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Unusual Ionic Hydrogen Bonds: Complexes of Acetylides and Fluoroform

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Abstract: Ion−molecule complexes of substituted acetylides, RCC^- (R = *tert*-butyl, H, phenyl, *p*-tolyl), and fluoroform, HCF_3, were studied using Fourier transform ion cyclotron resonance mass spectrometry. These complexes, $RCC^-\cdot HCF_3$, all have complexation energies of approximately −19 kcal/mol and are, therefore, hydrogen bonded. The acetylides vary in basicity over a 6 kcal/mol range, but all have the same complexation energy with fluoroform. The structure of these complexes was verified by deuterium isotopic exchange reactions and equilibrium fractionation experiments. The relationship between acid−base thermochemistry and hydrogen bond stability is discussed.

Introduction

Hydrogen bonds to ions have been widely studied.[1−5] However, relatively little information, aside from theory[6] is known about the strength of the interaction between carbanions and carbon acids in either the gas phase[7,8] or in solution.[9,10] We report here our results on the stability and structure of gas-phase hydrogen-bonded ion−molecule complexes of substituted acetylides with fluoroform. By studying these complexes we can gain insight into the factors affecting hydrogen bond stability as well as learn about intermediates in proton-transfer reactions.[11,12]

Considerable effort has been directed at exploring the connections between acid−base chemistry and hydrogen bond stability in both the gas-phase and in solution. The structure of hydrogen bonded complexes is typically assumed to reflect the acidity difference of the molecules in the complex. That is, the structure is $A^-\cdot HB$ if AH is a stronger acid than BH, and $AH\cdot B^-$ if BH is the stronger acid. Linear relationships are observed between the acidity of the hydrogen bond donor (or the basicity of the hydrogen bond acceptor) and the complexation energy.[2,3,5] These observations appear to hold for many anionic and many cationic systems as well. Information about the shape of the proton transfer potential energy surface is frequently inferred from these linear relationships.

The connection between acid−base thermochemistry and hydrogen bond stability is widely held to be intrinsic because of the many successful correlations that have been observed. We studied complexes of carbon acids as hydrogen bond donors and carbanions as hydrogen bond acceptors to better understand the correlation between acid−base chemistry and hydrogen bond strength. We found that ion−molecule complexes of fluoroform and aliphatic alkoxides have the structure $RO^-\cdot HCF_3$, even when proton transfer to the alkoxide is favorable in the separated reactants.[11] In a study of methanol−acetylide complexes, we found that the complexation energy had a different dependence on acid−base thermochemistry depending on whether the donor or acceptor was varied.[12] This result suggested that the dependence of the complexation energy on the acid−base thermochemistry is not always related to the shape of the potential energy surface. The results from studies of deuterium exchange proton-transfer reactions also support these claims.[13,14] These studies indicate that the apparent relation between complexation energies of ionic systems and acid−base chemistry is not a causal one.

Here we have synthesized complexes of fluoroform with several substituted acetylides, $RCC^-\cdot HCF_3$ (R=H, phenyl, *p*-tolyl). Their equilibrium complexation energies were determined relative to the corresponding methanol complex, $RCC^-\cdot HOCH_3$. Their complexation energies are all ∼−19 kcal/mol and are moderately stronger than a typical ion−dipole complex (∼−10−15 kcal/mol). Therefore, they are hydrogen bonded. Bimolecular proton/deuterium transfer solvent exchange experiments and ab initio molecular orbital calculations were performed to verify the structure of the complexes. This work clearly demonstrates the importance of charge distributions to hydrogen bond stability for anionic complexes.

Experimental Section

Materials. Acetylene and d_2-acetylene were synthesized by the standard literature procedure for the reaction of calcium carbide with

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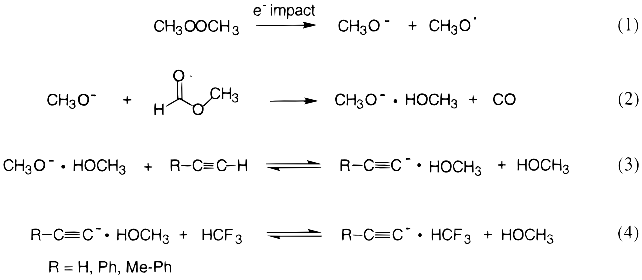
Scheme 1



water and deuterium oxide, respectively.[15] The products were purified by a trap-to-trap vacuum distillation. Dimethyl peroxide was synthesized by a literature procedure.[16] The product was purified by a trap-to-trap vacuum distillation. d_3-Methyl formate, $HCOOCD_3$, was synthesized by a literature procedure.[17] The product was purified by distillation and preparative gas chromatography using a Hewlett-Packard Series 6890 GC with a carbowax column. d_3-Methyl nitrite, CD_3ONO, was synthesized in situ by Bartmess's technique using CD_3OH and isoamylnitrite.[18] Phenylacetylene and *p*-tolylacetylene (4-ethynyltoluene) were obtained from Aldrich. They were purified before use by preparative gas chromatography. Tetrafluoromethane, CF_4, was obtained from Matheson. 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.[19] An additional Varian leak valve was added to perform experiments requiring five reagent gases. The magnetic field strength was 0.6 T. The temperature in the cell is estimated to be 350 K. Background pressures were on the order of $2.0-5.0 \times 10^{-9}$ Torr and operating pressures ranged from 0.7 to 3.0×10^{-6} Torr. Pressure measurements were made using an ion gauge (Granville Phillips 330) that 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%.

Ion−Molecule Chemistry. Acetylide−fluoroform complexes, $RCC^-{\cdot}HCF_3$, were synthesized through a sequence of ion−molecule reactions. The Riveros reaction was used to synthesize methanol−methoxide, $CH_3O^-{\cdot}HOCH_3$ (Scheme 1).[20,21] Acetylene, phenylacetylene, and *p*-tolylacetylene, RCCH, were observed to undergo a reversible exchange reaction with methanol-methoxide to form $RCC^-{\cdot}HOCH_3$ complexes (eq 3, in Scheme 1). The $RCC^-{\cdot}HOCH_3$ complexes then underwent a reversible solvent exchange reaction with fluoroform (eq 4, Scheme 1).

Appreciable amounts of the trimeric complex, $CH_3O^-{\cdot}(HOCH_3)_2$ ($m/z = 95$), were observed at long delay times (∼2 s) under the reaction conditions used. We were unable to resolve this peak from the $HCC^-{\cdot}HCF_3$ ($m/z = 95$), peak using our instrumentation. Therefore, CD_3OH was substituted for CH_3OH during the studies of HCC^- complexes. d_3-Methyl nitrite was used as the CD_3O^- source and deuterated methyl formate, $HCOOCD_3$, was used in place of methyl formate.

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 constant obtained at several pressure ratios was 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 based on our estimate for the error in the absolute pressure readings (±20%). The relative values should be more accurate because the relative pressure errors should be smaller (±10%).

Scheme 2

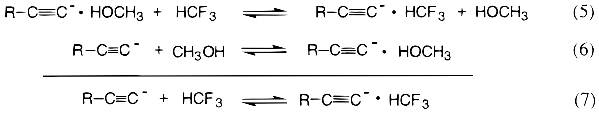


Table 1. Gas-Phase Acidities for the Reaction $AH \rightleftharpoons A^- + H^+$

AH	$\Delta G°$ (kcal/mol)	$\Delta H°$ (kcal/mol)
CH_3OH	375.1[a]	381.5
CD_3OH	375.5[b]	381.9
CF_3H	370.5[b]	378.0
HCCH	369.8[c]	377.8
p-CH_3-C_6H_4CCH	365.3[d]	372.8
C_6H_5CCH	364.2[b]	371.7

[a] Experimental values from ref 28. [b] Reference 29 re-anchored to data in ref 30. [c] Reference 30. [d] Reference 31.

Kinetics. The rate constants for proton transfer between CF_3^- and acetylene and phenylacetylene were measured. CF_3^- was generated from electron ionization of CF_4. 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

Complexation Energies. The complexation energies (eq 7, Scheme 2) of the substituted acetylide−fluoroform complexes, $RCC^-{\cdot}HCF_3$, were measured relative to substituted acetylide−methanol complexes, $RCC^-{\cdot}HOCH_3$. We previously determined these values in another study (see Tables 1 and 2).[12] The scale is anchored to the complexation energy of methanol−methoxide. The absolute values of its free energy of binding, $\Delta G°_{complex}$, and the enthalpy of binding, $\Delta H°_{complex}$, were determined by Meot-Ner[22] and Kebarle.[23] We used Meot-Ner's value here for consistency with our previous work. The free energies of complexation of the acetylide−fluoroform complexes were determined from the thermochemical cycle in Scheme 2.[24]

The complexation energy of fluoroform−acetylide was determined relative to deuterated methanol, CD_3OH, because of the difficulty of overlapping mass peaks. We determined the equilibrium complexation energy of deuterated methanol−methoxide, $CD_3O^-{\cdot}HOCD_3$, on a scale relative to methanol−methoxide using our instrumentation. Our value for the complexation energy of $CD_3O^-{\cdot}HOCD_3$ is consistent with the value obtained from kinetic measurements by Bierbaum, but is 0.5 kcal/mol larger (less stable).[25] We used our value because it

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Table 2. Measured Thermochemical Values for Equilibrium Reactions

reaction	$\Delta G°$ (kcal/mol)	$\Delta H°$ (kcal/mol)
$CH_3O^-{\cdot}HOCH_3 + CD_3OH \rightleftharpoons CH_3OH + CH_3O^-{\cdot}HOCD_3$	0.0	0.5
$CH_3O^-{\cdot}HOCD_3 + CD_3OH \rightleftharpoons CH_3OH + CD_3O^-{\cdot}HOCD_3$	1.0	0.5
$CD_3O^-{\cdot}HOCD_3 + H{-}C{\equiv}C{-}H \rightleftharpoons CD_3OH + H{-}C{\equiv}C^-{\cdot}HOCD_3$	1.7	2.7
$H{-}C{\equiv}C^-{\cdot}HOCD_3 + HCF_3 \rightleftharpoons CD_3OH + H{-}C{\equiv}C^-{\cdot}HCF_3$	2.1	2.1
$p\text{-}CH_3{\cdot}C_6H_5\text{-}C{\equiv}C^-{\cdot}HOCH_3 + HCF_3 \rightleftharpoons CH_3OH + p\text{-}CH_3\text{-}C_6H_5\text{-}C{\equiv}C^-{\cdot}HCF_3$	2.8	2.8
$C_6H_5{-}C{\equiv}C^-{\cdot}HOCH_3 + HCF_3 \rightleftharpoons CH_3OH + C_6H_5{-}C{\equiv}C^-{\cdot}HCF_3$	2.2	2.2

Table 3. Thermochemical Values for Complexation Energies for the Reaction $B^- + HA \rightleftharpoons B^-{\cdot}HA$

$B^-{\cdot}HA$	$\Delta G°$ (kcal/mol)	$\Delta H°$ (kcal/mol)
$CH_3O^-{\cdot}HOCH_3$	-19.4^a	-28.8^a
$CH_3O^-{\cdot}HOCD_3$	$-19.4,^b -19.6^c$	$-28.3,^b -28.5^c$
$CD_3O^-{\cdot}HOCD_3$	$-18.8,^b -19.4^c$	$-28.2,^b -28.8^c$
$H{-}C{\equiv}C^-{\cdot}HOCH_3$	-11.6^d	-21.6^d
$H{-}C{\equiv}C^-{\cdot}HOCD_3$	-11.3^b	-21.4^b
$p\text{-}CH_3{\cdot}C_6H_4{-}C{\equiv}C^-{\cdot}HOCH_3$	-11.1^d	-21.6^d
$C_6H_5{-}C{\equiv}C^-{\cdot}HOCH_3$	-11.0^d	-21.5^d

[a] All values measured at 350 K. Reference 22. [b] This work. [c] Reference 25. [d] Reference 12.

Table 4. Complexation Energies for Fluoroform and Acetylides for the Reaction $R{-}C{\equiv}C^- + HCF_3 \rightleftharpoons R{-}C{\equiv}C^-{\cdot}HCF_3$

RCC^-	$\Delta G°$ (kcal/mol)	$\Delta H°$ (kcal/mol)
HCC^-	−9.2	−19.3
$p\text{-}CH_3\ C_6H_4CC^-$	−8.3	−18.8
$C_6H_5CC^-$	−8.8	−19.3

[a] All values measured at 350 K. The absolute error in each values is estimated to be ±1 kcal/mol. The relative error should be less than ±0.5 kcal/mol.

will have a consistent relative error with our other measurements and because it relies on a direct equilibrium measurement rather than measurements of multiple rate constants. The complexation energy of $RCC^-{\cdot}HOCD_3$ was determined relative to our value of the complexation energy of $CD_3O^-{\cdot}HOCD_3$. All experimentally determined values are listed in Tables 2−4.

To derive $\Delta H°_{complex}$ from $\Delta G°_{complex}$, a value of $\Delta S°_{complex}$ is needed. Obtaining accurate estimates of the entropies for ion−molecule complexes is difficult. The vibrational modes with the greatest contribution to the entropy are the six low-frequency modes created upon complexation. These soft modes are very anharmonic and are generally not reproduced accurately by standard ab initio harmonic frequency calculations.[26] Consequently, we chose to assume that $\Delta S°$ of eq 5 in Scheme 2 is due only to the symmetry of the molecules.[27] 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 assuming a temperature of 350 K. The resulting values are listed in Table 4.

Solvent Switching/Isotopic Exchange Experiments. Incorporation of a deuterated neutral molecule into the complex followed by solvent switching or by proton exchange and loss of a protiated neutral molecule would be indicated by a change in mass. Isotopic exchange reactions were studied for both deuterated fluoroform and deuterated acetylenes. Deuterated acetylenes were not observed to exchange a deuterium with the $RCC^-{\cdot}HCF_3$ complexes on the time scale and attainable pressures of our experiments (eq 8). We can estimate the maximum efficiency to be less than 1.0% based on our detection limits and the pressures used.

Table 5. Deuterium Fractionation Factors for Fluoroform−Acetylide Complexes $R{-}C{\equiv}C^-{\cdot} + HCF_3 + DCF_3 \rightleftharpoons R{-}C{\equiv}C^-{\cdot}DCF_3 + HCF_3$

RCCH	K_{eq}
HCCH	0.94 ± 0.1
C_6H_5CCH	0.93 ± 0.1

$$R{-}C{\equiv}C^-{\cdot}HCF_3 + R{-}C{\equiv}CD \not\rightleftharpoons R{-}C{\equiv}C^-{\cdot}DCF_3 + R{-}C{\equiv}CH \quad (8)$$

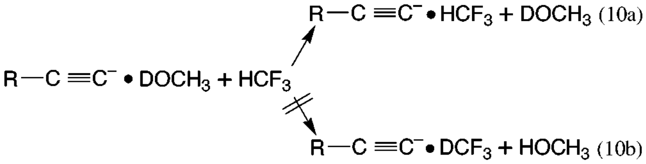
where, R = D, C_6H_5.

In contrast, deuterated fluoroform, DCF_3, was found to reversibly exchange into the $RCC^-{\cdot}HCF_3$ complexes (eq 9). For both phenylacetylene and acetylene, the process was efficient. Only one proton exchanged on the time scale examined (∼3 s) for the acetylide−fluoroform complex, $HCC^-{\cdot}HCF_3$. The deuterium fractionation factors (the equilibrium constant for eq 9) for phenylacetylide and acetylide−fluoroform complexes were measured. The ratio of DCF_3/HCF_3 was measured in situ by the ratio of DCF_2^+/HCF_2^+ in a positive ion spectra. This method for ascertaining neutral ratios of DCF_3/HCF_3 has been used previously and established to be reliable.[11] The fractionation values are listed in Table 5.

$$R{-}C{\equiv}C^-{\cdot}HCF_3 + DCF_3 \rightleftharpoons R{-}C{\equiv}C^-{\cdot}DCF_3 + HCF_3 \quad (9)$$

where R = D, C_6H_5.

We also examined the exchange reaction of fluoroform with $RCC^-{\cdot}DOCH_3$. The only product for acetylide and phenylacetylide complexes was protiated $RCC^-{\cdot}HCF_3$ (eq 10).



where R = H, Ph, Me-Ph.

Kinetics. The rate constants for proton transfer from acetylene and phenylacetylene to CF_3^- were measured (eq 11). The capture rate constants were calculated using the Su−Chesnavich model.[33] The efficiency of the reaction was calculated by eq 12. All values are listed in Table 6.

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Table 6. Kinetic Data for the Proton Transfer Reaction $CF_3^- + R-C\equiv C-H \rightarrow CF_3H + R-C\equiv C^-$

RCCH	$k_{obs} \times 10^{-9}$ (cm^3s^{-1})	$k_{cap} \times 10^{-9}$ (cm^3s^{-1})	efficiency Φ	μ-VTST RRKM barrier height (kcal/mol)
HCCH	0.20 ± 0.04	0.98	0.20	−8.2
C_6H_5CCH	0.29 ± 0.06	1.43	0.20	−7.2

[a] k_{cap} was calculated using the Su−Chesnavich collision capture model (ref 33) with the following parameters: dipole moment in D, molecular polarizability in Å^3, geometric mean of moments of inertia in amu Å^2: HCCH (0.0, 3.3, 13.9), C_6H_5CCH (0.66, 13.0, 228.6).

$$CF_3^- + R-C\equiv CH \rightarrow R-C\equiv C^- + HCF_3 \qquad (11)$$

$$\Phi = \frac{k_{obs}}{k_{cap}} \qquad (12)$$

Microcanonical variational transition state (μ-VTST) Rice−Ramsperger−Kassel−Marcus (RRKM) calculations were performed to derive the proton-transfer transition state barrier height.[34] Calculations were performed with the HYDRA program.[35] The reaction was modeled using a double well potential and the steady-state approximation. The parameters for the RRKM calculations were determined from ab initio calculations. The height of the central barrier was adjusted until the RRKM efficiency matched the experimental efficiency. The experimentally derived and ab initio barriers are in good agreement (see Table 6, Figures 1 and 2).

Theoretical Methods. Molecular orbital calculations were performed using Gaussian94.[36] Calculations on the acetylide−fluoroform system were done at the MP2/6-311++G**//HF/6-311++G** level of theory. All stationary points were confirmed by vibrational analyses at the HF/6-311++G** level. Calculations on the phenylacetylide−fluoroform system were done at the MP2/6-311++G**//HF/6-31+G* level of theory. Vibrational frequencies were calculated at the HF/6-31+G* level of theory. Thermochemistry was calculated using standard statistical mechanics with ab initio vibrational frequencies scaled by 0.89.[37] All results are summarized in Table 7 and in Figures 1 and 2.

Discussion

Background. The hydrogen bond is one of the most widely studied molecular interactions. A hydrogen bond is defined as an intermolecular (or intramolecular) interaction specifically involving a proton donor, A−H, and a proton acceptor, B.[38] Ionic hydrogen bonds are observed in solvent−ion interactions,[39] intermediates in proton-transfer reactions,[40] and in enzymatic active sites.[41] Their existence is substantiated by characteristic 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).[1,2] Because solvation has dramatic effects on the energetics and reactivity of ions,[32] it is difficult to understand the properties of hydrogen bonds to ions in the condensed phase.

$$B^- + HA \rightleftharpoons B^-{\cdot}HA \qquad (13)$$

Ionic gas-phase complexes provide a measure of the intrinsic stability of hydrogen-bonded complexes. We focus here on hydrogen bonds to anions.[42] Anionic complexes have been

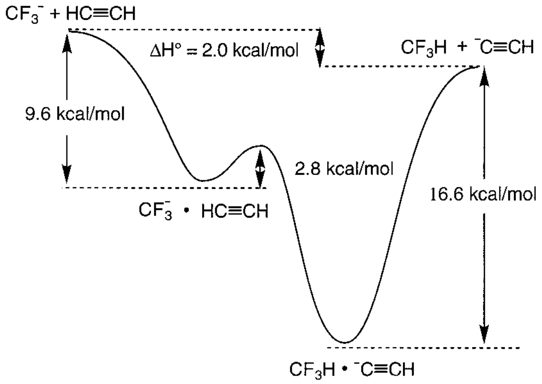

Figure 1. Potential energy surface for the reaction of CF_3^- and HCCH. Energies were calculated at the MP2/6-311++G**//HF-6-311++G** level of theory. Zero point energies were obtained from ab initio vibrational frequencies scaled by 0.89.

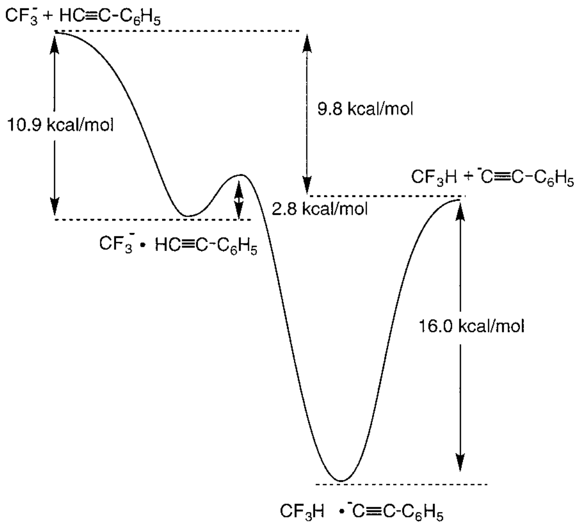

Figure 2. Potential energy surface for the reaction of CF_3^- and C_6H_5-CCH. Energies were calculated at the MP2/6-311++G**//HF-6-31+G* level of theory. Zero point energies were obtained from ab initio vibrational frequencies scaled by 0.89.

Table 7. Ab Initio Results for Complexation Energies

reaction	ΔH° (kcal/mol)
$R-C\equiv C^- + HCF_3 \rightleftharpoons H-C\equiv C^-{\cdot}HCF_3$	−16.6[a]
$C_6H_5\text{-}C\equiv C^- + HCF_3 \rightleftharpoons C_6H_5\text{-}C\equiv C^-{\cdot}HCF_3$	−16.0[b]
$H-C\equiv C^- + H-C\equiv C-H \rightleftharpoons H-C\equiv C^-{\cdot}H-C\equiv C-H$	−10.1[a]
$CF_3^- + HCF_3 \rightleftharpoons CF_3^-{\cdot}HCF_3$	−15.0[a]

[a] Energies calculated at the MP2/6-311++G**//HF/6-311++G** level of theory with vibrational corrections from 0.89 scaled HF/6-311++G** frequencies. [b] Energies calculated at the MP2/6-311++G**//HF/6-31+G* level of theory with vibrational corrections from 0.89 scaled HF/6-31+G* frequencies.

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studied by mass spectroscopy,[3,7,22,43] by photodissociation spectroscopy,[44] by electron photodetachment spectroscopy,[45,46] and by multiple photon infrared dissociation spectra.[47] The complexation energy ($\Delta H°$ for eq 13) is generally referred to as the hydrogen bond strength. However, this definition does not provide any indication of how much extra stabilization the hydrogen bond provides relative to a simple ion−dipole complex. Simple ion−dipole complexes in the gas phase can be bound by ∼10−12 kcal/mol, whereas hydrogen-bonded complexes can be bound by ∼25−35 kcal/mol.

The relation of the hydrogen bond strength to acid−base properties has been widely studied in the gas phase.[3,22,43] In general, strong acids appear to be good H-bond donors and strong bases appear to be good H-bond acceptors. However, polarity is also important. For instance, toluene is as acidic as methanol but is a poor hydrogen bond donor.[48] Because hydrogen-bonded complexes are intermediates in proton-transfer reactions, their structure is assumed to reflect the thermodynamic endpoints of the reaction. That is, the structure is $A^-{\cdot}HB$ if AH is the stronger acid (compared to HB), and $AH{\cdot}B^-$ if BH is the stronger acid.[49] This assumption has been tested for several systems by isotopic exchange,[50,51] electron photodetachment,[52] and computation.[53] A linear relationship is frequently observed between the difference in acidity of the two partners in the complex and the complexation energy.[54] These relationships have been suggested to provide information about the potential surface near the complexes or the degree of proton transfer in the complex. A value of 0.5 has been suggested to indicate that the proton is equally shared between the two molecules in the complex.[55] The connections between acidity and hydrogen bond stability have generally derived using a limited range of structural components. Therefore, it is uncertain how general these empirical rules are.

We recently studied complexes with carbanions as H-bond acceptors and carbon acids as H-bond donors in an attempt to better understand the relation between acid−base properties, the shape of the potential energy surface, and the stability of hydrogen-bonded complexes. These systems demonstrate that previous assumptions about hydrogen-bonded complexes are not completely general. For complexes of alkoxides with fluoroform, $RO^-{\cdot}HCF_3$, we found that the structure of the complex is not determined by the acid−base chemistry.[11] That is, the complex remains $RO^-{\cdot}HCF_3$ even when proton transfer from HCF_3 to the alkoxide is favorable in the separated reactants. The results from studies of deuterium exchange proton-transfer reactions suggest that other carbanions may behave similarly.[13,14] We studied complexes of acetylides with methanol, $RCC^-{\cdot}HOCH_3$. In this system the complexation energy is nearly constant with varying acetylides over ∼8 kcal/mol range of basicities.[12] However, the corresponding plot with a constant acetylide and varying alcohols, $C_6H_5CC^-{\cdot}HOR$, has a slope of ∼0.5. This work indicates that the frequent assumption that the trend in complexation energy is related to the shape of the potential energy surface does not hold. These results suggested that examination of the charge density of the separated ion and neutral is more useful than acid−base properties to interpret complexation energy data.

Our results on carbanions and carbon acids suggested that we could synthesize strongly bound carbon acid−carbanion complexes. Here we report our work on the synthesis of complexes of substituted acetylides with fluoroform, $RCC^-{\cdot}HCF_3$. We measured their stability and verified their putative structures. These complexes are unusual because neither of the homodimers, $RCC^-{\cdot}HCCR$ and $CF_3^-{\cdot}HCF_3$, are observed to have similar stability. Unlike alcohols, which are good donors and whose conjugate bases are good acceptors, only one species in each homodimer is a good hydrogen bond donor (or acceptor).

Structure of $RCC^-{\cdot}HCF_3$ Complexes. The structure of hydrogen-bonded complexes is frequently assumed to be related to the acid−base chemistry of the separated ion and neutral. Because we have shown that this assumption does not always hold, we investigated the structure of the assumed $RCC^-{\cdot}HCF_3$ complexes by deuterium exchange experiments. These experiments are completely consistent with the $RCC^-{\cdot}HCF_3$ structure for R = H and C_6H_5 and also provide information about the potential energy surface.

We performed deuterium exchange experiments using both acetylenes and fluoroform as the deuterium source. The reactions of RCCD (R = H, C_6H_5) with the acetylide−fluoroform complexes were examined. If the complex resembled $RCCH{\cdot}^-CF_3$, we would expect a simple solvent switching reaction with RCCD. We do not observe incorporation of deuterium from RCCD.[56] Therefore, the $RCCH{\cdot}^-CF_3$ structure is unlikely because solvent switching reactions are generally kinetically efficient.[25] These results suggest that the complex has the structure $RCC^-{\cdot}HCF_3$. To test this hypothesis, we examined the exchange reaction with DCF_3. We observe efficient exchange to incorporate DCF_3, suggesting a simple solvent switching mechanism and supporting the $RCC^-{\cdot}HCF_3$ structure. Although we cannot rule out the possibility of proton transfer in the collision complex, we suggest that it probably does not occur. The lack of deuterium incorporation from the RCCD exchange experiments suggests that the $RCC^-{\cdot}HCF_3$ complex must pass through an unfavorable intermediate to incorporate deuterium.

The $HCC^-{\cdot}HCF_3$ complex is a more complicated case because it has two possible sites of exchange. Incorporation of DCF_3 is facile. In the resulting complex, $HCC^-{\cdot}DCF_3$, the remaining acetylenic proton could still be exchanged. One plausible mechanism involves the isomerization of the putative $HCC^-{\cdot}DCF_3$ complex to $DCC^-{\cdot}HCF_3$ followed by simple

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solvent exchange of DCF_3. We know that the solvent exchange process should be facile. Therefore, if complexes of $DCC^-{\cdot}HCF_3$ were present, they would exchange with DCF_3. We do not observe $DCC^-{\cdot}DCF_3$, indicating that the isomerization−exchange reaction does not occur during the collision event. This result further suggests that processes involving the $HCCH{\cdot}^-CF_3$ structure are not energetically favorable.

In addition to the results from the acetylide−fluoroform complexes, the reaction of $RCC^-{\cdot}DOCH_3$ with HCF_3 produces $RCC^-{\cdot}HCF_3$ only. Plausible mechanisms for formation of the nonobserved product, $RCC^-{\cdot}DCF_3$, involve activated intermediates with CF_3^-. All of our results are consistent with the hypothesis that all intermediates containing CF_3^- are energetically unfavorable.

Stability and Potential Energy Surface (PES). All three $RCC^-{\cdot}HCF_3$ complexes have complexation energies of ~ -19 kcal/mol. These complexes are the most stable complexes of carbanions and carbon acids that have been observed.[57] Note that although we observed the heterodimeric complex of the comparably acidic components, $RCC^-{\cdot}HCF_3$, we do not observe formation of the symmetric, homodimeric complexes, $RCC^-{\cdot}HCCR$ and $CF_3^-{\cdot}HCF_3$, under our conditions. We estimate that these homodimeric complexes have complexation energies that are weaker than −16 kcal/mol.[58] We performed ab initio calculations on $HCC^-{\cdot}HCCH$ and $CF_3^-{\cdot}HCF_3$ to predict their stability. They are calculated to have complexation energies of −10 and −15 kcal/mol, respectively. Both are weaker than the calculated complexation energies for $RCC^-{\cdot}HCF_3$ (see Table 7). This result is markedly different from the behavior of alcohol−alkoxides, where the homodimers and heterodimers have comparable stabilities, and the behavior of CH_3CN, where neither the homodimer nor its heterodimers are exceptionally stable.[8]

We have also calculated the potential energy surfaces proton transfer between CF_3^- and acetylene and phenylacetylene (See Figures 1 and 2). Although the well depths of the $RCC^-{\cdot}HCF_3$ complexes are underestimated by ∼2 kcal/mol, the agreement is still reasonable.[59] The difference in energy between the $RCCH{\cdot}^-CF_3$ complex and the tautomeric $RCC^-{\cdot}HCF_3$ complex is predicted to be greater than the exothermicity of the overall proton transfer reaction for both R=H and phenyl. The result is especially striking for the CF_3^- + acetylene surface where the difference in complexes is ∼9 kcal/mol while the reaction is only calculated to be ∼2 kcal/mol exothermic. These results agree with our isotopic exchange experiments that suggest that complexes where CF_3^- is the hydrogen bond acceptor are energetically unfavorable.

To further explore the stationary points on the potential energy surfaces, we measured the rate constants for the two proton-transfer reactions. The proton-transfer reactions of acetylene and phenylacetylene with CF_3^- were both ∼20% efficient (See Table 6).[60] Although the reactions are relatively rapid compared to proton-transfer reaction of delocalized carbanions, the efficiency indicates that an energetic barrier exists on the potential surface. Microcanonical variational transition state RRKM modeling of the proton-transfer efficiencies was performed to determine the height of the central barrier. For acetylene and phenylacetylene, the barriers were calculated to be ∼8 and 7 kcal/mol below the entrance channels, respectively. These values are in reasonable agreement with the calculated barriers (see Figures 1 and 2).

We measured the deuterium fractionation factors of $RCC^-{\cdot}HCF_3$ with HCF_3/DCF_3 (eq 9) to learn about the shape of the potential surface near the complex. The fractionation factors are nearly unity for both (see Table 5). $\Delta G°$ for the reaction is approximately equal to the difference in zero point energies between the complexes and H/D fluoroform (eq 14). Our isotopic exchange experiments demonstrate that the structure of both complexes is $RCC^-{\cdot}HCF_3$. In this case, a fractionation factor of ∼1 indicates that the C−H stretch in fluoroform is not strongly perturbed in the complex.[61,62] Using our measured complexation energies for $RCC^-{\cdot}HCF_3$, the proton-transfer barrier is ∼10 kcal/mol higher than the $HCC^-{\cdot}HCF_3$ complex and ∼17 kcal/mol higher than the $C_6H_5CC^-{\cdot}HCF_3$ complex. Both results suggest that the proton transfer coordinate looks essentially like HCF_3 at the $RCC^-{\cdot}HCF_3$ minima for both systems.

$$\Delta G°_{\mathrm{eq}} \approx (\mathrm{ZPE}_{\mathrm{RCC^-{\cdot}DCF_3}} - \mathrm{ZPE}_{\mathrm{RCC^-{\cdot}HCF_3}}) - (\mathrm{ZPE}_{\mathrm{DCF_3}} - \mathrm{ZPE}_{\mathrm{HCF_3}}) \quad (14)$$

Charge Distributions and H-Bond Stability. The majority of gas phase anionic complexes for which data are available are structurally similar pairs. In these strongly bound systems, the acids and their conjugate base are good hydrogen bond donors and acceptors, respectively. For example, both alcohols, ROH, and alkoxides, RO^-, form strongly bound hydrogen bonded complexes with a variety of partners.[5] For weakly bound systems, many acids and their conjugate base are poor hydrogen bond donors and acceptors. For example, neither acetonitrile nor its conjugate base have been observed to form strongly bound hydrogen-bonded complexes.

The substituted acetylide−fluoroform system presents a case where the hydrogen bonding character of the acid and its conjugate base are substantially different. Both HCCH and HCF_3 have similar acidities (within <1 kcal/mol) and show efficient proton transfer reactions such as those for the alcohols. However, they are completely different in regard to their ability to participate in hydrogen bonds. HCF_3 is a good hydrogen bond donor to both anions[11] and neutrals.[63] In contrast, CF_3^- is a poor hydrogen bond acceptor. The stability of this ion is due to polarization of the charge away from the carbon into the fluorine atoms. On the basis of electrostatics alone, CF_3^- should be a poor acceptor compared to an anion with highly localized charge.[64] Although acetylene, HCCH, has been observed to form hydrogen bonds to neutrals in the gas phase,[65] it is a poor hydrogen bond donor toward anions—no complexes of the

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[57] Only two carbanion−carbon acid complexes have been examined. $CH_2CN^-{\cdot}CH_3CN$ has $\Delta H_{\mathrm{complex}} = -12.8$ kcal/mol and $C_5H_5^-{\cdot}CD_3CN$ has $\Delta H_{\mathrm{complex}} = -15.5$ kcal/mol (ref 8).

[58] Estimates are based on the pressure range obtainable and typical signal-to-noise ratios.

[59] The origin of the underestimation is uncertain. We found similar underestimations for $RCC^-{\cdot}HOCH_3$ complexes. Calculations at the MP2/aug-cc-p-VDZ//HF/aug-cc-p-VDZ level gave similar results, ruling out the possibility of a basis-set-dependent error. One possibility is basis set superposition error, but this error would tend to make the complexation energies less exothermic.

[60] Both reactions have the same efficiency despite the higher exothermicity of the CF_3^- + phenylacetylene reaction. We observed a similar result with the proton-transfer reaction of methoxide with these acetylenes. It is unclear whether the origin is a true thermodynamic barrier or dynamic effects during the reaction. Chabinyc, M. L.; Brauman, J. I. ref 31.

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structure $HCCH\cdot B^-$ have been observed experimentally and calculations indicate that they would be weakly bound.[66] In contrast, acetylide, HCC^-, is a good hydrogen bond acceptor. The charge is highly localized in a sigma orbital on the terminal carbon.[67] The anion forms stable complexes with both alcohols and fluoroform.

The results for the acetylide−fluoroform system demonstrate clearly that matched acidities do not imply any special hydrogen bonding interaction as has been suggested by some.[68] Both of the homodimers, $HCC^-\cdot HCCH$ and $CF_3^-\cdot HCF_3$, are less stable than the heterodimer, $HCC^-\cdot HCF_3$, based on experimental evidence, and they are both calculated to be weakly bound. In addition, all of our isotopic exchange data suggests that the structure $HCCH\cdot^-CF_3$ is energetically unfavorable. All of the weak complexes contain a good donor (or acceptor) with a poor acceptor (or donor). However, when a good donor, CF_3H, and a good acceptor, HCC^-, are brought together the complex is strongly bound (see Figure 1). This suggests that the stability of the homodimeric complex in no way determines the stability of heterodimeric complexes. As a consequence, Marcus-type additivity rules for complexation energies based on homodimers and heterodimers are certain to fail for systems where the hydrogen bonding properties of an acid and its conjugate base differ. This result has been suggested previously based on limited computational studies, but we believe our results are the first to demonstrate this hypothesis experimentally.[69,70]

The relation between the complexation energies and acid−base properties also can be understood by examining charge distributions.[11,12] A plot of the complexation energy vs the basicity of the acetylide shows almost zero slope (<0.1) over a 6 kcal/mol range (see Figure 3). The complexation energy shows no extra stability for the acetylide−fluoroform complex where the acidities are nearly matched. The complexation data show that the substituent on the acetylide provides the same stabilization to the free anion as it does to the complex. We believe that the charge distribution in the acetylide determines the trend in complexation energies. A simple model to explain this behavior is to treat the substituent as a remote dipole.[71] If the charge distribution at the terminal carbon remained nearly constant for all the acetylides, a dipolar substituent would provide similar stabilization in both the free ion and the complex. We obtained the same result for a series of methanol−acetylide complexes.[12]

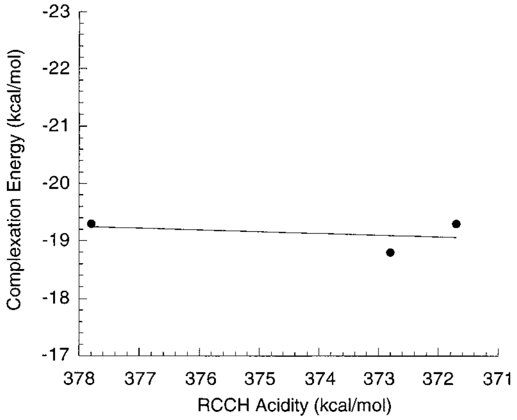

Figure 3. Complexation energies, $\Delta H^\circ_{\mathrm{complex}}$, of $RCC^-\cdot HCF_3$ vs the gas-phase acidities, $\Delta H^\circ_{\mathrm{acid}}$, of RCCH.

Conclusions

The substituted acetylide−fluoroform complexes clearly demonstrate the need to examine charge distributions rather than acid−base chemistry to understand hydrogen bonding ability. The acetylide−fluoroform system shows that the difference in energy between the intermediate hydrogen-bonded complexes can be large even when the proton transfer reaction between the separated species is nearly thermoneutral. Few hydrogen-bonded systems that have been studied so far have this type of potential surface, but there are likely to be more.[13,14,72]

The relationships between the magnitude of the deuterium fractionation factor and the difference in energy between wells on a double-well proton-transfer surface have been verified. Complexes with proton-transfer barriers that are large compared to the energy of the complex produce fractionation factors near unity. However, these results do not address how the magnitude of the complexation energy affects the fractionation factor.

This work further demonstrates that the correlations between acid−base thermochemistry and complexation energies observed for many systems are not an intrinsic property of hydrogen-bonded anionic complexes. These relationships are frequently used to predict the strength of unknown hydrogen bonds and appear to be correct in many cases.[3,5] While these relationships can be useful tools, caution should be used in applying them to new systems. Careful analysis of the origin of these relationships must be made before they can be applied to new systems.

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