

# Acidity, Basicity, and the Stability of Hydrogen Bonds: Complexes of $\text{RO}^- + \text{HCF}_3$

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**Abstract:** Ion–molecule complexes of  $\text{RO}^-$  ( $\text{R} = \text{Me}, \text{Et}, i\text{-Pr}$ ) and  $\text{HCF}_3$  have been studied with Fourier transform ion cyclotron resonance spectrometry. The  $\text{RO}^-$  complexation energies with  $\text{HCF}_3$  were measured relative to  $\text{RO}^- \cdot \text{H}_2\text{O}$ . These complexes,  $[\text{ROHCF}_3]^-$ , have complexation energies on the order of  $-20$  kcal/mol and have low deuterium fractionation factors and are, therefore, hydrogen bonded. The structure of the complexes was studied by isotopic equilibrium experiments and ab initio calculations. All of the complexes studied have the structure  $\text{RO}^- \cdot \text{HCF}_3$  even when  $\text{HCF}_3$  is a stronger acid than  $\text{ROH}$ . The structure of the complexes can be understood through electrostatic arguments rather than the difference in acidity between the ion and neutral.

## Introduction

Hydrogen bonds are 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  $\text{A-H}$  and a proton acceptor  $\text{B}$ .<sup>1</sup> Its existence is often characterized by spectroscopic features such as intense IR bands, unusual NMR shifts, and structural features such as short contact distances (smaller than van der Waals radii).<sup>2–4</sup> Hydrogen bonds are observed in both neutral and ionic systems. Understanding the ability of hydrogen bonds to stabilize ions is especially important because they are essential to a wide variety of phenomena, including solvation of ions,<sup>5,6</sup> stabilization of intermediates in proton-transfer reactions,<sup>7,8</sup> enzymatic stabilization of complexes and transition states,<sup>9,10</sup> and molecular recognition in biological and nonbiological systems.<sup>11</sup> In addition, knowledge of the structure of gas-phase proton-bound ions is critical to the interpretation of results from kinetic method determinations of thermodynamic quantities.<sup>12</sup> In this paper we address the question of how the

structure and stability of hydrogen-bonded complexes is related to the structure and stability of their ionic and neutral components.

Several key issues remain unresolved about hydrogen bonding in ionic systems. Hydrogen bonds to ions are thought to be stronger than those to neutral molecules, but the difference in magnitude is still debated.<sup>13,14</sup> Empirically, a linear free energy relationship (LFER) is seen between the complexation energy and the difference in acidity and basicity of the molecules involved for systems in both the gas phase and solution.<sup>15–19</sup> 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 molecules (e.g., proton bound amine dimers, alcohol–alkoxides).<sup>19–22</sup> Solvation is known to play a large role in both the stability and the structure of hydrogen-bonded complexes.<sup>23</sup> By uncovering the intrinsic character of hydrogen bonds we can begin to understand the basis by which these factors affect the interaction.

Gas-phase studies can provide information about the intrinsic stability of hydrogen-bonded ionic intermediates by eliminating solvation effects. Hydrogen-bonded complexes of both positive and negative ions have been widely studied. Most of these complexes are considered to have strong hydrogen bonds and generally involve nitrogen and oxygen for both positive and negative ions.<sup>15,17,19,22</sup> For example, alcohol–alkoxide dimers

(1) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; Freeman: San Francisco, 1960.

(2) Buckingham, A. D. In *Theoretical Treatments of Hydrogen Bonding*; Hadzi, D., Ed.; John Wiley & Sons: New York, 1997.

(3) Perrin, C. L.; Nielson, J. B. *Annu. Rev. Phys. Chem.* **1997**, *48*, 511–544.

(4) Emsley, J. *Chem. Soc. Rev.* **1980**, *9*, 91–124.

(5) Jorgensen, W. *Adv. Chem. Phys.* **1988**, *70*, 469–488.

(6) *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley-Interscience: New York, 1972.

(7) Eigen, M. *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 1–19.

(8) Bell, R. P. *The Proton in Chemistry*; Cornell University Press: Ithaca, NY, 1973.

(9) Jencks, W. P. *Catalysis in Chemistry and Enzymology*; Dover Publications: New York, 1987.

(10) Walsh, C. *Enzymatic Reaction Mechanisms*; W. H. Freeman: San Francisco, 1979.

(11) *Comprehensive Supramolecular Chemistry*; Lehn, J.-M.; Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vögtle, F., Ed.; Pergamon: New York, 1996.

(12) Cooks, R. G.; Patrick, J. S.; Kotaiho, T.; McLuckey, S. A. *Mass Spectrom. Rev.* **1994**, *13*, 287–339.

(13) Guthrie, J. P. *Chem. Biol.* **1996**, *3*, 163–170.

(14) Gerlt, J. A.; Kreevoy, M. M.; Cleland, W. W.; Frey, P. A. *Chem. Biol.* **1997**, *4*, 259–267.

(15) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445–476.

(16) Shan, S.-O.; Loh, S.; Herschlag, D. *Science* **1996**, *272*, 97–101.

(17) Caldwell, G.; Rozeboom, M. D.; Kiplinger, J. P.; Bartmess, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 4660–4667.

(18) Meot-Ner, M.; Sieck, L. W. *J. Am. Chem. Soc.* **1986**, *108*, 7525–7529.

(19) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1987**, *109*, 6230–6236.

(20) Kreevoy, M. M.; Liang, T. M. *J. Am. Chem. Soc.* **1980**, *102*, 3315–3322.

(21) Stahl, N.; Jencks, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 4196–4205.

(22) Meot-Ner, M. *J. Am. Chem. Soc.* **1984**, *106*, 1257–1264.

(23) Perrin, C. L.; Nielson, J. B. *J. Am. Chem. Soc.* **1997**, *119*, 12734–12741.

have complexation energies in the range from 20 to 28 kcal/mol,<sup>17,18</sup> and proton-bound amine dimers have energies of 18 to 25 kcal/mol.<sup>22</sup> Linear free energy relationships are often observed between the complexation energy and the difference in acidity and basicity of the neutral and ion. Because these relationships are known only for a limited range of structural types, e.g., alcohols, amines, carboxylic acids, etc., it is not possible to fully understand their origin.<sup>22</sup>

Many anionic hydrogen-bonded complexes appear to be the most stable when they consist of an ion and neutral which form a nearly conjugate acid–base pair. That is, the better the match of the gas-phase acidities of the neutral and the conjugate acid of the ion, the more stable the complex. There are, however, examples in which matched acidities are not sufficient to form strong hydrogen bonds. For example, carbon acids are as acidic as many alcohols in the gas phase; toluene and methanol have comparable acidities. Nevertheless, the hydrogen-bonded complex of methoxide and toluene is not known, and our efforts to generate this complex have been unsuccessful.<sup>24</sup> Caldwell and Bartmess have examined complexes of phenylacetylide with a series of alcohols whose acidity is comparable to that of phenylacetylene.<sup>17</sup> These ion–molecule complexes have complexation energies ranging from 21.4 kcal/mol for methanol to 26.6 kcal/mol for benzyl alcohol.<sup>17</sup> Meot-Ner has studied complexes of cyclopentadienide with alcohols which have strengths near 20 kcal/mol, but whether these complexes are best termed “hydrogen bonded” is unclear.<sup>25</sup> Thus, the acidity and basicity of the neutral and ion are not the only factors governing the stability of hydrogen-bonded intermediates.<sup>19,26</sup> Clearly polarity has an effect on the stability of the complex, but its role is uncertain due to the lack of experimental studies.

To better understand the factors affecting hydrogen bonding, we have chosen to study ion–molecule complexes of fluoroform, HCF<sub>3</sub>. Fluoroform is known to form hydrogen bonds with other neutrals such as ammonia<sup>27</sup> and has a similar acidity<sup>28</sup> and polarity<sup>29</sup> as the simple aliphatic alcohols. Furthermore, proton-transfer reactions between fluoroform and alkoxides are rapid, indicating that there are no large barriers on the potential surface as observed for other carbon acids such as substituted toluenes.<sup>30</sup> Fluoroform should therefore provide a good case for comparison with other hydrogen-bonded complexes.

In this paper we report studies of the hydrogen-bonded intermediates in the reaction of HCF<sub>3</sub> with several alkoxides. We have characterized these complexes through equilibrium binding studies as well as isotopic equilibrium fractionation experiments. Our studies show that the structure of the complex is not solely determined by the overall thermochemistry of the proton-transfer reaction. Our results suggest that electrostatics provide an important key to understanding the structure and strength of the hydrogen-bonded complexes.

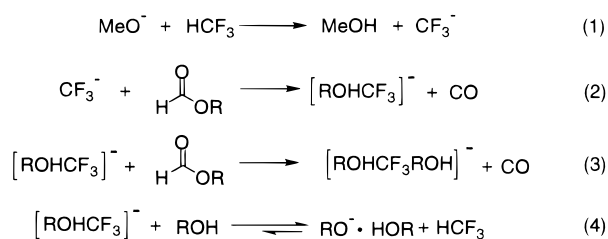
## Experimental Section

**Chemicals.** Fluoroform-*d*<sub>1</sub>, DCF<sub>3</sub>, was synthesized by a literature procedure.<sup>31</sup> The synthesized gas was purified by a trap-to-trap vacuum distillation. The product obtained contained 5% HCF<sub>3</sub> as an impurity as determined by mass spectrometry. Dimethyl peroxide was synthesized by a standard literature procedure.<sup>32</sup> The product was purified by a trap-to-trap vacuum distillation and characterized by mass spectrometry. All other chemicals were obtained commercially and used without further purification. Alkyl ethers were obtained from Aldrich Chemical. N<sub>2</sub>O (99% pure grade) was obtained from Matheson. All samples used were subjected to multiple freeze–pump–thaw cycles before introduction into the ICR spectrometer.

**Instrumentation.** All experiments were performed on an IonSpec Fourier transform ion cyclotron resonance (FT-ICR) spectrometer. Details of the spectrometer have been given previously.<sup>33</sup> The magnetic field strength was 0.6 T. The temperature in the cell is estimated to be 350 K.<sup>30</sup> Background pressures were on the order of 2.0–5.0 × 10<sup>−9</sup> Torr, and operating pressures ranged from 0.7 to 1.6 × 10<sup>−6</sup> Torr. Pressure measurements were made with 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%.

**Ion–Molecule Chemistry.** Reactions of CF<sub>3</sub><sup>−</sup> have previously been studied in the flowing afterglow environment.<sup>34</sup> We have reinvestigated its reaction with alkyl formates, the Riveros reaction,<sup>35,36</sup> to see if similar results would be obtained in the ICR (Scheme 1). CF<sub>3</sub><sup>−</sup> was produced from electron impact on CF<sub>4</sub> or the proton-transfer reaction of HCF<sub>3</sub> with CH<sub>3</sub>O<sup>−</sup>, which was generated by electron impact on dimethyl peroxide. CF<sub>3</sub><sup>−</sup> was isolated and allowed to react with various alkyl formates, HCO<sub>2</sub>R (R = Me, Et). Although ion–molecule complexes of HCF<sub>3</sub>, [ROHCF<sub>3</sub>]<sup>−</sup>, can be isolated from the reaction of CF<sub>3</sub><sup>−</sup> with the formates, they further undergo a solvated Riveros reaction with the alkyl formate precursor to produce [ROHCF<sub>3</sub>ROH]<sup>−</sup>, a cluster of three molecules (eq 3, Scheme 1).<sup>37</sup> These results are consistent with the flowing afterglow results.<sup>34</sup> Attempts to obtain [ROHCF<sub>3</sub>]<sup>−</sup> from the exchange reaction of HCF<sub>3</sub> with RO<sup>−</sup>·HOR were not fruitful. Alcohol·alkoxide complexes are sufficiently stable that they do not undergo a solvent switch with HCF<sub>3</sub> (eq 4, Scheme 1).

### Scheme 1



Alkoxide–water complexes, RO<sup>−</sup>·H<sub>2</sub>O, were synthesized from the proton-transfer/elimination reaction of hydroxide with dialkyl ethers (Scheme 2).<sup>38</sup> O<sup>−</sup>· was generated by electron impact upon N<sub>2</sub>O; OH<sup>−</sup> was then produced by the H atom abstraction reaction of O<sup>−</sup>· with either HCF<sub>3</sub> or the alkyl ethers present. The elimination reaction of OH<sup>−</sup> with the alkyl ethers was competitive with proton transfer from HCF<sub>3</sub> at pressure ratios of ether:HCF<sub>3</sub> of ~4:1, so reasonable quantities of RO<sup>−</sup>·H<sub>2</sub>O could be obtained (eq 6, Scheme 2). Alkoxide·water complexes of MeO<sup>−</sup>, EtO<sup>−</sup>, and *i*-PrO<sup>−</sup> were generated from *tert*-butyl

(24) Gatev, G. G.; Zhong, M.; Brauman, J. I. *J. Phys. Org. Chem.* **1997**, *10*, 531–536.

(25) Meot-Ner, M. *J. Am. Chem. Soc.* **1988**, *110*, 3858–3862.

(26) French, M. A.; Ikuta, S.; Kebarle, P. *Can. J. Chem.* **1982**, *60*, 1907–1918.

(27) Fraser, G. T.; Lovas, F. J.; Suenram, R. D.; Nelson, D. D., Jr.; Kemperer, W. *J. Chem. Phys.* **1986**, *84*, 5983–5988.

(28) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. **1988**, *17*, Suppl. 1.

(29) *CRC Handbook of Chemistry and Physics*, 75th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, 1994.

(30) Han, C.-C.; Brauman, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 6491–6496.

(31) Andreades, S. *J. Am. Chem. Soc.* **1964**, *86*, 2003–2010.

(32) Hanst, P. L.; Calvert, J. G. *J. Phys. Chem.* **1959**, *63*, 104.

(33) Wilbur, J. L. Ph.D. Dissertation, Stanford University, 1993.

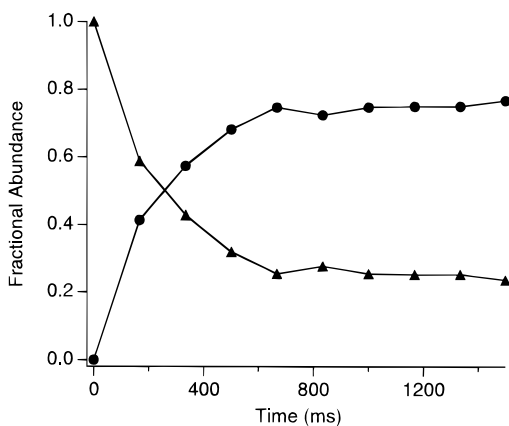
(34) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 7267–7271.

(35) Blair, L. K.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 1057–1060.

(36) DePuy, C.; Grabowski, J. J.; Bierbaum, V. M.; Ingemann, S.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1985**, *107*, 1093–1098.

(37) RO<sup>−</sup>·HOR is also observed, presumably from decomposition of the [ROHCF<sub>3</sub>ROH]<sup>−</sup> product.

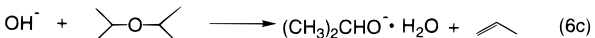
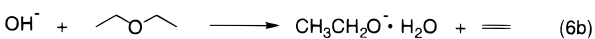
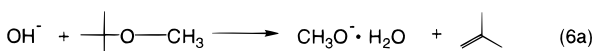
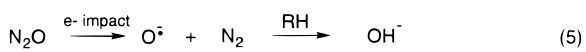
(38) DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 5034–5038.



**Figure 1.** Fractional ion intensities as a function of time until equilibrium for the reaction. MeO<sup>-</sup>·H<sub>2</sub>O + HCF<sub>3</sub> ⇌ [MeOHCF<sub>3</sub>]<sup>-</sup> + H<sub>2</sub>O: ▲, [CH<sub>3</sub>OHCF<sub>3</sub>]<sup>-</sup>; ●, [CH<sub>3</sub>OH<sub>2</sub>O]<sup>-</sup>. P<sub>HCF<sub>3</sub></sub> = 2.2 × 10<sup>-7</sup> Torr, P<sub>H<sub>2</sub>O</sub> = 1.9 × 10<sup>-7</sup> Torr.

methyl ether, ethyl ether, and isopropyl ether, respectively. No side reactions with the alkyl ethers were observed. No other ion–molecule complexes such as [HOHCF<sub>3</sub>]<sup>-</sup> were observed. Equilibrium was found to be measurable between alkoxide complexes of H<sub>2</sub>O and HCF<sub>3</sub> (eq 7, Scheme 2).

### Scheme 2



Deuterium isotope fractionation experiments were performed in a similar manner. The [ROHCF<sub>3</sub>]<sup>-</sup> complexes were synthesized as shown in Scheme 2. The equilibrium constant for exchange of DCF<sub>3</sub> and HCF<sub>3</sub> into the alkoxide complex was then measured (eq 8).



**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 s. A typical plot for the equilibrium between [ROHCF<sub>3</sub>]<sup>-</sup> and RO<sup>-</sup>·H<sub>2</sub>O is shown in Figure 1. 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%). The relative values are more important for our discussion than the absolute values.

The isotopic exchange measurements were performed in a similar manner. To obviate the difficulty of absolute pressure measurements we determined the ratio of DCF<sub>3</sub>/HCF<sub>3</sub> in situ by measuring the ratio of the DCF<sub>2</sub><sup>+</sup>/HCF<sub>2</sub><sup>+</sup> peaks in the positive ion spectra. The ratio was found to be nearly independent of electron-impact energy and delay time of detection. The ratio of ion intensities was also very similar to the ratio of pressures as measured by the ion gauge. The equilibrium

**Table 1.** Equilibrium Constants and Thermochemical Values for the Exchange Reaction<sup>a</sup>

$$\text{RO}^- \cdot \text{H}_2\text{O} + \text{HCF}_3 \rightleftharpoons [\text{ROHCF}_3]^- + \text{H}_2\text{O}$$

RO <sup>-</sup>	K <sub>eq</sub>	ΔG° (kcal/mol)	ΔH° (kcal/mol)	ΔH° <sub>ab initio</sub> (kcal/mol)
MeO <sup>-</sup>	0.29 ± 0.06	0.86 ± 0.1	0.38	0.70
EtO <sup>-</sup>	0.34 ± 0.07	0.75 ± 0.1	0.27	0.60
<i>i</i> -PrO <sup>-</sup>	0.39 ± 0.08	0.65 ± 0.1	0.17	0.60

<sup>a</sup> All values measured at 350 K. ΔH°<sub>ab initio</sub> was calculated at the MP2/6-311++G\*\*//HF/6-311++G\*\* level and corrected to 350 K with vibrational frequencies scaled by 0.89.

**Table 2.** Gas-Phase Acidities

$$\text{AH} \rightleftharpoons \text{A}^- + \text{H}^+$$

AH	ΔH° (kcal/mol)	ΔH° <sub>ab initio</sub> <sup>d</sup> (kcal/mol)
MeOH	381.5 ± 0.1 <sup>a</sup>	383.6
EtOH	378.6 ± 0.8 <sup>b</sup>	379.5
<i>i</i> -PrOH	376.7 ± 0.8 <sup>b</sup>	377.1
<i>t</i> -BuOH	375.9 ± 0.8 <sup>b</sup>	375.8
HCF <sub>3</sub>	377.8 ± 0.5 <sup>c</sup>	380.5

<sup>a</sup> From: Meot-Ner, M.; Siek, L. W. *J. Phys. Chem.* **1986**, *90*, 6687–6690. <sup>b</sup> From Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750–5759. <sup>c</sup> From ref 28 re-anchored to values from footnote b. <sup>d</sup> ΔH°<sub>ab initio</sub> was calculated at the MP2/6-311++G\*\*//HF/6-311++G\*\* level and corrected to 298 K with vibrational frequencies scaled by 0.89.

fractionation factor, Φ, was determined by the method outline above. All of the RO<sup>-</sup>·H<sub>2</sub>O was consumed before the equilibrium constant was measured. The deuterium fractionation factor, Φ (the equilibrium constant for eq 8), is defined in eq 9. The ratios, [M + 1]/[M], were corrected for the contribution from the natural abundance of <sup>13</sup>C in the [M + 1] ion to the [M + 1] peak. We have assigned the errors in Φ based upon the statistical error in the measured values.

$$\Phi = \frac{[\text{RODCF}_3]^- / [\text{ROHCF}_3]^-}{[\text{DCF}_3] / [\text{HCF}_3]} \quad (9)$$

**Theory.** All ab initio calculations were performed with Gaussian94<sup>39</sup> on an IBM RS6000-590. Geometries were optimized at the Hartree–Fock level with the 6-311++G\*\* basis set. All stationary points were characterized by vibrational frequency analyses. MP2 single-point calculations were performed at the HF/6-311++G\*\* geometry to account for electron correlation. Frequencies were scaled by 0.89 for use in thermochemical calculations.<sup>40</sup> This level of theory has been shown to reproduce experimental gas-phase acidities with an error of approximately ±1–2 kcal/mol.<sup>41</sup> The experimental and ab initio gas-phase acidities are given in Table 2. Visualization of electrostatic potential surfaces was performed with Spartan and MacSpartan.<sup>42</sup>

Proton-transfer potential energy surfaces were calculated by optimizing the geometry of the complexes at fixed values of the C–H or O–H distance. MP2 single-point calculations were performed at each of these points along the reaction path.

The calculation of the eigenvalues in model potentials was accomplished with Truhlar's FDBVM program.<sup>43</sup> The program uses the finite difference boundary value method for obtaining the eigenvalues and eigenfunctions of an arbitrary potential function. Model double well potentials were constructed to represent the calculated reaction barrier and energy difference between wells for the proton-transfer reactions.<sup>20</sup> Both fourth- and sixth-order polynomials were used, and

(39) Frisch, M. J.; et al. *Gaussian94RevC.3*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(40) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502–16513.

(41) Smith, B. J.; Radom, L. *Chem. Phys. Lett.* **1995**, *245*, 123–128.

(42) *MacSpartan*; Wavefunction, Inc.: Irvine, 1996.

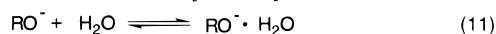
(43) Truhlar, D. G. *J. Comput. Phys.* **1972**, *10*, 123–132.

each gave similar results.<sup>44</sup> The reduced mass of the vibration was taken to be that of hydrogen or deuterium.<sup>45</sup>

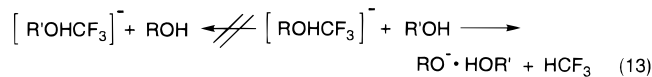
## Results

**RO<sup>-</sup>·H<sub>2</sub>O ⇌ RO<sup>-</sup>·HCF<sub>3</sub>.** The equilibrium constants for exchange of HCF<sub>3</sub> with alkoxide–water complexes, RO<sup>-</sup>·H<sub>2</sub>O (R=Me, Et, *i*-Pr), were measured at 350 K (eq 10, Scheme 3). Experimental values for *K*<sub>eq</sub> and Δ*G*<sup>o</sup> are shown in Table 1. The value of Δ*H*<sup>o</sup> can be derived from Δ*G*<sup>o</sup> if Δ*S*<sup>o</sup> for the exchange reaction is known. However, obtaining accurate estimates of the entropies for ion–molecule complexes is difficult.<sup>17,46</sup> The vibrational modes with the greatest contribution to the entropy are the six low-frequency modes created upon complexation. These modes are very anharmonic and are generally not reproduced accurately by standard ab initio harmonic frequency calculations.<sup>46,47</sup> Due to this difficulty we have chosen to assume the intrinsic Δ*S*<sup>o</sup> for eq 10 is zero and to correct for symmetry only.<sup>48</sup> We expect that this will introduce an error of no more than ±1.0 kcal/mol in the derived value of Δ*H*<sup>o</sup>. The relative error between values should be smaller because the Δ*S*<sup>o</sup> of complexation for these structurally similar complexes should be nearly equivalent. Values for Δ*H*<sup>o</sup> obtained from ab initio calculations agree well with the experimental values (Table 1).

### Scheme 3



**RO<sup>-</sup> + H<sub>2</sub>O ⇌ RO<sup>-</sup>·H<sub>2</sub>O.** We cannot measure the relative fluoroform·alkoxide, [ROHCF<sub>3</sub>]<sup>-</sup>, binding energies directly due to preferential formation of the alcohol·alkoxide, RO<sup>-</sup>·HOR' dimer (eq 13). However, they can be derived via the thermochemical cycle in Scheme 3.



The values of the water complexation energies of the alkoxides are needed to derive the fluoroform complexation energies. The ion–molecule complexation energy of MeO<sup>-</sup> and *t*-BuO<sup>-</sup> to H<sub>2</sub>O has been measured.<sup>18,49</sup> Values for complexes of EtO<sup>-</sup> and *i*-PrO<sup>-</sup> are not available in the literature, and we are unable to determine them experimentally using our instrumentation. However, these values can be estimated or calculated. The binding energies of alcohols to alkoxides are known to follow a linear free energy relationship with the acidity of the alcohol. We expect water binding energies to exhibit similar behavior. Indeed, a plot of the experimentally known RO<sup>-</sup>·H<sub>2</sub>O complexation energies versus the acidity of ROH has a slope of 0.5 similar to the value of 0.4 for alcohol–alkoxide complexes.<sup>17</sup> The gas-phase acidity values used are listed in Table 2. The

(44) Laane, J. *Appl. Spectrosc.* **1970**, *24*, 73–80.

(45) Examination of the normal coordinates shows that this is a reasonable approximation for the systems considered here.

(46) Paul, G. J. C.; Kebarle, P. *J. Phys. Chem.* **1990**, *94*, 5184–5189.

(47) East, A. L. L.; Radom, L. *J. Chem. Phys.* **1997**, *106*, 6655–6674.

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

(49) We believe the literature value for the complexation of energy of *tert*-butoxide to water in ref 18 is too large due to the estimated entropy value. We have assumed here that the difference in Δ*G*<sup>o</sup> of complexation between MeO<sup>-</sup> and *t*-BuO<sup>-</sup> is equal to the difference in Δ*H*<sup>o</sup>.

**Table 3.** Complexation Energies of Alkoxides with Water<sup>a</sup>

RO <sup>-</sup> + H <sub>2</sub> O ⇌ RO <sup>-</sup> ·H <sub>2</sub> O		
RO <sup>-</sup>	Δ <i>H</i> <sup>o</sup> (kcal/mol)	Δ <i>H</i> <sup>o</sup> <sub>ab initio</sub> (kcal/mol)
MeO <sup>-</sup>	-23.9	-23.0
EtO <sup>-</sup>	[-22.3]	-21.5
<i>i</i> -PrO <sup>-</sup>	[-21.2]	-21.0
<i>t</i> -BuO <sup>-</sup>	-20.9	-20.1

<sup>a</sup> Experimental values are from ref 18 and have errors of ±1 kcal/mol; values in brackets are interpolated from experimental values. Δ*H*<sup>o</sup><sub>ab initio</sub> was calculated at the MP2/6-311++G\*\*//HF/6-311++G\*\* level and corrected to 350 K with vibrational frequencies scaled by 0.89.

**Table 4.** Complexation Energies of Alkoxides with Fluoroform<sup>a</sup>

RO <sup>-</sup> + HCF <sub>3</sub> ⇌ [ROHCF <sub>3</sub> ] <sup>-</sup>		
RO <sup>-</sup>	Δ <i>H</i> <sup>o</sup> (kcal/mol)	Δ <i>H</i> <sup>o</sup> <sub>ab initio</sub> (kcal/mol)
MeO <sup>-</sup>	-23.5	-22.3
EtO <sup>-</sup>	[-22.0]	-20.9
<i>i</i> -PrO <sup>-</sup>	[-21.1]	-20.4

<sup>a</sup> Values were derived as described in the text; values in brackets were derived from interpolated values. Δ*H*<sup>o</sup><sub>ab initio</sub> was calculated at the MP2/6-311++G\*\*//HF/6-311++G\*\* level and corrected to 350 K with vibrational frequencies scaled by 0.89.

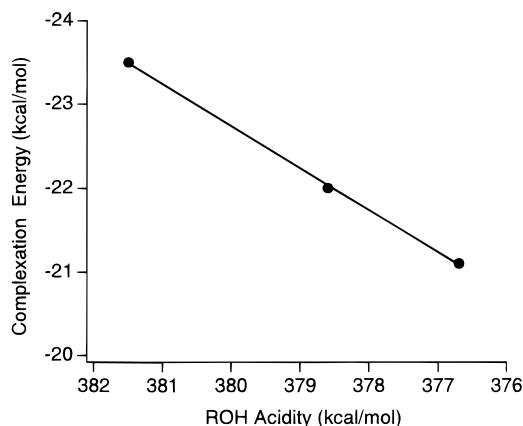
values for the water complexation energies of EtO<sup>-</sup> and *i*-PrO<sup>-</sup> have been obtained by interpolation from this plot and are listed in Table 3.

We have also performed ab initio calculations to determine the binding energies of the RO<sup>-</sup>·H<sub>2</sub>O (R = Me, Et, *i*-Pr, *t*-Bu) complexes (Table 3). The calculated values of Δ*H*<sup>o</sup> for MeO<sup>-</sup>·H<sub>2</sub>O and *t*-BuO<sup>-</sup>·H<sub>2</sub>O are systematically lower than the experimental values (Table 2). One possible source of this discrepancy is the inability to accurately calculate the O–H stretch of water in the ion–molecule complex that is expected to be highly anharmonic.<sup>50,51</sup> This frequency is expected to be red-shifted in the complex, which would lead to an increase in the binding energy because of the change in zero-point energy. However, these discrepancies are small (less than 1 kcal/mol) and the relative values agree well with the experimental values. A plot of the ab initio values versus the ab initio acidities of ROH gives a slope of 0.4 that is in reasonable agreement with the slope of 0.5 from the experimental values. We therefore believe that we can safely use interpolated values from the experimental LFER plot for the water complexation energies of EtO<sup>-</sup> and *i*-PrO<sup>-</sup>.

**RO<sup>-</sup> + HCF<sub>3</sub> ⇌ RO<sup>-</sup>·HCF<sub>3</sub>.** The values of the fluoroform–alkoxide complexation energies can be derived from the thermochemical cycle in Scheme 3. We have used the experimental value of the complexation energy of MeO<sup>-</sup>·H<sub>2</sub>O to derive the HCF<sub>3</sub> binding energy of MeO<sup>-</sup>. Interpolated values of the water complexation energies were used to obtain the HCF<sub>3</sub> binding energies of EtO<sup>-</sup> and *i*-PrO<sup>-</sup>. The values show the expected decrease in binding energy with acidity as seen in other systems (Table 4). The derived values from the thermochemical cycle also compare well with the [ROHCF<sub>3</sub>]<sup>-</sup> complexation energies calculated purely by ab initio methods (Table 4). Again the calculated values are systematically too low compared to the derived values, but the relative values are nearly identical. If the complexation energies are plotted versus

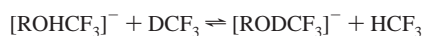
(50) Yates, B. F.; Schaefer, H. F., III; Lee, T. J.; Rice, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 6327–6332.

(51) Del Bene, J. E.; Jordan, M. J. *J. Chem. Phys.* **1998**, *108*, 3205–3212.



**Figure 2.** Alkoxide–fluoroform complexation energies as a function of acidity of ROH. The slope of the least squares line is 0.5.

**Table 5.** Deuterium Fractionation Factors,  $\Phi$ , for Alkoxide–Fluoroform Complexes<sup>a</sup>



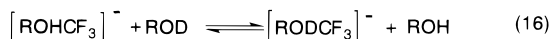
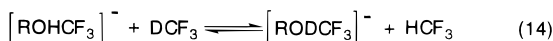
RO <sup>-</sup>	$\Phi$ (HCF <sub>3</sub> /DCF <sub>3</sub> )	$\Phi'$ (ROH/ROD)
MeO <sup>-</sup>	0.57 ± 0.03	[0.37]
EtO <sup>-</sup>	0.68 ± 0.02	[0.44]
<i>i</i> -PrO <sup>-</sup>	0.74 ± 0.02	[0.48]

<sup>a</sup> All values measured at 350 K. Values in brackets were derived as indicated in the text.

the acidity of the alcohol, the slopes of the derived and ab initio values are 0.5 and 0.3, respectively (See Figure 2).

**Fractionation Factors.** The deuterium isotopic fractionation factors,  $\Phi$ , of the [ROHCF<sub>3</sub>]<sup>-</sup> complexes were measured by the equilibrium exchange reaction with DCF<sub>3</sub> and HCF<sub>3</sub> (eq 8). The measured values are shown in Table 5. Fractionation factors, by definition, are measured relative to one of the compounds in the hydrogen-bonded dimer, in our case HCF<sub>3</sub> and DCF<sub>3</sub>. Although we cannot experimentally measure the fractionation factor,  $\Phi'$  (eq 17), relative to ROH and ROD, we can easily derive it from a thermochemical cycle (Scheme 4). We have experimentally measured the equilibrium constant,  $\Phi$ , for eq 14 and can obtain the equilibrium constant for eq 15 from the difference in zero-point energies of HCF<sub>3</sub>/DCF<sub>3</sub> and ROH/ROD.<sup>52</sup> The resulting values of  $\Phi'$  are shown in Table 5.

#### Scheme 4



$$\Phi' = \frac{[\text{RODCF}_3]^- / [\text{ROHCF}_3]^-}{[\text{ROD}] / [\text{ROH}]} \quad (17)$$

#### Discussion

Hydrogen bonds are defined by their unique properties relative to other intermolecular interactions, that is, their strength and structure. We focus here on hydrogen bonds to ions. In solution, ionic hydrogen bonds are characterized spectroscopically by energetic shifts in IR and UV absorption spectra and

large downfield shifts in NMR spectra.<sup>3,4</sup> In the gas phase these techniques are difficult to perform on ionic systems, so hydrogen-bonded complexes have been characterized by their complexation energies ( $\Delta H^\circ$  for eq 18) relative to typical ion–molecule complexes, e.g., 20–30 kcal/mol vs 10–15 kcal/mol.<sup>53</sup>



The magnitude of the complexation energy that an ion–molecule complex must have to be considered as hydrogen bonded is not defined. Most systems that have been studied have large complexation energies.

In the gas phase a linear free energy relationship between the complexation energy and the difference in acidity and basicity of the hydrogen-bonded molecule and ion is often observed.<sup>17,19</sup> The slope from these plots for negative ion complexes such as [ROHF]<sup>-</sup> and [ROHOR']<sup>-</sup> is typically near 0.5.<sup>17,54</sup> McMahon has also derived a predictive model for the complexation energy based on the electronegativities of the heteroatoms, A and B, and acid–base acidities.<sup>19</sup> Because there is a lack of data for complexes that contain dissimilar hydrogen bond donors and acceptors, it is not well understood how acidity and basicity contribute to the hydrogen bond strength. For example, phenylacetylide, whose basicity is comparable to that of alkoxides, forms strong hydrogen-bonded complexes with alcohols, but its complex with phenylacetylene has not been observed.<sup>17</sup> By studying hydrogen-bonded complexes of dissimilar ions and neutrals we can begin to understand the basis of these relationships.

To understand the factors which contribute to the stability of the complex, the identity of the hydrogen bond donor and acceptor within the complex must be known. The structures of hydrogen-bonded intermediates of proton transfer reactions are generally assumed to reflect the acidity difference of the endpoints of the proton-transfer reaction. That is, the structure is A<sup>-</sup>·HB if AH is the stronger acid (compared to HB), and AH·B<sup>-</sup> if BH is the stronger acid. This assumption has been tested in several ways including photodetachment spectroscopy,<sup>55–57</sup> isotopic equilibrium effects,<sup>58</sup> and computational analysis.<sup>59–61</sup> Proton-transfer reactions of various alcohols with F<sup>-</sup> have been widely studied. Deuterium isotopic fractionation experiments and computational studies suggest that the potential energy surface (PES) near the intermediates is nearly flat,<sup>58,61</sup> indicating that the two possible complexes RO<sup>-</sup>·HF and ROH·F<sup>-</sup> have similar energies. Photodetachment spectroscopy has shown that despite the flatness of the PES, the structure of the intermediate complex is influenced by the acidity difference of the two reactants.<sup>56,62</sup> The isolated intermediate resembles

(53) Note that the difference between these values is ~10–15 kcal/mol, which is similar to the estimated strength of the hydrogen bonds in solution, refs 13 and 16.

(54) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1983**, *105*, 2944–2950.

(55) Moylan, C. R.; Dodd, J. A.; Han, C.-C.; Brauman, J. I. *J. Chem. Phys.* **1987**, *86*, 5350–5357.

(56) Mihalick, J. E.; Gatev, G. G.; Brauman, J. I. *J. Am. Chem. Soc.* **1996**, *118*, 12424–12431.

(57) de Beer, E.; Kim, E. H.; Neumark, D. M.; Gunion, R. F.; Lineberger, W. C. *J. Chem. Phys.* **1995**, *99*, 13627–13636.

(58) Wilkinson, F. E.; Szulejko, J. E.; Allison, C. E.; McMahon, T. B. *Int. J. Mass. Spectrom. Ion Proc.* **1992**, *117*, 487–505.

(59) Cao, H. Z.; Allavena, M.; Tapia, O.; Evleth, E. M. *J. Phys. Chem.* **1985**, *89*, 1581–1592.

(60) Gronert, S. *J. Am. Chem. Soc.* **1993**, *115*, 10258–10266.

(61) Wladkowski, B. D.; East, A. L. L.; Mihalick, J. E.; Allen, W. D.; Brauman, J. I. *J. Chem. Phys.* **1993**, *100*, 2058–2088.

(62) Bradforth, S. E.; Arnold, D. W.; Metz, R. B.; Weaver, A.; Neumark, D. M. *J. Phys. Chem.* **1991**, *95*, 8066–8078.

(52) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies Consolidated*; National Standard Reference Data Service: Washington, 1972; Vol. I.

$\text{RO}^- \cdot \text{HF}$  when ROH is a stronger acid than HF and resembles  $\text{ROH} \cdot \text{F}^-$  when HF is the stronger acid. This relationship between the structure of the intermediates and the thermodynamic endpoints is not always the case, however. In the proton-transfer reaction of  $\text{H}^-$  with  $\text{H}_2\text{O}$ , the most stable intermediate has been shown to be  $\text{H}^- \cdot \text{H}_2\text{O}$  although  $\text{H}_2\text{O}$  is a stronger acid than  $\text{H}_2$ .<sup>57,63</sup> The  $\text{H}_2 \cdot \text{OH}^-$  complex is observed to be in equilibrium, but only comprises a small fraction of the population.<sup>57</sup> This suggests the structure of the intermediate is not solely determined by the acidity difference.<sup>64</sup> To understand these effects we have attempted to fully characterize the hydrogen-bonded complexes of  $\text{HCF}_3$  and several alkoxides.

**Strength.** The complexation energies between  $\text{RO}^-$  and  $\text{HCF}_3$  range from  $-21.1$  to  $-23.5$  kcal/mol (Table 4). These energies are larger than those for typical ion–dipole complexes (10–15 kcal/mol). For example, the binding energy of  $\text{Cl}^-$  to  $\text{HCF}_3$  is 16 kcal/mol.<sup>28</sup> The fluoroform complexation energies to alkoxides are almost the same as those for  $\text{H}_2\text{O}$  to alkoxides. However, the  $\text{HCF}_3$  complex energies are not as large as the complexation energies of alcohol·alkoxides or alcohol·phenylacetylide complexes which are near 25–28 kcal/mol. Therefore the complexes,  $[\text{ROHCF}_3]^-$ , can be said to exhibit a reasonable, but not exceptionally strong, hydrogen bond.

The complexation energies follow the basicity of the alkoxides similarly to the LFER seen for other hydrogen-bonded complexes (Figure 2). The complexation energy of  $[\text{EtOHCF}_3]^-$ , where the acidities of the two molecules are nearly matched ( $\Delta\Delta H_{\text{acid}}^\circ = 0.8$  kcal/mol), does not show any enhanced stabilization.<sup>13,14</sup> The slope of the least-squares fit line is 0.5, which is equivalent to that for the water·alkoxide complexes (0.5) and also similar to the slope (0.4) for alcohol·alkoxide complexes.<sup>17</sup> The values for the fluoroform·alkoxide complexes cover a limited range, so we do not wish to make a quantitative comparison of these slopes. We only note here that there is a striking similarity despite the substantial structural differences between fluoroform and an aliphatic alcohol.

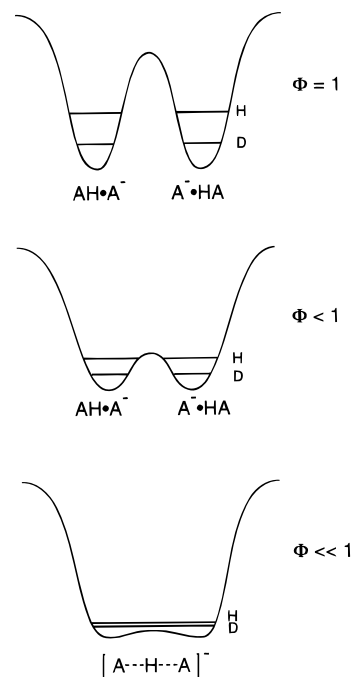
**Structure.** To probe the structure of the  $[\text{ROHCF}_3]^-$  complexes we have carried out deuterium fractionation experiments. The value of the fractionation factor,  $\Phi$ , arises from the differences of the zero-point energies (ZPE) in the separated reactants and in the complex.<sup>20</sup> The enthalpy change of the exchange reaction (eq 8) is approximately equal to the change in ZPE (eq 19).

$$\Delta H^\circ \cong (\text{ZPE}_{[\text{ROHCF}_3]^-} - \text{ZPE}_{[\text{ROHCF}_3]^-}) - (\text{ZPE}_{[\text{DCF}_3]^-} - \text{ZPE}_{[\text{HCF}_3]^-}) \quad (19)$$

The difference in zero-point energy of the C–H bond in the free molecule and in the complex can be understood from a simple one-dimensional model corresponding to the proton-transfer reaction coordinate.<sup>20</sup> If the barrier to proton transfer is high, the potential of the stretch is nearly harmonic and therefore the vibrational frequency is not strongly perturbed in the complex. The fractionation factor in this case would be 1.0. As the barrier between the two complexes decreases, the stretching frequency becomes more anharmonic and the difference in ZPE between H and D decreases<sup>51,65,20</sup> (Figure 3). In

(63) Miller, T. M.; Viggiano, A. A.; Stevens-Miller, A. E.; Morris, R. A.; Henchman, M.; Paulson, J. F.; Doren, J. M. *V. J. Chem. Phys.* **1994**, *100*, 5706–5714.

(64) There are similar interesting observations involving proton-bound cluster ions where the structure is determined by interactions between multiple protonation sites of differing basicity. See: Böhringer, H.; Arnold, F. *Nature* **1981**, *290*, 321–322. Graul, S. T.; Squires, R. R. *Int. J. Mass. Spectrom. Ion Proc.* **1989**, *94*, 41–61.



**Figure 3.** Zero-point energies of H and D atoms in double well potentials with varying barrier heights.

this case the fractionation factor would decrease and reach a lower limit as the barrier becomes negligible compared to the zero-point energy.<sup>20,65</sup> The contributions due to other normal modes, such as bending, are expected to be small compared to that of the C–H stretch.<sup>66</sup>

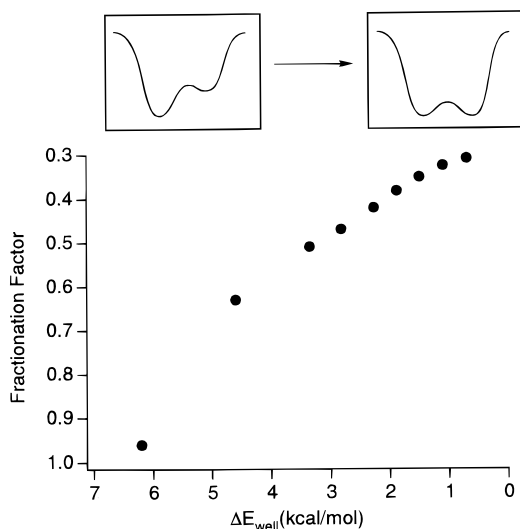
The value of the fractionation factor is also affected by symmetry aspects of the potential surface. For systems with a single well potential, the fractionation factor should be nearly constant for a series of complexes. McMahon and co-workers have shown that the fractionation factors for  $[\text{ROHF}]^-$  are nearly constant over the range of alcohol acidities.<sup>58</sup> This is consistent with quantum calculations which predict that these systems have a very flat potential surface near the hydrogen-bonded complexes.<sup>61</sup> For a double well potential, the fractionation factor is expected to increase as the difference in the energy between the wells increases. As the difference in energy between the wells increases, a concomitant increase in barrier height is also expected.<sup>67</sup> This increase in barrier should cause the potential of the H stretch to become more harmonic, and thus the fractionation factor should approach the limiting value of 1. To substantiate this qualitative prediction, model calculations were performed to calculate the anharmonic H/D stretching frequency in a double well (see Figure 4). These calculations indeed show a trend to larger values of  $\Phi$  with a larger difference in energy between wells. Similar results have been obtained by Kreevoy and Liang,<sup>20</sup> and also Huskey.<sup>65</sup>

To analyze the possible structure of the  $[\text{ROHCF}_3]^-$  complexes, we first examine the magnitudes of the measured fractionation factors. If the PES has a high barrier and the structure of the complex is  $\text{RO}^- \cdot \text{HCF}_3$ , we would expect the fractionation factor relative to  $\text{HCF}_3/\text{DCF}_3$ ,  $\Phi$ , to have a value near 1.0. If the structure of the complex is  $\text{ROH} \cdot \text{CF}_3^-$  and the barrier is high we would expect the fractionation factor relative to  $\text{ROD}/\text{ROH}$ ,  $\Phi'$ , to have a value near 1.0. For a low barrier complex,  $\Phi$  and  $\Phi'$  should both be less than 1.0 as the difference

(65) Huskey, W. P. *J. Am. Chem. Soc.* **1996**, *118*, 1663–1668.

(66) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265–273.

(67) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155–196.



**Figure 4.** Fractionation factors calculated for H and D in asymmetric double-well potentials relative to  $HCF_3/DCF_3$  with varying differences in energy between the two minima ( $\Delta E_{\text{well}}$ ).

in zero-point energies of the protiated and deuterated complex should be smaller than the difference in zero-point energies between  $HCF_3$  and  $DCF_3$  or  $ROD$  and  $ROH$ .

The barriers on the PES's for the proton-transfer reactions between  $RO^-$  and  $HCF_3$  are small, as indicated by the high efficiencies of these reactions.<sup>68</sup> The fractionation factors should therefore reflect the limiting case of the low barrier. The values of  $\Phi$ , the fractionation factor relative to  $HCF_3/DCF_3$ , for the  $[ROHCF_3]^-$  complexes are given in Table 5. All values are less than 1.0 as expected for a low-barrier PES. The values of  $\Phi'$ , the fractionation factor relative to  $ROH/ROD$ , are also given in Table 5. The values of  $\Phi'$  are lower than those for  $\Phi$  because the difference in zero-point energy between  $ROH$  and  $ROD$  is larger than that for  $HCF_3$  and  $DCF_3$ . These values can be compared to those for  $MeO^- \cdot HOME$ <sup>69,70</sup> and  $EtO^- \cdot HOEt$ <sup>71</sup> which are both near 0.40. The absolute magnitude of the fractionation factor does not indicate the structure of the ion-molecule complex directly in our case.

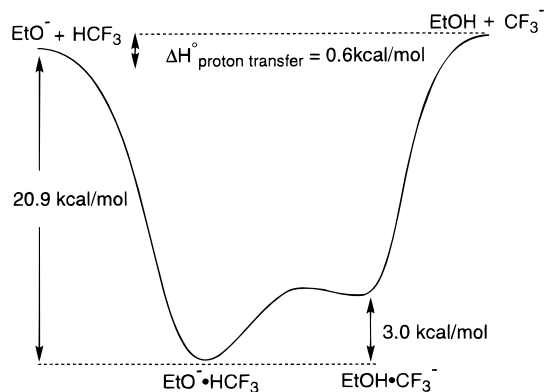
The trend in the fractionation factors suggests that the structure of these three complexes is similar. The experimental values of  $\Phi$  for the  $[ROHCF_3]^-$  complexes decrease with decreasing acidity of the alcohol. This behavior is consistent with a model of the proton-transfer potential surface as a double well; as the difference in energy between the wells decreases, the difference in zero-point energies for H and D in the complex decreases causing the fractionation factor to decrease (see Figure 4). The lowest fractionation factor should occur when the two wells have the same energy, that is, the PES where the vibration is the most anharmonic. The fractionation factor should then begin to increase as the difference in energy between wells increases (i.e., the plot should be nearly symmetric around matched energies).<sup>65</sup> The agreement with our model calculations is not expected to be quantitative due to the simplicity of our model.<sup>72</sup> From simple considerations of the acidities, we

(68) We have measured the rate constant for the  $EtO^- + HCF_3$  proton-transfer reaction. Its value is  $4.11 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and the collision capture rate from the Su-Chesnavich model is  $1.65 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . S. L. Craig and M. L. Chabinyk, unpublished results.

(69) Weil, D. A.; Dixon, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 6859–6865.

(70) Barlow, S. E.; Dang, T. T.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1990**, *112*, 6832–6838.

(71) Ellenberger, M. R.; Farneth, W. E.; Dixon, D. A. *J. Phys. Chem.* **1981**, *85*, 4–7.



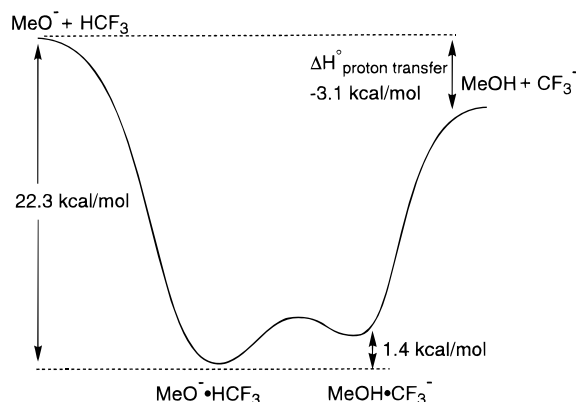
**Figure 5.** Calculated potential energy surface for the reaction of  $EtO^-$  with  $HCF_3$  at the MP2/6-311++G\*\*//HF/6-311++G\*\* level of theory. Relative energies include corrections from zero-point energies.

would expect the structure of the  $i\text{-PrO}^-$  complex to resemble  $i\text{-PrO}^- \cdot HCF_3$ , as isopropyl alcohol is more acidic than fluoroform by 1.1 kcal/mol.<sup>28</sup> Since ethanol and fluoroform have nearly matched acidities ( $HCF_3$  is 0.8 kcal/mol more acidic, based on  $\Delta\Delta H_{\text{acid}}^\circ$ ), we might assume that the two structures,  $EtO^- \cdot HCF_3$  and  $EtOH \cdot CF_3^-$ , have similar energies. However,  $\Phi$  is smaller for  $[MeOHCF_3]^-$  than for  $[EtOHCF_3]^-$ . Our model predicts that the fractionation factor should reach a minimum when the wells have equal energies and then begin to increase as the difference in energy increases. This suggests that the two structures,  $EtO^- \cdot HCF_3$  and  $EtOH \cdot CF_3^-$ , do not have equal energies and that  $EtO^- \cdot HCF_3$  is more stable. The observation that the fractionation factor is lowest for  $[MeOHCF_3]^-$ , where the acidities are not matched, suggests that the two structures,  $MeO^- \cdot HCF_3$  and  $MeOH \cdot CF_3^-$ , have similar energies (or at least are closer in energy than for the  $EtO^-$  complex). We believe that the continual decrease in fractionation factor with difference in acidity indicates that all of the complexes have the  $RO^- \cdot HCF_3$  structure.

To further investigate the structure of these complexes we performed ab initio calculations to map the proton-transfer potential energy surfaces. The calculated ab initio potential energy surface for the proton-transfer reaction between  $EtO^-$  and  $HCF_3$  is shown in Figure 5. Although the proton transfer is nearly thermoneutral, the complexes have different stabilities. The complex with the structure  $EtO^- \cdot HCF_3$  is calculated to be more stable than  $EtOH \cdot CF_3^-$  by 3.0 kcal/mol. For the proton-transfer reaction of  $MeO^-$  with  $HCF_3$ , the  $MeO^- \cdot HCF_3$  complex is more stable by 1.4 kcal/mol despite  $MeOH$  being 3.1 kcal/mol less acidic than  $HCF_3$  (see Figure 6). With this energy difference reasonable populations of both structures will be present, but  $MeO^- \cdot HCF_3$  should be dominant. The  $i\text{-PrO}^- \cdot HCF_3$  complex is calculated to be more stable than  $i\text{-PrOH} \cdot CF_3^-$  by 4.8 kcal/mol. We believe these calculations are consistent with all the experimental data.<sup>73</sup> The calculated well depths for the  $RO^- \cdot HCF_3$  complexes agree with our experimentally determined values better than those for  $ROH \cdot CF_3^-$ . The calculated barriers are low, consistent with the magnitude of the fractionation factors and kinetic data. The trend in the fractionation factors suggests a changing double well potential

(72) The one-dimensional model may not produce quantitatively accurate vibrational frequencies, refs 50 and 51, and also neglects the other modes, such as bending, that are affected by isotopic substitution. However, these effects are expected to be small compared to the shift of the H/D stretching frequency, ref 66.

(73) Fluoroform is calculated to be less acidic than ethanol by 1.0 kcal/mol at this level of theory compared to the experimental difference of  $-0.8$  kcal/mol. This deficiency should not affect the conclusions from the calculated PES's.



**Figure 6.** Calculated potential energy surface for the reaction of  $\text{MeO}^-$  with  $\text{HCF}_3$  at the MP2/6-311++G\*\*//HF/6-311++G\*\* level of theory. Relative energies include corrections from zero-point energies.

energy surface as seen in the calculations.  $\text{RO}^- \cdot \text{HCF}_3$  is the only structure consistent with all the data.

The calculated barrier in these proton-transfer reactions is small in agreement with the observation of rapid proton-transfer kinetics in these systems.<sup>68</sup> The barrier is high enough for these reactions, however, so that the ground-state wave function of the minimum energy complex would be expected to be localized in the  $\text{RO}^- \cdot \text{HCF}_3$  well, based on our estimates of the C–H stretching frequency. The PES for the reaction of  $\text{H}^-$  with  $\text{H}_2\text{O}$  has been widely studied,<sup>57,74</sup> and is calculated to have a small barrier, about 3.5 kcal/mol higher than the minimum energy complex. In this case, 2-D discrete variable representation calculations suggest the wave function is localized in the  $\text{H}^- \cdot \text{H}_2\text{O}$  well.<sup>57</sup> The complexes studied here should behave similarly. In contrast, while the  $\text{ROH} \cdot \text{CF}_3^-$  structure is calculated to be a stationary point on the potential surface, the zero-point energy is high enough that hydrogen should be able to freely access the  $\text{RO}^- \cdot \text{HCF}_3$  structure.

**Conclusions.** We believe our data require the structure of all three ( $\text{MeO}^-$ ,  $\text{EtO}^-$ ,  $i\text{-PrO}^-$ ) proton-transfer complexes to be  $\text{RO}^- \cdot \text{HCF}_3$ . For the case of nearly matched acidities ( $\text{EtO}^-$ ) the two intermediates have substantially different energies. The  $\text{MeO}^- \cdot \text{HCF}_3$  complex is especially striking, because this is a case where the acidity difference between the reactants does not determine the structure of the hydrogen-bonded complexes in the reaction. In other words, although  $\text{HCF}_3$  is a stronger acid than  $\text{MeOH}$ , this acidity difference is not reflected in the structure of the hydrogen-bonded complex.

Our results can be rationalized by examining the ability of the ions and neutrals to respectively accept and donate hydrogen bonds. The electrostatic surface of the alkoxides shows that the charge is localized mainly on the oxygen.<sup>75</sup> Conversely,  $\text{CF}_3^-$  gains its stability as an anion by polarizing the charge

away from the carbon into the fluorine atoms. As the hydrogen bond donor approaches the ion, it sees a lower effective charge in the case of  $\text{CF}_3^-$  than for the alkoxides. This can also be understood based on the larger electron affinity ( $\sim 2\text{--}3$  kcal/mol) of  $\text{CF}_3^-$  relative to the alkoxy radicals.<sup>28</sup> Because  $\text{CF}_3^-$  is able to internally stabilize its charge effectively by delocalization, it is not stabilized as much as an alkoxide by a hydrogen bond. Thus, the hydrogen bond accepting ability of the anions is different.<sup>76</sup> To examine the donating abilities of  $\text{HCF}_3$  and  $\text{ROH}$ , we can consider the stability of ion–molecule complexes where the molecules are expected to be the hydrogen bond donor.  $\text{EtOH}$  is a better hydrogen bond donor than  $\text{HCF}_3$  by 4.1 kcal/mol, based on their  $\text{F}^-$  affinities,<sup>54</sup> and the  $\text{EtO}^- \cdot \text{HCF}_3$  complex readily reacts with  $\text{EtOH}$  to form  $\text{EtO}^- \cdot \text{HOEt}$ . On the basis of  $\text{EtOH}$  we can characterize the alcohols as generally being better hydrogen bond donors than  $\text{HCF}_3$ . Even so,  $\text{CF}_3^-$  is such a poor hydrogen bond acceptor that the structure  $\text{EtO}^- \cdot \text{HCF}_3$  is calculated to be 3 kcal/mol more stable than  $\text{EtOH} \cdot \text{CF}_3^-$ . In short, in contrast to alcohols which are good hydrogen bond donors and whose conjugate bases are good acceptors, fluoroform is a reasonably good donor, but its conjugate base is a poor acceptor.

Our results indicate that care must be taken in analyzing data from studies of hydrogen-bonded complexes. The ability to donate and accept hydrogen bonds may not be a simple function of the acid–base properties of the molecule. If generalizations are to be made from ion–molecule complexation energies about the hydrogen bond accepting and donating abilities of ions and neutrals, the structure of the complex must be known.

## Summary

We have studied the hydrogen-bonded complexes on the proton-transfer surface of several alkoxides with fluoroform. The ion–molecule complexes are strongly bound and are best described as hydrogen bonded. The structures of the complexes have been studied by isotopic fractionation equilibria and by ab initio calculations. Our data show that the structure of these complexes does not reflect the difference in acidity of the two acids. This is in contrast to the usual assumption that acidity determines structure. The difference can be understood in terms of electrostatics in the isolated acid and base and their influence on the structure of the complexes.

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(75) Wiberg, K. B. *J. Am. Chem. Soc.* **1990**, *112*, 3379–3385.

(76) Electrostatics do not provide a quantitative means to calculate the hydrogen bond strength since the charge distributions are certainly perturbed at the close range of interaction of the ion and neutral. They do, however, provide a useful model to interpret the energy difference between the two isomeric hydrogen bonded complexes.

(74) Chalasinski, G.; Kendall, R. A.; Simons, J. *J. Chem. Phys.* **1987**, *87*, 2965–2975.