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Ab Initio Study of Structures and Binding Energies for Anion-Water Complexes

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Abstract: Results of ab initio molecular orbital calculations are reported for complexes of eleven anions with a water molecule. Optimized geometries obtained with the 6-31G(d) basis set were used in calculations including diffuse functions and the correlation energy. The present structural and energetic results complement and extend experimental studies of gas-phase acidities and single-molecule hydration energies. Trends for the hydrogen bonding are also elucidated.

The quantitative study of ion-molecule interactions in the gas phase has provided important characterization of chemical bonding and a fundamental basis for understanding solvent effects on the thermodynamics and kinetics of organic reactions.[1] In particular, relative binding affinities for a wide range of anions and cations with single solvent molecules have become available from measurements of equilibrium constants by use of ion-cyclotron resonance (ICR), high-pressure mass spectrometry, and the flowing afterglow technique.[1,2] Since the experiments do not yield detailed structural information, ab initio molecular orbital methods have been nicely complementary in providing both energetic and structural results for the ion-molecule complexes.[3] This combination of theory and experiment has also been most valuable in developing the ion-molecule potential functions needed for statistical mechanics and molecular dynamics simulations of simple ions in solution as well as biomolecular systems.[4] As part of our efforts in this area, we have undertaken ab initio studies of numerous ion-molecule complexes. Results for cation-molecule complexes have been described previously,[3a,b] while our findings for eleven anions solvated by a single water molecule are reported here.

Related experimental studies of hydrogen bonding to anions in the gas phase have been pioneered by Kebarle and co-workers.[2,5-10] They have determined absolute binding energies for halide,[5-8] hydroxide,[9,10] cyanide,[9] nitrite,[9] and nitrate[9] anions with water, alcohols, and acids. Strong binding suggestive of a covalent component is found for $F(H_2O)^-$ and $OH(H_2O)^-$, while the weaker interactions for larger, more polarizable ions such as I^- are dominated by electrostatics. Larson and McMahon have also examined the binding of F^- and Cl^- to many Brønsted acids.[11] Rough correlations with the gas-phase acidities of the solvent molecules were found and reflect the greater importance of electrostatics and multiple binding sites for Cl^-.[11] Another extensive ICR study has been carried out by Caldwell et al., who measured hydrogen bond strengths for alkoxide, acetylide, and dithianide ions with alcohols.[12] The hydrogen bonding for the carbanions is significantly weaker than expected on the basis of acidity and emphasizes the importance of the electronegativity of the anionic site.

On the theoretical side, early ab initio studies of F^- and Cl^- with water were performed by Kistenmacher et al. using large basis sets.[13] Their energetic results compare well with experiment, and similar structural results have been obtained by others.[14] Several groups have also performed calculations for $OH(H_2O)^-$ and various $RO(ROH)^-$ complexes.[15] These results are discussed below in comparison with the present findings for water interacting with F^-, Cl^-, OH^-, OOH^-, SH^-, CN^-, HC_2^-, CH_3O^-, CH_3S^-, $HCOO^-$, and CH_2CHO^-. Besides the hydration energies, gas-phase acidities of the conjugate acids have been calculated. Correlations of acidity with water binding strength are analyzed, and detailed characterization of the structures of the anion-water complexes is presented.

Computational Details

The ab initio MO calculations have been performed with the GAUSSIAN/80 series of programs on a Harris 800 computer at Purdue.[16] Geometries of all structures were optimized by use of analytical energy gradients[17] with the split-valence 6-31G(d) basis set (formerly denoted 6-31G*)[18] which inclues a set of d-type polarization functions on all non-hydrogen atoms. One symmetry constraint was often used as indicated in Figure 1 in order to study the conformational dependence of the energy. The optimized geometries were employed subsequently in single point calculations with the 6-31+G(d) basis set (6-31+G*) containing diffuse s and p functions on atoms other than hydrogen.[19] Diffuse functions

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Table I. Calculated Total Energies[a]

species		6-31G(d)//6-31G(d)	6-31+G(d)//6-31G(d)	MP2/6-31+G(d)
F^-		99.350 48	99.418 59	99.623 85
Cl^-		459.526 00	459.539 66	459.681 35
OH^-		75.326 60	75.376 33	75.588 16
HO_2^-		150.125 56	150.158 29	150.544 36
SH^-		398.093 22	398.106 89	398.240 34
CN^-		92.285 76	92.314 87	92.600 20
HC_2^-		76.175 89	76.210 11	76.464 27
CH_3O^-		114.384 47	114.410 47	114.742 62
CH_3S^-		437.114 86	437.126 90	437.395 62
HCO_2^-		188.182 63	188.208 11	188.707 68
CH_2CHO^-		152.283 93	152.311 47	152.762 58
H_2O		76.010 75	76.017 71	76.208 70
HF		100.002 91	100.014 86	100.201 96
HCl		460.059 98	460.061 02	460.204 52
H_2O_2		150.764 79	150.771 12	151.140 91
H_2S		398.667 32	398.668 11	398.800 76
HCN		92.875 20	92.878 63	93.160 13
$HC{\equiv}CH$		76.817 83	76.823 05	77.070 76
CH_3OH		115.035 42	115.040 92	115.356 45
CH_3SH		437.700 32	437.701 29	437.966 56
HCO_2H		188.762 31	188.769 16	
CH_3CHO		152.915 96	152.921 11	
$F(H_2O)^-$	(1a)	175.422 45	175.474 40	175.875 02
	(1b)	175.411 69	175.465 99	175.865 21
$Cl(H_2O)^-$	(2a)	535.559 47	535.577 38	535.914 15
	(2b)	535.558 69	535.576 54	535.912 30
$OH(H_2O)^-$	(3a)	151.393 46	151.432 63	151.840 68
	(3b)	151.393 06	151.432 35	151.840 20
	(3c)	151.391 63	151.430 26	151.837 98
	(3d)	151.391 53	151.428 78	151.839 16
	(3e)	151.379 51	151.426 56	151.832 69
$HOO(H_2O)^-$	(4a)	226.178 26	226.210 63	226.792 81
	(4b)	226.175 00	226.207 62	226.789 91
$SH(H_2O)^-$	(5a)	474.126 75	474.144 57	474.473 86
	(5b)	474.125 90	474.143 76	474.472 90
	(5c)	474.125 74	474.143 35	474.472 38
$CN(H_2O)^-$	(6a)	168.325 87	168.353 94	168.834 06
	(6b)	168.324 10	168.355 59	168.834 80
$HC_2(H_2O)^-$	7	152.219 57	152.252 54	152.702 32
$CH_3O(H_2O)^-$	(8a)	190.435 53	190.463 77	190.992 44
	(8b)	190.435 39	190.462 79	190.991 71
	(8c)	190.435 72	190.462 87	190.991 73
	(8d)	190.435 44	190.463 65	190.992 32
$CH_3S(H_2O)^-$	(9a)	513.147 60	513.164 25	513.628 88
	(9b)	513.147 38	513.163 90	513.628 67
	(9c)	513.147 20	513.163 68	513.628 61
	(9d)	513.147 35	513.164 08	513.628 61
$HCO_2(H_2O)^-$	(10a)	264.228 17	264.254 80	
	(10b)	264.220 80	264.250 24	
	(10c)	264.220 62	264.249 15	
$CH_2CHO(H_2O)^-$	(11a)	228.324 88	228.355 68	
	(11b)	228.324 86	228.354 67	
	(11c)	228.324 80	228.355 02	
	(11d)	228.326 03	228.355 60	

[a] Negative of the total energy is given in au.

are well-known to be important for describing the electronic structure of anions, particularly with first-row elements.[19,20] Electron correlation effects were considered by means of Møller–Plesset perturbation theory up to the second order (MP2/6-31+G(d)//6-31G(d)).[21] Only valence shell orbitals have been included in the correlation calculations.

Results

The total Hartree–Fock and correlated energies of the monomers and complexes calculated with the 6-31G(d) and 6-31+G(d) basis sets are reported in Table I. The computed solvation energies for the reaction $A^- + H_2O \rightarrow A(H_2O)^-$ are compared with the experimental enthalpies in Table II. Table III lists the computed protonation energies at various levels of theory and the experimental proton affinities. Some of the key geometrical parameters obtained at the 6-31G(d) level are shown in Figure 1. The full geometry entries for all the species considered in this paper are given as supplementary material in "*Z*-matrix" format. Figures 2 and 3 compare the calculated protonation energies and experimental proton affinities for the anions. The correlation of computed hydration energies and basicities for the anions is presented in Figure 4.

Some general comments on the energetic comparisons are in order before consideration of the individual systems. The conversion of the computed energies to enthalpies for comparison with the experimental data is represented by eq 1.[3c] ΔE_e° is the

$$\Delta H^{298} = \Delta E_e^\circ + \Delta E_v^\circ + \Delta(\Delta E_v)^{298} + \Delta E_r^{298} + \Delta E_t^{298} + \Delta PV \quad (1)$$

computed electronic energy change including correlation corrections, while ΔE_v° is the change in zero-point vibrational energy. $\Delta(\Delta E_v)^{298}$ is then the change in the vibrational energy difference in going from 0 to 298 K. The final terms are for changes in the number of rotational and translational degrees of freedom and the work term. For the present basis sets and system sizes, the zero-point energy change is very time consuming to compute. However, to assess the importance of the nonelectronic terms in eq 1, we have carried out the full computation for $OH(H_2O)^-$ and $SH(H_2O)^-$ using vibrational frequencies obtained at the 6-31G(d) level. The ΔE_e° for $OH^- + H_2O \rightarrow OH(H_2O)^-$ of −24.2 kcal/mol at the Hartree–Fock level is lowered to −27.5 kcal/mol including the MP2 correlation correction. Proceeding to MP3, which typically yields results similar to CI with full double excitations, provides little additional change, −27.3 kcal/mol. ΔE_v° is +2.1 kcal/mol and the temperature correction is +0.9. The vibrational modes were all treated harmonically which may introduce an error of ca. 0.3 kcal/mol due to the low-frequency torsional mode.[3c] The remaining terms can be evaluated classically as $-RT$ for ΔE_r^T, $-{}^3/_2RT$ for ΔE_t^T and $-RT$ for ΔPV which sum to −2.1 kcal/mol at 298 K. Thus, the net sum of the nonelectronic terms provides a correction of +0.9 kcal/mol to convert the computed energy of hydration to an enthalpy at 298 K. For $SH(H_2O)^-$, ΔE_v° is +2.0 kcal/mol and the temperature correction is +1.5 kcal/mol which lead to a net correction of +1.4 kcal/mol. Thus, the computed electronic energy change of −15.6 is translated to an enthalpy of hydration of −14.2 kcal/mol.

The correction for the protonation reaction $A^- + H^+ \rightarrow AH$ can be larger due to the covalent bond formation.[20] For formation of water, the correction to the electronic energy can be estimated from the 6-31G(d) frequencies. In this case, ΔE_v° is +9.1 kcal/mol and the temperature factor is 0 since there are no low-frequency modes. The remaining terms, ΔE_r^T, ΔE_t^T, and ΔPV, are $+{}^1/_2RT$, $-{}^3/_2RT$, and $-RT$, and they sum to −1.2 kcal/mol at 298 K. Thus, the computed protonation energy for OH^- needs to be made ca. 8 kcal/mol less exothermic for direct comparison with the experimental proton affinity. Corrections of 0–8 kcal/mol have been reported for other anions.[20]

Discussion

The individual complexes $A(H_2O)^-$ will be discussed first followed by examination of general trends.

$F(H_2O)^-$ and $Cl(H_2O)^-$. For both species, the C_s structures **1a** and **2a** are the global minima at the Hartree–Fock level as well as with electron correlation. The C_s structures have F–H and Cl–H distances of 1.384 and 2.375 Å with F–H–O and Cl–H–O angles of 172° and 154°. In order to assess the effect of geometry optimization including the diffuse functions, **1a** and **2a** were also fully optimized with the 6-31+G(d) basis set. The changes in the geometrical variables in comparison to 6-31G(d) are insignificant except for the hydrogen bond lengths. For **1a**, the F···H distance increases to 1.531 Å and the length of the hydrogen-bonded O–H bond decreases from 1.039 to 1.000 Å. For **2a**, the

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Table II. Calculated Complexation Energies (kcal/mol) with 6-31G(d) Geometries[a]

species		6-31G(d)	6-31+G(d)	MP2/6-31+G(d)	ΔH(exptl)
$F(H_2O)^-$	(1a)	38.4	23.9	26.6	23.3[b]
	(1b)	31.7	18.6	20.5	
$Cl(H_2O)^-$	(2a)	14.3	12.6	15.1	13.1,[b] 14.4[c]
	(2b)	13.8	12.0	14.0	14.9[d]
$OH(H_2O)^-$	(3a)	35.2	24.2	27.5	25[b]
	(3b)	35.0	24.0	27.2	
	(3c)	34.1	22.7	25.8	
	(3d)	34.0	21.8	26.5	
	(3e)	26.5	20.4	22.5	
$HOO(H_2O)^-$	(4a)	26.3	21.7	24.9	
	(4b)	24.3	19.8	23.1	
$SH(H_2O)^-$	(5a)	14.3	12.5	15.6	
	(5b)	13.8	12.0	15.0	
	(5c)	13.7	11.8	14.6	
	(5d)	12.0	10.7	12.0	
$CN(H_2O)^-$	(6a)	18.4	13.4	15.8	13.8[b]
	(6b)	17.3	14.4	16.3	
$HC_2(H_2O)^-$	7	20.7	15.5	18.4	
$CH_3O(H_2O)^-$	(8a)	25.3	22.3	25.8	19.9[e]
	(8b)	25.2	21.7	25.3	
	(8c)	25.4	21.8	25.4	
	(8d)	25.2	22.3	25.7	
$CH_3S(H_2O)^-$	(9a)	13.8	12.3	15.4	
	(9b)	13.7	12.1	15.3	
	(9c)	13.5	12.0	15.2	
	(9d)	13.6	12.2	15.2	
$HCO_2(H_2O)^-$	(10a)	21.8	18.2		
	(10b)	17.2	15.3		
	(10c)	17.1	14.6		
$CH_2CHO(H_2O)^-$	(11a)	19.0	16.6		
	(11b)	18.9	16.0		
	(11c)	18.9	16.2		
	(11d)	19.7	16.6		

[a] Energy and enthalpy changes for $A(H_2O)^- \rightarrow A^- + H_2O$. [b] Reference 2. [c] Reference 11b. [d] Reference 23. [e] Reference 12.

Table III. Calculated Energies of Protonation with HF/6-31G(d) Geometries (kcal/mol)

ions	HF/ 6-31G(d)	HF/ 6-31+G(d)	MP2/ 6-31+G(d)	exptl PA[a]
F^-	409.4	374.2	362.8	371.3
Cl^-	335.1	327.2	328.3	333.4
OH^-	429.3	402.5	389.4	390.7
HO_2^-	401.1	384.6	374.3	374.4
SH^-	360.3	352.2	351.7	353.5
CN^-	369.9	353.8	351.4	353.1
HC_2^-	402.8	384.6	380.6	375.4
CH_3O^-	408.5	395.6	385.2	381.4
CH_3S^-	367.4	360.4	358.3	359.0
HCO_2^-	363.8	352.1		345.2
CH_2CHO^-	396.6	382.6		366.4

[a] Bartmess, J. E. *Gas Phase Anion Thermodynamic Data Base*, 1985, personal communication. See, also: Bartmess, J. E.; McIver, R. T., Jr. in ref 1, Chapter 11 and ref 28.

increase in the Cl···H distance is slight (2.375 to 2.415 Å) and the O–H bond length remains at 0.961 Å. There is more charge transfer to the water molecule with the smaller basis set according to the Mulliken populations. Thus, the shorter hydrogen bonds at the 6-31G(d) level appear to be an attempt to compensate for the basis set limitations. The effect is clearly greatest for the least stable anions which form the strongest hydrogen bonds. Nevertheless, the energetic effects of these distortions are modest. The computed 6-31+G(d)//6-31G* hydration energy for $F(H_2O)^-$ is lowered from −23.9 to −24.8 when the 6-31+G(d) geometries are used, while the hydration enerrgy for $Cl(H_2O)^-$ remains unchanged at −12.6 kcal/mol.

The bifurcated C_{2v} forms for **1** and **2** are less stable at all levels of computation. However, the difference is much smaller for Cl^-. This along with the more bent hydrogen bond in **2a** is consistent with greater ion–dipole (electrostatic) character for the interaction with Cl^-. Kistenmacher et al. examined these systems and found hydrogen bonds bent by 4.5° for $F(H_2O)^-$ and 14.6° for $Cl(H_2O)^-$.[13] Recently, Yamabe, Ihira, and Hirao computed the solvation energy of Cl^- with a 4-31+G+p basis set and CI using single and double excitations.[14d] Their calculated interaction energy of 13.9 kcal/mol is similar to our results and the experimental values (Table II). They also obtained a Cl–H–O angle (151.6°) close to ours. The present solvation energies of 26.6 kcal/mol for $F(H_2O)^-$ and 15.1 kcal/mol for $Cl(H_2O)^-$ at the MP2/6-31+G(d)//6-31G(d) level may be compared with the experimental enthalpies of solvation of 23.3 and 13.1 to 14.9 kcal/mol. Electron correlation increases the binding energies by 2.7 and 2.5 kcal/mol for **1a** and **2a**; however, the zero-point and thermal corrections are expected to lower the result by ca. 1 kcal/mol based on $H_3O_2^-$ as a model. Thus, the present results favor the more recent experimental binding energies of 14–15 kcal/mol for $Cl(H_2O)^-$ over Kebarle's older data.[2,11,22,23]

The origins of the hydrogen bonding have been analyzed in terms of charge transfer, orbital overlap, and electrostatic interactions.[8,11,14] The stronger preference for linear hydrogen bonding in $F(H_2O)^-$ is consistent with greater covalent bond character than for $Cl(H_2O)^-$. Further increase in the ionic radius by passing to $I(H_2O)^-$ may lead to perference for the bifurcated C_{2v} structure.[8] With some purely electrostatic calculations, the bifurcated structures are predicted to be the most stable for all halide ions.[14a,24] However, simple potential functions with point charge models do reproduce the preference for the bent forms with F^- and Cl^-.[4,13]

$OH(H_2O)^-$. Five structures were examined on the $OH(H_2O)^-$ surface at the HF/6-31G(d) level. The asymmetric form **3a** is the global minimum, though rotation to **3b** requires only 0.2 kcal/mol. The syn conformer **3c** is higher in energy than the anti by 0.9 to 1.4 kcal/mol. The planar, symmetric structure **3d** with C_{2h} symmetry resembles a transition state for proton transfer between OH^- and H_2O; the computed energy relative to **3a** is

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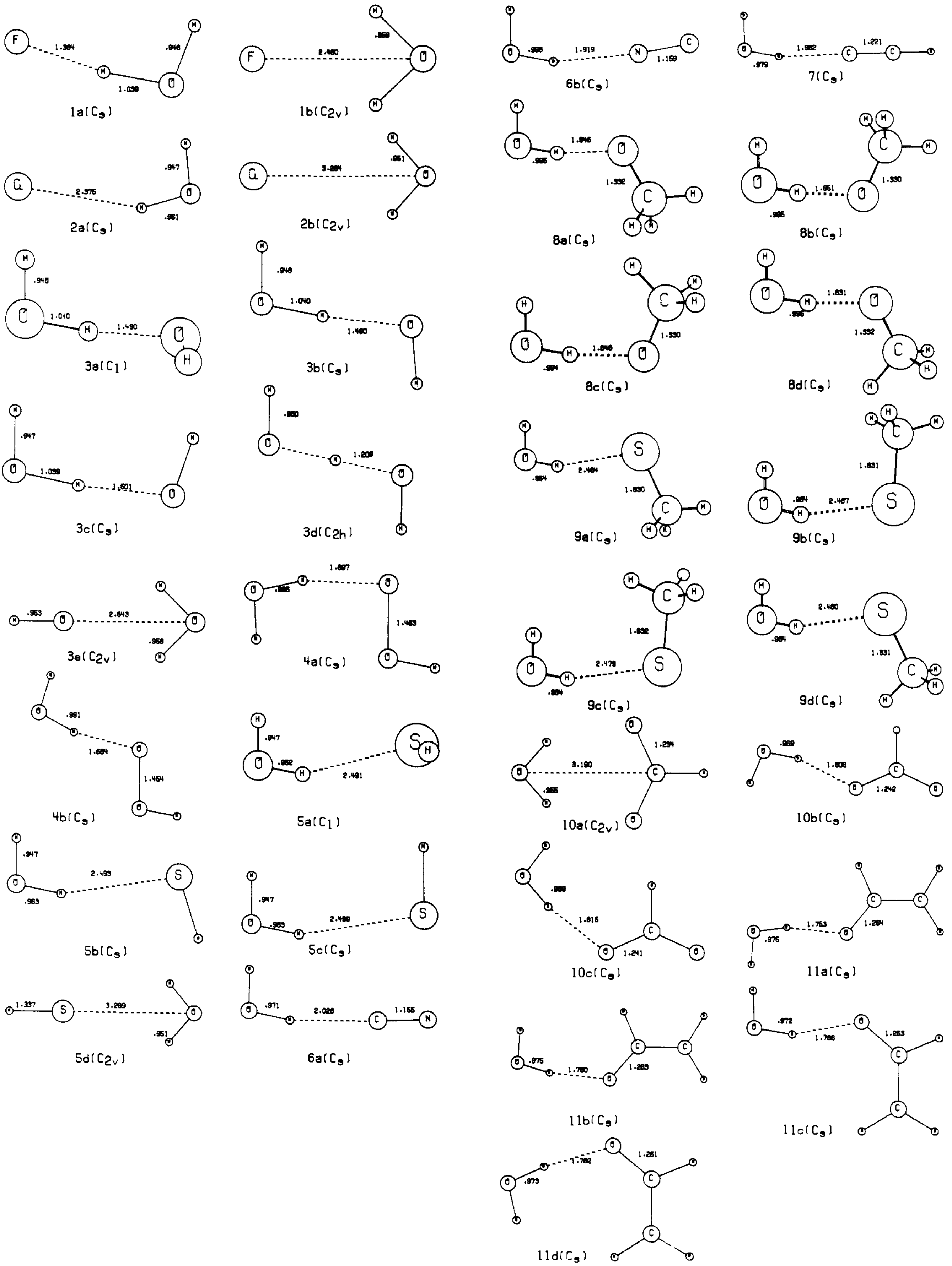

Figure 1. Optimized geometries for anion-water complexes with the 6-31G(d) basis set. Full geometrical details are available in the supplementary material.

reduced from 2.4 kcal/mol at the 6-31+G(d) level to 1.0 kcal/mol by the correlation correction. Geometry optimization at higher levels and zero-point considerations may therefore lead to the C_{2h} form or a C_2 rotamer as the global minimum; this point has been discussed at length by Rohlfing et al.[15e] The bifurcated form **3e** is significantly higher in energy. Previous theoretical work at the

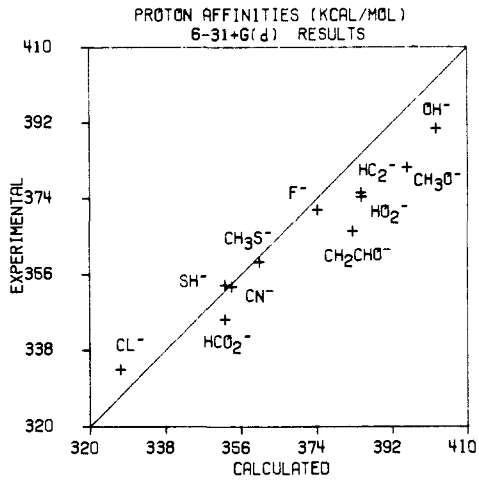

Figure 2. Correlation of experimental proton affinities and protonation energies from 6-31+G(d) calculations with the 6-31G(d) geometries.

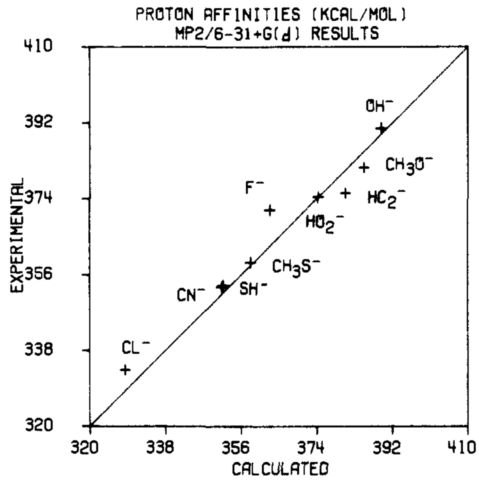

Figure 3. Correlation of experimental proton affinities and protonation energies from MP2/6-31G(d) calculations with the 6-31G(d) geometries.

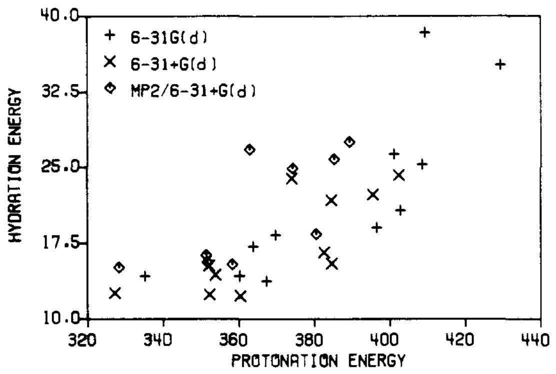

Figure 4. Correlation of calculated anion–water interaction energies and protonation energies in kcal/mol.

SCF level is consistent with the present findings, i.e., **3a** is the minimum energy form using 4-31G, 6-31G(d), and 6-31G(p,d) basis sets.[15] Furthermore, the calculations all yield a quite flat potential surface for motion of the central hydrogen in the hydrogen bond and for the internal rotation.[15]

The solvation energy of 35 kcal/mol at the 6-31G(d) level is substantially reduced by addition of the diffuse functions of 24 kcal/mol. The correlation correction raises it to 27.5, while the vibrational and thermal corrections yield a final computed enthalpy of 26.6 kcal/mol as discussed above. This is in good accord with the experimental value of 25 kcal/mol which has an uncertainty of 1–2 kcal/mol.[2,10] An alternative experimental result of 35 kcal/mol is not reasonable.[25]

$OOH(H_2O)^-$. Only the two planar forms, **4a** and **4b**, were optimized in this case. The syn conformer is preferred at all levels by ca. 2 kcal/mol. This structure undoubtedly benefits from added electrostatic attraction between the remote hydrogen on water and the hydroxyl oxygen of the peroxy anion. Some lengthening of the hydrogen bond relative to **4b** is apparently tolerated to optimize the effect. As in the cases of $OH(H_2O)^-$ and $SH(H_2O)^-$ discussed next, the global minimum for $OOH(H_2O)^-$ is probably a C_1 form obtained by small torsional changes in **4a**. The computed interaction energy including electron correlation of 24.9 kcal/mol is 2.6 kcal/mol less than that for $OH(H_2O)^-$. This may be attributed to charge delocalization between the two oxygens in HOO^-. The Mulliken population for the oxygen in OH^- with the 6-31+G(d) basis set is −1.34 while the values for the oxygens in HOO^- are −0.72 and −0.71.

$SH(H_2O)^-$. Similar to the monosolvated hydroxide ion, the C_1 geometry **5a** with an asymmetric, nonlinear hydrogen bond is the most stable form among the species considered. The anti and syn conformers **5b** and **5c** are less bound than **5a** by only 0.6 and 1.0 kcal/mol at the MP2/6-31+G(d) level. Thus, the torsional potential surface of $SH(H_2O)^-$ is also quite flat. Though the C_{2v} structure **5d** is still the highest energy form, the energy difference is smaller than for $OH(H_2O)^-$, 3.6 vs. 5.0 kcal/mol including the correlation energy. The S···H distance in **5a** of 2.49 Å is much longer than the corresponding O···H distance (1.49 Å), and the S–H–O angle of 154.7° is 18.2° farther from linearity than the O–H–O angle in **3a**. This is consistent with diminished covalent character and more dominant electrostatic interaction in $SH(H_2O)^-$ than $OH(H_2O)^-$. The greater ionic radius again leads to weaker hydration. The interaction energies for Cl^- and SH^- are both close to 12 kcal/mol less than for their first-row counterparts. To our knowledge, experimental and theoretical hydration energies have not been reported previously for SH^-.

$CH(H_2O)^-$. For $CN(H_2O)^-$ the C vs. N debate is found to be basis set dependent. The C hydrated form **6a** is preferred to the N hydrated alternative **6b** at the 6-31G(d) level by 1 kcal/mol. Reversal to a 1 kcal/mol preference for N hydration is found with the diffuse functions and is diminished to a 0.5-kcal/mol difference including electron correlation. The calculated binding energies of 16 kcal/mol are somewhat higher than Kebarle's value of 13.8 kcal/mol[9] even after a reasonable reduction for the zero-point and thermal corrections. The C vs. N dispute has been used by Payzant et al. to rationalize the deviation of CN^- from a plot of $\Delta H_{0,1}$ for hydration vs. basicity of anions.[9] In view of the energetic similarity for C and N hydration found here another explanation seems necessary. The charge delocalization in CN^- appears to reduce the hydration energy relatively more than it increases its gas-phase acidity. The electronegativity of the anionic site is also relevant.[12]

$HC_2(H_2O)^-$. The structure **7** was found as the minimum energy form in C_s symmetry with the 6-31G(d) basis set. The hydrogen bond has a computed length of 1.982 Å, and the C–H–O angle is 167.3°. The interaction energy of 20.7 kcal/mol at the 6-31G(d) level is reduced to 18.4 kcal/mol by including the diffuse functions and correlation energy. Caldwell et al. performed 4-31G calculations for this system with the hydrogen bond constrained to be linear and reported an interaction energy of 17.9 kcal/mol.[12] Although an experimental value for the enthalpy of hydration of HC_2^- is not available, Caldwell et al. did determine the binding energies of PhC_2^- with MeOH and *n*-PrOH via ICR; the experimental results are 13.3 and 15.4 kcal/mol, respectively.[12] Interaction with water is generally 1–2 kcal/mol weaker than with methanol,[12] while the lesser charge dispersal in HC_2^- than PhC_2^- should significantly increase the interaction. Thus, the computed hydration energy for HC_2^- is in the right range. It should be noted that there is considerable charge delocalization for both the cyanide and acetylide ions. The 6-31G(d) Mulliken charges for the C and N in CN^- are −0.35 and −0.65, while they are −0.42 and −0.66 for the carbons in C_2H^-. Surprisingly, the terminal carbon is the

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(25) DePaz, M.; Guidoni, A. G.; Friedman, H. L. *J. Chem. Phys.* **1970**, *52*, 687.

less negative one, though this qualitative result is basis set dependent.

$CH_3O(H_2O)^-$. Four structures with C_s symmetry were considered for $CH_3O(H_2O)^-$. The energy differences among them are very small at all theoretical levels. Nonetheless, the anti, staggered geometry **8a** is predicted to be lowest in energy except at the 6-31G(d) level. The O···H distances and O–H–O angles are essentially the same for all structures, ca. 1.65 Å and 170°. The calculated binding energy of 25.8 kcal/mol for **8a** at the MP2/6-31+G(d) level is significantly greater than the experimental value, 19.9 kcal/mol.[12] This result may also be compared with that of Ikuta, who used 6-311G(p,d)+p and [5s4p1d/3s1p] basis sets and found binding energies of 21.7 and 22.3 kcal/mol.[15f] The latter is identical with our 6-31+G(d) value, so the best theoretical results suggest that the experimental figure is low by 2–3 kcal/mol when all effects are considered. It has been noted previously that $HO^-\cdots HOCH_3$ and $CH_3O^-\cdots H_2O$ are proton transfer isomers and the latter is ca. 7.5 kcal/mol more stable.[15d]

$CH_3S(H_2O)^-$. The analogous four structures were examined for CH_3S^- with the same qualitative outcome. The anti, staggered form **9a** is only lower in energy than **9b–9d** by 0.1–0.2 kcal/mol. The S···H bond lengths are now 2.48 Å, and the hydration energy for **9a** is 15.4 kcal/mol including electron correlation. Thus, we find very little effect of methylation on the interaction energy for HS^-. The difference is greater in going from OH^- to CH_3O^-. Due to the long S–C bond length and 3p–2p interactions, the methyl group is not very effective in stabilizing the negative charge in CH_3S^- through polarization or anionic hyperconjugation. This is emphasized by the fact that CH_3SH is a weaker acid in the gas phase than H_2S while the opposite is true for CH_3OH and H_2O (vide infra).

$HCO_2(H_2O)^-$. Ab initio calculations have been performed previously for formate–water by several groups.[26] Lukovits et al. studied ten geometries and found structures similar to **10a–10c** to be lowest in energy.[26c] In fact, all of the computations predict the bifurcated form **10a** to be the most stable. At the 6-31+G(d) level, we obtained interaction energies of 18.2, 15.3, and 14.6 kcal/mol for **10a–10c**. On the basis of the many other results in Table II, it is expected that these values would be increased by 2–3 kcal/mol including electron correlation. This would put the interaction energies in good accord with the estimates of 20 kcal/mol for **10a** and 17 kcal/mol for **10b** and **10c** made by Lukovits et al. using a basis set comparable to 6-31G(p,d) with counterpoise and dispersion corrections. One interesting geometric point from the present 6-31G(d) optimizations is that the computed H–O–H angle from water in **10a** is 97.6° whereas as it deviates little from 102° in most of the other complexes. The distortion is understandable from an electrostatic standpoint since it keeps the centers of negative charge farther apart. Lukovits et al. did not optimize the intramolecular variables so that effect is not apparent in their results; however, the present C–O_w distance of 3.19 Å in **10a** is close to their value of 3.23 Å. It is also interesting to note that in Monte Carlo simulations of formate and acetate ions in dilute aqueous solution little occurrence of bifurcated hydrogen bonds as in **10a** has been found.[4c,26e] Interactions as in **10b** and **10c** are more common, though the total number of strong carboxylate–water interactions in dilute solution averages about seven.[4c,26e] Thermal averaging and the need to accommodate complete hydration shells are clearly important in understanding structure in condensed phases.

$CH_2CHO(H_2O)^-$. Four structures for solvated CH_2CHO^- anion have been examined in C_s symmetry with the water molecule bound to the enolate oxygen. Previous theoretical studies at the 4-31+G level have shown that the planar structure of the anion is the most stable conformer with a rotational barrier of 40 kcal/mol.[20] Structure **11d** is predicted to be the lowest in energy at the 6-31G(d) level. However, the addition of diffuse functions makes **11a** and **11d** isoenergetic and only more favorable than **11b** and **11c** by 0.4–0.6 kcal/mol. The computed binding energies are 19.0 and 19.7 kcal/mol for **11a** and **11d** at the 6-31G(d) level and 16.63 and 16.58 kcal/mol when diffuse functions are included. The hydrogen bonds in all structures are nonlinear with a largest divergence of 20°. One related ab initio study was carried out by Rachid et al. for the proton transfer in eq 2.[27] They used a minimal basis set and were primarily concerned with the stereochemistry in the deprotonation. A π complex structure for the products was found to be bound by 17 kcal/mol.

$$OH^- + CH_3CHO \rightarrow H_2O + CH_2CHO^- \qquad (2)$$

Proton Affinities

Discussion of basicities of anions are often in terms of proton affinities defined by the reaction $A^- + H^+ \rightarrow AH$; $PA = -\Delta H$. The 6-31G(d) protonation energies are too high compared with the experimental PAs (Table III). As discussed previously,[20] diffuse functions are particularly important for bettering the agreement. The average error for the computed data in Table III at the 6-31+G(d) level is 7 kcal/mol and is further improved to 3 kcal/mol by the MP2 correction. The accord may actually worsen a little after subtracting 0–8 kcal/mol from the computed values for the zero-point and thermal corrections discussed above and elsewhere.[20] Overall, the computed protonation energies are in good agreement with experiment and show improvement over earlier work with smaller basis sets.[20] The present results are also illustrated in comparison with experiment in Figures 2 and 3. The benefit of including the correlation energy is primarily for the less stable anions.

The computed protonation energies are in the order $OH^- > CH_3O^- > HC_2^- = HOO^- > CH_2CHO^- > F^- > CH_3S^- > CN^- > SH^- > HCO_2^- > Cl^-$ at the 6-31+G(d) level. The only significant discrepancy with the experimental order is for the enolate anion which might be rectified by the correlation correction. The calculations also reproduce the interesting reversal mentioned above of $OH^- > CH_3O^-$, but $CH_3S^- > SH^-$.[28]

Trends in Interaction Energies and Structures

The order of computed hydration energies at the 6-31+G(d) level is $OH^- > F^- > CH_3O^- > HOO^- > HCOO^- > CH_2CHO^- > HC_2^- > CN^- > Cl^- > SH^- > CH_3S^-$ and is consistent with the limited experimental data. There is clearly some correlation with basicity, though it is far from perfect as noted by others and illustrated in Figure 4.[2,9,11,12] The most aberrant points from the MP2 results are for the carbon acids, HCCH and HCN, and HF. The former yield anions that are less well hydrated than expected from their basicities, while F^- has an unusually strong interaction with water. In general, charge delocalization in the anions lowers the affinity for water relatively more than the proton affinity. This effect is apparent for CN^- and C_2H^- as well as CH_2CHO^- in the 6-31+G(d) results and for $HCOO^-$ if the bifurcated form was not considered. The pattern is reasonable since hydrogen bonding is dominated by electrostatics,[29] while the strength of the covalent bond to hydrogen in the acids is a key factor for the PAs along with the stability of the anion. Under the circumstances, correlations of the hydrogen bond strengths with electrostatic potential values should be good.[29b] Correlations with more readily accessible quantities such as Mulliken charges and the energy of the HOMO for the anions were examined and found to be poor. A rough correlation does exist between the hydration energies and the

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[26] (a) Port, G. N. J.; Pullman, A. *Int. J. Quantum Chem., Quantum Biol. Symp. No. 1* **1974**, *32*, 21. (b) Berthod, H.; Pullman, A. *J. Comput. Chem.* **1981**, *2*, 87. (c) Lukovits, I.; Karpfen, A.; Lischka, H.; Schuster, P. *Chem. Phys. Lett.* **1979**, *63*, 151. (d) Alagona, G.; Ghio, C.; Kollman, P. *J. Am. Chem. Soc.* **1983**, *105*, 5226. (e) Alagona, G.; Ghio, C.; Kollman, P. *J. Am. Chem. Soc.* **1986**, *108*, 185.

[27] Rachid, H. A.; Larrieu, C.; Chaillet, M.; Elguero, J. *Tetrahedron* **1983**, *39*, 1307.

[28] Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046, 6056.

[29] (a) Umeyama, H.; Morokuma, K. *J. Am. Chem. Soc.* **1977**, *99*, 1316. (b) Kollman, P. A.; McKelvey, J.; Johansson, A.; Rothenberg, S. *J. Am. Chem. Soc.* **1975**, *97*, 955. (c) Kollman, P. A. *J. Am. Chem. Soc.* **1978**, *100*, 2974.

amount of charge transferred to the water molecule.

A related observation from Table II is the weaker hydrogen bonding for the ions with second-row elements than the analogous first-row species. Ionic radius and polarization are obvious factors in this case. A useful rule-of-thumb for the halide, oxide, and thiolate ions is that the second-row species have hydrogen bonds 10–12 kcal/mol weaker than for their first-row counterparts. Furthermore, the maximal hydrogen bond energies are fairly constant at 26–27 kcal/mol for the first-row anions and near 15 kcal/mol for the second-row species. This discrepancy is the source of the pronounced leveling effect on, for example, the acidity of alcohols and thiols in going to aqueous solution. The gas-phase acidity difference for methanol and methanethiol of 22 kcal/mol (Table III) is cut to 12 by one water molecule and becomes 1.3 in aqueous solution.[28] Charge delocalization as in the enolate, carboxylate, and cyanide anions also gives an 8–10-kcal/mol reduction in hydrogen bond strengths.

On the technical side, the importance of diffuse functions for the first-row anions is clear for both the hydrogen bond and protonation energies. The relatively small effect of the diffuse functions for hydrogen bonding with second-row anions is largely offset by the correlation correction which in most cases increases the interaction energy by 2–3 kcal/mol. However, the diffuse functions have greater importance in obtaining accurate proton affinities for the second-row anions. The addition of diffuse functions and the correlation energy has little effect on the energetic order for alternate geometries of the hydrogen-bonded complexes, though geometry optimization at the higher levels would be necessary for full assessment of this issue.

Some generalizations can also be noted for the geometries of the hydrogen-bonded complexes. Naturally, hydrogen bond lengths $A^-\cdots H$ tend to decrease with increasing interaction energy. The crude linear correlation has a slope of ca. 12 kcal/(mol·Å); the most deviant points are for the two forms of $CN(H_2O)^-$, **6a** and **6b**, which are again found to have weaker interactions with water than expected. In general, the $A^-\cdots H$ hydrogen bonds are 0.9–1.0 Å longer for the second-row anions than their first-row analogues. Delocalization as in CH_2CHO^- and $HCOO^-$ also leads to longer hydrogen bonds by ca. 0.2 Å. Hydrogen bond bending is likewise correlated with hydrogen bond strengths. The optimal hydrogen bonds are typically bent less than 12° for the localized first-row and sp-hybridized anions, about 20° for the second-row anions and to intermediate values for the first-row anions delocalized by resonance. The drift toward bifurcated structures for the second-row anions was discussed above and is attributable to the increased dominance of ion–dipole attraction with increasing ionic radius.

Conclusion

High-level ab initio calculations have been carried out for complexes of eleven anions with water. Inclusion of diffuse functions, the correlation energy, and zero-point corrections provide favorable comparisons with available experimental data on gas-phase acidities and single molecule hydration enthalpies. The present results also yielded detailed structural characterization of the complexes, recognition of trends for both structure and energetics, and a basis for developing intermolecular potential functions for use in fluid simulations.

Acknowledgment. Gratitude is expressed to the National Science Foundation and National Institutes of Health for support of this work. Discussions with Dr. J. Chandrasekhar were also valuable.

Registry No. F^-, 16984-48-8; Cl^-, 16887-00-6; OH^-, 14280-30-9; HO_2^-, 14691-59-9; SH^-, 15035-72-0; CN^-, 57-12-5; HC_2^-, 29075-95-4; CH_3O^-, 3315-60-4; CH_3S^-, 17302-63-5; HCO_2^-, 71-47-6; CH_2CHO^-, 35731-40-9; H_2O, 7732-18-5.

Supplementary Material Available: Full geometrical details for the separated species and complexes in *Z*-matrix format (18 pages). Ordering information is given on any current masthead page.

Radical Chain Mechanism for Alkyl Rearrangement in Organocobalt Complexes

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Abstract: The molecular rearrangement of a series of 5-hexenylcobalt(III) complexes of various Schiff bases is demonstrated to proceed via an unusual radical chain process. Thus the facility with which the 5-hexenyl → cyclopentylmethyl rearrangement occurs is highly dependent on the presence of trace impurities which can vary from the age of a highly purified sample to the presence of air. We find that the rearrangement of (5-hexenyl)Co^{III}(salen) I can be deliberately controlled by inhibiting it completely or by promoting it rapidly. For example, the addition of cobalt(II), nitroxide (TEMPO), dioxygen, or dihydroanthracene as well as an electrochemical prereduction procedure can effectively squelch the 5-hexenyl rearrangement. Conversely, chemical and electrochemical oxidations with a ferrocenium salt and a platinum anode at 0.4 V, respectively, trigger the rearrangement. In each case, the limited molar amounts of additives (or faradays of charge) are sufficiently small to ensure high kinetic chain lengths. Inhibition and initiation of the chain process by these techniques relate directly to the destruction and generation, respectively, of alkyl radicals as the prime reactive intermediates. Accordingly, a homolytic displacement (S_H2) of the alkylcobalt(III) complex is proposed, in conjunction with the well-known rearrangement of the hexenyl radical, to constitute the two-step propagation cycle in Scheme III. Such a mechanism accounts for the intermolecular character of the hexenyl rearrangement as established by crossover experiments and the observation of a concurrent alkyl exchange which would otherwise be difficult to explain. The spontaneous rearrangement of a freshly prepared sample of (hexenyl)Co^{III}(salen) and the dichotomous effect of pyridine as a donor ligand are both readily accommodated within the content of the mechanism in Scheme III.

Molecular rearrangements are known in a wide variety of compounds, and their mechanisms are among the most difficult to delineate.[1,2] This is especially true of organometallic compounds in which the energetics of various pathways are often not strongly

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