behavior. However, $\phi(F)$ almost has a monotonic behavior, the calculated value for NF_2 being 0.003 au too small. The same problem occurs for θ_{yy}, with only the calculated NF_2 value preventing a monotonic increase across the series.

In summary, then, most of the theoretical properties follow one of two patterns: (a) a monotonic increase or decrease across the series or (b) a potential curve-like behavior with maximum or minimum at CF_2. The simplest understanding of these two patterns may be in the fact that the electron distribution may appear to behave differently, depending on the expectation value through which we observe it. For example, inspection of the $\langle 1/r_A \rangle$ values in Table V implies that the average distance of electrons from nucleus A decreases monotonically across the series. This behavior might be interpreted to imply that the "size" of the molecules decreases monotonically from BeF_2 to OF_2. Thus, the $\langle 1/r_A \rangle$ description of the electron distribution is consistent with properties of type a above. However, the calculated values of $\langle r^2 \rangle$ with respect to the center of mass show a different pattern, in which the molecular "size" decreases from BeF_2 to CF_2, but then *increases* at NF_2 and again at OF_2. We see that this picture of the electron distribution is harmonious with those properties following pattern b described above. We conclude that a major factor in determining the two patterns of periodic behavior for BeF_2 through OF_2 is the ambiguity involved in the concept of molecular size.

Electronic Structure of SiH_5^- and Model Studies of Inter- and Intramolecular Exchange in Pentacoordinate Silicon Species. An *ab Initio* Investigation[1]

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Abstract: The reaction $SiH_4 + H^- \rightarrow SiH_5^-$ is investigated by employing *ab initio* quantum chemical techniques. With respect to silane and a hydride ion, a trigonal-bipyramidal form of SiH_5^- is found to be stable by 16.9 kcal/mol and a tetragonal-pyramidal form by 14.0 kcal/mol. The attack of hydride ion on silane is found to proceed with the hydride ion approaching a face of the tetrahedron of silane with an activation energy of 8.6 kcal/mol. In addition, a model derived from SiH_5^- is employed to discuss conformational equilibria in $SiH_{5-n}X_n$ species, where X corresponds to a strongly electronegative substituent. It is found that the axial positions of the trigonal bipyramid are energetically preferred sites for the electronegative substituents and that the preferred mechanism for Berry pseudorotation proceeds *via* a tetragonal-pyramidal intermediate with an electropositive substituent in the apical position.

Pentacoordinate silicon intermediates have been postulated for nucleophilic displacement reactions occurring at silicon and conformational changes in the intermediate have been invoked to explain the stereochemistry of such reactions.[3] Stable pentacoordinate silicon species have been observed in the vapor[4] and solution phases[5] and the conformational changes have been studied in the latter case.[6]

In order to investigate further these processes, there was performed a series of both semiempirical CNDO[7] and *ab initio* LCBF-MO-SCF (Hartree-Fock) calculations on the model system SiH_5^-, considering both the formation of the intermediate, *i.e.*, the reaction

$$SiH_4 + H^- \longrightarrow SiH_5^-$$

as well as intramolecular rearrangement processes in the intermediate itself. In addition, similar calculations were performed on a series of model compounds derived from SiH_5^- in order to investigate the energetics of inter- and intramolecular exchange processes in pentacoordinate silicon species.

Computational Techniques

The CNDO technique was utilized to determine the geometry of the various conformers of the intermediate as well as that of the SiH_5^- systems at various positions along the reaction paths considered. This was done for reasons of economy, but it is expected that the resulting geometries are reasonable.[8] In order to investigate the energetics of the system, a series of *ab initio* calculations utilizing a fairly large basis of gaussian lobe functions,[9] including functions of d symmetry on silicon, was performed. The Si basis employed is the 12s, 9p set of Veillard,[10] using the (6 3 1 1 1 1/6 1 1 1) contraction of Rothenberg, *et al.*,[11] to which d functions of exponent

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(1) Presented in part at the Third International Symposium on Organosilicon Chemistry, Madison, Wis., Aug 1972.

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Table I. SCF Molecular Orbital Energies[a] for D_{3h} and C_{4v} SiH_5^- Species

	D_{3h}			C_{4v}	
	No d fns	d fns		No d fns	d fns
$1a_1'$	−68.6313	−68.6115	$1a_1$	−68.6317	−68.6121
$2a_1'$	−5.9505	−5.9252	$2a_1$	−5.9507	−5.9256
$1e_1'$	−4.0662	−4.0416	$3a_1$	−4.0669	−4.0431
$1e_1'$	−4.0662	−4.0416	1e	−4.0657	−4.0407
$1a_2''$	−4.0652	−4.0398	1e	−4.0657	−4.0407
$3a_1'$	−0.5065	−0.4876	$4a_1$	−0.5059	−0.4872
$2a_2''$	−0.2647	−0.2551	2e	−0.2679	−0.2602
$2e_1'$	−0.2575	−0.2538	2e	−0.2679	−0.2602
$2e_1'$	−0.2575	−0.2538	$5a_1$	−0.2369	−0.2342
$4a_1'$	−0.0783	−0.0942	$1b_1$	−0.0807	−0.0972
E_T	−291.6674	−291.7252	E_T	−291.6635	−291.7207

[a] Energies are in atomic units; 1 au = 627.13 kcal/mol.

Table II. Atomic and Overlap Populations for the D_{3h} and C_{4v} Geometries of SiH_5^-

		D_{3h}			C_{4v}	
		No d fns	d fns		No d fns	d fns
Atomic populations	Si	13.311	13.534	Si	13.316	13.543
	H_{ax}	1.414	1.331	H_{ap}	1.230	1.232
	H_{eq}	1.287	1.267	H_{bas}	1.364	1.306
Overlap populations	Si–H_{ax}	0.461	0.637	Si–H_{ap}	0.703	0.714
	Si–H_{eq}	0.660	0.689	Si–H_{bas}	0.549	0.652

0.30 and 0.15 were added. Fink and Allen's[12] 5s hydrogen function was contracted (4 1) with $\mu_H{}^2 = 1.5$. In addition, a single Gaussian was added for each hydrogen with an exponent of 0.095 to improve the description of the hydride ion. Hence, the basis is fairly complete, the main omission being that of not including p-type functions on the hydrogens. In addition, electron correlation is neglected in this series of calculations. Such effects are not expected to be important because of the approximate additivity of correlation energy in closed shell systems.[13] In the present case, only comparisons of the energies of closed-shell species are made.

SiH_5^-

The equilibrium geometry of SiH_5^-, as predicted by a series of CNDO calculations, is a trigonal bipyramid (D_{3h} symmetry) with Si–H_{eq} = 1.62 Å, Si–H_{ax} = 1.64 Å. For a later discussion of Berry pseudorotation,[14] a tetragonal pyramid (C_{4v} symmetry) was also considered. A geometry search using the CNDO technique indicates the C_{4v} structure of lowest energy to be that with Si–H_{bas} = 1.63 Å, and $\angle H_{ap}SiH_{bas} = 101.3°$. This form is predicted to be 1.51 kcal/mol higher in energy than the D_{3h} structure.

Tables I and II contain the results of *ab initio* calculations on these two geometrical forms of SiH_5^- both with and without silicon d functions included in the basis (exponent = 0.30). As can be seen, the inclusion of silicon d functions lowers the total energy of each species by an appreciable amount (0.06 au in each case). However, the qualitative nature of the results is unaffected. That is, the eigenvalue of the MO of d symmetry (the highest occupied MO in each case) has its eigenvalue changed no more than are those of the other MO's, and the ordering of the eigenvalues remains the same. Inclusion of a second d function (exponent = 0.15) lowers the energies to −291.7257 au for the D_{3h} structure and −291.7212 au for the C_{4v} structure, while negligibly affecting the eigenvalues. It is quite obvious from these results that the inclusion of d-type functions on silicon is not necessary to describe qualitative features of SiH_5^- but that such functions only increase the flexibility of the basis (serving mainly as polarization functions) and hence lower the total energy of the system. However, in order to obtain quantitative results for the remainder of this study, the basis which contains functions of d symmetry on silicon will be employed.

The computed barrier to Berry pseudorotation in the SiH_5^- system is 2.87 kcal/mol (about 1 kcal/mol lower than that reported by Mislow[15]). That the barrier is so low is not surprising if one compares the eigenvalues of the D_{3h} and C_{4v} structures from Table I. Except for MO 9, the eigenvalues change from 0.0004 to 0.002 au during the conversion of the D_{3h} structure into the C_{4v} structure, indicating that only small perturbations in the electronic structure occur. Reference to Table II also indicates that little charge rearrangement accompanies the process of Berry pseudorotation. The charge differences, however, are significant in that they correspond to semiempirical rules concerning pseudorotation in substituted species.[16] That is to say, in the D_{3h} structure, the axial protons are somewhat (0.064) more negative than the equatorial protons, indicating that the more electronegative substituents would be found in the axial positions. In the C_{4v} structure, the basal protons are more negative (by 0.074) than the equatorial protons indicating that in a substituted system Berry pseudorotation would preferentially take place by a mechanism whereby the "pivot position" is one of the more electropositive substituents. Similar results were found for PH_5 by Rauk, *et al.*[17] In order to investigate the stability of SiH_5^- relative to silane and a hydride ion, *ab initio* calculations were performed on SiH_4 and H^- using the basis described above. Total energies of −291.2254 au for silane and −0.4733 au for hydride ion were obtained. Hence, the D_{3h} structure of SiH_5^- is stable with respect to silane and a hydride ion by 16.93 kcal/mol. This is in agreement with the observed stability of SiF_5^- in solution[6] and the reported observation of $SiH_5\cdot$ species in the gas phase.[4]

The mode of attack of the hydride ion on silane was investigated by considering two possibilities: edge and

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(12) W. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1967).

(13) (a) A. Rauk, L. C. Allen, and E. Clementi, *ibid.*, **52**, 4133 (1970); (b) L. C. Snyder, *ibid.*, **46**, 3602 (1967).

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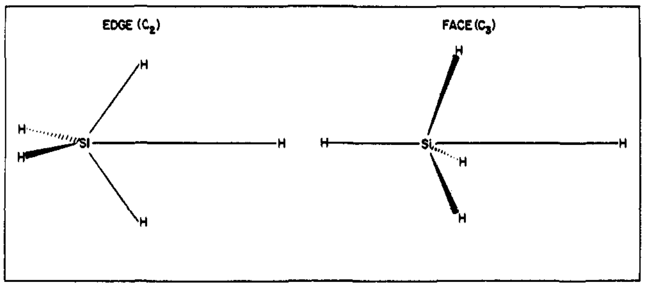

Figure 1. Modes of attack of hydride ion on silane.

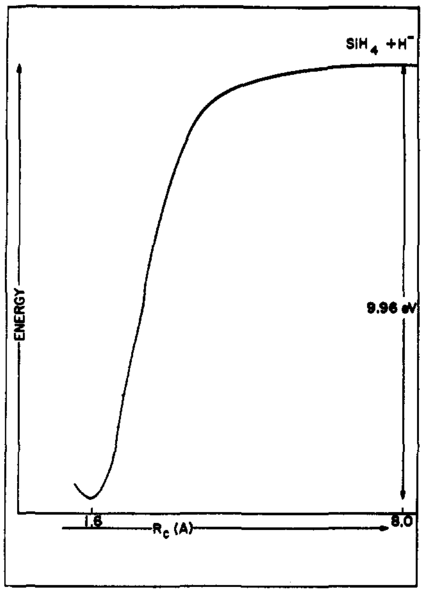

Figure 2. CNDO results for face attack of hydride ion on silane.

face attack of the hydride ion on the tetrahedron of silane. This corresponds to constraining the symmetry of the system to be C_2 (or C_3), for edge (or face) attack, with the silicon–hydride ion axis being the principal symmetry axis of the system (see Figure 1). The calculations were performed (using the CNDO technique) by specifying the distance between the silicon and the incoming hydride ion (R_c) and varying the positions of the silane protons (subject only to the symmetry constraints) until an energy minimum was found. This was accomplished by a simple three- or four-dimensional (for C_3 or C_2 attack, respectively) steepest-descent minimization technique. The contour for the lowest energy path, face attack, is presented in Figure 2. The contour for edge attack has essentially the same shape but is slightly higher in energy (1.5 kcal at R_c = 4 Å). Note also that neither of the two modes of attack occurs with an activation barrier, when the CNDO technique is employed.

In order to confirm these results, *ab initio* calculations were performed for a number of points along each of the (CNDO-determined) reaction coordinates. These results are summarized in Figure 3. Again, only the contour for face attack (that of lowest energy) is presented. The contour for edge attack has a similar shape and is 9 kcal/mol higher in energy at R_c = 4 Å. Differences between the CNDO and *ab initio* results are immediately apparent. First of all, the *ab initio* results predict an activation barrier of 8.6 kcal/mol at R_c = 3.5 Å, while the CNDO results predict no barrier at all. In addition, the CNDO results drastically overestimate the stability of the intermediate, due to the computed energy of the hydride ion being much too high (−0.17 au). The results in parentheses in Figure 3 are for calculations performed with the silicon d functions excluded from the basis. Again, it is found that these results are in qualitative agreement with those obtained by including silicon d functions in the basis.

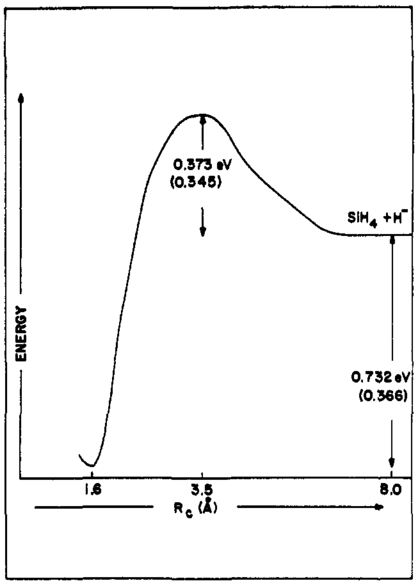

Figure 3. *Ab initio* results for face attack of hydride ion on silane (numbers in parentheses are for calculations excluding d functions).

Model Studies of Pseudorotation in Pentacoordinate Silicon Species

In order to investigate conformational equilibria *via* the mechanism of Berry pseudorotation in pentacoordinate silicon species a procedure analogous to that of Rauk, *et al.*[17] (employed in a similar study of substituted phosphoranes) was used. Model compounds of the form $SiH_{5-n}X_n$ were constructed, where X is a hydrogen atom in which the nuclear charge has been increased to +1.1. This corresponds to substitution by a strongly electronegative substituent with a value of 2.9 on the Pauling electronegativity scale.[18] This model then considers only the inductive effects of the ligands; interaction of ligand π orbitals and steric effects are excluded.

The energies of the various trigonal bipyramidal and tetragonal pyramidal systems were computed for $0 \leq n \leq 5$ (employing the geometries for SiH_5^- noted above). The energies of similarly substituted silanes were also computed. The results for the conformational equilibria as well as for the related exchange processes are presented in Figures 4–9 and Table III.

The exchange reactions listed in Table III proceed with the more electronegative substituent (X^-) as the leaving group. The corresponding exchange reactions with hydride ion as leaving group are less favored energetically by an amount that increases with increasing substitution by electronegative (X^-) groups. This in-

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(18) (a) T. L. Cottrell and L. E. Sutton, *Proc. Roy. Soc., Ser. A*, **207**, 48 (1951); (b) A. C. Hurley, *ibid.*, **218**, 333 (1953).

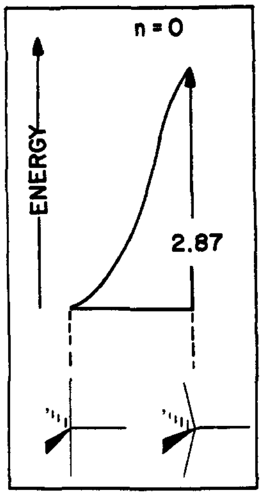

Figure 4. Potential energy curve for berry pseudorotation in SiH_5^-. The numbers are in kcal/mol.

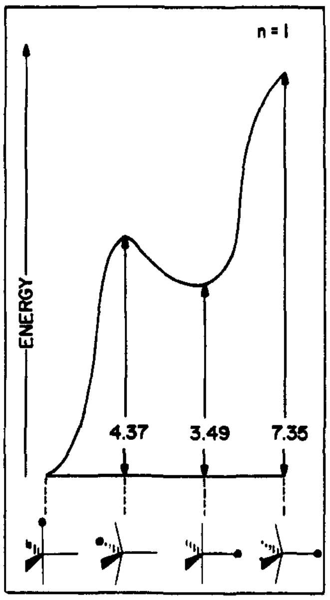

Figure 5. Potential energy curve for Berry pseudorotation in SiH_4X^- species. The more electronegative X is represented by a black circle. The numbers are in kcal/mol.

Table III. ΔH Values Computed for the Exchange Processes Occurring in $SiH_{5-n}X_n$ Systems

n		ΔH, kcal/mol
0	$SiH_4 + H^- \rightleftharpoons SiH_5^-$	16.97 (16.97)[a]
1	$SiH_4 + X^- \rightleftharpoons SiH_4X^-$	12.59 (35.77)
2	$SiH_3X + X^- \rightleftharpoons SiH_3X_2^-$	30.16 (55.08)
3	$SiH_2X_2 + X^- \rightleftharpoons SiH_2X_3^-$	44.05 (70.72)
4	$SiHX_3 + X^- \rightleftharpoons SiHX_4^-$	58.27 (86.73)
5	$SiX_4 + X^- \rightleftharpoons SiX_5^-$	72.79

[a] Values in parentheses are for the reaction occurring with the hydride ion as the leaving group.

crease in ΔH for exchange is given by (for n = 1–4)

$$\delta(\Delta H) = 23.1 + 1.8(n - 1)\ \text{kcal/mol}$$

where n is the number of X groups.

Consideration of the conformational equilibria in the various systems (Figures 4–9) shows features similar to those found in the aforementioned study of substituted phosphoranes.

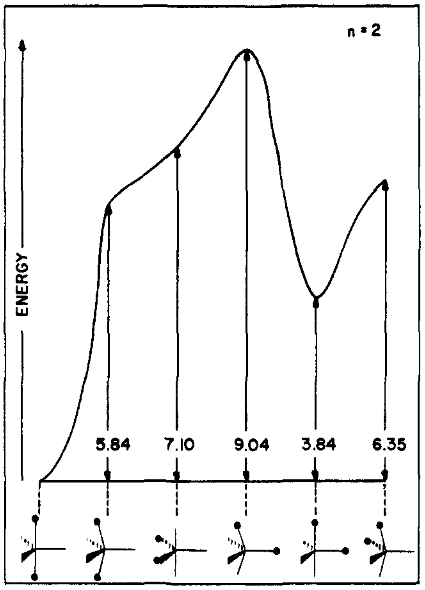

Figure 6. Potential energy curve for Berry pseudorotation in $SiH_3X_2^-$ species. The more electronegative X is represented by a black circle. The numbers are in kcal/mol.

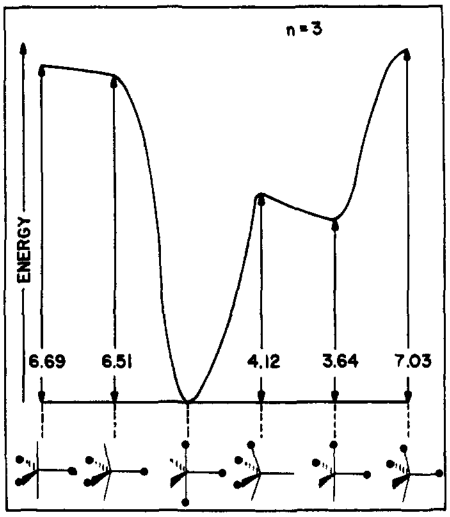

Figure 7. Potential energy curve for Berry pseudorotation in $SiH_2X_3^-$ species. The more electronegative X is represented by a black circle. The numbers are in kcal/mole.

SiH_4X^-. Both of the possible trigonal-bipyramidal species are expected to be stable. The form with the electronegative substituent in an equatorial position is 3.49 kcal/mol less stable than the species with the substituent in an axial position. A barrier of 0.88 kcal/mol separates the two species.

$SiH_3X_2^-$. Of the three possible trigonal-bipyramidal structures for this system, two are predicted to be stable; that with the two electronegative substituents axial is 3.84 kcal/mol more stable than the form with one substituent axial and one equatorial.

$SiH_2X_3^-$. Here, two of the three possible trigonal bipyramids represent energy minima. The structure with both axial positions substituted is 3.64 kcal/mol more stable than the structure with only one axial position substituted. Here, these two structures are separated by a barrier of 0.48 kcal/mol.

$SiHX_4^-$. For this system both of the two possible

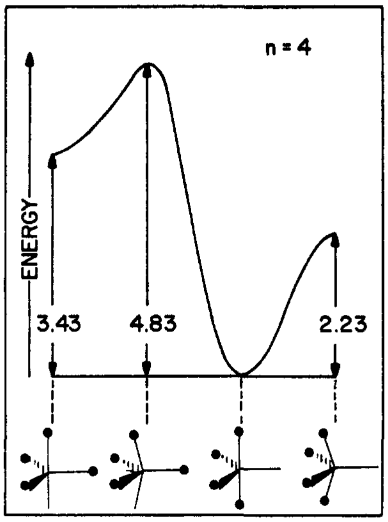

Figure 8. Potential energy curve for Berry pseudorotation in $SiHX_4^-$ species. The more electronegative X is represented by a black circle. The numbers are in kcal/mol.

trigonal bipyramidal species are predicted to be stable. The structure with both axial positions substituted is 3.43 kcal/mol more stable than the form with only one axial position substituted.

SiX_5^-. The predicted barrier to Berry pseudorotation for the pentasubstituted species is 2.94 kcal/mol compared with 2.87 kcal/mol for the unsubstituted SiH_5^- species.

Conclusions

It is predicted that the gas-phase reaction

$$SiH_4 + H^- \longrightarrow SiH_5^-$$

proceeds *via* attack of the hydride ion on a face of the tetrahedron of silane with an activation energy of 8.6 kcal/mol yielding a trigonal bipyramidal form of SiH_5^- that is 16.93 kcal/mol stable with respect to the reactants. A barrier of 2.87 kcal/mol to Berry pseudorotation is determined.

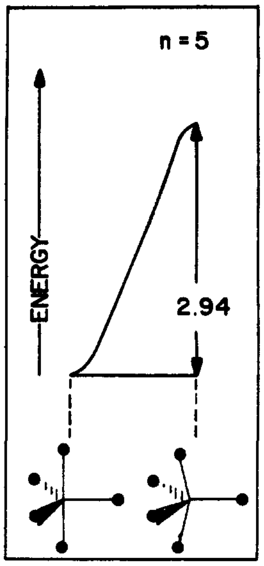

Figure 9. Potential energy curves for Berry pseudorotation in SiX_5^- species. The numbers are in kcal/mol.

In a study of Berry pseudorotation in electronegatively substituted $SiH_{5-n}X_n^-$ species, justification is found for empirical rules that state that trigonal bipyramidal species with a high degree of axial substitution are more stable than those with a low degree of axial substitution. In addition, it is found that the preferred mechanism for Berry pseudorotation involves a tetragonal-pyramidal intermediate with an electropositive substituent in the apical position.

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