# Properties of Clusters in the Gas Phase. 3. Hydration Complexes of $CO_3^-$ and $HCO_3^-$

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**Abstract**: Employing high-pressure mass spectrometry, the $\Delta H°_{n,n+1}$ and $\Delta S°_{n,n+1}$ for the gas-phase reactions $A^-(H_2O)_n + H_2O = A^-(H_2O)_{n+1}$ (where $A^- = CO_3^-$ and $HCO_3^-$) were measured from $n = 0$ to $n = 2$ and 3, respectively. In the case of $CO_3^-$, comparison of $\Delta G°_{n,n+1}$ ($n = 0, 1$) derived from these data at 296 K shows good agreement with previous measurements made only at that single temperature (Fehsenfeld and Ferguson). As an aid in understanding the bonding resulting from hydration of the ions, CNDO/2 calculations on the $HCO_3^-\cdot H_2O$ system were also performed and the results are discussed herein. In particular, the magnitude of the bonding for one and two water molecules to $HCO_3^-$ at different sites is discussed. The gas-phase results, when compared with those for other negative ions, have revealed interesting features and have led to a determination of the lower bound for the aqueous phase total single ion hydration energy of $HCO_3^-$.

## Introduction

Studies of ion clustering reactions have been prompted by their application to understanding a variety of subjects such as phase-transition phenomena,[1] solution chemistry,[2] and aeronomy.[3] Data concerning the hydration of $CO_3^-$, $HCO_3^-$, and other negative ions of polyatomic molecules find application, in comparison to results on spherical halide ions, for investigating the role of ion structure in clustering reactions and nucleation phenomena.[4] Furthermore, $HCO_3^-$ is often prevalent in natural and industrial waters,[5] and the properties of $HCO_3^-$ are also of interest in regard to biological processes.[6]

Direct observations have confirmed the presence of a variety of negative ions in considerable concentrations in the lower ionosphere (65–80 km above the earth's surface).[7,8] Even before direct observation, $CO_3^-$ was predicted to be an important negative ion in atmospheric processes,[9,10] and Arnold et al.[7] have also identified $HCO_3^-$ as a major ion at these altitudes. The existence of $CO_3^-$ and $HCO_3^-$ in the atmosphere has prompted studies of their properties and reactions. The photodissociation of both ions and their monohydrates[11] and the photodetachment of $CO_3^-$ [12] have been investigated. Furthermore, a study of the kinetics of several of their reactions has also been made,[13] but only limited information is available concerning their bonding and stability. In the present work, equilibrium thermodynamic data on the hydration of these ions are reported for the first three hydrates of $CO_3^-$ and the first four of $HCO_3^-$. In comparison with theoretical calculations, ion hydration is inferred from the data; the atmospheric implications will be discussed in another paper.[14]

## Experimental Section

The basic apparatus and general procedure for making the high-pressure mass spectrometric measurements have been described elsewhere.[15] In the present study, electrons are emitted from a platinum filament coated with $BaZrO_3$[16] upon the application of a current of approximately 7 A through a filament maintained at a negative voltage. Gas mixtures containing typically 1% $N_2O$, 10–50% $H_2O$, and remainder $CO_2$ are introduced into the reaction cell. The dissociative attachment of $N_2O$ readily produces $O^-$, which subsequently reacts rapidly with $CO_2$ to produce $CO_3^-$.[13] Negative ions produced in $N_2O$-$CO_2$ mixtures have been thoroughly studied by Parkes.[17] The $HCO_3^-$ is formed when water is present, presumably via the production of $OH^-$ followed by reaction with $CO_2$. Introduction of water also leads to the appearance of hydrates of $CO_3^-$ and $HCO_3^-$.

Earlier studies[18] showed that only the first one or two clustering reactions, if any, would be influenced by the presence of moderate values of field energy. Such effects could occur due to the lack of ion thermalization. To measure equilibria, the temperature must be well defined and the ions must be at thermal energies. In the present study, during production the ion is first subjected to electric fields imposed by focusing electrodes. Therefore, for the ion to become thermalized, it must collide sufficiently often with the neutral gas molecules in the low-field or field-free regions of the reaction cell. For the moderate values of electric field energy employed in the present study, even the first step of the $CO_3^-$ hydration is not influenced. This is seen by referring to Figure 1, which is a plot of equilibrium constant vs. field energy. The constant is found to be independent of electric field energy, thereby demonstrating the fact that ion thermalization is indeed occurring over the range of field energy investigated. Regarding pressure, Figure 2 shows that, from 6 Torr up to moderate pressures above, the equilibrium constant is independent of both total pressure and water partial pressure as expected for equilibrium conditions. The data plotted in Figure 2 at pressures below 6 Torr correspond to conditions in which $E/N \geq 45$ Td (1 Td = $10^{-17}$ V/cm$^2$). At the lower pressures, thermalization was incomplete and residence time in the reaction cell was insufficient for establishing equilibrium at the particular water concentration employed in the studies.

## Results

The equilibrium constant for the $(n, n + 1)$ reaction

$$A^-(H_2O)_n + H_2O(+M) \rightleftarrows A^-(H_2O)_{n+1}(+M) \quad (1)$$

is determined from the measured ion ratio $I_{n+1}/I_n$ and the known water partial pressure $p$ by

$$K_{n,n+1} = I_{n+1}/I_n p \quad (2)$$

where the usual assumptions[15] have been employed. The enthalpy and entropy changes for each clustering reaction $(n, n + 1)$ are determined from least-squares fits of van't Hoff plots based on the equation

$$\ln K_{n,n+1} = -\frac{\Delta H°_{n,n+1}}{R} T^{-1} + \frac{\Delta S°_{n,n+1}}{R} \quad (3)$$

where the standard state is 1 atm.

The van't Hoff plots and least-squares fitted lines for the hydration reactions of $CO_3^-$ and $HCO_3^-$ are shown in Figures 3 and 4, respectively. Enthalpy and entropy values derived from these data are given in Tables I and II. The error limits represent one standard deviation about the least-squares fit. Additionally, a small systematic error in the entropies might arise from inaccuracy in the calibration of the quadrupole mass spectrometer. However, the effect should be small since an error of 50% in the measured ratio of ion intensities would lead to only a 0.8 eu error in the entropy and essentially none in the enthalpy value.

No other values of enthalpy and entropy for these reactions

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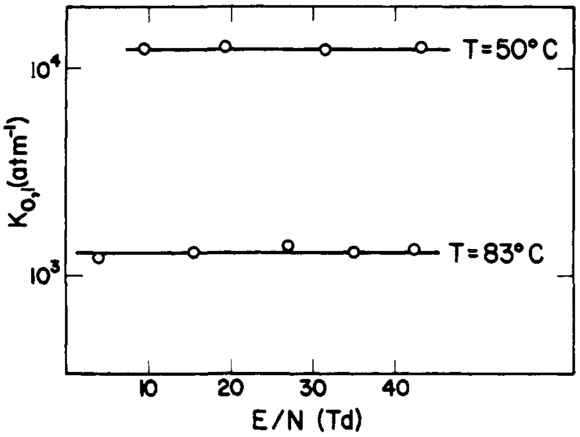

**Figure 1.** Equilibrium constant as a function of field energy for the reaction $CO_3^- + H_2O = CO_3^-(H_2O)$. 1 Td = $10^{-17}$ V/cm$^2$.

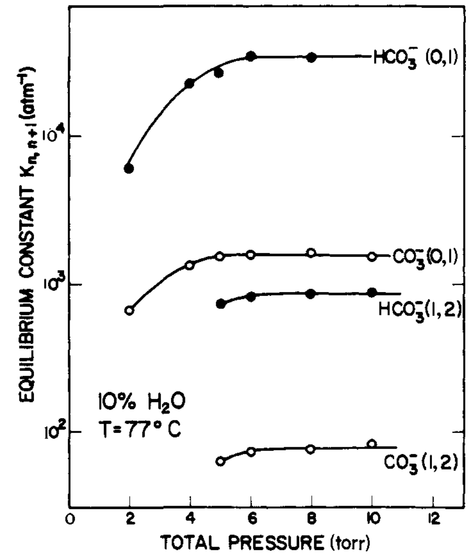

**Figure 2.** Equilibrium constants as a function of total gas pressure.

have been reported in the literature. However, Fehsenfeld and Ferguson[13] have reported $\Delta G°_{296}$ for the (0,1) and (1,2) hydration reactions of $CO_3^-$ and it is interesting to compare their results with those of the present study. Although the present work did not extend to the temperature employed in their measurements, $\Delta G°_{296}$ was calculated for comparison using the $\Delta H°$ and $\Delta S°$ data we obtained. The results, given in Table III, show good agreement between the two laboratories.

## Discussion of Structure and Bonding

Enthalpy and entropy data aid in understanding the bonding and structure of ion clusters. In Figure 5, the stepwise enthalpy changes are plotted vs. the hydration step $(n, n + 1)$ for $CO_3^-$ and $HCO_3^-$; included are data reported for other negative ions[19-21] as well. Concerning the attachment of the first ligand molecule, the enthalpy change, $-\Delta H°_{0,1}$, is approximately inversely proportional to the ion size. This is seen from the data plotted in Figure 6. In making the plot Goldschmidt radii[22] were chosen for the halide ions and Yatsimirski thermochemical radii[23] for radii of the polyatomic ions.

The pattern of enthalpy changes with successive clustering number $n$, shown in Figure 5, appear to fall into three categories. The negative ions $F^-$ and $OH^-$ are seen to display an initial rapid decrease of $-\Delta H°_{n,n+1}$, while for the larger halides the enthalpy change decreases much more slowly. In the cases of $NO_2^-$, $O_2^-$, and $HCO_3^-$, $-\Delta H°_{n,n+1}$ appears to decrease most appreciably in the formation of the third ($n = 2$ in the plot) instead of the second cluster. In related work, Kebarle and co-workers[19-21] have discussed the behavior of $\Delta H°_{n,n+1}$, with $n$, for several ions. They account for the large drop from $-\Delta H°_{0,1}$ to $-\Delta H°_{1,2}$ for $F^-$ and $OH^-$ as being due to resonance structures for the monohydrate. In the case of hydration energies of the larger halides, no special bonding features are apparent, and their hydration is taken as being primarily electrostatic in nature as expected for these simple spherical ions.

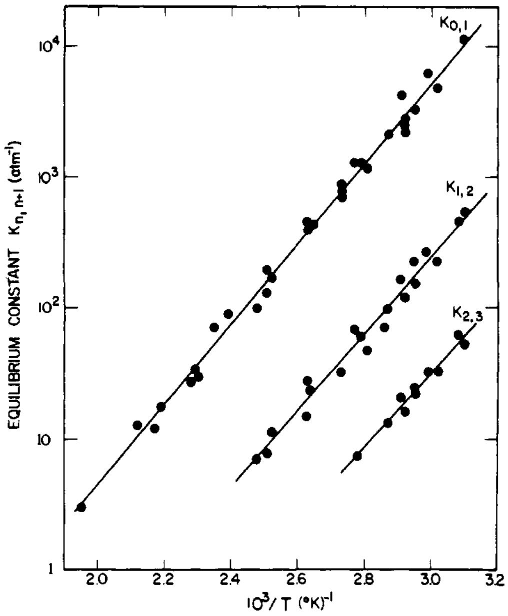

**Figure 3.** van't Hoff plots of equilibrium constants for the gas-phase reactions $CO_3^-(H_2O)_n + H_2O = CO_3^-(H_2O)_{n+1}$.

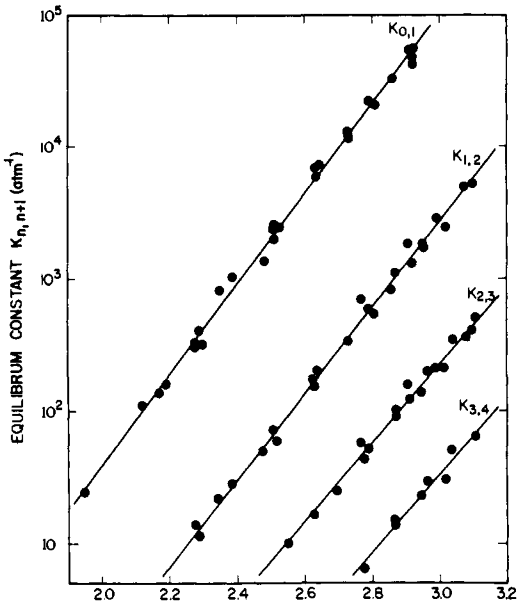

**Figure 4.** van't Hoff plots of equilibrium constants for the gas-phase reactions $HCO_3^-(H_2O)_n + H_2O = HCO_3^-(H_2O)_{n+1}$.

In the case of $NO_2^-$ and $O_2^-$, both have two oxygen atoms with favorable sites for hydrogen bonding by water. Kebarle and co-workers[19,20] have therefore suggested that the addition of the third water would be less favorable, thereby accounting for the larger drop of $-\Delta H°_{n,n+1}$ between $n = 1$ and $n = 2$. In a similar manner, the functional dependence of $-\Delta H°_{n,n+1}$ on $n$ has been used to suggest bonding features in other systems such as $Li^+$-$NH_3$[15] and $Sr^+$-$H_2O$.[24]

**Table I.** Enthalpies of Hydration $\Delta H^\circ_{n,n+1}$

| $A^-$ | $-\Delta H^\circ_{n,n+1}$, kcal/mol | | | |
|---|---|---|---|---|
| | (0,1) | (1,2) | (2,3) | (3,4) |
| $CO_3^-$ | 14.1<br>± 0.2 | 13.6<br>± 0.5 | 13.1<br>± 0.8 | |
| $HCO_3^-$ | 15.7<br>± 0.2 | 14.9<br>± 0.2 | 13.6<br>± 0.3 | 13.4<br>± 0.9 |

**Table II.** Entropies of Hydration $\Delta S^\circ_{n,n+1}$

| $A^-$ | $-\Delta S^\circ_{n,n+1}$, eu | | | |
|---|---|---|---|---|
| | (0,1) | (1,2) | (2,3) | (3,4) |
| $CO_3^-$ | 25.2<br>± 0.6 | 29.6<br>± 1.4 | 32.5<br>± 2.3 | |
| $HCO_3^-$ | 24.1<br>± 0.5 | 29.1<br>± 0.6 | 30.2<br>± 1.0 | 33.3<br>± 2.7 |

**Table III.** Comparison of Free Energies of Hydration for $CO_3^-$ at 296 K (kcal/mol)

| | $-\Delta G^\circ_{296}$ (0,1) | $-\Delta G^\circ_{296}$ (1,2) |
|---|---|---|
| this work | 6.6 | 4.8 |
| ref 13 | 6.7 | 4.3 |

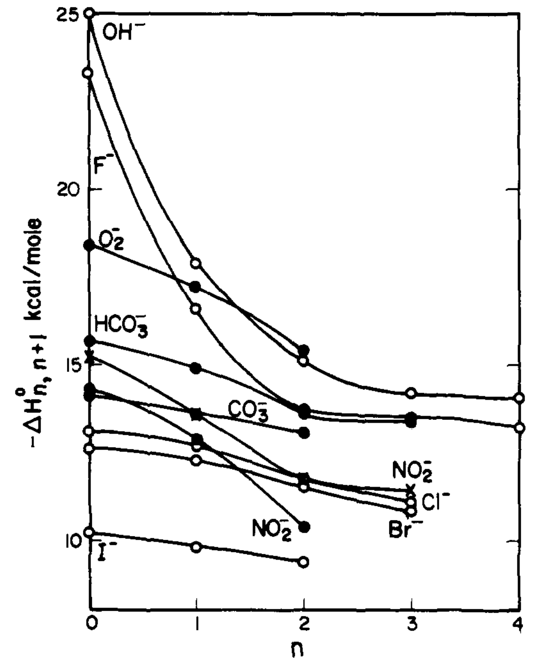

**Figure 5.** Gas-phase hydration enthalpy changes of several negative ions as a function of clustering step: (X)-$NO_2^-$ are recent results from this laboratory; (O)-$NO_2^-$ are from ref 19.

Since $CO_3^-$ and $HCO_3^-$ are nonspherical ions, in the early stages of hydration the energies should be strongly dependent on their structure. Unfortunately, the gas-phase structures of the ions are not known experimentally. However, in the case of $CO_3^-$, experimental studies[25] in condensed media have indicated a $C_{2v}$ geometry and support a unique OCO angle of greater than 120°. In contrast, semiempirical calculations[26,27] for the radical negative ion predict an angle much less than 120°. A recent ab initio calculation[28] predicts a structure (Figure 7a) consistent with the experimental results and with the simple notion of $O^-$ weakly bonding to $CO_2$ [$D(CO_2\text{-}O^-)$ = 1.8 eV (~40 kcal/mol)[11]].

More recently an ab initio molecular orbital calculation of the gas-phase structure of the bicarbonate ion $HCO_3^-$ has been reported.[29] It is interesting to compare the results with those made in this laboratory using CNDO/2 (a semiempirical molecular orbital method); the optimized geometries are shown in Figure 7. Both the CNDO/2 (Figure 7b) and the ab initio results (Figure 7c) predict a similar structure which is comparable to the gas-phase structure of the isoelectronic molecule $HNO_3$ (Figure 7d) determined from microwave studies.[30]

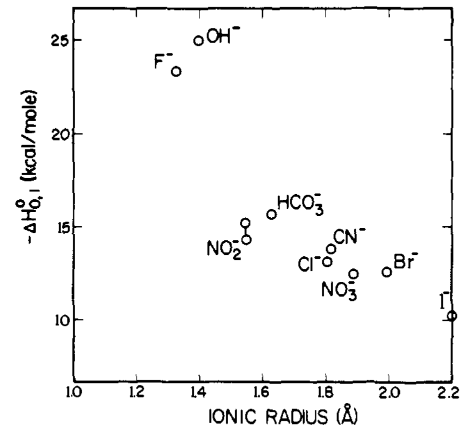

**Figure 6.** $-\Delta H^\circ_{0,1}$ vs. ionic radii: Goldschmidt ionic radii for monatomics. Yatsimirski thermochemical radii for polyatomics.

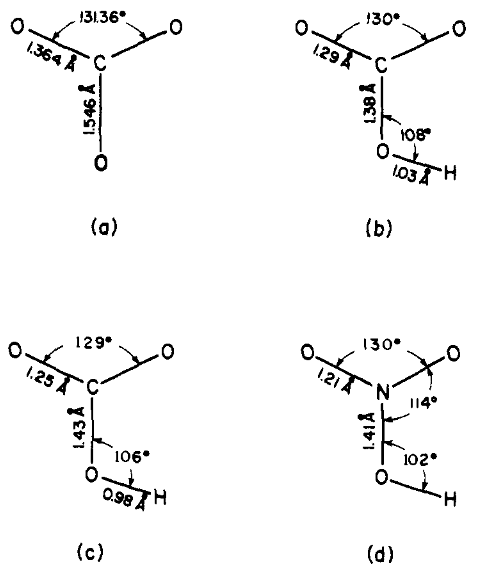

**Figure 7.** (a) The ab initio calculated structure for $CO_3^-$ from ref 20. (b) The CNDO/2 energy minimized structure for $HCO_3^-$ from this work. The two C-O bond lengths and angles were assumed to be equivalent. (c) Optimized ab initio geometry of $HCO_3^-$ from ref 29. (d) Gas-phase structure of $HNO_3$ from ref 30.

CNDO/2 calculations were also performed to gain some insight into the hydration structure of $HCO_3^-$ complexes. The results are in Figures 8 and 9. Although some geometric alterations might occur upon hydration, in making the calculations the ion and water monomer were assumed rigid with the CNDO optimized geometries. A configuration of water hydrogen bonded to the tightly bonded oxygens of the anion, thereby forming a C-O···H angle 115° and an O···H distance of 1.35 Å, was found to be most favorable (see Figure 8a). This result is analogous to predictions concerning the hydration of $OH^-$ based on other calculations.[31-33] Additionally, the $HCO_3^-$ hydration configuration with the water lying out of the plane of the ion was found to be slightly more favorable (about 0.5 kcal/mol) than one with the water in the plane. The resulting hydration or stabilization energy ($E_{\text{hydration}} = E_{\text{hydrate}} - E_{\text{ion}} - E_{\text{water}}$) was calculated as 29.6 kcal/mol.

Other stable configurations are in water binding with both hydrogens to an oxygen atom (13 kcal/mol, Figure 8b) and

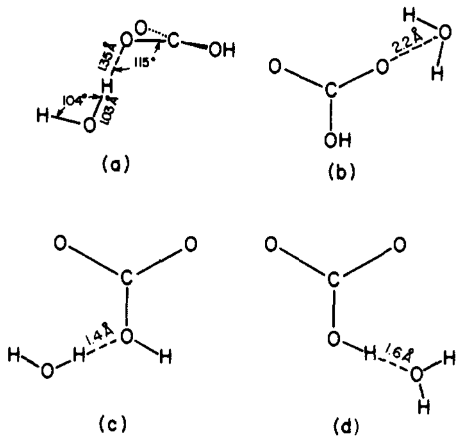

Figure 8. Geometries of the $HCO_3^-$-$H_2O$ complex from CNDO/2 calculations for various configurations. The free water and $HCO_3^-$ geometries were assumed in the complex. Stabilization energy: (a) 29.6, (b) 13, (c) 18, (d) 2 kcal/mol.

a water hydrogen bonded to the oxygen atom of the OH group on the ion (18 kcal/mol, Figure 8c). Hydrogen bonding of the hydrogen atom of $HCO_3^-$ to a water oxygen is calculated to be stable by only 2 kcal/mol (Figure 8d).

By examining the Mulliken populations of CNDO calculations, the stabilization energy for hydration is seen to be roughly proportional to the respective degrees of charge transfer from the ion to the water ligand. For the most stable configuration, about 12% of the charge of the anion is transferred to the water.

The CNDO calculations also predict a strong interaction (33 kcal/mol) between the carbon atom and a nonbonding orbital of the oxygen of the water, where the plane of the water molecule is orthogonal to the plane of the ion. In this configuration, the orientation of the dipole of the water is electrostatically repulsive to the overall charge of the ion. Furthermore, a considerable amount of additional negative charge is transferred from the water molecule into the already negative ion. The surprising strength of this interaction is probably an artifact of the CNDO approximation as has been encountered before with other nonbonding interactions of the oxygen atom of water.[34] Therefore this configuration is not considered to be physically reasonable.

The actual experimental hydration energy probably results from several contributing structures. Also, the most stable structure may not be the one obtained experimentally since the orientation of the ion with respect to the water molecule during a collision might allow a less stable configuration to first form. Therefore, for comparison with experimental hydration energies, a molecular dynamic[35] or Monte Carlo[4] approach would be required in order to properly average over various configurations resulting from different orientations of reactive collisions. In general, the CNDO stabilization energies are larger than those determined by ab initio calculations, and the hydrogen-bonded O···H bond lengths are somewhat shorter.[36] Owing to the approximate nature of CNDO calculations, the calculated energies are expected to be only reflective of the general trends and not necessarily quantitative.

Other calculations were made in which the addition of a second water was also considered. In making these computations the most stable hydrogen-bonded configuration shown in Figure 8a was taken for the monohydrate structure. The addition of water to the second oxygen of the ion was most favorable: only a slight decrease in the stabilization energy occurs for the second step compared to the first (~26.3 vs. 29.6 kcal/mol, Figure 9a). This corresponds to a decrease in the overall relative charge transfer per water. The other water configurations should show similar small decreases in stabilization energy when considered as the second step. In accounting for the second hydration step, two other possibilities must be considered. These are (1) the second water bonds to the oxygen atom of the ion already hydrogen bonded to the first water (stabilization energy ~24 kcal/mol, Figure 9b) and (2) a water molecule hydrogen bonds to the first water ligand already present (stabilization energy ~17 kcal/mol, Figure 9c).

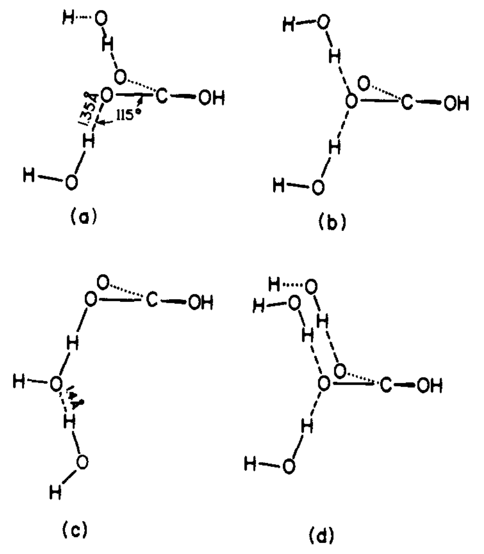

Figure 9. Hydrate structures for addition of a second water to $HCO_3^-$ giving additional stabilization energies of (a) 26.3, (b) 24, (c) 17 kcal/mol, and (d) for the third water addition, 20.7 kcal/mol.

Referring to Figure 5, one notices that the change of $-\Delta H°_{n,n+1}$ for $HCO_3^-$ from $n = 1$ to $n = 2$ is greater than from $n = 0$ to $n = 1$. Although this trend is not entirely outside the experimental error, it is apparent that the enthalpy changes for the first two hydration steps are similar in magnitude, while the third is appreciably less owing to less favorable bonding sites. With the first two hydration steps being those discussed above for which the stabilization energies are 29.6 and 26.3 kcal/mol (Figures 8a and 9c, respectively), the third step would be most favorable by the addition of a second water to one of the oxygen atoms for which the additional stabilization energy is 20.7 kcal/mol (Figure 9d). The CNDO calculations, therefore, also indicate that the stabilization energy (to which $\Delta H$ is related) for the third clustering step would be significantly smaller than for the first two steps.

For $CO_3^-$, the first three hydrations might be expected to have shown decreasing enthalpy changes as water molecules successively hydrogen bond to each oxygen atom of the parent ion. The relative decrease in $-\Delta H_{n,n+1}$ may be expected to be greater for the fourth step. But, unfortunately, data on the fourth hydration step was not obtained and this hypothesis cannot be confirmed.

Entropy changes also reflect the influence of structure in a reaction. The geometries of $CO_3^-$ and $HCO_3^-$ are rather similar, and it is not surprising that their entropy changes for hydration are rather similar, especially for the first two hydration steps.

## Considerations of Solvation

The experimentally determined gas-phase hydration values are not only of interest in themselves, but also because they can be related to aqueous-phase hydration via the Born–Haber cycle. The sum of the individual stepwise enthalpies correspond to the enthalpy change for the reaction

$$A^-(g) + nH_2O(g) \rightarrow A^-(H_2O)_n \qquad (4)$$

At sufficiently large values of $n$ the product is equivalent to that

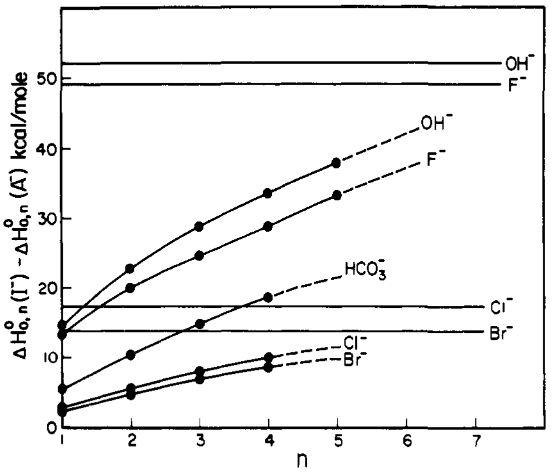

**Figure 10.** Experimental $\Delta H^\circ_{0,n}$ as a function of $n$ with iodide as reference. The $\Delta H_{\text{solv}}$ ($\Delta H^\circ_{0,\infty}$) reference to iodide is shown as the horizontal lines for comparison.

Table IV. Single Ion Hydration Enthalpies[a]

| ion | $OH^-$ | $F^-$ | $Cl^-$ | $Br^-$ | $I^-$ |
|---|---|---|---|---|---|
| $-\Delta H_{\text{solv}}$, kcal/mol | 116.3 | 113.3 | 81.3 | 77.9 | 64.1 |

[a] Data taken from ref 19.

of an ion in an aqueous droplet. The above can be written as a sequence of reactions

$$H_2O(g) + H_2O(g) \rightarrow (H_2O)_2 \tag{5}$$

$$(H_2O)_{n-1} + H_2O \rightarrow (H_2O)_n \;\; \Delta H^{\circ\omega}_{n-1,n} \tag{6}$$

$$A^-(g) + (H_2O)_n \rightarrow A^-(H_2O)_n \tag{7}$$

For large $n$, $\Delta H^{\circ\omega}_{n-1,n}$ is just the heat of condensation of water. The last step, eq 7, represents the hydration of $A^-$ in the aqueous phase; the enthalpy change for this step is represented by $\Delta H_{\text{solv}}$. In principle this quantity could be determined from the results of the gas-phase clustering experiments. This would be accomplished by summing the enthalpy changes for the successive clustering reactions, thereby determining the overall enthalpy change for 4 at very large $n$. The resulting value would then be corrected for each appropriate $\Delta H^{\circ\omega}_{n-1,n}$. Since the enthalpy change for reaction 1 would be expected to approach the value of the heat of condensation of water at moderate values of $n$,[37,38] this could be done with only moderate extrapolation of the experimental measurements. Unfortunately, however, the $\Delta H^{\circ\omega}_{n-1,n}$ values for forming the small water clusters are not known and the requisite correction cannot be readily made.

In order to compare the gas-phase clustering results with those expected in the liquid phase, it has become common[21] to reference the results with respect to a chosen ion. In this way, the influence of the series of water cluster reactions (eq 5 and 6) is eliminated. The iodide ion was taken as the reference negative ion.

Using this reference, $\Delta H^\circ_{0,n}(I^-) - \Delta H^\circ_{0,n}(A^-)$ are plotted for a number of ions, as a function of $n$, in Figure 10. Calculated heats of solvation are given in Table IV. The $\Delta H_{\text{solv}}$ for $OH^-$ given in ref 19 is used in preference to other values given in the literature. The value of 101.2 kcal/mol given in ref 37 is inconsistent with the gas-phase results obtained by Kebarle et al.[19] In fact, the hydration enthalpies of $OH^-$ references to iodide ion already exceed the lower (limiting) value of $\Delta H_{\text{solv}}$ ($\Delta H^\circ_{0,\infty}$) at $n = 5$.

Referring to Figure 10, $\Delta H^\circ_{0,n}$ values can be seen to asymptotically approach $\Delta H_{\text{solv}}$ for each individual ion. From

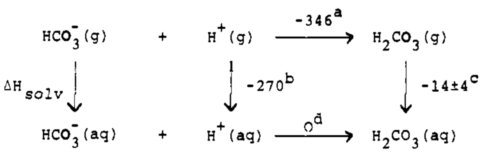

**Figure 11.** Reaction scheme for the determination of the enthalpy of solvation of $HCO_3^-$. The values are enthalpy charges in kcal/mol: (a) ref 29, (b) ref 19, (c) ref 40, (d) ref 41 and 42.

the present work, $-\Delta H_{\text{solv}}$ for $HCO_3^-$ is found to be greater than 83 kcal/mol. At only a value of $n = 4$ the ratio

$$[\Delta H_{\text{solv}}(I) - \Delta H_{\text{solv}}(A^-)]/[\Delta H^\circ_{0,n}(I^-) - \Delta H^\circ_{0,n}(A^-)]$$

is found to be constant (1.65 ± 0.05) for both the halides and hydroxide. This is remarkable considering the fact that $F^-$ and $OH^-$ interact strongly with water, while in the case of the larger halides the interaction is basically electrostatic and much weaker. Taking this constant ratio to be valid for $HCO_3^-$ leads to a value for its solvation $\Delta H_{\text{solv}}$, enthalpy, of −95 kcal/mol. The $\Delta H_{\text{solv}}(HCO_3^-)$ may also be calculated from experimental measurements by employing the recent ab initio molecular orbital calcualtions. Using the reaction scheme shown in Figure 11, $\Delta H_{\text{solv}}(HCO_3^-)$ is calculated to be −90 kcal/mol. This is in good agreement with the value derived from the gas-phase measurements presented here. The gas-phase experiments give a definite lower bound to $-\Delta H_{\text{solv}}$ and allow a reasonable estimate to be made for comparison with other thermochemical data.

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# Bonding Capabilities of Transition Metal Clusters. 2.[1] Relationship to Bulk Metals

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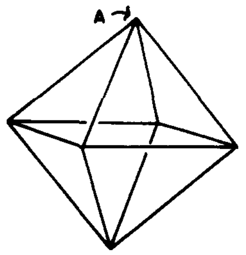
**Abstract:** The bonding capabilities of individual metal atoms of a cluster or of an infinite lattice have been estimated, based upon extended Hückel calculations. Each atom can be assigned a characteristic number of cluster valence molecular orbitals (CVMOs), which is dependent upon the site geometry. The CVMOs can contain metal electrons or can be used as ligand acceptor orbitals. The number of CVMOs located on an atom at a given site is inversely dependent upon the number of nearest neighbors.

A popular assumption as of late is that discrete organometallic transition metal cluster compounds are good models for chemisorption on to bulk metal surfaces and that catalysis by small metal particles involves species similar to known stoichiometric compounds.[2-5] Unfortunately, to date there has been little theoretical justification for any direct connection. This is due primarily to the fact that for bulk metals the observables of most concern to theoreticians are the diverse bulk electronic and magnetic properties, while for cluster compounds, which are almost always diamagnetic, the primary observables are structure and stoichiometry. Theoretical studies have generally been directed toward an understanding of one of these problems or the other; seldom have their direct relationships been explored. In this work we will explore such relationships and will offer a unified method for determining the bonding capabilities of an individual atom of a cluster or an individual atom of a bulk metal surface.

**Clusters.** It has been known for some time that structure and stoichiometry are closely related in group 8 organometallic cluster compounds.[5,6] A given cluster tends to have its stoichiometry determined not by the identity of the metal or the ligands, but by the geometry of the cluster. For example, if six metal atoms are arranged in an octahedral geometry they will in general form stable chemical compounds only if the sum of the cluster valence electrons (CVEs) is equal to 86 electrons.



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One such cluster is the anion $[Fe_6(CO)_{16}C]^{2-}$, which has 48 Fe electrons, 32 electrons from the CO ligands, 4 from the intersitial carbide, and a dinegative charge; the sum is 86 electrons.[7] Other diverse examples[6] include $[Co_6(CO)_{16}]$, $[Ni_6(CO)_{12}{}^{2-}]$, $[Ru_6(CO)_{17}C]$, $[Rh_6(CO)_{16}]$, and $[Ni_2Co_4(CO)_{14}]^{2-}$.

Recently we reported a simple, reliable MO method for determining the bonding capabilities or stoichiometries of small metal clusters.[1] As aggregates of metal atoms are built up one atom at a time, the atomic orbitals combine to form molecular orbitals, which evolve at the infinite limit into the band structure of bulk metal. At the intermediate cluster stage we have found that the MOs can be conveniently divided into two classes on the basis of energy. The high-lying antibonding orbitals (HLAOs) are destabilized by metal-metal antibonding interactions and are too high in energy to contain electrons or to serve as ligand acceptor orbitals. The cluster valence molecular orbitals (CVMOs) are lower in energy, are suitable for containing metal electrons, and can serve as acceptor orbitals for ligand bonding.

The preference shown for 86 CVEs by the octahedral clusters is due to the presence of exactly 43 CVMOs. To determine the number of CVMOs of a given cluster we have used extended Hückel calculations[8] as a guide and have determined empirically that a reliable upper energy limit for the CVMOs is the level of the p orbitals of a single metal atom. Thus any orbital significantly destabilized with respect to the p level of a single atom is classified as a HLAO.

**Bulk Metals.** Transition metals have diverse physical properties and have thus been of interest to theoreticians for many years. Generally the bonding with metals is treated by various band theories, discussions of which can be found in standard texts.[9,10] Inherent in such theories is a delocalization of states, which sometimes makes information regarding discrete atomic sites difficult to abstract. Actually it is also difficult to determine the properties of individual atoms by most physical measurements as well.

To make comparisons with the discrete cluster compounds, we need to know the number of states or orbitals contributed by each metal atom to the energy band and which are available for electron occupancy. This information is most readily available for the group 8, ferromagnetic metals, Fe, Co, Ni, and their alloys. From the spontaneous magnetic moments of

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