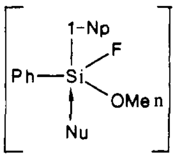

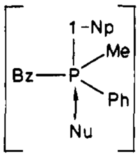

In each case, the results are consistent with axial attack, followed by pseudorotation to bring the departing group to an axial site.

In conclusion, present theoretical and experimental data suggest that pathways for substitution reactions at tetracoordinated silicon that proceed via five-coordinated states bear a close resemblance to pathways advanced for analogous reactions at tetracoordinated phosphorus.[20b]

Summary. On the basis of our treatment, we summarize the following main points.

For both X = F and Cl in the system $H^- + SiH_3X \rightarrow [H\text{–}SiH_3X]^-$, axial entry is a lower energy pathway than equatorial entry, axial departure is the preferred route rather than equatorial departure, and retention via pseudorotation is of lower energy than retention via equatorial attack.

For F vs. Cl as the leaving group, retention via pseudorotation is preferred for fluorine because the retention pathway is comparable in energy to the inversion pathway, and fluorine is more tightly bound in the trigonal bipyramidal intermediate, thus enhancing the possibility of ligand rearrangement before departure. For chlorine as the leaving group, inversion is the favored energy pathway.

Acknowledgment. The support of this research by the National Science Foundation (CHE8504737) is gratefully acknowledged. We thank the University of Massachusetts Computing Center for generous allocation of computer time. The authors also express appreciation to Professor John Ragle for many helpful discussions.

Supplementary Material Available: Angles for minimum strain energy conformations from molecular mechanics for the system $SiH_3X + H^-$ (Table SI); bond overlap for the Si–X bond for the system $[SiH_3X\text{–}H]^-$ for attack at H–H and H–X edges (Table SII); and energy of $[SiH_3X\text{–}H]^-$ minimized with respect to the length of the Si–X bond (Table SIII) (5 pages). Ordering information is given on any current masthead page.

Effect of Entering and Leaving Groups on Nucleophilic Substitution Reactions at Silicon. A Molecular Orbital Approach

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Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003. *Received March 31, 1986*

Abstract: Molecular orbital calculations are carried out for regular trigonal bipyramidal and square pyramidal conformations of $[SiH_3XY]^-$ (X = H and Y = H, OH, SH, Cl, F; X = Cl, F, OH, SH and Y = Cl, F), where $[SiH_3XY]^-$ is a proposed five-coordinated transition state for applicable nucleophilic substitution reactions of tetracoordinated silicon. The results of these calculations are correlated with experimental data on retention and inversion at silicon centers. For a given nucleophile, the experimentally established tendency toward retention in terms of leaving group ($H^- > OH^- > SH^- \sim F^- > Cl^-$) is shown to correlate with a corresponding decrease in calculated overlap population of the bond between silicon and the leaving group. Data for barriers to retention support a retention mechanism with axial nucleophilic attack orthogonal to the leaving group followed by pseudorotation and axial departure of the leaving group. The apicophilicity of the leaving group is found to vary with the type of nucleophile being used and enters into the determination of relative tendency toward a retention vs. an inversion pathway. A softer nucleophile increases the apicophilicity of the leaving group and thus tends to favor an inversion process in accord with experimental data.

For nucleophilic displacement at tetracoordinated silicon, a pentacoordinate activated state is commonly invoked to explain products resulting from both retention and inversion of configuration.[2] The accepted inversion mechanism is that the nucleophile attacks trans to the leaving group in the center of a tetrahedral face, giving rise to a trigonal bipyramidal activated state with entering and leaving groups in axial positions. See Figure 1a. This mechanism has been well established for inversion reactions at tetrahedral phosphorus[3] and carbon centers.

Two possible retention mechanisms have been proposed. The first, illustrated in Figure 1b, is the same mechanism invoked for retention in nucleophilic displacement reactions of phosphorus.[3,4] This mechanism invokes axial attack (in the center of a tetrahedral face containing the leaving group) and results in a five-coordinated, trigonal bipyramidal activated state with the leaving group in an equatorial position. Pseudorotation through a square pyramid with the leaving group and the nucleophile in cis-basal positions brings the leaving group to an axial position and the nucleophile to an equatorial position of the resultant trigonal bipyramid. Departure of the leaving group from the axial position completes the mechanism.

An alternate retention mechanism (Figure 1c), proposed by Corriu,[5] does not require a pseudorotation step. Instead, attack by a nucleophile is invoked on a tetrahedral edge between a ligand and a leaving group with the ligand and the leaving group assuming axial positions and the nucleophile an equatorial position of the five-coordinated activated state.

Our earlier calculations[6] have shown that for the leaving groups F^- and Cl^-, in the initial approach of a nucleophile, H^-, axial entry and departure are preferred routes. In agreement with experi-

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[1] Department of Chemistry, Vassar College, Poughkeepsie, NY 12601.

[2] Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 231 and references cited therein.

[3] Holmes, R. R. *Pentacoordinated Phosphorus—Reaction Mechanisms*; American Chemical Society: Washington, D.C., 1980; Vol. II, ACS Monograph No. 176, pp 87–88.

[4] Westheimer, F. H. *Acc. Chem. Res.* **1968**, *1*, 70.

[5] Reference 2, pp 295f.

[6] (a) Presented at the XIX Organosilicon Symposium, L.S.U., Baton Rouge, LA, April 26, 1985. (b) Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.*, previous paper in this issue.

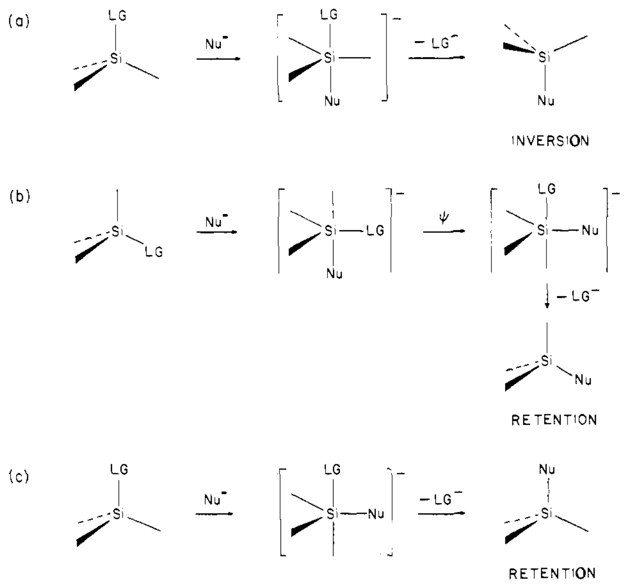

Figure 1. Mechanisms for nucleophilic substitution reactions of silicon: (a) inversion, (b) retention involving axial attack and pseudorotation to give axial departure, and (c) retention involving equatorial attack and axial depature. ψ symbolizes a pseudorotational process.

mental results,[2,7] these calculations determined that chlorine is a better leaving group than fluorine and exhibits a strong preference for an inversion pathway.

In this present work, we extend the molecular orbital calculations to a series of nucleophiles in addition to H^- and to leaving groups other than Cl^- and F^-. Experimentally, it is known[2,7] that the degree of retention of configuration for chiral derivatives increases along the series of leaving groups in the order $ROCO^-$, Br^-, $Cl^- < SR^-$, $F^- < OR^- < H^-$ and that use of hard nucleophiles promotes retention. Here we study the series of groups Cl^-, F^-, OH^-, SH^-, and H^-, considering both variations in nucleophilicity and leaving group tendencies. By looking at the electronic properties of five-coordinated transition states of simple silicon anions, we wish to establish factors associated with the leaving group and nucleophile which alter leaving group ability and the ratio of inversion and retention of products. In this way, underlying features controlling nucleophilic substitution at silicon may reveal themselves.

Calculation and Results

GAUSSIAN 82[8] (STO-3G minimal basis set) was used to calculate the energy and optimum bond lengths for ideal trigonal bipyramidal, TBP, and square pyramidal, SP, geometries for the system $[SiH_3XY]^-$, where X = H and Y = H, OH, SH, Cl, F; X = Cl, F, OH, SH and Y = Cl, F. Relative energies, charge densities, bond overlap populations, and optimum bond lengths are given in Table SI. TPB angles are 180°, 90°, 120°, and the SP apical-basal angle is set at 105°. All bond lengths are minimized (to the nearest 0.01 Å) to give the lowest total energy for the system.

The minimal basis set STO-3G was used since we wished to explore a wide range of entering and leaving groups to examine the major factors which are influencing retention and inversion. In obtaining this overview, it is necessary to consider only energy differences, either among isomeric structures for a given composition or between the same structural form for compositions differing by one ligand, the ligand being either a leaving group or a nucleophile. However, a trend toward inversion or retention obtained at the STO-3G level may be invalid if energy difference calculations performed on an expanded basis set resulted in a different ordering. To test the validity of the approach, a limited number of higher level calculations (6-31+G*) employing diffuse orbitals and d functions were carried out for some of the molecules involved. These results are presented in Table II. The data shown on the figures are the data from the STO-3G level calculations.

Table I. Energy Barriers to Retention for $[NuSiH_3(LG)]^-$ (kcal/mol)

Nu[a]	LG[b]	apicophilicity of LG, ΔE_{12}[c]	pseudorotation barrier, ΔE_{13}[c]	apicophilicity of Nu, ΔE_{14}[c]
H	Cl	25.6[d]	12.2	
	F	5.6	6.4[d]	
	SH	9.7	12.1[d]	
	OH	4.3	11.7[d]	
	H		7.2[d]	
F	Cl	20.6[d]	12.2	3.7
	F	1.9	4.3[d]	1.9
	SH	7.5	11.5[d]	3.4
OH	Cl	19.9[d]	18.6	6.0
	F	1.9	10.0[d]	2.6
SH	Cl	24.8[d]	24.7	10.2
	F	3.4	11.5[d]	7.5

[a] Nu = nucleophile. [b] LG = leaving group. [c] ΔE_{12}, ΔE_{13}, and ΔE_{14} are defined in reference to structures **1**, **2**, **3**, **4**. These structures are as follows: (**1**) TBP, LG, Nu(axial); (**2**) TBP, Nu(axial), LG(equatorial); (**3**) SP, LG, Nu(cis basal); (**4**) TBP, Nu(equatorial), LG(axial). [d] Determines total barrier height for retention mechanism 1b.

Table II. Basis Set Comparison. Relative Energy (ΔE) and Apicophilicity (A) of Leaving Groups, LG (kcal/mol)

				6-31+G*		STO-3G
Nu	LG	conformation		ΔE, kcal/mol	A(LG)[a]	A(LG)[a]
H	Cl	H_{ax}	Cl_{ax}	0	20.0	25.6
H	Cl	H_{ax}	Cl_{eq}	20.0		
H	SH	H_{ax}	SH_{ax}	0	12.0	9.7
H	SH	H_{ax}	SH_{eq}	12.0		
H	F	H_{ax}	F_{ax}	0	11.4	5.6
H	F	H_{ax}	F_{eq}	11.4		
H	OH	H_{ax}	OH_{ax}	0	2.9	4.3
H	OH	H_{ax}	OH_{eq}	2.9		

[a] $A = \Delta E_{12}$ as defined in Table I.

Since the treatment presented here relies on the use of relative energies in support of preferred reaction paths, the conclusions assume a more qualitative character, especially since kinetic factors, not treated here, may have some influence.

Discussion

Leaving Group Effect. In Figure 2, we show a plot of overlap population for the Si-LG bond (LG = potential leaving group) of $[SiH_3(Nu)(LG)]^-$ (Nu = nucleophile) with Nu and LG in axial positions of a TBP, as a function of the potential leaving group for nucleophiles H^-, F^-, and Cl^-. Data for the plot are found in Table SI. For a given nucleophile, the tendency toward inversion is greatest for chloride as the leaving group. This is reflected in the small overlap population of the Si–Cl bond. As the nucleophile attacks, the weak Si–Cl bond is easily broken. On the other hand, the large value of Si–H overlap population might reasonably be associated with retention in that the hydrogen is more tightly bound and could preferentially allow a ligand rearrangement (pseudorotation) to occur.

As the incoming nucleophile group Nu (trans to the LG) is varied from Cl^- to F^- to H^-, the overlap population of the Si–LG bond is altered, but the leaving group order $Cl^- > SH^- \sim F^- > OH^- > H^-$ is preserved, i.e., the best leaving group has the smallest Si–LG overlap population. A tightly bound incoming group, i.e., H^-, exhibits a greater weakening effect on the trans axial Si–LG bond as compared to a more weakly bound incoming group, i.e., Cl^-.

The latter trend in overlap population caused by varying the incoming nucleophile agrees with the conclusion of Corriu and co-workers[2,9] that the ability of the leaving group to be cleaved

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[7] Corriu, R. J. P.; Guerin, C. *Adv. Organomet. Chem.* **1982**, *20*, 265 and references cited therein.

[8] Binckley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN 82, Carnegie Mellon University, Pittsburgh, PA.

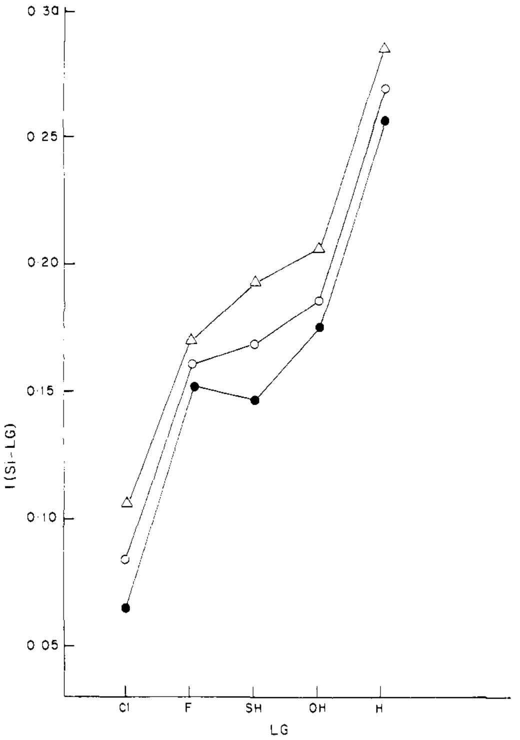

Figure 2. Overlap population, l, of the bond undergoing cleavage, Si–LG in the TBP, $[SiH_3(LG)(Nu)]^-$, as a function of the potential leaving groups, LG = Cl^-, F^-, SH^-, OH^-, H^-. The attacking nucleophiles are Nu = H^-, F^-, Cl^-. LG and Nu are in axial positions of the TBP. Solid circles, Nu = H^-; open circles, Nu = F^-; triangles, Nu = Cl^-.

(and hence the tendency toward inversion) is altered by the incoming nucleophile. Also the experimentally determined leaving group order for inversion, $Cl^- > F^- \sim SH^- > OH^- > H^-$, is clearly evident in the trend in overlap populations expressed in Figure 1 in this same order, i.e., the better leaving group has the lower Si–LG overlap.

The leaving group SH^- shows somewhat anomalous behavior. The Si–SH bond trans to the H^- nucleophile is somewhat weaker than that expected in $[SiH_4(SH)]^-$ (Figure 2).

A second point that we considered was the relationship between calculated retention barrier and LG ability. Table I summarizes the pertinent energies and footnote *c* defines the positions of the leaving group and nucleophile in the referenced trigonal bipyramidal (TBP) and square pyramidal (SP) structures. If the mechanism under consideration is b of Figure 1 (axial entry orthogonal to the LG, pseudorotation, and axial departure of the LG), then the barrier to retention by this process is related to the energy difference between structures **1** and **2** or **1** and **3** (depending on whether **2** or **3** is higher in energy), i.e., to ΔE_{12} or ΔE_{13}. The barrier for mechanism b of Figure 1 may be considered in two components: the barrier to attack orthogonal to the LG (as compared to attack by the nucleophile trans to the LG), i.e., ΔE_{12}; and the energy barrier encountered in Berry pseudorotation, ΔE_{13}. The first component of the barrier, ΔE_{12}, is really a measure of the apicophilicity of the leaving group.

The relative energies shown in Table SI may be used to assess barrier heights ΔE_{12} or ΔE_{13} and ΔE_{14}. For convenience, Table I tabulates these barrier heights for both retention mechanisms and the data for mechanism b of Figure 1 are plotted in Figure 3. For example, in the system $SiH_3F + OH^- \rightarrow [SiH_3FOH]^-$, the barrier for retention mechanism b of Figure 1 is 10.0 kcal/mol, i.e., ΔE_{13} is greater than ΔE_{12}. The barrier consists of two parts: the apicophilicity of F, 1.9 kcal/mol, and the additional barrier to pseudorotation of 8.1 kcal/mol. In the system $SiH_3Cl + OH^- \rightarrow [SiH_3ClOH]^-$, the barrier for retention mechanism b is 19.9 kcal/mol, i.e., ΔE_{12} is greater than ΔE_{13}. Here the SP (structure **3**) encountered in the pseudorotational process is 1.3 kcal/mol lower in energy relative to the TBP (structure **2**) which is the initial activated state. Experimentally,[7] the LG order is

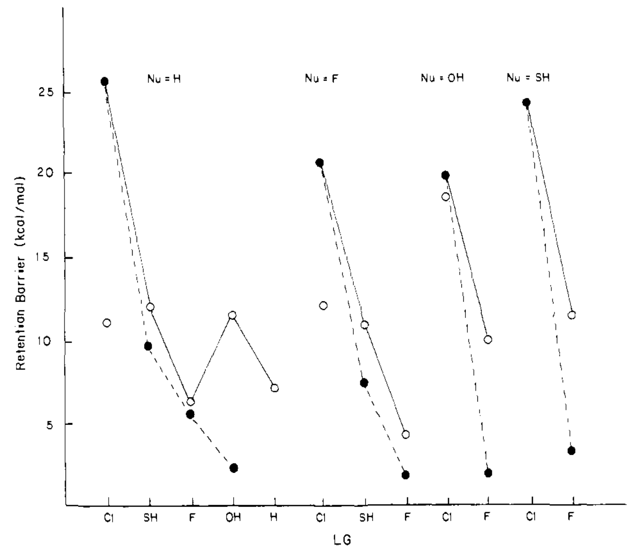

Figure 3. Retention barriers for $[SiH_3(Nu)(LG)]^-$ based on axial attack and a pseudorotation mechanism, Figure 1b. The filled circle indicates the apicophilicity of the LG and the open circle indicates the relative energy of the SP. The solid line represents the total retention barrier, and the dotted line shows the barrier due to the apicophilicity of the LG.

$$\begin{array}{c} Cl^- > SH^-, F^- > OH^- > H^- \\ \text{IN} \xrightarrow{\hspace{3cm}} \text{RN} \end{array}$$

The order predicted by this calculation of retention barriers (mechanism b of Figure 1) with H^- as the nucleophile is

$$\begin{array}{c} Cl^- \gg SH^- \sim OH^- > H^-, F^- \\ \text{IN} \xrightarrow{\hspace{3cm}} \text{RN} \end{array}$$

which, with the exception of fluorine, is the same as the order determined experimentally. The order of barrier height calculated for F^- as the attacking nucleophile is

$$\begin{array}{c} Cl^- \gg SH^- > F^- \\ \text{IN} \xrightarrow{\hspace{2cm}} \text{RN} \end{array}$$

The order determined by the apicophilicity of the LG, ΔE_{12}, is with one exception (LG = OH^-, Nu = H^-) the same as the order determined by the total barrier height. From Figure 3, it can be seen that the calculated apicophilicity of the LG correlates with the experimentally determined tendency toward retention, i.e., groups with low apicophilicity are poor leaving groups and tend toward the retention processes. It is to be appreciated that the order of apicophilicities, e.g., with H^- as the nucleophile, $Cl^- > SH^- > F^- > OH^- > H^-$, does not follow that expected from the relative electronegativities of these elements. In the case of chloride as the LG, experimental data show that nucleophilic substitution proceeds invariably with inversion. The high apicophilicity and LG ability of chlorine calculated here support this process.

Since the apicophilicity of the LG, ΔE_{12}, correlates with the experimentally observed LG order for nucleophilic displacement without exception, we chose the variation of this parameter as a test on the validity of our approach by performing calculations at the 6–31+G* level. Using H^- as the nucleophile, the results in Table II show that the same LG order obtained at the STO-3G level persists at the 6–31+G* level. While the relative changes in the LG apicophilicities are not directly comparable, the fact that the same trend exists lends some assurance that the underlying conclusions based on the less extensive STO-3G calculations are valid.

Equatorial Nucleophilic Attack. If the mechanism under consideration is c of Figure 1 (equatorial entry of nucleophilic and axial departure of LG) then one needs to consider ΔE_{14}, the apicophilicity of the nucleophile, as well as the energy expenditure for edge attack.[5] The edge attack pathway was shown to be a

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(9) (a) Corriu, R. J. P.; Royo, G.; De Saxce, A. *J. Chem. Soc., Chem. Commun.* **1980**, 892. (b) Breliere, C.; Carre, F.; Corriu, R. J. P.; De Saxce, A.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1981**, *205*, C1. (c) Corriu, R. J. P.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1982**, *233*, 165.

Table III. Apicophilicity of Leaving Group, LG (kcal/mol), and Overlap Population of Si–LG Bond

LG	Nu	apicophilicity of LG	overlap population LG_{ax}	overlap population LG_{eq}
Cl	H	25.6	0.065	0.114
	F	20.6	0.083	0.119
	Cl	27.0	0.106	0.164
	SH	24.8	0.086	0.086
	OH	19.9	0.084	0.084
F	H	5.6	0.154	0.174
	F	1.9	0.161	0.169
	SH	3.4	0.163	0.174
	OH	1.9	0.162	0.172

high-energy process in our earlier work[6] and hence is not considered to be a serious possibility, especially in the context of the evidence to follow. In addition, there is little correlation between the apicophilicity of the nucleophile and the tendency toward inversion or retention for the edge attack process. For example, compare Cl^- and F^- as leaving groups when F^- is the attacking nucleophile (Table I). If mechanism c of Figure 1 were the mechanism for retention, one might expect to see a sizable difference in the apicophilicity of the nucleophile, i.e., when F^- is the leaving group, a low apicophilicity for the nucleophile F^- would promote retention, whereas when Cl^- is the leaving group, one might expect, since experimentally inversion predominates for Cl^-, that the apicophilicity of the nucleophile might be much larger than in the case of F^- as leaving group. However, the difference in apicophilicity amounts to only 1.8 kcal/mol. This compares with a difference in barrier heights of 16.3 kcal/mol for these same groups proceeding by retention mechanism b. Comparisons with other nucleophiles and leaving groups in Table I leads to the same conclusion that little support exists for mechanism c.

Effect of Nucleophile on Apicophilicity of Leaving Group. For a given leaving group, experimentally, variation in the nucleophile may shift the reaction toward a retention or inversion process.[10] This shift is also reflected in our calculations by a change in the overlap population of the bond between silicon and the leaving group and by a change in the apicophilicity of the leaving group.

Insight into the primary factor controlling reaction stereochemistry, as influenced by the type of nucleophile used, results by considering how the choice of nucleophile alters the apicophilicity and covalency of the leaving group. For a given leaving group, Table III shows that variation in the nucleophile is accompanied by a sizable change in the apicophilicity of the leaving group. This variation is not in the same order that the overlap population of the LG varies with change in nucleophile. It does, however, correlate with the difference between the equatorial and axial overlap population of the LG. In Figure 4, a plot is shown of apicophilicity vs. the change in overlap population of the Si–LG bond when the LG is moved from an axial to an equatorial position (with the nucleophile in an axial position). This population difference is an expression of the relative tendency to form the initial transition states in the retention and inversion processes in Figure 1, b and a, respectively.

For a given leaving group, such as Cl^-, the apicophilicity of Cl^- (Figure 4 or Table III) decreases with nucleophile in the following order: $Cl^- > H^- > SH^- > F^- > OH^-$. The same order is observed for F^- as the LG: $H^- > SH^- > F^-, OH^-$.

As we have seen, for a given leaving group, the apicophilicity of the leaving group varies as the nucleophile varies. We now wish to consider how this correlates with the hardness or softness of the nucleophilic agent. Corriu[11] has noted that for a given LG, softer nucleophiles tend to promote an inversion process and harder nucleophiles tend toward retention of configuration.[12] Klopman[13] has calculated a set of characteristic numbers, $E\ddagger$, which are an index of softness or hardness of acids and bases. These numbers are based on charge, ionization potential, electron affinity, ion size, and hydration energy. A plot of apicophilicity of the LG vs. nucleophile hardness (Figure 5) shows that harder nucleophiles

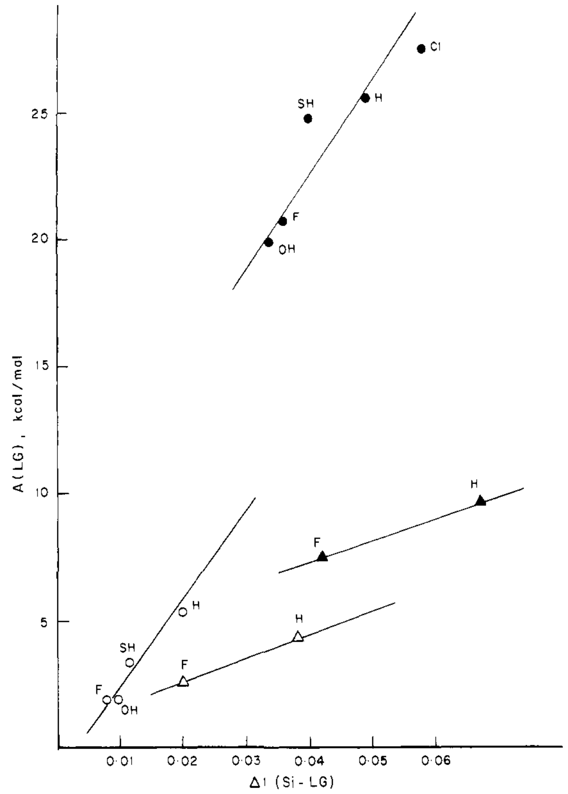

Figure 4. Apicophilicity of LG, ΔE_{12}, as a function of the change in overlap population, $\Delta 1$(Si–LG), with the LG in an axial or equatorial position of a TBP. $\Delta 1$(Si–LG) varies with each different nucleophile. The labels near the line identify the nucleophile. Each line corresponds to one LG. Closed circles, LG = Cl^-; open circles, LG = F^-; closed triangles, LG = SH^-; open triangles, LG = OH^-.

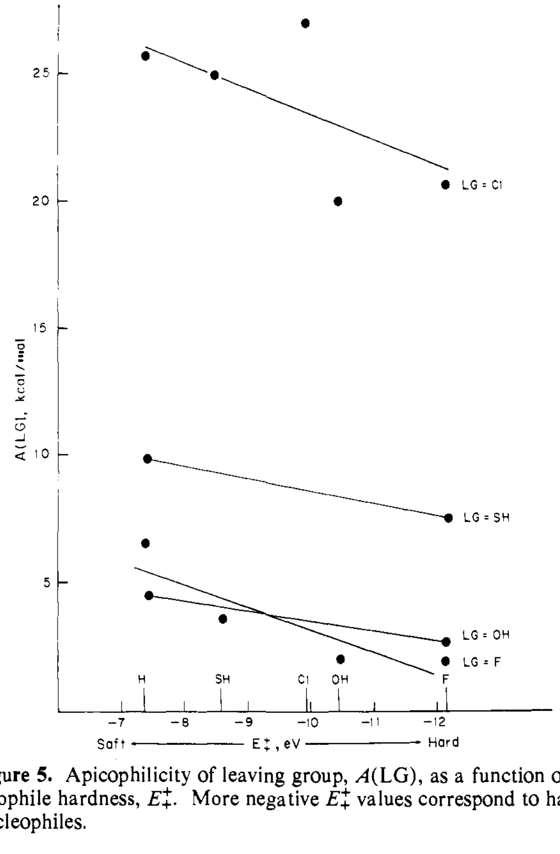

Figure 5. Apicophilicity of leaving group, A(LG), as a function of nucleophile hardness, $E\ddagger$. More negative $E\ddagger$ values correspond to harder nucleophiles.

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(10) Reference 7, pp 275f.

(11) Reference 2, pp 278f.

(12) Reference 2, p 259.

(13) Klopman, G., *J. Am. Chem. Soc.* **1968**, *90*, 223.

J. Am. Chem. Soc. **1987**, *109*, 1696–1701

tend to impart lower apicophilicities to the leaving group and hence favor a retention mechanism compared to softer nucleophiles.

Conclusions

With a constant nucleophile, the experimental LG order, $Cl^- > F^- \sim SH^- > OH^- > H^-$, and tendency toward inversion, $Cl^- > F \sim SH^- > OH^- > H^-$, are reflected in the context of these calculations by (1) an increase in overlap population of the Si–LG bond, $Cl^- < F^- < SH^- < OH^- < H^-$ (Figure 2), and (2), with the exception of SH^-, a decrease in apicophilicity of the LG (Figure 3). For example, with $Nu = H^-$, the apicophilicity decreases in the order $Cl^- > SH^- > F^- > OH^- > H^-$. These results support retention proceeding via the pseudorotation mechanism, increasing in this order. Since there is no correlation between the apicophilicity of the nucleophile and the experimental tendency toward inversion or retention, this calculation provides no support of a retention mechanism involving equatorial attack. Together with the evidence presented elsewhere,[6] namely, the relative high energy of edge attack, we can rule out equatorial attack as a feasible mechanism.

With a constant LG, the apicophilicity of the LG is affected by the nucleophile. For example, with $LG = Cl^-$, the apicophilicity of Cl^- decreases as the nucleophile is varied in the order (of nucleophiles) $Cl > H > SH > F \sim OH$. A change in nucleophile alters to a different extent the overlap population of the LG in both axial and equatorial positions (Figure 4) and the apicophilicity of the LG varies with the hard–soft character of the nucleophile. Softer nucleophiles increase the apicophilicity of the LG, which favor inversion, and harder nucleophiles decrease the apicophilicity of the LG, which favors retention (Figure 5).

Acknowledgment. The support of this research by the National Science Foundation (CHE8504737) is gratefully acknowledged. We thank the University of Massachusetts Computing Center for generous allocation of computer time.

Registry No. SiH_4, 7803-62-5; SiH_3OH, 14475-38-8; SiH_3SH, 14044-97-4; SiH_3F, 13537-33-2; SiH_3Cl, 13465-78-6; H^-, 12184-88-2; F^-, 16984-48-8; OH^-, 14280-30-9; SH^-, 15035-72-0; Cl^-, 16887-00-6; Si, 7440-21-3.

Supplementary Material Available: Relative energy, charge density, overlap populations, and bond distances for $[SiH_3XY]^-$ (Table SI) (3 pages). Ordering information is given on any current masthead page.

The Microwave Spectra, Electric Dipole Moment, and Molecular Structure of 1,1,2,2-Tetrafluorocyclopropane

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Abstract: The microwave spectra of the normal, monodeuteriated, dideuteriated, and carbon-13 isotopic species of 1,1,2,2-tetrafluorocyclopropane have been investigated and assigned in the region 26.5–40.0 GHz. The spectral assignments have yielded sufficient data to enable a complete determination of the molecular geometry in the frameworks of both the normal and dideuteriated isotopic species. The partial r_s parameters in the framework of the normal isotopic species are $r(C_1C_2) = 1.471$ (3) Å, $r(C_3C_{1,2}) = 1.497$ (10) Å, $r(C_{1,2}F) = 1.344$ (4) Å, $r(C_3H) = 1.088$ (5) Å, $\theta(FC_{1,2}F) = 109.9$ (4)° and $\theta(HC_3H) = 118.0$ (4)°. The electric dipole moment is determined to be 2.16 (3) D. The rotational spectra and symmetry of two low lying vibrational modes were assigned in the dideuteriated isotopic species. The frequencies of the modes were determined from relative intensity measurements to be 188 (9) cm^{-1} for the symmetric (A) vibrational state and 178 (13) cm^{-1} for the antisymmetric (B) vibrational state in accord with the previous vibrational assignments. All the ring bonds in 1,1,2,2-tetrafluorocyclopropane are found to shorten relative to cyclopropane with the greater reduction occurring in the C_1–C_2 bond. The FCF and HCH methylene angles, however, are larger in 1,1,2,2-tetrafluorocyclopropane than in 1,1-difluorocyclopropane. These results are related to structural trends established by several experimental and theoretical studies which examined the effect of fluorine substitution on the geometry of substituted cyclopropanes and oxiranes.

A number of experimental[1-10] and theoretical[11-15] investigations have been conducted to elucidate the effect of fluorine substitution upon the ring geometries of the fluorinated cyclopropanes and ethylene oxides. In the latter series, microwave spectroscopic studies have enabled the determination of complete molecular structures for ethylene oxide,[16] *cis*- and *trans*-1,2-difluoroethylene oxide[8,9] and 1,1,2,2-tetrafluoroethylene oxide.[10] The carbon–oxygen and carbon–carbon ring bond lengths of the 1,2-difluoroethylene oxides are found to shorten, relative to ethylene oxide, with the greater reduction occuring in the trans isomer.[9] A near-linear reduction in ring bond lengths is found to occur from ethylene oxide to *cis*-1,2-difluoroethylene oxide to 1,1,2,2-tetrafluoroethylene oxide.[10]

Molecular structures of *cis*- and *trans*-1,2-difluorocyclopropane[4,5] have recently been obtained from analysis of microwave spectra. The C_1–C_2 and C_3–$C_{1,2}$ ring bond lengths of both species are found to shorten, relative to cyclopropane,[17] with the greater reduction occurring in the trans isomer.[5] These results parallel

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