Do Barriers Exist for Nucleophilic Substitution at Tetravalent Silicon in the Gas Phase? An ab Initio and Ion Cyclotron Resonance Study

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Abstract: Ab initio calculations predict that the low-pressure gas-phase reaction of H^- with silane should produce H_3Si^- by (i) reaction at hydrogen and (ii) by elimination of hydrogen from the energized trigonal-bipyramidal intermediate H_5Si^-. Similar reactions are suggested for MeO^- with silane (with the elimination of methanol), and this is confirmed by ICR experiments. The attack of either nucleophile on silane proceeds without energy barriers. In contrast, calculations indicate that HO^- and MeO^- should initially react with methylsilanes through a methyl hydrogen to give species of the type $[NuH\text{---}{}^-CH_2SiH_3]$. These complexes are expected to be short lived since only a small barrier [20–35 kJ mol^{-1} (3-21G)] separates them from the more stable trigonal-bipyramidal species $[Me(Nu)SiH_3^-]$. ICR experiments fail to detect long-lived H-bonded species between various methylsilanes and RO^- or $[RO^-\text{---}HOR]$. Barriers in these and similar reactions do not affect the rates of formation of adducts since these are observed to be very high and apparently collision controlled. Ab initio and MNDO calculations predict that when the nucleophile and the attached groups are large (e.g., I^-/SiI_4), five-coordinate silicon adducts are still stable. Thus the S_N2 mechanism on silicon never resembles that of carbon.

Introduction

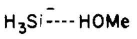
Dewar and Healy have suggested that tetrahedral carbon is less reactive than tetrahedral silicon toward nucleophilic reagents because of its smaller size rather than its lack of valence shell d orbitals.[1] They proposed that the five-coordinate state along the substitution path of tetrahedral carbon is raised in energy and is a transition state because of steric overcrowding, whereas the larger silicon atom can accommodate five attached atoms and its five-coordinate state can be a discrete intermediate. These features are illustrated in Figure 1.

We concur with Dewar and Healy that these contrasting features do not arise from d orbitals on silicon since the energy profiles shown in Figure 1 can be obtained without the use of d orbitals. Nevertheless, we undertook the present study because there is room for debate on the details and interpretation of silicon reactions. Thus we have studied both experimentally and theoretically to what degree it is true that typical nucleophilic attack (say by H^-, HO^-, MeO^-, and $[MeO^-\text{--}HOMe]$) on silane and methylsilane involves exothermic additions to silicon with (or without) the impediment of barriers and whether such five-coordinate adducts are the favored intermediates or products. In this paper we address the following questions: (i) Is nucleophilic addition to silicon the major path even in the most favorable case of silane, or is some other reaction (e.g., deprotonation) the major pathway? (ii) Are the hydrogens of silane or methylsilanes acidic enought to "trap" the incoming nucleophile into H bonding sufficient to produce a discrete potential well of associating reactants from which trigonal-bipyramidal adducts can only be formed by surmounting an energy barrier? (iii) If energy barriers do occur, do these affect the rate of reaction, i.e., is the observed rate slower than the collision rate? (iv) Does silicon revert to "carbon-like" behavior with no stable five-coordinate intermediate when the nucleophile and the attached groups are large?

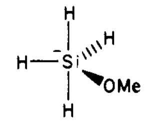
Results and Discussion

Ion cyclotron resonance experiments were carried out on a Dynaspec ICR 9 spectrometer equipped with a three-section cell operating at 70 eV and using an ion transit time of 1×10^{-3} s.[2] Full experimental details are given in the Experimental Section. Ab initio calculations were carried out with use of GAUSSIAN 80[3] at 6-21G or 3-21G level as indicated.[4,5]

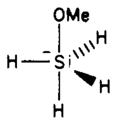
(a) The Reactions of Silane with H^-, RO^-, and $[RO^-\text{---}HOR]$. We have explored the fully relaxed motion of the hydride ion toward silane (at the 6-21G level) from starting points on a 180° arc in the plane embracing two H–Si bonds and the C_{2v} and C_{3v} axes. The relaxation runs started (at 3.5 Å from silicon) from points at 10° intervals along the arc, and the results are shown in Figure 2. It was found, for example, that a hydride ion within ±30° of the H–Si bond (chosen to define a direction of 0°) will react at hydrogen to ultimately form H_3Si^-.[6] The spread of angles from which the three possible kinds of products eventuated leads to a statistical expectation of yield as follows: 29% deprotonation (to SiH_3^-), 19% equatorial addition (to SiH_5^-), and 52% apical addition (to SiH_5^-). Thus with even the smallest nucleophile, there is a reasonable probability for reaction at hydrogen rather than silicon. We find no barriers for the direct attachment of hydride to silicon or to hydrogen. Once formed, SiH_5^- is separated from SiH_3^- and H_2 by a substantial barrier (estimated to be 300 kJ mol^{-1} at 6-21G), involving the concerted deflection and rupture of one apical and one equatorial Si–H bond leading to the elimination of H_2. The estimated barrier is somewhat high since no allowance has been made for configuration interaction in the transition state, yet the present estimate of the crest of this barrier lies 13 kJ mol^{-1} below the reactants. Thus SiH_5^- should have sufficient excess energy immediately after formation for it to cross the barrier and convert irreversibly into SiH_3^- and H_2. *Consequently five-coordinate SiH_5^- is expected to be short lived at low pressures and not directly observed.*[7]



1
(−233 kJ mol^{-1})



2
(−199 kJ mol^{-1})



3
(−206 kJ mol^{-1})

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[1] Dewar, M. J. S.; Healy, E. *Organometallics* **1982**, *1*, 1705.

[2] Bowie, J. H. *Acc. Chem. Res.* **1980**, *13*, 76.

[3] Binkley, J. S.; Whitehead, R. A.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. GAUSSIAN 80, Department of Chemistry, Carnegie-Mellon University, 1980. Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

[4] The molecular complexity of many of these systems has obliged us to work at the 3-21G level of atomic bases through limitations in file space.

[5] We recognize that the best representations of negatively charged species require expanded bases (e.g., see: Radom, L. *Mod. Theor. Chem.* **1977**, *4*, 333. Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609) preferably with a low exponent Gaussian in each set to represent the diffuse outer region of negative ions. Nevertheless, we believe that systematic exploration of the relative energies in the transition states, intermediates, and products in complex reaction pathways is indispensible if reaction sequences are to be evaluated and characterized.

[6] A weak complex $[H_3Si^-\text{--}H\text{-}H]$ appears at $d_{Si\cdots H}$ = 3.6 Å with a binding energy of −6 kJ mol^{-1}. Its existence must be regarded as at best transitory on the pathway to SiH_3^- and H_2.

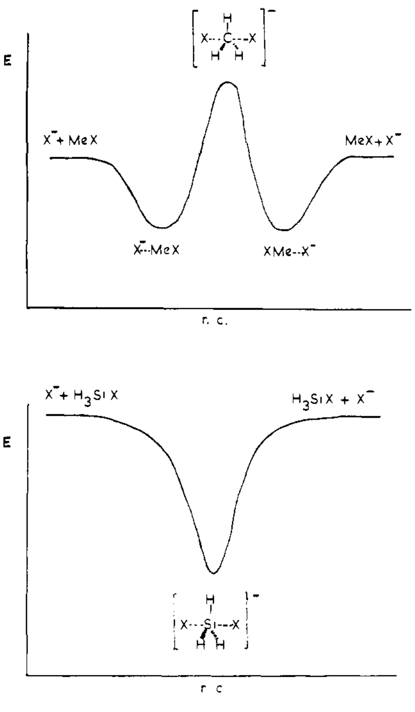


Figure 1. Minimum energy reaction paths proposed[1] are (a, top) a degenerate S_N2 reaction and (b, bottom) addition of X^- to H_3SiX.

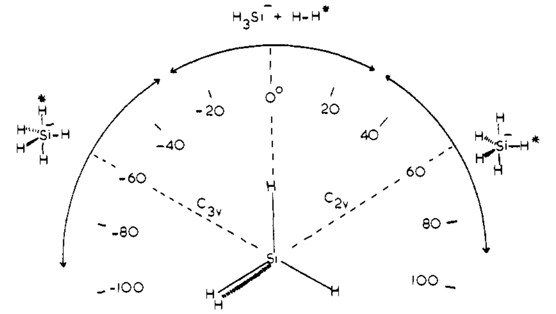


Figure 2. Preferred motion of H^- toward SiH_4 from an initial distance of 3.5 Å from silicon within a plane embracing two Si-H bonds and the C_{2v} and C_{3v} axes.

Calculations at the 6-21G level for the approach of MeO^- toward silane along (i) the H-Si axes, (ii) the twofold axes bisecting the H-Si-H angles, and (iii) the threefold axes leading into an H_3Si trigonal face indicate no barriers on the way to the formation of the respective adducts **1**, **2**, and **3**. Species **1** may eliminate methanol to yield H_3Si^- since its excess energy of formation exceeds its dissociation energy of 51 kJ mol^{-1}. Thus the reactions of the system MeO^-/silane should be deprotonation and adduct formation. Alkoxide negative ions RO^- (R = Me, Et, Pr, Bu, and *t*-Bu) all react with silane in ICR experiments to yield H_3Si^-, but adducts $[SiH_4 + RO^-]$ are *not* observed.[8] The formation of $(SiH_4 + RO^-)$ species can be effected if alkanol alkoxide negative ions $[RO^- \cdots HOR]$[10] are used instead of RO^-; i.e., the eliminated molecule of ROH takes off some of the excess energy of the reaction effectively stabilizing the adduct. Interestingly, the abundance of adduct peaks is in the following order—MeO < EtO < PrO < BuO ≫ *t*-BuO. Elaboration of R offers a wider partitioning of excess energy in the adduct, except for *t*-BuO whose shape renders adduct formation less favorable.

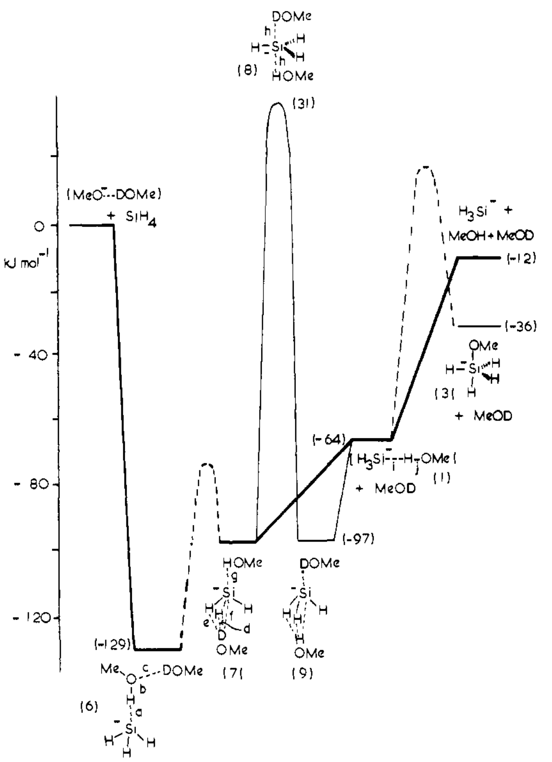
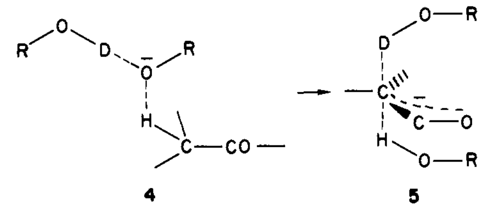


Figure 3. Calculated (6-21G) reaction channels following attachment of $[MeO^- \text{--} DOMe]$ to a silane hydrogen. Bond lengths (Å) are as follows: **6** ($a = 2.62$, $b = 0.99$, $c = 1.75$); **7** ($d = 2.34$, $e = 2.36$, $f = 3.04$, $g = 2.08$); **8** ($h = 2.87$), and **1** ($i = 2.75$, $j = 0.98$). Reaction intermediates are drawn as originating from **7**, i.e., assuming no equilibration between **7** and **9**. The height of the barrier (**6** → **7**) has not been calculated: the barrier crest must be below −64 kJ mol^{-1} (i.e., less than the energy required for the process **6** → **1** + MeOD).

Two questions now need to be addressed, viz (a) do the adducts correspond to solvated species (like **1**) or are they five coordinate (like **3**)? (b) If they correspond to **3**, are they formed by direct nucleophilic attack at silicon or by a sequential process involving initial attack of the nucleophile at hydrogen? ICR solvent exchange experiments were carried out to answer the former question. The species $[SiH_4 + EtO^-]$ was formed in the cell with an excess of (i) CD_3OD and (ii) butanol. *No solvent exchange was noted.* Thus the adducts observed should be five-coordinate species (e.g., **3**). To resolve the second question is a more difficult undertaking.



4 **5**

In our studies of >CH—CO—/$[RO^- \cdots DOR]$ systems we were able to demonstrate the attachment of the nucleophile to hydrogen because of the occurrence of H/D equilibration, and we proposed the intermediacy of the species **4** and **5** to rationalize the equilibration reaction.[11] If we could demonstrate a similar H/D

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(7) We have been unable to form SiH_5^- by reaction of silane with either MeO^- (cf.: Ingemann, S.; Kleingeld, J. C.; Nibbering, N. M. M.; *J. Chem. Soc., Chem. Commun.* **1982**, 1009. Sheldon, J. C.; Bowie, J. H.; Hayes, R. N. *Nouv. J. Chim.* **1984**, *8*, 79) or the cyclohexadienyl negative ion (cf.: DePuy, C. H.; Bierbaum, V. M.; Schmitt, R. J.; Shapiro, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 2920).

(8) Experimental conditions—total pressure 1×10^{-5} torr, maximum ion residence time 1×10^{-3} s. In contrast, RO^- negative ions react with Me_4Si to produce stable $[Me_4Si + RO^-]$ adducts.[9] The exception is *t*-BuO^- which does not react with Me_4Si.

(9) Klass, G.; Trenerry, V. C.; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1981**, *34*, 519.

(10) Alkoxide–alkanol negative ions are produced by the Riveros reaction: Blair, L. K.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 1057. Isolani, P. C.; Riveros, J. M. *Chem. Phys. Lett.* **1975**, *33*, 362. Faigle, J. F. G.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 2049.

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Table I. Energies (kJ mol^{-1} at the 3-21G Level) of H-Bonded and Five-Coordinate Adducts between Nu$^-$ (HO$^-$ and MeO$^-$) and Methylsilanes

substrate	H-bonded adduct		five-coordinate adduct (apical attack)	
	HO$^-$	MeO$^-$	HO$^-$	MeO$^-$
$MeSiH_3$	-195	-86	-310	-213
Me_3SiH	-191	-81	-307	-194
Me_4Si	NS[a]	NS[a]	-297	-183

[a] NS = not studied.

exchange with silane/[MeO$^-$- - -DOMe] we could confirm the attachment of the solvated nucleophile at a substrate hydrogen. ICR experiments demonstrate for this system that only [SiH_4 + MeO$^-$] species are formed—*no H/D equilibration is observed.* We found this observation sufficiently interesting to test, using ab initio calculations, whether it is theoretically possible for [RO$^-$- - -HOR] to react with a silane hydrogen, and if so whether that species could rearrange to a symmetrically disolvated intermediate (analogous to **5**). The results are summarized in Figure 3.

The results shown in Figure 3 summarize the reaction channels for the [MeO$^-$- - -DOMe]/silane system following nucleophile attack at hydrogen: direct attack at silicon is not considered. The H/D equilibration reaction is not observed since initial intermediate **6** (see Figure 3) does not relax into a symmetrical intermediate in which the alkanol residues are equivalent. Instead, **7** is formed and the alkanol residues can only be "equilibrated" by conversion to **9** through the symmetrical transition state **8**. Since this involves a considerable barrier, conversion **7** $\rightleftarrows$ **9** is unlikely. Intermediate **7** can eliminate MeOD to form **1** which should then decompose to H_3Si^-.[12] We have already shown that **1** is not a product in this reaction, and it is arguable whether it has sufficient internal energy to convert to five-coordinate **3**.[13] Taking all these factors into consideration it is likely that the major route to **3** involves direct attack of the solvated nucleophile at silicon.

(b) The Reactions of Methylsilane with HO$^-$ and MeO$^-$. There must be a reasonable probability that a nucleophile will interact first with tetramethylsilane via H bonding since the methyl hydrogens must be encountered first even when Nu$^-$ passes on its most favorable trajectory toward the central silicon.

Discrete H-bonded adducts of the type [ROH- - -$^-CH_2SiH_{(3-n)}Me_n$] (R = H or Me; n = 0 or 2) and trigonal-bipyramidal adducts of the type [$Me_n(RO)Si^-H_{(4-n)}$] (R = H or Me; n = 1, 3, and 4; RO in the apical position) have been identified by ab initio calculations; their energies of formation (from Nu$^-$ and the neutral substrate) are listed in Table I. Since the two types of adduct are local potential energy minima, barriers must exist between them. There is thus a prima facie case that such barriers must be overcome when a basic nucleophile attacks (say) Me_4Si at the silicon centre, provided the H-bonded species is the first stable intermediate in the reaction pathway.

(i) The Reaction Trajectory of HO$^-$ on MeSiH$_3$. The potential surfaces leading to the two forms of adduct in the HO$^-$/$MeSiH_3$ model system have been searched as a series of fully relaxed geometries proceeding from the incipient formation of the H-bonded intermediate to the formation of the trigonal-bipyramidal ion. The results are summarized in Figure 4. An HO$^-$ ion placed in the vicinity of the methyl group of $MeSiH_3$ strongly relaxes to the H-bonded adduct **10** (see Figure 4). A deeply defined channel leads to the formation of **10** because of its large formation energy (−195 kJ mol^{-1}). Within the concerted changes of C- -H and H–O bonds and C- -H–O angles explored, a barrier of 35 kJ mol^{-1} is estimated for conversion of **10** to **11**. These calculations indicate that HO$^-$ will react with a substrate of the type Me_4Si initially via H bonding, and that there is a barrier to be surmounted[14] before the five-coordinate adduct can be formed.

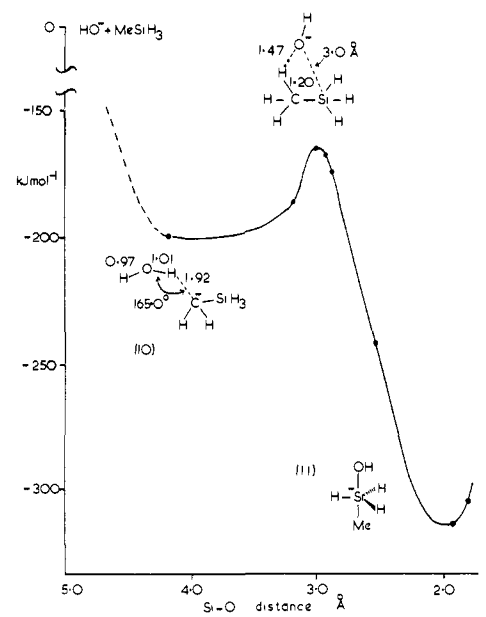

Figure 4. The HO$^-$/$MeSiH_3$ reaction. Calculations at the 3-21G level.

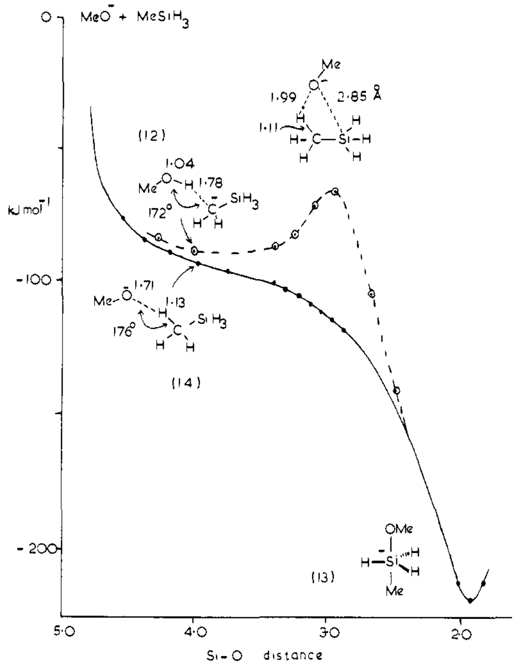

Figure 5. The MeO$^-$/$MeSiH_3$ reactions. Calculations at the 3-21G level.

(ii) The Reaction Trajectory of MeO$^-$ on MeSiH$_3$. The results obtained for the MeO$^-$/$MeSiH_3$ reaction are summarized in Figure 5. The formation energy of [MeOH- -$^-CH_2SiH_3$] (**12**) is smaller than that of [HOH- -$^-CH_2SiH_3$] (**10**), viz −86 and −195 kJ mol^{-1}, respectively. Thus the channel leading to **12** (Figure 5) is less strongly defined that that leading to **10** (Figure 4). Two reaction paths lead to the trigonal-bipyramidal species **13**. The first channel involves initial formation of H-bonded adduct **12**, subsequent to which there is a small barrier (20 kJ mol^{-1}) which

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(12) The reaction [MeO$^-$- -HOMe] + SiH_4 → H_3Si^- + 2MeOH was not detected by cyclotron ejection; the major precursor of H_3Si^- is MeO$^-$.

(13) We have not computed the barrier for the conversion **1** to **3**, but it is certainly not less than 50 kJ mol^{-1}. As much of the excess energy of formation of **1** will be removed by the methanol, it is not certain that conversion **1** to **3** can occur.

(14) Such a barrier (35 kJ mol^{-1}) should be compared with those calculated for nucleophilic addition to carbon systems; e.g., for the MeO$^-$/MeCHO system the barrier is suggested to be 65 kJ mol^{-1} for the process [MeOH- -$^-CH_2CHO$] → [(MeO)(Me)(H)C–O$^-$].[9] Barrier heights of a variety of S_N2 reactions are calculated to be in the range 5-60 kJ mol^{-1}.[15]

Table II. Rates (Flowing Afterglow) of Typical Methylsilane Reactions

reaction	rate *k*, cm^3 $molecule^{-1}$ s^{-1}
$Me_4Si + MeO^- \rightarrow Me_4Si^-OMe$	2×10^{-9}
$Me_4Si + F^- \rightarrow Me_4SiF^-$	1.9×10^{-9}
$Me_3SiOMe + MeO^- \rightarrow Me_3Si^-(OMe)_2$	2×10^{-9}
$Me_4Si + HO^- \rightarrow Me_3SiO^- + CH_4$	1.9×10^{-9}

must be surmounted prior to formation of **13**. In the second channel, MeO^- skirts the methyl substituent, approaches, and bonds to silicon with monotonically decreasing energy. This channel has no barrier and lies a few kilojoules lower than **12**. The interatomic distances in the second channel at the point of closest approach of MeO^- to a methyl hydrogen are quite different from those of **12** (see formulae **12** and **14** in Figure 5).

We have been unable to detect H-bonded complexes in ICR experiments involving nucleophilic addition to methylsilanes. The reaction of $[MeO^- {\cdot}{\cdot} DOMe]$ with Me_4Si gives only an adduct $[Me_4(MeO)Si^-]$—no H/D equilibration is observed. This adduct does not undergo "solvent exchange" with other alcohols, so the proposed intermediate $[MeOH {\cdot}{\cdot} {}^-CH_2SiMe_3]$ is not detected by ICR. In order to increase the possibility of the H/D exchange reaction, we carried out a similar reaction between $[MeO^- {\cdot}{\cdot} DOMe]$ and $MeSiF_3$; however, even in this system only a single adduct $[Me(MeO)SiF_3^-]$ is produced.

(c) The Relationship between Barriers and Reaction Rates. Although the reactions which occur between nucleophiles and either trigonal or tetrahedral carbon in the gas phase are normally exothermic or thermoneutral, the rates of such reactions range from collision controlled to too slow to be observed.[15-17] Brauman explains this variation in observed rates (with particular reference to tetrahedral carbon) by (a) a central barrier whose crest may be even lower in energy than reactants and (b) the internal energy levels of the transition state being more widely spaced than those of the reactants so that the back reaction is favored by entropy.[15,17] It is worth noting that molecular orbital calculations typically characterize the barriers in simple S_N2 reactions on tetrahedral carbon as lying higher in energy than reactants. On the other hand, recent theoretical studies[9,18,19] of nucleophilic addition or substitution at trigonal carbon indicate the existence of barriers (in support of Brauman's suggestion and in contradiction to earlier studies[20] which found no barriers in restricted surveys of potential surfaces). Nucleophilic approach toward a trigonal carbon generally proceeds with the initial formation of an H-bonded complex between the nucleophile and a hydrogen of the substrate. There is then an energy barrier to be surmounted as the nucleophile detaches itself and approaches the carbon center.[9,18,21]

Alkylsilanes undergo a variety of reactions with nucleophiles,[9,22-24] and our ab initio calculations indicate that there are energy barriers in certain of these reactions. Do the barriers affect the rates of these reactions? Damrauer, De Puy, and Bierbaum have shown that nucleophiles react with trimethylchlorosilane in the gas phase at the collision rate for exothermic reactions, or not at all for endothermic reactions.[24] DePuy and colleagues have measured for us the rates of formation of the four representative reactions shown in Table II.[25] *These reactions are fast and proceed at or near the collision rate.*[26] We would expect a similar situation for the corresponding reactions of silane and methylsilane.

An explanation for this observation may be that for an energy barrier of this type, the energy difference between reactants and transition state is too wide for the "entropy effect"[15] to affect the rate of a strongly exothermic reaction. In the particular examples of Figures 4 and 5, these differences are of the order −160 and −60 kJ mol^{-1}, respectively. We do not know how small this energy difference must become in order to lessen the reaction rate for Nu^-/silicon reactions.

(d) Does Silicon Form Stable Five-Coordinate Intermediate when the Attached Groups Are Large? Dewar and Healy rejected the orbital explanation for the lower rates of nucleophilic substitution at four-coordinate carbon relative to silicon and concluded that the only remaining and possible explanation lay in the greater steric repulsion within a five-coordinate species centered on the smaller carbon.[1] We have tested this proposal by calculating whether a variety of five-coordinate silicon species with increasingly large groups are local energy minima lying below reactant energies or whether they are unstable and dissociating species, i.e., potential transition states. In short, will silicon revert to "carbon-like" behavior if it becomes overcrowded in the five-coordinate state?

We have found that $[SiH_3(SMe)_2]^-$, $[SiH_3(SiH_3)_2]^-$, and $SiCl_5^-$ are true energy minima with formation energies of −94, −5, and −151 kJ mol^{-1}, respectively (6-21G).[27] Since GAUSSIAN 80 does not extend to atoms heavier than argon, we employed the semiempirical MNDO package MOPAC[28] for calculations on the species $SiCl_5^-$, $SiBr_5^-$, and SiI_5^-. Again, all are local energy minima with formation energies of −235, −211, and −194 kJ mol^{-1}, respectively. Bromine and iodine atoms are larger relative to silicon than hydrogen or fluorine (say) are to carbon.[29] If carbon is, in purely steric terms "overcrowded" in the five-coordinate state of the exemplary S_N2 reaction $F^- + MeF \rightarrow FMe + F^-$, then silicon cannot escape being "overcrowded" in the five-coordinate states of $SiBr_5^-$ and SiI_5^-. Steric effects (i.e., secondary repulsive forces between substituents) do play a role in certain Nu^-/silicon reactions, e.g., the adduct formed in ICR experiments between *t*-BuO^- and silane is much less abundant than that formed between BuO^- and silane. Yet in the simpler silicon systems described here, it appears that repulsive forces between substituents do not provide

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(26) We can be no more precise than this since it is likely that collision rates calculated by ADO theory are at best correct to ±20%, see: Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347. Su, T.; Bowers, M. T. "Gas Phase Ion Chemistry"; Bowers, M. T., Eds.; Academic Press: New York, 1979; Vol. 1, Chapter 3.

(27) Reaction of Cl^- with tetrachlorosilane in ICR experiments does not lead to a detectable $SiCl_5^-$ species; presumably its excess energy of formation renders it unstable with respect to products. Similarly, MeS^- does not yield a stable adduct with tetramethylsilane.

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(29) The normal covalent radii (Å) are the following: C 0.77, H 0.37, F 0.72, Si 1.17, Br 1.14, I 1.33 (Wells, A. F. "Structural Inorganic Chemistry"; 4th ed.; Oxford University Press: Oxford, 1975; p 236). The ratios of H and F to C are 0.48 and 0.94, whereas the ratios of Br and I to Si are 0.97 and 1.14, respectively.

an explanation for the different behavior of carbon and silicon.

The difference between carbon and silicon is due to the increase in atomic size (from C to Si) having an effect on bond formation and, in particular, on favoring a greater number of bonds formed. For example, increasing the size of the central atom increases the separation between it and the donor atoms and implies diminished repulsion between the effective nuclear charges of their atomic cores. An increase in the coordination number in the cluster of atoms is then favored both by the diminished repulsion between cores and by the consequential reduction in localization (the mutual repulsion) of valence electrons within the larger cluster.[30]

Conclusions

We have gone some way to answering the four equations posed in the introduction. In brief the answers are the following:

(i) Nucleophilic addition to silicon is the major pathway in silane and methylsilanes. The formation of a *stable* five-coordinate intermediate in such an exothermic reaction depends both upon possible decomposition modes of the intermediate, and upon its ability to dissipate (some of) its excess energy of formation.

(ii) Theoretical calculations predict that H^- and MeO^- should react with silane without energy barriers to form $[H_4SiNu^-]$. In contrast, the hydrogens of methylsilanes should initially trap a basic nucleophile (e.g., HO^-, MeO^-) and there is then a small energy barrier (20 to 35 kJ mol^{-1}) to be overcome before the five-coordinate adduct is formed. The predicted H-bonded intermediates are not detected in ICR experiments.

(iii) The energy barriers described in ii (above) do not affect the rates of the reactions which (within experimental and computational error) are equal to the collision rates.

(iv) Theoretical calculations show that silicon can (in theory) form stable five-coordinate adducts even with the bulkiest of donor atoms. This contrasts with carbon, which is unable to form five-coordinate adducts even with the smallest donor atoms. This difference is unlikely to result solely from steric factors.

Experimental Section

ICR spectra were measured with a Dynaspec ICR 9 spectrometer. Spectra can either be obtained in the 0–5 eV range (primary negative ions formed by dissociative thermal electron capture) or in the range 40–80 eV (primary negative ions formed by dissociative secondary electron capture). The latter range gives the better sensitivity, hence spectra were obtained at a nominal 70 eV. Other reaction conditions are the following: $\omega_c/2\pi$ = 153.7 kHz; RONO pressure 5×10^{-6} torr; pressure of silyl compound 1×10^{-5} torr. In the case of $[RO^- \text{--} HOR]$ experiments, HCO_2R was also added at a partial pressure of 5×10^{-6} torr. The ion current was in the 10^{-10} A range, emission current 0.2 μA, and ion transit time 1×10^{-3} s.

Alkyl nitrites were prepared on the day of the ICR experiment by a standard method.[31] Silane was prepared from tetrachlorosilane by reaction of lithium aluminum hydride,[32] and trifluoromethylsilane was prepared by a standard method.[33]

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(30) As an illustration, the most stable crystalline forms of the native group 4A elements display the following coordination numbers (bonds to nearest neighbors): C 3, Si 4, Ge 4, Sn 6, and Pb 12. This is an example of an increase in coordination number down a group in the Periodic Table, yet it cannot be attributed to increasing atomic size since the relative sizes of any atom to its neighbors is constant (and equal) in any one of these elemental structures. It must be inferred that the capacity of larger atoms to achieve higher coordination number is related to the characteristics of the longer bonds formed. For an example of a model that relates coordination number to variations of repulsions between atomic cores, see: Allison, G. B.; Sheldon, J. C. *Inorg. Chem.* **1967**, *6*, 1493.

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Cyclopropylidenemethanone: A Quasi-Symmetrical Molecule

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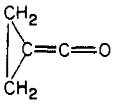
Abstract: The structure of cyclopropylidenemethanone has been investigated via microwave spectroscopy. Analysis of the spectra of the ground and nine excited vibrational states has revealed the form of two bending potentials involving motion of the methanone group relative to the cyclopropylidene ring. The vibration perpendicular to the plane containing the ring carbon atoms has a double-minimum potential with the ground state lying just 2 cm^{-1} below the 29 cm^{-1} high central barrier. Analysis of this motion using the rigid bender method shows that the two potential minima lie 17.5° away from the ring plane. The proximity of the ground state to the top of the barrier leads to the designation of the molecule as *quasi-symmetric*, being close to C_{2v}, despite its less symmetric C_s equilibrium structure. The vibration in the plane of the ring has a near harmonic potential, with a fundamental of 154 cm^{-1}. Analysis of the Stark effect indicates a dipole moment of 2.60 (1) D.

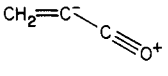
Cyclopropylidenemethanone (**1**) would be expected to have a symmetrical C_{2v} structure, with all heavy atoms in a plane were it not for the fact that the closely related molecule propadienone (**2**) has recently been shown to be kinked, the heavy atoms being in a zigzag arrangement in the methylene plane.[1,2] The question therefore arises as to whether **1** will exhibit an analogous structural abnormality. The cyclopropane ring has long been regarded as electronically similar to a double bond.[3,4] The electronic pe-



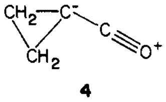
1

$CH_2{=}C{=}C{=}O$

2



3



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