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LETTERS

Hydrogen Bond Strength and Acidity. Structural and Energetic Correlations for Acetylides and Alcohols

Michael L. Chabinyc and John I. Brauman*

Department of Chemistry, Stanford University, Stanford, California 94305-5080

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Ion−molecule complexes of acetylide anions, RCC^- (R = *tert*-butyl, H, phenyl, *p*-tolyl), and methanol have been studied using Fourier transform ion cyclotron resonance mass spectrometry. The RCC^- complexation energies with $HOCH_3$ were measured relative to $CH_3O^-{\cdot}H_2O$ and $CH_3O^-{\cdot}HOCH_3$. 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. 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. Thus, the existence, and magnitude, of these correlations cannot be used to infer structural information about the complexes. The stability of hydrogen-bonded complexes appears to be related to the charge distributions of the separated ion and neutral.

Introduction

The stability of hydrogen-bonded complexes of neutrals with ions is frequently correlated with the acidity and basicity of the hydrogen bond donor and acceptor.[1−3] In both the gas phase and the condensed phase, linear relationships between the acidity of the hydrogen bond donor or the basicity of the hydrogen bond acceptor and the hydrogen bond strength have been observed. These relationships have been found for a variety of positively and negatively charged hydrogen-bonded complexes including proton-bound amines, carboxylate−carboxylic acids, phenoxide−phenols, and alcohol−alkoxides.[4] Inferences about the structure of hydrogen-bonded complexes and the nature of the proton transfer potential energy surface are frequently made from these correlations.[5,6] We report here results that show that one should not draw conclusions about the potential energy surface solely on the basis of these correlations. Although the structural inferences may be correct in many cases, they are not inherently related to the existence and magnitude of the correlations.

We have recently shown that acid−base thermochemistry does not determine the structure of complexes of fluoroform, CF_3H, with aliphatic alkoxides.[7] That is, the most stable complex had the structure $CF_3H{\cdot}^-OR$ even when proton transfer to the alkoxide was favorable for the separated ion and molecule. This surprising result suggests that our understanding of the relationship between hydrogen bond properties and acid−base chemistry is substantially inadequate.

We report here our results on a study of gas-phase complexes of substituted acetylides with methanol (eq 1). We find that the complexation energy is nearly constant over a range of basicities (∼8 kcal/mol) of the hydrogen bond acceptor for this system. This outcome is unprecedented for strongly hydrogen-bonded anionic complexes.[8] We analyze the significance of these results, and we suggest that the charge distributions of the separated ion and molecule, rather than the acid−base thermochemistry, provide a better rationale to understand the trend in complexation energies for this system.

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* Corresponding author.

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$$\text{R-C}{\equiv}\text{C}^- + \text{CH}_3\text{OH} \rightleftharpoons \text{R-C}{\equiv}\text{C}^-{\cdot}\text{HOCH}_3 \qquad (1)$$

Experimental Section

Equilibrium exchange studies were performed using an IonSpec Fourier transform ion cyclotron resonance spectrometer.[9] Methanol−methoxide, $CH_3O^-{\cdot}HOCH_3$, was synthesized by the reaction of methoxide with methyl formate.[10] Methoxide−water, $CH_3O^-{\cdot}H_2O$, was synthesized by the elimination reaction of hydroxide with *tert*-butyl methyl ether.[11] Various acetylenes were observed to undergo a reversible exchange reaction with either $CH_3O^-{\cdot}HOCH_3$ or $CH_3O^-{\cdot}H_2O$ to form $RCC^-{\cdot}HOCH_3$ (eq 2). The relative complexation free energies, $\Delta G^\circ_{\text{complex}}$, of the conjugate bases of *tert*-butyl acetylene (3,3-dimethylbutyne), acetylene, phenylacetylene, and *p*-tolylacetylene (4-ethynyltoluene) to methanol were determined. Overlapping equilibrium reactions were measured to verify the internal consistency of the data (See Figure 1). Our derived difference between the complexation free energies of methanol−methoxide and water−methoxide is within 0.5 kcal/mol of Meot-Ner's value[12] and our complexation free energy of phenylacetylide and methanol agrees well with Bartmess's value.[13] The complexation energies of the methanol−methoxide and water−methoxide complexes have been measured previously using high-pressure mass spectrometry.[14] Using these literature values and a standard thermochemical cycle[13] the complexation energies, $\Delta H^\circ_{\text{complex}}$, of methanol with the acetylides were derived (eq 1) and are listed in Table 1.[15]

$$\text{R-C}{\equiv}\text{C-H} + \text{CH}_3\text{O}^-{\cdot}\text{HA} \rightleftharpoons \text{R-C}{\equiv}\text{C}^-{\cdot}\text{HOCH}_3 + \text{HA} \qquad (2)$$

$$\text{R} = \text{H, } \textit{tert}\text{-butyl, phenyl, 4-CH}_3\text{-phenyl}$$

$$\text{HA} = \text{H}_2\text{O, CH}_3\text{OH}$$

Results and Discussion

The $RCC^-{\cdot}HOCH_3$ complexation energies are all near −21.5 kcal/mol. Typical ion−molecule complexes have complexation energies near −10 to −12 kcal/mol. The additional stability of the acetylide complexes is evidence that they are hydrogen-bonded.

To best interpret the complexation energy data, the structure of the ion−molecule complex should be known. Ab initio molecular orbital calculations at the MP2/6-311++G**//HF/6-311++G** level of theory were performed to investigate the structure of two of the complexes.[16] The complexation energies of the acetylide and phenylacetylide complexes were reproduced within typical expected agreement (~2 kcal/mol). The potential energy surface for both acetylides is a near single well with the proton highly localized on the methanol in both cases, $RCC^-{\cdot}HOCH_3$. The O−H bond distance of methanol in the complex is only ~0.03 Å longer than in the free molecule. The single well shape is in agreement with the observed rapid proton transfer kinetics in this system.[17] We therefore assume the acetylide is the hydrogen bond acceptor and the methanol is the hydrogen bond donor for the complexes studied here (all of the acetylenes are stronger acids than methanol). This is consistent with our[7] and others'[2,18−20] suggestion that electrostatic forces are important. The acetylene C−H bond is not very polar, whereas in the acetylide the charge is significantly localized on the terminal carbon. Consequently, acetylenes should be relatively poor hydrogen bond donors, but acetylides should be good hydrogen bond acceptors.

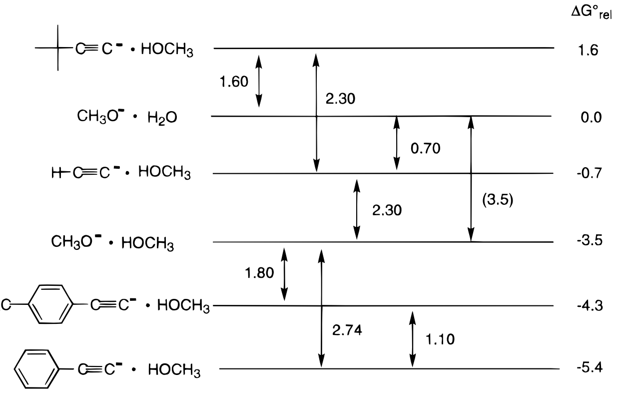

Figure 1. Ladder of relative ΔG° for equilibrium exchange reactions, eq 2. Value in parentheses from ref 11. All other values were measured at 350 K.

TABLE 1: Acetylide−Methanol Complexation Energies[a,b] $\text{R-C}{\equiv}\text{C}^- + \text{CH}_3\text{OH} \rightleftharpoons \text{R-C}{\equiv}\text{C}^-{\cdot}\text{HOCH}_3$

RCC^-	$\Delta G^\circ_{\text{complex}}$ (kcal/mol)	$\Delta H^\circ_{\text{complex}}$ (kcal/mol)	$\Delta H^\circ_{\text{acid}}$ RCCH (kcal/mol)
$(CH_3)_3CC^-$	−10.7	−20.8	379.1
HCC^-	−11.6	−21.6	377.8
$4\text{-}CH_3C_6H_4CC^-$	−11.1	−21.6	372.8
$C_6H_5CC^-$	−11.0	−21.5	371.7

[a] All values measured at 350 K. [b] Acidities from ref 20.

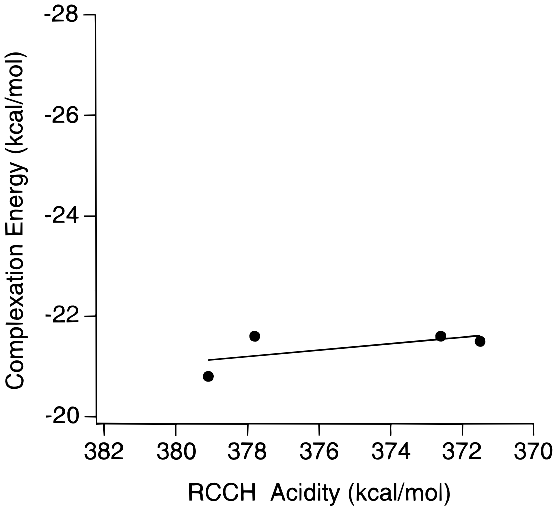

Figure 2. Complexation energies, $\Delta H^\circ_{\text{complex}}$, of substituted acetylides with methanol, $\text{R-C}{\equiv}\text{C}^- + \text{HOCH}_3 \rightleftharpoons \text{R-C}{\equiv}\text{C}^-{\cdot}\text{HOCH}_3$, vs the gas-phase acidity, $\Delta H^\circ_{\text{acid}}$, of RCCH.

A plot of $\Delta H^\circ_{\text{complex}}$ as a function of the acidity of the acetylenes[21] is shown in Figure 2. The slope is essentially zero (<0.1). The slope of this correlation between the complexation energy and acidity is surprising. For example, a similar plot for a series of aliphatic alkoxide−methanol complexes, $RO^-{\cdot}HOCH_3$, has a slope of ~0.5.[13] The more basic alkoxides form the strongest complexes, and as the alkoxide becomes less basic, the stability of the complex is only weakened half as much as the change in basicity. In contrast, a slope of ~0 suggests that the $RCC^-{\cdot}HOCH_3$ complexes are stabilized by the substituent R to the same extent as the free anion. We believe the behavior in these two cases can be explained by the difference in how the substituents stabilize the charge in alkoxides and acetylides.

Uncovering the origin of the stabilizing effect of substituents on acetylides is difficult because there is no unambiguous theoretical method to separate π- and σ-orbital effects.[22] The complexation data shows that the substituent provides the same stabilization to the free anion as it does to the complex. A simple

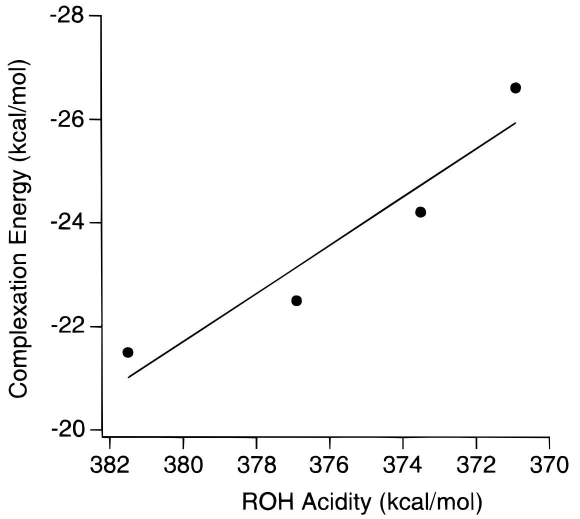

Figure 3. Complexation energies, $\Delta H^\circ_{\mathrm{complex}}$, of substituted alcohols with phenylacetylide, $C_6H_5\text{-}C{\equiv}C^- + HOR \rightleftharpoons C_6H_5\text{-}C{\equiv}C^-{\cdot}HOR$, vs the gas-phase acidity, $\Delta H^\circ_{\mathrm{acid}}$, of ROH.

model to explain this behavior treats the substituent as a remote dipole. If the charge distribution at the terminal carbon remained nearly constant, a dipolar substituent would provide similar stabilization in both the free ion and the complex.[23] Wiberg has shown that for a variety of substituted acetylenes the charge distribution at the terminal C−H is essentially the same.[24] Our ab initio results—CHELPG charges[25] and values of the electrostatic potential near the terminal carbons—suggest that this is true also for the charge distribution in acetylides. While there is no unambiguous quantitative measure for this interpretation, it provides a good qualitative model to understand the experimental data.

In contrast, the effect of substituents on aliphatic alkoxides has been explained by a perturbation molecular orbital model.[26,27] Alkyl substituents stabilize the charge on the oxygen because the occupied orbital on the oxygen atom can mix with the antibonding orbitals of the alkyl group. Alkoxides with the lowest basicities are poorer hydrogen bond acceptors. From a simple electrostatic model, a lower charge density would lead to a weaker interaction.[23] The alkoxides with the lowest basicities have the most delocalized charge and are therefore poorer acceptors.

Our data indicate that the dependence of the stability of hydrogen-bonded complexes on acid−base chemistry should not be used to infer information about the proton transfer potential energy surface. For example, a slope of 0.5 has been suggested to indicate “half” transfer of the proton in the complex, or equivalently a very broad potential minima.[3,6] If this interpretation is correct, the slope should only depend on the acid−base chemistry of the hydrogen bond donor and acceptor as long as the molecular structures of the partners are not substantially altered. Data for alcohol−alkoxides, for example, appear to be consistent with this hypothesis. The slope of a plot of $\Delta H^\circ_{\mathrm{complex}}$ vs $\Delta H^\circ_{\mathrm{acid}}$ for alcohol−alkoxides complexes is ∼0.5 if either the alkoxide, $RO^-{\cdot}HOCH_3$, or the alcohol, $C_6H_5CH_2O^-{\cdot}HOR$, is varied.[13] The data for the acetylide−alcohol system, however, are not. For acetylide−alcohol complexes, $RCC^-{\cdot}HOCH_3$, the slope is ∼0 if the acetylide is varied (Figure 2) and ∼0.5 if the alcohol, $C_6H_5CC^-{\cdot}HOR$, is varied (Figure 3).[13] Furthermore, our calculations indicate that the proton in the $RCC^-{\cdot}HOCH_3$ complexes is highly localized on the methanol moiety and that the potential surface has a near single well shape. This result is completely inconsistent with the interpretation that the slope is dependent on the shape of the potential energy surface. This does not mean that the proton in alcohol/alkoxide complexes is not significantly delocalized or transferred, nor does it mean that acetylide complexes described here have some universal properties. What these results tell us is that these linear free energy relationships are not fully general. Therefore the observation of these correlations is not a direct consequence of the acid−base energetics, nor is it a predictor of the structure of the hydrogen-bonded complex.

Interpretation of our results using an analysis of charge distributions allows us to reconcile why the $C_6H_5CC^-{\cdot}HOR$ complexation energies are sensitive to the acidity of the alcohol while the $RCC^-{\cdot}HOCH_3$ complexation energies are insensitive to acidity of the acetylenes. For alcohols, the charge distribution near the O−H group appears to be correlated to the acidity. Several observations lead us to this conclusion. The slope of a plot of $\Delta H^\circ_{\mathrm{complex}}$ vs $\Delta H^\circ_{\mathrm{acid}}$ for a variety of structurally dissimilar systems, for example, $C_5H_5^-{\cdot}HOR$[28] and $F^-{\cdot}HOR$[6] is also ∼0.5. Gas-phase NMR data shows that the chemical shift of the hydroxyl protons of aliphatic alcohols is linearly correlated with the gas-phase acidity.[29] 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 with its acidity. Thus, on the basis of electrostatics alone we would expect that the alcohols would have different hydrogen bonding characteristics. For acetylides, the charge distribution at the terminal carbon does not appear to be related to the basicity of the anion as discussed above.

Stated most in most general terms, we have demonstrated experimentally that the shape of the potential energy surface does not necessarily influence the relationship between complexation energy and acid−base chemistry. Careful consideration of the effect of substituents on ions and neutrals must be made to understand fully why acid−base properties appear to be related to the stability of hydrogen-bonded complexes.

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