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Hydrogen-Bonded Complexes of Methanol and Acetylides. Structure and Energy Correlations

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Abstract: We examine the connection between acid−base chemistry and hydrogen bond stability for anionic ion−molecule complexes. Ion−molecule complexes of substituted acetylides, RCC^- (R = *tert*-butyl, H, phenyl, *p*-tolyl), and methanol were studied using Fourier transform ion cyclotron resonance mass spectrometry. These complexes, $RCC^- \cdot HOCH_3$, all have complexation energies of −21 kcal/mol and are, therefore, hydrogen bonded. The acetylides vary in basicity over an 8 kcal/mol range, but all have the same complexation energy with methanol. In contrast, results reported by Bartmess show that the complexation energies of aliphatic alcohols with phenyl acetylide vary with the acidity of the alcohol. These results show that the frequently observed relationship between acid−base energetics and complexation energy is a property of the specific system and not a general one. We believe that these results demonstrate that the existence, and magnitude, of these correlations cannot be used to infer structural information about the complexes.

Introduction

The ability to predict the stability of hydrogen-bonded complexes is important. The stability of many ionic hydrogen-bonded complexes appears to be related to the acidity of the donor and the basicity of the acceptor.[1,2] This relationship is frequently used to predict the stability and structure of hydrogen-bonded complexes in both the gas phase and solution. The connections between hydrogen bond stability, structural features, and acid−base thermochemistry, however, are derived from a limited data set. The origins of these relationships must be explored to determine when they are likely to succeed and when they are likely to fail.

Studies of hydrogen-bonded complexes in the gas phase can reveal the intrinsic stability of the interaction. Much experimental work has been performed on both positively[3−5] and negatively[1,6] charged complexes. Anionic hydrogen bonds are especially important because they are observed in intermediates in proton-transfer reactions[7] and in enzymatic active sites.[8] The only gas-phase data available for a constant donor with a series of structurally similar acceptors are those for the alcohol−alkoxide and alcohol−halide series.[9] Fewer computational studies of asymmetric systems have been performed compared to those of symmetric systems.[10,11] By studying dissimilar ions we can begin to disaggregate the contributions of the donor and the acceptor to these relationships.

We report here a study of gas-phase ionic hydrogen-bonded complexes of methanol with substituted acetylides. Acetylenes behave like "normal" acids in the condensed phase,[7] and acetylides are thought to be localized carbanions.[12] They both appear to behave similarly in the gas phase.[13,14] In the gas phase, phenyl acetylide is known to form strong hydrogen bonds to alcohols with strengths similar to those of alcohol−alkoxides.[15] While some work has been performed using carbanions as hydrogen bond acceptors, none has used a structurally similar set of anions.[16] We have previously communicated our initial results[17] and now provide a more detailed analysis here.

Our work here shows that the energies of complexation of substituted acetylides to methanol are constant over a range of acidity differences. In contrast, Bartmess and co-workers have shown that the stabilities of the complementary complexes of phenyl acetylide with aliphatic alcohols do depend on the acidity difference.[15] This result contrasts with that for alcohol−fluoride[18] and alcohol−alkoxide complexes.[15] Our results have important consequences for understanding the generality of the relationship between acid−base properties and complexation energies.

Experimental Section

Materials. Acetylene was synthesized by the standard literature procedure for the reaction of calcium carbide and water.[19] The product

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(14) The rate constant for the identity proton-transfer reaction $HCC^- + HCCH$ is 3.42×10^{-10} mol cm^3 s^{-1}. The reaction efficiency is 0.30 based on the Su−Chesnavich capture rate. C. DePuy, personal communication.

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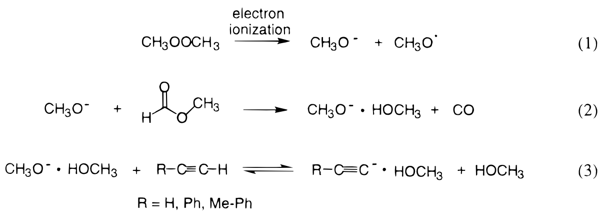
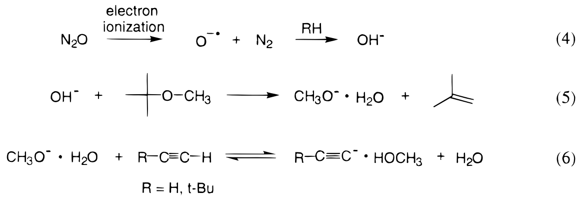
10.1021/ja994191l CCC: $19.00

Scheme 1



Scheme 2



was purified by a trap-to-trap vacuum distillation. No impurities were detected in either the negative or the positive ion mass spectra. Dimethyl peroxide was synthesized by a literature procedure.[20] The product was purified by a trap-to-trap vacuum distillation. Phenylacetylene and *p*-tolylacetylene (4-ethynyltoluene) were obtained from Aldrich. They were purified before use by preparative gas chromatography using a Hewlett-Packard Series 6890 GC with a Carbowax column. All other chemicals were obtained from Aldrich Chemical and used without further purification.

Instrumentation. All experiments were performed using an IonSpec Fourier transform ion cyclotron resonance (FT-ICR) spectrometer. Details of the spectrometer have been given previously.[21] The magnetic field strength was 0.6 T. The temperature in the cell is estimated to be 350 K.[22] Background pressures were on the order of $(2.0-5.0) \times 10^{-9}$ Torr, and operating pressures ranged from 0.7×10^{-6} to 3.0×10^{-6} Torr. Pressure measurements were made using an ion gauge (Granville Phillips 330) which was calibrated against a capacitance manometer (MKS 170 Baratron with a 315BH-1 sensor). We estimate the absolute pressure measurements to have an error of ±20%. Relative pressure measurements should be more accurate (±10%).

Ion−Molecule Chemistry. The Riveros reaction[23,24] was used to synthesize $CH_3O^-{\cdot}HOCH_3$ (Scheme 1). Substituted acetylenes, RCCH, were observed to undergo a reversible exchange reaction with methanol-methoxide to form $RCC^-{\cdot}HOCH_3$ dimers (eq 3 Scheme 1). Equilibrium between the complexes was measurable for phenylacetylene, *p*-tolylacetylene and acetylene. No mass peaks were observed that corresponded to $RCC^-{\cdot}HCCR$ complexes.

The methoxide−water dimer was synthesized by the elimination reaction of hydroxide with *tert*-butyl methyl ether (Scheme 2).[25] Acetylide−methanol complexes were generated by an exchange reaction with acetylene and 3,3-dimethylbutyne (eq 6, Scheme 2). Small amounts of the acetylide−water complexes, $RCC^-{\cdot}H_2O$, were observed at high water pressures with long delay times but did not have an effect on the equilibration of $CH_3O^-{\cdot}H_2O$ and $RCC^-{\cdot}HOCH_3$. The presence of the acetylide−water complex at high water pressures is consistent with its complexation energy ($\Delta G°_{\mathrm{complex}} = -9.6$ kcal/mol).[16] Again, no mass peaks corresponding to $RCC^-{\cdot}HCCR$ were observed.

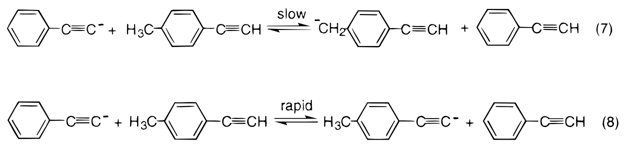
Equilibrium Measurements. All equilibrium measurements were obtained as an average of at least five trials at several pressure ratios on different days. At the pressures used, the system reached equilibrium in ∼1−2 s. Several methods were used to test whether a true equilibrium had been achieved. After a constant ratio of ion intensities was obtained, one species was ejected and the reaction was followed in time until a constant ratio was reached again. The final ratio of ion intensities was found to be independent of ejected ion. The equilibrium constants obtained at several pressure ratios were found to be in good agreement. The major source of error in these experiments is the accuracy of the measurement of the absolute pressures. We have assigned the error in the equilibrium constants on the basis of our estimate for the error in the absolute pressure readings (±20%). The relative values should be more accurate since the relative pressure errors should be smaller (±10%).

Kinetics. The measured rate constants are an average of at least three trials at several pressure ratios on different days. The reaction was measured over at least two half-lives at each pressure. The main error in the rate constants is due to the absolute pressure readings, and we have therefore assigned an error of ±20% to the measured rate constants.

Results

Acidity of *p*-Tolylacetylene. The gas-phase acidity of *p*-tolylacetylene is not available in the literature. *p*-Tolylacetylene contains two plausible sites of deprotonation, the benzylic protons and the acetylenic proton. The acidity of the benzylic protons can be estimated on the basis of known substituent effects.[26] A Hammett plot of measured gas-phase acidities of substituted toluenes has a slope of ∼18.[9,27] Using a σ_p value of 0.23 for the acetylene group,[27] the gas-phase acidity, $\Delta G°_{\mathrm{acid}}$, of the benzylic protons is estimated to be 367 kcal/mol; 3 kcal/mol less acidic than phenylacetylene. Unfortunately, there are no data in the literature to estimate the acidity of the acetylenic proton.

To determine the acidity of the acetylenic proton we investigated the proton-transfer reaction between phenyl acetylide and *p*-tolylacetylene. Proton-transfer reactions of delocalized carbanions are known to be slow.[22,28] Consequently, the equilibrium between the benzylic anion of *p*-tolylacetylene and phenylacetylene (e-q 7) should not be attainable on the time scale of our experiment. Conversely, equilibrium between the acetylenic anion and phenylacetylene (eq 8) should be attainable because the proton-transfer reactions of localized carbanions are faster.[14]



The production of the two isomeric anions of *p*-tolylacetylene was observed when MeO^- was used as the base. When the initially formed *p*-tolylacetylene, $m/z = 115$ [(M − 1) peak], was isolated, it reacted with phenylacetylene to produce phenyl acetylide, $m/z = 101$. The ratio of m/z 115/101 was nearly constant after ∼3 s at total pressures of $\sim(6-10) \times 10^{-7}$ Torr. Under the same conditions with initial isolation of phenyl acetylide, a different final ratio of m/z 115/101 was observed. After the apparent equilibration, phenyl acetylide was ejected from the ICR cell and the $m/z = 101$ peak grew back in. The observed ratio of m/z 115/101 was the same before and after ejection of phenyl acetylide (Figure 1). In the first experiment,

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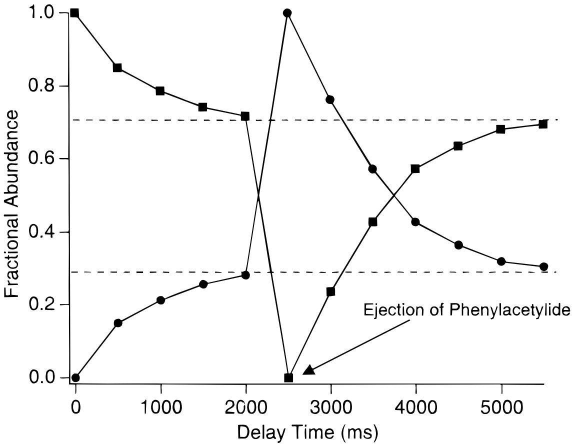

Figure 1. Time plot of the proton-transfer reaction of phenylacetylide (■) with *p*-tolylacetylene (●). Pressures: phenylacetylene, 2 × 10^{-7} Torr; *p*-tolylacetylene, 4 × 10^{-7} Torr. Dashed lines indicate equilibrium fractional abundances. Ejection of phenyl acetylide occurs just prior to the data point indicated by the arrow.

both isomers of deprotonated *p*-tolylacetylene are present, and presumably the fraction of the population that is the acetylenic isomer equilibrates with the phenylacetylene, while the benzylic isomer does not. In the second experiment, only the acetylenic isomer should be produced from the reaction with phenyl acetylide for kinetic reasons. This isomer can equilibrate with phenylacetylene as evidenced by the identical *m*/*z* 115/101 ratio before and after ejection of phenyl acetylide (Figure 1). Experiments at different pressure ratios of phenylacetylene:*p*-tolylacetylene all gave the same equilibrium constant, 0.19 ± 10%.

Our reactivity data indicate that we can measure the equilibrium acidity of the acetylenic proton of *p*-tolylacetylene relative to that of phenylacetylene. Based on our estimate of the acidity of the benzylic protons of *p*-tolylacetylene, the equilibrium constant for eq 7 is ~0.01. Because the estimated value of K_7 is small, we have ignored the contribution of the benzylic isomer in our determination of the acidity of the acetylenic proton. The error introduced should be no more than ~0.1 kcal/mol. We therefore assign the $\Delta G^\circ_{\mathrm{acid}}$ of the acetylenic proton of *p*-tolylacetylene to be 365.3 kcal/mol, 1.1 kcal/mol less than that in phenylacetylene. This result is consistent with the typical acidity weakening effect of a methyl substituent attached to an aromatic ring.[26] We assign $\Delta H^\circ_{\mathrm{acid}}$ to be 372.8 kcal/mol on the basis of the estimated ΔS° of 0 eu for eq 8.

Complexation Energies. The equilibrium constants for binding of methanol to the acetylides were measured relative to $CH_3O^-{\cdot}H_2O$ and $CH_3O^-{\cdot}HOCH_3$. Values for the absolute free energies of binding, $\Delta G^\circ_{\mathrm{complex}}$ (eq 10), of these two complexes have been measured using high-pressure techniques by Meot-Ner[29] and Kebarle.[30] The literature values of $\Delta G^\circ_{\mathrm{complex}}$ for $CH_3O^-{\cdot}HOCH_3$ differ by 1.0 kcal/mol. We have used Meot-Ner's value here because we are using his value of $\Delta G^\circ_{\mathrm{complex}}$ for $CH_3O^-{\cdot}H_2O$.[31] Figure 2 shows the measured ladder of complexation energies.[32] We have overlapped as many values as possible to test for internal consistency. The agreement in the ladder is very good, with the largest deviation being 0.5 kcal/mol between our derived difference between the methoxide complexation energies of water and methanol and the difference in Meot-Ner's measured values. Our measured equilibrium constant between methanol−methoxide and methanol−phenyl acetylide agrees well with the literature value.[15] The derived values of $\Delta G^\circ_{\mathrm{complex}}$ for the acetylides are given in Table 2. They were obtained from the thermodynamic cycle in Scheme 3, where HA was either H_2O or CH_3OH. The values of the gas-phase acidities, $\Delta G^\circ_{\mathrm{acid}}$, used to derive ΔG° for eq 11 are listed in Table 1.

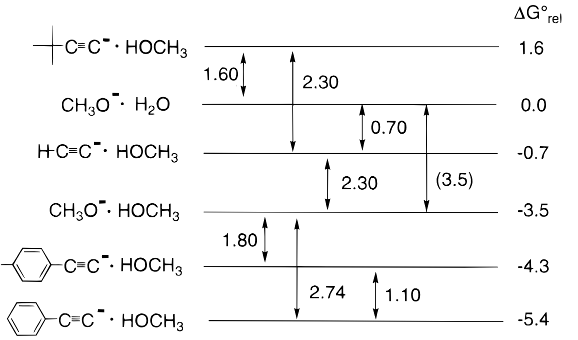

Figure 2. Ladder of complexation equilibria of hydrogen-bonded complexes. All values are given in kilocalories per mole. Value in parentheses are derived from ref 29.

Table 1. Gas-Phase Acidities

AH	ΔG° (kcal/mol)	ΔH° (kcal/mol)
CH_3OH	375.1[a]	381.5
$(CH_3)_3CCH$	371.4[c]	379.1
HCCH	369.8[b]	377.8
p-CH_3 C_6H_4CCH	365.3[d]	372.8
C_6H_5CCH	364.2[c]	371.7

Table 2. Acetylide−Methanol Complexation Energies[a]

$$RCC^- + HOCH_3 \rightleftharpoons RCC^-{\cdot}HOCH_3$$

RCC^-	ΔG° (kcal/mol)	ΔH° (kcal/mol)
$(CH_3)_3CC^-$	−10.7	−20.8
HCC^-	−11.6	−21.6
4-CH_3 $C_6H_4CC^-$	−11.1	−21.6
$C_6H_5CC^-$	−11.0	−21.5

Scheme 3

$$R{-}C{\equiv}C{-}H + CH_3O^-{\cdot}HA \rightleftharpoons R{-}C{\equiv}C^-{\cdot}HOCH_3 + HA \qquad (9)$$

$$CH_3O^- + HA \rightleftharpoons CH_3O^-{\cdot}HA \qquad (10)$$

$$R{-}C{\equiv}C^- + CH_3OH \rightleftharpoons R{-}C{\equiv}C{-}H + CH_3O^- \qquad (11)$$

$$R{-}C{\equiv}C^- + CH_3OH \rightleftharpoons R{-}C{\equiv}C^-{\cdot}HOCH_3 \qquad (12)$$

To derive $\Delta H^\circ_{\mathrm{complex}}$ from $\Delta G^\circ_{\mathrm{complex}}$, a value of $\Delta S^\circ_{\mathrm{complex}}$ is needed. Obtaining accurate estimates of the entropies for ion−molecule complexes is difficult.[15,30,33] The vibrational modes with the greatest contribution to the entropy are the six low-frequency modes created upon complexation. These modes are best described as torsions and are generally not reproduced accurately by standard ab initio harmonic frequency calculations.[34] Due to this difficulty we have chosen to assume that ΔS° of eq 9 in Scheme 3 is due only to the symmetry of the

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(31) Meot-Ner's values are $\Delta G^\circ_{\mathrm{complex}} = -19.4$ and $\Delta H^\circ_{\mathrm{complex}} = -28.8$ for $CH_3O^-{\cdot}HOCH_3$, and $\Delta G^\circ_{\mathrm{complex}} = -15.9$ and $\Delta H^\circ_{\mathrm{complex}} = -23.9$ for $CH_3O^-{\cdot}H_2O$.

(32) While it is conceivable that the complex of deprotonated *p*-tolylacetylene might have the structure $CH_3OH{\cdot}{}^-CH_2C_6H_5CCH$, it is unlikely. The structurally similar complex of benzyl anion and methanol has been calculated to be weakly bound, ~12 kcal/mol, and has not been observed experimentally. See ref 23 and the following: Gatev, G.; Zhong, M.; Brauman J. I. *J. Phys. Org. Chem.* **1997**, 10, 531−536.

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Table 3. Proton-Transfer Rate Constants for the Reaction of Methoxide and Acetylenes

$$CH_3O^- + R{-}C{\equiv}C{-}H \rightarrow CH_3OH + R{-}C{\equiv}C^-$$

RCCH	$k_{obs} \times 10^{-9}$ (cm^3 s^{-1})	$k_{cap} \times 10^{-9}$ (cm^3 s^{-1})[a]	Φ
HCCH	1.00 ± 0.2	1.13	0.89
C_6H_5CCH	0.71 ± 0.2	1.88	0.38

[a] k_{cap} was calculated using the Su−Chesnavich collision capture model (ref 36) with the following parameters (dipole moment in debye, molecular polarizability in cubic angstroms, geometric mean of moments of inertia in atomic mass units·square angstroms): for HCCH, 0.0, 3.3, 13.9; for C_6H_5CCH, 0.66, 13.0, 228.6.

molecules.[35] We expect that this will introduce an error of no more than ±3 eu in the value of $\Delta S°_{complex}$ and ±1.0 kcal/mol in the derived value of $\Delta H°_{complex}$. The relative error between values should be smaller because $\Delta S°_{complex}$ for these structurally similar complexes should be nearly equivalent. All values were calculated using a temperature of 350 K. The values listed in Table 2 are averages of the overlapped values where possible.

Kinetics. The rate constants for proton transfer from acetylene and phenylacetylene to CH_3O^- were measured (eq 13). The capture rate constants were calculated using the Su−Chesnavich model.[36] The efficiency of the reaction was calculated by eq 14. All values are listed in Table 3.

$$CH_3O^- + R{-}C{\equiv}C{-}H \rightarrow CH_3OH + R{-}C{\equiv}C^- \quad (13)$$

$$\Phi = k_{obs}/k_{cap} \quad (14)$$

Computational Details. Ab initio molecular orbital calculations were performed to examine the potential energy surfaces of the proton-transfer reaction of methoxide with acetylene and phenylacetylene. All calculations were performed with Gaussian94.[37] Calculations with acetylene were performed at the MP2/6-311++G**//HF/6-311++G** levels of theory. Due to the size of the system, the MP2/6-311++G**//HF/6-31+G* level of theory was used for phenyl acetylide. Both levels of theory generally yield good relative energetics for gas-phase organic anions.[38] In addition, the thermochemistry for the acetylene system was similar (within ~2 kcal/mol) for both the MP2/6-311++G**//HF/6-311++G** and the MP2/6-311++G**//HF/6-31+G* levels of theory. Both the relative gas-phase acidities and relative complexation energies are in reasonable agreement with the experimental values. All stationary points were confirmed by full vibrational analyses. Vibrational frequencies were scaled by 0.90 for use in thermochemical calculations.[39] Calculated energetics are shown in Figures 3 and 4.

Discussion

Background. The hydrogen bond is one of the most important noncovalent interactions in chemistry. A hydrogen bond is defined most generally as an intermolecular (or intramolecular) interaction specifically involving a proton donor A−H and a proton acceptor B.[40] Hydrogen bonds to ions are observed in solvent−ion interactions,[41] as intermediates in proton-transfer reactions,[7] and in enzymatic active sites.[8] Their existence is often characterized by spectroscopic features, such as intense IR bands and unusual NMR shifts, and structural features, such as short contact distances (smaller than van der Waals radii).[2,42]

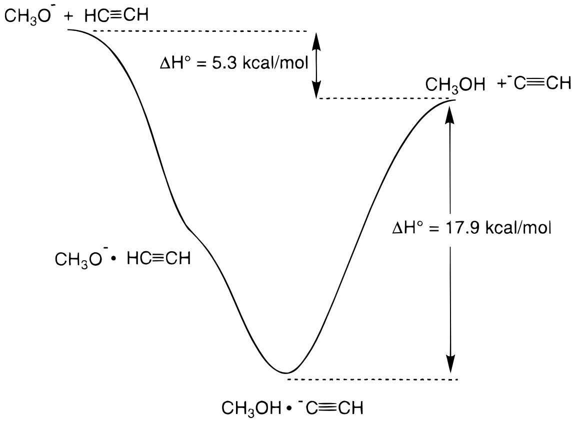

Figure 3. Potential energy surface for the proton-transfer reaction between methoxide and acetylene. All values were calculated at the MP2/6-311++G**//HF/6-311++G** level of theory and are corrected for contributions from the zero point energies.

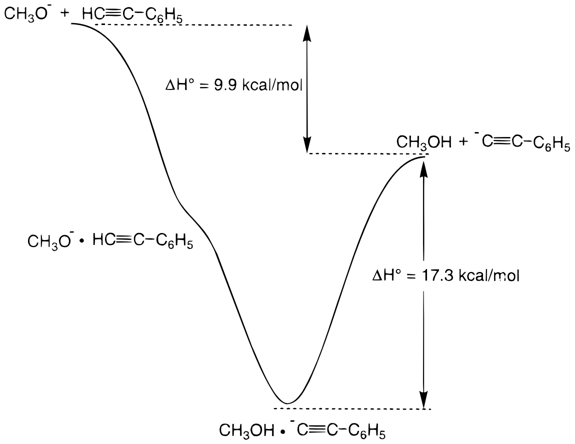

Figure 4. Potential energy surface for the proton-transfer reaction between methoxide and phenylacetylene. All values were calculated at the MP2/6-311++G**//HF/6-31+G* level of theory and are corrected for contributions from the zero point energies.

Several issues remain unresolved about hydrogen bonding in ionic systems in both the gas phase and the condensed phase. Hydrogen bonds to ions in solution are thought to be stronger than those to neutral molecules, but the difference in magnitude is still debated.[43−45] The height of the barrier to proton transfer has been suggested to be related to the stability of the hydrogen-bonded complex.[44] The validity of this statement is uncertain because few observations have been made of complexes with high barriers to proton transfer. Linear free energy relationships are frequently observed between the complexation energy and the difference in acidity and basicity of the molecules in the complex.[1,45,46] Our knowledge of the dependence of hydrogen bond strength on structure is limited, however, as most data are known for hydrogen bonds between structurally similar

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molecules (e.g., proton-bound amine dimers, phenol−phenoxides). Solvation is also known to play a large role in both the stability and the structure of hydrogen-bonded complexes.[2,47] By uncovering the intrinsic character of hydrogen bonds, we can begin to understand the basis by which solvation affects the interaction.

Gas-phase hydrogen-bonded complexes have been widely studied. While neutral complexes in the gas phase can be studied by many spectroscopic techniques, such as IR and microwave spectroscopy,[48] application of these techniques to ions is generally difficult.[49,50] The majority of the work on gas-phase ionic complexes has centered on mass spectrometric determinations of complexation energies[1,6,51] (eq 15) and electron photodetachment studies of negative ion complexes.[52,53]

$$AH + B^- \rightleftharpoons AH{\cdot}B^- \qquad (15)$$

Most known gas-phase ionic hydrogen-bonded complexes are strongly bound, near 20−25 kcal/mol, whereas typical ion−dipole complexes are bound by ∼10−15 kcal/mol. This “extra” stability of ∼10 kcal/mol is surprisingly similar to the suggested strength of ionic complexes in solution. In the literature the terms “complexation energy” and “hydrogen bond strength” are frequently used interchangeably. There is no unambiguous definition of the complexation energy required to conclude that a complex is hydrogen bonded.

The relation of acid−base properties to hydrogen bond strength has been widely studied.[1,15,51,54] In general, strong acids appear to be good hydrogen bond donors and strong bases appear to be good acceptors. A linear relationship is frequently observed between the difference in acidity of the two partners in the complex and the complexation energy.[11,51] The value of the slope has been widely suggested to indicate the degree of proton transfer in the complex, analogous to the interpretation of a Brønsted coefficient for kinetic data.[2,18,51,55,56] For example, a slope of 0.5 has been interpreted as an indication that the proton is equally shared between the donor and acceptor in the complex. However, while this conclusion has been demonstrated for some systems,[57] relatively few computational studies have been performed on asymmetric systems to determine whether this interpretation is fully general.[10,11] In addition, relatively few structural types have been studied for anionic systems, making it difficult to disaggregate the contributions of the donor, AH, and the acceptor, B^-, to the slope.[6]

In this study we focus on the relationship between acid−base properties and complexation energy. We have chosen to study substituted acetylides, RCC^-, as hydrogen bond acceptors. The complexes of phenyl acetylide with simple alcohols have been studied previously by Caldwell and Bartmess.[15] Here we perform the complementary experiment by studying complexes of various acetylides with a constant alcohol, methanol. Methanol was chosen so that the largest range of acetylides available could be studied in our instrument.

Stability and Structure. The complexation energies, $\Delta H°_{\text{complex}}$, of the acetylides with methanol are all approximately −21 kcal/mol (see Table 2). No complexes of the acetylides with acetylenes, $RCC^-{\cdot}HCCR$, were observed despite the ability of RCCH to form hydrogen bonds in neutral complexes.[58−60] These results are consistent with previous observations by Bartmess for phenyl acetylide.[15] Calculations by Scheiner indicate that the $HCC^-{\cdot}HCCH$ complex is bound by approximately 10−12 kcal/mol.[61] We expect the complexation energies of the other acetylene−acetylide complexes to be similar. Although we cannot observe these complexes in the presence of the corresponding $RCC^-{\cdot}HOCH_3$ complex, we can estimate[62] that they must be less stable by at least 3 kcal/mol.

The kinetic data indicate that there is little barrier to proton transfer between acetylenes and methoxide (Table 3). For acetylene, the proton-transfer reaction is nearly unit efficient, and the rate constant is close to that for propoxide with acetylene.[13] It is surprising that the efficiency of the reaction of methoxide and phenylacetylene is lower than that for methoxide and acetylene despite the greater exothermicity of the reaction. We do not believe that the lower efficiency is caused by a higher enthalpic barrier to proton transfer. There are several possible explanations for the result, such as the existence of a rotor-locking transition state on the potential surface or non-RRKM dynamic effects.[63,64] The proton-transfer reaction path involves the locking of the phenylacetylene rotor without a substantial compensating decrease in potential energy (Figure 4). This could lead to a minimum in the sum of states along the reaction path after the orbiting transition state. Thus, the reaction rate would be slowed by an entropic bottleneck rather than an enthalpic barrier. Similar “barrierless” proton-transfer reactions of alkoxides with alcohols exhibit less than unit efficient proton-transfer kinetics and have been suggested to have rotor-locking transition states on the reaction path.[65]

The ab initio potential energy surface for the proton-transfer reaction of methoxide and acetylene is shown in Figure 3. The calculated $\Delta H°$ of the overall proton-transfer reaction is ∼1 kcal/mol greater than the experimental value, and the complexation energy of methanol with acetylide is ∼3 kcal/mol weaker than the experimental value. These differences are relatively small and within usual agreement for this level of theory.[11] The $CH_3O^-{\cdot}HCCH$ complex is a stationary point on the Hartree−Fock (HF) surface. There is a slight barrier to proton transfer of ∼0.2 kcal/mol at this level, but the barrier disappears at the MP2 level. The absence of a barrier is consistent with the high efficiency of the reaction. Similar results are observed for the reaction of methoxide and phenylacetylene. The hydrogen-bonded $CH_3O^-{\cdot}HCCC_6H_5$ complex is 3.5 kcal/mol more stable

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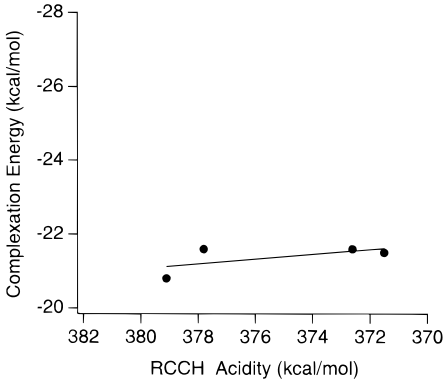

Figure 5. Complexation energies, $\Delta H°$, of substituted acetylides vs the gas-phase acidity, $\Delta H°_{\text{acid}}$, of RCCH:

$$RCC^- + HOCH_3 \rightleftharpoons RCC^-{\cdot}HOCH_3$$

than the isomeric ion−molecule complex where methoxide is complexed to the aromatic proton para to the ethynyl group.[66] For both acetylene and phenylacetylene, the difference in energy between the two isomeric "hydrogen-bonded" complexes is large (∼6−9 kcal/mol), indicating that the proton is highly localized on the methanol (see Figures 3 and 4). The O−H bond of methanol in both complexes is elongated by only 0.02 Å relative to the value in uncomplexed methanol. The agreement between the calculated potential surface and the experimental kinetic and thermodynamic data is good. On the basis of these calculations, we assume that the minimum energy complex has the structure $RCC^-{\cdot}HOCH_3$ for all R studied because all of the acetylenes studied are more acidic than methanol.

Our calculated potential energy surfaces indicate that complexes of the type $RO^-{\cdot}HCCR$ are substantially less stable than $ROH{\cdot}^-CCR$. This suggests that this system may behave similarly to the $CF_3H{\cdot}^-OR$[67] and $H^-{\cdot}H_2O$[68] systems, where the acid−base chemistry does not determine the structure of the most stable hydrogen-bonded complex. We predict that the structure of the complex will remain $ROH{\cdot}^-CCR$ for complexes where the acetylide is more basic than the alkoxide of the complexed alcohol, as the isomeric complex, $RO^-{\cdot}HCCR$, should be much less stable. There must be a difference in acidity where the structure does change, but it is not likely to be near matched acidities. Unfortunately we cannot test this hypothesis experimentally because we are unable generate complexes that would exhibit this behavior using our current synthetic method.

Stability and Acid−Base Chemistry. Our experimental results for complexes of $RCC^-{\cdot}HOCH_3$ show that the complexation energy is almost completely insensitive to the acidity of RCCH. The slope of a plot of $\Delta H°_{\text{complex}}$ vs $\Delta H°_{\text{acid}}$ is about 0.1 (Figure 5). A plot of the complexation energy vs the electron affinities of the acetylides similarly has little slope. This result contrasts with that for the aliphatic alkoxides, whose energies of complexation with methanol give a slope of ∼0.5. The only other anionic system that we are aware of that exhibits an insensitivity of complexation energy to changes in basicity is a series of water−carboxylate complexes.[69] However, these complexes are more weakly bound (∼15 kcal/mol), so it is uncertain whether this result would also occur for more strongly bound complexes, e.g., alcohol−carboxylates.

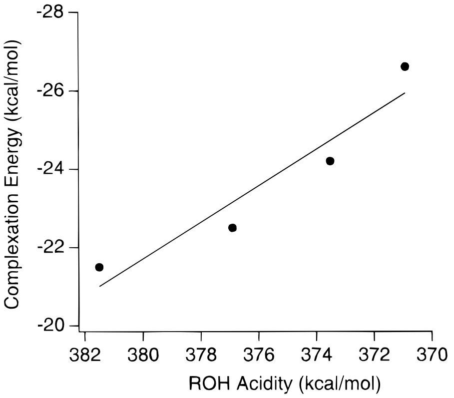

Figure 6. Complexation energies, $\Delta H°$, of phenyl acetylide with alcohols vs the gas-phase acidity, $\Delta H°_{\text{acid}}$, of ROH. All values are from ref 9.

The value of the slope for plots such as these has been suggested to indicate the degree of proton transfer in the complex analogous to a Brønsted coefficient for kinetic data.[11,18,70] Within this hypothesis, a slope of 0.5 indicates a broad potential surface where the proton is equally shared between the donor and the acceptor in the hydrogen-bonded complex. For example, data for alcohol−alkoxides appear to agree with this hypothesis. A plot for the series $RO^-{\cdot}HOCH_3$ gives a slope of ∼0.5, and the complementary series, $C_6H_5CH_2O^-{\cdot}HOR$, has the same slope.[15] Computational results for $CH_3O^-{\cdot}HOCH_3$ and $CH_3CH_2O^-{\cdot}HOCH_3$ support a low-barrier surface with a nearly shared proton.[57] If this hypothesis is true for all proton-transfer potential energy surfaces, we would expect a similar result for the complementary series to the methanol−acetylide series. However, unlike the case for the substituted acetylide−methanol complexes, a plot of $\Delta H°_{\text{complex}}$ for phenyl acetylide−alcohol complexes vs $\Delta H°_{\text{acid}}$ of the alcohol gives a slope of ∼0.5 (see Figure 6).[15] This result is inconsistent with the interpretation that the slope is related to the degree of proton transfer in the complex. For this hypothesis to be internally consistent, the slopes for both plots would have been 0.5 (an equally shared proton), or the slope of one would have been near 0.0 and the other near 1.0 (a fully transferred proton). In addition, our calculated potential energy surfaces do not indicate a broad potential surface near the methanol−acetylide complexes, suggesting that the slope is not indicative of the nature of the potential energy surface for the phenyl acetylide−alcohol complexes.

Understanding Donors and Acceptors. We believe that our data and those of others suggest that the slopes of these plots are related to molecular properties of the varying donor or acceptor and are not necessarily indicative of the shape of the potential energy surface. For example, the complexation energies of a series of alcohol−cyclopentadienide, $C_5H_5^-{\cdot}HOR$, complexes have a dependence on the acidity of the alcohol nearly identical to that of the alcohol−alkoxides, $R'O^-{\cdot}HOR$.[16] While the alcohol−alkoxides have low-barrier potential energy surfaces, the alcohol−cyclopentadienide surface is unlikely to have a similar shape. To gain insight into the origin of these empirical

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relationships, we compare and contrast the behavior of two systems— the alcohol−alkoxides and acetylene−acetylides— for which data for the molecule as a donor and its conjugate base as an acceptor are available.

A variety of theoretical methods to decompose the energy of hydrogen-bonded complexes into a conceptual useful form have been explored.[71−75] We do not believe that any of them is easily interpreted for strongly bound ionic complexes. In addition, they are sensitive to basis sets and levels of correlation for ionic species.[11] Simple models based on electrostatic charges have also been shown to be inadequate for strongly bound anionic systems.[76−78] Therefore, we choose to analyze the features in the electronic structure of the free hydrogen bond donor and acceptor that cause the change in acidity (or basicity) and semiquantitatively analyze our results.

Alcohols are good hydrogen bond donors, as evidenced from the strength of their complexes with a variety of anions.[9] The stabilities of a variety of hydrogen-bonded complexes of alcohols with structurally diverse anions have similar dependencies on the acidity of the alcohol, suggesting that the slope is not necessarily related to the shape of the proton-transfer potential energy surface.[15,51,54] Ab initio studies show that the charge on the proton does not change for the series of aliphatic alcohols, although there is a shift of charge between the carbon and oxygen.[79] Gas-phase NMR spectra, a sensitive probe of the electron density near protons, show that the chemical shift of the hydroxyl proton varies with the gas-phase acidity of the alcohol.[80] The origin of this correlation has not been examined in detail, but it suggests that the electronic environment of the proton in the unperturbed alcohol is correlated to its acidity. Furthermore, the polarizability of the aliphatic alcohols increases linearly with increasing acidity. On the basis of simple electrostatic forces alone, we would expect alcohols to have different hydrogen-bond-donating abilities.[81]

Alkoxides are good hydrogen bond acceptors.[15,54] The more basic alkoxides appear to be the best hydrogen bond acceptors. Or, stated in another way, the alkoxides with the lowest electron detachment energies are the best acceptors.[9] The origin of the difference in electron detachment energies of the aliphatic alkoxides has been explained through a perturbation molecular orbital model.[82,83] Alkyl substituents stabilize the charge on the oxygen because the orbitals of the oxygen atom can interact with the antibonding orbitals of the alkyl substituents. The difference in their ability to accept hydrogen bonds is most easily interpreted as being caused by the resulting changes in the charge distribution at the oxygen. For a substituent to be a good acceptor, more charge is needed. Hence, alkoxides with low detachment energies are better acceptors. Interestingly, AIM calculations by Wiberg show that the charge at the oxygen for free alkoxides does not appear to change with basicity.[79] His results show that there is a charge shift from the carbon bonded to the oxygen into the substituents with little change at the oxygen. These results are in apparent opposition to those from the perturbation theory model. Whether this is a result of the charge distribution model is uncertain. What is certain, however, is that there are changes in the orbital interactions through the series of alkoxides, and these changes affect the total charge distributions in the alkoxides. We believe that these charge shifts are the origin of the differing abilities of the alkoxides to accept hydrogen bonds.

Acetylenes are known to be modest hydrogen bond donors in neutral complexes. The C−H bond is polarized in the opposite direction of sp^3-hybridized C−H bonds, leading to a partial positive charge on the hydrogen.[84] Acetylenes are known to be weaker hydrogen bond donors to neutrals than are alcohols.[59] This is also the case for hydrogen bonding to anions. The calculated potential surface in Figures 3 and 4 and the lack of observation of acetylene−acetylide, $RCC^-{\cdot}HCCR$, complexes demonstrate that these complexes are relatively weak.[61] The calculated energetics suggest that complexes of acetylenes and anions should be considered simple ion−molecule complexes. Wiberg has shown that the charge distribution at the terminal hydrogen does not appear to depend on the substituent.[85] Thus, the complexation energies of these complexes are likely to be simply correlated with the dipole moment and polarizability of the acetylene. The calculated phenylacetylene−methoxide complex is slightly more stable (~2 kcal/mol) than the acetylene−methoxide complex, consistent with this interpretation. In summary, acetylenes are modest H-bond donors to neutrals and relatively poor donors to anions.

Acetylides are good hydrogen bond acceptors. Their complexes with alcohols are strongly bound. Most importantly, our results show that the ability of a series of acetylides to accept hydrogen bonds does not vary with their basicity (the acidity of the acetylene). We therefore expect that in the substituted acetylides the charge distribution at the terminal carbon should be only slightly perturbed by the substituent. Unfortunately, there is no unambiguous computational method to separate π and σ orbital effects for acetylenes to analyze the effect of the substituent.[85,86] A simple conceptual model treats the substituent as a dipole that interacts through space with the terminal charged carbon atom. The polar substituent should provide the same stabilizing effect to the free anion and the hydrogen-bonded complex.[87] This analysis is consistent with our experimental result that substituents have little effect on the stability of the hydrogen-bonded complexes of acetylides with methanol. In

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addition, the calculated CHELPG charges at the terminal carbon and the values of the electrostatic potential are similar for all the acetylides studied. Another possible interpretation is that the charge at the terminal carbon is stabilized by shifts in the π electron density due to the substituents. Because the dominant contribution to the hydrogen bond is expected to be the interaction with the charge in the sp orbital on the terminal carbon, the complexation energy would be affected weakly by the substituent. Either interpretation leads to the conclusion that the acetylides are equally good acceptors despite the differences in basicity.

This interpretation allows us to reconcile why the $C_6H_5CC^-\cdot HOR$ and the $RCC^-\cdot HOCH_3$ complexation energies have different dependencies on acid−base thermochemistry. For alcohols, the charge distribution near the O−H group appears to be correlated to the acidity. As expected, the hydrogen bond strength for the $C_6H_5CC^-\cdot HOR$ complexes varies with acidity. For acetylides, the charge distribution at the terminal carbon is not related to the basicity of the anion. In this case, the complexation energies of the $RCC^-\cdot HOCH_3$ complexes are invariant with respect to basicity. We suggest that other hydrogen bond donors and acceptors that derive their stability from remote substituents should behave similarly to the acetylides. Inferences about potential energy surfaces based on hydrogen−deuterium exchange reactions of carbon acids with the hydroxide anion also support this hypothesis.[88,89] These results demonstrate the importance of charge distributions to hydrogen bond strength in anionic complexes.

Stated in most general terms, the complexation energy does not appear to be directly related to the acidity (or basicity) of one of the partners but is instead related to a feature of the molecular electronic structure that may or may not be related (or correlated) to the acidity.[81] This result does not imply that alcohol−alkoxides do not have low-barrier surfaces or that structural correlations derived from these relations are not correct in some cases. Nor does it mean that the properties of the acetylide−alcohol complexes are universal. We only suggest that these correlations are not fully generalizable. Therefore, caution should be used when using these energetic relationships to make structural inferences.

Conclusion

We have presented an ionic hydrogen-bonded system in which the complexation energy is not a simple function of acid−base properties of the H-bond donor and acceptor. The complexation energies of substituted acetylides with methanol are strong, −21 kcal/mol, and are nearly constant over an acidity range of 8 kcal/mol. The complementary data for complexes of phenyl acetylide with aliphatic alcohols show that the stability of the complex varies with the alcohol. These results can be understood by examining the origin of substituents on the acidity difference in the acetylenes versus the origin of the acidity differences in the alcohols. Careful consideration of the effect of substituents on ions and neutrals must be made to fully understand why acid−base properties appear to be related to the stability of hydrogen-bonded complexes. In some cases, inferences made from energetic relationships about the shape of potential energy surfaces and the structure of hydrogen-bonded complexes may not be correct.

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