changes of ketone solutes. It is obvious that many other reactions and processes are amenable to study in these media.

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Hypervalent Silicon Hydrides: SiH_5^-

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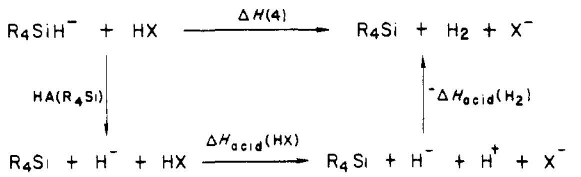
The rich diversity and practical utility of organosilicon chemistry continues to engender widespread research interests.[1] A key issue in the field involves the role of the low-lying vacant Si d-orbitals in the properties and reactivity of silicon-containing compounds. A familiar manifestation of d-orbital participation is the aptitude of silicon for hypervalency in the form of (10-Si-5) pentavalent anions.[2] Examples of pentavalent silicon anions have been isolated and structurally characterized,[3] and they are frequently invoked as intermediates in nucleophilic addition reactions of organosilanes in solution.[4-7] Moreover, several 10-Si-5 negative ions bearing alkyl, alkoxyl, and halogen ligands have been identified as products of gas-phase ion-molecule reactions.[8-10] We now wish to report the synthesis and characterization of the archetype pentavalent silicon anion, SiH_5^- (**1**), along with several of its simple alkyl derivatives in a flowing afterglow apparatus at 298 K.[11]

Scheme I



Hydride ion is a potent gas-phase base (PA = 400.4 kcal/mol)[12] which can be generated by electron impact on either NH_3 or CH_4. Its direct reaction with SiH_4 in a flow reactor at 0.4 torr has been previously reported by Bohme and co-workers to yield exclusively SiH_3^- by proton transfer.[13] Interestingly, when D^- is the reactant ion, H^- and SiH_2D^- also appear as products, implying that reversible addition of the nucleophilic ion to silicon occurs during the course of reactive collisions. We have now found that H^- reacts with *alkyl*silanes in a flowing afterglow at 0.4 torr total pressure by exclusive addition (eq 1). These reactions are most likely

$$H^- + R_4Si \xrightarrow[He]{} R_4SiH^- \qquad (1)$$

$$R_4Si = Me_4Si,\ Et_3SiH,\ Et_2SiH_2,\ n\text{-}C_5H_{11}SiH_3$$

saturated termolecular processes as shown by their large bimolecular rate coefficients at 0.4 torr (e.g., 4.5×10^{-9} cm^3 s^{-1} for Et_3SiH) and their pressure-independent product distributions from 0.3 to 0.9 torr. Relative to SiH_4, termolecular addition is facilitated in the larger alkylsilanes by the greater complexity and, thus, longer lifetimes of the intermediate collision complexes.[14] Adduct formation appears to be unique to hydride ion since other strongly basic anions such as NH_2^- (PA = 403.6 kcal/mol)[12] and OH^- (PA = 390.7 kcal/mol)[12] react only by proton abstraction and condensation reactions.[10]

The alkylsilyl hydride anions formed by reaction 1 behave as potent hydride donors, reducing a wide variety of substrates in bimolecular hydride transfer reactions such as CO_2, Et_3B, and $Fe(CO)_5$.[15] Of special significance is the observation of facile hydride transfer among the silanes themselves. In particular, both n-$C_5H_{11}SiH_4^-$ (**2**) and $Et_3SiH_2^-$ (**3**) transfer hydride to SiH_4 to produce the parent ion of the series, SiH_5^- (eq 2). The major

$$\underset{\mathbf{3}}{Et_3SiH_2^-} + SiH_4 \xrightarrow{68\%} \underset{m/z\ 31}{SiH_3^-} + Et_3SiH + H_2$$
$$\xrightarrow{32\%} \underset{\substack{m/z\ 33\\ \mathbf{1}}}{SiH_5^-} + Et_3SiH \qquad (2)$$

primary product with $Et_3SiH_2^-$ is SiH_3^- (68%), which is also observed to build up as a secondary product at the expense of SiH_5^- at higher SiH_4 flow rates. This latter observation indicates that an 'autocatalyzed' decomposition reaction is occurring (eq 3). The

$$SiH_5^- + SiH_4 \rightarrow SiH_4 + H_2 + SiH_3^- \qquad (3)$$

occurrence of such a reaction in the gas phase requires that SiH_5^- be thermodynamically unstable with respect to H_2 dissociation but may survive intact under the present conditions by virtue of a kinetic barrier preventing prompt fragmentation. Computational studies of SiH_5^- support this conclusion since it has been determined at quite high levels of theory that although H_2 dissociation is ca. 6 kcal/mol exothermic, a D_{3h} trigonal-bipyramidal SiH_5^- structure represents a local minimum on the potential energy surface.[16-19]

Reaction 3 is but one example of a more general protolytic reaction which may occur between silyl hydride anions and Brønsted acids (HX) (eq 4). We have exploited this reaction

$$R_4SiH^- + HX \rightarrow [R_4\overset{\delta^-}{Si}\cdots H\cdots H\cdots \overset{\delta^-}{X}] \rightarrow R_4Si + H_2 + X^- \qquad (4)$$

in the determination of thermochemical data for SiH_5^- and two of its alkyl derivatives. Equation 4 may be formulated in terms

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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),

$$Et_3SiH \xrightarrow{D^-} \underset{\textbf{3-}d}{Et_3SiHD^-} \xrightarrow{CO_2} \underset{68\%}{HCO_2^-},\ \underset{32\%}{DCO_2^-} \qquad (5)$$

$$n\text{-}C_5H_{11}SiH_3 \xrightarrow{D^-} \underset{\textbf{2-}d}{n\text{-}C_5H_{11}SiH_3D^-} \xrightarrow{CO_2} \underset{86\%}{HCO_2^-},\ \underset{14\%}{DCO_2^-} \qquad (6)$$

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

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

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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