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Relationship between Donor and Acceptor Numbers and Intrinsic Molecular Properties from Gas-Phase Ion Equilibria

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Molecular and bulk solvent properties of protic and aprotic solvent molecules were discussed in the respects of donor numbers (DN) and acceptor numbers (AN) proposed recently by Gutmann, and the intrinsic molecular properties obtained from gas-phase ion equilibria measurements. For aprotic solvent molecules, good correlations are generally found between the gas-phase thermochemical data and both of DN and AN. This indicates that DN and AN for aprotic solvents well reflect the intrinsic molecular properties. On the other hand, the correlations for H_2O and lower alcohols are not good. This is due to the more effective enhancement effect in the intermolecular interactions for protic solvents than for aprotic solvents.

Several empirical parameters have been proposed for characterizing the solvent properties. Grunwald and Winstein proposed the Y value as a scale for the ionizing properties of solvents.[1] This was based on a comparison of the rate constant for the solvolysis of *t*-butyl chloride in one solvent with that in the reference solvent mixture of 80% ethanol and 20% water.

Kosower introduced the Z value which characterizes the ionizing property of solvent.[2–4] This value is based on the UV spectra of 1-ethyl-4(methoxycarbonyl)-pyridinium iodide. The charge-transfer energy of this compound in a particular solvent was considered as an empirical measure of the ionizing property.

The E_t values proposed by Dimroth and Reichhardt[5,6] are based on the solvent sensitivity of optical absorption of a 4-(1-pyridinio)phenolate due to the intramolecular charge-transfer transition. All these parameters, Y, Z, and E_t, are known to be a good measure for the acceptor properties of solvents.[7]

In order to obtain a solvent-independent representation for the donor ability of a molecule, the donor numbers (DN) were introduced by Gutmann and Wychera.[8] The donor number is defined as a molar enthalpy value for the reaction of the donor (D) with $SbCl_5$ as a reference acceptor in a 10^{-3} M[†] solution of 1,2-dichloroethane.[7]

$$D + SbCl_5 = D\cdot SbCl_5 \qquad (1)$$
$$(-\Delta H_{D\cdot SbCl_5} = DN)$$

Recently, an empirical parameter for the acceptor properties of solvents has been proposed by Mayer et al.[9,10] which is based on the ^{31}P NMR chemical shift in triethylphosphine oxide in the respective pure solvent. In constrast to classical solvent parameters such as dielectric constant, dipole moment, or polarizability, the acceptor number (AN) allows the interpretation of numerous solvent dependent NMR-, IR, Raman-, UV-spectroscopic, and kinetic data.

The extended donor-acceptor concept presented by Gutmann[7] can be applied to very weak (electrostatic) as well as to strong (covalent or coordinate) interactions, because in both cases rearrangement of the charges in the interacting species takes place. The objective of this work is to investigate the molecular and solvent properties of protic and aprotic solvent molecules by examining the relations between the donor and acceptor numbers and gas-phase thermochemical data which represent the intrinsic molecular properties.

Discussion

DN's vs. Gas-Phase Proton Affinities. In the determination of DN's, the adducts of $D\cdot SbCl_5$ are formed in a 1:1 molar ratio with all donor molecules.[7] Thus DN's represent molecular donicities rather than donicities for bulk solvents.

The gas-phase proton affinity (PA) is defined as the negative of the enthalpy change for the protonation Reaction (2).

$$A + H^+ = AH^+, \; -\Delta H^\circ = PA(A) \qquad (2)$$

Namely, the proton affinity is a measure of the Brönsted basicity. On the protonation, a sort of coordinate bond is formed between A and H^+, i.e., $A \rightarrow H^+$. Thus the proton affinity may also be regarded as a scale of the gas-phase Lewis basicity.

Figure 1 shows the relationship between the gas-phase PA's[11] and DN's[7] for protic and aprotic solvent molecules. A fair correlation is seen between these two parameters for aprotic solvent molecules. This indicates that PA's could be a measure of molecular donicity for aprotic solvents.

Contrary to the aprotic solvent molecules, the correlation is not good for protic solvent molecules. The H_2O, CH_3OH, and C_2H_5OH molecules have about the same DN's. This means that the bond energies of D–$SbCl_5$ is more or less the same for D= C_2H_5OH, CH_3OH, and H_2O. On the contrary, proton affinities for these compounds are quite different. The smallest value of the PA for H_2O is due to the localization of positive charge in three protic hydrogens in H_3O^+. Almlöf and Wahlgren examined the electronic structure of H_3O^+ by ab initio MO calculations.[12] They deduced an HOH angle of 117° and net positive charges on H and O of 0.328 and 0.015, re-

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[†] 1 M = 1 mol dm^{-3}.

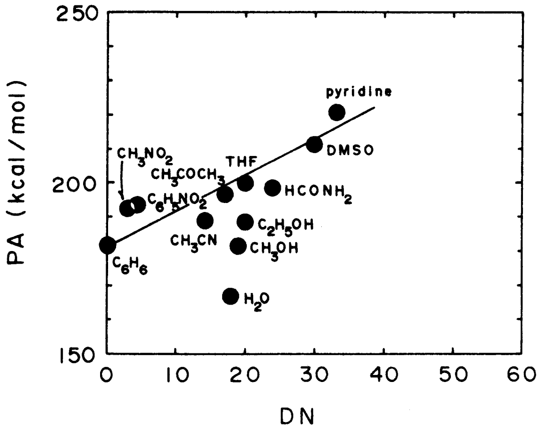


Fig. 1. Relationship between donor numbers (DN's) and gas-phase proton affinities (PA's) for protic and aprotic solvents. THF: tetrahydrofuran, DMSO: dimethyl sulfoxide.

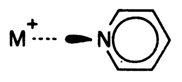
spectively. Nearly all the positive charge in H_3O^+ is on three hydrogen atoms. In the protonated alcohols, the positive charge can be more delocalized owing to the electron-donating ability of the alkyl, making the value of PA larger than H_2O. As shown in Fig. 1, alcohols are seen to approach to the correlation curve for aprotic solvents as the alkyl gets larger. Thus the gas-phase proton affinities may be used for the measure of the molecular donicities for aprotic solvents and higher alcohols. However, PA's cannot be the measure of the molecular donicities for water and lower alcohols, and may be not for ammonia and lower amines, either.

DN's vs. Bond Energies of Li^+ and K^+ with Solvent Molecules Measured in the Gas Phase. Figure 2 shows the relationship between DN's and the bond energies ($-\Delta H°$'s) of the complexes $Li^+ \cdot D$ and $K^+ \cdot D$ for D=various protic and aprotic solvents.[13]

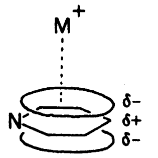
Since Li^+ and K^+ have inert closed shells, they refuse the acceptance of electrons from the solvent molecule, D. Thus the stabilization of the clusters of $Li^+ \cdot D$ and $K^+ \cdot D$ comes from electrostatic and polarization interactions.[14]

As shown in Fig. 2, a fair correlation is found between DN and $-\Delta H°$ for aprotic solvents, except for pyridine.

For the complex of the alkali ion M^+ with pyridine, the two stable structures may exist as shown below.



(I)



(II)

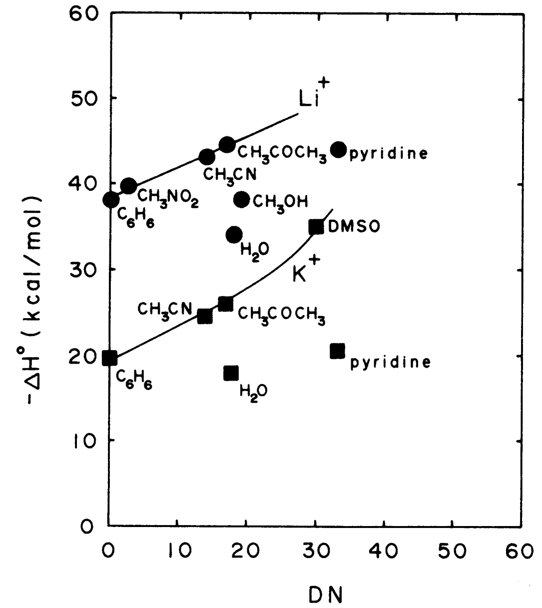


Fig. 2. Relationship between donor numbers (DN's) and enthalpy changes ($\Delta H°$'s) for reaction: M^++solvent=M^+(solvent), measured in the gas phase. M^+=Li^+ and K^+. $-\Delta H°$ corresponds to the bond energy of the cluster M^+---solvent. DMSO: dimethyl sulfoxide.

The structure (I) assumes the importance of the ion-dipole interaction. The relatively large dipole moment of pyridine (μ_D=2.2 D) is mainly due to the large size of the molecule, i.e., pyridine is a rather soft Lewis base. Thus the interaction of the molecule with hard Lewis acids such as Li^+ and K^+ could not be so strong as would be expected from the large μ_D of pyridine. In addition, the exchange repulsion between the closed shells of alkali ions and the lone pair plus diffuse π electrons of the pyridine molecule would make the interaction of the structure (I) less favorable. This might explain the deviation of pyridine from the correlation curve.

If the bond energy of the structure (I) is small, the complex may prefer the structure (II), in which the stabilization is due to the ion-quadrupole interaction. Such a structure is found to be most stable for the complex of K^+ with benzene.[15,16]

As the case of PA vs. DN, the protic solvents deviate from the correlation curve for aprotic solvents. In Fig. 2, the deviation of H_2O is larger than CH_3OH. This suggests that the ion-induced dipole moment interaction plays an important role for the stabilization of the bonds of $M^+ \cdot D$. The polarizability of CH_3OH(3.25 Å^3) is larger than that of H_2O(1.45 Å^3) while the dipole moment of CH_3OH(1.70 D) is smaller than that of H_2O(1.84 D). Although the data points are rather scarce, it may be worthwhile nothing that the DN's which represent the measure of the mainly covalent (or coordinate) bond strengths can also be a good measure for the electrostatic bond strengths for aprotic solvents.

AN's vs. Gas-Phase Acidities. The gas-phase acidity scale may be given by the enthalpy change $-\Delta H^\circ_{acid}$ of Reaction (3),

$$AH = A^- + H^+ \qquad (3)$$

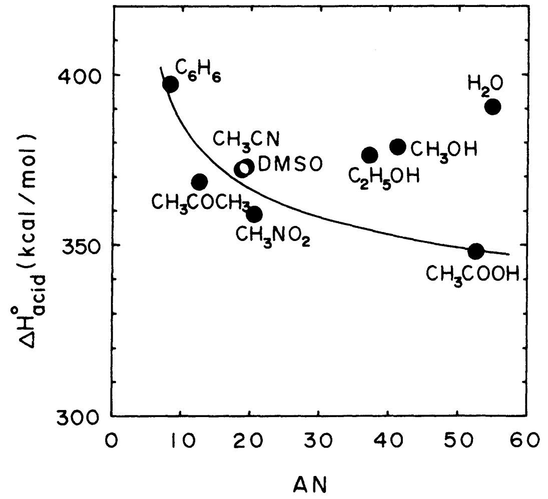


Fig. 3. Relationship between acceptor numbers (AN's) and gas-phase acidities ($-\Delta H^\circ_{acid}$) for protic and aprotic solvents. DMSO: dimethyl sulfoxide.

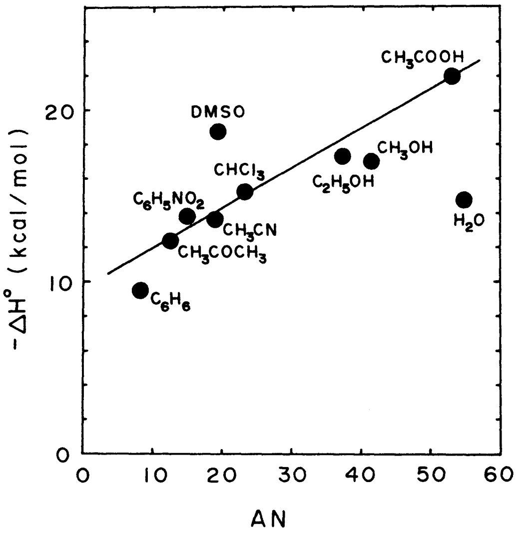


Fig. 4. Relationship between acceptor numbers (AN's) and enthalpy changes (ΔH°'s) for reaction: Cl^-+solvent=Cl^----solvent, measured in the gas phase. $-\Delta H^\circ$ corresponds to the bond energy of the cluster Cl^----solvent.

$-\Delta H^\circ_{acid}=DH^\circ(A\text{-}H)+IP(H)-EA(A)$ where $DH^\circ(A\text{-}H)$ is the bond energy of A-H, IP(H) is the ionization energy of the hydrogen atom, and EA(A) is the electron affinity of the radical A. Any molecule containing a hydrogen atom is potentially a proton donor, or Brönsted acid. For the complex of an acceptor AH and a donor D, $\overset{\delta-}{A}-\overset{\delta+}{H}\leftarrow D$, the stronger interaction may be expected for AH which has a larger gas-phase acidity (smaller value of $-\Delta H^\circ_{acid}$).

Figure 3 shows the relationship between $-\Delta H^\circ_{acid}$[17] and AN's for protic and aprotic solvents. A fair correlation exists between these two parameters for aprotic solvents, i.e., $-\Delta H^\circ_{acid}$ decreases with an increase of AN. However, just the opposite correlation is found for protic solvents, i.e., $-\Delta H^\circ_{acid}$ *increases* with an increase of AN in the order $C_2H_5OH \rightarrow CH_3OH \rightarrow H_2O$. This is ascribed to the fact that AN is a measure of the acceptor ability for the bulk solvent rather than that for a free molecule (see the following section).

AN's vs. Bond Energies of Cl^- with Solvent Molecules Measured in the Gas Phase. Figure 4 shows the relationship between AN's and bond energies of Cl^- with protic and aprotic solvents.[13]

A good correlation is seen for aprotic solvents and acetic acid as the case of gas-phase acidities vs. AN's. These results suggest that there is some correlation between the gas-phase acidity and the bond strength of the complex $AH\cdots Cl^-$. Actually it is already pointed out that the bond strength of $AH\cdots X^-$ increases with the acidity of AH where X^- corresponds to halide or O_2^- ion.[18,19,20] An approximate correlation of the bond strength with the gas-phase acidity can be expected on the grounds that the bond strength of the bond $AH\cdots X^-$ should be related to $D(A^-\cdots H^+)$ since the bridging H atom in the complex must carry appreciable positive charge induced by the negative ion X^-.

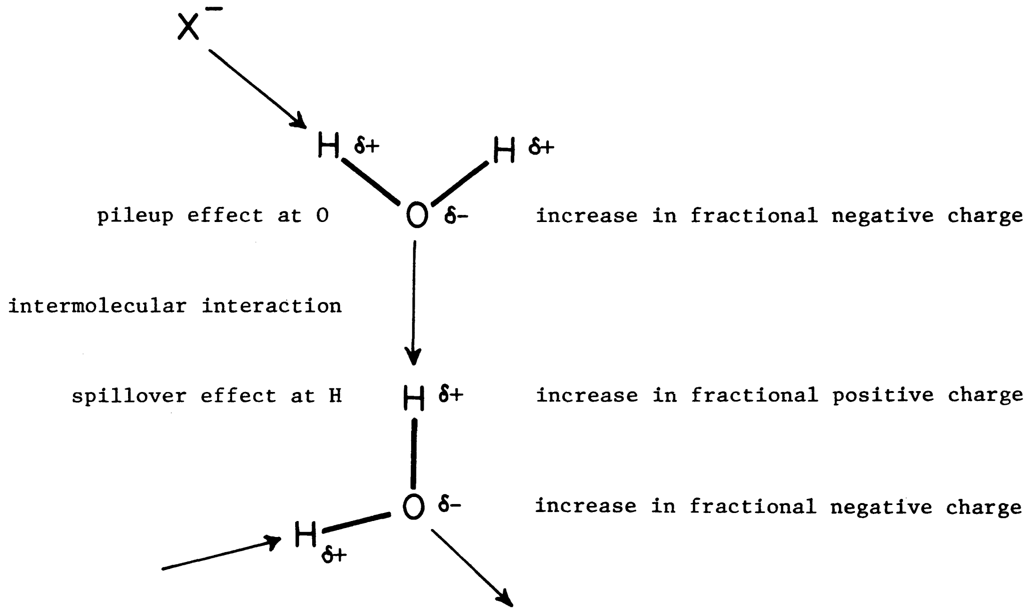
Contrary to a good correlation observed for aprotic solvents, just the opposite correlation is found for protic solvents, i.e., $-\Delta H^\circ$ *decreases* with an increase of AN in the order $C_2H_5OH \rightarrow CH_3OH \rightarrow H_2O$. The H_2O molecule which has the largest AN as a solvent has the least $-\Delta H^\circ$. This is somewhat puzzling because the larger AN suggests the stronger bond of $AH\cdots Cl^-$ as is observed for aprotic solvents. This must be due to the characteristic solvent properties which arise from the intrinsic molecular properties. The stepwise solvation enthalpies $\Delta H^\circ_{n-1,n}$ for Reaction (4),

$$\text{Ion(solvent)}_{n-1} + \text{solvent} = \text{Ion(solvent)}_n \qquad (4)$$

and the heats of solvation ΔH°_s are related as

$$\Delta H^\circ_s = \sum_{n=1}^{n=N} \Delta H^\circ_{n-1,n}(\text{Ion(solvent)}_n) - \sum_{n=2}^{n=N} \Delta H^\circ_{n-1,n}(\text{solvent})_n \qquad (5)$$

The value of $\Delta H^\circ_{n-1,n}$ (Ion(solvent)_n) and $\Delta H^\circ_{n-1,n}$ $(\text{solvent})_n$ converge at $n=N$. It may be reasonable to assume that the solvent of large AN is a good solvent for negative ions, namely, AN and $-\Delta H^\circ_s$ correlate with each other. The large value of AN for H_2O suggests that the value of $-\Delta H^\circ_s$ is also large. The small value of $-\Delta H^\circ$ for H_2O (Fig. 4) is understandable because of the low gas-phase acidity of the H_2O molecule. When the H_2O molecule interacts with the ion, the H_2O molecule is polarized. The polarized H_2O molecule would enhance the further hydrogen bonding with the H_2O molecule in the outer shell. This enhancement effect would extend from inner ligands to outer ligands in the shells surrounding the core ion and thus make the value of $-\Delta H^\circ_s$ ultimately large. This kind of enhancement effect may be envisaged more clearly by the donor-acceptor concept, i.e., the spillover effect of the acceptor and the pileup



effect of the donor.[7] As an example, the interaction between a negative ion X^- and water molecules is shown above in a version of pileup and spillover effects.

A donor-acceptor interaction leads to increasing polarities of the bonds originating from the donor and acceptor atoms, respectively. Increasing polarity is related to an increase in fractional positive charge at the acceptor atom and an increase in fractional negative charge at the donor atom. The original decrease of fractional positive charge at the acceptor atom due to both the charge-transfer and polarization effects is overcompensated by passing over the negative charges, including part of those originally situated at the accepter atom to other areas of the acceptor molecule. In this way the fractional negative charges of other nuclei in the acceptor component are increased, in particular those terminating the acceptor molecule. This has been described as the spillover effect of negative charge from the acceptor atom. The original loss of negative charge at the donor atom by charge transfer toward the acceptor molecule is overcompensated by attracting electronic charge from other parts of the donor molecule to the donor atom. In this way the electron density at the donor atom is increased with appropriate changes of fractional nuclear charges in other areas of the donor component. This has been termed by the pileup effect of negative charges at the donor atom.

The enhancement effect for alcohols may be weaker than that for H_2O. The induced charge in the alcohol molecule is more or less dispersed in the alkyl, and this makes the net negative charge on the oxygen atom smaller. The charge dispersion leads to the weaker intermolecular interactions for alcohols. Thus the value of $-\Delta H^\circ_s$ or $-\sum_{n=1}^{n=N}\Delta H^\circ_{n-1,n}$ (Ion(solvent)$_n$) for alcohol may be expected to be smaller than that for H_2O. In fact, a positive enthalpy change (2.0 kcal mol^{-1}) is found for the transfer of Cl^- from H_2O to CH_3OH.[23] Figure 5 shows the n dependence of the sum of the stepwise solvation of the Cl^- ion $-\Delta H^\circ_{o,n}$ (i.e. $-\sum_{n=1}^{n=n}\Delta H^\circ_{n-1,n}$ ($Cl^-(solvent)_n$) for solvents=H_2O and CH_3OH up to $n=4$ or 5.[14,24] The value of $-\Delta H^\circ_{o,n}$ for CH_3OH is larger than that for H_2O up to $n=5$. This is reasonable because the first solvation shell around the Cl^- ion is composed of more than 5 solvent molecules[20,25] and the interaction of Cl^- with ligand molecules in the first shell is stronger (or nearly equal) for CH_3OH than for H_2O mainly due to the larger gas-phase acidity of CH_3OH than that of H_2O. In the cluster ion which is composed of several solvation shells, the strength of the intermolecular interactions between molecules belonging to the neighboring solvation shells would become stronger for H_2O than for alcohols, because of the greater enhancement effect for H_2O than for alcohols. This effect would make the ultimate value of $-\Delta H^\circ_s$ for H_2O larger than that for alcohols. The

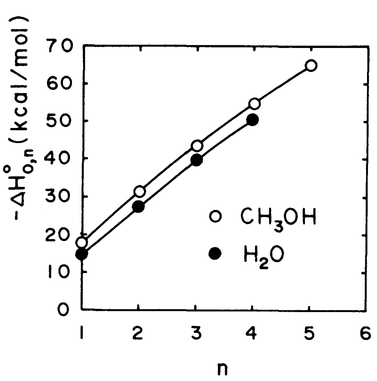


Fig. 5. The n dependence of the sum of the stepwise solvation enthalpies $\Delta H^\circ_{n-1,n}$ for reaction: $Cl^-(solvent)_{n-1}$+solvent=$Cl^-(solvent)_n$. $\Delta H_{o,n}=\sum_{n=1}^{n=n}\Delta H_{n-1,n}$ ($Cl^-(solvent)_n$). Solvents=H_2O and CH_3OH.

strong and extensive enhancement effect expected for H_2O suggests that the number N in Eq. 5 for H_2O is larger than that for alcohols.

The relatively small values of AN for aprotic solvents compared to protic solvents may partly due to the less effective enhancement effect. The positive charge in the aprotic solvent molecule can be well dispersed in the hydrophobic groups and the electrostatic intermolecular interactions must be weaker than those for protic solvents. Thus the solvation shells surrounding the core ion may not grow so large as the case of protic solvents, i.e., the number N for the aprotic solvent may be generally smaller than those for the protic solvents.

Concluding Remarks

The relationships between DN's and AN's and intrinsic molecular properties from gas-phase ion equilibria are studied.

For aprotic solvents, good correlations are generally found between DN's and AN's and intrinsic molecular properties. Since DN's represent the molecular properties, good correlations between DN's and intrinsic molecular properties are reasonable. It is of interest that there are also good correlations between intrinsic molecular properties and AN's which represent the bulk solvent properties. This indicates that AN's for aprotic solvents reflect more or less the molecular properties. From the observed good correlations and relatively small values of AN's, it is tentatively concluded that the negative ions in aprotic solvents are solvated by only a restricted number of ligands. We think that the negative ion in aprotic solvents is composed of rather tight single solvation shell which is further solvated by sorrounding solvent molecules only weakly. In such a case, the molecular properties of solvent molecules would be reflected on the AN's.

For protic solvents, just the opposite correlations between AN's and intrinsic molecular properties are found compared to those for aprotic solvents. This may be mainly due to the extensive solvation of ions in protic solvents owing to the enhancement effects in the intermolecular interactions, i.e., the formation of multiple solvation shells which is realized by the pileup and spillover effects of protic solvent molecules. The enhancement effects are the most prominent for H_2O.

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