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Abstract: We have performed a theoretical study of the decomposition of the five-coordinate silicon anions (siliconates) $H_3(CH_3)SiOH^-$ and $(CH_3)_4SiOH^-$. These ions can be formed from hydroxide ion attack on methylsilane or tetramethylsilane, 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 methide 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 the series. In previous papers we discussed a comparison of fluorine atom and fluoride ion attack on methane and silane[1] and the stabilities of some small five-coordinate siliconates.[2] 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.[3]

Our eventual goal is to perform theoretical calculations for rather large molecular systems involved in the polymerization of silanols to form silica. 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.[4] 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[1] and an inability to predict the correct energy ordering of isomers of five-coordinate silicon complexes.[2] 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.[5] There have been only a few published theoretical works on silicon chemistry using semiempirical techniques,[5,6] but recently quite a number of ab initio studies of small silicon systems have appeared.[7-18]

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 XH, in which X is a ligand other than hydroxyl. These processes have been invoked in explaining the gas-phase data of DePuy, Bierbaum, and Damrauer.[3]

Calculations on compounds related to those of interest here have been considered in a recent paper by Sheldon, Hayes, Bowie, and DePuy (SHBD).[16] The calculations performed by these authors at the self-consistent field (SCF) level with the 6-31G basis set predict that the addition of hydroxide ion to methylsilane to form the five-coordinated silicon anion is downhill by 45.7 kcal mol^{-1}. Elimination of ethane from methoxymethylsilane and methane from methoxydimethylsilane is reported to occur with large barriers. It should be noted, however, that these calculations on hypervalent silicon anions were performed without either d or diffuse functions in the basis set or correlation corrections for the computation of energetics. Since no actual transition states were obtained by SHBD, the reported barriers may be particularly unreliable.

Calculations

The semiempirical calculations were performed with the MNDO method developed by Dewar and co-workers.[4] The silicon parameters were obtained from a later communication by Dewar.[19] All stationary

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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)[21] SCF level for the monomethylsiliconate ($H_3SiMeOH^-$) and its reactions and at the 3-21G*[22] SCF level for the tetramethylsiliconate and its reactions. For energy comparisons on the monomethylsiliconate system, single-point calculations were performed with second-order perturbation theory[23] 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 C_s symmetry was assumed within the methyl groups. Since no such assumptions were made for fragments of the siliconate, 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 states 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 Komornicki[26] as implemented by Schmidt, Gordon, and Dupuis[27] 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, $(CH_3)_4SiOH^-$, since this is the one suspected to have formed in the experiments of DePuy, Bierbaum, and Damrauer.[3] For comparison and ease of calculation, the species formed from the addition of hydroxide to methylsilane, $H_3(CH_3)SiOH^-$, was also studied. At least one methyl group was required to study the formation of methane from the resultant siliconate, since methane was one of the presumed
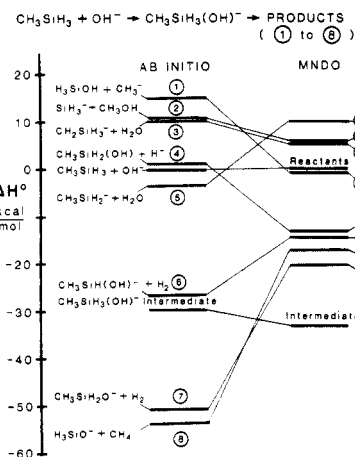
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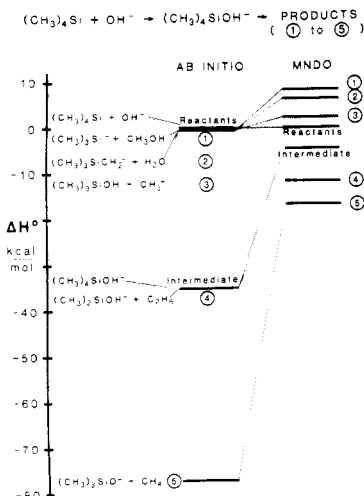**Figure 1.** Calculated energies for dissociation of monomethylsiliconate.

Figure 2. Calculated energies for dissociation of tetramethylsiliconate.

products in the experimental work.

We will begin with a discussion of the formation of the siliconate from hydroxide addition to the parent neutral compound. This will be followed by a consideration of the properties of the siliconates and finally by a discussion of the various decomposition pathways.

Formation of the Pentavalent Siliconates. Addition of hydroxide ion to either the methylsilane or tetramethylsilane (TMS) resulted in a monotonic decrease in energy to form a stable five-coordinate siliconate at the MNDO level of theory. Because of computer time considerations, the actual path calculation was only carried out at this semiempirical level of theory. Figure 1 shows the relative energy of the reactants and products of the hydroxide addition to methylsilane, and Figure 2 shows the same quantities for the hydroxide addition to TMS. For all cases the zero of energy is taken to be that of the isolated reactants, hydroxide ion plus methylsilane or TMS. In the case of the MNDO calculations, the experimental gas-phase heat of formation for hydroxide ion is used, since previous work has shown that MNDO predicts this ion to be too unstable by about 30 kcal mol^{-1}.[1] Both ab initio and MNDO results indicate that the monomethyl siliconate is approximately 30 kcal mol^{-1} downhill from its reactants. Note that both methods used here predict a substantially smaller exoergicity for the hydroxide addition than does the earlier work by SHBD (45.7 kcal mol^{-1}).[16] This is probably a reflection of the inadequacy of the basis set used in the earlier work. This inadequacy is, in principle, also present in the MNDO calculations but is apparently overcome to a large degree by the parameterization procedure and the use of the experimental gas-phase heat of formation for hydroxide ion. There is substantial disagreement between the ab initio calculations and the MNDO calculations in the case of the tetramethyl siliconate compared with its reactants, TMS and

Table I. Relative Energies of the Siliconate Isomers (kcal mol⁻¹)

isomer	ab initio	MNDO
Monomethylsiliconate		
OH axial, Me equatorial	0.0	unstable
OH axial, Me axial	0.3	9.5
OH equatorial, Me equatorial	1.5	0.0
OH equatorial, Me axial	4.4	unstable
Tetramethylsiliconate		
OH axial	0.0	1.3
OH equatorial	8.5	0.0

hydroxide. Ab initio results indicate a slight further stabilization of the siliconate relative to the reactants compared with the smaller siliconate, with a total stabilization energy of 35 kcal mol⁻¹. The MNDO results indicate a substantially different conclusion: that the siliconate 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 siliconate, which results in the siliconate being too unstable relative to the isolated reactants. There is no evidence in either case at the MNDO level for any barrier to formation of the pentavalent siliconate from isolated reactants.

Properties of the Pentavalent Siliconates. Addition of hydroxide ion to either methylsilane or TMS results in stable trigonal-bipyramidal siliconates according to all levels of theory. In the case of the monomethylsiliconate, H₃SiMe(OH)⁻, four different isomers are possible depending on the locations of the hydroxyl and the methyl groups. The tetramethylsiliconate 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 monomethylsiliconate 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 hydroxyl 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 (equatorial methyl, equatorial hydroxyl) isomer to be about 10 kcal mol⁻¹ more stable than the AA (apical methyl, apical hydroxyl) isomer.

The ab initio results for the tetramethylsiliconate indicate that the isomer with the hydroxyl apical is more stable than the one with the hydroxyl equatorial by 8.5 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.[2]

Figure 3 shows the calculated geometries of the EE isomer of the monomethylsiliconate. 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 hydroxide group is stretched by several hundredths of an angstrom relative to the other apical hydrogen.

Figure 4 shows the geometries of the isomer of the tetramethylsiliconate 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 monomethylsiliconate 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.
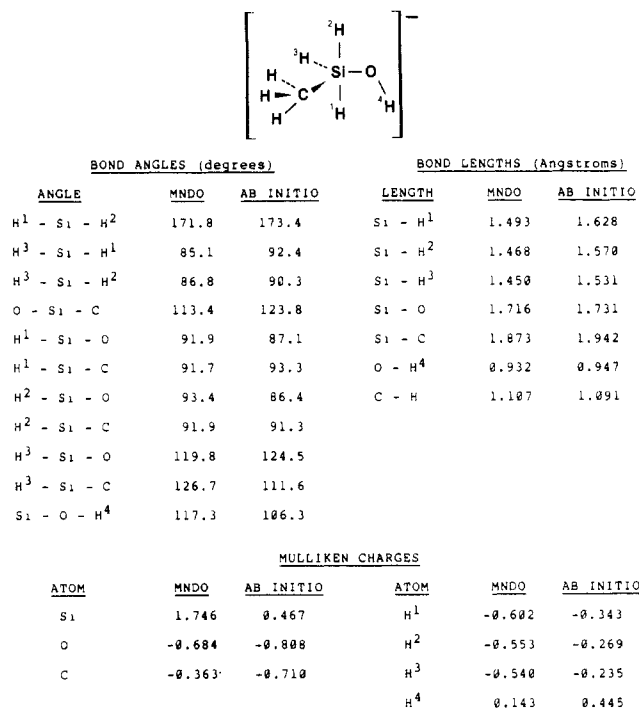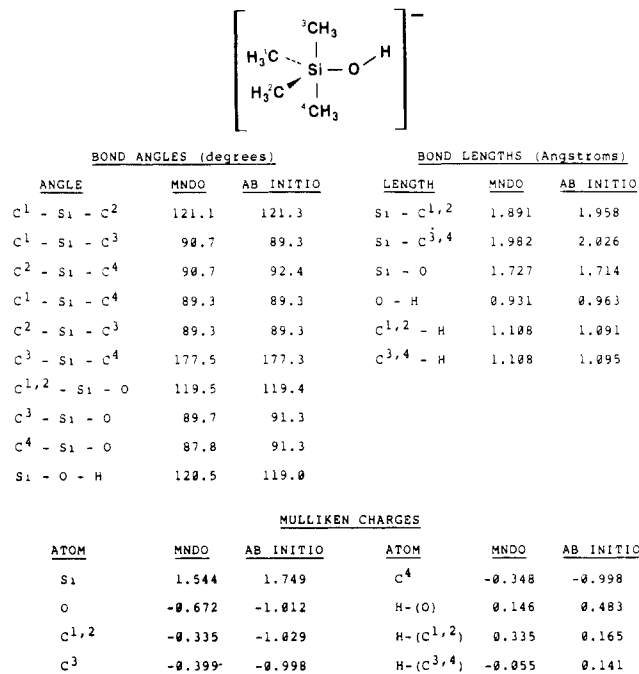
BOND ANGLES (degrees)			BOND LENGTHS (Angstroms)		
ANGLE	MNDO	AB INITIO	LENGTH	MNDO	AB INITIO
H¹ - Si - H²	171.8	173.4	Si - H¹	1.493	1.628
H³ - Si - H¹	85.1	92.4	Si - H²	1.468	1.570
H³ - Si - H²	86.8	90.3	Si - H³	1.450	1.531
O - Si - C	113.4	123.8	Si - O	1.716	1.731
H¹ - Si - O	91.9	87.1	Si - C	1.873	1.942
H¹ - Si - C	91.7	93.3	O - H⁴	0.932	0.947
H² - Si - O	93.4	86.4	C - H	1.107	1.091
H² - Si - C	91.9	91.3			
H³ - Si - O	119.8	124.5			
H³ - Si - C	126.7	111.6			
Si - O - H⁴	117.3	106.3			

MULLIKEN CHARGES					
ATOM	MNDO	AB INITIO	ATOM	MNDO	AB INITIO
Si	1.746	0.467	H¹	-0.602	-0.343
O	-0.684	-0.808	H²	-0.553	-0.269
C	-0.363	-0.710	H³	-0.540	-0.235
			H⁴	0.143	0.445

Figure 3. Geometry and Mulliken charges for EE (methyl equatorial, hydroxyl equatorial) isomer of monomethylsiliconate. Ab initio populations are taken from the 6-31+G(d) basis set.

BOND ANGLES (degrees)			BOND LENGTHS (Angstroms)		
ANGLE	MNDO	AB INITIO	LENGTH	MNDO	AB INITIO
C¹ - Si - C²	121.1	121.3	Si - C¹,²	1.891	1.958
C¹ - Si - C³	90.7	89.3	Si - C³,⁴	1.982	2.026
C² - Si - C⁴	90.7	92.4	Si - O	1.727	1.714
C¹ - Si - C⁴	89.3	89.3	O - H	0.931	0.963
C² - Si - C³	89.3	89.3	C¹,² - H	1.108	1.091
C³ - Si - C⁴	177.5	177.3	C³,⁴ - H	1.108	1.095
C¹,² - Si - O	119.5	119.4			
C³ - Si - O	89.7	91.3			
C⁴ - Si - O	87.8	91.3			
Si - O - H	120.5	119.0			

MULLIKEN CHARGES					
ATOM	MNDO	AB INITIO	ATOM	MNDO	AB INITIO
Si	1.544	1.749	C⁴	-0.348	-0.998
O	-0.672	-1.012	H-(O)	0.146	0.483
C¹,²	-0.335	-1.029	H-(C¹,²)	0.335	0.165
C³	-0.399	-0.998	H-(C³,⁴)	-0.055	0.141

Ab initio calculation treats as equivalent C¹ and C²; C³ and C⁴.

Figure 4. Geometry and Mulliken charges for isomer of tetramethylsiliconate with hydroxyl equatorial. Ab initio populations are taken from the 6-31+G(d) basis set.

It appears that in general the predicted MNDO charges on the hydrogens are too negative by about 0.2–0.3 e. This error accounts for almost all of the discrepency in the predicted charges.

This effect of the hydrogen charges becomes even more apparent when the charges on the tetramethylsiliconate are analyzed (Figure 4). For this siliconate, the predicted charges on silicon are in much closer agreement (+1.544 MNDO vs +1.749 ab initio) than those for the monomethylsiliconate. Note that in this case there are no hydrogens attached directly to the silicon. Again, the charges on the methyl carbons are quite different, probably due to the larger negative charges on hydrogen predicted by MNDO. Thus,

the only serious problem with MNDO charges appears to be 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 monomethylsiliconate, 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 relative energies shown in Figure 1 were calculated with a 6-31++G(d,p) basis set, because diffuse functions are needed on hydride ion to correctly predict its energy. The ab initio results predict that methide production is more endoergic than hydroxide, while MNDO predicts that it takes about the same energy to produce either methide or hydroxide. In all cases reaction path calculations performed with MNDO show no evidence of a barrier; the energy rises monotonically from the siliconate to the products.

The tetramethylsiliconate 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 tetramethylsiliconate; 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 siliconate should be accompanied by substantial internal energy in the siliconate because of the predicted 35 kcal mol^{-1} greater stability of the siliconate 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 (H$_2$) 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 monomethylsiliconate, this could produce either H$_2$ or methane. For the tetramethylsiliconate, 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.[3]

The ab initio calculations (Figure 1) predict the products of both H$_2$ and methane elimination from the monomethylsiliconate to be lower in energy than the siliconate itself, with the methane elimination products slightly more stable. MNDO, however, predicts both sets of products to be higher in energy than the siliconate. Since we have already deduced that in this case MNDO gives reasonable results for the stability of the siliconate and the MNDO errors in H$_2$ and methane are small, the only logical conclusion is that the MNDO predictions for the heats of formation of the remaining anions (CH$_3$SiH$_2$O$^-$ and H$_3$SiO$^-$) 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 tetramethylsiliconate should be exoergic by over 40 kcal mol^{-1}. MNDO also predicts this reaction to be exoergic, but by much less, approximately 10 kcal mol^{-1}. However, as discussed previously, the stability of the tetramethylsiliconate as calculated by MNDO is too small, resulting in the exoergic prediction for loss of methane.

Table II. Activation Energies for Pentavalent Siliconate Dissociation (kcal mol^{-1})

product	monomethylsiliconate		tetramethylsiliconate: MNDO
	ab initio	MNDO	
H$_2$	10.0	41.8, 54.1[a]	
CH$_4$	16.0	45.3	21.2
H$_2$O		96.2, 82.9[b]	70.3
CH$_3$OH		104.4	78.1

[a] The first entry is for H$_2$ removal using the hydroxyl proton; the second entry is for H$_2$ removal by H-ligand combination. [b] The first entry is for H$_2$O removal by direct ligand combination; the second entry is for H$_2$O removal using a methyl proton.

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

In the case of the monomethylsiliconate, there is another feasible way to remove H$_2$: the combination of two of the hydrogens attached to the silicon to form H$_2$, leaving the CH$_3$SiHOH$^-$ anion. In this case, as shown by Figure 1, MNDO predicts these products to be slightly more endoergic than the products of H$_2$ elimination to leave the siloxide anion. The ab initio results also indicate that the CH$_3$SiHOH$^-$ set of products are 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 CH$_3$SiHOH$^-$ anion but by much less than it underpredicts the stability of the siloxide anion.

Table II shows the calculated activation energies for formation of H$_2$ 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 H$_2$ 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 H$_2$ removal via H-ligand combination has a somewhat higher activation energy than that of H$_2$ removal involving the hydroxyl proton, probably because in the case of H-ligand combination two negatively charged hydrogens must be brought together in the transition state on the way to forming an H$_2$ molecule. The MNDO activation energy for methane removal from the tetramethylsiliconate is significantly less than that of the small monomethylsiliconate, but this is undoubtedly due to the underprediction of stability for the larger siliconate itself. (The ab initio transition states for tetramethylsiliconate 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 tetramethylsiliconate, 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 siliconate, 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 H$_2$-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
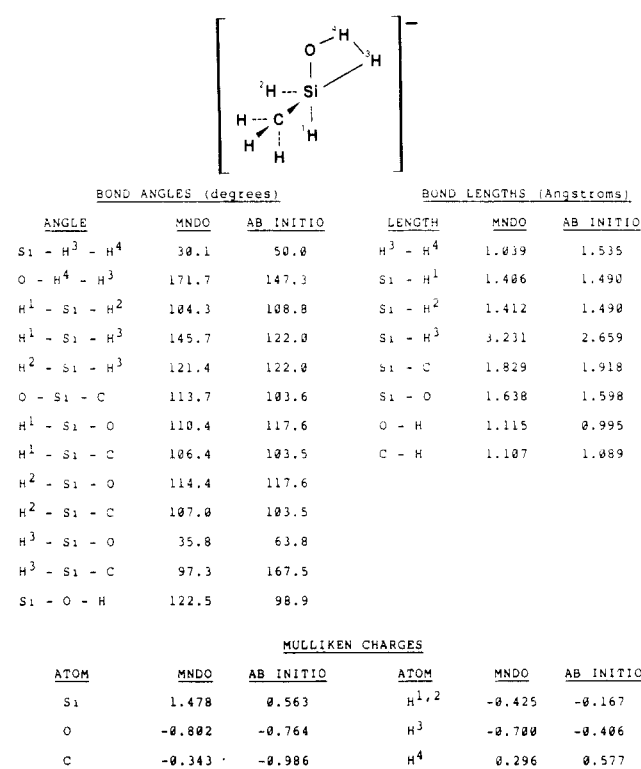
BOND ANGLES (degrees) / BOND LENGTHS (Angstroms)

ANGLE	MNDO	AB INITIO	LENGTH	MNDO	AB INITIO
$Si - H^3 - H^4$	30.1	50.0	$H^3 - H^4$	1.039	1.535
$O - H^4 - H^3$	171.7	147.3	$Si - H^1$	1.406	1.490
$H^1 - Si - H^2$	104.3	108.8	$Si - H^2$	1.412	1.490
$H^1 - Si - H^3$	145.7	122.0	$Si - H^3$	3.231	2.659
$H^2 - Si - H^3$	121.4	122.0	$Si - C$	1.829	1.918
$O - Si - C$	113.7	103.6	$Si - O$	1.638	1.598
$H^1 - Si - O$	110.4	117.6	$O - H$	1.115	0.995
$H^1 - Si - C$	106.4	103.5	$C - H$	1.107	1.089
$H^2 - Si - O$	114.4	117.6			
$H^2 - Si - C$	107.0	103.5			
$H^3 - Si - O$	35.8	63.8			
$H^3 - Si - C$	97.3	167.5			
$Si - O - H$	122.5	98.9			

MULLIKEN CHARGES

ATOM	MNDO	AB INITIO	ATOM	MNDO	AB INITIO
Si	1.478	0.563	$H^{1,2}$	-0.425	-0.167
O	-0.802	-0.764	H^3	-0.700	-0.406
C	-0.343	-0.986	H^4	0.296	0.577

Figure 5. Geometry and Mulliken charges for transition state for H_2 elimination from monomethylsiliconate by abstraction of hydroxyl proton.

BOND ANGLES (degrees) / BOND LENGTHS (Angstroms)

ANGLE	MNDO	AB INITIO	LENGTH	MNDO	AB INITIO
$Si - C - H^4$	39.9	43.7	$C - H^4$	1.855	1.939
$O - H^4 - C$	149.0	148.8	$Si - H^1$	1.406	1.517
$H^1 - Si - H^{2,3}$	104.5	101.9	$Si - H^2$	1.393	1.489
$H^2 - Si - H^3$	109.8	109.4	$Si - H^3$	1.393	1.489
$O - Si - C$	55.2	71.0	$Si - C$	1.633	1.641
$H^1 - Si - O$	106.8	102.6	$Si - C$	3.317	2.902
$H^1 - Si - C$	162.0	173.5	$O - H^4$	0.974	0.989
$H^2 - Si - O$	119.1	119.1	$C - H$	1.094	1.101
$H^2 - Si - C$	86.0	88.5			
$H^3 - Si - C$	84.9	82.8			
$H^3 - Si - O$	114.9	118.6			
$Si - O - H^4$	115.9	91.5			

MULLIKEN CHARGES

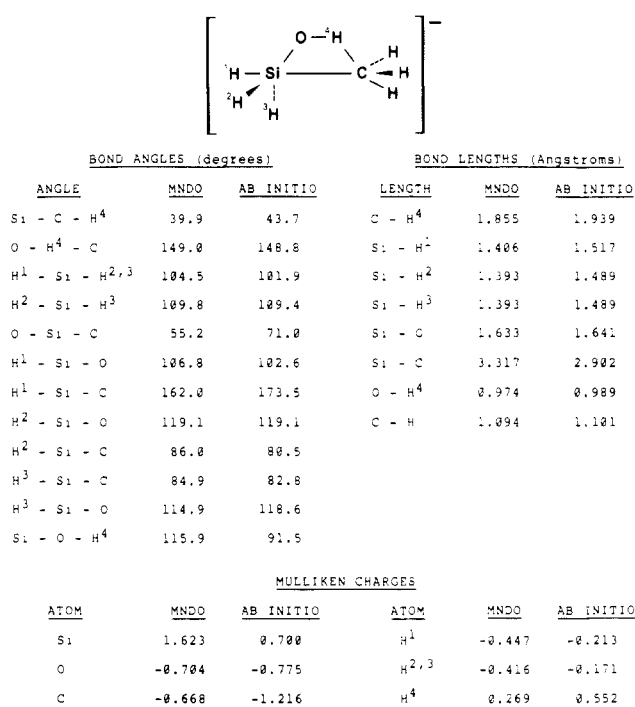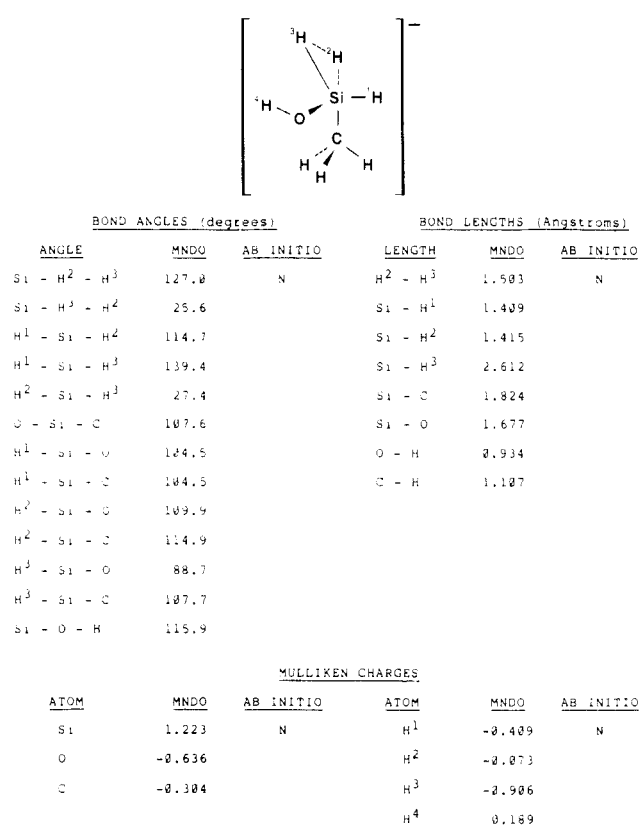| ATOM	MNDO	AB INITIO	ATOM	MNDO	AB INITIO
Si	1.623	0.700	H^1	-0.447	-0.213
O	-0.704	-0.775	$H^{2,3}$	-0.416	-0.171
C	-0.668	-1.216	H^4	0.269	0.552

Figure 6. Geometry and Mulliken charges for transition state for methane elimination from monomethylsiliconate.

charge at the transition state. This type of process we term anionic dissociative proton transfer, because the departing group is significantly anionlike at the transition state. Thus, a substantial part of the barrier is the dissociation of the ligand from the silicon atom.

This terminology is even more appropriate when we consider the removal of methane from the monomethylsiliconate. The transition-state geometries and charges are given in Figure 6. In this transition state, the Si–C bond is significantly stretched at the transition state, and the charge on the methyl group is approximately –0.9. Thus, the transition state is indeed close to a

BOND ANGLES (degrees) / BOND LENGTHS (Angstroms)

ANGLE	MNDO	AB INITIO	LENGTH	MNDO	AB INITIO
$Si - H^2 - H^3$	127.0	N	$H^2 - H^3$	1.503	N
$Si - H^3 - H^2$	25.6		$Si - H^1$	1.409	
$H^1 - Si - H^4$	114.7		$Si - H^2$	1.415	
$H^1 - Si - H^3$	139.4		$Si - H^3$	2.612	
$H^2 - Si - H^3$	27.4		$Si - C$	1.824	
$O - Si - C$	107.6		$Si - O$	1.677	
$H^1 - Si - O$	104.5		$O - H$	0.934	
$H^1 - Si - C$	104.5		$C - H$	1.107	
$H^2 - Si - O$	109.9				
$H^2 - Si - C$	114.9				
$H^3 - Si - O$	88.7				
$H^3 - Si - C$	107.7				
$Si - O - H$	115.9				

MULLIKEN CHARGES

ATOM	MNDO	AB INITIO	ATOM	MNDO	AB INITIO
Si	1.223	N	H^1	-0.409	N
O	-0.636		H^2	-0.073	
C	-0.304		H^3	-0.906	
			H^4	0.189	

N: Ab initio values were not calculated.

Figure 7. Geometry and Mulliken charges for transition state for H_2 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 tetramethylsiliconate (not shown) is very similar to that for removal from the monomethylsiliconate; the Si–C distance is approximately 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 tetramethylsiliconate, 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 H_2 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 monomethylsiliconate, possible products that could result from this type of process include H_2, methane, water, and methanol. The reaction producing H_2 in this manner was discussed in the previous section, and the reaction producing methane would be expected to be qualitatively similar. For the tetramethylsiliconate, 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
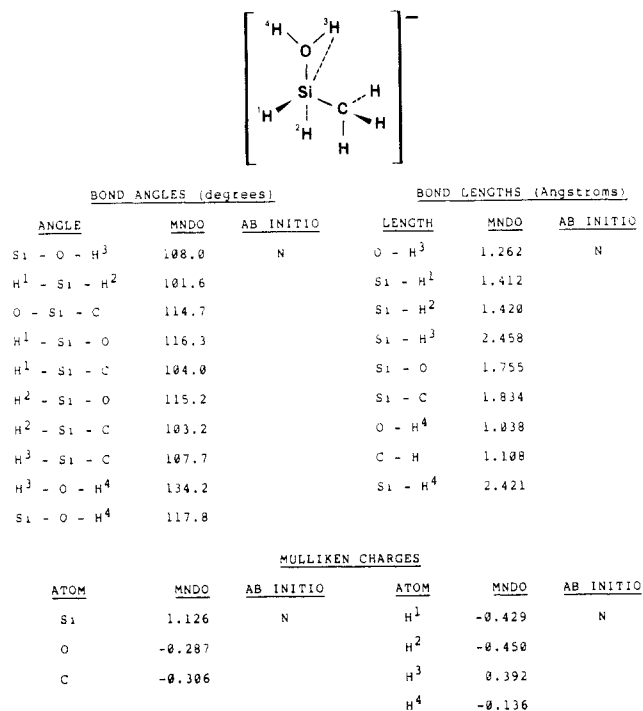
2, and the activation energies are given in Table II.

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 monomethylsiliconate, 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 tetramethylsiliconate. 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 tetramethylsiliconate and one for the monomethylsiliconate) 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 $583i$ and $163i$ cm^{-1}, respectively, for the monomethylsiliconate.) 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 the methanol plus silyl anion product in both cases. Thus, even though the transition states have not been determined exactly, they are probably close enough to the true transition states to give reasonable estimates of their properties.

The transition-state geometry for the monomethylsiliconate indicates that the methanol C–O bond is almost completely formed before appreciable stretching of the Si–C bond occurs, although the Si–O bond is appreciably stretched. The geometry of the transition state for the tetramethylsiliconate is very similar to that of the monomethylsiliconate. 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 tetramethylsiliconate, 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 monomethylsiliconate. 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 monomethylsiliconate by direct ligand combination is expected to be endoergic, although by much more in the case of MNDO than ab initio. Thus, MNDO predicts the silyl anion left upon water removal to be too endoergic by approximately 15 kcal mol^{-1}. Water removal using a hydrogen from a methyl group is predicted to be significantly endoergic by both ab initio (40 kcal mol^{-1}) and MNDO (38 kcal mol^{-1}) for the monomethylsiliconate but much less endoergic by MNDO for the tetramethylsiliconate. Most of the discrepency in the case of the tetramethylsiliconate is again due to the destabilization of this five-coordinate siliconate by MNDO.
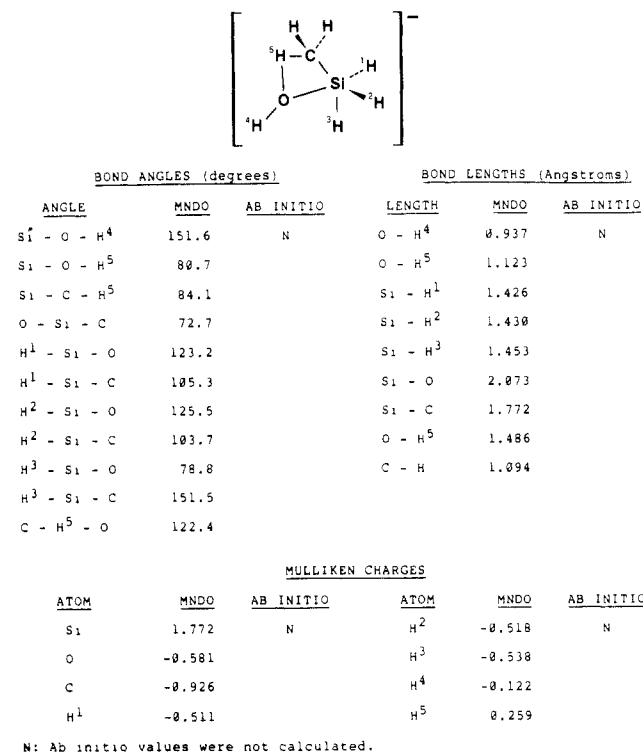
Table II shows that the MNDO-predicted activation energies for water removal are quite high by both kinds of processes, again probably due to the fact that the process attempts to bring together two negatively charged ligands or pieces of ligands to produce a neutral product. The second entry in the case of the monomethylsiliconate 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 tetramethylsiliconate is lower by about 13 kcal mol^{-1}, probably due to the destabilization of the pentavalent siliconate by MNDO.

Figure 8 shows the transition-state geometry and the charges for water removal from the monomethylsiliconate 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 ($1271i$ cm^{-1} for the reaction

BOND ANGLES (degrees)			BOND LENGTHS (Angstroms)		
ANGLE	MNDO	AB INITIO	LENGTH	MNDO	AB INITIO
$Si - O - H^3$	108.0	N	$O - H^3$	1.262	N
$H^1 - Si - H^2$	101.6		$Si - H^1$	1.412	
$O - Si - C$	114.7		$Si - H^2$	1.420	
$H^1 - Si - O$	116.3		$Si - H^3$	2.458	
$H^1 - Si - C$	104.0		$Si - O$	1.755	
$H^2 - Si - O$	115.2		$Si - C$	1.834	
$H^2 - Si - C$	103.2		$O - H^4$	1.038	
$H^3 - Si - C$	107.7		$C - H$	1.108	
$H^3 - O - H^4$	134.2		$Si - H^4$	2.421	
$Si - O - H^4$	117.8				

MULLIKEN CHARGES					
ATOM	MNDO	AB INITIO	ATOM	MNDO	AB INITIO
Si	1.126	N	H^1	-0.429	N
O	-0.287		H^2	-0.450	
C	-0.306		H^3	0.392	
			H^4	-0.136	

N: Ab initio values were not calculated.

Figure 8. Geometry and Mulliken charges for transition state for water elimination from monomethylsiliconate by abstraction of proton from silicon.

BOND ANGLES (degrees)			BOND LENGTHS (Angstroms)		
ANGLE	MNDO	AB INITIO	LENGTH	MNDO	AB INITIO
$Si - O - H^4$	151.6	N	$O - H^4$	0.937	N
$Si - O - H^5$	80.7		$O - H^5$	1.123	
$Si - C - H^5$	84.1		$Si - H^1$	1.426	
$O - Si - C$	72.7		$Si - H^2$	1.430	
$H^1 - Si - O$	123.2		$Si - H^3$	1.453	
$H^1 - Si - C$	105.3		$Si - O$	2.073	
$H^2 - Si - O$	125.5		$Si - C$	1.772	
$H^2 - Si - C$	103.7		$O - H^5$	1.486	
$H^3 - Si - O$	78.8		$C - H$	1.094	
$H^3 - Si - C$	151.5				
$C - H^5 - O$	122.4				

MULLIKEN CHARGES					
ATOM	MNDO	AB INITIO	ATOM	MNDO	AB INITIO
Si	1.772	N	H^2	-0.518	N
O	-0.581		H^3	-0.538	
C	-0.926		H^4	-0.122	
H^1	-0.511		H^5	0.259	

N: Ab initio values were not calculated.

Figure 9. Geometry and Mulliken charges for transition state for water elimination from monomethylsiliconate by abstraction of proton from methyl group.

coordinate vs $22i$ cm^{-1} for the second negative mode, a rotation of the H_2O being formed). The IRC calculation showed unequivocally that this transition state connects the pentavalent siliconate with the water plus $CH_3SiH_2^-$ products. Figure 9 shows the transition-state geometry and the charges for water removal from the monomethylsiliconate utilizing a proton from the methyl group (MNDO only). Results for the tetramethylsiliconate 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 ($1524i$ cm^{-1} for the reaction coordinate mode vs $368i$, $198i$, and $63i$ cm^{-1} for the other negative modes). IRC calculations again showed unequivocally that the transition state connected the pentavalent siliconate with the products of water removal.

The final possible product of direct ligand-combination processes is ethane, and this only for the tetramethylsiliconate. 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 siliconate 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 siliconate 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 of H_2 compared 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 siliconate 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 siliconate (anionic dissociative proton transfer). These other potential processes involve com-

bination 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 AM1[29] 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.

Registry No. ($CH_3)_4SiOH^-$, 113773-32-3; $H_3SiMe(OH)^-$, 113773-33-4.

(29) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.