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The Ionic Hydrogen Bond and Ion Solvation. 5. OH···O$^-$ Bonds. Gas-Phase Solvation and Clustering of Alkoxide and Carboxylate Anions

Michael Meot-Ner (Mautner)* and L. Wayne Sieck

Contribution from the Chemical Kinetics Division, Center for Chemical Physics, National Bureau of Standards, Gaithersburg, Maryland 20899. Received May 2, 1986

Abstract: Dissociation energies, ΔH°_D, of RO$^-$·HOR, RCOO$^-$·HOR, and RCOO$^-$·HOOCR complexes range from 14 to 29 kcal/mol. Large values of ΔH°_D are observed for the symmetric dimers $CH_3O^-{\cdot}HOCH_3$ (28.8 kcal/mol) and $CH_3COO^-{\cdot}HOOCCH_3$ (29.3 kcal/mol). ΔH°_D decreases as the difference between the acidities of the components increase; e.g., for dimers with large $\Delta\Delta H^\circ_{acid}$ such as $CH_3COO^-{\cdot}H_2O$ and $HCOO^-{\cdot}H_2O$ ($\Delta\Delta H^\circ_{acid}$ = 42.2 and 45.5 kcal/mol, respectively), ΔH°_D = 16.0 kcal/mol. For 13 dimers, a linear correlation of the form $\Delta H^\circ_D = 28.4 - 0.29\Delta\Delta H^\circ_{acid}$ is obtained. Some dimers deviate substantially from the correlation, suggesting special structural effects. For example, the large value of ΔH°_D = 36.8 kcal/mol for HCOO$^-$·HOOCH suggests double hydrogen bonding, involving a CH···O$^-$ type bond. On the other hand, the data suggest that only one hydrogen bond is formed in $RCOO^-{\cdot}H_2O$. Comparison between anionic and cationic hydrogen bonded systems shows that the bonding energies are similar for RO$^-$·B and $ROH_2^+{\cdot}B$ complexes involving the same ligand B, suggesting primarily electrostatic interactions in both, while RCOO$^-$·B is weaker by 4–6 kcal/mol than $RCOOH_2^+{\cdot}B$, probably due to charge delocalization in RCOO$^-$. The weakening of O$^-$···HO hydrogen bonds to charge delocalized anions is also shown in $CH_2{=}CHO^-{\cdot}H_2O$, where ΔH°_D = 15.3 kcal/mol. The anion CH_3COO^- may form a polydentate complex with the polyether triglyme, but the thermochemistry indicates a loose polydentate structure. By using the present data, it is estimated that hydration by four water molecules is necessary for zwitterion formation by amino acids (neglecting intramolecular charge interactions and cooperative effects.)

Strong hydrogen bonds between ions and neutral molecules play a central role in ion solvation and may also be important in biocatalysis and in determining the structure of biopolymers. In preceding papers in this series we investigated bonds of the type NH$^+$···N, NH$^+$···O, OH$^+$···O,[1] NH$^+$···S, SH$^+$···O, SH$^+$···S[2] as well as RCNH$^+$···X and XH$^+$···NCR.[3] In all the bond types, the partial proton transfer is most efficient when the proton affinities of the components A and B in AH$^+$···B are similar, and the dissociation energy of the hydrogen bond decreases as the difference between the proton affinities of A and B increases. This trend was observed first by Yamdagni and Kebarle.[4] Recently, more extensive sets of data from this laboratory led to a set of correlations (eq 1) for the various AH$^+$···B bonds.[1,2] It was also

$$\Delta H^\circ_D = a - b\Delta PA \qquad (1)$$

shown that a correlation between hydrogen bonding and basicities can be extended to include neutral hydrogen bonds, but this extended correlation is nonlinear.[5]

We wish to develop analogous relations between the strengths of anionic hydrogen bonds RO$^-$···HOR′ and the difference between the gas-phase acidities of the components, ΔH°_{acid}, eq 2.

$$\Delta H^\circ_D = a - b\Delta\Delta H^\circ_{acid} \qquad (2)$$

In the present paper we seek to develop correlations (eq 2), by using data over a significant range of dissociation energies and relative acidities. These correlations, although they have no fundamental interpretation, are useful for predicting hydrogen bond strengths in clusters and in systems where direct gas-phase measurement is not possible, such as large biomolecules. Correlations for OH···O$^-$ bonds, drawn from data over a narrow range or involving a smaller series of dimers, were presented by Caldwell et al.[6] and by Yamdagni and Kebarle.[7]

The present data may be used to compare the strengths of OH$^+$···O cationic hydrogen bonds with OH···O$^-$ hydrogen bonds of identical partners. Furthermore, the thermochemical data on hydrogen bonded complexes are also of interest because structural details can be inferred. For example, unusually large values of ΔH°_D and ΔS°_D were observed in some polydentate complexes, indicating the formation of mutiply hydrogen bonded complexes.[8,9] In the present case, the carboxylate anions RCOO$^-$ contain two equivalent electron donor sites for hydrogen bonding, and the question whether multiply bonded complexes are formed will also be addressed.

Results and Discussion

1. Correlation between ΔH°_D and ΔH°_{acid} and Resonance Effects. The van't Hoff plots for the association reactions are shown in Figure 1, and the results are summarized in Table I. Also included in Table I are results from this laboratory for the dimers $OD^-{\cdot}D_2O$, $CH_3O^-{\cdot}H_2O$, and $CH_3O^-{\cdot}CH_3OH$, which we reported recently.[10]

Inspection of Table I reveals an inverse relation between ΔH°_D and $\Delta\Delta H^\circ_{acid}$ (where $\Delta H^\circ_{acid} = \Delta H^\circ_D$ (RO$^-$–H$^+$)) throughout the whole series of dimers. Figure 2 shows that the data may be divided into separate series, one for the complexes of OH$^-$ and RO$^-$ and a second for complexes of the carboxylate anions RCOO$^-$. However, a single correlation can include all the data with a standard deviation of ΔH°_D(calcd) − ΔH°_D(experimental) = 0.9 kcal/mol, which is still within the experimental error of ±1 kcal/mol for ΔH°_D. The correlation parameters are given in eq 3–5.

RO$^-$···HO

$$\Delta H^\circ_D = 27.5 \pm 0.4 - 0.29 \pm 0.02\Delta\Delta H^\circ_{acid}$$
$$\text{8 points, corr coeff} = 0.987 \qquad (3)$$

RCOO$^-$···HO

$$\Delta H^\circ_D = 29.6 \pm 0.3 - 0.31 \pm 0.01\Delta\Delta H^\circ_{acid}$$
$$\text{7 points, corr coeff} = 0.997 \qquad (4)$$

O$^-$···HO (all data)

$$\Delta H^\circ_D = 28.1 \pm 0.4 - 0.29 \pm 0.01\Delta\Delta H^\circ_{acid}$$
$$\text{13 points, corr coeff} = 0.981 \qquad (5)$$

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Table I. Thermochemistry of Cluster Dissociation and Related Parameters

A^-	B	$\Delta H°_D$[a]	$\Delta H°_D$ ($OH^+\cdots O$)[a,b]	$\Delta S°_D$[c]	$\Delta\Delta H°_{acid}$[a,d]
OD	D_2O	26.8[e]	31.8	22.2	0
CH_3O^-	H_2O	23.9[e]	25.4	22.9	9.1
CH_O^-	CH_3OH	28.8[e]	32.1	26.7	0
$C_2H_5O^-$	C_2H_5OH	27.6		26.8	0
t-$C_4H_9O^-$	H_2O	23.4[f]	22.2	(28)[f]	15.0
t-$C_4H_9O^-$	CH_3OH	25.5	26.8	27.9	5.9
$C_6H_5O^-$	H_2O	15.4	21.1	23.9	40.9
$C_6H_5O^-$	C_2H_5OH	19.3	28.0	27.0	28.7
$C_6H_5O^-$	CH_3COOH	27.4[g]		24.0[g]	−1.3
$HCOO^-$	H_2O	16.0	24.1	23.0	45.5
$HCOO^-$	CH_3OH	17.6		23.6	36.4
$HCOO^-$	HCOOH	36.8	(30.4)	39.1	0
$C_2H_3COO^-$	H_2O	16.0	20.1	22.5	42.2
CH_3COO^-	C_2H_5OH	20.7	(29.8)	29.2	30.0
CH_3COO^-	CH_3COOH	29.3	(30.4)	29.6	0
CH_3COO^-	C_6H_5OH	26.1	(29.8)	24.0	1.3
CH_oCOO^-	$CH_3OCH_2CH_2OCH_2CH_2OCH_3$	15.1		18.5	
$(CH_3)_2CHCOO^-$	H_2iO	15.7[i]	(22.2)	(23)[i]	44[j]
$(CH_3)_2CHCOO^-$	$(CH_3)_2CHCOOH$	29.9	30.4	33.4	0
CF_3COO^-	H_2O	13.7		23.9	68.0
CH_3COO–$\cdot H_2O$	H_2O	12.9		20.5	
($CH_3COO^-\cdot CH_3COOH$)	CH_3COOH	19.6		28.6	
($CH_3COO^-\cdot 2CH_oCOOH$)	CH_3COOH	16.2		33.2	

[a] kal/mol. [b] From ref 1. Values in parentheses are calculated from correlation 5, see text. [c] cal/mol·K. [d] Relative $\Delta H°_{acid}$ of alcohols from ref 19. $\Delta H°_{acid}$ (CH_3OH) = 381.6 kcal/mol from ref 20. $\Delta\Delta H°_{acid}$ values for acids using data from ref 20 as tabulated in ref 19. [e] Reference 10. [f] From $\Delta G°_D(505)$ = 9.3 kcal/mol, and $\Delta S°$ estimated on the basis of similar complexes. [g] Calculated from $\Delta H°_D$ of $CH_oCOO^-\cdot C_6H_5OH$, by using $\Delta H°_{acid}(CH_3COOH) - \Delta H°_{acid}(C_6H_5OH)$ = 1.3 kcal/mol (Bartmess tabulation) and assuming $\Delta S°_D(CH_3COO^-\cdot C_6H_5OH) = \Delta S°°_D(C_6H_5O^-\cdot CH_3COOH)$. [h] In relation to acidity of $CH_2{=}CHOH$, calculated from $\Delta H°_f$ of $CH_2{=}CHOH$ and $CH_2{=}CHO^-$. [i] From $\Delta G°_D(514)$ = −3.9 kcal/mol, and $\Delta S°$ estimated on the basis of similar complexes. [j] Estimated.

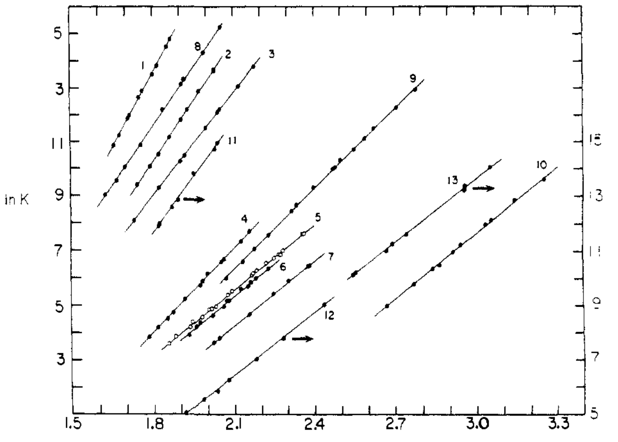


Figure 1. van't Hoff plots for clustering equilibria: 1, $HCOO^-\cdot HCOOH$; 2, $(CH_3)_2CHCOO^-\cdot HOOCCH(CH_3)_2$; 3, t-$C_4H_9O^-\cdot HOCH_3$; 4, $CH_3COO^-\cdot HOC_2H_5$; 5, $CH_3COO^-\cdot HOH$; 6, $HCOO^-\cdot HOH$; 7, $C_6H_5O^-\cdot HOH$; 8, $CH_3COO^-\cdot HOOCCH_3$; 9, $CH_3COO^-\cdot (HOOCCH_3)_2$; 10, $CH_3COO^-\cdot (HOOCCH_3)_3$; 11, $C_2H_5O^-\cdot HOC_2H_5$; 12, $CH_2{=}CHO^-\cdot H_2O$; 13, $CH_3COO^-\cdot CH_3OCH_2CH_2OCH_2CH_2OCH_3$.

In comparison, the correlation line for the cationic $OH^+\cdots O$ hydrogen bonds, eq 6, gave very similar parameters,[1] as is shown graphically in Figure 2.

$OH^+\cdots O$

$$\Delta H°_D = 30.0 \pm 0.4 - 0.30 \pm 0.01\ \Delta\Delta H°_{acid}$$

$$\text{20 points, corr coeff} = 0.979 \qquad (6)$$

With respect to correlations 3 and 4 we note that slopes of the two correlation lines are equal within the standard deviations but that the intercept for the $RCOO^-$ series is higher by 2 kcal/mol. Correspondingly, Figure 2 shows that for a given $\Delta\Delta H°_{acid}$ complexes of $RCOO^-$ are stronger by 1–2 kcal/mol than complexes RO^-.

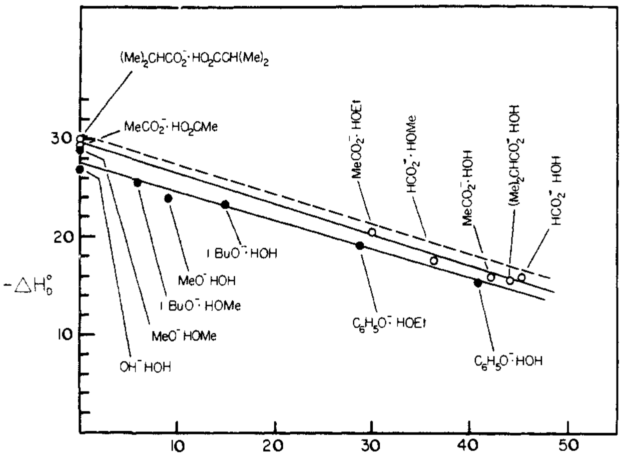
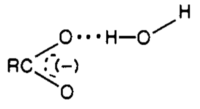


Figure 2. Correlation lines for association ions: ○ = $RCOO^-\cdots HO$ bonds, ● = $RO^-\cdots HO$ bonds, — for proton bonded association ions of the type $OH^+\cdots O$.

The stronger hydrogen bonding of $RCOO^-$ vs. RO^- ions is surprising, since charge delocalization in ion **1** should decrease, rather than increase, the bonding energy. In fact, the analogous charge resonance in the cationic dimers **2** decreased $\Delta H°_D$, i.e., the values for $RCOOH_2^+\cdot ROH$ deviated below the line for $ROH_2^+\cdot ROH$ in plots analogous to those shown in Figure 2.[1]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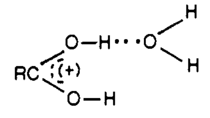
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The apparent strengthening of hydrogen bonding to carboxylate anions may be an artifact of interpretation, however. The correlation lines in Figure 2 display $\Delta H°_D$ vs. $\Delta\Delta H°_{acid}$ of alcohols and carboxylic acids, and the effects of resonance may primarily increase the acidities by stabilizing the ion. In other words, the correlation line for $RCOO^-\cdot B$ may be shifted to the right by about 4 kcal/mol from the line for $RO^-\cdot ROH$, rather than being shifted up by 2 kcal/mol. This interpretation follows if going from $RCH_2O^-\cdot B$ to the corresponding $RCOO^-\cdot B$ complexes is done in two steps, the first decreasing $\Delta\Delta H^\circ_{acid}$ and the second decreasing ΔH°_D. A horizontal displacement of the lines then occurs if the relation between the intramolecular ion stabilizing effect of carbonyl substitution vs. the effect on ΔH°_D is larger than, for example, the analogous relation for alkyl substitution. This added ion stabilizing effect may be ascribed to charge resonance in $RCOO^-$.

The recent paper by Caldwell et al.[5] gave a two-parameter correlation line for the strengths of $ROH\cdots OR'$ bonds (eq 7), and another two-parameter correlation (eq. 8) for several types of hydrogen bonds $X^-\cdots HY$ was given by Yamdagni and Kebarle.[4]

for $ROH\cdot{}^-OR'$

$$\Delta H^\circ_D = -0.31\Delta H^\circ_{acid}(ROH) + 0.40\Delta H^\circ_{acid}(R'OH) - 15.0 \tag{7}$$

for $X^-\cdot HY$

$$\Delta H^\circ_D = -0.134\Delta H^\circ_{acid}(YH) + 0.20\Delta H^\circ_{acid}(XH) \tag{8}$$

The correlation of Caldwell et al.[6] is more relevant to the present data. For complexes of a given anion $R'O^-$ with a series of alcohols ROH, the slopes given by eq 3 and 7 are similar, while for complexes of a given alcohol with a series of anions, the slope of eq 7 is higher. However, eq 7 was obtained from data derived from single-temperature measurements, by using calculated or assumed entropies. Also, the data ranged over $\Delta\Delta H^\circ_{acid}$ values of only 10 kcal/mol and was referred to a low absolute reference value of $\Delta H^\circ_D(CH_3O^-\cdot CH_3OH)$ = 21.8 kcal/mol.

2. Comparison between Anionic and Cationic Hydrogen Bonds. Cationic hydrogen bonds $OH^+\cdots O$ and anionic hydrogen bonds $OH\cdots O^-$ show remarkably similar trends. For example, we recently studied anionic and cationic mixed clusters of water and methanol containing up to five molecules clustered to $CH_3OH_2^+$ or CH_3O^-.[10] Each cationic cluster was more stable by 2–4 kcal/mol than the corresponding anionic cluster, and the variation of stabilities with cluster size and composition was parallel. The excess stabilities of the cationic vs. anionic clusters could be related primarily to the difference between the dissociation energies of the first $CH_3OH_2^+\cdot OR_2$ vs. $CH_3O^-\cdot HOR$ bond in each cluster.

The extra stabilities of cationic vs. analogous anionic clusters apply in general to the present data. Table I lists the values for ΔH°_D of $OH^+\cdots O$ vs. the analogous $OH\cdot O^-$ clusters, e.g., $H_3O^+\cdot H_2O$ vs. $OH^-\cdot OH_2$, $CH_3COOH_2^+\cdot CH_3OH$ vs. $CH_3COO^-\cdot CH_3OH$, etc. In each case, except for the anomalous formic acid dimer (see below), the cationic complex is more stable. However, the differences between the ΔH°_D of cationic and anionic clusters vary significantly, in accordance with the proton affinity and $\Delta\Delta H^\circ_{acid}$ correlations. In general, the increased stability of $RCOOH_2^+\cdot ROH$ vs. $RCOO^-\cdot ROH$ complexes is substantial, because in this case the high acidity of the carboxylic acids leads to large $\Delta\Delta H^\circ_{acid}$ and therefore small ΔH°_D values.

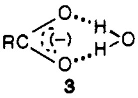
On the other hand, for all five complexes of the aliphatic alcohols (see Table I), $CH_3O^-\cdot H_2O$, $CH_3O^-\cdot CH_3OH$, $C_2H_5O^-\cdot C_2H_5OH$, $t\text{-}C_4H_9O^-\cdot H_2O$, and $t\text{-}C_4H_9O^-\cdot CH_3OH$, the dissociation energies are similar within 3 kcal/mol or less to those for the corresponding cationic complexes $CH_3OH_2^+\cdot H_2O$, etc. This would be expected from the simplest electrostatic model, where in both the $AH^+\cdot B$ and $(A-H)^-\cdot B$ complexes a pointlike unit charge interacts with the same dipole and the same polarizable entity.

3. Effects of Charge Delocalization. In contrast to the alkoxide complexes, bonding in the complexes $RCOO^-\cdot B$ and $C_6H_5O^-\cdot B$ is weaker by 4–6 kcal/mol than in $RCOOH_2^+\cdot B$ and $C_6H_5OH_2^+\cdot B$, respectively. This may suggest the weakening of the electrostatic interactions in these complexes resulting from charge delocalization in the $RCOO^-$ and $C_6H_5O^-$ ions.

In order to further investigate the effects of charge delocalization, we measured the bonding energy in the complex $CH_2{=}CHO^-\cdot H_2O$. The result, 15.3 kcal/mol, is substantially lower than the 21.1 kcal/mol predicted by the correlation eq 5, based on the acidity of CH_3CHO. We note, however, that, if the structure of the complex is $CH_2CHO^-\cdots HOH$, the correlation of interest would be that to ΔH°_{acid} of $CH_2{=}CHOH$, which can be calculated as 356 kcal/mol. By using this value, eq 5 gives $\Delta H^\circ_D(CH_2{=}CHO^-\cdot HOH)$ = 18 kcal/mol, reasonably close to the experimental value. This supports the application of eq 5 to charge-delocalized oxygen-containing anions. Of course, correlation 5 was derived by using complexes of $C_6H_5O^-$ and of $RCOO^-$, which are also charge-delocalized anions.

The present complex may also have the structure $HOH\cdots{}^-CH_2{=}CHO$. The solvation of charge-delocalized carbanions and the relative stabilities of isomeric cluster ions such as $CH_2{=}CHO^-\cdots HOH$ and $HOH\cdots{}^-CH_2{=}CHO$ are of interest and will be further investigated.

4. Structure of the Complexes. The presence of two electron donor sites in $RCOO^-$ ions allows doubly hydrogen bonded structures such as **3**.



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The formation of a second hydrogen bond is expected to affect ΔH°_D and ΔS°_D. For example, ΔH°_D for complexes of RNH_3^+ with some esters and amides are larger by 7 ± 2 kcal/mol than expected for singly bonded complexes,[1,9] presumably due to the formation of doubly hydrogen bonded complexes. Other multiple electron pair donors such as polyethers,[8] amino acid derivatives,[9] and nucleic bases[11] also give complexes with thermochemistry indicative of multiple bonding, and in these complexes each additional hydrogen bond adds approximately 7 ± 2 kcal/mol to the dissociation energy. In addition to the enthalpy effect, the formation of a second hydrogen bond eliminates an internal rotation in the complex, which usually increases ΔS°_D by 6 ± 2 cal/mol·K.

In the present case, we can compare complexes where double hydrogen bonding is possible with other complexes in which the second bond is blocked. Double bonding, as in ion **3**, is possible in $HCOO^-\cdot H_2O$ but not in $HCOO^-\cdot CH_3OH$ or $C_6H_5O^-\cdot H_2O$. Nevertheless, the ΔH°_D and ΔS°_D values for the three complexes are very similar, and the small differences in ΔH°_D can be attributed to the correlation with $\Delta\Delta H^\circ_{acid}$. Similarly, $CH_3COO^-\cdot H_2O$ could form the doubly bonded structure **3** but $CH_3COO^-\cdot C_2H_5OH$ and $C_6H_5O^-\cdot C_2H_5OH$ cannot, yet the thermochemistries of the three complexes are similar. These observations suggest that the $RCOO^-\cdot H_2O$ complexes are singly bonded as in ion **1**, and the doubly hydrogen bonded structure **3** is not formed.

The above conclusions are in contrast with a recent ab initio calculation, which showed that E_D for structure **3** of $HCOO^-\cdot H_2O$ is larger by 2.5 kcal/mol than for structure **1**.[12] It should be noted that our results do not rule out this possibility. As noted above, the formation of **3** would entail an entropy contribution of approximately 6 cal/mol·K to ΔS°_D, corresponding to a $-T\Delta S$ free energy contribution of −3 kcal/mol to ΔG°_D at the experimental temperature of 500 K. Therefore, the observed equilibrium conformation of $HCOO^-\cdot H_2O$ would be predominantly the singly bonded isomer **1** even if the dissociation energy of the doubly hydrogen bonded isomer **3** is somewhat larger.

One complex that does exhibit unusual thermochemistry is $HCOO^-\cdot HCOOH$. Compared with $CH_3COO^-\cdot CH_3COOH$, ΔH°_D is increased by 7.5 kcal/mol, and ΔS°_D is increased by 9.5 cal/mol·K, both in the range characteristic of the formation of a second hydrogen bond. Therefore, the doubly bonded structure **5** rather than the singly bonded structure **4** is suggested.

Structure **5** is interesting because the second hydrogen bond is of the $CH^+\cdots O^-$ type. Similar $CH^+\cdots X^-$ bonds are formed in complexes of halide ions with CH_3CN.[13] Analogous cationic

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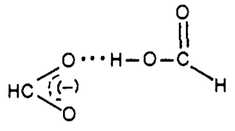
[10] Meot-Ner (Mautner), M.; Sieck, L. W., submitted for publication.

[11] Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1979**, *101*, 2396.

[12] Stevens, W., unpublished results. Ab initio results using geometry optimization and total energy calculations from double-ζ plus polarization SCF and zero-point energy corrections from double-ζ SCF harmonic analysis at double-ζ optimized geometries. Results: $HCOO^-\cdot H_2O$, singly bonded geometry (ion **1**, text), 13.5 kcal/mol; doubly bonded geometry (ion **3**, text), 16.0 kcal/mol.



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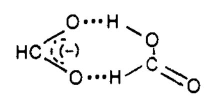


5

$CH^+\cdots O$ hydrogen bonds are also observed in the complexes $(CH_3)_4N^+\cdot OR_2$.[14] The latter bond strengths were 7–9 kcal/mol, similar to the present case. The reason that double hydrogen bonding is formed in **5** but not in **3** may be that in **5** the configuration allows closer approach to the optimal 180° geometry for the hydrogen bonds.

The thermal stability of a second hydrogen bond may be estimated from thermochemical considerations. Thermal opening can be considered to occur when the equilibrium populations of **4** and **5** are equal (eq 9–11).

$$K(\mathbf{4}/\mathbf{5}) = 1 \qquad (9)$$

$$\Delta G°(\mathbf{4}\rightarrow\mathbf{5}) = \Delta H°(\mathbf{4}\rightarrow\mathbf{5}) - T\Delta S°(\mathbf{4}\rightarrow\mathbf{5}) = 0 \qquad (10)$$

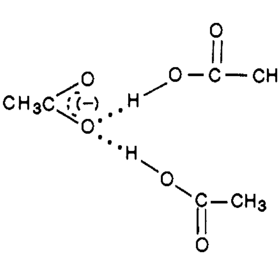
$$T_{\mathrm{op}} = \Delta H°(\mathbf{4}\rightarrow\mathbf{5})/\Delta S°(\mathbf{4}\rightarrow\mathbf{5}) = 789\ \mathrm{K} \qquad (11)$$

The thermochemistry suggests that the temperature required to open the second hydrogen bond in **5** is approximately 800 K. This explains why the doubly bonded structure seems to dominate under our experimental conditions of 520–560 K.

Another complex with an unusually large $\Delta S°_D$ is $C_6H_5O^-\cdot C_6H_5OH$. Molecular models show that the two phenyl rings can overlap in the complex and inhibit several internal rotations. The overlap of the rings can also bring the 2 and 6 carbons of the two rings sufficiently close to allow attractive dispersion interactions. This would explain why $\Delta H°_D$ for this dimer is higher by 3 kcal/mol than that for $CH_3O^-\cdot CH_3OH$.

Because of the above structural effects, the $HCOO^-\cdot HCOOH$ and $C_6H_5O^-\cdot C_6H_5OH$ complexes deviate from the correlation lines in Figure 2. The complex $CH_3COO^-\cdot C_6H_5OH$ also deviates from the correlation line of eq 2. However, in this clustering system, the acidities of the two components are similar, and the dimer and the monomer anions CH_3COO^- and $C_6H_5O^-$ were also present in the equilibrium system. From the thermochemical data, $\Delta H°_D$ of $C_6H_5O^-\cdot CH_3COOH$ is calculated as 27.4 kcal/mol, and with a $\Delta\Delta H°_{\mathrm{acid}} = -1.3$ kcal/mol, the resulting point fits well on the correlation line for the RO^- anions. This may indicate that a proton shift occurs in the complex and that the $C_6H_5O^-\cdot HOOCH_3$ structure is the more stable form.

5. Higher Clustering of the Acetate Anion. The CH_3COO^- anions possess two equivalent hydrogen bonding acceptor sites, and both **6** and **7** may be formed upon higher clustering.



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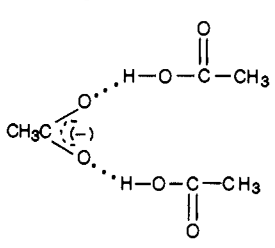
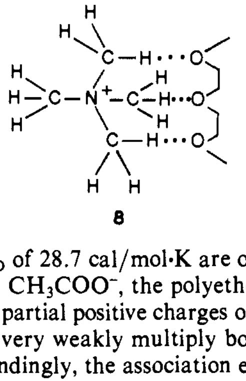


7

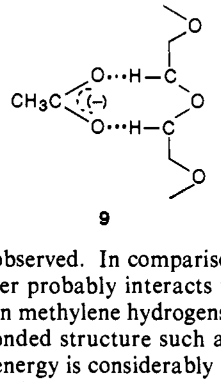
Consecutive clustering energies usually decrease with increasing cluster size due to the mutual repulsion and charge delocalization effects of the two ligands. Structure **7** should decrease interactions between the ligands and facilitate higher clustering. It is, therefore, of interest to compare the higher clustering energies of acetic acid clusters with those of other anionic clusters in which only structures analogous to **6** are possible.

The consecutive attachment energies of three CH_3COOH molecules to CH_3COO^- are 29.3, 19.6, and 16.2 kcal/mol. In comparison, the consecutive attachment energies of three CH_3OH molecules to CH_3O^- are 28.8, 21.4, and 15.0.[10] Evidently, for each clustering step, the attachment energies in the two systems are equal within the combined experimental error. Consequently, the thermochemical data do not show special effects due to the possibility of structure **7**.

In relation to the interaction of carboxylate groups with multiple ligands, it is also of interest to examine a ligand where multiple polar groups are present but hydrogen bonding is not possible. As a model for such interactions, we investigated the complex $CH_3COO^-\cdot CH_3OCH_2CH_2OCH_2CH_2OCH_3$. An analogous cationic complex of the same polyether with the non-hydrogen bonding cation $(CH_3)_4N^+$ was investigated previously.[14] In this complex the polyether ligand can interact by a favorable alignment of dipoles such as in ion **8**. An interaction energy of 20.6 kcal/mol and $\Delta S°_D$ of 28.7 cal/mol·K are observed. In comparison, with the anion CH_3COO^-, the polyether probably interacts through the small partial positive charges on methylene hydrogens, giving at best a very weakly multiply bonded structure such as ion **9**. Correspondingly, the association energy is considerably smaller, 15.1 kcal/mol, and the $\Delta S°_D$ of 18.5 cal/mol·K also indicates a loose structure.



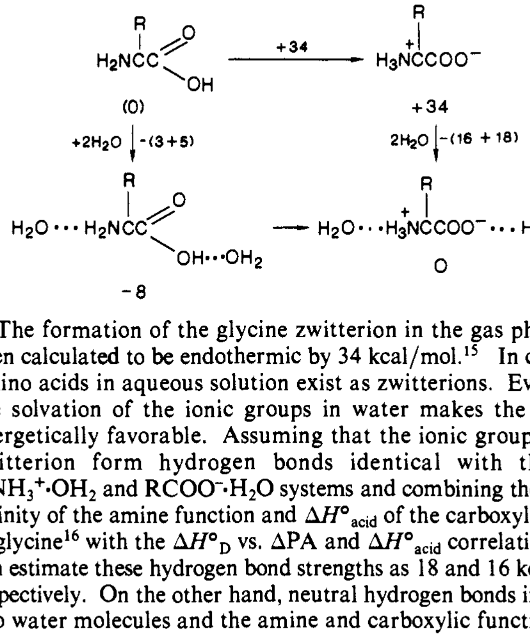
8



9

6. Some Implications for Biomolecules. The solvation of carboxylate groups is relevant to the acid dissociation of biological acids, including amino acids. One particular question of interest is the formation of zwitterions in aqueous solution.

The role of solvation in this process may be illustrated by a thermochemical cycle.



The formation of the glycine zwitterion in the gas phase has been calculated to be endothermic by 34 kcal/mol.[15] In contrast, amino acids in aqueous solution exist as zwitterions. Evidently, the solvation of the ionic groups in water makes the process energetically favorable. Assuming that the ionic groups of the zwitterion form hydrogen bonds identical with those in $RNH_3^+\cdot OH_2$ and $RCOO^-\cdot H_2O$ systems and combining the proton affinity of the amine function and $\Delta H°_{\mathrm{acid}}$ of the carboxylic group in glycine[16] with the $\Delta H°_D$ vs. ΔPA and $\Delta H°_{\mathrm{acid}}$ correlations, one can estimate these hydrogen bond strengths as 18 and 16 kcal/mol, respectively. On the other hand, neutral hydrogen bonds involving two water molecules and the amine and carboxylic functions can be estimated as only 3 and 5 kcal/mol, respectively. Therefore, as the thermochemical cycle shows, solvation by two water molecules is not sufficient for zwitterion formation. However, considering the $CH_3NH_3^+\cdot 2H_2O$ cluster and $CH_3COO^-\cdot 2H_2O$ clusters as models for the double hydration of each ionic group further adds 14.6 and 12.9 kcal/mol, respectively (data from ref

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(14) Meot-Ner (Mautner), M.; Deakyne, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 469.

(15) Wright, L. R.; Borkman, R. F.; Gabrielli, A. M. *J. Phys. Chem.* **1982**, *86*, 3951.

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17 and Table I, respectively), to the hydration of the zwitterion clustering, compared with 8 kcal/mol for two more neutral hydrogen bonds. Therefore, solvation by four water molecules would be sufficient to make the transition to the zwitterion exothermic by 12 kcal/mol.

The above estimate considers the two ionic functions in the zwitterion to hydrogen bond as separate ions. In fact, the presence of the opposite charge in the molecule will decrease the charge on each group, which weakens the hydrogen bonds at each site and creates a situation more analogous to neutral hydrogen bonds. Therefore, solvation by substantially more than four water molecules may be necessary to make the formation of zwitterions exothermic.

The present data also demonstrate that $OH^- \cdots O$ hydrogen bonds can make substantial contribution to protein conformation and enzyme action. For example, carboxylic functions of aspartic acid and glutamic acid residues are found near the active sites in enzyme cavities. The present data show that if optimal geometric alignment is allowed, such ionized carboxylic functions may form bonds as strong as 30 kcal/mol with neutral OH or COOH groups in the enzyme or the substrate.

Experimental Section

The measurements were carried out with the NBS pulsed electron beam mass spectrometer, which has been described elsewhere.[18] Negative ions were generated by adding an electron scavenger, such as $C_2H_5NO_2$, N_2O, CH_3ONO, or SF_6 (for carboxylic acid reaction systems) to the carrier gas, which was CH_4 or c-C_6H_{12}. In some cases, neat N_2O or SF_6 was used the as the carrier gas. The primary anions, formed by electron capture or dissociative electron capture, reacted rapidly with the sample components to yield the RO^- and $RCOO^-$ ions of interest.

For all equilibria, checks were made to ensure that the equilibrium constant was independent of total source pressure and of the partial pressure of the ligand. In particular, $CH_3O^- \cdot CH_3OH$ was checked thoroughly because of a discrepancy of our value for $\Delta H°$, 28.8 kcal/mol, with a low value, 21.8 kcal/mol, quoted in ref 6. For this reaction, we obtained van't Hoff plots by using neat N_2O and by using 2% N_2O in c-C_6H_{12} as carrier gases, and another van't Hoff plot was obtained for $CD_3O^- \cdot CD_3OD$ by using trace N_2O in CH_4 as a carrier gas. Further, we did detailed studies with varying partial pressures of CH_3OH at three temperatures, varying the concentration of CH_3OH between 0.2 and 2.0 $\times 10^{14}$ molecules/cm^3. The results of all of the studies were consistent within ±1 kcal/mol for $\Delta H°$ and ±2 cal/(mol·K) for $\Delta S°$, which are our usual error limits.

To study the cluster $C_2H_5O^- \cdot C_2H_5OH$, we used C_2H_5OH in CH_4 and trace N_2O as the carrier gas. In this system, we observed the overall reaction

$$C_2H_5O^- \rightarrow C_2H_3O^- + H_2 \qquad (12)$$

The reaction appeared to be catalyzed by the presence of C_2H_5OH, i.e., the apparent first-order rate constant increased with increasing concentration of C_2H_5OH. The apparent second-order rate constant was $\sim 10^{-10}$ cm^3 s^{-1} at 600 K and showed a small positive temperature coefficient. The observed high rates ruled out reactions with an impurity, e.g., CH_3CHO, as the source of the product $C_2H_3O^-$ ion. Analogous dehydrogenation reactions were observed with n-$C_3H_7O^-$ and i-$C_3H_7O^-$. Because of reaction 12 and its dependence on the concentration of C_2H_5OH, the clustering studies in this system were carried at a low concentration, 0.0001, of C_2H_5OH.

For measurements involving other symmetric dimers ($RO^- \cdot ROH$ and $RCOO^- \cdot RCOOH$) the sample ROH and RCOOH compounds were usually 0.01 or less of the total gas mixture in the ion source. For $RCOO^- \cdot H_2O$, $RCOO^- \cdot ROH$, $C_6H_5O^- \cdot H_2O$, and $C_6H_5O^- \cdot ROH$, however, the formation of $RCOO^- \cdot RCOOH$ and $C_6H_5O^- \cdot C_6H_5OH$ dimers competed with the equilibria under study, and in some cases the formation of these dimers depleted the monomer anions irreversibly. When this occurred trace amounts, less than 0.0001 of RCOOH and C_6H_5OH, and large amounts, up to 0.50 of the reaction mixture, of H_2O and ROH were used to slow the depleting reactions and maximize the formation of the complexes of interest. In some systems, such as $CH_3COO^- \cdot H_2O$, van't Hoff plots were obtained at various concentrations of CH_3COOH to verify that the competing dimerization did not effect the results for the thermochemistry of $CH_3COO^- \cdot H_2O$.

The total gas pressure in the ion source was in the range of 0.5–2.5 torr. Checks were made to demonstrate that the measured equilibrium constants were independent of total source pressure and mixture composition.

The chemicals were obtained from commerical sources, with nominal purities of 98% or greater, and used as supplied.

Acknowledgment. We thank Dr. W. Stevens for unpublished results of ab initio calculations. This work was supported in part by the Office of Basic Energy Sciences, U.S. Department of Energy.

Registry No. $C_2H_5O^-$, 16331-64-9; t-$C_4H_9O^-$, 16331-65-0; $C_6H_5O^-$, 3229-70-7; $HCOO^-$, 71-47-6; $C_2H_3O^-$, 35731-40-9; CH_3COO^-, 71-50-1; $(CH_3)_2CHCOO^-$, 5711-69-3; CF_3COO^-, 14477-72-6; C_2H_5OH, 64-17-5; H_2O, 7732-18-5; CH_3OH, 67-56-1; CH_3CO_2H, 64-19-7; HCO_2H, 64-18-6; C_6H_5OH, 108-95-2; $H_3CO(CH_2)_2O(CH_2)_2OCH_3$, 111-96-6; $(CH_3)_2CHCO_2H$, 79-31-2.

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Selectivity in the Laser-Induced Photochemistry of $I_2 + C_2H_2$ in the Gas Phase

M. Cecilia Yappert and Edward S. Yeung*

Contribution from the Ames Laboratory-USDOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011. *Received June 20, 1986*

Abstract: The reaction between I_2 and acetylene has been carefully studied to establish its potential use for the separation of radioactive isotopes of iodine. The two possible photoproducts, *cis*- and *trans*-1,2-diiodoethylene, were prepared and then characterized by GC, GC–MS, and FTIR in both condensed and gas phases. For the first time the IR spectra of both cis and trans isomers in the gas phase are reported. Below the dissociation energy, when either the ortho or para modifications of I_2 were excited, only the trans isomer was found as a product. Studies conducted with isotopic mixtures of $^{127}I_2$, $^{129}I_2$ and ^{127}I, ^{129}I revealed that the reaction proceeds by the addition of iodine atoms to acetylene. The production of atoms leads to isotopic scrambling. Consequently, this reaction cannot be used to separate the isotopes of iodine, as previously postulated.

The reaction between halogens, especially iodine, and hydrocarbons is extensively documented in the chemical literature.[1] Surprisingly, there is still confusion about the gas-phase photochemical addition of iodine to unsaturated hydrocarbons, for

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