Gas-Phase Chemistry of Pentacoordinate Silicon Hydride Ions

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Abstract: The formation, thermochemical properties, and reactivity of gas-phase pentacoordinate silicon hydride anions are described. These ions are produced as the major products of reactions between H^- and alkylsilanes under flowing afterglow conditions at room temperature. Substituted silicon hydride ions are formed by addition of nucleophilic anions such as F^-, alkoxides, nitrile anions, and CF_3^- to SiH_4 and to primary, secondary, or tertiary alkylsilanes. The parent ion of the series, SiH_5^-, is formed by hydride transfer from alkyl silicon hydride ions to SiH_4. Pentacoordinate silicon hydride ions are shown to be reactive hydride reducing agents, transferring H^- to a wide variety of organic, inorganic, and transition-metal organometallic species. Silicon hydride ions undergo sequential hydride−deuteride exchange reactions with SiD_4 by a mechanism analogous to protonic H/D exchange in gas-phase carbanions. Reactions with Brønsted acids lead to protolytic cleavage of an Si−H bond in the anion and formation of H_2. Depending upon the structure and acidity of the reactant acid, these reactions produce the corresponding silyl anion and both the free and silicon-complexed conjugate base anion. Reactions between alkylhydridosiliconate ions and neutral silanes occur by hydride transfer, protolytic cleavage and alkyl group transfer with accompanying H_2 loss. The observation of "self-cleavage" of an alkylhydridosiliconate ion by its alkylsilane precursor to produce the corresponding silyl anion and H_2 indicates that simple alkylhydridosiliconates are metastable with respect to H_2 loss. Reactions between CO_2 and monodeuterated alkylhydridosiliconate ions formed by addition of D^- to alkylsilanes produce statistical yield ratios of DCO_2^- and HCO_2^-, indicating complete scrambling of hydrogen and deuterium ligands in the siliconate ion, and a negligible isotope effect for the exothermic transfer of H^- to CO_2. The hydride affinity (HA) ordering of alkylsilanes is determined from bracketing methods and equilibrium measurements to be $HA(Et_3SiH) \leq HA(Et_2SiH_2) \leq HA(n\text{-}C_5H_{11}SiH_3) \leq HA(SiH_4)$, where the differences among all the silanes are less than 1−2 kcal/mol. The absolute hydride affinities for SiH_4 and the alkylsilanes are estimated to be 19−20 kcal/mol. Collisional activation of SiH_5^- and alkylhydridosiliconate ions results in inefficient fragmentation by H_2 loss, with estimated threshold energies of about 0.6 eV. CID of Et_3SiHD^- occurs by loss of both HD and H_2, indicating that the alkyl hydrogens are partially involved in these dissociations.

Introduction

Mass spectrometric and gas-phase ion techniques can provide access to information about the physical properties and reactivity of exotic or unusual chemical species that would otherwise be too reactive or unstable for condensed-phase studies. Experimental information of this kind is especially important for the continued refinement of theoretical models for chemical bonding and electronic structure. At the same time, the practical pursuit of molecules exhibiting rare or unusual bonding patterns or novel structural features often inspires the development of useful new experimental techniques such as preparative pyrolysis,[1] neutralization−reionization mass spectrometry,[2] and low-temperature matrix isolation,[3] to name a few.

Hypervalent[4] (or, preferably, "hypercoordinate"[5]) main-group molecules are one such class of compound that has long intrigued both experimental and theoretical chemists. While there are many examples of stable hypercoordinate compounds (e.g. SF_6, XeF_2, ClF_5, etc.), it is most often the case that formal octet-rule violations in a molecule lead to kinetic and thermodynamic instability. Accordingly, this class of compound has provided great synthetic challenges over the years.[6] Establishing a proper electronic description of the bonding in hypercoordinate molecules has also posed a formidable theoretical challenge.[7,8] Traditional views made use of empty d orbitals on the central atom to achieve the required hybridization for hypervalency, e.g., dsp^3, d^2sp^3, etc.[9] However, *ab initio* molecular orbital calculations of the electronic structures of small hypercoordinate molecules such as SO_2Cl_2, PH_5, F_3^-, etc. indicate that the d-orbital populations are quite low.[7,10] While the issue is still somewhat controversial,[11] the growing consensus is that 3-center, 4-electron bonding involving s and p orbitals,[12] with the d orbitals acting primarily as polarization functions,[7,13] represents

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a better description of compounds containing hypercoordinate main-group elements.

Pentacoordinate silicon anions ([10-Si-5] species;[14] siliconate anions) are an important class of hypercoordinated compounds. These species have been proposed as intermediates in nucleophilic displacement reactions at silicon,[15] and numerous examples of stable pentacoordinate siliconates have been isolated and characterized.[16−20] Moreover, several pentacoordinated silicon anion complexes have been prepared recently that show potential for use as versatile hydride reducing agents.[21] Various physical and chemical aspects of gas-phase pentacoordinate silicon ions have been investigated over the past 25 years in several different laboratories.[22] Beauchamp and co-workers determined fluoride binding energies for a series of fluoromethylsilanes by ion cyclotron resonance (ICR) spectroscopy.[23] Larson and McMahon have produced quantitative scales of F^-, Cl^-, and CN^- binding energies for neutral molecules, including selected silanes.[24] Bowie and co-workers used ICR experiments in combination with ab initio calculations to characterize the ion/molecule reactions of silane and various derivatives with both bare and solvated negative ions.[25] The long-lived adducts observed in some of these reactions are believed to be trigonal-bipyramidal (tbp) siliconate ions. DePuy, Damrauer, Bierbaum, and co-workers extensively investigated the negative ion chemistry of cyclic and acyclic organosilanes by the flowing afterglow technique.[26] A variety of pentacoordinate silicon anions were observed and chemically characterized, including the first example of a pentaalkylsiliconate anion made by direct addition of allyl anion to dimethylsilacyclobutane.[26b] Damrauer, Burggraf, Davis, and Gordon described[27] a combined experimental and theoretical study of an extensive series of siliconate anions of the general forms H_3SiXY^- and Me_3SiXY^-. Qualitative and quantitative estimates of X^- affinities were obtained that are generally consistent with the trends established for nucleophilic substitution reactions at silicon in solution. Recently, Brauman and co-workers demonstrated the intermediacy of a pentacoordinate silicon adduct in the gas-phase reactions of various anionic bases with a β-hydroxysilane.[28]

Theoretical investigations of pentacoordinate silicon anions include numerous studies of SiH_5^-,[25b,29,30] its halogenated derivatives,[31] and various mono- and disubstituted siliconates.[25df,27,32] A stable tbp structure is calculated for SiH_5^- with a hydride binding energy of 16−22 kcal/mol and a small pseudorotation barrier of less than 3 kcal/mol.[29,30] SiH_5^- is computed to be unstable with respect to H_2 loss by ca. 7−11 kcal/mol[29,30a] but is prevented from doing so by an energy barriers of *ca.* 17 kcal/mol.[29]

We recently described[33] the preparation of a series of pentacoordinate silicon hydride ions (hydridosiliconates) in the gas phase, as well as the archetype hydridosiliconate, SiH_5^-. The alkylsiliconate ions were formed by the direct attachment of H^- to various alkylsilanes (eq 1), while SiH_5^- could be

$$R_4Si + H^- \rightarrow R_4SiH^- \tag{1}$$

generated by H^- transfer from hydridosiliconates to SiH_4. Over the past several years, we have employed pentacoordinate silicon hydride ions as convenient reducing agents in gas-phase ion syntheses[34] and in mechanistic studies of gas-phase hydride

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reduction reactions.[35] We present here a detailed description of their formation, thermochemical properties, and gas-phase reactivity.

Experimental Section

All experiments were carried out at room temperature (296 ± 2 K) either in a flowing afterglow apparatus or a modified version of the instrument equipped with a triple quadrupole mass analyzer.[36,37] Unless otherwise noted, the total pressure and flow rate of the helium buffer gas used was 0.4 Torr and 190 STP cm^3/s, respectively. Hydride ions were generated by electron impact on either NH_3 (NH_2^- also formed) or CH_4, and were always accompanied by variable amounts of HO^- resulting from traces of water impurity in the instrument. Direct detection of H^- was possible with the single-stage mass analyzer (Extranuclear Laboratories 7-270-9; Model 15 High-Q Head), while it could only be indirectly detected with the triple quadrupole system (EXTREL C50 TQMS, 3-1200 amu mass range). Hydroxide ions were formed by electron ionization of a N_2O/CH_4 mixture, and F^- was produced by electron ionization of NF_3.

Kinetic measurements were performed by standard methods using either a moveable neutral reagent inlet or a pair of fixed-position ring inlets located at calibrated distances from the sampling orifice of 38 and 48 cm.[37] Neutral reagent flow rates were determined by measuring the pressure increase with time when the reagent flow was diverted from the flow tube to a calibrated volume. Absolute rate coefficients are determined with typical precision of better than ±10% and an estimated accuracy of ±20%. Product branching ratio measurements were determined either directly from the observed mass spectra when no secondary reactions occurred or from the slopes of plots of the product ion yields *versus* the extent of reactant ion conversion. For all quantitative measurements of reaction product distributions, the detector resolution was kept as low as possible so as to minimize ion mass discrimination. No corrections were made for differences in the diffusive loss rates for different ions. The estimated uncertainties in the product yields are ±10%.

Collision-induced dissociation (CID) measurements and mass-selected ion/molecule reactions were carried out in the gas-tight, rf-only quadrupole collision chamber (Q2) of the triple quadrupole mass analyzer. Argon and neon target gases were used, with pressures maintained in the single- (<0.05 mTorr) or multiple-collision (0.05–0.12 mTorr) range as read from an MKS Baratron 390H pressure transducer. The axial kinetic energy of the reactant ion is determined by the Q2 rod offset voltage, which can be varied up to 200 V. Ions are detected with a Channeltron electron multiplier operated in pulse counting mode. The methods used for measurement and analysis of CID threshold energies have been described in detail previously.[37,38] Briefly, the cross section for dissociation of the mass-selected reactant ion is measured as a function of the collision energy in the center-of-mass (CM) frame with argon or neon target gas maintained in Q2 at pressures less than 0.05 mTorr. The product ion appearance curves are fit with an analytical model which takes into account the ion beam kinetic energy spread, the Doppler broadening due to target motion, the internal energy content of the reactant ion (assumed to be at a temperature of 298 K), and kinetic shifts due to slow dissociation on the instrument time scale.[37,38] The reactant ion vibrational frequencies required for the internal energy and kinetic shift calculations were obtained from semiempirical molecular orbital calculations (MOPAC 6.0; AM1 Hamiltonian[39]) and were scaled by a factor of 0.9.

Materials. Gas purities were as follows: He (99.995%), Ar (99.955%), N_2O (99%), CH_4 (99%), CD_4 (99% d_4), NH_3 (anhydrous, 99.5%), ND_3 (99% d_3), SiH_4 (99.995%), SiD_4 (98% d_4), NF_3 (99%), CO_2 (99.5%), COS (97.5%). The alkylsilanes were obtained from Silar, Aldrich and Hüls. All other reagents were obtained from commercial vendors and used as supplied except for degassing of liquid samples prior to use.

Results and Discussion

Ion Formation. Several previous studies of gas-phase negative ion/molecule reactions of organosilanes under flowing afterglow conditions have reported the formation of adducts, formulated as pentacoordinate siliconates, as well as proton transfer and various types of condensation products.[26] For example, direct attachment of F^-, allyl anion, and alkoxide ions is reported to occur with high efficiency to tetramethylsilane and various cyclic and acyclic quaternary silanes,[26a,b] while HO^- and NH_2^- react predominantly by addition/alkane elimination pathways.[25d,26a,e] In contrast, in the only prior flowing afterglow study of negative ion/molecule reactions with the parent silane, SiH_4, Bohme and co-workers observed only proton transfer and condensation products.[40] For example, H^- was reported to yield only SiH_3^- upon reaction with SiH_4. However, the reaction between D^- and SiH_4 was found to produce H^- and SiH_2D^- as well, suggesting the intermediacy of a metastable $[SiH_4D^-]^*$ adduct in these reactions.

We have found that H^-, formed by electron ionization of either NH_3 or CH_4, reacts with primary, secondary, tertiary, and quaternary silanes to yield mainly or exclusively the corresponding $[M + H]^-$ adduct, *i.e.* hydridosiliconate ions.[33] For example, *n*-pentylsilane (eq 2) and triethylsilane (eq 3) both

$$n\text{-}C_5H_{11}SiH_3 + H^- \rightarrow n\text{-}C_5H_{11}SiH_4^- \tag{2}$$

$$Et_3SiH + H^- \rightarrow Et_3SiH_2^- \tag{3}$$

yield predominantly the pentacoordinate adducts upon reaction with hydride ion at room temperature and 0.4 Torr total pressure in the flowing afterglow. This is remarkable selectivity, considering the great base strength of H^- ($\Delta H_{acid}(H_2) = 400.4$ kcal/mol)[41] and the availability of both the SiH ($\Delta H_{acid} \approx 385$ kcal/mol)[42] and α-CH ($\Delta H_{acid} \approx 388-393$ kcal/mol)[42] positions in these alkylsilanes for exothermic proton transfers. A conceivable explanation might be that proton abstraction by H^- from the kinetically acidic α-CH position in the alkyl group does occur,[25f,43] but it is followed by rapid hydride transfer from the resulting α-silyl carbanion to the neutral silane (e.g., eq 4).

$$CH_3CH_2SiH_3 \xrightarrow{H^-} CH_3CHSiH_3^- \xrightarrow{CH_3CH_2SiH_3} CH_2{=}CHSiH_3 + CH_3CH_2SiH_4^- \tag{4}$$

However, this can be ruled out by the fact that reaction between alkylsilanes and NH_2^- carried out in the absence of H^- does not produce any hydridosiliconate ions but does form a significant yield of the proton abstraction product.

Figure 1 shows a representative product mass spectrum resulting from the reaction of H^- with Et_2SiH_2, which illustrates the relative simplicity of these reactions. The typical side-products[25d,26a,e] from reactions with the unavoidable impurity ions HO^- and NH_2^- are also formed in variable amounts. The peak labeled "x" is a $Et_3Si^-/Et_2SiHCHCH_3^-$ ion mixture (*m/z*

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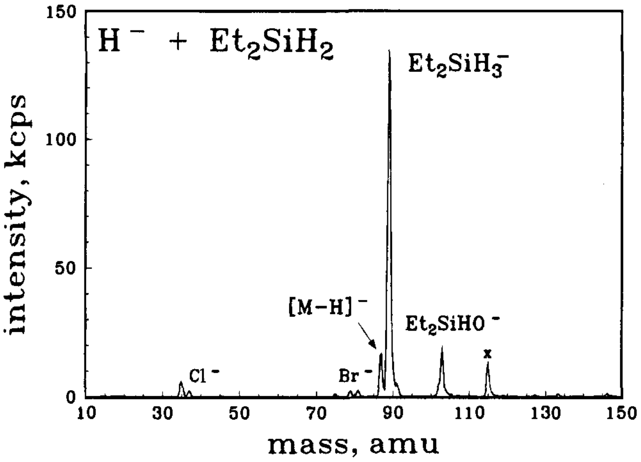

Figure 1. Mass spectrum illustrating the formation of $Et_2SiH_3^-$ from reaction of H^- with Et_2SiH_2 in the flowing afterglow apparatus at room temperature. Et_2SiHO^- arises from the HO^- ions present in the initial reactant ion mixture; the peak labeled "x" (*m/z* 115) is a mixture of Et_3Si^- and $Et_2SiHCHCH_3^-$ formed by a secondary reaction. See text for discussion.

115) resulting from a secondary reaction between $Et_2SiH_3^-$ and Et_2SiH_2 (*vide infra*).

The apparent bimolecular reaction rate coefficients measured for these H^- attachment reactions indicate that they are highly efficient. At 0.40 Torr the overall rate coefficient for the reaction of H^- with n-$C_5H_{11}SiH_3$ (eq 2) is $4.6 \pm 0.4 \times 10^{-9}$ cm^3/s, and for Et_3SiH (eq 3) it is $4.4 \pm 0.4 \times 10^{-9}$ cm^3/s. Estimates of the dipole moments and polarizabilities for these compounds[44] suggest collision rate coefficients[45] for H^- in the range of $8-9 \times 10^{-9}$ cm^3/s, indicating overall efficiencies for the apparent bimolecular reactions of *ca.* 50%. For comparison, Damrauer and DePuy report that addition of F^- to tetamethylsilane "occurs on every encounter" at 0.4 Torr.[26e] The measured rate coefficients and product distributions are independent of the total helium pressure from 0.3 to 0.9 Torr. This indicates that the H^- addition reactions are saturated termolecular processes in this pressure regime. Given the large number of internal degrees of freedom in alkylsilanes and the moderate exothermicity for H^- addition (*vide infra*), it is not surprising that the excited intermediates should have microsecond lifetimes and exhibit efficient three-body stabilization under flowing afterglow conditions.

An alternative method of forming pentacoordinate silicon hydride ions is the addition of nucleophilic anions such as F^-, alkoxides, nitrile anions, or enolates to primary, secondary, or tertiary silanes. For example, the fast reaction between F^- and n-$BuSiH_3$ ($k_{obsd} = 2.2 \pm 0.1 \times 10^{-9}$ cm^3/s, efficiency[45] = 1.0) gives exclusively the pentacoordinate adduct (eq 5), as does addition of CH_3O^- to Et_2SiH_2 (eq 6). With weakly-basic alkoxide ions and other nucleophiles, this approach works even with SiH_4; selected tetrahydrosiliconate anions have been prepared by this method, such as the (trifluoromethyl)siliconate ion shown in eq 7. However, note that with SiH_4 as the reactant,

$$F^- + n\text{-}BuSiH_3 \rightarrow n\text{-}BuSiH_3F^- \qquad (5)$$

$$CH_3O^- + Et_2SiH_2 \rightarrow Et_2SiH_2OCH_3^- \qquad (6)$$

$$CF_3^- + SiH_4 \rightarrow CF_3SiH_4^- \qquad (7)$$

$$\rightarrow CHF_3 + SiH_3^-$$

the apparent proton transfer product is also usually produced if it is thermodynamically accessible ($\Delta H_{acid}(SiH_4) = 372.3 \pm 2.1$ kcal/mol[41]).

All attempts to produce pentacoordinate silicon hydride ions by H^- transfer to neutral silanes from conventional gas-phase hydride transfer reagents such as cyclohexadienyl anion,[46] HNO^- [46,47] and CH_3O^- [48] have failed. It will be shown later that this is simply a reflection of the thermochemistry. However, we have observed facile transfer of hydride ion from one silane to another. We previously showed how this provides a means to synthesize the archetype hydridosiliconate ion, SiH_5^- (eq 8).[33] For example, the reaction of SiH_4 with $Et_3SiH_2^-$ yields both SiH_5^- and SiH_3^- as primary products, with the latter ion also formed as a secondary product. The implications of this observation will be discussed later. For chemical reactivity studies, the greatest yields of SiH_5^- are obtained with tetrahydridosiliconate ion precursors such as n-$C_5H_{11}SiH_4^-$ or n-$BuSiH_4^-$.

$$Et_3SiH_2^- + SiH_4 \xrightarrow{32\%} Et_3SiH + SiH_5^- \qquad (8)$$

$$\xrightarrow{68\%} Et_3SiH + SiH_3^- + H_2$$

Reactivity. (a) Hydride Reductions. Pentacoordinate silicon hydride ions behave as gas-phase hydride transfer reagents with a wide variety of compounds. For example, n-$BuSiH_4^-$ readily reduces CO_2, COS, and CS_2 to form the corresponding formates (eq 9) and transfers H^- to a variety of transition metal carbonyls to form the corresponding formyl complexes (eq 10).[34a,b] Substituted borohydride ions are also easily formed from reactions between hydridosiliconates and boranes (eq 11).[34c] All of these reactions occur rapidly ($k_{obsd}/k_{collision}$ >

$$n\text{-}BuSiH_4^- + CXY \rightarrow n\text{-}BuSiH_3 + HCXY^- \qquad (X, Y = O, S) \quad (9)$$

$$n\text{-}BuSiH_4^- + Cr(CO)_6 \rightarrow n\text{-}BuSiH_3 + (CO)_5CrCHO^- \qquad (10)$$

$$n\text{-}C_5H_{11}SiH_4^- + Et_3B \rightarrow n\text{-}C_5H_{11}SiH_3 + Et_3BH^- \qquad (11)$$

0.5),[45] forming the corresponding $[M + H]^-$ species as the major or exclusive product. With simple aliphatic aldehydes and ketones, somewhat different behavior is observed in that adducts, formulated as *monoalkoxysiliconate ions*, are formed as the major or exclusive product (e.g., eq 12).[35] The occurrence of

$$n\text{-}BuSiH_4^- + Me_2C{=}O \rightarrow [Me_2CH{-}O{-}SiH_3Bu^-] \leftarrow Me_2CHO^- + n\text{-}BuSiH_3 \qquad (12)$$

carbonyl group reduction in these addition reactions is shown by the formation of the free alkoxide ion (i.e., Me_2CHO^- in eq (12)) as the major fragment ion from CID of the adducts and by the fact that the CID spectra are identical to those of the corresponding reference ions formed by directly adding the pre-

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[44] Dipole moments taken from: McClellan, A. L. *Table of Experimental Dipole Moments*; Rahara Enterprises: El Cerrito, CA, 1989; Vol. 3. The polarizability for $C_4H_{12}Si$ was estimated to be 12.8 Å^3 from the molar refractive index for $BuSiH_3$ (n_D^{20} = 1.3922, cf.: *Dictionary of Organometallic Compounds*; Chapman and Hall: New York, 1984; Vol. 2) and the Clausius–Mossotti equation (cf.: Atkins, P. W. *Physical Chemistry*, 4th ed.; W. H. Freeman and Co.: New York, 1990). The derived atomic polarizability parameter for a tetravalent silicon atom is 3.69 Å$^{3/2}$, see: Miller, K. J. *J. Am. Chem. Soc.* **1990**, *112*, 8533.

[45] Su, T.; Chesnvich, J. *J. Chem. Phys.* **1982**, *76*, 5183.

[46] DePuy, C. H.; Bierbaum, V. M.; Schmitt, R. J.; Shapiro, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 2920.

[47] Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 1433.

[48] Ingemann, S.; Kleingeld, J.; Nibbering, N. M. M. *J. Chem. Soc., Chem. Commun.* **1982**, 1009.

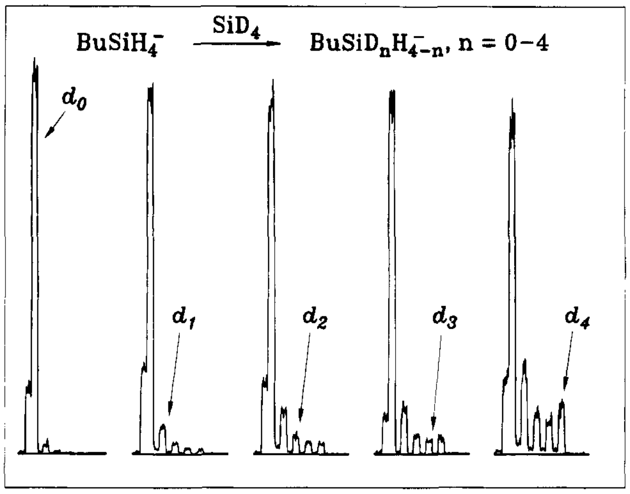
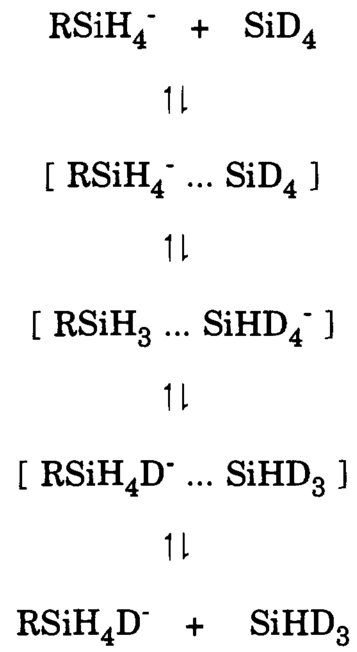


Figure 2. Mass spectrum illustrating four sequential hydride−deuteride exchanges between mass-selected $BuSiH_4^-$ (*m/z* 89) and SiD_4 in Q2 of the triple quadrupole analyzer; collision energy <0.5 eV, lab frame, $P(SiD_4)$ = 0.13−0.30 mTorr.

formed alkoxide ion to the same silane. The details of these reactions will be published elsewhere.[49] We recently demonstrated the use of mono- and dialkoxysiliconate ions for determining the diastereoselectivity[35a] and regioselectivity[35b] involved in gas-phase hydride reductions of various organic carbonyl compounds.

(b) **Hydride−Deuteride Exchange.** Monodeuterated siliconate ions can be formed by adding D^-, formed by electron ionization of CD_4 or ND_3, to alkylsilanes. In the course of examining the reactions of these ions (*vide infra*), it was found that the deuterium label was lost if relatively high flow rates of the neutral silane were used. That is, upon addition of increasing amounts of neutral silane to the flow reactor in which D^- is present, the relative abundance of the d_1 siliconate ion product displays an initial rise followed by a decrease, along with a concomitant rise in the d_0 siliconate ion yield. Such behavior is interpreted as evidence for reversible hydride−deuteride exchange reactions between the d_1 siliconate ion and the neutral silane. This was verified by examining the reactions of several different hydridosiliconate ions with SiD_4. Because of the more economical use of the deuterated material, these reactions were carried out in the collision chamber (Q2) of the triple quadrupole at total pressures of 0.08−0.30 mTorr, with low collision energies (<0.5 eV, lab frame). As illustrated in Figure 2 for n-$BuSiH_4^-$, four *sequential* H/D exchanges occur. A mechanism for the exchange is shown in Scheme 1, which is analogous to those proposed by DePuy and co-workers for protonic H/D exchanges in carbanions[50] and by Nibbering and co-workers for hydride/deuteride exchange between CD_3O^- and $CH_2{=}O$.[48] First, hydride transfer from the siliconate ion to SiD_4 occurs within the long-lived collision complex. The thermochemical results described later indicate that this step is approximately thermoneutral, or slightly exothermic. Therefore, the $SiHD_4^-$ ion can either dissociate from the complex or, alternatively, transfer D^- back to the alkylsilane and thereby effect the overall exchange. In principle, multiple hydride−deuteride exchanges can occur in this way during a single ion/molecule encounter, although the data are more consistent with a sequence of slow, single exchanges per collision. Note that in Figure 2 the observed abundance for the d_4 siliconate ion (*m/z* 93) remains similar to that for the d_2 and d_3 ions throughout the range of SiD_4 pressures used. This rules out carbanion (n-Bu^-) transfer from n-$BuSiH_4^-$ to SiD_4 forming $BuSiD_4^-$ as an important contributing mechanism, since it would lead to an anomalously high d_4 ion signal intensity. However, the unusually high relative abundance of the d_1 ion that is evident in Figure 2 may be indicative of carbanion transfer, as described below.

Scheme 1



(c) **Alkyl Group Transfer Reactions.** Although direct carbanion transfer from alkylhydridosiliconate ions to SiD_4 does not take place, secondary reactions of these ions occur in the presence higher concentrations of neutral alkylsilanes in the flow reactor which lead to alkyl group transfer with accompanying H_2 loss. For example, the $Et_3Si^-/Et_2SiHCHCH_3^-$ ion mixture indicated by peak "x" in Figure 1 arises from the following reaction (eq 13):

$$Et_2SiH_3^- + Et_2SiH_2 \rightarrow Et_3Si^- \text{ and } Et_2SiHCHCH_3^- + H_2 + EtSiH_3 \quad (13)$$

That the observed $C_6H_{15}Si^-$ (*m/z* 115) product consists of a mixture of silyl anion and α-silylcarbanion structures is shown by the characteristic ionic products formed upon reaction with N_2O, in accordance with the general prescription given by DePuy and Damrauer.[26d] Reaction of the $C_6H_{15}Si^-$ ions formed as shown above with N_2O in Q2 produces both Et_3SiO^- (*m/z* 131, eq 14a) and Et_2SiHO^- (*m/z* 103, eq 14b) in an approximately 1:3 yield ratio.

$$Et_3Si^- + N_2O \rightarrow Et_3SiO^- + N_2 \quad (14a)$$

$$Et_2SiHCHCH_3^- + N_2O \rightarrow Et_2SiHO^- + CH_3CHN_2 \quad (14b)$$

Therefore, the H_2 molecule expelled during the ethyl transfer reaction originates mainly from one of the ethyl groups in the product. Similar behavior is observed with other alkylsiliconates, e.g., reaction of $BuSiH_4^-$ with $BuSiH_3$ gives a mixture of Bu_2SiH^- and $BuSiH_2CHC_3H_7^-$, and $HexSiH_4^-$ (Hex = n-C_6H_{13}) reacts with $HexSiH_3$ to yield a mixture of Hex_2SiH^- and $HexSiH_2CHC_5H_{11}^-$. In view of these results, we propose that the anomalously high relative abundance of the nominal "d_1" product ion with *m/z* 90 indicated in Figure 2 is due, in part, to transfer of the butyl group from n-$BuSiH_4^-$ to SiD_4 with accompanying loss of HD from the product (eq 15). Loss of D_2 giving n-$BuSiD_2^-$ also probably occurs, but this product ion cannot be observed since it has the same mass

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[49] Ho, Y.; Squires, R. R., to be published.

[50] Stewart, J. H.; Shapiro, R. H.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1977**, *99*, 7650.

as the n-BuSiH$_4^-$ reactant (m/z 89).

$$n\text{-BuSiH}_4^- + \text{SiD}_4 \rightarrow \underset{m/z\ 90}{\text{C}_3\text{H}_7\text{CHSiD}_3^-} + \text{HD} + \text{SiH}_4 \qquad (15)$$

$$\rightarrow \underset{m/z\ 89}{n\text{-BuSiD}_2^-} + \text{D}_2 + \text{SiH}_4$$

Reactions involving hydridosiliconates and silanes bearing different alkyl groups show very specific behavior. For example, BuSiH$_4^-$ reacts with HexSiH$_3$ to produce a C$_{10}$H$_{23}$Si$^-$ product ion which is shown by subsequent N$_2$O reactions to be a mixture of (Hex)(Bu)SiH$^-$ and BuSiH$_2$CHC$_5$H$_{11}^-$. In contrast, the analogous reaction between HexSiH$_4^-$ and BuSiH$_3$ yields a product ion mixture consisting of (Hex)(Bu)SiH$^-$ and HexSiH$_2$CHC$_3$H$_7^-$. Furthermore, HexSiH$_4^-$ reacts with Et$_2$SiH$_2$ to yield only C$_{10}$H$_{23}$Si$^-$ and *no* C$_8$H$_{19}$Si$^-$, while Et$_2$SiH$_3^-$ reacts with HexSiH$_3$ to give C$_8$H$_{19}$Si$^-$ and *no* C$_{10}$H$_{23}$Si$^-$. These results, taken together, indicate that the observed silyl anion/α-silylcarbanion product mixture is derived exclusively from the *neutral silane reactant* and, further, that hydride transfer does not precede alkyl transfer since this would necessarily interconvert the siliconate and neutral silane. The mechanistic details of these alkyl transfer reactions are under further investigation.

(d) Protolytic Cleavage. Siliconate ions undergo protonolysis reactions with a variety of Brønsted acids, HA (eq 16). These

$$\text{R}_3\text{SiH}_2^- + \text{HA} \xrightarrow{a} \text{R}_3\text{SiH} + \text{H}_2 + \text{A}^- \qquad (16)$$

$$\xrightarrow{b} \text{R}_3\text{SiH(A)}^- + \text{H}_2$$

$$\xrightarrow{c} \text{R}_3\text{Si}^- + \text{H}_2 + \text{HA}$$

$$\xrightarrow{d} \text{R}_2\text{SiH}_2 + \text{RH} + \text{A}^-$$

$$\xrightarrow{e} \text{R}_2\text{SiH}_2\text{(A)}^- + \text{RH}$$

$$\xrightarrow{f} \text{R}_2\text{SiH}^- + \text{RH} + \text{HA}$$

reactions are analogous to the familiar acid-cleavage reactions of neutral organosilanes that are observed in both solution[51] and the gas phase.[52] Gas-phase protonolysis reactions have also been observed with other main-group organometallic "ate" complexes such as aluminates[53] and borates.[54] The mechanisms of these types of reactions are believed to involve protonation of a high-lying σ-bonding orbital in the ligand sphere of the electropositive element, with simultaneous development of strong H−H or R−H bonding interactions.[55]

Reaction 16 indicates two different types of protolytic processes involving cleavage of either an Si−H bond or an Si−R bond. In the case of reactions 16a and 16d, a common product ion, A$^-$, is formed. However, the observed product distributions for reactions of various types of acids with the simple alkylsiliconates examined in the present work (R = H, ethyl, butyl, pentyl, etc.) suggest that the alkane-cleavage pathways (16d−f) are of little or no importance compared to the H$_2$-cleavage channels (16a−c). For instance, the reaction between n-BuSiH$_4^-$ ions (m/z 89) and EtOH yields the butylsilane [M − H]$^-$ ion as the major product (m/z 87, eq 17c), and lesser amounts of the free alkoxide ion, EtO$^-$ (m/z 45, eq 17a), and the ethoxysiliconate ion n-BuSiH$_3$OEt$^-$ (m/z 133, eq 17b).

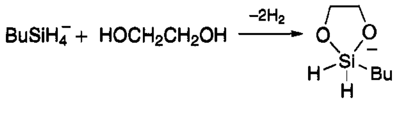
$$n\text{-BuSiH}_4^- + \text{EtOH} \xrightarrow{a} n\text{-BuSiH}_3 + \text{H}_2 + \text{EtO}^- \qquad (17)$$

$$\xrightarrow{b} n\text{-BuSiH}_3\text{OEt}^- + \text{H}_2$$

$$\xrightarrow{c} n\text{-BuSiH}_2^- + \text{H}_2 + \text{EtOH}$$

Variable BuSiH$_3$ concentration studies of this reaction taking place in the flow tube, and control experiments with the reaction carried out in Q2 of the triple quadrupole indicate that the ethoxysiliconate ion is a true primary product. The measured yields for reactions 17a, 17b, and 17c taking place in Q2 are 13 ± 3%, 15 ± 4%, and 72 ± 7%, respectively. These results indicate that siliconate protonolysis by an acid HA can occur in two ways: with and without retention of the conjugate base anion A$^-$ in the organosilane product. However, the complete absence of the corresponding alkane-cleavage products, EtOSiH$_4^-$ (m/z 77) or SiH$_3^-$ (m/z 31), from reaction 17 indicates that protonolysis of the Si−Bu bond does not occur.

Protonolysis of hydridosiliconate ions has been observed with a wide variety of acid types, including CH acids such as ketones and nitriles and heteroatom acids such as thiols, carboxylic acids, and polybasic acids. In each case the conjugate base anions, A$^-$, are observed as a major or exclusive product ion along with variable yields of the corresponding siliconates, R$_3$SiH(A)$^-$, and silyl anions, R$_3$Si$^-$. The relative yields of these three products appear to be controlled, in part, by the relative acidities of the acid HA and the silane. For example, formic acid (ΔH_{acid}(HCO$_2$H) = 345 kcal/mol[41]) reacts with hydridosiliconates to produce only HCO$_2^-$, while the weaker acid EtOH (ΔH_{acid}(EtOH) = 377 kcal/mol[41]) forms all three products (eq 17). With alcohols and other heteroatom acids, the overall reactions are quite efficient. For instance the measured rate coefficient for reaction between CF$_3$CH$_2$OH and Et$_3$SiH$_2^-$ is 1.4×10^{-9} cm^3/s, corresponding to an efficiency near 100%.[45] Depending on the structure of the hydridosiliconate ion, *sequential* protonolysis of up to two SiH bonds can be observed. Reaction of BuSiH$_4^-$ with excess EtOH in the helium flow reactor yields significant amounts of BuSiH$_2$(OEt)$_2^-$ (m/z 177), but only traces of BuSiH(OEt)$_3^-$ (m/z 221). Diols are a particularly interesting class of reactant in this regard, as loss of *two* equivalents of H$_2$ occurs to produce cyclic siliconate products (eq 18). Synthesis



(18)

of this same ion can also be accomplished by reacting the deprotonated diol HOCH$_2$CH$_2$O$^-$ with the neutral silane; in this case, addition and protonolysis occur in a single step. In a later section, we will demonstrate the use of these protonolysis reactions for estimating thermochemical properties of hydridosiliconates.

Of particular significance is the observation that neutral silanes are also capable of protonolyzing hydridosiliconates. This is generally evident from the slow disappearance of the hydridosiliconate ions, e.g. RSiH$_4^-$, and appearance of the corresponding silyl anions, RSiH$_2^-$, in addition to the alkyl transfer product R$_2$SiH$^-$ with increasing concentration of the silane precursor RSiH$_3$ in the flow reactor. For example, the

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(51) (a) Bamford, C. H., Tipper, C. F. H., Eds, *Comprehensive Chemical Kinetics*; American Elsevier Publishing Co.: New York, 1973; Vol. 12. (b) Dessy, R. E.; Kitching W. *Adv. Organomet. Chem.* **1966**, *4*, 267.

(52) (a) Wojtyniak, A. C. M; Stone, J. A. *Int. J. Mass Spectrom. Ion Process* **1986**, *74*, 59. (b) Oppenstein, A.; Lampe, F. W. *Rev. Chem. Intermed.* **1986**, *6*, 275.

(53) Damrauer, R.; Krempp, M.; Damrauer, N. H.; Schmidt, M. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 5218.

(54) Kiplinger, J. P.; Crowder, C. A.; Sorensen, D. N.; Bartmess, J. E. *J. Am. Soc. Mass Spectrom.* **1994**, *5*, 169.

(55) Matteson, D. S. *Organomet. Chem. Rev. A* **1969**, *4*, 1969.

reaction between $Et_3SiH_2^-$ and SiH_4 produces both SiH_5^- and SiH_3^-, the latter ion being formed by protolytic cleavage (eq 8). As the SiH_4 flow rate is further increased, the SiH_5^- signal intensity is depleted and the SiH_3^- signal increases. This indicates that SiH_5^- undergoes a secondary reaction with SiH_4 that produces SiH_3^-, i.e., reaction 19 is taking place.

$$SiH_5^- + SiH_4 \rightarrow SiH_4 + SiH_3^- + H_2 \qquad (19)$$

The occurrence of this process was verified by examining the reaction of mass-selected $^{28}SiH_5^-$ (*m/z* 33) ions with SiH_4 in Q2 of the triple quadrupole analyzer. Reaction at low collision energy (<0.5 eV, lab frame) produces $^{28}SiH_3^-$ (*m/z* 31) and traces of $^{29}SiH_5^-$ (*m/z* 34) and $^{30}SiH_5^-$ (*m/z* 35). These latter products indicate that thermoneutral H^- transfer accompanies the indicated protonolysis reaction (eq 20).[56]

$$\underset{(m/z\ 33)}{^{28}SiH_5^-} + {}^{*}SiH_4 \rightarrow \underset{(m/z\ 31)}{^{28}SiH_3^-} + {}^{*}SiH_4 + H_2 \qquad (20)$$

$$\rightarrow {}^{28}SiH_4 + \underset{(m/z\ 33,34,35)}{{}^{*}SiH_5^-}$$

$*$ = natural isotopic abundance

Reaction 19 is unusual because it corresponds to the net dehydrogenation of the reactant ion by a catalyst. Reactions such as this are normally thermodynamically unfavorable, e.g., for neutral binary hydrides, dehydrogenation is endothermic by 50−110 kcal/mol, and for SiH_5^+, H_2 loss is endothermic by 20 kcal/mol.[41] The occurrence of this reaction requires (1) that SiH_5^- be thermodynamically unstable with respect to H_2 loss and (2) that an energy barrier must exist that prevents spontaneous decomposition of this ion, i.e. it is a *metastable* species. In fact, both of these conclusions were predicted nearly 20 years ago by *ab initio* molecular orbital calculations on SiH_5^-.[30j] The most recent calculations on this system by Boldyrev and Simons[30a] and by Reed and Schleyer,[29] carried out at high levels of theory including estimates for the correlation and zero-point energies, indicate that H_2 loss from SiH_5^- is exothermic by 7−11 kcal/mol but has a barrier of 17.5 kcal/mol. The C_{3v} transition structure for dehydrogenation **C** located by Reed and Schleyer,[29] somewhat resembles a $(SiH_4)H^-$ complex, which suggests that unimolecular decomposition of SiH_5^- by H_2 loss occurs by a hydride elimination−deprotonation mechanism. Indirect evidence in support of this conclusion is presented in a later section. In view of the fact that all of the simple alkyl hydridosiliconates we have examined also exhibit protolytic cleavage by their neutral alkylsilane precursor, we tentatively conclude that metastability toward H_2 loss is a general characteristic of this class of ion.

$$[H_3Si{-}H{-}H^-]$$
$$\mathbf{C},\ C_{3v}$$

Fluxional Behavior. An important aspect of [10-Si-5] anions and many other pentacoordinate species is the fluxionality of the trigonal bipyramidal (tbp) structures that are usually preferred.[6,57] For example, Corriu and co-workers recently characterized by ^{29}Si and ^{1}H NMR the intramolecular hydrogen exchange processes occurring in a series of $H_2Si(OR)_3^-\ M^+$ complexes and reported a free energy of activation of 16.9 kcal/mol for interchange of apical and equatorial hydrogens in the complexes with RO = ^{i}PrO and $M^+ = K^+$.[21e] Damrauer and co-workers used dynamic ^{19}F NMR to measure intramolecular exchange barriers of 10−12 kcal/mol for a series of trifluorophenylsiliconate salts in the presence of 18-crown-6,[17] and similar values have been reported by Holmes and co-workers for a related series of fluorosiliconates[58] Martin and co-workers examined substituent effects on the pseudorotation barriers for a series of phenyl spirosiliconates[18] and demonstrated a linear correlation between the measured barrier height and the phenyl ligand electron-withdrawing ability.

The mechanism for ligand scrambling in simple pentacoordinate silicon anions has been examined in detail with *ab initio* molecular orbital theory. Calculations carried out with several different levels of theory over the last 20 years[29−31] suggest a barrier of 2.6−2.9 kcal/mol for Berry pseudorotation of SiH_5- *via* a C_{4v} transition state. Wilhite and Spialter characterized the potential energy profiles for pseudorotation of hypothetical $SiH_{5-n}X_n^-$ species, where X is a generic electronegative substituent.[30k] Barriers ranging from 2 to 9 kcal/mol were found, depending upon the substitution pattern in the siliconate ions. Recently, Gordon and co-workers reexamined the pseudorotation potential energy surface for SiH_4F^- and showed that only a single minimum exists, i.e., that the structure with an equatorial fluorine ligand is actually a transition state.[30e,31a]

The occurrence of hydrogen ligand scrambling in pentacoordinate silicon hydride ions was briefly examined in our earlier flowing afterglow study.[33] In these experiments, deuterium-labeled hydridosiliconate ions were produced by addition of D^- to neutral alkylsilanes in the flow tube, and the relative yields of HCO_2^- and DCO_2^- formed in reactions with added CO_2 were measured (e.g., eq 21).

$$n\text{-}C_5H_{11}SiH_3 \xrightarrow{D^-} n\text{-}C_5H_{11}SiH_3D^- \xrightarrow{CO_2} HCO_2^-, DCO_2^- \qquad (21)$$

The formation of a statistical yield ratio of HCO_2^- and DCO_2^- (i.e., 3:1 in the above example) would indicate that complete H/D ligand scrambling had occurred at some point during the lifetime of the d_1 hydridosiliconate ion, presumably by way of a sequence of Berry pseudorotations that renders the hydrogen and deuterium ligands structurally equivalent. In the original study,[33] we reported the measurement of a 6:1 HCO_2^-/DCO_2^- yield ratio for reaction 21 and a 2:1 yield ratio for the analogous reaction between Et_3SiHD^- and CO_2. The occurrence of a consistent factor of 2 deviation in both experiments from the corresponding statistical yield ratios was taken as evidence for a kinetic isotope effect for H^- *vs* D^- transfer from the completely scrambled siliconate ions.

However, these experiments were complicated by the unavoidable presence of *unlabelled* hydridosiliconate ions in the flow tube, and by the occurrence of H/D exchange reactions between the d_1 hydridosiliconates and the neutral silane precursors throughout the reaction region where the CO_2 probe reagent was being added (cf. Scheme 1). Despite our efforts to correct for these effects in the earlier experiments,[33] the results are now known to be incorrect. Re-measurement of the HCO_2^-/DCO_2^- yield ratios from the reactions of various mass-selected $R_nSiH_{5-n}D^-$ ions with CO_2 in Q2 of the triple quadrupole, where the above complications are absent, indicates that the H^-/D^- transfer ratios are in fact *equal* to the statistically predicted values. Table 1 lists the isotopically-corrected HCO_2^-/DCO_2^- yield ratios determined from reactions of three different d_1 hydridosiliconate ions with CO_2 in Q2 under conditions of the

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[56] The total signal available in this experiment was insufficient to permit detection of any $^{29}SiH_3^-$ (*m/z* 32) that may have formed.

[57] (a) Sommer, L. H. *Stereochemistry, Mechanism and Silicon*; McGraw-Hill: New York, 1965. (b) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933. (c) Ugi, I.; Marquarding, D.; Klusacek, H.; Gillespie, P.; Ramirez, F. *Acc. Chem. Res.* **1971**, *4*, 288.

[58] Johnson, S. E.; Payne, J. S.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *Inorg. Chem.* **1989**, *28*, 3190.

Table 1. Corrected Yield Ratios for HCO_2^- and DCO_2^- Obtained from Reactions of d_1 Hydridosiliconate Ions with CO_2[a]

	HCO_2^-/DCO_2^-		
reactant ion	obsd[b]	stat[c]	k_H/k_D[d]
$n\text{-}C_5H_{11}SiH_3D^-$	3.33 ± 0.15	3.0	1.10 ± 0.05
$Et_2SiH_2D^-$	2.05 ± 0.21	2.0	1.03 ± 0.11
Et_3SiHD^-	1.03 ± 0.06	1.0	1.03 ± 0.06

[a] All reactions carried out in Q2 of the triple quadrupole analyzer with mass-selected reactant ions; $P(CO_2) = 0.15$ mTorr, collision energy <0.5 eV (center-of-mass). [b] Measured yield ratio corrected for ^{13}C and ^{29}Si isotopic impurities in the mass-selected d_1 reactant ion beam and the ^{13}C isotopes in the formate ion products. [c] Statistically-predicted yield ratio. [d] Apparent kinetic isotope effect for H^- *vs* D^- transfer to CO_2.

Table 2. Kinetic Data for Reactions of d_0 and d_1 Hydridosiliconate Ions with CO_2[a]

reactant ion	k_{obsd}[b]	$r = k(d_0)/k(d_1)$	k_H/k_D[c]
$n\text{-}C_5H_{11}SiH_4^-$	4.6 ± 0.5	1.0 ± 0.2	1.0 ± 0.2
$n\text{-}C_5H_{11}SiH_3D^-$	4.6 ± 0.3		
$n\text{-}BuSiH_4^-$	5.9 ± 0.2	0.98 ± 0.04	0.92 ± 0.04
$n\text{-}BuSiH_3D^-$	6.0 ± 0.1		
$Et_2SiH_3^-$	3.5 ± 0.2	0.95 ± 0.05	0.86 ± 0.05
$Et_2SiH_2D^-$	3.7 ± 0.2		
$Et_3SiH_2^-$	3.7 ± 0.2	1.03 ± 0.06	1.06 ± 0.06
Et_3SiHD^-	3.6 ± 0.2		

[a] All reactions carried out in the flowing afterglow at room temperature. [b] Measured overall rate coefficient in units of $\times 10^{-10}$ cm^3/s. [c] Apparent kinetic isotope effect for H^- *vs* D^- transfer to CO_2.

Scheme 2

$$\begin{tikzcd}
R_4SiH^- + HX \arrow[r, "\Delta G_{rxn}"] \arrow[d, "\Delta G_{HA}(R_4Si)"'] & R_4Si + H_2 + X^- \\
R_4Si + H^- + HX \arrow[r, "\Delta G_{acid}(HX)"] & R_4Si + H^- + H^+ + X^- \arrow[u, "-\Delta G_{acid}(H_2)"']
\end{tikzcd}$$

Table 3. Protonolysis Bracketing Results for Pentacoordinate Silicon Hydride Ions[a]

HA	$\Delta G_{acid}(HA)$[b]	SiH_5^-	$n\text{-}C_5H_{11}SiH_4^-$	$Et_2SiH_3^-$	$Et_3SiH_2^-$
NH_3	396.1 ± 0.7	−	−	−	−
D_2O	387.0 ± 0.2	−	−	−	−
H_2O	384.1 ± 0.2	−	−	−	−
furan	380.0 ± 3.0	+(slow)	+(slow)	+(slow)	+(slow)
fluorobenzene	378.9 ± 2.0	+	+	+	+(slow)
1,3-diazine	376.9 ± 2.0	+	+	+	+
MeOH	374.0 ± 2.0	+[c]	+	+	+
EtOH	370.8 ± 2.0	+	+	+	+

[a] + and − correspond to observance and non-observance of the protonolysis reaction shown in eq 16a, as indicated by the formation of the conjugate base anion A^- of the reference acid HA; by "slow" it is meant that the apparent yield for the reaction was <0.1%. [b] Reference 41. [c] Reaction carried out with CD_3OD to avoid mass overlap between CH_3O^- and SiH_3^- (both *m/z* 31).

lowest possible collision energy (<0.5 eV, CM; $P(CO_2) \sim 0.15$ mTorr). Close agreement between the measured and statistically-predicted H^-/D^- transfer ratios is obtained, indicating that the hydrogen and deuterium ligands have become structurally equivalent in the adducts and that the overall isotope effect for H^- *vs* D^- transfer to CO_2 is negligibly small.

The absence of a significant kinetic isotope effect for H^- *vs* D^- transfer to CO_2 was further verified by noting the identical rates of decay of the monodeuterated and undeuterated hydridosiliconate ions formed in the flow reactor in the presence of added CO_2. It is a straightforward matter to derive expressions that interrelate the kinetic isotope effect for H^- vs D^- transfer, k_H/k_D, and the ratio of observed overall reaction rate coefficients for undeuterated (d_0) and monodeuterated (d_1) ions. For reactions of CO_2 with $R_nSiH_{5-n}^-$ *vs* $R_nSiH_{4-n}D^-$ ions, k_H/k_D is given by $r/[(5 - n) - (4 - n)r]$, where $r = k(d_0)/k(d_1)$. Table 2 summarizes the data collected for mono-, di-, and trialkylsilicon hydride ions. The k_H/k_D values are all found to be essentially equal to unity, indicating negligible kinetic isotope effects for H^- *vs* D^- transfer to CO_2.

Thermochemistry. (a) Hydride Affinities. A key physical property of pentacoordinate silicon hydride ions is the absolute and relative hydride binding energies, *i.e.*, the hydride affinities (HA) of silanes. The hydride affinity[41,59] of a neutral compound, X, is given by the enthalpy of dissociation of H^- from the hydride adduct HX^-. Hydride affinities are known for a little over one hundred neutral species, spanning a range of 6.5 kcal/mol for CO to 168 kcal/mol for C_2.[41] These quantities can be determined from various thermochemical cycles, H^- transfer equilibrium measurements and bracketing experiments. The facile hydride transfer reactions observed to occur between hydridosiliconate ions and numerous types of neutral molecules suggest that silanes possess relatively low hydride affinities. However, because of the limited number of compounds with known hydride affinities in the lower end of the scale, bracketing of absolute hydride affinities for silanes, and resolution of possible differences among the mono-, di-, tri-, and tetraalkylsilanes is not practical. Hydride transfer is observed from $Et_3SiH_2^-$, $Et_2SiH_3^-$, and $n\text{-}BuSiH_4^-$ to NO (HA = 40.2 ± 1.1 kcal/mol), but not to C_6H_6 (HA = 21.5 ± 4.2 kcal/mol) or CO (HA = 6.5 ± 0.8 kcal/mol). However, it is likely that the absence of hydride transfer to benzene has kinetic rather than thermodynamic origins (*vide infra*). Cyclohexadienyl anion, the species with the lowest hydride binding energy that can be generated in the flowing afterglow, does not transfer H^- to any alkylsilanes.

(b) Protonolysis Reactions. An alternative approach to determining absolute hydride affinities for silanes involves a bracketing procedure based upon the protolytic cleavage reactions between pentacoordinate silicon hydride ions and Brønsted acids (eq 16a). A simple thermodynamic cycle formulated in terms of the hydride binding free energy of the silane (ΔG_{HA}) and the gas-phase acidities (ΔG_{acid}) of HX and H_2 can be derived, as illustrated in Scheme 2. Assuming favorable kinetic behavior, this reaction will occur only when the overall free energy change, ΔG_{rxn}, is negative. Therefore, the occurrence of this reaction with a particular reference acid implies that $\Delta G_{HA}(R_4Si) + \Delta G_{acid}(HX) - \Delta G_{acid}(H_2) \leq 0$ or, since $\Delta G_{acid}(H_2)$ is well known,[41] $\Delta G_{HA}(R_4Si) \leq 394.4 - \Delta G_{acid}(HX)$ kcal/mol. Table 3 lists the results of a series of protonolysis bracketing experiments with four different silicon hydride ions carried out with the mass-selected siliconate ion in Q2 of the triple quadrupole analyzer under conditions of the lowest possible collision energy. Each of the hydridosiliconate ions undergoes protonolysis with fluorobenzene, 1,3-diazine, MeOH, and EtOH, as indicated by the appearance of the corresponding conjugate base anions with signal intensities greater than ten times the background level. Protonolysis of the siliconates by furan appears to be very inefficient, and ammonia does not react with any of the siliconate ions. In the earlier study[33a] we reported that H_2O and D_2O were capable of protonolyzing $n\text{-}C_5H_{11}SiH_4^-$ and $Et_3SiH_2^-$. However, new measurements performed under better-defined conditions in the flow tube, and additional control experiments with these reactions carried out in Q2 of the triple quadrupole analyzer indicate that, in fact, protonolysis with H_2O and D_2O does *not* occur.[33b] Thus, all four siliconate ions behave similarly, with an apparent upper limit to ΔG_{HA} of about 14 kcal/mol. If we

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(59) Squires, R. R. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds., D. Reidel: Dordrecht, 1987, p 373.

assume that the non-occurrence of protonolysis with H_2O is thermodynamic in origin, then we can assign $\Delta G_{HA} = 12 \pm 3$ kcal/mol to these silanes, where the uncertainty is estimated.

In order to convert ΔG_{HA} to a hydride affinity (HA), the entropy of H^- binding to a neutral silane, ΔS_{HA}, is required since HA = $\Delta G_{HA} + T\Delta S_{HA}$. As with proton binding,[60] this quantity can be reasonably estimated from $\Delta S_{HA} = S°(H^-) + \Delta S_{rot}$, where ΔS_{rot} is the change in rotational entropy accompanying H^- dissociation from a hydridosiliconate ion and $S°(H^-)$ is the absolute entropy of hydride ion (26.0 ± 0.1 eu).[61] For SiH_5^- (D_{3h}, $\sigma = 6$) and SiH_4 (T_d, $\sigma = 12$), $\Delta S_{HA} = 26.0 + R \ln (6/12) = 24.6$ eu, so HA(SiH_4) at 298 K is determined to be 19 ± 4 kcal/mol. This experimental value is consistent with the values predicted from molecular orbital calculations, which are in the range of 16–22 kcal/mol.[29,30] For the alkylsiliconates, the rotational entropies are harder to estimate since the alkyl groups may occupy either apical or equatorial positions in the idealized trigonal-bipyramidal siliconate structures, and the magnitudes of the internal rotational barriers associated with the alkyl groups may differ in the siliconates and corresponding neutral alkylsilanes. Since the apicophilicity[15b] of *n*-alkyl groups in the siliconate ions is probably not large,[32b] and since these ions probably exist as mixtures of fluxional structures anyway, we will simply neglect the ΔS_{rot} term and assume $\Delta S_{HA} = 26$ eu for each of the alkylsilanes. Therefore, the final value for the 298 K hydride affinity of each of the alkylsilanes is determined to be 20 ± 4 kcal/mol. The only theoretical values available in the literature for comparison are for methylsilane; Damrauer, Burggraf, Davis, and Gordon[27] report HA($MeSiH_3$) = 17.8 and 18.2 kcal/mol from MNDO and *ab initio* calculations, respectively.

(c) Equilibrium Hydride Transfer Reactions. In principle, the relative hydride affinities of the alkylsilanes can be more accurately defined by examining the preferred direction for H^- transfer from one silane to another. Hydride transfer reactions involving selected hydridosiliconate and alkylsilane pairs have been carried out in the flow tube at room temperature and in Q2 of the triple quadrupole analyzer at low collision energies. In the flow tube experiments, reversible H^- transfer is observed to occur between the following pairs of silanes: Et_3SiH/Et_2SiH_2, Et_2SiH_2/*n*-$C_5H_{11}SiH_3$, and Et_3SiH/*n*-$C_5H_{11}SiH_3$. From these results, it is concluded that the hydride affinities of mono-, di-, and trialkylsilanes are quite similar. This conclusion is qualitatively verified by the fact that $Et_3SiH_2^-$, $Et_2SiH_3^-$, and *n*-$C_5H_{11}SiH_4^-$ each appear to react by hydride transfer with any of the other two neutral silanes in Q2 and display kinetic energy-dependent product yields that are typical for exothermic or weakly endothermic reactions. In all of the above reactions, variable amounts of protolytic cleavage and alkyl transfer (<5%) are observed to accompany H^- transfer.

In contrast, although H^- transfer to SiH_4 from any one of the three hydridosiliconate ions listed above can be observed in both the flow tube and Q2, SiH_5^- does not appear to transfer H^- to any of the corresponding alkylsilanes, even in Q2 with excess kinetic energy. This suggests that either SiH_4 has a significantly greater hydride affinity than any of the other alkylsilanes, or the rate of protolytic cleavage of SiH_5^- by neutral alkylsilanes is much greater than that for hydride transfer. In light of the protonolysis results, which suggest that the hydride affinities of all the silanes are essentially the same, plus the fact that a significant amount of SiH_3^- is usually formed from reactions of SiH_5^- with alkylsilanes, the latter explanation is more likely.

We have attempted to further quantify the difference in hydride affinity between Et_3SiH and *n*-$C_5H_{11}SiH_3$ with hydride transfer equilibrium measurements in the flowing afterglow (eq 22). These measurements were carried out in two ways: by

$$n\text{-}C_5H_{11}SiH_3 + Et_3SiH_2^- \rightleftharpoons n\text{-}C_5H_{11}SiH_4^- + Et_3SiH \qquad (22)$$

direct determination of the equilibrium ratio of the hydridosiliconate ion signal intensities that result from known concentrations of the two neutral silanes, and by measurement of the rate coefficients for forward and reverse hydride transfer between the two silanes. For the direct equilibrium experiments, a measured flow rate of Et_3SiH ($F(Et_3SiH) \approx 0.04$ atm cm^3/s) was added to the flow reactor at a distance from the sampling orifice of 85 cm and allowed to react with H^- formed at the ion source. A measured flow rate of *n*-$C_5H_{11}SiH_3$ (also about 0.04 atm cm^3/s) was then added through the moveable inlet at different positions to establish the range of reaction distances where the ratio of hydridosiliconate ion signal intensities, I_{103}/I_{117}, became constant (typically 30–40 cm from the sampling orifice). Three determinations of the equilibrium constant in this way give an average value for $K(22) = [I_{103}/I_{117}][F(Et_3SiH)/F(C_5H_{11}SiH_3)]$ of 2.9 ± 0.7. For the kinetic determination of the equilibrium constant, the variable distance method was used and the flow rate of the neutral silane precursor for the hydridosiliconate reactant ion was kept as low as practical so as to minimize the effects of back hydride transfer. Replicate measurements of the total decay rate coefficients give average values for $k(22, \text{forward}) = 4.9 \pm 0.6 \times 10^{-10}$ cm^3/s and $k(22, \text{reverse}) = 4.4 \pm 0.3 \times 10^{-10}$ cm^3/s. In both the reaction between *n*-$C_5H_{11}SiH_3$ and $Et_3SiH_2^-$, and the reaction between Et_3SiH and *n*-$C_5H_{11}SiH_4^-$, hydride transfer represents greater than 95% of the total (the remainder being protonolysis). Therefore, the equilibrium constant is determined to be $K(22) = k_f/k_r = 1.1 \pm 0.1$, in fair agreement with the value obtained by direct measurement. The average value from the two different determinations is 2 ± 1, corresponding to a difference in ΔG_{HA} for *n*-$C_5H_{11}SiH_3$ and Et_3SiH at 298 K of -0.4 ± 0.2 kcal/mol. Using an estimate for $\Delta S(22)$ of $R \ln (1/2) = -1.4$ eu, the enthalpy change, $\Delta H(22)$, is determined to be -0.8 ± 0.2 kcal/mol.

The qualitative behavior and quantitative results described above suggest the following hydride affinity order: HA(Et_3SiH) ≤ HA(Et_2SiH_2) ≤ HA(*n*-$C_5H_{11}SiH_3$) ≤ HA(SiH_4). Thus, increasing alkyl substitution decreases hydride affinity, but the effects are quite small. There are no thermochemical data in the literature involving simple alkylsilanes and other anions with which the present result might be compared. Electron-releasing inductive effects of alkyl substituents should decrease the Lewis acidity of the silicon atom, while negative charge stabilization through alkyl group polarization would lead to increased Lewis acidity in the larger silanes. For these reasons, one might expect to observe only small changes in hydride affinity with increasing alkyl substitution. MOPAC/AM1 semiempirical molecular orbital calculations[39] support this prediction and corroborate the hydride affinity ordering given above. For the simple methylsilanes the computed ordering is HA(Me_4Si) < HA(Me_3SiH) < HA(Me_2SiH_2) < HA($MeSiH_3$) ~ HA(SiH_4), with all of the hydride affinities falling within a range of only 2 kcal/mol.

(d) Unimolecular Reactions: Collision-Induced Dissociation. Theoretical studies and the present experimental results suggest that SiH_5^- and its simple alkyl derivatives are thermodynamically unstable with respect to H_2 loss. Therefore, it is of interest to examine the energy-resolved CID behavior of these

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[60] Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, NY, 1979; Vol. 2, Chapter 11.

[61] Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1 (JANAF Tables).

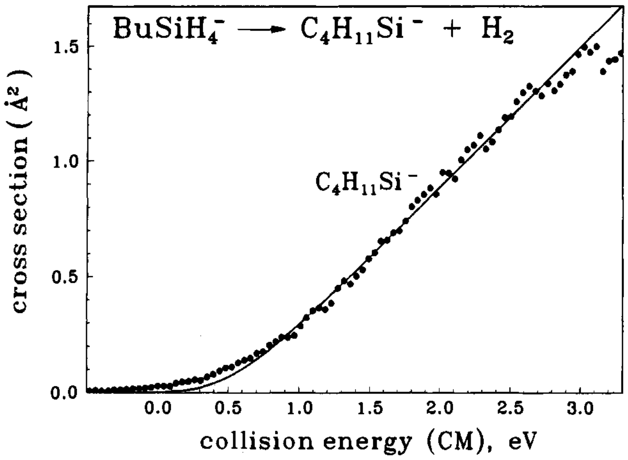

Figure 3. Cross section for dissociation of H_2 from *n*-$BuSiH_4^-$ resulting from collisional activation with neon target at 0.045 mTorr. The solid line is the optimized, fully-convoluted model appearance curve obtained with the model described in the Experimental Section.

ions since, in principle, this could provide a means to determine the H_2 dissociation barrier. Collisional activation of SiH_5^- and the mono-, di-, and trialkylsiliconate ions described in the preceding sections was carried out in the triple quadrupole analyzer with argon target gas under a range of conditions of target pressure and collision energy. Inefficient fragmentation by loss of H_2 is observed to occur in each case, with estimated maximum cross sections in the 5–10 eV (lab) collision energy range of <1.5 Å². Formation of SiH_3^- from CID of SiH_5^- can only be observed with relatively high target gas pressures (ca. 0.10–0.20 mTorr), and the product ion appearance curve is poorly defined. Figure 3 shows a plot of the energy-dependent cross sections obtained for CID of $BuSiH_4^-$ under single-collision conditions using neon target gas. The threshold (ΔE_0) for H_2 loss is determined from this appearance curve to be 0.56 ± 0.10 eV (12.9 ± 2.3 kcal/mol). Collisional activation of Et_3SiHD^- (*m/z* 118) using 0.18 mTorr argon target pressure and 17 eV (CM) collision energy results in product ions with *m/z* 115 and 116 arising by loss of *both* HD and H_2 (eq 23). This indicates that hydrogen loss from the activated ion can occur by both 1,1- (geminate) and 1,2- (vicinal) elimination mechanisms.

$$\underset{(m/z\ 118)}{Et_3SiHD^-} \rightarrow \underset{(m/z\ 115)}{C_6H_{15}Si^-} + HD \qquad (23)$$

$$\rightarrow \underset{(m/z\ 116)}{C_6H_{14}SiD^-} + H_2$$

The nature of the H_2 loss transition structure for SiH_5^- described by Reed and Schleyer provides some useful clues regarding the origins of the behavior described above.[29] They found that H_2 dissociation occurs by way of a C_{3v} structure, **C**, that resembles a hydride ion engaged in a tight hydrogen bond to one of the SiH_4 hydrogens. Formation of this structure from D_{3h} SiH_5^- requires that a (apical) hydride ligand undergoes almost complete dissociation from the silicon atom and then adopts a collinear orientation with one of the Si–H bonds. This certainly represents a "tight", dynamically disfavorable transition state. Moreover, the activation energy calculated for this rearrangement process (17.5 kcal/mol) was found to be slightly greater than the energy required for direct cleavage to $H^- + SiH_4$ (16.0 kcal/mol). Therefore, H^- dissociation from SiH_5^- is kinetically and energetically preferred over H_2 loss. This could account for the apparent inefficiency of the dissociation reaction involving SiH_5^-, since one would predict that CID of SiH_5^- should occur mainly by loss of H^-—an ion that cannot be detected directly by our instrument. Formation of a relatively free H^- ion during unimolecular decomposition of a siliconate is also consistent with the observed loss of H_2 from Et_3SiHD^- (eq 23), since this strongly basic ion could deprotonate the α-CH position in one of the ethyl groups of the nascent Et_3SiD molecule prior to its departure from the complex.

Summary. Hydridosiliconate ions represent a fascinating class of hypercoordinate species that exhibit unique chemical behavior and unusual physical properties. These ions are relatively easily accessed for gas-phase studies under flowing afterglow conditions by direct addition of hydride ion or other nucleophilic anions to alkylsilanes. Pentacoordinate silicon ions have been found to be reactive hydride reducing reagents that can be used to prepare a variety of other negative ions in the gas phase, including the archetype hydridosiliconate ion, SiH_5^-. Sequential hydride–deuteride exchange reactions have been shown to occur between hydridosiliconate ions and SiD_4. These reactions may find practical use as ion structure and mechanistic probes in future studies of gas-phase siliconate ion chemistry. Alkylhydridosiliconate ions react with neutral silanes by alkyl group transfer with accompanying H_2 loss to yield mixtures of tricoordinate silyl anions and α-silylcarbanions. The chemical reactivity results described in this study indicate that simple alkylhydridosiliconate ions are thermodynamically unstable with respect to dissociation of H_2 and that they are fluxional molecules in which all of the hydride ligands become chemically equivalent. Protonolysis of Si–H bonds (but not Si–C bonds) in hydridosiliconate ions readily occurs with Brønsted acids to yield H_2, silyl anions, and either the free or silicon-complexed conjugate base of the acid. These reactions can be used to estimate the hydride affinities of SiH_4 and alkylsilanes, which are all found to be in the vicinity of 20 kcal/mol. Collision-induced dissociation of hydridosiliconate ions occurs by inefficient loss of H_2, with estimated activation energies around 0.6 eV (13 kcal/mol). CID results for a deuterium-labeled alkylsiliconate indicate that both 1,1- and 1,2-elimination mechanisms are involved in these dissociations.

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