agreement with the experimental $\Delta H_{O,1}^\circ$ values. The $Cl^-$ lines up with the dipole of the functional group (S=O or CN). The approach of the negative ion to the functional group is hindered due to the presence of methyl for both DMSO and acetonitrile, but since DMSO is pyramidal the two methyl groups keep partially out of the way and the approach of $Cl^-$ is not completely barred. This is not so for the linear acetonitrile where the methyl group is completely in the way of the negative ion. The same strong steric blockage should also occur for acetone. The net atomic charges obtained from Mulliken population analysis also are given in Fig. 6. These show that only 0.002 electrons are transferred to $K^+$ on formation of the DMSO complex. The electron transfer on formation of the $Cl^-$ DMSO complex (0.060 electrons) is somewhat larger but still quite small. The bonding in both cases is largely electrostatic.

Considering the negative ions $X^-$ in protic and dipolar aprotic solvents, one may conclude from the data in Table 2 and structures in Fig. 6 that because the dipole and polarizability of the aprotic molecule is located some distance away from the ion, the strength of interaction will decrease relatively less rapidly with increase of ion radius, than would be the case for protic solvents like water whose dipole can approach the immediate vicinity of the ion. The $\Delta H_{O,4}^\circ$ for attachment of four solvent molecules to $Cl^-$ and $I^-$ are given in Table 2 for $H_2O$, CH3CN and DMSO. The $\Delta H_{O,1}^\circ = \Delta H_{O,4}^\circ (I^-) - \Delta H_{O,4}^\circ (Cl^-)$ and the corresponding $\delta \Delta H_{O,4}^\circ$ also are shown in Table 2. Acetonitrile and acetone when compared to water show the expected trend i.e. the $\delta \Delta H_{O,4}^\circ$ values for these two aprotic solvents are considerably smaller than that for...
For example, $\delta H^0_{\text{H}_2\text{O}} = 11 \text{ kcal/mol}$ while that for MeCN is only $\sim 3 \text{ kcal/mol}$. Thus, for these two solvents, the lesser decrease of solvation in the liquid solvent with increase of $X^-$ radius is at least partially due to the large distance between the ion and the dipole of the solvent molecules in the first shell. For DMSO the decrease of solvation ($\delta H^0_{\text{DMSO}}$) between Cl$^-$ and I$^-$ is not smaller than that in H$_2$O but approximately the same. This special behaviour of DMSO should be attributed to the aforementioned ability of the negative ion to approach the S=O dipole, due to the pyramidal structure of Me$_2$SO, and the very high dipole moment of this solvent molecule. These result in strong binding to $X^-$. The binding energies $X^-$ to DMSO are appreciably higher than those for $X^-$H$_2$O, thus Cl$^-$H$_2$O, 14.6 kcal/mol while Cl$^-$DMSO 18.6 kcal/mol (Table 2). Thus, the lesser sensitivity of DMSO solvation on $X^-$ radius (Fig. 3) can not be based on first shell solvation.

An examination, Magnera (11), of the solvation past the first shell, largely on basis of the Born eq. 11 where $r$ is the radius of the inner shell cluster,

$$\Delta G^0_{\text{Born}} = -\frac{165.2}{r(A)^2} \left(1 - \frac{1}{D}\right) \text{kcal/mol}$$

D the dielectric constant of the solvent, shows that for small protic molecules like water solvation past the first shell makes a substantial contribution to the total solvation. Furthermore, the solvation past the first shell decreases significantly with increase of the radius of the core ion $X^-$. Dipolar aprotic molecules like acetonitrile, acetone, DMSO are bulky and lead to a large inner shell cluster radius, weak solvation past the inner shell and only small decreases of this solvation with increase of $X^-$ radius.

In summary, dipolar aprotic solvents like acetonitrile, acetone and probably also DMF and DMA and others, lead to $X^-$ solvation which is insensitive to ion radius because effective steric interference of the alkyl groups keeps the dipole of the functional group of inner shell molecules at a large distance from $X^-$. In addition to this the solvation past the inner shell in dipolar aprotic solvents is weak and the decreases resulting from ion radius increase small. For DMSO, this second effect seems to be the major one.

Results in Figs. 4, 5, 6 demonstrated that positive ions are strongly solvated by dipolar aprotic solvents due to particularly strong interactions of the ion with the solvent molecules in the first shell. The $\Delta H^0_{\text{DMSO}}$ and $\Delta G^0_{\text{DMSO}}$ results in Table 3, from Sunner (15), expand the data to a larger number of solvents. The binding energies of K$^+$ with DMSO, DMA and DMF are seen to be even bigger than those with the bidentate ligands MeOCH$_2$CH$_2$OMe (Glyme) and 1,2 diaminoethane. The strong solvation of the positive ions in dipolar aprotic solvents is particularly useful in synthetic work (reactions 8 and 9). It promotes the solubility of the MX salt and by complexing with M$^+$ prevents the formation of ion pairs $M^+X^-$, thus keeping the reactivity of $X^-$ high.

### Table 3. Energy changes for reactions: $K^+ + L = K^+L$ in the gas phase.

<table>
<thead>
<tr>
<th>L</th>
<th>$-\Delta H^0$ (kcal/mol)</th>
<th>$-\Delta G^0$ (kcal/mol)</th>
<th>$\mu^b$</th>
<th>L</th>
<th>$-\Delta H^0$ (kcal/mol)</th>
<th>$-\Delta G^0$ (kcal/mol)</th>
<th>$\mu^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>35</td>
<td>25</td>
<td>3.9</td>
<td>Me$_2$CO</td>
<td>26</td>
<td>19</td>
<td>2.9</td>
</tr>
<tr>
<td>DMA</td>
<td>31</td>
<td>24</td>
<td>3.8</td>
<td>MeCN</td>
<td>24</td>
<td>18</td>
<td>3.9</td>
</tr>
<tr>
<td>DMF</td>
<td>31</td>
<td>23</td>
<td>3.9</td>
<td>Me$_2$O</td>
<td>21</td>
<td>13</td>
<td>1.3</td>
</tr>
<tr>
<td>(MeOCH$_2$)$_2$</td>
<td>31</td>
<td>23</td>
<td></td>
<td>NH$_3$</td>
<td>18</td>
<td>12</td>
<td>1.5</td>
</tr>
<tr>
<td>(NH$_2$CH$_2$)$_2$</td>
<td>26</td>
<td>19</td>
<td></td>
<td>H$_2$O</td>
<td>17</td>
<td>11</td>
<td>1.8</td>
</tr>
</tbody>
</table>

a. Sunner (15); b. dipole moment in Debye; c. standard state 1 atm., 298K.

c. Acidities and delocalized anions in dipolar aprotic solvents.

A comparison between the acidities for substituted phenols in the gas phase, McMahon (16), Taft (17), H$_2$O, and DMSO, Bordwell (18) is shown in Fig. 7. The plots show that an approximately linear relationship exists between the acidities in the gas phase and the aqueous or DMSO solution. This can be
Ions-gas phase and solution-dipolar aprotic solvents

Fig. 7. Acidities of substituted phenols in the gas phase, in H$_2$O and in DMSO solution. $\Delta G_{PT}^{\circ}$ for proton transfer reaction: $A^- + AH = AO^+ + A^-$, where $AO^+$ is phenol and $AH$ is a substituted phenol. $\Delta$ para, $\Delta$ meta substituent.

expressed by eq. 12 for the proton transfer reaction 13 where $AO^+$ is phenol

$$\Delta G_{PT}^{\circ}(g) = \rho \Delta G_{PT}^{\circ}(s)$$

(12)

$$A^- + AH = AO^+ + A^- \quad (PT)$$

(13)

and $AH$ is a substituted phenol. The value of $\rho$ is approximately 7 for H$_2$O and 2.5 for DMSO, i.e. the substituent effect is attenuated by a factor of 7 in H$_2$O and 2.5 in DMSO. It is easy to show, see Born cycle (4—5), that eq. 12 leads to the approximate relationship 14, if the small solvation energy

$$\delta \Delta G_S(A^-) = \Delta G_S(A^-) - \Delta G_S(AO^-) = -c \Delta G_{PT}^{\circ}(g)$$

(14)

c = (1 - \frac{1}{\rho}) \approx 0.86 \quad (H_2O) 

\approx 0.6 \quad (DMSO)

difference $\delta \Delta G_S(AH) = \Delta G_s(AH) - \Delta G_s(AO^+)$ is neglected. An acidifying substituent, like CN, in $AH$ which increases the gas acidity relative to $AH$ by say 10 units, decreases the solvation of $A^-$ by $-8.6$ units in H$_2$O and $-6$ units in DMSO.

It is well known that a substituent like CN that increases the charge delocalization in $A^-$ causes a decrease of $A^-$ solvation. The question why this decrease is smaller for dipolar aprotic solvents has been often answered on basis of an argument by Grunwald (19). The formation of $A^-$ from $AH$ leads to an increase of polarizability of $A^-$ relative to $AH$ because of the expansion of the delocalized electrons into a larger space. This increase of polarizability in $A^-$ leads to an increase in dispersion forces between $A^-$ and the solvent molecule. When solvent molecules with large polarizabilities (i.e. dipolar aprotic molecules) are present the increase of dispersion energy is larger than that for the small protic molecules like water. We believe that the higher dispersion energy for aprotic solvents is not the most important effect. Charge delocalization away from the oxygen of the phenoxide ion may be also considered as an increase of the effective radius of the charge center. The arguments presented in the preceding section showed that the solvation by protic i.e. hydrogen bonding solvents like H$_2$O is very sensitive to ion radius, while that by dipolar aprotic solvents is not. Thus the factors involved in the lesser sensitivity of aprotic solvents to $X^-$ radius increase may also be the applied to the lesser decrease of solvation by aprotic solvents in the presence of charge delocalization.
As pointed out in the preceding section, the pyramidal DMSO is somewhat closer to protic solvents than acetonitrile or acetone. On this basis one would expect the slopes $p$ for the latter two solvents to be less than the $p = 2.5$ observed for DMSO.

**LITERATURE**