

Ionic Hydrogen Bond and Ion Solvation. 6. Interaction Energies of the Acetate Ion with Organic Molecules. Comparison of CH_3COO^- with Cl^- , CN^- , and SH^-

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Abstract: The interaction energies of CH_3COO^- with protic and aprotic molecules were measured by pulsed high-pressure mass spectrometry. The attachment energies of the first three water molecules are 15.8, 12.8, and 11.8 kcal/mol. The rapid approach to $\Delta H_{\text{conden}}(\text{H}_2\text{O})$ shows that ionic interactions are accounted for mostly by the first two solvent molecules. CH_3COO^- hydrogen bonds strongly to NH acids such as pyrrole, amides, and aniline, with $\Delta H_{\text{D}}^\circ = 25\text{--}31$ kcal/mol. With the carbon acids CH_3CHO , CH_3COCH_3 , and CH_3CN as ligands, the attachment energies are 14-16 kcal/mol and the interactions may involve multiple $\text{O}^-\text{--HC}$ bonds. Despite the fact that the ions CH_3COO^- , Cl^- , CN^- , and SH^- differ in size, structure, electronegativity, isotropy, and available bonding sites, they bond with similar strengths to most OH, NH, and CH hydrogen donors, from H_2O to large organic molecules such as the dipeptide analogue $\text{CH}_3\text{CO-Ala-OCH}_3$. Also, the four ions show similar clustering energies with n H_2O and HCN molecules ($n = 1\text{--}4$).

Carboxylate anions are common charge carriers in biological environments. These ionic groups are expected to interact strongly with a large variety of organic molecules and functional groups. For example, we found recently that acetate ions hydrogen bond to water, alcohols, and CH_3COOH by 15-30 kcal/mol.¹ To broaden the understanding of ionic hydrogen bonding in biological systems, it is of interest to measure the interaction energies of CH_3COO^- also with NH donors such as pyrrolic, amide, and aniline systems. Bonding to polar carbon acids is also of interest since $\text{O}^-\text{--HC}$ interactions can occur. These would be anionic analogies of $\text{CH}^{\delta+}\text{--O}$ type hydrogen bonds that were investigated recently.²

The acetate anion is a structured, anisotropic ion with two equivalent bonding sites, high polarizability, high electronegativity, and strong gas-phase acidity of the parent molecule. These properties are expected to affect the electron-donor properties of anions in ionic hydrogen bonds. It is of interest therefore to compare the ligand bonding energies of the acetate ion with those of a series of anions that vary in these properties. In the present work, we examine new and literature data on clustering energies of CH_3COO^- , Cl^- , CN^- , and SH^- with a series of OH, NH, and CH hydrogen-donor ligands, including some common solvent molecules and biological model molecules.

In relation to the effects of anisotropy, we found recently that the bonding energies in the clusters $\text{CN}^- \cdot n\text{HCN}$ ($n = 1\text{--}6$) were similar to those in $\text{Cl}^- \cdot n\text{HCN}$.³ This showed that the anisotropy of the field about CN^- did not affect significantly the interaction energies. Similarly, Larson and McMahon found recently that the hydrogen-bonding energies of a variety of ligands to Cl^- and CN^- are comparable.⁴ The acetate ion is even more structured and anisotropic than CN^- , and it is of interest whether this affects the clustering thermochemistry. We shall compare clusters of CH_3COO^- , Cl^- , and CN^- with one to four H_2O and HCN molecules in relation to this question.

Experimental Section

The measurements were performed with the NBS pulsed high-pressure mass spectrometer and standard methods.¹ The carrier gas was CH_4 , and the anions were generated by pulsed chemical ionization using trace CH_3ONO and/or 1-10% N_2O for electron capture. In particular, N_2O proved inefficient below about 180 °C, and at lower temperatures

CH_3ONO was always used. The reactant OH^- or CH_3O^- ions then reacted with trace CH_3COOH to yield CH_3COO^- anions or with the ligands BH to give B^- . The ions CN^- and SH^- were similarly generated by chemical ionization of HCN and H_2S , and Cl^- was generated by direct electron capture by trace CHCl_3 .

The concentration of CH_3COOH was kept to a minimum so that the formation of $\text{CH}_3\text{COO}^- \cdot \text{CH}_3\text{COOH}$ will proceed slowly, allowing the measurement of the fast equilibria of interest. Attempts to use $\text{CH}_3\text{COOCOCH}_3$ as a source of CH_3COO^- anions failed to prevent the self-clustering problem, possibly due to impurities of CH_3COOH . The reaction mixture also contained 0.1-5% of the ligand BH. Under these conditions the primary reactant ions OH^- or CH_3O^- can react first with BH to give B^- , which in turn can react with CH_3COOH to give CH_3COO^- , or cluster with BH to give $\text{B}^- \cdot \text{BH}$. The latter can then exchange with CH_3COOH to give $\text{CH}_3\text{COO}^- \cdot \text{BH}$.

The preliminary fast chemical ionization processes therefore result in the stable species CH_3COO^- and $\text{CH}_3\text{COO}^- \cdot \text{BH}$. Under our conditions the preliminary processes are mostly completed during the 1-ms ionizing pulse, and equilibrium between CH_3COO^- and $\text{CH}_3\text{COO}^- \cdot \text{BH}$ is also achieved during the ionizing pulse. The ions observed during the subsequent 2-10-ms equilibrium period are therefore these ions in a constant equilibrium ratio, both in slow decay and in parallel as $\text{CH}_3\text{COO}^- \cdot \text{CH}_3\text{COOH}$ builds up.

Total source pressures were 0.8-2.4 Torr, and checks were performed to ensure that the equilibrium constant was independent of pressure in this range. Checks were also made by varying the pressure of CH_3COOH and therefore the buildup rate of $\text{CH}_3\text{COO}^- \cdot \text{CH}_3\text{COOH}$. It was found that this consecutive reaction does not affect significantly the equilibrium ion ratio. Nevertheless, the rate of this clustering reaction increases with decreasing temperature, and it can become significant once the pseudo-first-order association rate approaches collision rate. This limits the temperature range of the van't Hoff plots for the equilibria for the formation of $\text{CH}_3\text{COO}^- \cdot \text{BH}$.

With low-volatility ligands such as indole, aniline, and $\text{CH}_3\text{CO-Ala-OCH}_3$, the mixture was allowed to flow to the source for up to 1 h until the measured equilibrium constant became independent of flow time, indicating that P_{BH} achieved a constant value in the source. Kinetic measurements on proton-transfer reactions involving these ligands showed that the reactions proceeded at the expected collision rate as calculated with the nominal concentrations. This confirmed that the ligand concentration after a sufficiently long flow time was the nominal value.

The reagents were purchased from commercial sources and used as purchased. HCN was generated by dropping KCN into concentrated H_2SO_4 .

Results

Equilibrium constants for the attachment of ligands BH to CH_3COO^- were obtained from eq 1.

$$K = I(\text{CH}_3\text{COO}^- \cdot \text{BH}) / I(\text{CH}_3\text{COO}^-) P_{\text{BH}} \quad (1)$$

Here, I is ion signal intensity, and P_{BH} is the partial pressure of BH in the source in atmospheres. Van't Hoff plots were obtained from temperature studies and are shown in Figures 1

(1) Meot-Ner (Mautner), M.; Sieck, L. W. *J. Am. Chem. Soc.* **1986**, *108*, 7525.

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(3) Meot-Ner (Mautner), M.; Scheiner, S.; Liebman, J. F., submitted for publication in *J. Chem. Phys.*

(4) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1988**, *110*, 1087-1093.

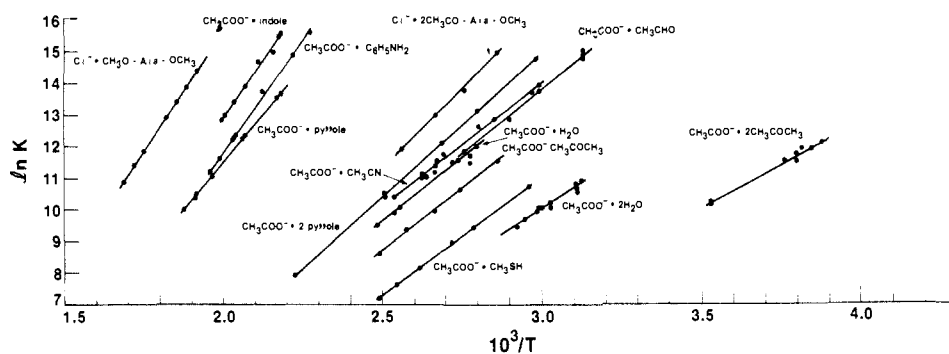


Figure 1. Van't Hoff plots for the clustering of various ligands with CH_3COO^- . The notation $\text{CH}_3\text{COO}^- \cdot 2\text{H}_2\text{O}$ stands for $\text{CH}_3\text{COO}^- \cdot 2\text{H}_2\text{O} \rightarrow (\text{CH}_3\text{COO}^- \cdot 2\text{H}_2\text{O}) + \text{H}_2\text{O}$, etc.

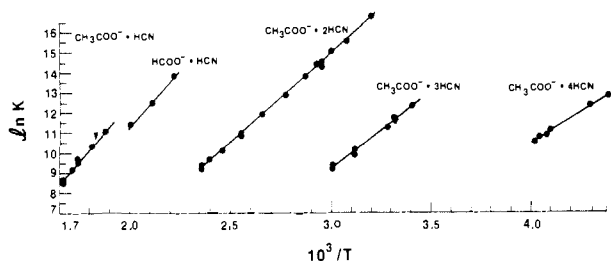


Figure 2. Van't Hoff plots for the clustering of HCOO^- and CH_3COO^- with HCN.

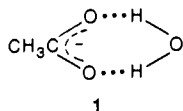
and 2. The results are summarized in Table I.

The present results are in very good agreement with literature data in most cases. In particular, good agreement is observed for five out of seven bonding energies that were measured also by Larson and McMahon.⁴ The agreement is notable since the latter ICR results were obtained from ligand-exchange equilibria at one temperature, using estimated entropy changes. The two cases where significant differences are noted are $\text{CN}^- \cdot \text{pyrrole}$ and $\text{CN}^- \cdot \text{CH}_3\text{CN}$. Both show somewhat unusual ΔS°_D values, and the error in the ICR enthalpies results from the entropy estimates.

Discussion

1. Hydration. We measured recently¹ the dissociation energy of $\text{CH}_3\text{COO}^- \cdot \text{H}_2\text{O}$, and the result was reproduced with excellent agreement in the present work. Further, the attachment energies of the second and third water molecules were also measured in the present work.

In the complex $\text{CH}_3\text{COO}^- \cdot \text{H}_2\text{O}$, the bidentate structure **1** is possible, and ab initio calculations suggest that it is more stable by 3 kcal/mol than a singly bonded isomer.⁵



However, several experimental observations argue against the bidentate structure **1**. First, the bonding energies of $\text{CH}_3\text{COO}^- \cdot \text{H}_2\text{O}$ and $\text{CH}_3\text{COO}^- \cdot \text{CH}_3\text{OH}$ are similar,¹ although the latter cannot form a bidentate structure. Also, ΔS°_D of $\text{CH}_3\text{COO}^- \cdot \text{H}_2\text{O}$ is similar to that of the other anions in Table I, indicating the absence of a special constrained structure in $\text{CH}_3\text{COO}^- \cdot \text{H}_2\text{O}$. Further, the thermochemistries of the second and higher clustering steps of the four ions are also similar, while displacement of the bidentate bond upon higher clustering of $\text{CH}_3\text{COO}^- \cdot \text{H}_2\text{O}$ could result in special thermochemical values for this ion.

The experimental results therefore argue against structure **1** under the experimental conditions. This structure may not form because of unfavorable entropy of the constrained structure. Even if present in the monohydrated cluster, the second hydrogen bond would be displaced by additional solvent molecules in the higher

clusters and in aqueous solution. Indeed, the bidentate structure is not observed in solution.⁵

The observed decrease of ΔH°_D from the first to the second solvent molecule by a factor of 0.8 follows the usual trend.⁶ With a further decrease to 11.8 kcal/mol with the third molecule, the attachment energy of the solvent molecules is already, within the experimental error, about the limiting value, which is $\Delta H^\circ_{\text{vap}}(\text{H}_2\text{O}) = 10.5$ kcal/mol. According to the usual trend, subsequent solvent molecules should continue to bond to the cluster with energies near the neutrallike condensation limit.⁶ Therefore, the ionic contribution to the solvation of carboxylate anions is contained mainly in the hydrogen bonds to the first two solvent molecules. A similar argument applies also to the hydration of Cl^- and Br^- , as well as of carbanions such as H_2C^- , CH_2CN^- , $\text{c-C}_5\text{H}_5^-$, (pyrrole-H)⁻, and (imidazole-H)⁻ and of deprotonated peptide links, for all of which the attachment energy of the first H_2O molecule is 13–16 kcal/mol.⁷ In all of these, the weak ionic contributions to solvation are largely dissipated within the first two water molecules.

2. Complexes with Nitrogen Acids. Table I lists the dissociation energies of $\text{CH}_3\text{COO}^- \cdot \text{HN}$ complexes involving five nitrogen acids. The $\text{CH}_3\text{COO}^- \cdot \text{HN}$ bonding in the complexes with pyrrole, indole, and an amide is substantial, 24–28 kcal/mol. These complexes model the bonding of aspartate COO^- functions to imidazole in protease enzyme centers. The structures of these complexes and their biological implications are discussed elsewhere.⁷

The strongest bond in Table I is between CH_3COO^- and the alanine derivative $\text{CH}_3\text{CONH}(\text{CH}_3)\text{COOCH}_3$ (i.e., $\text{CH}_3\text{CO-Ala-OCH}_3$), which models a peptide link. The main bonding site here is the amide NH group. However, the bonding of this large molecule with anions is also enhanced by secondary $\text{CH} \cdot \text{X}^-$ interactions and nonionic dispersion forces, which arise upon multiple contact between the large ligand and the ion. Further evidence of this will be given below.

Table I shows the attachment energies of a second molecule of pyrrole, $\text{CH}_3\text{CONHCH}_3$, and $\text{CH}_3\text{CO-Ala-OCH}_3$ to CH_3COO^- . The point of interest is that the ion has two separate but equivalent attachment sites. The question is whether attachment to two sites decreases the mutual interactions of the ligand molecules. In the clustering of ligands to an attachment site in ions, such as, for example, a protonated oxygen or nitrogen atom in cationic complexes, the usual trend is that the attachment energy of the second molecule is decreased by a factor of 0.7–0.8 because of charge delocalization and mutual repulsion of the ligands.⁶ For pyrrole, $\text{CH}_3\text{CONHCH}_3$, and $\text{CH}_3\text{CO-Ala-OCH}_3$, the ratio $\Delta H^\circ_{1,2}/\Delta H^\circ_{0,1}$ is 0.74, 0.64, and 0.68, respectively, and for H_2O , we found the ratio 0.81. The mutual effects of two ligands attached to CH_3COO^- are therefore at least as large as is usual for ligands attached to a single bonding site. Therefore, the results suggest that the charge delocalization and repulsion effects of the ligands are transmitted effectively through the O–C–O⁻ system. The same conclusion is reached below from energies of higher clustering.

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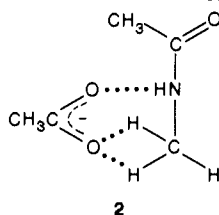
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Table I. Thermochemistry^a of Complexes of Anions A⁻ with Ligands BH

BH	ΔH°_D				ΔS°_D			
	CH ₃ COO ⁻	Cl ⁻	CN ⁻	SH ⁻	CH ₃ COO ⁻	Cl ⁻	CN ⁻	SH ⁻
Protic Oxygen and Sulfur Ligands								
H ₂ O	15.8 18.2 ^f (17.1)	14.8 ^b 15.1 ^l (13.7)	14.6 15.8 ^l (14.4)	14.2 15.6 ^l (14.4)	20.3	19.7	19.6	18.7
2 H ₂ O ^c	12.8	12.8 ^b	11.7	12.6	19.1	21.0	18.1	20.4
3 H ₂ O ^c	11.8 ^d	11.7 ^b	10.7	11.7	20 ^p	22.4	19.8	23.5
CH ₃ OH	17.6 (20.4)	17.4 ⁿ (16.3)	16.6 16.5 ^m (17.2)	17 (17.2)	23.6	24.1	20.8	20 ^p
C ₂ H ₅ OH	20.7 ^e (21.7)	17.3 ^o (17.4)	17.4 17.4 ^m (18.2)	16.2 (18.2)	29.2	23.1	22.5	19.8
C ₆ H ₅ OH	26.1 ^e (31.2)	25.0 ⁱ (25.0)			24.0	26.0		
CH ₃ COOH	29.3 ^e (31.0)	21.6 ^f (24.8)			29.6	19.3		
H ₂ S		21 ^m (17.7)	18.9 ^k 19.8 ^m (18.9)	13.2 (18.9)			20.1	19.7
CH ₃ SH	14.9 (22.2)				22.8			
Protic Nitrogen Ligands								
pyrrole	24.0 (23.8)		23.4 19.5 ^m (19.7)	23.0 (19.7)	25.1		27.1	24.4
2 pyrrole ^c	17.9				24.2			
indole	27.9 (25.1)				30.4			
CH ₃ CONHCH ₃	25.4 ^g (23.6)					27.4		
2 CH ₃ CONHCH ₃ ^c	16.4 ^g				18.7			
CH ₃ CO-Ala-OCH ₃	31.4 ^g (26.0)	29.4 (20.2)	26.4 (21.4)	27.5 (21.4)	35.6	28.3	28.7	27.8
2 CH ₃ CO-Ala-OCH ₃ ^c	21.2 ^g	19.8			34.1	27.0		
Aprotic Ligands								
HCN	23.5 ^h (23.6)	21.8 21 ^m (17.7)	20.7 21.7 ^m (18.9)	21 (18.9)	22.2	18.9	20.6	20 ^p
2 HCN ^c	16.6 ^h	17.9	16.4		20.2	22.7	21.8	
3 HCN ^c	14.8 ^h	13.6	12.6		25.6	21.4	21.2	
4 HCN ^c	12.0 ^h	11.2	10.9		27.2	23.4	24.8	
HCOO ⁻ -HCN	22.0 (22.2)				21.4			
HCOO ⁻ -2HCN ^c	17.8				23.6			
CH ₃ CHO	16.3 (19.8)				21.7			
CH ₃ COCH ₃	15.7 (19.6)	13.7 ⁱ (14.8)			21.9	19.6		
2 CH ₃ COCH ₃ ^c	10.8				17.9			
CH ₃ CN	14.8 (18.6)	13.5 ^j (14.0)	13.8 16.4 ^m (14.9)		18.0	15.0	14.2	

^a ΔH°_D in kcal/mol, error estimate ± 1 kcal/mol; ΔS°_D in cal/mol·K, error estimate ± 2 cal/mol·K. Present results unless stated otherwise. Values in parentheses calculated from the empirical equation of Larson and McMahon. ^b Reference 8. ^c Shorthand for Cl⁻·2H₂O → (Cl⁻·H₂O)·H₂O, etc. ^d From $\Delta G^\circ_D(298) = 5.9$ kcal/mol; ΔS°_D estimated 20 cal/mol·K. ^e Reference 1. ^f Reference 16. ^g Reference 7. ^h Reference 3. ⁱ Reference 17. ^j Reference 8. ^k From ligand exchange equilibrium CN⁻·H₂S + HCN → CN⁻·HCN + H₂S; $\Delta H^\circ = -1.8$ kcal/mol; $\Delta S^\circ = -0.5$ kcal/mol·K. ^l Reference 5. ^m Reference 4. ⁿ Reference 8b. ^o Reference 14. ^p Estimated.

In fact, the mutual effects of two ligand molecules of CH₃C-O-NHCH₃ or CH₃CO-Ala-OCH₃ attached to CH₃COO⁻ are somewhat larger than usual. A possible reason may be that the attachment of the first ligand molecule involves secondary O⁻·HC interactions such as in ion 2. The energy required to displace



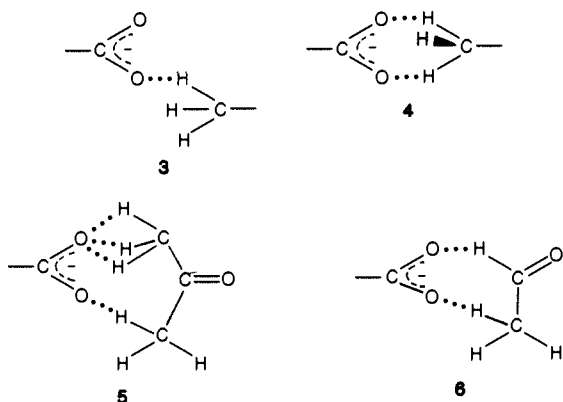
the weaker O⁻·HC bonds by the second O⁻·HN bond would make

this bond appear weaker and would result in a small $\Delta H^\circ_{1,2}/\Delta H^\circ_{0,1}$ ratio.

3. Interactions with Aprotic Solvents. RCOO⁻·HC Bonds. The positive end of the dipole of the aprotic polar molecules CH₃CHO, (CH₃)₂CO, and CH₃CN are on the methyl groups, and the most favorable structures should be 3-6.

In analogy with, for example, Cl⁻·CH₃CN, the methyl hydrogens are expected to interact with the anionic center.⁸ The simplest structure is 3. However, structures with multiple interactions such as 4-6 may be more stable. For example, in the analogous cationic CH^{δ+}·O type complex N(CH₃)₄⁺·H₂O, ab initio

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calculations showed that the most stable geometry was a "cavity complex" where the oxygen atom fits into a cavity formed by three methyl hydrogens from two methyl groups.² An analogous complex is illustrated in 5. However, because of the presence of two bonding sites in CH_3COO^- , other multiply bonded structures such as 4 and 6 also may be possible.

The mutual effect of two acetone ligands as expressed by $\Delta H_{1,2}^\circ/\Delta H_{0,1}^\circ$ is 0.68. This is within the usual range, though somewhat large, which may reflect the disruption of a multiply bonded structure such as 4-6.

In relation to $\text{CH}_3\text{COO}^- \cdot \text{CH}_3\text{CHO}$, a point of interest is whether the aldehyde hydrogen bears a large fractional charge and whether it attaches then strongly to the anion. Comparison with the CH_3COCH_3 complex shows similar bonding energies, and we note also that the gas-phase acidities of the two ligands are similar. The observations suggest that CH_3CHO attaches to the anion by the methyl group.

An O-HC bond also occurs in $\text{CH}_3\text{COO}^- \cdot \text{HCN}$. In comparison with the other aprotic ligands, the bonding energy is increased however by 6-8 kcal/mol, due to the large partial charge on the hydrogen in HCN.

The complexing energies of HCOO^- with one and two molecules of HCN are similar to the complexing energies with CH_3COO^- . This is consistent with the empirical ΔH_D° vs $\Delta\Delta H_{\text{acid}}^\circ$ correlations,^{1,19} which, given the acidity difference of 5 kcal/mol between the two acids,⁹ predict a difference of only about 1 kcal/mol between bonding to the two ions. Similarly, the acid dissociation energies $\Delta H_{\text{acid}}^\circ$ of all carboxylic acids are within 5 kcal/mol of that of CH_3COOH , and the bonding energies of all the $\text{RCOO}^- \cdot \text{HB}$ complexes should be similar to those of $\text{CH}_3\text{COO}^- \cdot \text{HB}$.⁹ Therefore, the values in Table I should be good models for the interaction energies of ligands with most carboxylate functions, including those in biological systems.

4. Comparison of CH_3COO^- , Cl^- , CN^- , and SH^- . Ionic hydrogen bonding is dominated by electrostatic interactions, but covalent electron transfer, attractive dispersion forces, and repulsive factors also play a role. The four ions differ significantly in size, charge delocalization, electron densities at the bonding site, and the spatial distribution of charge, i.e., isotropy. On this basis it may be expected that the hydrogen-bonding energies to a given ligand would vary significantly. However, the four ions exhibit bonding energies nearly identical with the OH donors H_2O and alcohols, the NH donors pyrrole and the peptide analogue $\text{CH}_3\text{CONHCH}(\text{CH}_3)\text{COOCH}_3$, and the CH donors HCN, CH_3COCH_3 , and CH_3CN .

It is noted that the attachment energies of H_2O to the four ions agree well with the ab initio results of Gao et al.⁵ These authors suggest that attachment energies of ligands to delocalized ions such RCOO^- and CN^- are weakened due to electrostatic effects. Bonding to anions with second-row atoms is also weakened by polarization and ionic radius effects and decreased covalent charge transfer. The results are increased hydrogen bond lengths, which are about 2.4 Å for second-row hydrates, 1.8-2 Å to hydrates of HCOO^- and CN^- , compared with 1.4-1.8 Å for $\text{RO}^- \cdot \text{H}_2\text{O}$.⁵ The

ab initio results therefore suggest that various hydrogen bond weakening factors operate in the four ions. It is remarkable that the various factors balance out to yield similar bonding energies that vary less than 2 kcal/mol across the four ions for diverse ligands such as H_2O , CH_3OH , pyrrole, $\text{CH}_3\text{CO-Ala-OCH}_3$, HCN, and CH_3CN .

The factors that affect anionic hydrogen bonding also affect the acidities of the components, and an inverse correlation is usually observed between $\Delta\Delta H_{\text{acid}}^\circ$ and ΔH_D° .¹ Larson and McMahon developed recently an improved empirical correlation, which also considers the electronegativities of the components.⁴ The predictions of this equation are quoted in parentheses in Table I. The agreement with experimental values for the complexes of CH_3COO^- , Cl^- , and CN^- with OH and NH ligands (except $\text{CH}_3\text{CO-Ala-OCH}_3$) is remarkably good; 14 out of 15 complexes agree better than 3 kcal/mol. The one larger deviation may be due to bond weakening in $\text{CH}_3\text{COO}^- \cdot \text{C}_6\text{H}_5\text{OH}$ where both components are strongly delocalized. However, other complexes of CH_3COO^- show good agreement with predicted values, and in this respect charge delocalization in the ion does not seem significantly bond weakening.

The bonding energies of the complexes of HCN with the four ions also agree well with predicted values. However, the weaker carbon acids CH_3CHO , $(\text{CH}_3)_2\text{CO}$, and CH_3CN show weaker bonding to CH_3COO^- than predicted. The agreement is also poorer for complexes involving sulfur, where three out of seven complexes show substantial differences.

On the whole, the equation of Larson and McMahon seems to predict reliably anionic hydrogen bond strengths. A useful application of the equation is to identify special structural effects. The complexes of the large flexible peptide-like alanine derivative $\text{CH}_3\text{CONHCH}(\text{CH}_3)\text{COOCH}_3$ are all stronger by 5-9 kcal/mol than expected. This strongly suggests multiple interactions where $\text{CH} \cdot \text{X}^-$ interactions and nonionic dispersion forces contribute 5-9 kcal/mol to the bonding to the four anions.

5. Higher Clustering. The similarity in the bonding energies of the four ions applies also in higher clustering, i.e., the attachment energies of the second and higher ligand molecules. This applies in all the cases observed, from the small weakly bonded ligand H_2O to the large strongly bonded ligand $\text{CH}_3\text{CO-Ala-OCH}_3$.

To compare the higher clustering properties of CH_3COO^- , Cl^- , and CN^- , we measured the clustering energies with up to four HCN molecules. HCN was selected as a strongly bonding small ligand that can approach closely and is therefore a good probe of the field about the ion. We find very similar clustering energies, which suggested that for clustering purposes CN^- and CH_3COO^- act in a manner similar to that of an isotropic core ion. Similar results were obtained in comparing the clustering of K^+ and NH_4^+ .¹⁰

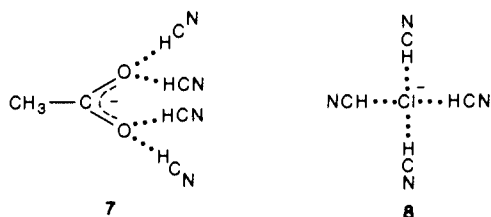
The results are unexpected since CH_3COO^- has two binding sites and the two oxygen atoms can provide a total of five lone pairs for hydrogen-bonding ligands. The structure of the solvent attached directly to CH_3COO^- as in 7 is quite different from structure 8 about Cl^- .

Conclusion

The four ions CH_3COO^- , Cl^- , CN^- , and SH^- show similar hydrogen-bonding and clustering energies with a variety of ligands. Electrostatic considerations and ab initio calculations⁵ suggest that this results from compensating variations of several bonding

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factors. The bonding energies are reproduced well by ab initio calculations⁵ and by a new empirical formula for anionic hydrogen bonds.⁴ This formula also helps to identify special structural effects such as secondary CH \cdots 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 $_3$ S $^-$,⁵ as well as H°_D vs $\Delta\Delta H^\circ_{\text{acid}}$ correlations,¹ and the empirical formula of Larson and McMahon⁴ all suggest that alkyl substitution on the anionic site, which changes the $\Delta\Delta H^\circ_{\text{acid}}$ 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 $^-$ ·HCN ($\Delta H^\circ_D = 22.0$ kcal/mol) are compared with CH $_3$ COO $^-$ ·HCN ($\Delta H^\circ_D = 23.5$ kcal/mol). Therefore, although the CH $_3$ COO $^-$ and SH $^-$ ions are simpler than biological ions, the attachment energies of CH $_3$ COO $^-$, 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 $_3$ CO-Ala-OCH $_3$ also suggest, however, that overall anion binding can be significantly strengthened by CH \cdots O $^-$ bonds and dispersion forces. The presence of bulk solvent will also have a significant effect.

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Registry No. CH $_3$ COO $^-$, 71-50-1; Cl $^-$, 16887-00-6; CN $^-$, 57-12-5; SH $^-$, 15035-72-0; CH $_3$ OH, 67-56-1; C $_2$ H $_5$ OH, 64-17-5; C $_6$ H $_5$ OH, 108-95-2; CH $_3$ COOH, 64-19-7; H $_2$ S, 7783-06-4; CH $_3$ SH, 74-93-1; CH $_3$ CO-NHCH $_3$, 79-16-3; CH $_3$ CO-Ala-OCH $_3$, 3619-02-1; HCN, 74-90-8; CH $_3$ CHO, 75-07-0; CH $_3$ COCH $_3$, 67-64-1; CH $_3$ CN, 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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Abstract: The bonding energy of a water molecule to carbanions ranges from 11.0 kcal/mol for $c\text{-C}_5\text{H}_5^-$ to 13-15 kcal/mol for CH $_2$ CN $^-$, CH $_2$ CHO $^-$, and CH $_2$ COCH $_3^-$ and to 16.2 kcal/mol for HCC $^-$. Alcohols bond to $c\text{-C}_5\text{H}_5^-$ more strongly, by up to 20.6 kcal/mol for the strongly acidic CF $_3$ CH $_2$ OH, and the attachment energies show an inverse linear correlation with the acidities of the alcohols. The $c\text{-C}_5\text{H}_5^-$ ion exhibits unusual behavior in that it bonds to the hydrogen donor H $_2$ O more weakly (11.0 kcal/mol) than to CH $_3$ CN (15.5 kcal/mol). In contrast, the more localized pyrrolide ion $c\text{-C}_4\text{H}_4\text{N}^-$ bonds to the two solvents by comparable strength, 15.8 and 15.7 kcal/mol, respectively. These observations indicate a specific N \cdots OH hydrogen bonding contribution in $c\text{-C}_4\text{H}_4\text{N}^-$ ·H $_2$ O, and/or an unusual C \cdots HC type hydrogen-bonding contribution in $c\text{-C}_5\text{H}_5^-$ ·CH $_3$ CN. As to structures, correlations between ΔH°_D and $\Delta H^\circ_{\text{acid}}$ suggest that ligands may hydrogen bond to the π system of $c\text{-C}_5\text{H}_5^-$, and to the oxygen atoms in CH $_2$ CHO $^-$ and CH $_2$ COCH $_2^-$. The latter is also supported by solvent shell effects in CH $_2$ COCH $_2$ · n H $_2$ O.

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 $^-$ ·HO interactions, is less efficient than the solvation of oxoanions that involves O $^-$ ·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 $c\text{-C}_5\text{H}_5^-$. The question of interest is whether the interaction with an H $_2$ O 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 $c\text{-C}_4\text{H}_4\text{N}^-$, where the formation of N \cdots 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.

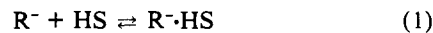
Experimental Section

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 $_3$ ONO 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 $^-$ · n H $_2$ O clusters, deprotonation and ligand switching reactions formed OH $^-$ · n H $_2$ O 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.



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