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Gas-Phase and Computational Studies of Pentacoordinate Silicon

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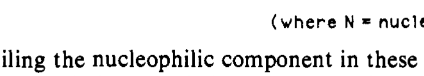
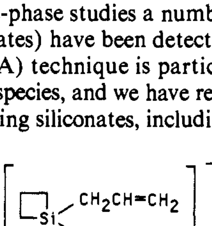
Abstract: We have demonstrated that a wide variety of pentacoordinate silicon anions (siliconates) should be stable and can be prepared by combining the predictive powers of MNDO and ab initio computational methods and the flowing afterglow (FA) experimental technique. MNDO has been used to compute the anion affinities of 91 siliconates; all but five of these are predicted to be stable with respect to the loss of an anion. Twenty-four siliconates, most of them previously unreported, have been prepared and studied in the FA. The MNDO predictions were, in general, consistent with the experimental results and with trends previously reported by Corriu and co-workers, but in some cases they were found deficient. For example, MNDO tends to underestimate the stability of fluorine-containing siliconates. In these cases, we have carried out ab intio computations and found these to be consistent with both the experimental studies reported here and the Corriu trends.

Nucleophilic substitution at silicon has been studied in detail for many years and is generally thought to involve the intermediacy of pentacoordinate silicon (eq 1).[1] Early studies established the scope of allowable substitution patterns at silicon as well as detailing the nucleophilic component in these reactions. Sommer and Corriu have made important contributions to understanding substitution reactions at silicon with both their fundamental chemical studies and their important reviews in this area.[2] Although the intermediacy of pentacoordinate silicon has long been alleged, such species have only in recent years become commonplace. In gas-phase studies a number of pentacoordinate silicon anions (siliconates) have been detected and studied.[3] The flowing afterglow (FA) technique is particularly well suited for the detection of these species, and we have reported the preparation of a variety of interesting siliconates, including **1** which is the most highly carbon substituted siliconate to be reported.[4,5] We have also demonstrated that a siliconate intermediate is involved in the reaction of a number of anions with trimethylchlorosilane (eq 2).[6] In this study we found that all substitution reactions that are exothermic occur at the collision rate while analogous endothermic reactions do not occur in the FA. For the isoenergetic case, where A = Cl, we observed the siliconate intermediate $[(CH_3)_3SiCl_2]^-$.



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-X + N \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-N + X \qquad (1)$$

(where N = nucleophile)



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$$(CH_3)_3SiCl + A^- \longrightarrow (CH_3)_3SiA + Cl^- \qquad (2)$$

(where A^- = anion)

There have also been a number of recent studies of siliconates in solution. Corriu,[7] Martin,[8] Holmes,[9] and their co-workers have prepared and studied a variety of cyclic species while we[10] have

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(1) Fleming, I. In *Comprehensive Organic Chemistry*; Pergamon Press: Oxford, 1979; Chapter 13.

(2) (a) Corriu, R. J. P. *Phosphorus and Sulfur* **1986**, *27*, 1. (b) Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. *Top. Stereochem.* **1983**, *15*, 43. (c) Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 231. (d) Corriu, R. J. P.; Guerin, C. *Adv. Organomet. Chem.* **1982**, *20*, 265. (e) Sommer, L. H. *Stereochemistry, Mechanism, and Silicon*; McGraw-Hill: New York, 1965.

(3) (a) Dillard, J. G. *Inorg. Chem.* **1974**, *13*, 1491. (b) Haartz, J. C.; McDaniel, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 8562. (c) MacNeil, K. A. G.; Thynne, J. C. J. *Int. J. Mass. Spectrom. Ion Phys.* **1970**, *3*, 455. (d) Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 4992.

(4) Sullivan, S. A.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1981**, *103*, 480.

(5) For a review of our flowing afterglow silicon studies, see: DePuy, C. H.; Damrauer, R.; Bowie, J. H.; Shelton, J. C. *Acc. Chem. Res.* **1987**, *20*, 127.

(6) Damrauer, R.; DePuy, C. H.; Bierbaum, V. M. *Organometallics* **1982**, *1*, 1553.

(7) (a) Boudin, A.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 473. (b) Breliere, C.; Carre, F.; Corriu, R. J. P.; Poirer, M.; Royo, G. *Organometallics* **1986**, *5*, 388.

(8) Stevenson, W. H., III; Wilson, S.; Martin, J. C.; Farnham, W. B. *J. Am. Chem. Soc.* **1985**, *107*, 6340.

(9) Holmes, R. R., personal communication. Although most of Professor Holmes' work on pentacoordinate silicon has been focused on their structural aspects, a variety of recent work has begun to uncover some of the solution chemistry of these species.

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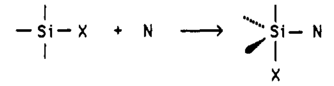
carried out dynamic NMR studies of acyclic siliconates like $[R(C_6H_5)SiF_3]^-$. Such studies have not only established that many siliconates are readily prepared but have shed additional light on their dynamic properties and on nucleophilic substitution reactions at silicon.

X-ray crystallographic studies on siliconates have provided structural data for many of these species, both cyclic and acyclic.[11] Such species generally have trigonal-bipyramidal structures. Particularly important to the work reported here is Schomburg and Krebs' X-ray analysis[12] of $[SiF_5]^-$ and $[(C_6H_5)_2SiF_3]^-$. Both are trigonal bipyramidal with the latter one being slightly distorted. Indeed, the distortion appears to result from interactions between the ortho hydrogens of the phenyl groups and the apically oriented fluorines. We have recently made $[Mes_2SiF_3]^-$ (where Mes is mesityl) and in collaboration with Professors R. Holmes and R. Day examined its X-ray structure.[13] As might be expected, it is even more distorted than $[(C_6H_5)_2SiF_3]^-$. Interestingly, there is also a strong interaction between an apically oriented fluorine and its counterion, a potassium ion complexed by 18-crown-6. A variety of other structural studies have established that the trigonal-bipyramidal geometry is generally favored in siliconates although, as Holmes and co-workers have shown, distortion of trigonal-bipyramidal geometry along a Berry pseudorotational path toward rectangular pyramidal geometry occurs in some cyclic siliconates.[11,14]

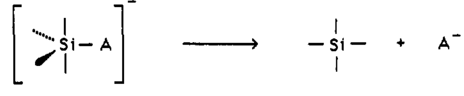
Several computational studies of siliconates have established that the pentacoordinate state for silicon is of lower energy than the reactant or product states in eq 1.[15] This is now well substantiated by using a variety of computational levels, although it is important to recognize that certain siliconates are less stable than alternate species. (For example, though $[SiH_5]^-$ is stable with respect to SiH_4 and H^-, it is not as stable as H_3Si^- and H_2.[16]) Moreover, such studies have indicated not only that siliconate formation is favored for a wide variety of neutral silanes directly reacting with anions,[15a] but generally that little energy separates apical and equatorial orientation for substituents,[15] and that barriers to dynamic properties like Berry pseudorotation are low.[15d]

In previously reported computational studies, we have compared MNDO and various ab initio levels for quite a number of siliconates.[15a] The MNDO method has been shown to adequately reproduce the major substituent trends in the formation of siliconates, but it is unable to accurately predict substituent orientation effects. Some of the reasons for the differences have been detailed in this previous report.

In the work reported here we have undertaken a systematic extension of our gas-phase and computational studies of siliconates in order to explore further the stability of these species. We also wanted to consider whether certain observations by Corriu and co-workers in recent years[2] could be understood in computational terms. They have noted in a variety of studies that the order Br, Cl > F, SR > OR, H applies to (a) the ease of pentacoordination, where these groups are X in eq 3, (b) the ease of nucleophilic substitution, where these groups are X in eq 1, and (c) the stereochemistry of substitution at a chiral silicon in a chiral analogue of eq 1 with substituents like Br and Cl favoring inversion and OR and H favoring retention. They have also noted that the apical orientation of substituents (apicophilicity) of pentacoordinate silicon species follows the order Cl > F, F > OR, and F > H. On the other hand, Corriu and Guerin[2b,c] have pointed out that analysis of the nucleophilic component in eq 1 is considerably more difficult in solution because a number of factors intervene (metal ion effects, solvent effects, hardness, etc.). Yet, in the gas phase nucleophilic species are easily characterized because solvent interactions are absent. Here, the affinity between a neutral silane and an anion (eq 4) is a quantity that can be measured.[17] Indeed, Larson and McMahon have established that fluoride ion bonds more strongly than chloride to neutral silanes in the gas phase.[17]



(3)



(4)

ΔH° = A Affinity

Our computational studies consider these trends, but they also explore in greater depth the formation of siliconates with particular emphasis on (1) detailing the energetics of their formation for a wider variety of substituent groups, (2) computing examples that are subject to experimental verification, and (3) comparing MNDO computations with the more authorative ab initio methodology. The gas-phase FA work reported not only examines the second point in detail but extends our knowledge of the behavior of siliconates in other ways. It is important to recognize that the observations of Corriu and co-workers on the ease of pentacoordination and nucleophilic substitution are based on kinetic studies while our computational studies relate only to thermodynamic considerations. We reconcile these differences easily because there are no barriers in any of our computations where stable siliconates form from a neutral silane and an anion.

Experimental Section

Flowing Afterglow Studies. These experiments were performed in a flowing afterglow (FA) system at 298 K as previously described.[5] Amide, fluoride, chloride, and bromide ions were made by electron impact on NH_3, NF_3, CCl_4, and CH_2Br_2, respectively. Hydroxide ions were made by dissociative electron attachment to N_2O to form O^- followed by hydrogen atom abstraction from methane; HS^- was produced by reaction of hydroxide ion and carbon disulfide. Other anions like CH_3O^-, H_2P^-, MeS^-, and H_3Si^- were prepared by reaction of their conjugate acid with amide ion. Typical helium pressures and flow rates were 0.4 Torr and approximately 160 STP cm^3/s, respectively. Neutral reactants, including the silanes, were obtained from commercial suppliers and used without purification. The identity of products was determined from mass-to-charge (m/z) ratios.

Computational Studies. MNDO computations[18] were carried out by using the MOPAC program[19] with recently revised silicon parameters.[20] To correct for inadequate treatment of isolated small anions with MNDO, experimental heats of formation have been used for these anions in the calculations as explained previously.[15a] Two basis sets were used for the ab initio calculations. Molecular structures for all species were determined at the restricted Hartree–Fock (RHF) SCF level by using the 6-31G* basis set[21] (hereafter referred to as 6-31G(d)). All structures

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(10) Damrauer, R.; Danahey, S. E. *Organometallics* **1986**, *5*, 1490.

(11) Numerous X-ray structures of pentacoordinate silicon have been carried out. Perhaps the best compilation of these is given in (a) below. An additional small sample of those that are not otherwise referenced in the text is given as (b) and (c). (a) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Current Chem.* **1986**, *131*, 99. (b) Klebe, G.; Hensen, K. *J. Chem. Soc., Dalton Trans.* **1985**, 5. (c) Schomburg, D. *Z. Naturforsch.* **1983**, *38b*, 938.

(12) Schomburg, D.; Krebs, R. *Inorg. Chem.* **1984**, *23*, 1378.

(13) Preliminary mention of this work has been made: Harland, J. J.; Payne, J. S.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1987**, *26*, 760.

(14) (a) Holmes, R. R.; Day, R. O.; Harland, J. J.; Sau, A. C.; Holmes, J. M. *Organometallics* **1984**, *3*, 341. (b) Holmes, R. R.; Day, R. O.; Harland, J. J.; Holmes, J. M. *Organometallics* **1984**, *3*, 347. (c) Holmes, R. R. *Five Coordinated Structures.* In *Prog. Inorg. Chem.* **1984**, *32*, 119. (d) Holmes, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 3745.

(15) (a) Gordon, M. S.; Davis, L. P.; Burggraf, L. W.; Damrauer, R. *J. Am. Chem. Soc.* **1986**, *108*, 7889. (b) Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 1686. (c) Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 1692. (d) Wilhite, D. L.; Spialter, L. *J. Am. Chem. Soc.* **1973**, *95*, 2100. References 15b and 15c are to a large extent focused on the bimolecular nucleophilic substitution of silicon. Of particular note along such lines is an early paper: Ahn, N. T.; Minot, C. *J. Am. Chem. Soc.* **1980**, *102*, 103.

(16) For a discussion of both experimental and computational work see: Hajdasz, D. J.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 3139.

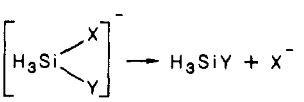
(17) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1985**, *107*, 766. A variety of other fluoride affinities have been calculated: O'Keeffe, M. *J. Am. Chem. Soc.* **1986**, *108*, 4341.

(18) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(19) Stewart, J. J. P. Quantum Chemistry Program Exchange, Program No. 455, Department of Chemistry, Indiana University, Bloomington, Indiana 47405.

(20) Dewar, M. J. S.; Friedheim, J.; Grady, G.; Healy, E. F.; Stewart, J. J. P. *Organometallics* **1986**, *5*, 375.

Table I. Energy Relationships for X^- Loss from $[H_3SiXY]^-$ in kcal/mol by MNDO (ab Initio in Parentheses)



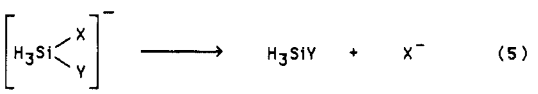
	X →	OH	CH_3	NH_2	OMe	F	H	PH_2	SH	Cl	SMe	I	Br	SiH_3
Y	OH	20.9 (41.3)	23.2	21.3	21.9	11.9 (39.5)	17.5 (31.6)	17.1	14.4	10.3 (9.1)	10.0	19.8	19.7	5.4
	CH_3	23.4	24.9 (32.4)	23.0	23.2	15.4 (29.0)	17.8 (18.2)	15.1	12.9	8.5	8.3	7.3	6.5	−6.9
↓	NH_2	22.5	24.0	22.3 (42.1)	22.7	14.1	17.6	15.9	13.5	9.3	9.0	8.0	7.4	−6.6
	OMe	28.5	29.6	28.1	28.3	20.0 (43.7)	23.4	20.3	17.7	13.4 (10.6)	12.9	11.6	11.1	−2.2
	F	22.0 (51.2)	25.3 (54.1)	23.0	23.5 (51.2)	12.8 (49.4)	20.5 (42.2)	19.7	16.9	12.7 (15.6)	12.6 (24.8)	11.7	11.1	−2.5
	H	30.9 (29.9)	31.0 (54.1)	29.8	30.2	23.8 (29.1)	23.3 (16.7)	18.8	16.8 (4.0)	12.3 (4.5)	11.8	10.2	9.6	−3.4 (−0.2)
	PH_2	63.8	61.6	61.4	60.4	56.3	52.1	39.5	38.7	32.7	32.3	27.6	27.8	18.0
	SH	60.1	58.4	58.0	56.8	52.5	49.1 (46.6)	37.7	36.6 (17.6)	30.7	30.2	26.3	26.3	16.3
	Cl	66.5 (62.8)	64.5	64.3	63.0 (60.2)	58.8 (57.7)	55.1 (58.2)	42.2	41.2	35.2 (21.0)	34.8 (31.4)	30.3	30.4	20.8
	SMe	63.4	61.5	61.2	59.7	55.9 (48.4)	51.8	39.0	37.9	32.0 (13.0)	31.4	27.2	27.2	17.7
	I	72.3	70.1	69.8	68.0	64.6	59.8	43.9	43.6	37.0	36.8	31.6	31.6	24.0
	Br	73.5	71.2	71.1	69.4	65.9	61.1	46.0	45.5	39.1	38.7	33.5	33.7	25.3
	SiH_3	47.3	45.6	44.9	43.9	40.1 (28.3)	35.9	24.0	23.3	17.3	17.0	13.7	13.1	3.6 (6.4)

were verified to be minima on their respective potential energy surfaces by establishing that their matrices of second derivatives were positive definite. The eigenvalues of these analytically determined 6-31G(d) second-derivative matrices were used to calculate the zero-point vibrational energies.

At the 6-31G(d) geometries, single-point calculations were carried out with the larger 6-31++G(d,p) basis set[22] in order to better accommodate the negative charges in the anions. To obtain accurate energetics for reaction 5, the SCF wave function with this basis set was augmented with second-order many-body perturbation theory as formulated by Pople and co-workers.[23] Previous calculations[15a] have shown that these MP2/6-31++G(d,p)//SCF/6-31G(d) calculations provide reliable gas-phase acidities and energies of pentacoordination. All ab initio calculations were carried out with the GAUSSIAN82 system of programs on the IBM 3081 at North Dakota State UNiversity and on the Cray XMP/48 at the San Diego Supercomputer Center.

Results and Discussion

Computational Studies. MNDO has been used to compute the X affinity of H_3SiY (eq 5) for X and Y = OH, CH_3, NH_2, OCH_3,



(5)

F, H, PH_2, SH, Cl, SCH_3, I, Br, and SiH_3. These groups were selected because each or a closely related analogue could be studied in the FA. The data collected in Table I indicate that all but five of the 91 siliconates computed are expected to be stable with respect to loss of X^-. Furthermore, Corriu trends a and b (ease of pentacoordination and ease of nucleophile substitution, respectively) referred to in the introduction are reproduced by these computations. Both trend a and trend b can be considered by examining any column in Table I. The most extensively studied column is X = F, where both MNDO and a number of ab initio (in parentheses) computations have been made. Here the MNDO computations show that Br and Cl form more stable siliconates than SCH_3 and that H and OCH_3 form still less stable siliconates. Thus, Corriu's experimental trend a, setting aside X = F for a moment, is properly represented by the MNDO computations.

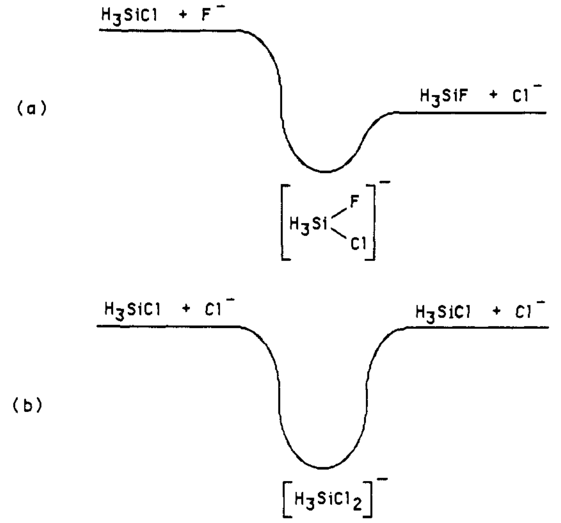


Figure 1. Typical reaction coordinate for (a) an exothermic substitution reaction at silicon and (b) an isoenergetic pentacoordination at silicon.

Moreover, the ease of formation of the siliconates (trend a) also controls the ease of nucleophilic substitution (trend b), a fact consistent with our earlier FA observations on trimethylchlorosilane in which we demonstrated that its nucleophilic substitutions took place through siliconate intermediates.[6] If we recall that no barriers to siliconate formation have been observed when stable siliconates result, Corriu's results and the MNDO computations are reasonably consistent. However, it is clear that MNDO does not adequately compute the stability of fluorine-substituted siliconates if the Corriu order is correct. Ab initio calculations (MP2/6-31++G[d,p]//SCF/6-31G[d]) give a far better agreement with the experimental trends as the numbers in parentheses in Figure 1 demonstrate. We do, however, see that Y = F, SCH_3, and OCH_3 have quite similar values (for H_3SiFY^- → $H_3SiY + F^-$). Similar trends are observed for other columns in Table I, but the comparisons are not as good since fewer ab initio computations were made. Nevertheless, it is clear that MNDO can seriously underestimate the stability of certain siliconates. This is particularly evident in Table I, where the siliconates of H_3SiF and X = OH, CH_3, OCH_3, F, and H are far less stable with MNDO than ab initio methods. When X = Cl

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(21) Gordon, M. S.; Boudjouk, P.; Anwari, F. *J. Am. Chem. Soc.* **1983**, *105*, 4972.

(22) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(23) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91.

and SCH_3, however, the two methods agree more closely. Because MNDO can seriously underestimate the stability of fluorine-containing siliconates, particularly ones bound to H and second-row elements, caution must be exercised in comparing columns in Table I with Corriu's trends if the corresponding fluorine-containing siliconate has not been computed at an ab initio level.

Examination of any row from Table I allows analysis of the nucleophilic component in substitution reactions at silicon (eq 1). Consequently, we see that the X = F > Cl order prevails throughout the table with both MNDO and ab initio methods. More generally, the affinity of any H_3SiY compound for X^- can be obtained by examining the appropriate row in Table I. A rough general order of $OH > CH_3 > NH_2 > OCH_3 > F > H > PH_2 > SH > Cl > SCH_3 > I > Br > SiH_3$ is found for nucleophiles attacking H_3SiY, where the atom of Y bound to silicon is in the third row. For second-row attachments, the order is somewhat different: $CH_3 > OH > OCH_3 > NH_2 > H > PH_2 > SH > Cl > SCH_3 > I > Br > SiH_3$ with X = F having no consistent order.

An examination of the rows in Table I allows a comparison between the X-affinity of various silanes and the corresponding Si–X bond dissociation energy (BDE). It is well-known[24] that the Si–F bond is extremely strong. It seems reasonable to expect that the Si–F bond in siliconates should also be very strong. Table I shows that this is only partially true. For example, in all cases studied the F-affinity exceeds that of the Cl-affinity for H_3SiY, which is what one might expect from BDEs. However, it is clear that the difference between these affinities is highly dependent on the nature of Y. Furthermore, in contrast to what might be predicted on the basis of Si–X BDEs, the X-affinities (for X = F, OH, NH_2, and OCH_3) of a number of H_3SiY compounds have similar values. In fact, in all four cases where the X-affinities for X = F and OH have been computed by ab initio methods, the OH-bonded siliconate is the more stable species. Although these points are not directly addressed in the experimental section of this paper, experimental studies are being planned to consider them.

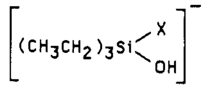
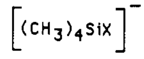
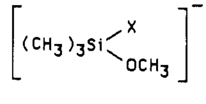
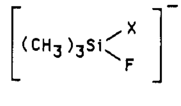
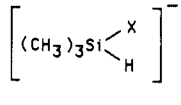
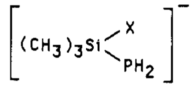
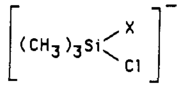
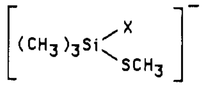
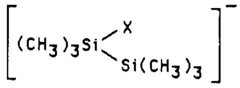
We and others previously have reported on the apical/equatorial orientation aspects of siliconate computations. Because these questions of orientation, as well as those dealing with substitution at chiral silicon, are impossible to address in the FA, we will not comment here on related computational work that is currently in progress. This work will be reported at a later time.

Flowing Afterglow Studies. The flowing afterglow technique has been used to examine the generality of our computations. Although we chose to carry out our computational studies on simple silyl (H_3Si) compounds, the FA studies were, with one exception, done with trimethylsilyl derivatives, both because such derivatives were much more widely available and because their greater complexity maximized siliconate stabilization. The increased number of vibrational modes in the trimethylsilyl group allows excess energy to be better dissipated in exothermic reactions.

The strategy employed in the FA studies is best understood with reference to parts a and b of Figures 1, which are diagramatic representations of the MNDO computations for $[H_3SiFCl]^-$ and $[H_3SiCl_2]^-$, respectively. Figure 1a shows a typical exothermic ion–molecule reaction along the path from left-to-right. This, of course, corresponds to an exothermic nucleophilic substitution at silicon (eq 6). When such a reaction is highly exothermic, the probability that the intermediate siliconate can be stabilized and detected is small despite the relatively high pressures in the FA and the large number of vibrational modes attending the trimethylsilyl groups. A far better approach for obtaining siliconates would be to follow the path in Figure 1a from right-to-left. Here, the siliconate is formed in a less exothermic way and escape by nucleophilic substitution is quite improbable because of the high exit channel barrier. Another approach that reasonably can be expected to give siliconates is represented in Figure 1b. Here, because the reaction is isoenergetic, the probability of stabilizing the siliconate is increased because its lifetime is increased. Both of these approaches, entering the endothermic side of the reaction channel and entering the isoenergetic reaction manifold, have produced stable siliconates in this FA study.

$$H_3SiCl + F^- \longrightarrow H_3SiF + Cl^- \qquad (6)$$

Table II. List of the Pentacoordinate Species Prepared in the Flowing Afterglow in This Study

	X = F, Cl
	X = OCH_3, F, Cl
	X = OH, OCH_3, F, Cl, Br
	X = OCH_3, F, Cl, Br, SiH_3
	X = OCH_3, F, Cl
	X = Cl
	X = Cl, Br
	X = Cl, SCH_3
	X = Cl

Reference to Table II shows the variety of new siliconates that have been prepared. Indeed, OH-, PH_2-, SCH_3-, $Si(CH_3)_3$-, and Br-substituted siliconates are reported for the first time. Pioneering work in the area of H-substituted siliconates has been carried out by Squires and co-workers, who not only prepared $[H_5Si]^-$ but studied the reactions of several other H-substituted siliconates.[16] We have prepared four new H-substituted siliconates as well as a number of other CH_3O-, F-, and Cl-containing species. Although we have been able to prepare quite a variety of siliconates consistent with the computational predictions, not all our efforts have been successful. This generally does not result because of difficulties in the computational predictions but arises for experimental reasons. All reactions with $(CH_3)_3SiN(CH_3)_2$ have failed because of inexplicable signal losses in the FA even for energetically favorable cases. Similarly, the use of H_2P^- and HS^- has led to signal loss difficulties. On the other hand, despite work with other halide ions and the favorable computational predictions, we have not used I^- in the FA because the siliconates formed with it would have $m/z > 200$, a mass region that is not easily sampled with our normal FA setup. The use of anions like HO^-, H_2N^-, and H^- was impractical because their high basicity made other reaction channels more probable.[25] Finally, CH_3^-, because its electron is bound by only 1.8 kcal/mol, readily undergoes electron detachment and cannot be made in the FA.[26] Even though some

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(24) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(25) Bartmess, J. E.; McIver, R. T., Jr., In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2. All acidity values quoted come from this source or an updated, but unpublished, version recently obtained from J. E. Bartmess.

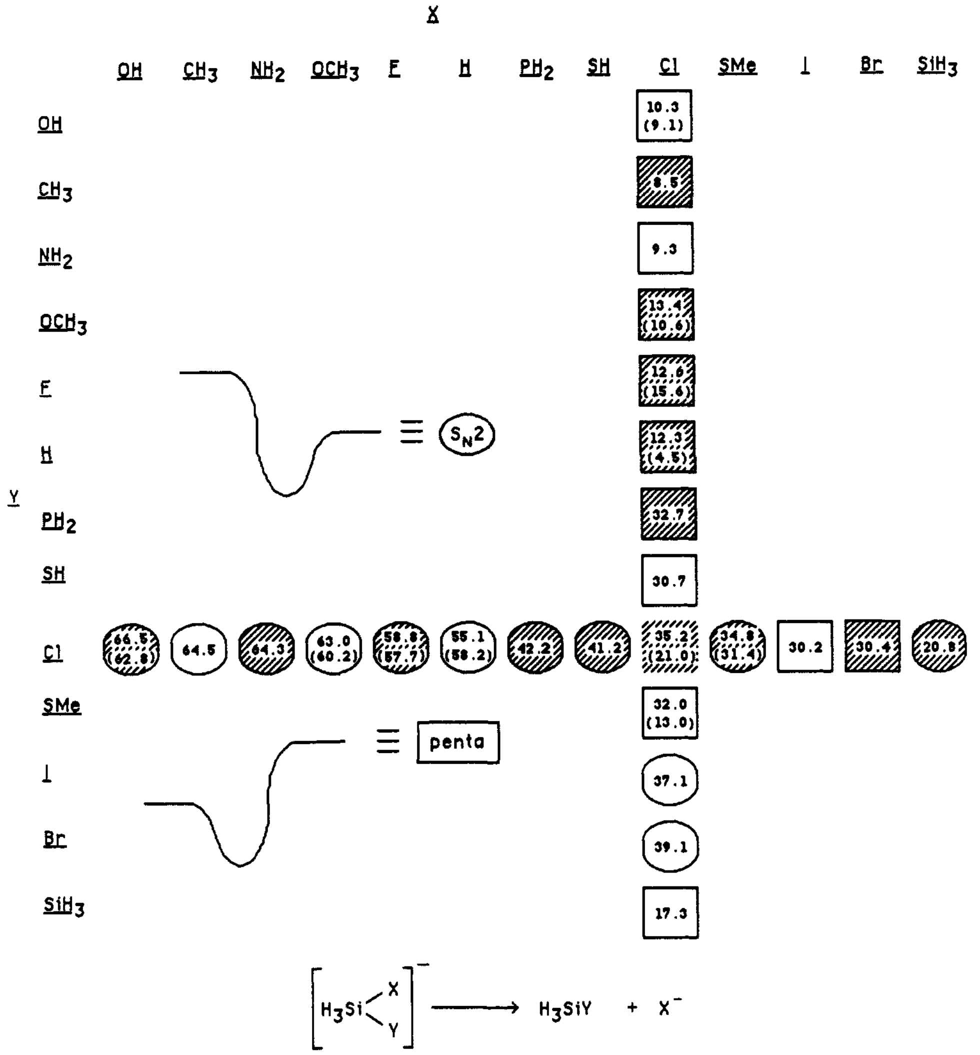


Figure 2. Energy relationships for X^- loss from $[H_3SiClX]^-$ and Cl^- loss from $[H_3SiYCl]^-$. Values in ovals predict S_N2 displacement of Cl^-. Those in rectangles predict formation of a siliconate. MNDO values (ab initio in parentheses) given in kcal/mol. Crosshatched entries represent experimental verifications of the computational predictions.

minor experimental difficulties are experienced with certain trimethylsilyl compounds and anions, we see that a wide variety of siliconates can be made by using the direct reaction approach outlined here and, thus, the computations have proved to be an excellent guide for these preparations.

A further test of these ideas comes when we consider our earlier work on nucleophilic substitution of $(CH_3)_3SiCl$ in light of the present work.[6] Figure 2 displays both the MNDO computations from Table I for $H_3SiCl + X^-$ and $H_3SiY + Cl^-$ as well as any ab initio computations we have carried out for these. All of the circled entries in Figure 2 represent nucleophilic substitution reactions that are predicted to be exothermic in the sense of going from left-to-right along a path like that illustrated in Figure 1a. All the boxed entries represent reactions that are predicted to be endothermic; these are ones following a right-to-left path in Figure 1a and should lead to siliconate formation. Thus, the reaction of H_3SiCl and HO^-, CH_3^-, H_2N^-, CH_3O^-, F^-, H^-, H_2P^-, HS^-, CH_3S^-, and H_3Si^- should occur with substitution. We have demonstrated this to be the case for reactions between $(CH_3)_3SiCl$ and HO^-, H_2N^-, CH_3O^-, F^-, H_2P^-, HS^-, CH_3S^-, and H_3Si^-. Similarly, we would predict that Cl^- and H_3SiY, for Y = OH, CH_3, NH_2, OCH_3, F, H, Cl, PH_2, SH, SCH_3, and SiH_3, would give stable siliconates. Indeed, reactions of Cl^- and $(CH_3)_3SiY$, for Y = CH_3, OCH_3, F, H, PH_2, and Cl, have all led to stable siliconates. Again, the agreement between the computations and the FA experiments is very good. Those predictions that have been successfully tested are represented in Figure 2 by the shaded circles and boxes.

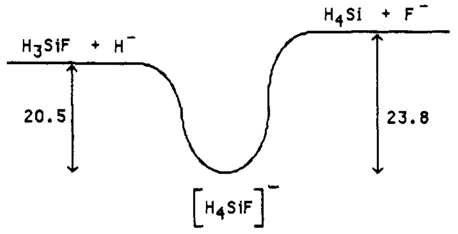
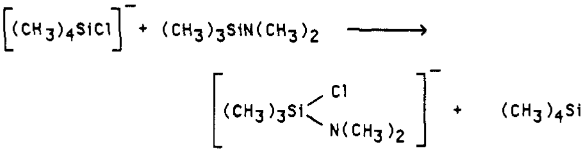


Figure 3. MNDO energetics (kcal/mol) for formation of $[H_4SiF]^-$.

The predictive power of the computations coupled with the flexibility of the FA method can lead to additional insights. For example, though we have shown that all direct reactions of $(CH_3)_3SiN(CH_3)_2$ and nucleophiles, even ones likely to form stable siliconates, fail to give any signals in the FA, we have been able to use $[(CH_3)_4SiCl]^-$ to transfer Cl^- to $(CH_3)_3SiN(CH_3)_2$ (eq 7). This so-called soft transfer is predicted by MNDO to be exo-



$$[(CH_3)_4SiCl]^- + (CH_3)_3SiN(CH_3)_2 \longrightarrow [(CH_3)_3Si(Cl)N(CH_3)_2]^- + (CH_3)_4Si \quad (7)$$

thermic by about 1 kcal/mol (Table I). Thus, even though this experiment does not give a large signal for the siliconate, it does

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(26) (a) Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556. (b) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 607.

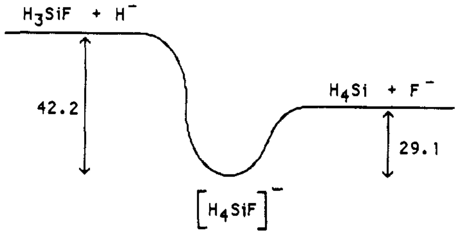


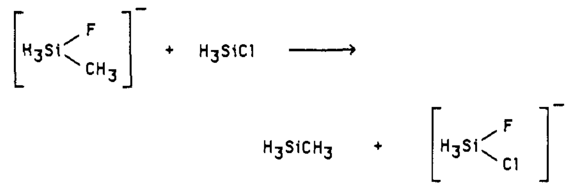
Figure 4. Ab initio energetics (kcal/mol) for formation of $[H_4SiF]^-$.

demonstrate that the computations presented in Table I can be used to predict the outcome of more complex reactions.

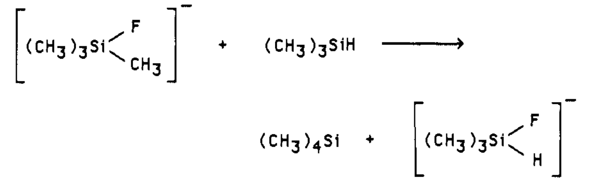
There are certain MNDO computations that do not fit our experimental results. One example is that of $[H_4SiF]^-$. Figure 3 depicts the energetics of $[H_4SiF]^-$ formation with the MNDO values. It indicates that reaction of H_3SiF and H^- should give this siliconate by analogy with our other successful direct siliconate syntheses from the endothermic side. Our experimental result is that the analogous methyl-substituted siliconate is made from $(CH_3)_3SiH$ and F^- (eq 8). Although MNDO gives a result irreconcilable with experiment, ab initio computations give a much more credible result (Figure 4). We see that reactions between H_4Si and F^- gives the siliconate, $[H_4SiF]^-$, which cannot escape through the substitution channel. Here is another example of MNDO calculations seriously underestimating the stability of the siliconate formed from a fluorosilane.

$$(CH_3)_3SiH + F^- \longrightarrow [(CH_3)_3SiFCl]^- \quad (8)$$

Other transfer reactions allow us to further probe the territory between computation and experiment. Transfer of F^- in reaction between $[H_3Si(CH_3)F]^-$ and H_3SiCl is predicted to be exothermic by 43 kcal/mol (29 kcal/mol by ab initio) (eq 9). The methyl-substituted reaction between $[(CH_3)_3Si(CH_3)F]^-$ and $(CH_3)_3SiCl$, however, gives no discernible $[(CH_3)_3SiFCl]^-$ even though $[(CH_3)_4SiF]^-$ rapidly reacts. On the other hand, reaction between $[H_3Si(CH_3)F]^-$ and H_4Si is exothermic by only 8 kcal/mol with MNDO (0.1 kcal/mol by ab initio). Experimentally, transfer between $[(CH_3)_3Si(CH_3)F]^-$ and $(CH_3)_3SiH$ gives a large signal for $[(CH_3)_3SiFH]^-$ (eq 10). Presumably, the first transfer is so exothermic that the siliconate product cannot be stabilized in the FA. When, as in the second case (eq 10), the transfer is less exothermic (a softer transfer), the product siliconate having a lower energy content can be stabilized and detected in the FA.



$$[H_3SiF(CH_3)]^- + H_3SiCl \longrightarrow H_3SiCH_3 + [H_3SiFCl]^- \quad (9)$$



$$[(CH_3)_3SiF(CH_3)]^- + (CH_3)_3SiH \longrightarrow (CH_3)_4Si + [(CH_3)_3SiFH]^- \quad (10)$$

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Gas-Phase Chemistry of Transition Metal–Imido and –Nitrene Ion Complexes. Oxidative Addition of N–H Bonds in NH_3 and Transfer of NH from a Metal Center to an Alkene

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Contribution from the Herbert C. Brown Laboratory of Chemistry, Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. *Received February 1, 1988*

Abstract: We report here on the gas-phase chemistry of a number of bare transition metal–nitrene and –imido ion complexes, MNH^+. Group 3, 4, and 5 atomic metal ions react with NH_3 at thermal energies to generate MNH^+ via dehydrogenation. A reaction mechanism is proposed involving initial oxidative addition to an N–H bond, in analogy to mechanisms proposed for reactions of gaseous atomic metal ions with hydrocarbons. Cr^+ reacts with NH_3 via slow condensation to form $CrNH_3^+$, as do all group 6–11 atomic metal ions investigated. However, excited-state Cr^+ reacts with NH_3 via bond-insertion reactions to form $CrNH_2^+$ and $CrNH^+$. An unidentified metastable electronic state of Cr^+, produced by direct laser desorption of chromium foil, reacts with much higher efficiency than does kinetically excited Cr^+. FeO^+ reacts with NH_3 to generate $FeNH^+$ with loss of H_2O. Thermochemical studies of VNH^+ and $FeNH^+$ involving ion–molecule reactions indicate values of $D°(V^+–NH) = 101 \pm 7$ kcal/mol and $D°(Fe^+–NH) = 54 \pm 14$ kcal/mol, the latter value in accord with $D°(Fe^+–NH) = 61 \pm 5$ kcal/mol obtained from photodissociation. The high bond strength for VNH^+ indicates multiple bonding, analogous to that in the isoelectronic VO^+, while the weaker bond strength for $FeNH^+$ indicates a single bond, analogous to that in the isoelectronic FeO^+. Proton-transfer experiments indicate $PA(VN) = 220 \pm 4$ kcal/mol from which $\Delta H_f(VN) = 111 \pm 9$ kcal/mol and $D°(V–N) = 125 \pm 9$ kcal/mol are obtained. VNH^+ is unreactive with ethene and benzene, but $FeNH^+$ transfers NH to ethene and benzene through metathesis and homologation reactions. A cyclic metalloaminobutane intermediate is consistent with the products of the $FeNH^+$/ethene reaction.

Studies have shown gas-phase atomic transition metal ions to be highly reactive species which exhibit many novel reaction pathways.[1] In particular, gas-phase atomic metal ions and highly unsaturated organometallic ions have been observed to activate

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[‡] NSF predoctoral fellow.

[1] For a recent review of gas-phase metal-ion chemistry, see: Allison, J. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley-Interscience: New York, 1986; Vol. 34, p 628.

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