Table I. Protonolysis Reactions of Silyl Hydride Anions, 298 K

	reference acids[a]					
anion	EtOH (376.1)	MeOH (381.4)	H_2O (390.7)	D_2O (392.9)	NH_3 (403.6)	inference[b]
SiH_5^- (**1**)	+	+	–	–	–	$18.0 \le HA \le 26.9$
n-$C_5H_{11}SiH_4^-$ (**2**)	+	+	+	+	–	$5.3 \le HA \le 16.3$
$Et_3SiH_2^-$ (**3**)	+	+	+	+	–	$4.7 \le HA \le 15.6$

[a] $\Delta H_{acid}(HX)$ shown in parentheses in kcal/mol.[12] A + sign indicates occurrence of protonolysis and formation of the corresponding conjugate base anion. [b] Estimated limits on the hydride affinity (HA) of the corresponding neutral silane in kcal/mol. Correction factors which take into account changes in rotational and translational entropy have been incorporated.

of the thermochemical cycle in Scheme I, where $HA(R_4Si)$ is the hydride affinity of the silane $D[R_4Si{-}H^-]$ and $\Delta H_{acid}(HX)$ and $\Delta H_{acid}(H_2)$ are known quantities.[12] Thus, by monitoring the occurrence or nonoccurrence of reaction 4 for a particular silyl hydride and a series of acids of varying acidity, one can derive limits on the hydride affinity of the silane. Table I presents the results of such "bracketing" experiments for three reactant ions. Our experimentally derived limits on the hydride binding energies are in good agreement with the computed values for SiH_4 reported by Baybutt (18.6 kcal/mol, HF),[16] Wilhite and Spialter (16.9 kcal/mol, HF),[17] Keil and Ahlrichs (20.3 kcal/mol, PNO CI),[18] and most recently by Schleyer (18.3 kcal/mol, MP4/6-31++G**).[19] Hydride affinities of this magnitude are among the lowest known for any neutral molecule and are comparable to those of NH_3 (8 kcal/mol),[20] H_2O (16 kcal/mol),[21] and benzene (25 kcal/mol).[22]

The facility with which the silyl hydride ions undergo binary hydride transfer reactions combined with their ready adaptability to isotope labeling makes them ideal systems for investigating the structures and fluxional behavior of isolated 10-Si-5 negative ions. Small Berry pseudorotational barriers have been computed for SiH_5^- (ca. 2.7 kcal/mol)[17,18] and measured experimentally for 10-Si-5 phenyl siliconates in solution.[4,23] Therefore, one may anticipate that the hydrogens in **1**–**3** undergo rapid intramolecular scrambling once the ions are formed. To test this, we have generated in situ monodeuterated alkylsilyl hydride ions using D^- (from ND_3) in conjunction with reaction 1. Addition of CO_2 to the system as a convenient hydride acceptor is followed by determination of the *primary* relative yields of HCO_2^- and DCO_2^- products. In the absence of a kinetic isotope effect for transfer of H^- vs. D^-, chemical equivalence of the hydrogens in the reactant ions would be indicated by statistical yields of HCO_2^- and DCO_2^-. The results for ions **2**-*d* and **3**-*d* are shown below (eq 5 and 6),

$$\mathrm{Et_3SiH} \xrightarrow{\mathrm{D^-}} \underset{\mathbf{3}\text{-}d}{\mathrm{Et_3SiHD^-}} \xrightarrow{\mathrm{CO_2}} \underset{68\%}{\mathrm{HCO_2^-}},\ \underset{32\%}{\mathrm{DCO_2^-}} \tag{5}$$

$$n\text{-}\mathrm{C_5H_{11}SiH_3} \xrightarrow{\mathrm{D^-}} \underset{\mathbf{2}\text{-}d}{n\text{-}\mathrm{C_5H_{11}SiH_3D^-}} \xrightarrow{\mathrm{CO_2}} \underset{86\%}{\mathrm{HCO_2^-}},\ \underset{14\%}{\mathrm{DCO_2^-}} \tag{6}$$

where the indicated branching ratios have been corrected for the natural isotope distributions in each ion and the contribution to the HCO_2^- yield from the unavoidable presence of unlabeled reactant ion.[24] An isotope effect is immediately evident since the determined yields deviate significantly from the 1:1 and 3:1 statistical values. However, the deviation is a *constant* $k_H/k_D = 2.1$ for the two systems, so we may conclude that complete scrambling of H and D has occurred in the silicon ions prior to the probe reaction with CO_2. Further experiments with $Et_2SiH_2D^-$, SiH_4D^-, and other isotopomers are in progress to confirm this finding.

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Proton Transfer as a Function of Hydration Number and Temperature: Rate Constants and Product Distributions for $OH^-(H_2O)_{0,1,2,3}$ + HF at 200–500 K

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Proton-transfer reactions which are exothermic in the gas phase are exceedingly efficient—most reacting at essentially every collision.[6–10] Several studies have shown how this extreme reactivity is influenced by solvation in the gas phase at 300 K.[8,9,11–16] Here we report how hydration influences the rate constants *and* the product distributions of the reaction

$$OH^- + HF = H_2O + F^- \qquad \Delta H^\circ = -19.5\ \text{kcal/mol}^{17} \tag{1}$$

throughout the temperature range 200–500 K. Such studies in the gas phase—where the solvation number is systematically changed—examine the role of solvate in the transfer of protons.[18]

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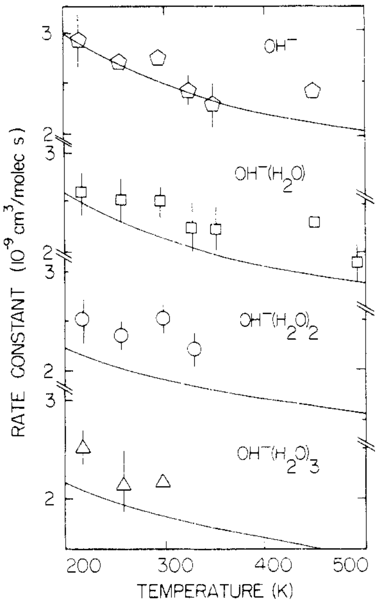

Figure 1. Rate constants for the reactions $OH^-(H_2O)_{0,1,2,3}$ + HF as a function of temperature. For each reaction, data points are compared with theoretical predictions, see text.

Reaction 1—a proton-transfer reaction involving only four atoms—has been studied in a selected ion flow tube (SIFT)[19] in the temperature range 200–500 K. Figure 1 shows how the experimental rate constants (each a mean of at least three determinations) decrease monotonically with increasing temperature. The data agree, within the limits of experimental error, with theoretical predictions for collision rate constants, shown as solid lines.[20,21] These are derived by using the adiabatic capture model (ACCSA) due to Clary:[22] this model has already shown impressive predictive success for proton-transfer reactions in this temperature range.[23] We therefore conclude that the temperature dependence shown in Figure 1 is that of the physical collision efficiency and not that of the chemical reaction efficiency. Proton transfer, efficient at 300 K,[6–10] is efficient throughout 200–500 K.[23,24]

The effect of hydration on reaction 1 is also indicated in Figure 1, where rate constants are shown for the hydroxide ion hydrated with one, two, and three water molecules. Agreement between experiment and theory is seen to be similar for the hydrated and for the unhydrated reactants.[25] Proton transfer occurs on essentially every collision throughout the range of hydration[8–16] *and* temperature[26] studied.

Hydrating the reactant gives identical reaction efficiencies: in contrast, it gives different reaction products. In Figure 2, the product distributions[27] are reported as branching ratios, and reaction enthalpies[28] are also shown for each possible channel.

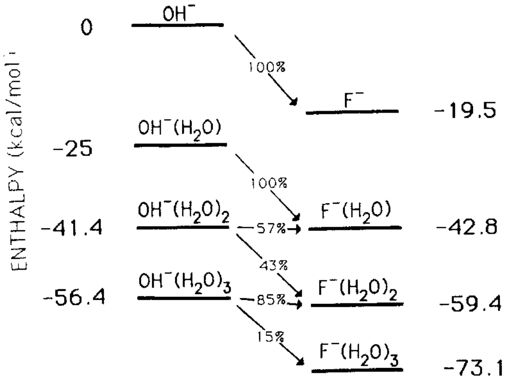

Figure 2. Enthalpy diagram for the reactants (left column) and for the products (right column), identified by the ionic species. Relative enthalpies[28] yield reaction enthalpies by subtraction. Experimental product distributions (independent of temperature) are reported with error limits of 0.25% for $OH^-(H_2O)$, ±5% for $OH^-(H_2O)_2$, and ±10% for $OH^-(H_2O)_3$.

Because the reactions are so efficient, they must be exothermic. For example, $OH^-{\cdot}H_2O$ gives $F^-{\cdot}H_2O$ ($\Delta H° = -17.8$ kcal/mol) exclusively and no F^- ($\Delta H° = +5.5$ kcal/mol). (Our shorthand notation for the reaction $OH^-{\cdot}H_2O + HF \rightarrow F^-{\cdot}H_2O + H_2O$ is $1 \rightarrow 1$, indicating ionic solvation numbers.) For $OH^-(H_2O)_2$, two reactions are possible: $2 \rightarrow 1, 2$, and for $OH^-(H_2O)_3$, there is also a choice: $3 \rightarrow 2, 3$. In both cases, the preferred channels, $2 \rightarrow 1$ and $3 \rightarrow 2$, are given by a simple *propensity rule*: The most efficient channel is the least exothermic, yielding the ionic product with the minimum number of solvate molecules.[12,15,16]

Up to three molecules of water have been observed to transfer efficiently from ionic reactant to ionic product, in order to drive the proton-transfer reaction. These experiments demonstrate solvate participation in proton transfer in the *absence* of solvent. They reflect, in the gas phase, what Grunwald's NMR studies demonstrated in solution over 2 decades ago.[18]

When a solvate molecule is transferred, a proton comes *to* the ionic reactant (or base) and a water molecule leaves *from* it (formally an OH^- transfer).

$$HOH{\cdot}\underset{H}{O^-} + HF \rightarrow [HOH{\cdot}\underset{H}{O^-}{\cdot}HF] \rightarrow HOH + \underset{H}{OH}{\cdot}F^-$$

Within the transition state, the transferred water molecule is at the center of charge. Concomitant transfer of solvate and negative charge (from left to right) is an efficient pathway of low energy because solvate and charge are never separated. This is in marked contrast to the nucleophilic displacement reactions described in the accompanying communication.[29]

Consider the following mechanism. Initially a substantial solvation energy (~15 kcal/mol) binds the HF to the ion within the intermediate,[28] then proton transfer within the intermediate liberates reaction exothermicity as excitation energy, and finally, to the maximum extent possible, solvate water molecules are "boiled off".[9,11,30] According to this mechanism, channels $2 \rightarrow 2$ and $2 \rightarrow 1$ result from the sequential loss of one and two waters, respectively, from the intermediate: $F^-(H_2O)_3 \rightarrow F^-(H_2O)_2 \rightarrow F^-{\cdot}H_2O$. If, in the loss of the first water, more than a total of 1.4 kcal/mol is released as relative translational energy and excitation energy in the expelled water, loss of a second water becomes endothermic: the experimental result is that 43% lose only one water. The mechanism predicts that the channels $3 \rightarrow 3$ and $3 \rightarrow 2$ follow the sequence $F^-(H_2O)_4 \rightarrow F^-(H_2O)_3 \rightarrow F^-(H_2O)_2$. Here "loss" of 3.0 kcal/mol in the expulsion of the first water makes the loss of the second water endothermic, and here only 15% lose only one water. The experimental product distributions are therefore qualitatively consistent with the predictions of the "boil-off" model.[30]

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Registry No. OH^-, 14280-30-9; HF, 7664-39-3; $OH^-(H_2O)$, 23138-14-9; $OH^-(H_2O)_2$, 34118-36-0; $OH^-(H_2O)_3$, 34118-37-1.

Supplementary Material Available: Table of numerical values of experimental and theoretical rate constants shown in Figure 1 (1 page). Ordering information is given on any current masthead page.

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Nucleophilic Displacement as a Function of Hydration Number and Temperature: Rate Constants and Product Distributions for $OD^-(D_2O)_{0,1,2}$ + CH_3Cl at 200–500 K

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Nucleophilic displacement reactions which are exothermic do not react on every collision in the gas phase.[6,7] They exhibit a negative temperature dependence, rate constants *decreasing* with *increasing* temperature,[8] and reaction at 300 K is quenched dramatically by the addition of only one–three solvate molecules.[9] In each respect nucleophilic displacement differs from proton transfer, as contrasted in the companion paper.[10] Here we report how hydration influences the rate constant *and* the product distribution of the nucleophilic displacement reaction

$$OD^- + CH_3Cl = CH_3OD + Cl^- \qquad \Delta H° = -50 \text{ kcal/mol}^{11} \tag{1}$$

within the temperature range 200–500 K. Such data invite interpretation using hypersurfaces calculated for hydrated reactants.[12]

Rate constants for reaction 1 have been measured with a selected ion flow tube (SIFT), using techniques similar to those used in the companion study.[10] Because the $OH^-(H_2O)$ reactant and the $^{35}Cl^-$ product have the same mass-to-charge ratio (m/e = 35), perdeuterated anions, produced from D_2O in the ion source, were used throughout. Rate constants, for the process $OD^-(D_2O)_n$ + CH_3Cl → products, were measured for the mono- and dihydrate (n = 1, 2) but were too small to measure for n = 3.[13] The data at 300 K agree, within ±30%, with data obtained by Bohme and colleagues using the flowing afterglow technique.[9]

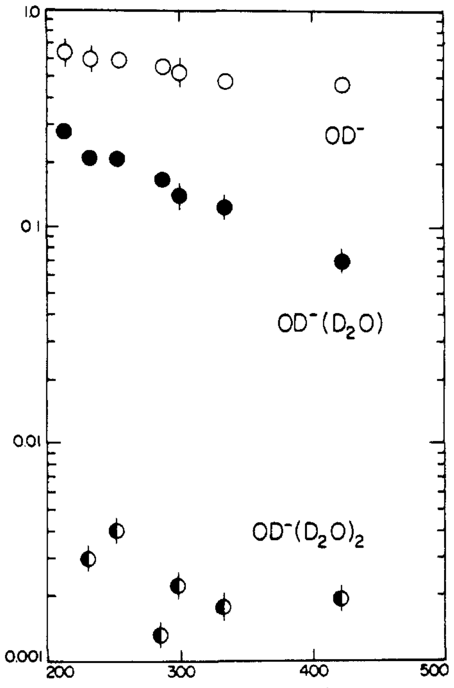

Figure 1. Reaction efficiencies for the reactions $OD^-(D_2O)_{0,1,2}$ + CH_3Cl as a function of temperature.

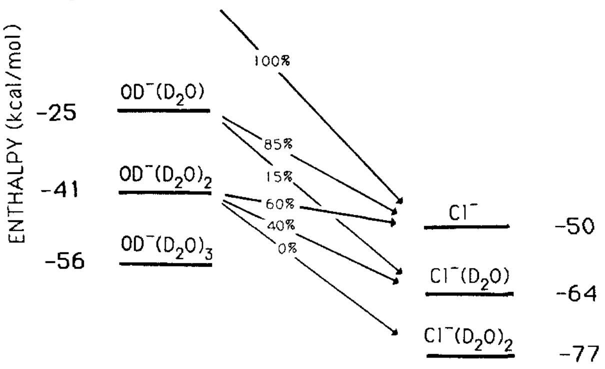

Figure 2. Ethalpy diagram for the reactants (left column) and products (right column), identified by the ionic species. Relative enthalpies are for undeuterated species[16] and yield reaction enthalpies by subtraction. Experimental product distributions (independent of temperature) are reported with error limits of ±3% for $OD^-(D_2O)$ and ±10% for $OD^-(D_2O)_2$.

Figure 1 shows the dependence of the rate constant on temperature and solvation number. What is represented is the *reaction efficiency*, which is the ratio of the experimental rate constant to a theoretical collision rate constant. Collision rate constants have been calculated by using the ACCSA procedure, developed by Clary.[13,14]

Reaction 1 shows the *negative* temperature dependence that has been shown experimentally[8] and has been predicted theoretically[15,8] for nucleophilic displacement at an sp^3 carbon atom.

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