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Theoretical Study of the Decomposition of Five-Coordinate Silicon Anions

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Abstract: We have performed a theoretical study of the decomposition of the five-coordinate silicon anions (siliconates) 

\[ \text{H}_4\text{Si(OH)}_2 \text{Si(OH)}_2 \text{Si(OH)}_2 \]  

and \( \text{H}_4\text{Si(OH)}_2 \text{Si(OH)}_2 \text{Si(OH)}_2 \). These ions can be formed from hydroxide ion attack on methylsilicate or tetramethylsilicate, respectively. Both MNDO and ab initio calculations show that removal of methane from the five-coordinate structure is likely, via a transfer of the proton from the OH group to an adjacent methyl substituent. This process we term anionic dissociative proton transfer, because the transition state is one in which the methyl group being removed is almost completely dissociated to methylene ion before the proton transfer takes place. This conclusion is in agreement with earlier experimental work by DePuy, Bierbaum, and Damrauer, which indicated a correlation between the rates for these reactions and the gas-phase acidities of the products. Detailed comparisons among the MNDO calculations, the ab initio calculations, and available experimental data indicate that great caution should be exercised in using MNDO calculations to draw even semiquantitative conclusions about these silicon-containing anion systems without resorting to reliable ab initio results on similar systems.

The chemistry of silicon and silicon compounds has become increasingly important to the creation of many new materials, including catalysts, polymers, ceramics, glasses, and composites. We have embarked on a theoretical study of the mechanisms of elementary silicon reactions, of which this paper is the third in this series. In previous papers we discussed a comparison of fluorine atom and fluoride ion attack on methane and silane and the stabilities of some small five-coordinate siliconates. In this paper we continue the discussions of five-coordinate siliconates and in particular the decomposition of siliconates substituted by both methyl and hydroxyl groups. Our consideration of these systems was spurred by the gas-phase studies conducted by DePuy, Bierbaum, and Damrauer of the attack of hydroxide ion onto various silanes and their subsequent decomposition.

Our eventual goal is to perform theoretical calculations for rather large molecular systems involved in the polymerization of silanols to form silicic acid. At present, available ab initio molecular orbital methods are much too time-consuming to attack directly the systems of interest. Therefore, we depend heavily on Dewar’s MNDO method to calculate properties for the large molecular systems involved in these processes. We have found, however, that because of known and suspected deficiencies of MNDO, it is necessary to carry out reliable ab initio calculations on smaller model systems whenever possible to verify and calibrate the MNDO results. In particular, this combination of techniques has uncovered and quantified several deficiencies in MNDO calculations on silicon compounds, including a tendency to overestimate heats of formation of small anions and certain transition states and an inability to predict the correct energy ordering of isomers of five-coordinate silicon complexes. Of great importance in this paper is the determination of the usefulness of MNDO in determining the properties and reactivities of five-coordinate siliconates, which appear to be quite prevalent in reactions of anions with tetrahedral silicon compounds, as discussed by Dewar and Healy in an earlier paper on MNDO calculations. There have been only a few published theoretical works on silicon chemistry using semiempirical techniques, but recently quite a number of ab initio studies of small silicon systems have appeared. Thus, we consider in this paper the formation and decomposition of siliconates containing both methyl and hydroxyl groups. There are a variety of possible decomposition routes, including simple removal of any of the ligands to form the negative ion of that ligand and the resultant silane and interaction of various ligands to produce a variety of leaving groups. Of particular interest are interactions of the proton of the hydroxyl group with other ligands to form neutral leaving groups of the form \( \text{XH} \), in which \( \text{X} \) is a ligand other than hydroxyl. These processes have been invoked in explaining the gas-phase data of DePuy, Bierbaum, and Damrauer.

Calculations

The semiempirical calculations were performed with the MNDO method developed by Dewar and co-workers. The silicon parameters were obtained from a later communication by Dewar. All stationary

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Decomposition of Five-Coordinate Silicon Anions

points on the potential surface were optimized by procedures supplied with the MOPAC package of programs available through QCPE.20 The ab initio geometries were predicted at the 6-31G(d) SCF level for the monomethylsiliconate (H3SiMeOH−) and its reactions and at the 3-21G* SCF level for the tetramethylsiliconate and its reactions. For energy comparisons on the monomethylsiliconate system, single-point calculations were performed with second-order perturbation theory23 and the 6-31+G(d) basis set.24 For the tetramethylsiliconate system MP2/6-31+G(d), energy differences were estimated by assuming correlation effects obtained from MP2/3-21G* and polarization effects resulting from RHF/6-31+G(d) energies are additive.25 To reduce the computational effort involved in the geometry predictions for the tetramethylsiliconate, all methyl groups were assumed to be staggered and C3 symmetry was assumed within the methyl groups. Since no such assumptions were made for fragments of the silicate, fragmentation energies will be calculated to be slightly too exoergic. Because of the restrictions placed on the structures of the tetramethylsiliconates, no force fields were calculated for these species.

Energy differences reported for the ab initio calculations correspond to enthalpies (or energies) calculated at 0 K but corrected for zero-point vibrational energies for the case of the monomethylsiliconate and energies at 0 K for the case of the tetramethylsiliconate (no zero-point correction). In the case of MNDO, the differences correspond to enthalpy differences at 298 K, since the output is given as standard heats of formation at 298 K. We estimate that reconciliation of these two quantities (correcting for the temperature difference) would amount to at most a correction of 1–3 kcal mol−1. Thus, the differences in both these quantities will be reported as energy differences, keeping in mind that they refer to different temperatures for the two methods.

Cartesian force constant calculations were carried out on suspected transition states. Transition state structures were verified by diagonalization of the force constant matrix in order to determine the presence of one, and only one, negative eigenvalue. Selected transition states were then further characterized by performing intrinsic reaction coordinate (IRC) calculations to determine the set of reactants and products connected by that transition state. For the ab initio transition states, the method developed by Ishida, Murokuma, and Komornicki26 as implemented by Schmidt, Gordon, and Dupuis27 was employed. This method calculates the path of steepest descent along the potential surface from the transition state forward to products and backward to reactants. For the MNDO transition states, the approximate intrinsic reaction-coordinate method developed by Stewart, Davis, and Burggraf and implemented as an option in MOPAC was used.28 This method follows the path of steepest descent via a classical trajectory whose kinetic energy is completely damped at each step along that trajectory.

Results and Discussion

The species of greatest interest in this study is the one formed from addition of hydroxide ion to tetramethylsilane, (CH3)4Si(OH), since this is the one that has been observed in the experiments of DePuy, Bierbaum, and Damraper.1 For comparison and ease of calculation, the species formed from the addition of hydroxide to methylsilane, H2(CH3)Si(OH), was also studied. At least one methyl group was required to study the formation of methane from the resultant silicate, since methane was one of the presumed

20) Stewart, J. J. P. QCPE, 455.

Figure 1. Calculated energies for dissociation of monomethylsilicate.

Figure 2. Calculated energies for dissociation of tetramethylsilicate.
hydroxide. Ab initio results indicate a slight further stabilization of the silicate relative to the reactants compared with the smaller silicate, with a total stabilization energy of 35 kcal mol⁻¹. The MNDO results indicate a substantially different conclusion: that the silicate is now stabilized relative to the reactants by only 4.3 kcal mol⁻¹. We believe that the MNDO results are in error due to substantial crowding of the methyl groups in the five-coordinate silicate, which results in the silicate being too unstable to be a significant reactant. There is no evidence in either case at the MNDO level for any barrier to formation of the pentavalent silicate from isolated reactants.

Properties of the Pentavalent Silicates. Addition of hydroxide ion to either methyl silane or TMS results in stable trigonal-bipyramidal silicates according to all levels of theory. In the case of the monomethylsilicate, H₂SiMe(OH)³⁻, four different isomers are possible depending on the locations of the hydroxy and the methyl groups. The tetramethylsilicate presents the possibility of two different isomers, depending on whether the hydroxyl group is apical or equatorial.

Table I presents the energies of each of the possible isomers at both the MNDO and the ab initio levels. Ab initio results indicate that all of the four possible isomers of the monomethylsilicate are stable minima, while MNDO predicts that only two of the four are stable, with attempted optimization of the other two possibilities reverting to an isomer with both the hydroxy and the methyl groups in equatorial positions. In addition, the ab initio prediction is that all of the possibilities lie within about 4 kcal mol⁻¹ of each other, while MNDO predicts the EE (methyl equatorial, hydroxyl equatorial) isomer to be about 4 kcal mol⁻¹ more stable than the AA (apical methyl, apical hydroxyl) isomer.

The ab initio results for the tetramethylsilicate indicate that the isomer with the hydroxyl apical is more stable than the one with the hydroxy equatorial by 8.9 kcal mol⁻¹. MNDO predicts the two isomers to be very close in energy, with the equatorial hydroxyl isomer more stable than the apical hydroxyl isomer by a little over 1 kcal mol⁻¹. These findings are consistent with our previous comparisons, which led to the conclusion that MNDO does not reliably predict the relative order of isomers in these trigonal-bipyramidal complexes.

Figure 3 shows the calculated geometries of the EE isomer of the monomethylsilicate. A comparison of the ab initio and MNDO geometries indicates that MNDO predicts Si–H distances to be consistently 0.1 Å shorter than the ab initio values. One interesting feature of the EE isomer is the marked asymmetry between the two axial hydrogens, which appears in both calculations. For this isomer the apical hydrogen closest to the proton from the hydroxy group is stretched by several hundredths of an angstrom relative to the other apical hydrogen.

Figure 4 shows the geometry of the isomer of the tetramethylsilicate with the hydroxyl group equatorial. In general, the ab initio and the MNDO geometries agree very well.

Figure 3 also shows calculated Mulliken charges for the monomethylsilicate with each theoretical method. The MNDO charges are substantially different from those obtained at the RHF/6-31+G(d) level of theory. In particular, the MNDO charge on silicon is +1.746, while the ab initio value is only +0.467. The charges on the methyl carbons are also rather different. Finally, MNDO assigns a much larger negative charge to the hydrogens attached to silicon than does the ab initio calculation.
the only serious problem with MNDO charges appears to be the systematic negative error in the hydrogen charges. The systematic negative error in the hydrogen charges.

**Decomposition of the Pentavalent Siliconates.** There are several kinds of products that may be formed when the five-coordinate siliconates decompose. Figures 1 and 2 show the relative energies of each of the possible sets of decomposition products. In each case, the zero of energy is chosen to be the energy of the isolated reactants (hydroxide ion and methylsilane or TMS), and the siliconate energy shown is for that isomer predicted to be most stable by that particular method. Each possible set of decomposition products will be discussed in turn.

**Removal of Anion Ligands.** The simplest decomposition process involves removal of one of the ligands from the siliconate as an anion. In the case of the monomethylsilicate, the possible anion products are hydroxide, hydride, or methide. The ab initio and MNDO results are in general agreement that removal of any of these ligands as anions is substantially uphill from the five-coordinate siliconate. (Note that the MNDO results are corrected for the experimental heats of formation of the anions.) Of course, removal of hydroxide takes the system back to the reactants. MNDO predicts that production of hydride is slightly less endoergic than production of hydroxide, while the ab initio results predict that production of hydride should be slightly more endoergic than production of hydroxide. For this case only, the ab initio results give reasonable results for the stability of the siliconate and the siliconate.

The tetramethylsilicate can produce only two possible ligand products: hydroxide or methide. The ab initio calculations predict that removal of either ligand is a substantially endoergic process. We have previously discussed MNDO’s problem with the stability of the tetramethylsilicate; this results in the ligand production being much less endoergic than it should be. MNDO reaction path calculations again show no evidence for any barrier in the ligand removal processes. Experimentally, formation of the silicate should be accompanied by substantial internal energy in the siliconate because of the predicted 35 kcal mol−1 greater stability of the silicate compared with the hydroxide and TMS reactants. Thermodynamically, there is just enough energy available to remove methide, but other processes are predicted to be more favorable, as shown in later discussions.

**Formation of Hydrogen (H₂) or Methane.** Another set of decomposition reactions involves removal of the hydroxyl proton in combination with one of the ligands. In the case of the monomethylsilicate, this could produce either H₂ or methane. For the tetramethylsilicate, only methane could be produced in this manner. This type of process is particularly interesting, because evidence for these products has been found in the gas-phase experimental work of DePuy, Bierbaum, and Damrauer. The ab initio calculations (Figure 1) predict the products of both H₂ and methane elimination from the monomethylsilicate to be lower in energy than the silicate itself, with the methane elimination products slightly more stable. MNDO, however, predicts both sets of products to be higher in energy than the silicate. Since we have already deduced that in this case MNDO gives reasonable results for the stability of the silicate and the MNDO errors in H₂ and methane are small, the only logical conclusion is that the MNDO predictions for the heats of formation of the remaining anions (CH₃SiHOH− and H₂SiO−) are far too endoergic. Both of these anions have a free oxide with most of the charge localized on this atom. Figure 2 indicates that the ab initio prediction for the loss of methane from the tetramethylsilicate is also exoergic, by about 10 kcal mol⁻¹. However, as discussed previously, the stability of the tetramethylsilicate as calculated by MNDO is too small, resulting in the exoergic predication for loss of methane.

### Table II. Activation Energies for Pentavalent Siliconate Dissociation (kcal mol⁻¹)

<table>
<thead>
<tr>
<th>Product</th>
<th>monomethylsilicate</th>
<th>tetramethylsilicate:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ab initio</td>
<td>MNDO</td>
</tr>
<tr>
<td>H₂O</td>
<td>10.0</td>
<td>41.8, 54.1</td>
</tr>
<tr>
<td>CH₄</td>
<td>16.0</td>
<td>45.3</td>
</tr>
<tr>
<td>H₂SiO₂</td>
<td>96.2, 82.9</td>
<td>78.1</td>
</tr>
</tbody>
</table>

*The first entry is for H₂ removal using the hydroxyl proton; the second entry is for H₂ removal by H-ligand combination. The first entry is for H₂O removal by direct ligand combination; the second entry is for H₂O removal using a methyl proton.

Apparently, MNDO once again predicts the remaining silicate anion to be much too unstable.

In the case of the monomethylsilicate, there is another feasible way to remove H₂: the combination of two of the hydrogens attached to the silicon to form H₂, leaving the CH₃SiHOH− anion. In this case, as shown by Figure 1, MNDO predicts these products to be slightly more endoergic than the products of H₂ elimination to leave the siloxide anion. The ab initio results also indicate that the CH₃SiHOH− set of products is less stable than the siloxide anion set of products, but by a much larger amount than MNDO (24 kcal mol⁻¹ (ab initio) vs 5 kcal mol⁻¹ (MNDO)). As Figure 1 shows, MNDO thus underpredicts the stability of the CH₃SiHOH− anion by much less than it underpredicts the stability of the siloxide anion.

Table II shows the calculated activation energies for formation of H₂ and methane from each of the siliconates, in addition to activation energies for several other processes that will be discussed later. The ab initio results indicate that the activation energy for H₂ removal by the more favorable route is slightly less than that for methane removal (both processes having fairly low activation energies), in spite of the greater stability of the products of methane removal compared with those of hydrogen removal. MNDO agrees with this trend, but the activation energies are far too high as noted previously for many types of reactions. MNDO predicts that H₂ removal via H-ligand combination has a somewhat higher activation energy than that of H₂ removal involving the hydroxyl proton, probably because in the case of H₂-ligand combination two negatively charged hydrogens must be brought together in the transition state on the way to forming an H₂ molecule. The MNDO activation energy for methane removal from the tetramethylsilicate is significantly less than that of the small monomethylsilicate, but this is undoubtedly due to the underprediction of stability for the larger siliconate. (The ab initio transition state for tetramethylsilicate were not calculated because of size and computer time restraints.)

For each transition state, the Cartesian force constant calculation gave the required one, and only one, negative eigenvalue of the force constant matrix. In addition, intrinsic reaction paths were followed to ensure that each transition state connected the assumed set of reactants and products. In the case of the MNDO transition state for elimination of methane from the tetramethylsilicate, the results in the direction of the complex were ambiguous, although the dissociation direction definitely led to the products. Initial steps in the direction toward the five-coordinate structure definitely headed in that direction; at later times the trajectory reversed itself and headed toward the dissociated products. The difficulty may have involved the different isomers of the five-coordinate silicate, an inappropriately large step size, or unevenness in the MNDO potential surface near the transition state. Because of the similarity of transition states for methane elimination from the two siliconates, we feel certain that the transition state discovered was indeed the correct one.

The calculated geometries for the H₂-elimination transition states (involving the hydroxyl proton) are given in Figure 5. The ab initio and MNDO results are qualitatively similar, in that the hydrogen atom attached to the silicon is significantly separated before the bond with the hydroxyl hydrogen begins to form. The charges, also given in Figure 5, indicate that the hydrogen being separated from the silicon has acquired a substantial negative charge.
The charge on the methyl group is approximately proximately 0.9.

This type of process we term anionic part of the barrier is the dissociation of the ligand from the silicon. In this transition state, the Si-C bond is significantly stretched at the removal of methane from the monomethylsiliconate. The methane elimination from monomethylsiliconate.

Figure 6. Geometry and Mulliken charges for transition state for H₂ elimination from monomethylsiliconate by abstraction of hydroxyl proton.

Figure 7. Geometry and Mulliken charges for transition state for H₂ elimination from monomethylsiliconate by direct ligand combination. methyl anion removing the hydroxyl hydrogen. The charges on the methyl group and its attaching hydrogen from the hydroxyl group were followed along the IRC toward the methane product with ab initio calculations. The transition from the highly negatively charged methyl group at the transition state to neutral methane proceeds very smoothly along the IRC.

The MNDO transition state for methane removal from the tetramethylsiloxane (not shown) is very similar to that for removal from the monomethylsiloxane; the Si-C distance is approx. 0.1 Å longer, and the C-H (hydroxyl hydrogen) distance is about 0.15 Å longer. This similarity, plus the very similar charges in the transition states, leads us to believe that we have indeed located the transition state for removal of methane from the tetramethylsiloxane, in spite of the difficulties with the intrinsic reaction coordinate calculation in this case.

The geometry and charges for the MNDO transition state for removal of H₂ via H-ligand combination are shown in Figure 7. Note that, at the transition state, one H is substantially removed from the silicon while the other is still fairly tightly bound. This type of unsymmetrical transition state is typical of MNDO predictions for a wide variety of reactions. The charges indicate that both hydrogens do carry a negative charge at the transition state, with one hydrogen being almost a free hydride. This general type of process (removal by combination of negatively charged ligands) is not likely to be as important as the combination of a ligand with the positively charged hydroxyl hydrogen.

Formation of Water, Methanol, and Ethane. Another set of possible decomposition products results from combination of two ligands and then removal of the combination. In the case of the monomethylsiloxane, possible products that could result from this type of process include H₂, methane, water, and methanol. The reaction producing H₂ in this manner was discussed in the previous section, and the reaction producing methane would be expected to be qualitatively similar. For the tetramethylsiloxane, only methanol and ethane could be produced by this type of process. We will discuss each in turn, beginning with the process that is common to both, elimination of methanol. Again, relative energies of products and reactants are shown in Figures 1 and
Decomposition of Five-Coordinate Silicon Anions


2, and the activation energies are given in Table II.

Formation of methanol is predicted to be significantly endoergic by both ab initio and MNDO calculations for both systems. The methods agree quantitatively for the monomethylsilicate, but for the tetramethyl compound, MNDO predicts the endoergicity to be much less than that predicted by the ab initio calculations, in large part due again to the fact that MNDO underestimates the stability of the tetramethylsilicate. Transition states for both complexes were calculated with MNDO. In both cases, refinement of the transition-state geometries could not eliminate additional negative eigenvalues of the Cartesian force constant matrix, but the additional negative components (two for the tetramethylsilicate and one for the monomethylsilicate) were significantly smaller than the negative force constant corresponding to the reaction coordinate. (For example, the corresponding frequencies for the reaction coordinate and the second negative mode were 583 cm\(^{-1}\) and 163 cm\(^{-1}\), respectively, for the monomethylsilicate.) In the monomethyl case, the additional negative mode was a wagging motion of the hydrogens attached to silicon.

In the tetramethyl case, these additional components were identified with (nearly free) internal rotation of the methyl groups. IRC calculations unequivocally connected the pentavalent siliconate with (nearly free) internal rotation of the methyl groups. The transition-state geometry for the monomethylsilicate indicates that the methanol C-O bond is appreciably stretched. The geometry of the transition state for the tetramethylsilicate is very similar to that of the monomethylsilicate. Activation energies are high for both siliconates, at least compared to those for removal of H\(_2\) or methane as discussed in the last section. The activation energy is considerably less for the tetramethylsilicate, again probably due to the underestimation of its stability because of steric crowding.

Formation of water by direct ligand combination (removing both complete ligands) is only possible for the monomethylsilicate. Both siliconates can also form water by a somewhat different process, the combination of the hydroxyl group with one of the hydrogens from a methyl group. Figure 1 shows that water removal from the monomethylsilicate by direct ligand combination is expected to be endoergic, although the Si-O bond is appreciably stretched. The geometry of the transition state for the tetramethylsilicate is very similar to that of the monomethylsilicate. Activation energies are high for both siliconates, at least compared to those for removal of H\(_2\) or methane as discussed in the last section. The activation energy is considerably less for the tetramethylsilicate, again probably due to the underestimation of its stability because of steric crowding.

Table II shows that the MNDO-predicted activation energies for water removal are quite high by both kinds of processes, again probably due to the fact that the process attempts to bring together two negatively charged ligands or pieces of ligands to produce a neutral product. The second entry in the case of the monomethylsilicate is for the process utilizing the methyl proton. Note that this process has a lower activation energy than the one for direct ligand combination by about 13 kcal mol\(^{-1}\). The corresponding activation energy for the tetramethylsilicate is lower by about 13 kcal mol\(^{-1}\), probably due to the destabilization of the pentavalent silicate by MNDO.

Figure 8 shows the transition-state geometry and the charges for water removal from the monomethylsilicate via direct ligand combination (MNDO only). Note that the water molecule is essentially formed by the transition state (although one of the O-H bonds is still appreciably stretched) but is still very closely associated with the silicon. The force constant calculation gave two negative eigenvalues of the Cartesian force constant matrix, but the second one was very near zero (1271 cm\(^{-1}\) for the reaction coordinate vs 22 cm\(^{-1}\) for the second negative mode, a rotation of the H\(_2\)O being formed). The IRC calculation showed unequivocally that this transition state connects the pentavalent siliconate with the water plus CH\(_3\)SiH\(_2\)\(^{+}\) products. Figure 9 shows the transition-state geometry and the charges for water removal from the monomethylsilicate utilizing a proton from the methyl group (MNDO only). Results for the tetramethylsilicate were quite similar. Again, the water molecule is appreciably formed by the transition state, with strong association remaining between
the oxygen and the silicon. In addition, however, because of the strength of a C–H bond, there is still an appreciable association between the hydrogen that is now part of the water molecule and its former bond partner, the carbon atom of the methyl group. Repeated attempts to completely refine the transition-state geometry failed to remove the multiple negative eigenvalues of the Cartesian force constant matrix, but three of the four negative eigenvalues were very much smaller than the one corresponding to the reaction coordinate (1524 cm$^{-1}$ for the reaction coordinate mode vs 3681, 1981, and 631 cm$^{-1}$ for the other negative modes). IRC calculations again showed unequivocally that the transition state connected the pentavalent silicate with the products of water removal.

The final possible product of direct ligand-combination processes is ethane, and this only for the tetramethylsilicate. Figure 2 shows that this process is expected to be essentially one of constant energy according to the ab initio results and slightly exoergic according to MNDO. In this case, MNDO underpredicts the stability of both the five-coordinate silicate and the resultant silyl anion by approximately the same amount. The search for the transition state for this process did not result in any low-energy pathway leading to the desired ethane products.

In general, all of the processes involving complete ligand removal after combination with another ligand are predicted to be highly unfavorable processes, even if an appreciable amount of energy is available from the formation of the complex. Only when a ligand can combine with a positively charged hydrogen from the hydroxyl group does the process become favorable.

**Conclusions**

When we attempt to interpret the gas-phase experiments, the prediction is that both H$_2$ and methane elimination from these five-coordinate siliconates should be facile when enough internal energy is available for these processes. The formation of the siliconates from hydroxide ion and a neutral silane is predicted to give a substantial excess of internal energy to overcome the barriers to these processes. In the absence of detailed dynamical predictions for these systems, the interpretation of DePuy, Bierbaum, and Damrauer that five-coordinate silicate intermediates are formed and then eliminate methane and/or other stable products is entirely consistent with these theoretical results. Furthermore, their correlation of the relative formation rates of possible products with the gas-phase acidities of these products seems reasonable given the acid-base character of the elimination reaction as shown by the calculated strongly anionic character of the departing species. The slightly smaller activation energy for formation H$_2$-coordinated with methane is consistent with the greater gas-phase acidity of hydrogen, making it easier for hydrogen to donate a proton to the oxygen of the silicate at the transition state.

Other possible decomposition modes of a five-coordinate intermediate have been shown by these calculations to be much less likely than the processes involving combination of the hydroxyl proton with other ligands in the silicate (anionic dissociative proton transfer). These other potential processes involve combination of two negatively charged ligands or parts of ligands, and the calculated activation barriers are much higher than those for the anionic dissociative proton-transfer processes, even though in some cases the thermodynamic energy differences of reaction are favorable. In addition, simple dissociation of any single ligand is predicted to be unfavorable compared with the anionic dissociative proton-transfer processes.

MNDO has serious problems when used alone in the study of these silicon reactions. Once again, we see that the improper steric repulsions at fairly long distances make overprediction of activation energies fairly common. The steric repulsion problem also destabilizes some pentavalent siliconates but apparently only those with an appreciable number of large ligands. Finally, the problems that MNDO has with small anions extends to much larger anions as well, at least for the case of silicon-containing anions. Thus, we feel that under the present circumstances it is essential that any MNDO study of silicon chemistry must be accompanied by a carefully coordinated ab initio or experimental study or both. Stand-alone MNDO predictions of silicon chemistry are unreliable, at least in a quantitative sense. On the other hand, it is certainly true that most of the essential features of the chemistry for this particular study, including the correlation with the gas-phase experimental study, are qualitatively reproduced by the MNDO calculations. Furthermore, MNDO structures, especially for the potential energy minima, are in good agreement with the ab initio geometries. There is a great need for a more reliable semiempirical tool to study larger silicon systems, and we hope that the new semiempirical method AM$1^{26}$ will fill this need when it is parameterized for silicon.

It should also be noted that, to be reliable, ab initio calculations on five-coordinated anions need to include adequate basis sets and computational levels. In particular, the omission of d orbitals from the five-coordinated center and of diffuse functions on anions can lead to substantial errors.

Further details of the calculated structures and total energies of any of the species discussed in the paper are available from us.

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**Registry No.** (CH$_3$)$_4$SiOH, 113773-32-3; H$_2$SiMe(OH)$_3$, 113773-33-4.