

the relativistic calculations of the shielding constants of atoms by Kolb et al.³¹ They are positive and about 7% of the shielding constant for Cu and Zn and about 16% for Ag and Cd. They increase up to about 41% for Au and Hg. However, since the effects of relativity are large for electrons in the inner core AO's, the relativistic effects on the chemical shifts are probably much smaller than these. Some of the effects would be incorporated within the form of the Pascal rule like formula given by eq 12.

A theory of chemical shift in which spin-orbit coupling is introduced through perturbation theory has been applied to hydrogen halides and halomethanes.³² These results may be used to estimate the relativistic effects due to ligands. They show that the effects are positive for the shielding constant (shift to a higher field). As seen from Figure 1, the experimental chemical shifts of AgBr_4^{3-} and AgI_4^{3-} are -623 and -739 ppm, respectively.^{12a} This change is reverse to that expected from the relativistic effect. In the present calculations, the heaviest ligand is the Cl atom, so the effects should be small.

Conclusion

In this paper, we studied the nuclear magnetic shielding constants of the metals in the Ag, Cd, Cu, and Zn complexes. The results of the ab initio calculations compare well with the experimental chemical shifts. Table III summarizes the results of the present calculations. The paramagnetic term is a major part of the chemical shift, and the diamagnetic term is a minor part. For the paramagnetic term the inner amplitudes of the valence MO's of the metal are important (e.g., see Figure 5), and for the diamagnetic term the core MO's give a dominant contribution.

Table VIII shows a summary of the mechanisms of the metal chemical shift. For the complexes of the metals whose electronic configuration is primarily $d^{10}s^1-2p^0$, the paramagnetic term is due to the electrons in the outer valence np orbital and the holes in

the valence $(n-1)d$ orbital of the metal. These electrons and holes are produced by the interactions between metal and ligands as illustrated in Figure 6. For the copper complexes, the metal chemical shift is due primarily to the d contributions so that it increases with increasing electron acceptability of the ligand. For the zinc and cadmium complexes, the p contribution is larger than the d contribution, so that the chemical shift is most affected by the ability of the electron donation of the ligand. However, the d contribution also becomes important when the ligand is a good electron acceptor like CN^- , because the d electrons have larger angular momentum than the p electrons. For the silver complexes, the p and d contributions are competitive. Therefore, both of the donating and withdrawing properties of the ligand are important. It is shown that these differences in the origin of the chemical shifts of the 1B and 2B metals are understood from the atomic energy levels of the metals.

The diamagnetic term is a minor part of the chemical shift. But the equation like Pascal's rule, as expressed by eq 12, is derived. So the diamagnetic term can be estimated very accurately at least for the series of the complexes calculated here.

The complexes studied here have the transition metals Cu, Ag, Zn, and Cd, which have the electronic structure $d^{10}s^1-2p^0$. So the balance of the valence d and p contributions makes the chemical shift in a full variety. The mechanism of the chemical shift for the complexes of the metals with incomplete d-valence shells should be different from those of the complexes studied here. Such study will be published in a forthcoming paper.

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Registry No. CuCl , 7758-89-6; CuCl_4^{3-} , 15444-92-5; $\text{Cu}(\text{CN})_4^{3-}$, 19441-11-3; $\text{Cu}(\text{NH}_3)_2^+$, 16089-31-9; $\text{Zn}(\text{H}_2\text{O})_6^{2+}$, 15906-01-1; ZnCl_2 , 7646-85-7; ZnCl_4^{2-} , 15201-05-5; $\text{Zn}(\text{CN})_4^{2-}$, 19440-55-2; $\text{Zn}(\text{NH}_3)_4^{2+}$, 17095-57-7; $\text{Ag}(\text{H}_2\text{O})_6^+$, 42566-53-0; AgF_4^{3-} , 90605-28-0; AgCl_2^- , 15955-35-8; AgCl_4^{3-} , 15723-80-5; $\text{Ag}(\text{CN})_4^{3-}$, 16743-34-3; $\text{Ag}(\text{NH}_3)_2^+$, 16972-61-5; $\text{Cd}(\text{H}_2\text{O})_6^{2+}$, 14752-06-8; CdCl_2 , 10108-64-2; CdCl_4^{2-} , 15974-49-9; $\text{Cd}(\text{CN})_4^{2-}$, 16041-14-8; $\text{Cd}(\text{CH}_3)_2$, 506-82-1.

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Anion-Alcohol Hydrogen Bond Strengths in the Gas Phase

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Abstract: The hydrogen bond strengths of a number of alcohol-alkoxide complexes have been determined by using ion cyclotron resonance spectrometry, as well as the bond strengths for a number of alcohol-carbanion complexes. The acceptor/donor properties of the anions and alcohols correlate with both Brønsted acid/base character and the electronegativity. Carbon acids are considerably worse as donors than the localized carbanions (acetylide, dithianide) are as acceptors. Ab initio MO calculations using the 4-31+G basis set reproduce the bond strengths fairly well.

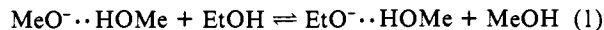
The role of solvation as one aspect of structure-reactivity relationships has long been recognized, but it is often regarded as of secondary importance compared to the effects of the intrinsic structure of the reacting species. The observation of Brauman and Blair,¹ that the acidity order of the aliphatic alcohols in the gas phase is completely reversed on going to bulk solution, revealed

that solvation can be the dominant factor in such reactions, and completely swamp out any effects due to the intrinsic structure alone. As a result, there has been considerable interest in gas phase ion/molecule reactions in the past decade, as a method of separating the effects of intrinsic structure and solvation on reactivity and energetics.

If a reversal in a reactivity order occurs on going from the nonsolvated ion to the bulk-solvated case, then there must be some

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point in the stepwise solvation where such a reversal happens. McIver, Scott, and Riveros² have shown, by quantitatively measuring equilibrium 1, that the reversal of the relative acidities



of methanol and ethanol on the change of phase is almost half complete with the first molecule of solvation. Clair and McMahon³ have obtained similar results for monosolvated acetate and propionate. Other workers,⁴ using techniques such as high-pressure mass spectrometry and flowing afterglow spectrometry, have also investigated the effects of stepwise solvation on ion reactivity, and they have shown that in some cases, the first molecule of solvent makes the behavior of the ion very solution-like, while in other cases many solvent molecules are necessary for the reactivity and solvation thermochemistry to approach that of the bulk solvated form. For anions other than the alkoxides cited above, most of the data deal with only a few simple anions, such as the halides, solvated by a wide variety of solvent molecules.^{4c,d,j,m,p} Such studies show a definite trend of increasing hydrogen bonding strength with increasing acidity of the donor and basicity of the anionic acceptor.^{4c} Larson and McMahon have recently measured solvent-switching reactions similar to (1) using ICR spectrometry for a number of donors bound to fluoride and chloride.⁵ They found a linear relationship between alcohol acidity and the hydrogen bond strength in $\text{ROH} \cdots \text{F}^-$, with most other donor functional groups bonded significantly less strongly, but HF being bonded much better.

The approach in this work to evaluating the thermochemistry of the first step of solvation involves measuring equilibria such as reaction 1 for a variety of alcohols and alkoxides, thus keeping the nature of the acceptor and donor sites constant while evaluating the effect of distant substituents on the hydrogen bonding strength. With a standard series of oxyacid hydrogen bonding abilities established, other acceptor and donor types may then be compared, to determine whether gas-phase acid/base character alone is the major factor in hydrogen bonding or whether other factors such as electronegativity or delocalization of charge are important. We report here the first cases of quantitative hydrogen bonding abilities of free, localized carbanions, specifically acetylides and 1,3-dithianide, as well as data on the ability of delocalized carbanions such as enolates to act as hydrogen bond acceptors.

Experimental Section

The instrumentation used is an ion cyclotron resonance (ICR) spectrometer, utilizing a McIver-type trapped ion cell and capacitance bridged detector.⁶ The techniques used to measure the equilibria were essentially those used in determination of the gas-phase acidity scale⁷ and

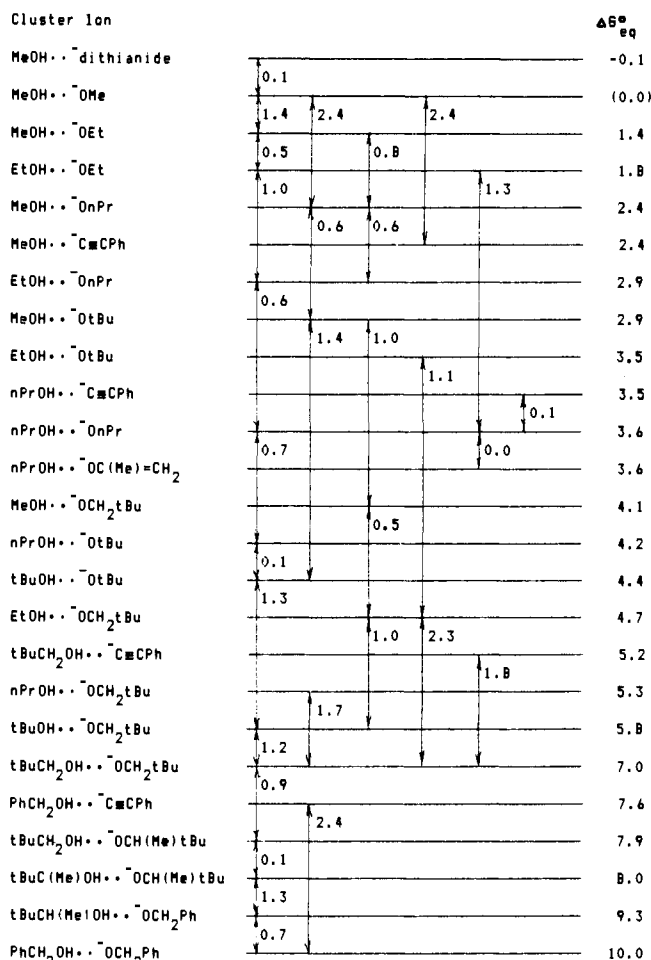
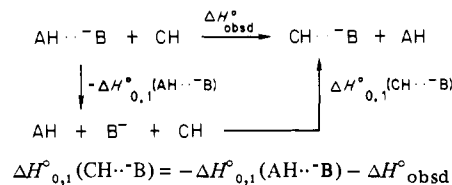


Figure 1. Scale of equilibria for anion-alcohol complexes. Values are free energies (kcal/mol).

Scheme I



other monosolvated equilibria.^{3,5,8,9} Time-dependent ion abundances were measured at constant magnetic field to reduce the effect of differential ion loss, and all reactions were confirmed by double resonance. The problem with the temperature of the cell being dependent on the filament current, encountered in the measurement of gas-phase acidities,⁷ has been corrected by modification of the filament block design¹⁰ so that the cell now varies less than 5°C with changing filament currents. The equilibria measured here were obtained at 307 ± 3 K.

Chemicals were obtained commercially, save for the nitrite and formate esters. The nitrite esters were prepared in situ from the appropriate alcohol.¹¹ The formate esters were made from formic acid and the appropriate alcohol by the previously described "stir-and-prepare" method.¹² All compounds were purified by distillation, sublimation, or preparative gas/liquid chromatography and then degassed on the foreline of the ICR

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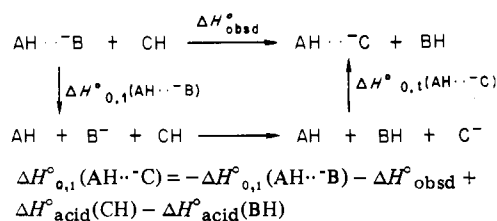
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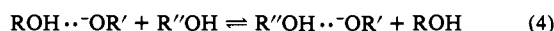
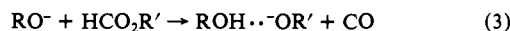
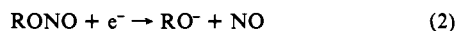
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Scheme II

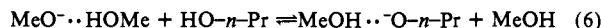


spectrometer by several freeze-pump-thaw cycles before being admitted to the vacuum system. The positive ICR mass spectra were consistent with the compounds used and showed negligible amounts of impurities. All ion abundance measurements were made with the ion gauge turned off to reduce the amount of pyrolytic species observed.

The reaction sequence in eq 2-5 was used to create the monosolvated species and to allow them to equilibrate. As a check on the attainment of equilibrium and the absence of excess energy in the products, for several of the measured equilibria (eq 5), the original monosolvated ion ROH \cdots OR' was generated from a variety of precursors. For example,



for equilibrium 6, the equilibrium constant was found to be independent



of whether the reactants in steps 2 and 3 were MeONO and HCO₂Me, MeONO and HCO₂nPr, or n-PrONO and HCO₂Me. Double resonance confirmed that reaction 6, entered by any of the methods, proceeded readily in both directions, at ca. 10% efficiency for the exothermic direction, and the derived $\Delta G^{\circ}(6)$ values were within 0.2 kcal/mol of each other on numerous trials.

Results

The $\Delta G^{\circ}_{\text{eq}}$ obtained for the various equilibria such as reaction 5 are given in Figure 1 along with $\Delta G^{\circ}_{\text{eq}}$ relative to MeOH \cdots OMe. The thermochemistry of the hydrogen bonds involved in these species can be calculated from the observed equilibria, using the thermochemical cycles in Schemes I and II. If it is assumed (see the Discussion section) that the cluster ion AH \cdots B exists primarily in the form where the more acidic partner is the acceptor, i.e., $\Delta G^{\circ}_{\text{acid}}(\text{BH}) < \Delta G^{\circ}_{\text{acid}}(\text{AH})$ for AH \cdots B, then for the entering neutral acid CH being between AH and BH in gas-phase acidity, Scheme I should be the most exergonic pathway, involving a simple solvent-switching reaction. In this case the observed $\Delta G^{\circ}_{\text{eq}}$ directly represents the difference in hydrogen-bonding ability. If the entering acid CH is a stronger acid than either acid in the cluster ion, then a proton transfer should occur, as in Scheme II. In this case the observed $\Delta G^{\circ}_{\text{eq}}$ must be corrected for the difference in acidity between the entering and departing acids. If CH is less acidic than either AH or BH by more than 2-3 kcal/mol, and of comparable bonding ability, then any exchange is too endergonic and is not observed.

For the experimental relative free energies in Table I to be converted to absolute enthalpies, there is needed both a method of obtaining the entropies for these equilibria and some absolute enthalpy value for anchoring the data. We adopt the nomenclature of Kebarle and co-workers in defining the thermochemistry of bonding the first solvent molecule to the bare ion (the reaction $\text{XH} + \text{Y}^- \rightarrow \text{XH} \cdots \text{Y}^-$) to be $\Delta G^{\circ}_{0,1}$. The relative $\Delta G^{\circ}_{0,1}$ values obtained here have been anchored to the absolute value for the bond strength of MeO \cdots HOMe of $\Delta G^{\circ}_{0,1} = -15.3 \pm 1.9$ kcal/mol ($\Delta H^{\circ}_{0,1} = -21.8 \pm 1.0$ kcal/mol and $\Delta S^{\circ}_{0,1} = -21.8 \pm 3.0$ eu) and $\Delta G^{\circ}_{0,1} = -16.9 \pm 1.9$ kcal/mol for PhCH₂OH \cdots OCH₂Ph ($\Delta H^{\circ}_{0,1} = -23.8 \pm 1.0$ kcal/mol and $\Delta S^{\circ}_{0,1} = -23.2 \pm 3.0$ eu),¹³ obtained by using pulsed high-pressure mass spectrometry in a manner similar to that used to obtain the value of HO \cdots HOH.^{4c} Scheme II predicts that the ΔG° values for these two cluster ions

Table I. Bond Strengths and Acidities of Alcohol-Anion Cluster Ions

XH \cdots Y	$-\Delta G^{\circ}_{0,1}$ ^a	$-\Delta H^{\circ}_{0,1}$ ^b	$\Delta S^{\circ}_{\text{tr,rot}}$ ^c	$\Delta H^{\circ}_{\text{acid}}$ ^d
HOH \cdots OH	18.8 ^e	25.0 ^e	-13.3	365.8
HOH \cdots OMe	13.3 ^f	19.9		359.2
MeOH \cdots dithianide ^g	8.2	14.8		358.1
MeOH \cdots OMe	(15.3) ^h	(21.8) ^h	(0.0)	357.4
MeOH \cdots OEt	13.6	20.2	0.9	355.9
EtOH \cdots OEt	14.0	20.6	4.8	355.5
MeOH \cdots O- <i>n</i> -Pr	13.2	19.8	1.8	354.9
MeOH \cdots C \equiv CPh	7.7	13.3		356.0
EtOH \cdots O- <i>n</i> -Pr	13.7	20.3	4.5	354.4
MeOH \cdots O- <i>t</i> -Bu	12.3	18.9	3.7	354.4
EtOH \cdots O- <i>t</i> -Bu	12.9	19.5	6.5	353.8
<i>n</i> -PrOH \cdots C \equiv CPh	8.8	15.4		354.9
<i>n</i> -PrOH \cdots O- <i>n</i> -Pr	14.4	21.0	8.0	353.7
<i>n</i> -PrOH \cdots	7.9	14.5	6.5	354.3
$\text{O}^-(\text{Me})=\text{CH}_2$				
MeOH \cdots OCH ₂ - <i>t</i> -Bu	12.0	18.6	3.0	353.2
<i>n</i> -PrOH \cdots O- <i>t</i> -Bu	13.6	20.2	8.2	354.5
<i>t</i> -BuOH \cdots O- <i>t</i> -Bu	13.8	20.4	12.8	354.3
EtOH \cdots OCH ₂ - <i>t</i> -Bu	12.6	19.2	6.3	352.6
<i>t</i> -BuCH ₂ OH \cdots C \equiv CPh	10.5	17.1		353.2
<i>n</i> -PrOH \cdots OCH ₂ - <i>t</i> -Bu	13.2	19.8	8.0	352.0
<i>t</i> -BuOH \cdots OCH ₂ - <i>t</i> -Bu	13.7	20.3	10.7	351.5
<i>t</i> -BuCH ₂ OH \cdots	14.9	21.5	11.5	350.3
$\text{O}^-(\text{Me})=\text{CH}_2$				
PhCH ₂ OH \cdots C \equiv CPh	12.9	19.5		350.8
<i>t</i> -BuCH ₂ OH \cdots	14.7	21.3	11.5	349.4
$\text{O}^-(\text{Me})-\text{t-Bu}$				
<i>t</i> -BuC(Me)OH \cdots	14.8	21.4	12.4	349.3
$\text{O}^-(\text{Me})-\text{t-Bu}$				
<i>t</i> -BuCH(Me)OH \cdots	15.0	21.6	12.5	348.0
$\text{O}^-(\text{CH}_2\text{Ph})$				
PhCH ₂ OH \cdots OCH ₂ Ph	15.7 ⁱ	22.3 ⁱ	12.9	346.7

^a For $\text{XH} + \text{Y}^- \rightarrow \text{XH} \cdots \text{Y}^-$, kcal/mol, 298 K. ^b $\Delta H^{\circ}_{0,1} = \Delta G^{\circ}_{0,1} + 298\Delta S^{\circ}_{0,1}$, kcal/mol, with $\Delta S^{\circ}_{0,1} = 22$ eu. ^c Translational plus rotational entropy, eu, from statistical mechanics, see text. ^d From eq 11. ^e Reference 4b. ^f Reference 19 relative to the data for MeOH \cdots OMe. ^g Dithianide is the (M-1)⁻ ion of 5,5-dimethyl-1,3-dithiane, see ref 23. ^h Reference 13, $\Delta S^{\circ}_{0,1} = 21.8 \pm 3.0$ eu. ⁱ Reference 13, $\Delta S^{\circ}_{0,1} = 23.2 \pm 3.0$ eu.

Table II. Entropy Terms from Statistical Mechanics for Reaction 1^a

species	S°_{tr} ^b	S°_{rot} ^c	S°_{sym} ^d	S°_{vib} ^e	S°_{tot}
MeOH	36.3	18.8	0.0	1.7	56.8
EtOH	37.4	21.9	0.0	5.5	64.8
MeOH \cdots OMe	38.3	25.1	-1.4	22.4	84.4
MeOH \cdots OEt	38.9	26.4	0.0	26.4	91.7
reaction 1 [ΔS°]	-0.5	-1.8	1.4	0.2	-0.7
exptl[ΔS°]					-1.2 \pm 1.3

^a All values in eu; nonexperimental entropies calculated as described in the text. ^b Translational entropy. ^c External rotational entropy, excluding symmetry terms. ^d Entropy of rotational symmetry. ^e Vibrational entropy.

should differ by 11.2 ± 4.0 kcal/mol, comparing favorably to the observed difference in Figure 1 of 10.0 kcal/mol.

Calculation of $\Delta S^{\circ}_{0,1}$ using statistical mechanics, as is done for gas-phase acidities,⁷ requires knowledge of the structure and frequencies of the hydrogen bond. These data are not readily available, and there have been several methods proposed to circumvent this lack. These involve use of only the rotational symmetry term for estimation of the entropy for equilibrium 4 or its cationic equivalent, assuming a cancellation of translational, vibrational, and nonsymmetry-related rotational terms,⁸ inclusion of the translational term $\Delta S^{\circ}_{\text{tr}}$,⁹ inclusion of $\Delta S^{\circ}_{\text{rot}}$, on the basis of standard geometries,^{5b} and a calculation based on the proportionality of the vibrations to $\Delta H^{\circ}_{0,1}$.⁵ An evaluation of these assumptions is undertaken here.

The equilibrium constant for reaction 1 has been measured in the ICR spectrometer for several temperatures in the range 307 to 364 K, decreasing by a factor of 2 over that range to give $\Delta H^{\circ}(1) = -1.8 \pm 0.4$ kcal/mol and $\Delta S^{\circ}(1) = -1.2 \pm 1.3$ eu, as shown in Figure 2. For comparison to these data, the various

(13) Caldwell, G.; Kebarle, P., private communication.

Table III. Molecular Orbital Calculations

	$-E^a$	$-\Delta E_{0,1}^b$	EA ^c	EA ^d	ΔE_{acid}^e	r^f	$-\Delta E_{0,1}^g$
HOH	75.91912				394.6 (390.8)		
HO ⁻	75.29023		69.2	42.1			
HO ⁻ ··HOH	151.25437	28.3	103.1	68.0 ^h		1.504	40.8 ⁱ
MeOH	114.87977				393.1 (379.2)		
MeO ⁻	114.25329		63.4	36.2			
MeO ⁻ ··HOME	229.17437	25.9	94.3			1.467	31.2 ⁱ
HC≡CH	76.71861				385.6 (375.4)		
HC≡C ⁻	76.10407		82.6	66.0			
HC≡C ⁻ ··HOH	152.05167	17.9	97.6			1.940	
HC≡C ⁻ ··HC≡CH	152.83963	10.6	92.9			2.234	
EtO ⁻ ··HOH	229.16183 ⁱ						29.3
EtO ⁻ ··HOME	268.12570 ⁱ						29.9
EtO ⁻ ··HOEt	307.11023 ⁱ						30.2

^a4-31+G//4-31+G basis set, hartrees, ref 17, except as noted. ^b4-31+G//4-31+G for $E(X^-) + E(YH) - E(X^- \cdots HY)$, kcal/mol. ^cHOMO energy (vertical IP), kcal/mol. ^dExperimental electron affinity, kcal/mol, ref 7, unless otherwise noted. ^e $\Delta E_{acid} = E(A^-) - E(AH)$, kcal/mol. Number in parentheses is ΔH_{acid}° , experimental, kcal/mol, ref 7. ^fHydrogen bond length for monosolvated anion, Å, 4-31+G calculations. ^g4-31G//4-31G for $-E(X^-) - E(YH) + E(X^- \cdots HY)$, kcal/mol, see ref 16f and 17b for monomer energies. ^hReference 32. ⁱ4-31G level calculations, see ref 17a.

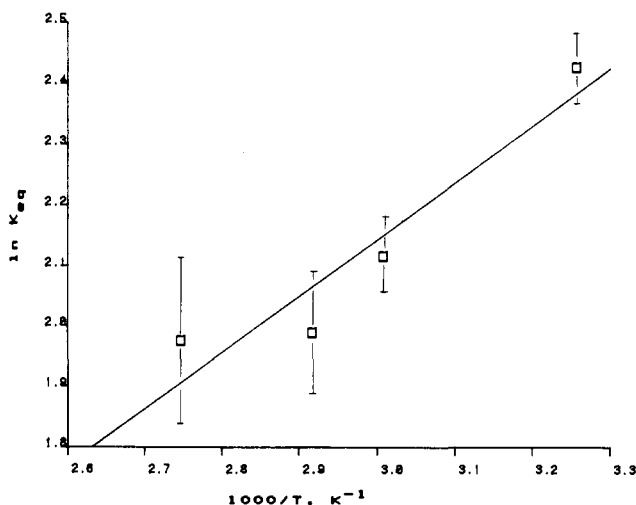


Figure 2. Van't Hoff plot of reaction 1.

components of ΔS° , as calculated by statistical mechanics,^{5,14} are given in Table II. The calculation of the translational term is straightforward. The symmetry term assumes that the barrier to proton transfer between the two methoxides is negligible (see the Discussion of molecular orbital calculations, below), so that for reasons of chemical reactivity, the donor and acceptor portions of RO⁻··HOR are equivalent.¹⁵ For the rotational and vibrational terms, a more extensive knowledge of the geometry is necessary. Following the lead of others,¹⁶ molecular orbital calculations at the 4-31G//4-31G level^{17a} have been done for the species in equilibrium 1, as reported in Table III. The alkyl group structure for the ethyl species was taken as that calculated for ethanol, and only the C-O, O-H, and O··HO bond lengths and associated angles were optimized. The non-optimization of the alkyl parts

of the ions and alcohols should not greatly affect the vibrational entropy, since the frequencies involved are present with little change in both neutrals and ions in reaction 1 and therefore cancel, and they also are of high enough frequency that they are insignificant contributors to ΔS_{vib}° . From the gradient force constants and structures obtained, the entropy terms in Table II are derived, resulting in a calculated $\Delta S^\circ(1)$ of -0.7 eu, within experimental error of the measured value. The vibrational term is small, $+0.2$ eu. The external rotational entropy was calculated on the basis of an extended geometrical structure for the alkyl groups in the cluster ions. Symmetry, rotational, and translational terms are all needed to adequately describe the experimental entropy change.

This does not prove that the vibrational entropy is negligible for the equilibria involving larger cluster ions, however. In Table I, we calculate $\Delta S_{tr,rot}^\circ$ for the various species involved in the equilibria, based on the O⁻··HO geometry of MeO⁻··HOME,^{16f} and standard geometries of the various alkyl groups. Increasing the alkyl group size results in a modest decrease in ΔS_{tr}° and a large decrease in ΔS_{rot}° such that ΔS° for PhCH₂O⁻··HOCH₂Ph is calculated to be 14 eu more negative than that for MeO⁻··HOME. This can be compared to the experimental $\Delta S_{0,1}^\circ$ for PhCH₂O⁻··HOCH₂Ph of -23.2 ± 3.0 eu, as determined by high-pressure mass spectrometry.¹³ This latter value is within experimental uncertainty of the $\Delta S_{0,1}^\circ$ for MeO⁻··HOME.¹³ The decrease in translational and rotational entropies must therefore be appreciably offset by an increase in ΔS_{vib}° as the alkyl groups increase in size. This is not unreasonable in that as 3 free rotations and 3 translations of the separated alkoxide and alcohol are traded for the 6 new low-frequency vibrations of the cluster ion, a net loss in entropy is expected, due to the restriction of motion involved, but the very low frequencies involved in the loose hydrogen bond may make this overall entropy decrease relatively small.

Larson and McMahon^{5b} have proposed eq 7, developed from a statistical mechanistic method that takes into account translational, rotational, and vibrational variation in the hydrogen-bonded species. In the present work, r is taken as the hydrogen bond

$$\Delta S_{0,1}^\circ = R \left[9.06 + 2.5 \ln (\Delta H_{0,1}^\circ) - 2 \ln (r) + \ln \left(\frac{\sigma_{ROHOR^-}}{\sigma_{ROOH}\sigma_{RO^-}} \right) \right] \quad (7)$$

length of 1.5 Å obtained from molecular orbital calculations (see below) and σ is the rotational symmetry number of the species subscripted. The equation was solved iteratively for the known $\Delta G_{0,1}^\circ$ values. The $\Delta S_{0,1}^\circ$ values obtained from it are consistently higher (29 to 34 eu) than the experimental ones for MeOH··OMe and PhCH₂OH··OCH₂Ph, but they show relatively little variation with structure. We thus believe that none of the above methods estimates $\Delta S_{0,1}^\circ$ to an accuracy better than ± 3 eu, and therefore we calculate $\Delta H_{0,1}^\circ$ by using a constant entropic change of -22

(14) Benson, S. W. "Thermochemical Kinetics"; 2nd ed.; Wiley: New York, 1976.

(15) Blair, L. K.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 1057.

(16) (a) Diercksen, G. H. F.; Kraemer, W. P. *Chem. Phys. Lett.* **1970**, *5*, 570. (b) Newton, M. D.; Ehrenson, S. *J. Am. Chem. Soc.* **1971**, *93*, 4971. (c) Sabin, J. R. *J. Chem. Phys.* **1971**, *54*, 4675. (d) Kraemer, W. P.; Diercksen, G. H. F. *Theor. Chim. Acta* **1972**, *23*, 398. (e) Roos, B. O.; Kraemer, W. P.; Diercksen, G. H. F. *Ibid.* **1976**, *42*, 77. (f) Jorgensen, W. J.; Ibrahim, M. J. *Comput. Chem.* **1981**, *2*, 7. (g) Szczesniak, M. M.; Scheiner, S. *J. Chem. Phys.* **1982**, *77*, 4586. (h) Rohlfing, C. M.; Allen, L. C.; Cook, C. M.; Schlegel, H. B. *Ibid.* **1983**, *78*, 2498.

(17) (a) 4-31G basis sets (Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724) as implemented in the GAUSSIAN 76 program, Quantum Chemistry Program Exchange No. 368, Indiana University, Bloomington IN 47405. (b) 4-31+G basis set (Chandrasekar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609, 5612) using the GAUSSIAN 80 program, Quantum Chemistry Program Exchange No. 446, Indiana University, Bloomington IN 47405.

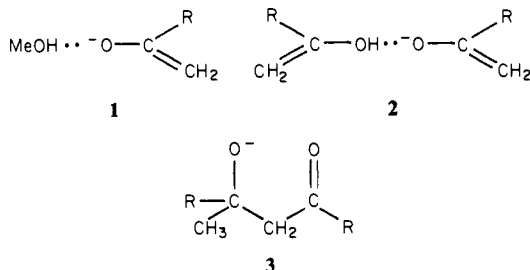
Table IV. Limits on $\Delta H^\circ_{0,1}$ for Compounds Not in Equilibrium

acid	reaction ^a MeOH ⁺ · -OMe		reaction ^a HOH ⁺ · -OH	
		$-\Delta H^\circ_{0,1}$ ^b		$-\Delta H^\circ_{0,1}$ ^b
<i>i</i> -Pr ₂ NH	N	<21.8	N	<25.0
CH ₃ CH=CH ₂	N	<21.8	N	<25.0
PhCH ₃	N	<21.8	N	<13.6
PhCHMe ₂	N	<20.1	N	<11.7
CH ₃ SOCH ₃	N	<15.3	N	<6.9
Et ₂ NOH	E	>12.5		
Me ₂ C=NOH	E	>9.3		
PhNH ₂	E	>9.7		
<i>n</i> -NO ₂ C ₆ H ₄ CH ₃	N	<8.6	N	<0.2
EtSH	E	<0.0		
<i>i</i> -PrSH	E	>0.0		
cyclopentadiene	D	<-1.3 ^c	D	
CH ₃ NO ₂	D		D	
Me ₂ CHNO ₂	D		D	
PhOH	E	>0.0		
CH ₃ CO ₂ H	E	>0.0		
MeCOCH ₂ COMe	D		D	

^aE = exchange observed, as in reaction 4 or 5; D = deprotonation of the acid, with no solvation; N = no reaction. ^bFrom Schemes I or II, for reaction with the ion shown. ^cMay denote a barrier to proton transfer.

eu, with an assigned uncertainty of ± 3 eu, for all alcohol-alkoxide ions. Relative uncertainties of ± 1.2 kcal/mol are assigned to the derived $\Delta H^\circ_{0,1}$ values, and absolute uncertainties of ± 2.2 kcal/mol are due to the uncertainty in the anchor value for MeO⁻··HOMe.¹³

In addition to the equilibria measured here, a number of acids were observed to exchange into MeO⁻··HOMe, MeO⁻··HOH, or HO⁻··HOH in an irreversible manner, so that equilibrium constants could not be obtained. If it assumed that only exothermic reactions are observed in the ICR spectrometer, then some limits on the hydrogen bond strength may be set. These are given in Table IV. In all cases in the table where exchange into MeO⁻··HOH occurred, both possible exchange products were observed, with that of the stronger donor, methanol, predominating. For the hydroxy and thiol compounds, a second exchange corresponding to reaction 5 generally occurs, while only a single exchange, as in (4), is observed for the carbonyl compounds. The ion arising from the latter is envisioned as **1**, with the enolate oxygen hydrogen bonded to the alcohol donor. For a second exchange of the carbonyl compound into this, either an energy penalty of ca. 8 kcal/mol¹⁸ must be paid to tautomerize the donor neutral to the enol, as in **2**, or a relatively weak bond involving a C-H donor group must be formed. A third possibility is the covalently bonded species **3**. Data from the flowing afterglow¹⁹ indicate that the acetone-acetone enolate ion has a relatively weak $\Delta G^\circ_{0,1}$ of -8.5 ± 0.5 kcal/mol, which can explain the lack of a second exchange in the ICR spectrometer.



Other acids listed in Table IV did not exchange into any of the monosolvated species tried. These include all the acids giving highly delocalized carbanions with no electronegative atoms present, such as benzyl anion and cyclopentadienide. This is in

(18) Pollack, S.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4845. Revised value, 8 ± 2 kcal/mol, W. J. Hehre, personal communication.

(19) Mackay, G. I.; Bohme, D. K. *J. Am. Chem. Soc.* **1978**, *100*, 327. Mackay, G. I.; Rakshit, A. B.; Bohme, D. K. *Can. J. Chem.* **1981**, *59*, 1615. Mackay, G. I.; Rakshit, A. B.; Bohme, D. K. *Ibid.* **1982**, *60*, 2594.

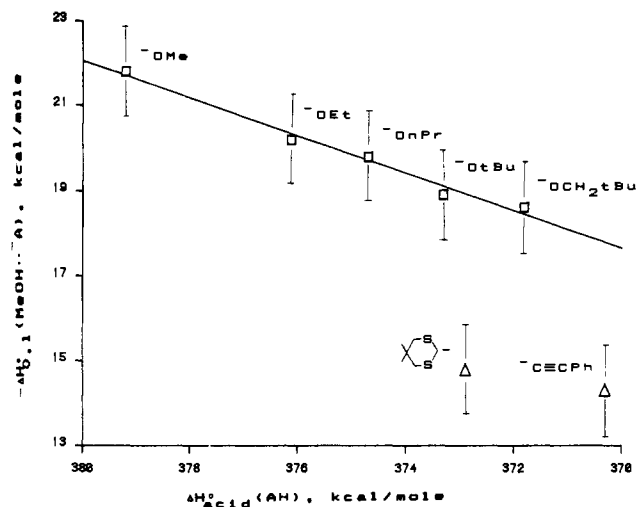


Figure 3. Hydrogen bond strengths vs. gas-phase acidities for methanol-anion complexes.

agreement with solution-phase results that highly delocalized anions are less solvated by protic solvents than localized anions.²⁰ For the carbon acids 2,4-pentanedione and nitromethane, (M-1)⁻ ions are observed to arise from HO⁻··HOH. In these cases, the proton-transfer reaction is more exothermic than a reasonable estimate of the hydrogen bond strength in the product ion, so the excess energy in the product results in cluster ion dissociation. This is not an absolute requirement, however, since oxyacids such as phenol and acetic acid do exchange into the cluster ions, even though the proton-transfer exothermicity is greater than the product hydrogen bond strength. Cyclopentadiene should fall into the first class here, with simple proton removal by MeOH⁻··OMe; however, no reaction is observed. Proton transfer and solvation are not simple functions of the thermochemistry; while oxygen/oxygen transfer and solvation appear to be facile, as with the bare ions,²¹ there are barriers to transfer for carbon acids of various kinds.¹⁹

Discussion

Relative Hydrogen Bond Strengths. The hydrogen bond strengths given in Table I show the expected pattern of increasing $\Delta H^\circ_{0,1}$ with more acidic donor alcohols and more basic alkoxide acceptors, for the smaller alcohols. For methanol as the donor, the bonding strengths of the C₁-C₅ alkoxides are best fit by eq 8 with a correlation coefficient of $r = 0.992$ and a 7% standard

$$-\Delta H^\circ_{0,1}(\text{RO}^- \cdot \cdot \text{HOMe}) = 0.443\Delta H^\circ_{\text{acid}}(\text{ROH}) - 146.2 \text{ kcal/mol} \quad (8)$$

deviation for the slope, as shown in Figure 3. The other alcohols give similar correlations with slightly smaller slopes (0.3-0.4), though the reduced number of points available for the successively better donors increases the uncertainty considerably. If the acceptor is held constant as neopentoxide, then the C₁-C₅ alcohols follow eq 9 with $r = 0.956$. The slope of -0.37 (standard deviation

$$-\Delta H^\circ_{0,1}(\text{ROH} \cdot \cdot \text{OCH}_2\text{-}t\text{-Bu}) = -0.37\Delta H^\circ_{\text{acid}}(\text{ROH}) + 160.2 \text{ kcal/mol} \quad (9)$$

0.07) is somewhat less than the slope of -0.5 found for alcohol variation in F⁻··HOR bond strengths by Larson and McMahan;⁵ the anion neopentoxide used in this work is only 0.3 kcal/mol less basic than fluoride. For all the C₁-C₅ alcohol-alkoxide data, a dual-substituent parameter correlation gives eq 10, with $r = 0.920$. Equation 10 can be compared to that of Kebarle and Yamdagni,^{4c}

$$-\Delta H^\circ_{0,1}(\text{ROH} \cdot \cdot \text{OR}') = -0.31\Delta H^\circ_{\text{acid}}(\text{ROH}) + 0.40\Delta H^\circ_{\text{acid}}(\text{R'OH}) - 15.0 \quad (10)$$

(20) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006.

(21) Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891.

Table V. Hydrogen Bond Strengths of MeOH...A Compared to Acidity and Electronegativity

cluster ion	$-\Delta H^{\circ}_{0,1}$	$\Delta H^{\circ}_{\text{acid}}(\text{AH})^a$	χ^b
MeOH...F	29.6 ^c	371.5	4.0
MeOH...OCH ₂ - <i>t</i> -Bu	18.6	371.8	3.5
MeOH...C≡CPh	14.3	370.3	3.3
MeOH...dithianide ^c	14.8	372.9	2.5

^aReference 7. ^bElectronegativity of the anionic atom, ref 33. ^cReference 5.

where for clustering equilibria for a wide variety of functional groups at the hydrogen bonded site they found that the data fit eq 11. While the signs and order of magnitude of the acceptor

$$-\Delta H^{\circ}_{0,1}(\text{X}^- \cdots \text{HY}) = -0.134\Delta H^{\circ}_{\text{acid}}(\text{YH}) + 0.20\Delta H^{\circ}_{\text{acid}}(\text{XH}) \quad (11)$$

and donor coefficients in eq 10 and 11 are comparable, a strict comparison may be too simple a view.²² Equation 11 is not limited to a single set of functional groups at the reactive site, but it represents an average over a number of acceptor and donor types. This includes the implicit assumption that the hydrogen-bonding ability is dependent only on acid/base properties. As noted below, our data and that of Larson and McMahon indicate that the electronegativity of the anionic atom is also important in determining hydrogen bond strengths, at constant basicity. Thus, eq 11 may have several kcal/mol uncertainty in the $\Delta H^{\circ}_{0,1}$ values that it gives, based on the exact functional groups involved. Equations 8-10, while more limited in intent than (11), indicate that alcohols and alkoxides are better than the general trend of acids and anions in hydrogen-bonding ability relative to their acidity. The comparable magnitude of the two coefficients in (10) is consistent with the similar nature of the acceptor and donor groups and the low barrier to proton-transfer involved.¹⁵

Figure 3 also reveals that the localized carbanions formed from phenylacetylene and 5,5-dimethyl-1,3-dithiane²³ are less effective as hydrogen bond acceptors than an alkoxide of equal gas-phase basicity should be. The weakening is 3.5 and 4.1 kcal/mol, respectively, based on eq 8. The acetylide ion shows a similar decrease in acceptor ability with *n*-propyl, neopentyl, and benzyl alcohols as donors. It is evident from this that the electronegativity of the anionic site can be as important as the basicity of the anion, if not more so, in determining hydrogen-bonding strengths. As further evidence, Larson and McMahon⁵ have determined the hydrogen bond strength of F⁻...HOCH₃ to be 29.6 kcal/mol, placing it 11 kcal/mol above the line in Figure 3. In Table V, it is seen that for a variation in $\Delta H^{\circ}_{\text{acid}}$ of only 2.6 kcal/mol, $\Delta H^{\circ}_{0,1}$ varies by over 15 kcal/mol, paralleling the trend of electronegativities. The hybridization of the carbanion in the 1,3-dithiane system has not been established in the gas phase, but molecular orbital calculations²⁴ support the assignment of the sp³ geometry as being the most stable, similar to the lithiocarbon in solution.

Acetone exchanges into MeO⁻...HOME in an irreversible fashion, but neopentyl alcohol will exchange into the resulting cluster ion in trade for the acetone. This brackets $\Delta H^{\circ}_{0,1}$ (MeOH...OCMe=CH₂) at -13.5 ± 3.1 kcal/mol relative to the other values reported here. The flowing afterglow results of Bohme and co-workers give a value of >-15.0 kcal/mol.¹⁹ Direct equilibrium of acetone with the *n*-PrOH...OnPr ion and *n*-PrOH gives a bond strength of 14.5 kcal/mol for *n*-PrOH...OC-

(22) Equation 10 is not a true dual substituent parameter equation, since the first coefficient is a single regression coefficient on data for $\Delta H^{\circ}_{0,1}$ for Cl⁻...HX, and the second coefficient is from a single point fit to the data for HO⁻...HOH. A true DSP fit to these data ($r = 0.920$) results in:

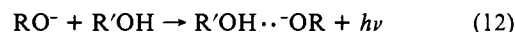
$$\Delta H^{\circ}_{0,1}(\text{X}^- \cdots \text{HY}) = -0.144\Delta H^{\circ}_{\text{acid}}(\text{YH}) + 0.191\Delta H^{\circ}_{\text{acid}}(\text{XH}) + 5.5$$

(23) Bartmess, J. E.; Hays, R. L.; Khatri, H. N.; Misra, R. N.; Wilson, S. r. *J. Am. Chem. Soc.* **1981**, *103*, 4746.

(24) Bernardi, F.; Csizmadia, I. G.; Mangini, A.; Schlegel, H. B.; Whangbo, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1975**, *97*, 2209. Lehn, J.-M. *Ibid.* **1976**, *98*, 7498. Streitwieser, A., Jr.; Ewing, S. P. *Ibid.* **1975**, *97*, 190, 191.

Me=CH₂. This is slightly stronger than the estimate for the methanol solvate, consistent with the greater donor ability of *n*-PrOH relative to MeOH as seen in Table I. Equation 8 predicts that the enolate of acetone with $\Delta H^{\circ}_{\text{acid}} = 368.8$ kcal/mol should bind to MeOH with $\Delta H^{\circ}_{0,1} = -17.0$ kcal/mol, 4 ± 2 kcal/mol stronger than the observed bond strength. Equation 8 is defined only for oxygen acids, however. If the acidity of the enol form¹⁸ of acetone is used, $\Delta H^{\circ}_{\text{acid}} = 361$ kcal/mol, then a $\Delta H^{\circ}_{0,1}$ of -13.7 kcal/mol is calculated, in good agreement with the bracketed value. If eq 9 is used to predict $\Delta H^{\circ}_{0,1}$ for **2**, a value of 21.3 kcal/mol is obtained, or $\Delta G^{\circ}_{0,1} = -15.2$ kcal/mol. The reported experimental $\Delta G^{\circ}_{0,1}$ of -8.5 kcal/mol,¹⁹ corrected for the 8-kcal/mol enolization energy, is comparable to that expected for **2**.

Hydrogen Bond Strengths of Symmetric Species. For symmetric proton-bound dimers of oxygen bases, such as R₂OH⁺...OR₂, the enthalpy change for separation to R₂O and R₂OH⁺ has been found to be 31 ± 2 kcal/mol, for R₂O ranging over 30 kcal/mol in gas-phase basicity, with certain small deviations due to steric and resonance effects.^{8,9} For the symmetric alcohol-alkoxide complexes in this work $\Delta H^{\circ}_{0,1}$ is -21.3 ± 0.7 kcal/mol. The trend of slightly increasing bond strengths for the larger alcohols is opposite to that expected if a steric effect were operating, as has been invoked to explain a decrease in the R₂OH⁺...OR₂ bond strengths for large R groups.⁹ This increase for the anions is believed to be due to a perturbation of the measured equilibrium by a radiative bimolecular clustering mechanism, previously studied.²⁵ Reaction 12 results in an increase in the amount of



cluster ion with time and becomes faster with increasing alkyl group size. Thus more of the larger cluster ion is present at long times, and the apparent equilibrium constant is larger. This process ($k \approx 1 \times 10^{10}$ cm³ molecule⁻¹ s⁻¹)²⁵ should only become comparable in rate to the exchange reactions that determine the equilibrium position for symmetric clusters for alcohols of C₅ and larger, and so it should not appreciably affect the data for any but the largest clusters, based on how the relative clustering scale are constructed. It does not seem to have been observed for the cationic dimers; however, smaller alkyl groups on the bases were involved in those studies.^{8,9}

There is a decrease of ca. 4 kcal/mol in hydrogen bond strength on going from HO⁻...HOH to the alcohol clusters. The corresponding oxyanion cluster ions display constant bond strengths on change of the substituent from H to alkyl,⁹ while for the nitrogen bases, H₃NH⁺...NH₃ is 2-3 kcal/mol more strongly bound than the symmetric alkylamine cluster ions.⁴⁸ This change in the anionic bond strength is consistent with two different structural effects. The O⁻...HO bond length is 0.16 Å shorter for HO⁻...HOH than for MeO⁻...HOME, by molecular orbital calculations,¹⁶⁸ thus increasing the bond strength. Also, the location of the net unit charge is different in the cationic and anionic cluster ions. For the cationic case, molecular orbital calculations¹⁶ indicate that the structure of H₃O₂⁺ resembles two water molecules bound by a symmetrically situated proton, in a broad shallow well. The central proton retains 66% of the positive charge. For the anionic species, our 4-31+G//4-31+G calculations indicate that the negative charge resides largely on the oxygen atoms in the species HO⁻...HOH and MeO⁻...HOME, proximate to the substituent and capable of direct interaction with it. Solvation of hydroxide by water results in transfer of -0.19 units of charge from HO⁻ to the water moiety, while solvation of methoxide by methanol results in -0.12 unit of charge being transferred. On the basis of simple electrostatics alone, this indicates a weaker bond for the methanol cluster of 2-5 kcal/mol. The stronger interaction of the charge and the substituent, due to proximity, can be taken as the reason for the changing effects in the anionic case, compared to the cations.

Absolute and Relative Basicities of Monosolvated Anions. The monosolvated gas-phase acidity can be defined as ΔH° for reaction

13. Data on hydrogen bond strengths of neutral-neutral systems



in the gas phase are relatively rare,²⁶ but in general for alcohols they seem to be fairly constant and of the order of 3–4 kcal/mol. Lacking specific data, we take reaction 13 as our defining system and ignore the neutral-neutral hydrogen bond. The derived monosolvated acidities for each species are given in Table I. In general, they lie in a small acidity range between ethanethiol and acetic acid.⁷ As noted above, for reaction with a carbon acid more acidic than $\Delta H_{\text{acid}}^{\circ}(\text{RO}^- \cdots \text{HOR}')$, such as $\text{MeO}^- \cdots \text{HOME}$ reacting with 2,4-pentanedione, only simple proton transfer is observed with no solvent switching occurring.

Earlier workers have shown that monosolvation of anions can affect their relative basicities. For example, methanol in aqueous solution is ca. 1.1 kcal/mol more acidic than ethanol,²⁷ while in the gas phase it is 3.1 kcal/mol less acidic. Solvation by one molecule of methanol decreases the difference in acidities, to methanol being only 1.7 less acidic than ethanol, or about halfway to the solution value. The present work provides further examples of this effect. Methanol is 5.9 kcal/mol less acidic than *tert*-butyl alcohol in the gas phase, but only 3.0 kcal/mol less acidic when solvated by one methanol. In solution methanol is more acidic by ca. 5 kcal/mol.²⁷ A true reversal of acidity is observed for the carbon acids. Phenylacetylene is 2.6 kcal/mol more acidic than neopentyl alcohol when nonsolvated, but 2.8 kcal/mol less acidic when solvated by a single methanol. There are no solution-phase data comparing these two species directly, but the effects of changing solvent and counterion can be seen in the relative acidities of phenylacetylene and fluorene. The acetylene is 5 pK units more acidic than fluorene in ether, comparable in acidity in cyclohexylamine, 6 pK units less acidic in DMSO,²⁰ and 12.5 pK units less acidic in the gas phase. Similarly, 5,5-dimethyl-1,3-dithiane is 7 kcal/mol more acidic than methanol nonsolvated but 0.7 kcal/mol less acidic when both are monosolvated by another methanol.

Additivity of the Hydrogen Bond Strengths. Magnoli and Murdoch have shown that for a variety of cationic proton bound dimers and a few anionic species, the bonding enthalpy of an unsymmetric species $\text{AH}^+ \cdots \text{B}$ or $\text{AH} \cdots \text{B}^-$ is closely approximated by the average of the enthalpy for the two symmetric cases AHA^{\pm} and BHB^{\pm} less half the difference in acidity or basicity of AH and BH ,²⁸ as expressed by eq 14. The alcohol-alkoxide cluster

$$\Delta H_{0,1}^{\circ}(\text{A}^- \cdots \text{HB}) = \frac{1}{2}[\Delta H_{0,1}^{\circ}(\text{A}^- \cdots \text{HA}) + \Delta H_{0,1}^{\circ}(\text{B}^- \cdots \text{HB})] - \frac{1}{2}[\Delta H_{\text{acid}}^{\circ}(\text{AH}) - \Delta H_{\text{acid}}^{\circ}(\text{BH})] \quad (14)$$

ions in this work follow eq 14 to a worst-case deviation of ± 0.3 kcal/mol, indicating that the enthalpies involved fit the additivity criteria of Magnoli and Murdoch. This must be taken only as an approximate fit since eq 10 and 14 are mathematically non-equivalent; the uncertainty in the data allow reasonable fits to both. We have no experimental data for symmetrical carbanion-carbon acid systems such as $\text{PhC}\equiv\text{C}^- \cdots \text{HC}\equiv\text{CPh}$, since the second carbon acid does not switch into any $\text{ROH} \cdots \text{C}\equiv\text{CPh}$ that we can generate. A rearrangement of eq 14, using the $\Delta H_{0,1}^{\circ}$ values for $\text{PhC}\equiv\text{C}^- \cdots \text{HOR}$, predicts that $\Delta H_{0,1}^{\circ}(\text{PhC}\equiv\text{C}^- \cdots \text{HC}\equiv\text{CPh})$ should be -16.9 to -18.4 kcal/mol, depending on the alcohol chosen, while the observed lack of exchange of the second acetylene implies that $\Delta H_{0,1}^{\circ}$ for the symmetric carbanion cluster must be less than 13.7 kcal/mol. A similar analysis for the dithiane results in the same upper limit on its $\Delta H_{0,1}^{\circ}$ value. Thus, these carbon acids are at least 3 kcal/mol weaker as donors than an alcohol of the same gas-phase acidity. This is not surprising for the sp^3 -hybridized site in 1,3-dithiane, but terminal acetylenes

are known to have hydrogen-bonding ability in solution.²⁹ The lack of any observed donating capability in the present studies does not rule out the existence of C–H hydrogen bond donation in the gas phase, but it indicates that it is less than the present method is sensitive to. As previously noted, the donor ability of acetone results in bond strengths considerably lower than those investigated here.¹⁹

Molecular Orbital Calculations. There have been a number of molecular orbital calculations performed on the simplest case of hydrogen bonded oxyanions, $\text{HO}^- \cdots \text{HOH}$,¹⁶ though only one study has done a complete geometry optimization on this species,^{16h} and only one study has extended the calculations to alcohols.^{16f} A minimal basis set results in a $\Delta E_{0,1}$ for $\text{HO}^- \cdots \text{HOH}$ of -70 kcal/mol, far too strongly bound. Use of the standard 4-31G split valence basis set gives a well depth of ca. 40 kcal/mol,^{16b,h} and inclusion of polarization functions bring the $\Delta E_{0,1}$ to the experimental range of -23 to -30 kcal/mol.¹⁶ Inclusion of configuration interaction makes the binding stronger by a few kcal/mol,^{16g,h} while a zero-point energy correction, to convert the calculated ΔE to ΔH for direct comparison to the experimental data, reduces the well depth by 5.3 kcal/mol,^{16b} so as to roughly offset the change due to CI inclusion. The nonsymmetric ion is found to be the most stable by the SCF calculations, with a central barrier for the symmetric form ranging from 0.1 to several kcal/mol. The highest level post-SCF calculations show the symmetric form to be favored by a fraction of a kcal/mol, but in general the entire potential surface is a broad, flat well.^{16h} Jorgensen and Ibrahim^{16f} at the 4-31G and 6-31G* level find $\text{HO}^- \cdots \text{HOME}$ to be more bound by 12 kcal/mol with respect to dissociation to its components than $\text{HOH} \cdots \text{OMe}$, but the latter is the more stable isomer by 4 kcal/mol at the 4-31G level, due to the exothermic proton transfer for the free acids. The $\text{MeOH} \cdots \text{OMe}$ ion is calculated to be 9 kcal/mol more weakly bound than $\text{HOH} \cdots \text{OH}$.

These calculations, at a sufficiently high level, reproduce the experimental data reasonably well. The recent development¹⁷ of the 4-31+G basis set for use with anions, employing additional diffuse s and p functions beyond the usual 4-31G basis set, has prompted us to re-examine these cluster ions with this possibly more appropriate basis set, both to evaluate its use with hydrogen bonded anions and to examine the orbital nature of the bonding. The results at the 4-31+G//4-31+G level are given in Table III. In these calculations, the hydrogen bond was constrained to be linear, and the groups attached to the acidic and basic heavy atoms were held antiperiplanar; while $\text{HO}^- \cdots \text{HOH}$ deviates from this by ca. 6° in bond linearity and 30° in torsion angle for the best totally optimized calculation, the energy difference is negligible.^{16h} The values calculated for $\Delta E_{0,1}$ in this work are ca. 3 kcal/mol too bound compared to the experimental $\Delta H_{0,1}^{\circ}$ for all examples, much closer to the experimental value than with the 4-31G basis set.^{16f} The zero-point energy effects can account for the remaining difference. The relative bond strengths of $\text{HO}^- \cdots \text{HOH}$ and $\text{MeO}^- \cdots \text{HOME}$ are of the right size and order, compared with the considerable overestimation for their difference given by the 4-31G basis set. The acetylide-water bond strength is likewise about 3 kcal/mol too strong on the basis of extrapolations from our data on $\text{ROH} \cdots \text{C}\equiv\text{CPh}$, and the acetylene-acetylide bond relatively weak, consistent with its not being observed experimentally. At the 4-31G level, with use of only a partial geometry optimization as noted above in the Results section, the relative bond strengths of $\text{MeO}^- \cdots \text{HOME}$, $\text{EtO}^- \cdots \text{HOME}$, and $\text{EtO}^- \cdots \text{HOEt}$ agree quite well with the experimental ordering, though they are ca. 50% too large.

The hydrogen bond length varies inversely with the bond strength for the water and acetylene complexes. The $\text{HO}^- \cdots \text{HOH}$ hydrogen bond is 0.03 Å longer than the weaker $\text{MeO}^- \cdots \text{HOME}$ bond, however, while the 4-31G calculations give the opposite trend by 0.2 Å. Higher level basis sets give an increase in the hydrogen bond length for $\text{HO}^- \cdots \text{HOH}$.^{16h} The lengthening of the OH bond in the donors MeOH and HOH in these complexes is nearly the

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same, from 0.950 in both free donors to 1.032 in complexed HOH and 1.038 in complexed MeOH.

By Koopman's theorem, the HOMO energies of the anions can be compared with the experimental vertical electron affinity (EA), as given in Table III. The HOMO energies for nonsolvated anions obtained from the calculations with the 4-31+G basis set are consistently too bound, by 16 to 35 kcal/mol relative to the experimental EA. We note that the electron affinities given by the 4-31+G calculations for all monosolvated anions (and by experiment for $\text{HO}^- \cdots \text{HOH}^{32}$) are larger than those for the bare anions by approximately the value of $-\Delta H_{0,1}^\circ$. For acetylide, the HOMO is not the σ orbital that the solvent bonds to, or that the proton was removed from in formation of the anion, but rather the π orbitals, for both the bare and monosolvated cases. The energies of both the acceptor and π orbitals increase by approximately $-\Delta H_{0,1}^\circ$ in this case.

The MNDO method³⁰ does not give reliable results for the energies or structures of the anion-alcohol complexes. The typical hydrogen bond length for $\text{RO}^- \cdots \text{HOR}$ is 2.65 Å, and the bond strength is 4 to 8 kcal/mol, with no discernable trend paralleling the experimental data. The acetylide complex $\text{MeOH} \cdots \text{C}\equiv\text{CH}$ is calculated to be unbound by 32 kcal/mol. The poor performance of the MNDO method involving localized anions and hydrogen bonds is a known flaw, however.³⁰

Conclusions

The hydrogen bond strengths of a number of anions bound to alcohols in the gas phase have been quantitatively shown to be

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a linear function of the acid/base character of the acceptor and donor species, as well as being affected by the electronegativity of the atoms involved. Enolates are oxyanion acceptors like alkoxides in this respect, while localized carbanions are significantly more weakly bound than expected on the basis of acidity alone. The first solvent molecule can invert reactivity orders in some cases.

In solution, the available thermochemical data on hydrogen bonds²⁹ deals largely with neutral-neutral species, with only a limited amount of data for halide/donor complexes. Linear free-energy relationships are observed for hydrogen bond strengths in solution, with acid/base and electronegativity being separate factors in correlating the data.³¹ Both the gas-phase and solution data indicate that hydrogen bonding is an attenuated function of the acid/base character of the species involved for a given reactive site, but the lack of quantitative acidity data in solvents such as CCl_4 where hydrogen bonding can be measured presents problems in such an analysis. In the gas phase, the lack of solvent not only obviates such problems but results in maximal effects due to the lack of solvent competition for the reactive site.

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Registry No. HOH, 7732-18-5; MeOH, 67-56-1; EtOH, 64-17-5; PrOH, 71-23-8; *t*-BuOH, 75-65-0; *t*-BuCH₂OH, 75-84-3; PhCH₂OH, 100-51-6; *t*-BuCHMeOH, 464-07-3; ⁻OH, 14280-30-9; ⁻OMe, 3315-60-4; ⁻OEt, 16331-64-9; ⁻OPr, 26232-83-7; ⁻C≡CPh, 25640-27-1; ⁻O-*t*-Bu, 16331-65-0; ⁻OC(Me)=CH₂, 71695-00-6; ⁻OCH₂-*t*-Bu, 55091-58-2; ⁻OCH(Me)-*t*-Bu, 91126-83-9; ⁻F, 16984-48-8; HC≡CH, 74-86-2; HC≡C⁻, 29075-95-4; CH₃CH=CH₂, 115-07-1; PhCH₃, 108-88-3; PhCHMe₂, 98-82-8; CH₃SOCH₃, 67-68-5; Et₂NOH, 3710-84-7; Me₂C=NOH, 127-06-0; PhNH₂, 62-53-3; *m*-NO₂C₆H₄CH₃, 99-08-1; EtSH, 75-08-1; *i*-PrSH, 75-33-2; CH₃NO₂, 75-52-5; Me₂CHNO₂, 79-46-9; PhOH, 108-95-2; CH₃CO₂H, 64-19-7; MeCOCH₂COMe, 123-54-6; *i*-Pr₂NH, 108-18-9; cyclopentadiene, 542-92-7; dithianide, 91126-82-8.

Nucleophilic Oxygenation of Carbon Dioxide by Superoxide Ion in Aprotic Media To Form the $\text{C}_2\text{O}_6^{2-}$ Species

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Abstract: The reaction chemistry for the combination of superoxide ion with carbon dioxide in acetonitrile, dimethylformamide, and dimethyl sulfoxide and the resulting products have been characterized by electrochemical and spectroscopic methods and by chemical analysis. The reaction kinetics, which have been studied by the rotated ring-disk voltammetric method, are first order with respect to each reactant; in dimethylformamide k_2 has an approximate value of $10^3 \text{ M}^{-1} \text{ s}^{-1}$. The overall stoichiometry is 1 O_2^- per CO_2 to give $\text{C}_2\text{O}_6^{2-}$ and O_2 [$\text{CO}_2 + \text{O}_2^- \rightarrow \frac{1}{2}\text{C}_2\text{O}_6^{2-} + \frac{1}{2}\text{O}_2$]. The primary step appears to be a nucleophilic addition of O_2^- to CO_2 to form the anion radical, CO_4^- . The apparent configuration of the $\text{C}_2\text{O}_6^{2-}$ group is $\text{OC}(\text{O})\text{OC}(\text{O})\text{OO}^{2-}$ on the basis of the vibrational spectroscopy and the hydrolysis products of $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_6$ (the isolated reaction product).

The one-electron reduction of dioxygen yields superoxide ion (O_2^-) in biological¹ and chemical systems.² In aqueous media the dominant chemistry of O_2^- is that of a strong Brønsted base ($\text{O}_2^- + \text{HA} \rightarrow \frac{1}{2}\text{H}_2\text{O}_2 + \frac{1}{2}\text{O}_2 + \text{A}^-$), whereas in aprotic media O_2^- also acts as an effective nucleophile. In particular, O_2^- undergoes facile nucleophilic addition to carbonyl carbon atoms that are bonded to electron-withdrawing leaving groups (acid

chlorides, acid anhydrides, and esters).³ The present paper summarizes the results of a systematic study of the chemical reactivity of superoxide ion in aprotic solvents with dissolved carbon dioxide.

This investigation also has been motivated by a desire to identify activated carbon dioxide species in biological reactions such as the vitamin K dependent carboxylation of glutamic acid residues of prothrombin.⁴⁻⁶ One proposal⁶ is that the carboxylating species

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