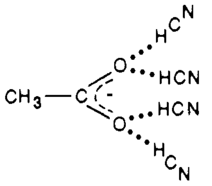

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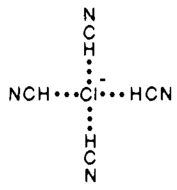

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factors. The bonding energies are reproduced well by ab initio calculations[5] and by a new empirical formula for anionic hydrogen bonds.[4] This formula also helps to identify special structural effects such as secondary $CH{\cdot}X^-$ bonds when the ligand is a large flexible molecule such as, for example, a peptide.

The present measurements are intended as models for interactions of anions with hydrogen donors in biological systems. While biological ions are more complex, theoretical results on SH^- vs CH_3S^-,[5] as well as $H°_D$ vs $\Delta\Delta H°_{acid}$ correlations,[1] and the empirical formula of Larson and McMahon[4] all suggest that alkyl substitution on the anionic site, which changes the $\Delta\Delta H°_{acid}$ of the parent carboxylate and sulfhydryl groups by 1–5 kcal/mol, will change anionic hydrogen bond strengths only by 1–2 kcal/mol. This is also indicated when the present results for $HCOO^-{\cdot}HCN$ ($\Delta H°_D$ = 22.0 kcal/mol) are compared with $CH_3COO^-{\cdot}HCN$ ($\Delta H°_D$ = 23.5 kcal/mol). Therefore, although the CH_3COO^- and SH^- ions are simpler than biological ions, the attachment energies of CH_3COO^-, SH^-, and Cl^- to the present ligands should be good models for interaction energies of carboxylate and sulfhydryl groups, as well as of Cl^-, with hydrogen-donor functions in biological molecules. The results with CH_3CO–Ala–OCH_3 also suggest, however, that overall anion binding can be significantly strengthened by $CH{\cdot}O^-$ bonds and dispersion forces. The presence of bulk solvent will also have a significant effect.

Acknowledgment. This work was funded in part by a grant from the U.S. Department of Energy, Office of Basic Energy Sciences.

Registry No. CH_3COO^-, 71-50-1; Cl^-, 16887-00-6; CN^-, 57-12-5; SH^-, 15035-72-0; CH_3OH, 67-56-1; C_2H_5OH, 64-17-5; C_6H_5OH, 108-95-2; CH_3COOH, 64-19-7; H_2S, 7783-06-4; CH_3SH, 74-93-1; $CH_3CONHCH_3$, 79-16-3; CH_3CO-Ala-OCH_3, 3619-02-1; HCN, 74-90-8; CH_3CHO, 75-07-0; CH_3COCH_3, 67-64-1; CH_3CN, 75-05-8; pyrrole, 109-97-7; indole, 120-72-9.

The Ionic Hydrogen Bond and Ion Solvation. 7. Interaction Energies of Carbanions with Solvent Molecules

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Contribution from the Chemical Kinetics Division, Center for Chemical Physics, National Bureau of Standards, Gaithersburg, Maryland 20899. *Received September 2, 1987*

Abstract: The bonding energy of a water molecule to carbanions ranges from 11.0 kcal/mol for $c\text{-}C_5H_5^-$ to 13–15 kcal/mol for CH_2CN^-, CH_2CHO^-, and $CH_2COCH_3^-$ and to 16.2 kcal/mol for HCC^-. Alcohols bond to $c\text{-}C_5H_5^-$ more strongly, by up to 20.6 kcal/mol for the strongly acidic CF_3CH_2OH, and the attachment energies show an inverse linear correlation with the acidities of the alcohols. The $c\text{-}C_5H_5^-$ ion exhibits unusual behavior in that it bonds to the hydrogen donor H_2O more weakly (11.0 kcal/mol) than to CH_3CN (15.5 kcal/mol). In contrast, the more localized pyrrolide ion $c\text{-}C_4H_4N^-$ bonds to the two solvents by comparable strength, 15.8 and 15.7 kcal/mol, respectively. These observations indicate a specific $N^-{\cdot}OH$ hydrogen bonding contribution in $c\text{-}C_4H_4N^-{\cdot}H_2O$, and/or an unusual $C^-{\cdot}HC$ type hydrogen-bonding contribution in $c\text{-}C_5H_5^-{\cdot}CH_3CN$. As to structures, correlations between $\Delta H°_D$ and $\Delta H°_{acid}$ suggest that ligands may hydrogen bond to the π system of $c\text{-}C_5H_5^-$, and to the oxygen atoms in CH_2CHO^- and $CH_3COCH_2^-$. The latter is also supported by solvent shell effects in $CH_3COCH_2^-{\cdot}nH_2O$.

Acid–base properties in solution are strongly affected by the efficiency of ion solvation. In particular, it is expected that the solvation of carbanions, which involves $C^-{\cdot}HO$ interactions, is less efficient than the solvation of oxoanions that involves $O^-{\cdot}HO$ bonds, which can be as strong as 30 kcal/mol.[1-3] For a better understanding of the solvation of carbanions, we shall examine here the interaction energies of carbanions with protic and aprotic solvent molecules.

As a model delocalized carbanion, we shall use $c\text{-}C_5H_5^-$. The question of interest is whether the interaction with an H_2O molecule involves specific hydrogen bonding or is it of a nonspecific electrostatic nature. For comparison, we shall investigate the gas-phase solvation of an anion of a molecule of comparable size and acidity, i.e., the pyrrolide anion $c\text{-}C_4H_4N^-$, where the formation of $N^-{\cdot}HO$ hydrogen bonds, with contribution from a covalent charge-transfer component, is possible.

Strong carbon acids such as carbonyl compounds contain in general electron-withdrawing groups, which become the negative charge center in the anions. Therefore, although the acidic site is carbon, the ligand bonding site may be a heteroatom lone pair, or a π system, rather than carbon. We shall examine empirical trends in bonding energies as indicators of preferred hydrogen bonding sites to carbanions.

Experimental Section

The measurements were done with the NBS pulsed high-pressure mass spectrometer and standard methods.[4] The carrier gas was CH_4 with trace amounts of CH_3ONO added as a chemical-ionization electron-capture agent. The gaseous mixture also contained 0.01–0.1% of the carbon acid RH and 1–10% of the solvent of interest. The reagents were obtained from commercial sources, were of purity over 98%, and were used as purchased.

In the solvation of ions of weak carbon acids such as HCCH, it was observed that instead of the formation of $R^-{\cdot}nH_2O$ clusters, deprotonation and ligand switching reactions formed $OH^-{\cdot}nH_2O$ clusters. This prevented studies of higher solvation in these systems.

Results

Van't Hoff plots for equilibria 1 are given in Figures 1 and 2, and the results are summarized in Table I.

$$R^- + HS \rightleftarrows R^-{\cdot}HS \tag{1}$$

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(1) Kebarle, P. *Ann. Rev. Phys. Chem.* **1977**, *28*, 445.

(2) Caldwell, G.; Rozeboom, M. D.; Kiplinger, J. P.; Bartmess, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 4660.

(3) Meot-Ner (Mautner) M. *J. Am. Chem. Soc.* **1986**, *108*, 6189.

(4) Sieck, L. W. *J. Phys. Chem.* **1985**, *89*, 5552.

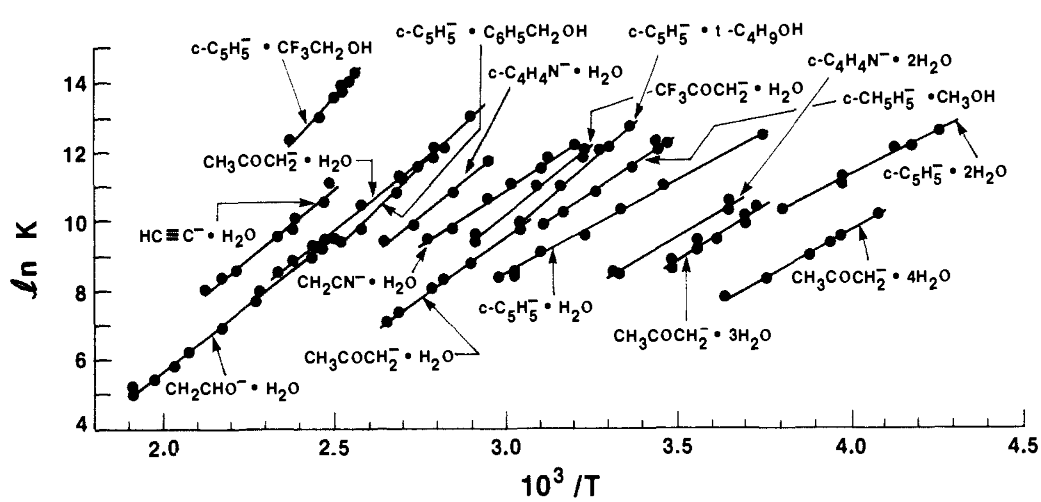

Figure 1. Van't Hoff plots for the dissociation of clusters involving water and alcohols.

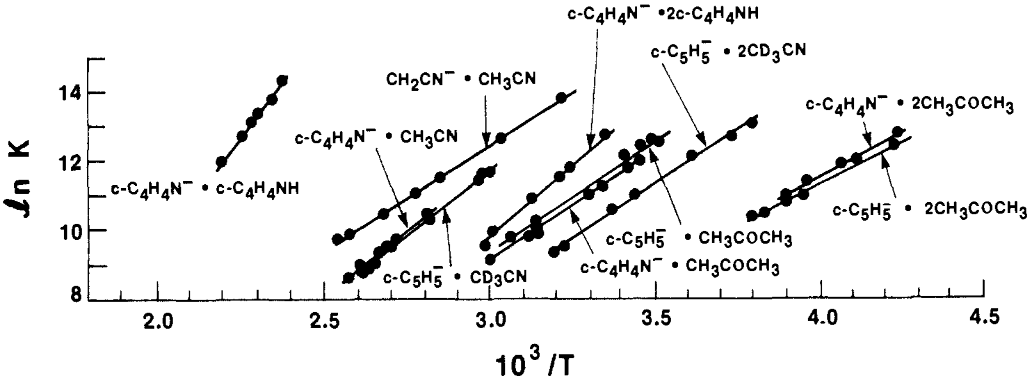

Figure 2. Van't Hoff plots for the dissociation of clusters involving aprotic solvents.

Reactions 1–12 in Table I show the solvation energies of carbanions and of the pyrrolide anion by H_2O. Although there are no experimental literature data on the present complexes, two of the present association energies were calculated by Gao et al.[5] For $HC_2^-{\cdot}H_2O$ two values were obtained, 15.5 kcal/mol with 6-31+G(d) and 18.4 kcal/mol with MP2/6-31+G(d). The experimental value of 16.2 kcal/mol agrees better with the former. For $CH_2CHO^-{\cdot}H_2O$, the 6-31+G(d) value, 16.6 kcal/mol, also agrees well with the experimental result of 15.4 kcal/mol. The ab initio calculation used the oxygen atom of the ion as the favored bonding site for H_2O. Experimental support for this configuration will be given below.

In the present data we observe the usual inverse correlation between dissociation energies, ΔH°_D, and the acidity difference, ΔH°_{acid}, of the components.[6] The largest series of this kind in the present results is for the $c\text{-}C_5H_5^-{\cdot}HOR$ complexes, and Figure 3 shows the correlation line for these complexes. From Figure 3, the correlation eq 2 is obtained.

$$\Delta H^\circ_D = 24.4 - 0.41\Delta\Delta H^\circ_{acid}\ (\text{kcal/mol}) \qquad (2)$$

Here $\Delta\Delta H^\circ_{acid}$ is the difference between the acid dissociation energies, $\Delta\Delta H^\circ_{acid}$, of $c\text{-}C_5H_6$ and ROH. The slope of the correlation line is somewhat larger than the value of about 0.30, which is usually observed for most types of anionic and cationic complexes. The intercept gives the intrinsic strength of this type of bond, i.e., the bond strength after accounting for acidity differences, as 24.4 kcal/mol. The intrinsic strength of $c\text{-}C_5H_5^-{\cdot}HOR$ hydrogen bonds is therefore considerably strong, but weaker than $O^-{\cdot}HO$ bonds whose intrinsic strength is 30.0 kcal/mol.[6b] It should be noted that the accuracy of the correlation line is limited by the short range of the acidity differences covered.

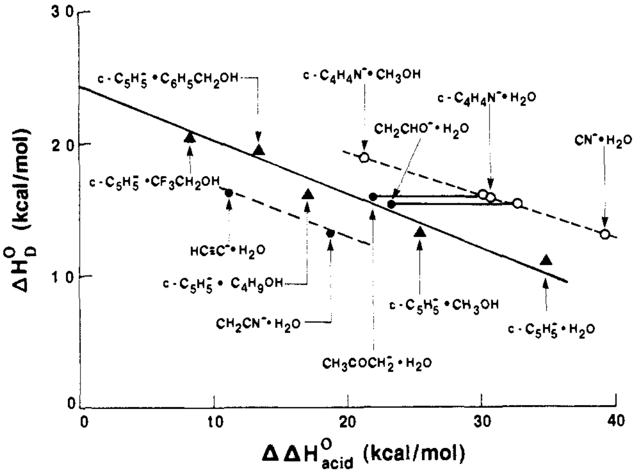

Figure 3. Correlations between ΔH°_D and $\Delta\Delta H^\circ_{acid}$ for complexes of $c\text{-}C_5H_5^-$ ions with water and alcohols (▲). Points for the solvation of other carbanions suggesting $C^-{\cdot}HO$ bonding (●), and for pyrrolide, $c\text{-}C_4H_4N^-$, and CN^-, suggesting $N^-{\cdot}HO$ bonding (○) are also shown. For $CH_2CHO^-{\cdot}H_2O$ and $CH_3COCH_2^-{\cdot}H_2O$, the oxygen enol acidities yield points (○) that fall on the correlation line for $N^-{\cdot}HO$ bonds and suggest analogous $O^-{\cdot}HO$ bonds while the consideration of $C^-{\cdot}HO$ bonds yields points (●) not consistent with the line (- -) for other $C^-{\cdot}HO$ complexes.

An alternative empirical equation that considers the electronegativities as well as $\Delta\Delta H^\circ_{acid}$ was developed by Larson and McMahon.[7] The predictions of this formula (in parentheses in Table I) for the $c\text{-}C_5H_5^-{\cdot}HOR$ complexes reproduce the variation of ΔH°_D with $\Delta\Delta H^\circ_{acid}$, but the predicted values are consistently too high by 3–4 kcal/mol. This may be because charge delocalization in the ion weakens the solvation energy. However, in

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(5) Gao, J.; Garner, D. S.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 4784.

(6) (a) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1971**, *93*, 7139. (b) Meot-Ner (Mautner), M.; Sieck, L. W. *J. Am. Chem. Soc.* **1986**, *108*, 7525.

(7) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1987**, *109*, 6230.

Table I. Thermochemistry[a] of Dissociation of Complexes of Carbanions and of the Pyrrolide Anion

	$\Delta H°_D$	$\Delta H°_D$ (L-M)[b]	$\Delta S°_D$	$\Delta\Delta H°_{acid}$[c]
		Protic Solvents		
$HC{\equiv}C^-{\cdot}H_2O$	16.2	18.4	18.6	11.0
$CN^-{\cdot}H_2O$	14.6	14.4	19.6	38.7
$CH_2CN^-{\cdot}H_2O$	13.2	17.8	17.6	18.7
$CH_2CHO^-{\cdot}H_2O$	15.4	18.9	19.5	32
$CH_3COCH_2^-{\cdot}H_2O$	15.8	19.5	20.3	29
$(CH_3COCH_2^-{\cdot}H_2O){\cdot}H_2O$	13.9		22.8	
$(CH_3COCH_2^-{\cdot}2H_2O){\cdot}H_2O$	13.0		27.4	
$(CH_3COCH_2^-{\cdot}3H_2O){\cdot}H_2O$	10.8		24.1	
$CF_3COCH_2^-{\cdot}H_2O$	12.8	15.8	17.3	32
$c\text{-}C_5H_5^-{\cdot}H_2O$	11.0	15.0	16.1	34.7
$(c\text{-}C_5H_5^-{\cdot}H_2O){\cdot}H_2O$	10.0		17.4	
$c\text{-}C_4H_4N^-{\cdot}H_2O$	15.7	17.5	23.1	30.7
$(c\text{-}C_4H_4N^-{\cdot}H_2O){\cdot}H_2O$	12.1		23.2	
$c\text{-}C_4H_4N^-{\cdot}CH_3OH$	18.6	20.8	27.5	21.5
$c\text{-}C_5H_5^-{\cdot}CH_3OH$	13.2	17.8	21.1	25.5
$c\text{-}C_5H_5^-{\cdot}t\text{-}BuOH$	17.0	21.1	32.0	17.2
$c\text{-}C_5H_5^-{\cdot}C_6H_5CH_2OH$	19.2	22.2	29.8	13.5
$c\text{-}C_5H_5^-{\cdot}CF_3CH_2OH$	20.6	23.8	24.3	8.3
		Aprotic Solvents		
$CH_2CN^-{\cdot}CH_3CN$	12.8	19.4	13.4	0
$c\text{-}C_4H_4N^-{\cdot}CH_3CN$	15.8		23.4	12.0
$CH_3COCH_2^-{\cdot}CH_3CN$	15.3	21.7	18.9	10
$c\text{-}C_5H_5^-{\cdot}CD_3CN$	15.5	15.6	22.8	16.0
$(c\text{-}C_5H_5^-{\cdot}CD_3CN){\cdot}CD_3CN$	13.1		22.8	
$(c\text{-}C_5H_5^-{\cdot}2CD_3CN){\cdot}CD_3CN$	<10.2		(22)[d]	
$c\text{-}C_4H_4N^-{\cdot}CH_3COCH_3$	13.1	20.2	20.5	8.7
$(c\text{-}C_4H_4N^-{\cdot}CH_3COCH_3){\cdot}CH_3COCH_3$	10.7		19.0	
$c\text{-}C_5H_5^-{\cdot}CH_3COCH_3$	13.5	16.5	21.8	12.7
$(c\text{-}C_5H_5^-{\cdot}CH_3COCH_3){\cdot}CH_3COCH_3$	9.8		16.4	
$c\text{-}C_4H_4N^-{\cdot}c\text{-}C_4H_4NH$	26.9	24.8	35.2	0
$(c\text{-}C_4H_4N^-{\cdot}c\text{-}C_4H_4NH){\cdot}c\text{-}C_4N_4NH$	17.1		31.2	
$c\text{-}C_5H_5^-{\cdot}c\text{-}C_5H_6$	<8.6	19.1	(20)[d]	0

[a] $\Delta H°$ and $\Delta G°$ in kcal/mol, $\Delta S°$ in cal/mol K. Error estimates: $\Delta H°$, ±1 kcal/mol, $\Delta S°$, ±2 cal/mol K. [b] Calculated from the empirical formula of Larsen and McMahon, ref 7. [c] References 15 and 16. For CH_2CHO^-, $CH_3COCH_2^-$ and $CF_3COCH_2^-$, the enol acidities of conjugate acids are considered. [d] $\Delta S°_D$ estimated from similar reactions, $\Delta H°$ calculated from $\Delta G°_D = \Delta H°_D - T\Delta S°_D$. For $(c\text{-}C_5H_5{\cdot}2CD_3CN){\cdot}CD_3CN$: $\Delta G°_D(232) > -5.1$ kcal/mol; for $c\text{-}C_5H_5^-{\cdot}c\text{-}C_5H_6$, $\Delta G°_D(250) > -3.6$ kcal/mol.

the more localized $HC_2^-{\cdot}H_2O$ complex, which also involves $C^-{\cdot}HO$ bonding, the predicted value is also too high by 2.2 kcal/mol.

The Larson and McMahon formula predicts well the bonding energies for anionic hydrogen bonds of nitrogen and oxygen compounds.[7] In the present data, the complexes of $c\text{-}C_4H_4N^-$ with H_2O, CH_3OH, and $c\text{-}C_4H_4NH$ belong to this category, and the predicted values are accurate within ±2 kcal/mol.

For the enolate anions $RCOCH_2^- \leftrightarrow RC(CH_2)CO^-$, theoretical[5] and experimental results (see below) indicate that H_2O bonds to the oxygen atom. Here the appropriate parameters are the acidities of the enols and the electronegativity of oxygen, and using these, the Larson–McMahon equation again predicts values too high by about 3 kcal/mol. Finally, for the bonding of the aprotic solvents CH_3CN and CH_3COCH_3 to several anions (Table I), the predicted values are too high by 0–7 kcal/mol.

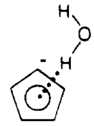
In summary, for the bonding of protic hydrogen donors to deprotonated carbon acids, the Larson–McMahon formula gives quite accurate results if the predictions are corrected by −3 kcal/mol. For the bonding of neutral carbon acids to anions, the predicted values are erratic and too high by up to 7 kcal/mol.

Discussion

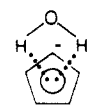
1. Comparison between Bonding Energies to $c\text{-}C_5H_5^-$ and $c\text{-}C_4H_4N^-$. Evidence for Covalent Contribution in $N^-{\cdot}HOR$ Bonds. The attachment energy of H_2O to the carbanion $c\text{-}C_5H_5^-$, 11.0 kcal/mol, is smaller than the attachment energy to the nitrogen-containing anion of similar ring size and aromaticity, the pyrrolide anion $c\text{-}C_4H_4N^-$, which is 15.7 kcal/mol. A similar relation is observed between the attachment energies of CH_3OH to $c\text{-}C_5H_5^-$ and $c\text{-}C_4H_4N^-$. The stronger bonding to $c\text{-}C_4H_4N^-$ may be due to several factors. First, in $c\text{-}C_4H_4N^-$, a nitrogen lone pair is present, and the $N^-{\cdot}HO$ hydrogen bond can have a significant covalent charge-transfer component. Alternatively, the stronger bonding of the hydrogen-bonding solvents to $c\text{-}C_4H_4N^-$ may be due to stronger electrostatic interactions due to the localization of charge on the nitrogen in $c\text{-}C_4H_4N^-$. In this case, however, $c\text{-}C_4H_4N^-$ should show stronger electrostatic interactions than $c\text{-}C_5H_5^-$ also with non-hydrogen-bonding polar solvents. To test this, we measured the bonding energies of the two ions to CH_3CN and CH_3COCH_3. The results show that, surprisingly, the bonding energies of the aprotic solvents to the two ions are similar. Therefore, the electrostatic bonding properties of the two ions seem to be similar, and stronger bonding between $c\text{-}C_4H_4N^-$ and H_2O would seem to reflect a covalent contribution to the $N^-{\cdot}HO$ hydrogen bond. Deprotonated amides and imidazole also form relatively strong $N^-{\cdot}HO$ bonds to H_2O with $\Delta H°_D$ of 15 kcal/mol.[17]

However, the present observations concerning the different behavior of H_2O and CH_3CN toward $c\text{-}C_5H_5^-$ and $c\text{-}C_4H_4N^-$ could be also explained on an electrostatic basis, following the arguments of Kebarle.[8] According to these arguments, CH_3CN would be less sensitive to charge localization differences between the ions because its dipole is more removed from the charge centers, due to the steric interference of the methyl group. Theoretical calculations on these systems would be helpful for a more definitive analysis.

2. $\pi^-{\cdot}HOR$ Hydrogen Bonds. Although the bonding in the complexes of $c\text{-}C_5H_5^-$ was denoted formally as $C^-{\cdot}HO$ interactions, the preferred structures may be $\pi^-{\cdot}HO$ complexes as in ion **1a**. This is likely if the negative charge of the anion is centered in the delocalized aromatic π system. An alternative, more constrained bidentate structure (**1b**) with the two water hydrogens bonded to the π system of the ion is not supported by the small value of $S°_D$ measured for this complex.



1a



1b

In relation to the π complex vs $C^-{\cdot}HO$ structure, the complexes of $c\text{-}C_5H_5^-$ can be compared with a complex that is known to involve a $C^-{\cdot}HO$ bond. An appropriate complex is $HC_2^-{\cdot}H_2O$, where ab initio results show an $HC{\equiv}C^-{\cdot}HOH$ bond.[5] Figure 3 shows that for the same $\Delta\Delta H°_{acid}$ a complex of $c\text{-}C_5H_5^-$ with HOR is stronger by about 4 kcal/mol than this true $C^-{\cdot}HOR$ complex. This may be seen as indirect evidence for a stronger type of bonding, probably of the $\pi^-{\cdot}HO$ type, in the complexes of $c\text{-}C_5H_5^-$.

Three complexes where even more efficient $N^-{\cdot}HO$-type bonding is possible lie by about a further 4 kcal/mol above the line for $c\text{-}C_5H_5^-{\cdot}HOR$. The $O^-{\cdot}H_2O$-type complexes similarly allow efficient hydrogen bonding involving two strongly electronegative centers and covalent charge transfer. It is of interest therefore that the $CH_2CHO^-{\cdot}H_2O$ and $CH_2C(CH_3)O^-{\cdot}H_2O$ complexes also lie on the highest line in Figure 3, if H_2O is considered bonded to the oxygen atoms and the oxygen acidities of the enols are used in calculating $\Delta\Delta H°_{acid}$. In contrast, $C^-{\cdot}HO$ bonding yields points (filled circles, Figure 3) that are not consistent with other $C^-{\cdot}HO$ complexes. These results are therefore consistent with $O^-{\cdot}H_2O$ hydrogen bonding in these complexes, in agreement with ab initio results.[5] Further evidence for this bonding site will be discussed below.

3. Solvation by Several Solvent Molecules. Table I shows the solvation energies of several carbanions by two to four solvent

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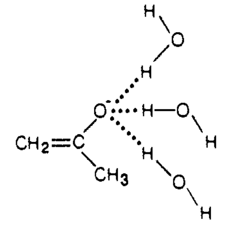
[8] (a) Kebarle, P. *J. Phys. Chem.* **1987**, *91*, 2551. (b) McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1977**, *99*, 2222.

molecules. Usually in clusters, the clustering energies approach the condensation energy of the solvent[9] as the lower limit. In c-$C_5H_5^-\cdot nH_2O$, the first clustering energy, $\Delta H°_{0,1}$ is already near $\Delta H°_{vap}(H_2O)$ = 10.5 kcal/mol, and $\Delta H°_{1,2}$ is also similar. Following the usual pattern, further attachment energies should remain similar. Overall, therefore, the condensation energy of the solvent about such a delocalized anion is not substantially larger than the condensation energy of a droplet of the neutral solvent. The solvation energies of the other carbanions and of (pyrrole-H)$^-$ by H_2O, CD_3CN and CH_3COCH_3 (Table I) also approach the respective condensation energies after two to three solvent molecules.

The sequence of attachment energies of H_2O molecules to $CH_3COCH_2^-$ shows a pattern of possible structural implications (Table I). The first three clustering energies seem to decrease asymptotically toward 13 kcal/mol, but with the fourth H_2O molecule a drop to 10.8 kcal/mol is observed. Such a drop usually implies the filling of a solvent shell, in this case after the third solvent molecule, and the start of an outer shell with the fourth. Our recent quantitative criteria for the filling of solvent shells[10] as applied to this system is expressed in eq 3, where $\Delta H°_{1,2}$ etc. are dissociation energies.

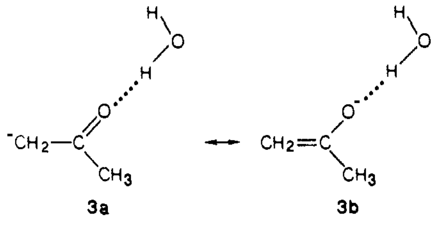
$$\Delta H°_s = (\Delta H°_{3,4} - \Delta H°_{2,3}) - (\Delta H°_{2,3} - \Delta H°_{1,2}) = -1.8 \text{ kcal/mol} \quad (3)$$

A negative value of $\Delta H°_s$ is taken as indicative of shell filling, and $\Delta H°_s < -2$ kcal/mol is taken as conclusive. The present results therefore constitute strong evidence for shell filling with the third H_2O molecule. A similar case was observed[10] recently in the solvation of OH^-, where the first three H_2O molecules attach to the three lone pairs of the oxygen atom.[11] Furthermore, recent crystallographic evidence shows that three H_2O molecules hydrogen bond to the oxygen in CH_3O^- to form the first shell.[12] In analogy, the filling of a solvent shell by three H_2O molecules about $CH_3COCH_2^-$ suggests that the water molecules bond to and form a solvent shell about the oxygen atom, as in structure **2**.



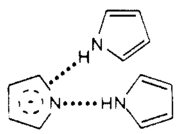
2

The shell structure effect provides further experimental support that the H_2O ligand attaches to the oxygen atom in $CH_2C(R)O^-$ to form efficient $O^-\cdot HO$ hydrogen bonds as discussed above. Therefore, hydration should shift the negative charge to the oxygen, or in terms of resonance structures, enhance resonance structure **3b** vs **3a**.



3a **3b**

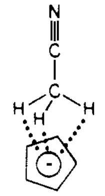
The higher clustering results also give an indication about hydrogen bonding involving an anionic π system. Such bonding is indicated in the pyrrolide trimer c-$C_4H_4N^-\cdot 2$c-C_4H_4NH. Here the second pyrrole molecule bonds to the dimer relatively strongly, by 17.1 kcal/mol, although the lone pair of the nitrogen of c-$C_4H_4N^-$ is already occupied. In contrast, hydrogen-bonded clusters where the only bonding site is blocked in the dimer, such as $(CH_3COCH_3)_2H^+$ and $(CH_3CN)_2H^+$ show a sharp drop in bonding energies in going to the trimer. Therefore, in the pyrrolide dimer an efficient bonding site seems to be available for the third molecule. Since the nitrogen atom in the pyrrolide anion has only one lone pair available, the second ligand molecule may be bonded to the ring in an $NH\cdot\pi^-$ interaction, as ion **4**. This is the anionic analogue of the $NH^+\cdot\pi$ interaction seen previously in the cationic $NH_4^+\cdot C_6H_6$ dimer.[13]



4

4. Interactions of Carbanions with Aprotic Solvents. Figure 3 and the preceding observations show that carbanions are more weakly hydrogen bonding than anions containing O^- and N^- centers, in agreement with electronegativity considerations.[7] The most unfavorable components for ion–ligand bonding are therefore carbanions interacting with aprotic, non-hydrogen-bonding solvents.

A complex of this type is $CH_2CN^-\cdot CH_3CN$, which indeed shows a weak interaction, 12.8 kcal/mol. In comparison, $CH_2C(CH_3)O^-\cdot CH_3CN$ is more strongly bonded (15.3 kcal/mol); here a hydrogen bond formally of the type $O^-\cdot HC$ is allowed. Surprisingly, however, c-$C_5H_5^-\cdot CH_3CN$ is also bonded by 15.5 kcal/mol. This is a stronger interaction than in $CH_2CN^-\cdot CH_3CN$ as well as in c-$C_5H_5^-\cdot H_2O$, both of which would be expected to be more strongly bonded based on charge localization and hydrogen-bonding considerations. In particular, the relation between the bonding of c-$C_5H_5^-$ to H_2O and CH_3CN is unusual since for every other anion, H_2O bonds more strongly than CH_3CN.[9] The unusual bonding strength in c-$C_5H_5^-\cdot CH_3CN$ suggests possible $\pi^-\cdot HC$ bonding, and the most favorable conformation may involve multiple HC interactions such as in ion **5**. The cationic analogy is a $\pi\cdot HC^+$ interaction in the benzene–$(CH_3)_4N^+$ complex.[13]



5

Another case where a carbanion would interact with an aprotic molecule is c-$C_5H_5^-\cdot$c-C_5H_6. Here also $\Delta H°_D$ is small, <8.6 kcal/mol. The weakness of carbanion–carbon acid interactions is consistent with the calculations of Scheiner et al. who find $\Delta H°_D$ = 10 kcal/mol for $HC\equiv C^-\cdot HC\equiv CH$.[14]

Conclusions

In the present work and recent papers,[3,17] we measured dissociation energies for the complexes of SH^-, $RCOO^-$, HC_2^-, CH_2CHO^-, OH^-, CH_3O^-, and CN^- with H_2O. Recently, Gao et al.[5] calculated these dissociation energies with an ab initio 6-31+G(d) basis set. In most cases, the experimental values are higher by only 1.5 kcal/mol than the ab initio values, and in most cases the ab initio values agree with experiment within 2 kcal/mol. The close agreement is encouraging.

In the present and preceding paper we also examined the new empirical equation of Larson and McMahon[7] for a large variety of anionic hydrogen-bonded complexes. In most cases, the pre-

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dictions of the formula are accurate within ±2 kcal/mol. Even complexes of a delocalized carbanion can be accomodated with a small correction of −3 kcal/mol. However, not surprisingly, the formula is not useful for complexes that are not properly hydrogen bonned, such as carbanions bonded to aprotic molecules.

After $\Delta\Delta H^\circ_{\text{acid}}$ relations are accounted for, the intrinsic hydrogen-bonding strengths of proper carbanions, i.e., carbanions without heteroatoms, to protic solvent molecules are weaker by 4–8 kcal/mol than for carbanions with electronegative oxygen or nitrogen functions. In the latter, experimental trends are consistent with ab initio calculations, indicating that the hydrogen-donor bonds to the electronegative heteroatom.

In c-$C_5H_5^-$ and c-$C_4H_4N^-$, trends in complexing energies suggest that the anionic aromatic π systems can serve as electron donors to protic and possibly to aprotic hydrogen-bonding ligands.

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Registry No. $HC{\equiv}C^-$, 29075-95-4; CN^-, 57-12-5; $^-CH_2CN$, 21438-99-3; $^-CH_2CHO$, 64723-93-9; $CH_3COCH_2^-$, 24262-31-5; $CF_3COCH_2^-$, 64723-97-3; c-$C_5H_5^-$, 12127-83-2; c-$C_4H_4N^-$, 23303-09-5; H_2O, 7732-18-5; CH_3OH, 67-56-1; *t*-BuOH, 75-65-0; $C_6H_5CH_2OH$, 100-51-6; CH_3CH_2OH, 75-89-8; CH_3CN, 75-05-8; CD_3CN, 2206-26-0; CH_3COCH_3, 67-64-1; c-C_4H_4NH, 109-97-7; c-C_5H_6, 542-92-7.

Distonic Ions as Reacting Species[†]

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Abstract: The characteristic reactions of a family of distonic radical cations show that the gas-phase chemistry of these species differs considerably from that of the isomeric conventional molecular ions. Fifteen distonic radical cations, derived from $^{\bullet}CH_2CH_2NH_3^+$ by introduction of alkyl substituents at C or N, have been demonstrated to be stable species whose reactions are characteristic of their structure. The predominant fragmentation and isomerization processes are the following: (i) simple cleavage of a C–N bond with formation of alkene ions or alkene molecules, (ii) 1,2-migration of protonated amino groups, and (iii) formation of ammonium ions by elimination of alkenyl radicals. Chain length permitting, these reactions may be preceded or accompanied by specific intramolecular hydrogen abstraction reactions, which lead to isomeric distonic ions with characteristically different reactions. The hydrogen abstraction reactions are generally reversible; in the presence of long alkyl groups isomerization to amine molecular ions (et vice versa) can occur. Correspondingly, the reactions of many low-energy amine molecular ions require isomerization to distonic intermediates prior to fragmentation.

A considerable number of recent papers have demonstrated the existence in the gas phase of stable distonic radical cations,[1-14] and distonic ions are with increasing frequency being suggested as key intermediates in unimolecular fragmentation reactions.[2,15-22] The collision-induced reactions of these species have often been used to establish their structural integrity, but the question of how the particular properties of distonic ions influence their reactions has not been addressed in the literature. We have studied the isomerization and dissociation reactions of a family of distonic amine ions, in order to discover the characteristic reactions of these species and to examine the difference between these reactions and those of the corresponding conventional molecular ions.

The term *distonic ion* was coined by Radom and co-workers[23] to describe radical cations arising (formally) by ionization of zwitterions or diradicals. The difference between the properties of stable distonic ions and those of conventional molecular ions generated by direct ionization of neutral molecules can be considerable, and Radom's neologism has rapidly gained acceptance among gas-phase ion chemists. However, the properties of distonic ions often vary with the number of heavy atoms separating the charge and radical bearing sites. In the present paper we employ the adjectives α-distonic, β-distonic, γ-distonic, etc., to denote respectively species with charge and radical at adjacent atoms (α-distonic ions or ylidions, e.g., **1**), with charge and radical separated by one heavy atom (β-distonic ions, e.g. **2**), by two heavy atoms (γ-distonic ions), etc.

Chart I

$CH_3NH_2^{+\bullet}$ $CH_3CH_2NH_2^{+\bullet}$

$^{\bullet}CH_2NH_3^+$ $^{\bullet}CH_2CH_2NH_3^+$

1 2

Recent experimental and ab initio studies[11-14,21,24,25] of the various $CH_5N^{\bullet+}$ and $C_2H_7N^{\bullet+}$ isomers have shown that α- and

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