JOURNAL

OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 108, NUMBER 25 DECEMBER 10, 1986

Theoretical Studies of the Reactions $XH_n \rightarrow XH_{n-1}^- + H^+$ and $XH_{n-1}^- + SiH_4 \rightarrow [SiH_4XH_{n-1}]^-$

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Abstract: Ab initio and MNDO calculations have been carried out to evaluate the gas-phase acidities of closed-shell XH_n compounds (X = C, N, O, F, Si, P, S, Cl) and the affinities of silane for the XH_{n-1}^- anions. Fourth-order perturbation theory with extended basis sets reproduces the experimental gas-phase acidities to within 2 kcal/mol. Stable pentacoordinated silicon anions are found for X = H, C, N, O, and F. In contrast, only marginally stable charge-dipole complexes are found for X = Si, S, and Cl.

I. Introduction

The relative acidities of protons in different chemical environments, either within the same molecule or in different molecular species, have important mechanistic implications for organic and organometallic chemistry. The simplest prototype reactions to study these trends are those in which the neutral hydride XH_n loses a proton.

$$XH_n \rightarrow XH_{n-1}^- + H^+ \tag{1}$$

The effect of substituents on the energetics of reaction 1 may then be assessed by replacing one or more of the hydrogens with various groups.

Related to the acidities described by reaction 1 is the affinity of a particular substrate for the nucleophiles XH_{n-1}^-. For hydrocarbon substrates, one expects to observe weakly bound long-range ion–molecule complexes separated by a barrier at the pentacoordinated structure.[1] Since atoms in the third (and lower) row(s) of the periodic table are more able to accommodate a pentacoordinate environment, the transition state found for second-row compounds may be replaced by an appreciable well. Indeed, such stable pentacoordinate anionic intermediates have been implicated in the polymerization mechanism of silanols.[2]

The purpose of this work is twofold: to systematically evaluate the gas-phase acidities of simple closed shell hydrides in the second and third rows of the periodic table (X = C, N, O, F, Si, P, S, Cl) and to evaluate the relationship, if any, between these gap-phase acidities and the stabilization of the pentacoordinate anionic intermediates formed in the reaction

$$XH_{n-1}^- + SiH_4 \rightarrow [H_{n-1}XSiH_4]^- \tag{2}$$

Because our ultimate goal is to systematically investigate substituent effects in reaction 1 and to analyze subsequent steps in the polymerization mechanism initiated by (2), with the hydrogens in silane replaced by alkyl groups, the calculations presented here have been carried out with both ab initio and semiempirical MNDO[3] wave functions. Thus, an ancillary goal of the present work is to evaluate the reliability of MNDO for calculations of this type.

The experimental gas-phase acidities of all of the simple hydrides of interest in this paper are known,[4,5] so that direct comparisons with theory are possible. Several related calculations have been carried out; however, to our knowledge, there has been no systematic theoretical evaluation of reaction 1 for all of the species of interest here. Schleyer and co-workers[6] evaluated the effect of substituents on C–H acidities, while Lee and Schaefer[7] investigated the gas-phase acidities of CH_4, NH_3, H_2O, hydrogen cyanide, and acetylene. Raghavachari[8] has very recently reported on the effects of both basis set and correlation on the electron affinities of first-row atoms, and Novoa and Mota[9] have done the same for a few small compounds. Feller and Davidson[10] have evaluated the electron affinities of atomic carbon and oxygen using

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multireference configuration interaction (CI) wave functions. Chandrasekhar et al.[11] have discussed the importance of diffuse functions for the description of anions containing second-period elements.

To our knowledge, the present work is the first systematic theoretical analysis of pentacoordinate anionic silicon. White and Spialter[12] predicted that SiH_5^- is more stable than silane + hydride ion by 16.9 kcal/mol, with a predicted barrier of 8.6 kcal/mol for the attachment process. Keil and Ahlrichs,[13] using a large basis set and a doubles CI corrected for size consistency, predicted reaction 2 with X = H to be exothermic by 20 kcal/mol, and a similar calculation by Brandemark and Siegbahn[14] predicts the exothermicity to be 21 kcal/mol. Both of the latter sets of authors predict SiH_5^- to be higher in energy than $SiH_3^- + H_2$. Dewar and Healy[15] have concluded on the basis of MNDO calculations that pentacoordinate silicon anions should form without barriers, and this has been verified for reaction 2 with X = H by the calculations of Brandemark and Siegbahn.[14]

II. Computation Approach

For the ab initio calculations, three basis sets were employed. Molecular structures for all species were determined at the restricted Hartree–Fock (RHF) SCF level, using the 6-31G* basis set,[16] hereafter referred to as 6-31G(d). All structures 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.

It is well-known that an adequate description of the energetics of electron attachment processes (to form anions) requires the addition of diffuse functions to the basis set.[6] This is not as necessary for closed shell anions formed in deprotonation reactions,[17] as is the case here. Nonetheless, the 6-31++G(d,p) basis set,[18] in which p polarization functions are added to the hydrogens and diffuse functions are added to all atoms (an sp set for heavy atoms and a single s for hydrogens), has been used for the prediction of the energetics of reactions 1 and 2. For this purpose, single-point calculations at the SCF geometries were performed in which second-order perturbation corrections (MP2)[19] have been added. Gas-phase acidities have additionally been calculated with full fourth-order perturbation theory (MP4),[20] using both the 6-31++G(d,p) basis set and the extended 6-311++G(3df,2pd) basis.[18] The latter has a triply split valence space, with three sets of d functions and one set of f's on the heavy atoms and two sets of p functions and one set of d's on the hydrogens. All ab initio calculations were performed with the IBM version of GAUSSIAN82.[21] Zero-point vibrational energies have been added to all energy differences, so that the calculated values can be more directly compared with the experimental ones and with those from MNDO. Lee and Schaefer have previously noted that temperature corrections to 298 K have no effect on the predicted gas-phase acidities.[7]

The semiempirical calculations were carried out with the MOPAC[22] network of programs. The silicon parameters were taken from a revised set recently proposed by Dewar.[23] To correct for the inadequate treatment of small anions at this level, experimental heats of formation have been used for the XH_{n-1}^- species, where they are available.[4,5]

Table I. 6-31G (d) Structures for XH_n and XH_{n-1}^- Compounds

molecule	bond length (Å)	angle (deg)
H_2	0.730	
CH_4	1.084	109.47
NH_3	1.002	107.2
H_2O	0.947	105.5
HF	0.911	
CH_3^-	1.119	101.7
NH_2^-	1.030	99.3
OH^-	0.962	
SiH_4	1.481	109.47
PH_3	1.403	95.4
H_2S	1.326	94.4
HCl	1.266	
SiH_3^-	1.543	95.4
PH_2^-	1.431	92.9
SH^-	1.342	

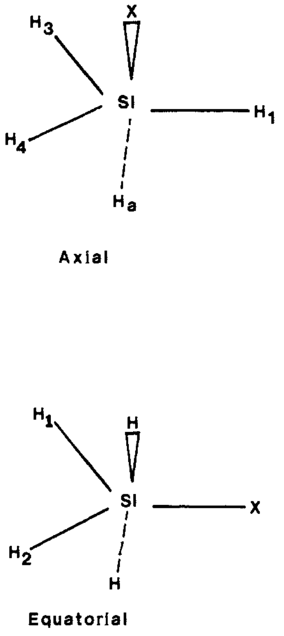

Figure 1. Schematics of pentacoordinate anion structures.

III. Results and Discussion

A. Structures. The predicted ab initio structures for the XH_n and XH_{n-1}^- compounds are listed in Table I. The structures for the neutral species have been published and compared with experiment previously.[14] Removal of a proton generally results in a small increase in the bond lengths to the remaining hydrogens and a concomitant decrease in the bond angles. The MNDO structures are similar, with two exceptions: (1) SiH bond distances are consistently predicted to be about 0.1 Å too short; and (2) CH_3^- is incorrectly predicted to have a trigonal planar structure.

The geometries of the $[H_{n-1}XSiH_4]^-$ species are summarized in Tables II and III, for axial and equatorial substituents, respectively (note that in these and later tables $H_{n-1}X$ is represented as Y). In general, the bond lengths to axial substituents are from 0.05 to 0.10 Å longer than are those to equatorial groups. This trend is consistent with standard VSEPR arguments[25] and appears to become increasingly pronounced as the electronegativity of the substituent decreases. Third-row substituents tend to be only marginally stable, particularly when they are placed in the equatorial position. Note the very long bond lengths for the

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Table II. Ab Initio Structures of $SiH_4Y^{-a,b}$ with Y Axial

Y	SiX	SiH_a	SiH_1	SiH_2	SiH_3	$XSiH_a$	$XSiH_1$	$XSiH_2$	$XSiH_3$	H_aSiH_1	H_aSiH_2	H_aSiH_3
H	1.622	1.622	1.531	1.531	1.531	180.0	90.0	90.0	90.0	90.0	90.0	90.0
CH_3	2.025	1.612	1.535	1.536	1.536	180.0	90.0	90.0	90.0	90.0	90.0	90.0
OH	1.791	1.611	1.513	1.530	1.530	180.0	89.2	91.9	91.9	90.8	88.1	88.1
F	1.713	1.608	1.518	1.518	1.518	180.0	90.6	90.6	90.6	90.0	90.0	90.0
SiH_3	2.755	1.604	1.496	1.496	1.496	180.0	90.0	90.0	90.0	90.0	90.0	90.0
SH	3.446	1.515	1.475	1.475	1.475	180.0	75.6	76.0	76.0	104.4	104.0	104.0
Cl	3.331	1.512	1.475	1.475	1.475	180.0	75.6	75.6	75.6	104.4	104.4	104.4

[a] Bond lengths in Å, angles in deg. [b] See Figure 1 for a description of the structures.

Table III. Ab Initio Structures of $SiH_4Y^{-a,b}$ with Y Equatorial

Y	SiX	SiH_1	SiH_2	SiH_3	SiH_4	$XSiH_1$	$XSiH_2$	$XSiH_3$	$XSiH_4$	H_3SiH_4	H_3SiH_1	H_3SiH_2
CH_3	1.949	1.527	1.530	1.629	1.623	120.4	122.1	88.6	91.7	180.0	90.2	89.4
OH	1.731	1.531	1.531	1.621	1.567	125.5	125.2	86.6	87.3	174.0	90.7	90.7
F	1.676	1.535	1.535	1.570	1.570	125.3	125.3	86.7	86.7	173.4	91.9	91.9
SiH_3	2.420	1.527	1.527	1.612	1.596	119.2	119.3	85.0	93.0	178.0	90.2	90.2

[a] Bond lengths in Å, angles in deg. [b] See Figure 1 for a description of the structures.

Table IV. Total Energies (Hartrees) for Reference Compounds[a]

species	Mp2/ 6-31++G(d,p)	MP4(SDTQ)/ 6-311++G(3df,2pd)[b]	ZPE[c]
H_2	-1.15776	-1.17165	6.64
CH_4	-40.36610	-40.43763	29.97
NH_3	-56.39242	-56.47640	23.02
H_2O	-76.23285	-76.33740	14.39
HF	-100.21564	-100.34231	6.18
SiH_4	-291.34135	-291.41240	20.86
PH_3	-342.58048	-342.66286	16.43
H_2S	-398.81214	-398.90165	10.32
HCl	-460.20775	-460.29734	4.55
H^-	-0.50363	-0.51859	
CH_3^-	-39.67844	-39.75707	18.64
NH_2^-	-55.73175	-55.81897	11.97
OH^-	-75.60259	-75.70375	5.55
F^-	-99.62385	-99.74113	
SiH_3^-	-290.73058	-290.80642	12.96
PH_2^-	-341.98095	-342.06732	8.54
SH^-	-398.24157	-398.33253	3.94
Cl^-	-459.67114	-459.75785	

[a] Calculated at 6-31G(d) geometries. [b] For third-row compounds, the basis set is 6-31++G(3df,2pd). [c] Zero-point energies in kcal/mol.

compounds with axial SiH_3, SH, and Cl and equatorial SiH_3. No stable 6-31G(d) structures were found when SH or Cl was placed in an equatorial position.

One significant difference between the ab initio and MNDO structural predictions (aside from the consistently short SiH distances) is that MNDO finds a stable tetragonal structure for SiH_4F^-. The optimized 6-31G(d) structure in tetragonal symmetry has one imaginary frequency, suggesting that the structure is a transition state in the pseudorotation of the fluorine from the axial to the equatorial position. Note that the very long Y–Si distances for Y = SH and Cl result in a structure which resembles the weak interaction between a nearly tetrahedral silane and an anion Y^-. This is further supported by the fact that for each species the charge on Y is nearly −1, while that on silane is nearly 0. This suggests that the structures are more appropriately thought of as charge-dipole complexes than pentacoordinated anions. For Y = SiH_3, the structure and charge distribution are intermediate between those of the second-row species and the charge-dipole complexes, with the negative charge on silyl being approximately $^2/_3$. MNDO predicts trigonal-bipyramidal structures for Y = SiH_3, SH, and Cl.

While Mulliken population analyses are particularly questionable for ions, it is worth noting that the importance of the diffuse basis functions is suggested by the fact that their net populations in the pentacoordinate species range from 0.4 to 0.6 e, in comparison with a value of 0.16 for the parent silane. As one would expect, the net negative charge on the SiH_4 moiety in the $SiH_4XH_{n-1}^-$ compounds increases by about 0.1 e/step as X varies from right to left across the periodic table (i.e., as the electronegativity decreases from F to C). The role of d orbitals in the ab initio calculations may be assessed by comparing the d orbital population P_d on the central silicon in the anion to that in the reference compound SiH_4 (0.22 e). When X is taken from the second row, P_d varies from 0.34 to 0.38 e, an increase of 0.12–0.16 e. In contrast, there is no increase in P_d for the charge-dipole complexes. As expected, silyl is again intermediate between the two cases, with an increase in P_d of 0.07 e.

B. Gas-Phase Acidities. Selected 6-31++G(d,p) and 6-311++G(3df,2pd) total energies for the XH_n and XH_{n-1}^- compounds are listed in Table IV. The corresponding gas-phase acidities, defined by reaction 1, are compared with the MNDO and experimental results in Table V. Experimentally, one observes three important trends:

Table V. Gas-Phase Acidities (eV)

method	H_2	CH_4	NH_3	H_2O	HF	SiH_4	PH_3	H_2S	HCl
MNDO(corr[a])	17.37	17.79	17.29	17.11	15.87	16.53	15.88	14.97	14.17
MNDO(uncorr[b])	19.10	18.91	18.26	18.32	17.78	17.90	15.77	15.36	14.22
6-31++G(d,p)									
SCF	17.24	18.41	17.92	17.23	16.48	16.32	15.96	15.09	14.16
MP2	17.51	18.22	17.57	16.78	16.10	16.28	16.02	15.24	14.40
MP3	17.53	18.36	17.80	17.08	16.09	16.29	16.10	15.35	14.51
MP4(SDQ)	17.51	18.33	17.72	16.94	15.95	16.29	16.12	15.35	14.52
MP4(SDTQ)		18.27	17.64	16.86	15.87	16.27	16.10	15.35	14.51
6-311++G(3df,2pd)[c]									
SCF	17.29	18.38	17.92	17.31	16.38	16.25	16.02	15.21	14.34
MP2	17.51	17.98	17.41	16.81	16.06	16.18	15.86	15.12	14.39
MP3	17.50	18.12	17.66	17.12	16.31	16.18	15.92	15.21	14.48
MP4(SDQ)	17.48	18.13	17.61	17.00	16.19	16.20	15.97	15.25	14.51
MP4(SDTQ)		18.03	17.48	16.86	16.09	16.15	15.91	15.21	14.48
experiment[d,e]	17.36	18.06	17.50	16.94	16.10	16.23	15.98	15.26	14.46

[a] MNDO values corrected for experimental heats of formation of anion. [b] Uncorrected MNDO values. [c] For third-row compounds, this basis set is 6-31++G(3df,2pd). [d] From ref 3 of text. [e] Experimental value for NH_3 taken from ref 4 of text.

Table VI. Total 6-31++G(d,p)//6-31G(d) Energies for SiH_4Y^- Anions (hartree)

Y	position	SCF	MP2	ZPE[a]
H		-291.73875	-291.87546	23.3
CH_3	axial	-330.78746	-331.07424	43.0
CH_3	equatorial	-330.78714	-331.07271	43.0
OH	axial	-366.66991	-366.99588	29.3
OH	equatorial	-366.66929	-366.99534	28.2
F	axial	-390.70121	-391.01316	21.8
F	equatorial	-390.68860	-391.00065	21.5
SiH_3	axial	-581.83880	-582.07052	34.9
SiH_3	equatorial	-581.83357	-582.06639	35.1
SH	axial	-689.34676	-689.59096	25.8
Cl	axial	-750.77614	-751.02063	21.5

[a] Zero-point energy in kcal/mol.

(1) The gas-phase acidity of XH_n increases (i.e., it is easier to remove a proton) as the electronegativity of the central atom X increases across a given row of the periodic table. Presumably, this occurs because the more electronegative atom is better able to accommodate the negative charge.

(2) The gas-phase acidity increases as one proceeds vertically from a lighter to a heavier atom. This is presumably related to the relative sizes of the atoms and the relative strengths of the HX bonds.

(3) It is easier to remove a proton from molecular hydrogen than from methane.

All levels of theory presented in Table VI correctly reproduce these trends (except uncorrected MNDO: see below).

At the highest level of theory, full MP4 with the largest basis set, all theoretical values are within 0.1 eV (2.3 kcal/mol) of the experimental ones, the average error at this level being 0.05 eV. The effect of correlation on the computed values (taken as the difference between the SCF and MP2 results for a given basis set) is generally a quite substantial 0.2–0.5 eV (4.6–11.5 kcal/mol). While there is some variation, this effect is roughly the same for the two basis sets. It is also generally observed that MP3 overcorrects the MP2 values, thereby leaving the MP2 results in better agreement with experiment. Indeed, the average MP2 error is only 0.08 eV with the smaller basis set. This is particularly important, since it suggests that calculations of the energetics for reaction 2 and for larger species will be reliable at this level of theory. It is gratifying that MNDO, corrected for the experimental heats of formation of the XH_{n-1}^- species (where available), is also in good quantitative agreement with experiment. However, this only indicates that MNDO accurately predicts the heats of formation of the neutral species. The uncorrected gas-phase acidities indicate that MNDO, as expected, calculates heats of formation for first- and second-row negative ions that are far too endothermic. It does a considerably better job for anions, such as those in the third row, which are larger in size.[26]

C. Pentacoordinate Anions. The 6-31++G(d,p) total energies for the SiH_4Y^- anions are summarized in Table VI, and the energetics for reaction 2 are given in Table VII. The value of −17 kcal/mol for Y = H is in good agreement with the previous ab initio predictions,[13,14] and all three theoretical predictions are close to the very recent experimental estimate of −18 to −27 kcal/mol.[27]

Table VII. Relative Energies (kcal/mol) for Reactions $Y^- + SiH_4 \rightarrow SiH_4Y^-$

Y	position	SCF	MP2	MNDO[a]
H		-10.4	-16.7	-23.3
CH_3	axial	-27.0	-30.7	-30.8
CH_3	equatorial	-26.8	-29.7	-34.0
OH	axial	-31.2	-29.9	-30.9
OH	equatorial	-31.9	-30.7	-37.3
F	axial	-31.2	-29.1	-23.8
F	equatorial	-23.7	-21.6	
F	tetragonal			-32.2
SiH_3	axial	+8.2	+0.2	+3.4
SiH_3	equatorial	+11.7	+4.8	+7.2
SH	axial	-1.6	-4.0	-16.8
Cl	axial	-2.6	-4.5	-11.0

[a] All energies corrected for experimental heats of formation of Y^- except SH and Cl.

Table VIII. Energy Differences (kcal/mol) for $SiH_4Y^- \rightarrow SiH_3^- + HY$

Y	E[MP2/6-31++G(d,p)][a]
H	-8.1
CH_3	-14.0 (a); -15.0 (e)
OH	+20.4 (a); +20.0 (e)
F	+42.0 (a); +34.2 (e)
SiH_3	-0.9(a); -3.5 (e)
SH	+30.2 (a)
Cl	+51.6 (a)

[a] a, e in parentheses refers to axial and equatorial substituents, respectively.

The most obvious general trends predicted by the ab initio calculations are that the second-row substituents (CH_3^-, OH^-, F^-) are more effective in stabilizing the pentacoordinate system than is hydride ion and much more effective than substituents in the third row. Indeed, as noted above, the latter are only marginally stable as charge-dipole complexes. The MNDO results are in agreement with both of these trends, although the semiempirical method finds both hydride and third-row substituents to be somewhat more stable than does the ab initio procedure. In addition, the MNDO third-row complexes are more tightly bound and therefore are more like true pentacoordinated species than charge-dipole complexes. Note that while correlation corrections (i.e., the addition of MP2) can have a substantial effect on the predicted stability of the pentacoordinate species, the effect is not always in the same direction. Thus, while MP2 increases the stability of the most species, those of OH^- and F^- are decreased slightly.

Note that while the silyl substituents are found to be minima at the 6-31G(d) level they are predicted to be higher in energy than the separated species when diffuse functions are added to the basis set. The addition of MP2 corrections preferentially stabilizes the two pentacoordinate anions, but not enough to bring them below the separated reactants. MNDO gives similar results. However, because MNDO incorrectly destabilizes the separated SiH_3^-, the Si–Si distance is too small.

There is generally little difference among the stabilities of the compounds with substituents from the second row. On the basis of these results there is not obvious correlation between the gas-phase acidities discussed above and the stabilization of the pentacoordinate compounds considered here. However, calculations on a more extensive set of compounds may uncover such a correlation. The ab initio calculations predict little difference between axially and equatorially substituted methyl and OH, while MNDO predicts the equatorial substitutions to be favored by 4 and 6 kcal/mol, respectively. The ab initio calculations do find axial fluorine to be 7.5 kcal/mol more stable than equatorial, while, as noted earlier, MNDO predicts a tetragonal SiH_4F^-, rather than equatorial. The tetragonal species is found to be 8.4 kcal/mol lower in energy than the axial structure.

So far, the stability of the pentacoordinated silicon anions has only been discussed relative to the separated species $SiH_4 + Y^-$, i.e., reaction 2. However, as noted in the introduction, it has been pointed out[13,14] that for Y = H, SiH_5^- is unstable relative to $H_2 + SiH_3^-$. The energetics for reaction 3 for the species considered

$$SiH_4Y^- \rightarrow SiH_3^- + HY \tag{3}$$

in this paper are listed in Table VIII. In agreement with the previous calculations, reaction 3 is found to be exothermic for Y = H. The same is true for methyl and silyl substituents. However, for the electronegative substituents F and OH, the pentacoordinated compound is more stable than the separated products in reaction 3. This is clearly related to the highly stable SiY bond when Y is an electronegative species. Interestingly, the weakly

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Table IX. Energy Differences (kcal/mol) for $Y^- + SiH_4 \rightarrow YH + SiH_3^-$

Y	*E*[MP2/ 6-31++G(d,p)]	*E*[MP4/ 6-311++G(3df,2pd)][a]
H	-27.2	-29.5
CH_3	-48.2	-46.8
NH_2	-31.3	-32.3
OH	-12.2	-17.4
F	+11.9	+3.0
SiH_3	0.0	0.0
PH_2	+7.1	+6.6
SH	+25.2	+23.1
Cl	+46.5	+41.7

[a] For third-row substituents this basis set is 6-31++G(3df,2pd).

bound ion–dipole complexes with Y = Cl, SH are also quite stable relative to the products in reaction 3. This may be explained in terms of reaction 4, the energetics for which are summarized in

$$Y^- + SiH_4 \rightarrow YH + SiH_3^- \qquad (4)$$

Table IX. This reaction is highly endothermic for Y = Cl, SH, and the exothermicity increases with decreasing electronegativity for second-row substituents. For Y = H and CH_3 the exothermicity of reaction 4 is sufficient to more than balance the exothermicity of reaction 2, resulting in an exothermic reaction 3. The trends displayed in Table VIII reflect the greater ability of more electronegative and more diffuse species to accommodate a negative charge, as well as the strength of SiY bonds when Y is electronegative. Finally, note that the two levels of theory presented in Table VIII for reaction 4 agree to within a few kcal/mol.

IV. Conclusions

The main conclusions to be drawn from this work are the following:

(1) The highest level of theory is able to predict gas-phase acidities with an accuracy of 2–3 kcal/mol. The use of a smaller, more tractable basis set and second-order perturbation theory results in very little loss of accuracy.

(2) The MNDO method, corrected for experimental heats of formation of the reference anions, reproduces all of the important trends in gas-phase acidities and provides a reasonable quantitative estimate of these values as well.

(3) Both ab initio and semiempirical calculations agree that substituents from the second row of the periodic table are much better able to stabilize pentacoordinated silicon anions relative to silane than are substituents from the third row. Indeed, no stable structures were found with SiH_3^-, SH^-, or Cl^- in the equatorial positions, and the axial substituents are only marginally stable as charge-dipole complexes.

(4) H^- is more stabilizing than the substituents from the third row, but less than those from the second row.

(5) MNDO does a good job of predicting which substituents stabilize pentacoordinated silicon anions, but not which isomers will be most stable.

(6) For the electronegative substituents Y = F, Cl, and SH, the negative charge prefers to reside on Y rather than on SiH_3^-; that is, the abstraction reaction 4 is endothermic. Consequently, the corresponding SiH_4Y^- complexes are found to be stable with respect to SiH_3^- + HY. The OH substituent is also stable to HY extrusion, because the exothermicity of reaction 4 is less than that for reaction 2.

Acknowledgment. This work was supported in part by grants to M.S.G. (CHE83-09948) and R.D. (CHE83-13826) from the National Science Foundation and to M.S.G. from the Air Force Office of Scientific Research (82-0190), and the donors of the Petroleum Research Fund, administered by the American Chemical Society. All of the *ab initio* calculations were performed on the IBM 3081/D computer at North Dakota State University, and the computer time made available by the NDSU Computer Center is gratefully acknowledged.

Registry No. H_2, 1333-74-0; CH_4, 74-82-8; NH_3, 7664-41-7; H_2O, 7732-18-5; HF, 7664-39-3; SiH_4, 7803-62-5; PH_3, 7803-51-2; H_2S, 7783-06-4; HCl, 7647-01-0; H^-, 12184-88-2; CH_3^-, 15194-58-8; NH_2^-, 17655-31-1; OH^-, 14280-30-9; F^-, 16984-48-8; SiH_3^-, 15807-96-2; PH_2^-, 13937-34-3; SH^-, 7783-06-4; Cl^-, 16887-00-6; SiH_5^-, 41650-16-2; axial-$SiH_4CH_3^-$, 104911-61-7; equatorial-$SiH_4CH_3^-$, 105015-58-5; axial-SiH_4OH^-, 73085-31-1; equatorial-SiH_4OH^-, 78853-67-5; axial-SiH_4F^-, 73173-71-4; equatorial-SiH_4F^-, 105015-59-6.

Supplementary Material Available: Tables of total 6-31++G(d,p) energies and 6-311++G(3df,2pd) energies for reference compounds (2 pages). Ordering information is given on any current masthead page.

Theoretical Evidence for Two Geometrical Isomers of AgO_2[†]

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Received October 8, 1985

Abstract: With use of nonempirical pseudopotentials and moderately large basis sets, SCF and CI calculations show that AgO_2 presents two nearly degenerate structures of C_{2v} and C_s symmetry, respectively. The ground state of these structures is found to be a $^2A_2$ and a $^2A''$. While the SCF and the CI description are almost coincident, the effect of electron correlation on the geometrical parameters is found to be quite important.

Because of its relevance in the silver-catalyzed oxidation reactions, a considerable amount of experimental work has been devoted to the isolation and characterization of the reaction products formed thorugh molecular oxygen and atomic silver interactions in rare gas matrices.

Of particular interest is the AgO_2 molecule which is only stable at low temperatures and has to be obtained by means of cryogenic techniques and isolated in an inert matrix. However, from the different experiments carried out to determine the molecular structure of this molecule two distinct geometrical arrangements

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