Journal of Organometallic Chemistry, 292 (1985) 159–166
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

QUANTUM-CHEMICAL ANALYSIS OF SILICON ATOM PENTACOORDINATION *

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(Received January 31st, 1985)

Summary

The energy characteristics and dynamics of charge redistribution in the $X_{ax}(H_3)_{eq}Si\ldots Y$ group in changing the $Si \leftarrow Y$ coordination bond length and rehybridization of the silicon atom valence shell have been calculated in MNDO approximation. The calculations are carried out with a complete optimization of molecular geometry of C_{3v} symmetry. The formation of complex anions X = H, F, Cl; $Y = H^-$ (I) and molecular complex $F_{ax}(H_3)_{eq}Si \leftarrow O{=}CH{-}OH$ (II) is discussed. The main difference between pentacoordinate structures I and II is a weaker perturbation of the $FSiH_3$ molecule caused by the O=CH–OH ligand as compared to that of H^-.

When tetrahedral silicon is involved in the formation of an additional donor–acceptor $Si \leftarrow Y$ bond, this atom acquires a higher positive charge as compared with the tetracoordinate state of its valence shell. In this case, the electronic density is transferred to the axial and equatorial atoms attached to silicon, affecting predominantly the substituent X_{ax} charge.

The complexing energies calculated are as follows, kJ/mol: -253.9 (X = H), -273.2 (X = F), -398.7 (X = Cl) for I and 72.4 for II.

Introduction

The increase in electronic charge of the silicon atom valence shell in the formation of coordinate $X_4Si \leftarrow Y$ bonds was used for the explanation of high dipole moments of 1-organylsilatranes [1,2] and until recently remained the only working hypothesis for the interpretation of numerous experimental data concerning pentacoordinate organosilicon compounds.

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* Dedicated to Professor Oleg A. Reutov on the occasion of his 65th birthday on September 5th, 1985.

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0022-328X/85/$03.30

In 1982 an analysis of chemical shifts in the X-ray fluorescent spectra (Si-K_α) revealed a higher positive charge on the silicon atom in silatranes, $XSi(OCH_2CH_2)_3N$ as compared with analogous Si-substituted triethoxysilanes, $XSi(OCH_2CH_3)_3$, which contradicted widely accepted ideas [3]. These unusual experimental data required further investigation. The occurrence of the positive charge per se on the pentacoordinate silicon atom is not unexpected and was postulated by non-empirical quantum-chemical calculations of the anions SiH_5^-, $FSiH_3F^-$, $FSiH_4^-$ [4,5] and the complex $FSiH_3 \ldots NH_3$ [6]. Our analysis of Mulliken's anion population, based on literature data [4] has shown that in going from the tetra- to the penta-coordination state the positive charge on the silicon atom increases by 0.16–0.20 e.

We intended to carry out a quantum-chemical qualitative analysis of changes in the energy parameters and charge redistribution in the $X_{ax}(H_3)_{eq}Si \ldots X$ group caused by variations in the coordinate Si ← Y bond length and rehybridization of the silicon atom valence shell. The following questions were put forward:

1. What changes in the $XSiH_3$ group parameters are due, firstly, to rehybridization of the silicon atom valence shell and secondly, what changes are solely associated with the coordinate bond formation?
2. What is the role of equatorial substituents?
3. What characteristics of the $XSiH_3$ fragment determine the complex stability?

Along with models $X_{ax}(H_3)_{eq}Si \ldots H^-$ with X = H, F, Cl (I), the coordination for a more complicated system $F_{ax}(H_3)_{eq}Si \ldots O{=}CH{-}CH$ (II) has been calculated in order to establish how much the data of the ion model (I) can be extended to molecular systems.

Results and discussion

$XSiH_4^-$ calculation

Earlier we suggested that the increase in the positive charge on the silicon atom in silatranes as compared to that of isostructural Si-substituted triethoxysilanes results from rehybridization of the silicon valence shell [3]. As can be seen from Table 1, if the coordination number of silicon in monosubstituted silanes, $XSiH_3$ with X = H, F, Cl is extended, the total energy increases by 60–90 kJ/mol. The energy of rehybridization, E_{hb} ($XSiH_3$) required for the silicon valence shell strain reduces in the series of substituents: F > H > Cl. The negative charge delocalization from H^- to the system $X_{ax}(H_3)_{eq}Si \leftarrow H^-$ leads to stabilization of $XSiH_4^-$ relative to individual $XSi_{sp^3}H_3$ and H^- fragments (Table 1). Considering the total energy as an

TABLE 1

ENERGIES ^{a} OF STABILIZATION, E_{st}, COMPLEXATION, E_c, AND REHYBRIDIZATION, E_{hb}, for all $X_{ax}(H_3)_{eq}Si \leftarrow H$ SYSTEMS (kJ/mol)

X	Y	E_{st}	E_c	E_{hb}
H	H^-	−335.5	−253.9	81.6
F	H^-	−361.6	−273.2	88.4
Cl	H^-	−465.3	−398.7	66.6
F	O=CH–OH	−17.4	72.4	89.8

^{a} $E(H^-) = -1058.3$ kJ/mol, calculated from [7]; E(O=CH–OH) = −77308.9 kJ/mol; $E_c = E_{min}(XH_3Si_{sp^2} \leftarrow Y) - [E(XSi_{sp^3}H_3) + E(Y)]$.

integral characteristic of rehybridization and coordination effects, the energy of complex anion formation can be calculated as shown in eq. 1, which leads to

$$E = E_{\min}(\mathrm{XSiH_4^-}) - \left[E(\mathrm{XSi}_{sp^3}\mathrm{H_3}) + E(\mathrm{H^-})\right] \qquad (1)$$

-253.9, -273.2 and -398.7 kJ/mol for X = H, F, Cl, respectively. The values obtained seem to be somewhat high, since the equatorial atoms were taken to be fixed in the same plane as the silicon atom. The essential role of angles deformation and bonds of the central atom in the complexation process was shown previously for $H_3B \leftarrow O{=}C$ [8]. In the case of a fixed planar triangle BH_3 geometry, the absolute value of the heat of complexation for this system is lowered by 33 kJ/mol.

The potential curve for the reaction of $X_{ax}(H_3)_{eq}Si\ldots H^-$ formation was calculated for the case when the anion H^- added is approaching the silicon atom along the third order symmetry axis. A narrow range (from 2.00 to 1.49 Å) in which the reaction coordinate $R(Si\ldots H^-)$ varies is due to unstable solutions at fairly long distances. Therefore, the energy of hydride ion addition, E_{st}, was estimated using calculated results of individual systems. The equilibrium $Si\ldots H^-$ distances for $XSiH_4{}^-$ are 1.49, 1.52 and 1.54 Å for X = Cl, H and F, respectively. The values obtained are consistent with the data of non-empirical calculations of $XSiH_4{}^-$ (-1.59 Å for X = H and F, respectively) [5]. The energy of $XSiH_4{}^-$ stabilization, corresponding to the reaction $XSi_{sp^2}\,H_3 + H^- \rightarrow XSiH_4{}^-$ increases in the substituent series H < F < Cl and follows the order of complexing energy change (Table 1). This series is in agreement with the reactivity of compounds R_3SiX (X = F, Cl, Br; R = OCH_3, C_2H_5) in the pentacoordination state [9].

The structural parameters of $XSiH_4{}^-$ anions and individual $XSiH_3$ molecules are presented in Table 2. From these data it may be concluded that in all the compounds considered the internuclear distances become markedly perturbed under the effect of H^-. This is manifested by the lengthening of the axial bonds by 0.01–0.03 Å in the series $F < H \ll Cl$ and by a slightly smaller (0.005–0.01 Å) increase of the equatorial bond lengths in the series H < Cl < F with shortening of the $Si\ldots H^-$ distance. The transition from the tetrahedral to the trigonal-bipyramidal configuration of silicon in the $XSiH_3$ molecule is accompanied by analogous structural changes in the equatorial $Si{-}H_{eq}$ bond lengths ($H \approx Cl < F$). At the same time, the order of the rehybridization-induced change of the axial $X_{ax}{-}Si$ distances (X < Cl < F) is different from that observed in the anionic complex. Consequently, the structure of the $XSiH_3$ group in anions I is determined by the sum of rehybridization and H^--coordination effects. All the $XSiH_3$ bond lengths increase in the series $XSi_{sp^3}H_3 < XSi_{sp^2}H_3 < XSiH_4^-$, the maximal changes in the internuclear $X_{ax}{-}Si$ distances exceeding two- or three-times the changes in $H_{eq}{-}Si$.

The predominant lengthening of the $X_{ax}{-}Si$ internuclear distances provides evidence for a *trans*-weakening effect of the axial bonds for substituents X = H, F, Cl with strengthening of the $Si \leftarrow H^-$ coordination. An adequate hypothesis relative to silatranes was first proposed by Voronkov [10]. This assumption was also confirmed experimentally [11–14]. The effect was analyzed on a quantum-chemical level in terms of hypervalent bonding of the $X_{ax}{-}Si \leftarrow N$ three-centered system model [15].

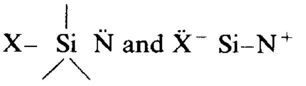
The hypervalent scheme is topologically similar to p,π-conjugation and seems to involve, without extending the silicon valence shell, the charge transfer to the

TABLE 2

BOND LENGTH CHANGES IN INDIVIDUAL MOLECULES $XSiH_3$ AND COMPLEXES I AND II (Å)

Compound	Si...Y	X–Si	H–Si
$Si_{sp^3}H_4$		1.434	1.434
$H_{ax}Si_{sp^2}(H_3)_{eq}$		1.450	1.440
$H_{ax}(H_3)_{eq}Si_{sp^2}\ldots H^-$	2.00	1.507	1.461
	1.52	1.522	1.477
$FSi_{sp^3}H_3$		1.644	1.442
$F_{ax}Si_{sp^2}(H_3)_{eq}$		1.679	1.458
$F_{ax}(H_3)_{eq}Si_{sp^2}\ldots H^-$	2.00	1.718	1.472
	1.54	1.729	1.483
$ClSi_{sp^3}H_3$		2.109	1.438
$Cl_{ax}Si_{sp^2}(H_3)_{eq}$		2.165	1.443
$Cl_{ax}(H_3)_{eq}Si_{sp^2}\ldots H^-$	2.00	2.279	1.448
	1.49	2.309	1.457
$F_{ax}(H_3)_{eq}Si_{sp^2}\ldots O{=}C\lt$	3.00	1.680	
	2.16	1.692	

substituent, which is reproduced by the resonance structures:



$$X\text{–}\ \overset{|}{\underset{/\ \backslash}{Si}}\ \ddot{N}\ \text{and}\ \ddot{X}^-\ Si\text{–}N^+$$

The orbitals of the equatorial bonds are described by a symmetric non-degenerate orbital of the a_1 type and by two antisymmetric degenerate orbitals of the e type. Since, according to symmetry requirements, the interaction of doubly degenerate orbitals with a lone electron pair of the coordinative electron-donor can be neglected, we should extend the hypervalent scheme to interaction with the equatorial orbital a_1.

The molecular orbitals, MO, and their energies in anions (X = F, Cl) which we have calculated for the equilibrium $R(Si\ldots H^-)$ distances are given in Table 3. Among occupied MOs of anions I one may recognize two MOs describing the $X_{ax}\text{–}Si \leftarrow H^-$ fragment, one of which, the higher occupied molecular orbital (HOMO), contains considerable contributions from equatorial substituents. The presence of these orbitals in all anions of I indicates that the complete hypervalent scheme must involve all AOs of the equatorial atoms attached to silicon. The population of atomic orbitals making the greatest contribution to the HOMO in different anions $XSiH_4^-$ decreases in the following order: $Cl > H > F$ for axial atoms and $H \approx F > Cl$ for the equatorial atom. The AO population of the hydride ions decreases in the following order: $F > Cl > H_{ax}$.

The HOMO analysis of complex anions of I reveals practically complete absence of electron charge localization ($c^2 \leqslant 0.03$) on the central silicon atom. The charge is completely transferred from H^- to the axial and equatorial atoms. Thus, the silicon atom involved in the donor–acceptor $Si \leftarrow H^-$ bonding acts as a bridge in the

TABLE 3

AO CONTRIBUTIONS TO VALENCE MOs OF $XSiH_4^-$ COMPLEX ANIONS IN THE EQUILIBRIUM STATE, c_i^2 (%)

MO	ε_{MO} (eV)	Si			F			H	H^-
		3*s*	$3p_x3p_y$	$3p_z$	2*s*	$2p_x2p_y$	$2p_z$	1*s*	1*s*
1*a*₁(Si–F)	−35.35	6	0	6	88	0	0	0	0
2*a*₁(Si–H)	−13.61	53	0	1	5	0	8	24	9
1*e* (F–Si–H)	−8.75	0	30	0	0	128	0	40	0
3*a*₁(F–Si–H⁻)	−8.64	0	0	15	2	0	71	0	12
2*e* (F–Si–H)	−6.10	0	30	0	0	70	0	100	0
4*a*₁(F–H–H⁻)	−3.43	0	0	3	0	0	10	36	51
					Cl				
					3*s*	$3p_x3p_y$	$3p_z$		
1*a*₁(Si–Cl)	−17.13	14	0	1	81	0	0	3	0
2*a*₁(Si–H)	−15.10	48	0	0	20	0	4	21	7
1*e* (Cl–Si–H)	−8.25	0	60	0	0	26	0	114	0
3*a*₁(Cl–Si–H⁻)	−8.10	0	0	25	1	0	47	0	27
2*e* (Cl–Si–H)	−5.72	0	4	0	0	170	0	26	0
4*a*₁(Cl–H–H⁻)	−4.02	0	0	3	0	0	36	21	39

electron density transfer from the hydride anion to adjacent atoms. It should be noted that the $XSiH_4^-$ stabilization is linearly (via three points) related to the LUMO energy (Fig. 1).

The results obtained are strongly confirmed by the change in charge distribution in the $X_{ax}(H_3)_{eq}Si\ldots H^-$ system. As seen from Fig. 2, the formation of complex anions of I decreases the electron density on the hydride anion in the following order: $F > Cl > H_{ax}$, which is in agreement with the values obtained from the corresponding eigen vectors in HOMO of anions of I. The extent of this change within the range $R_{min} - R = 2$ Å decreases in the series $H > Cl > F$. Contrary to widely accepted ideas, the silicon atom displays an increase in the positive, rather than the negative charge (Fig. 2c). The change $+q(\mathrm{Si})$, with respect to tetracoordi-

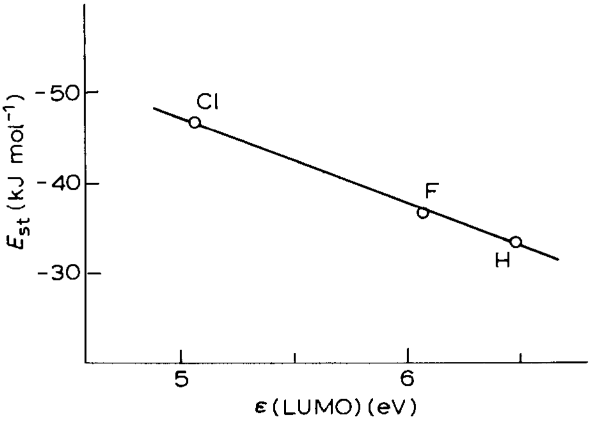


Fig. 1. Linear dependence of stabilization energy, E_{st}(I) upon LUMO energy.

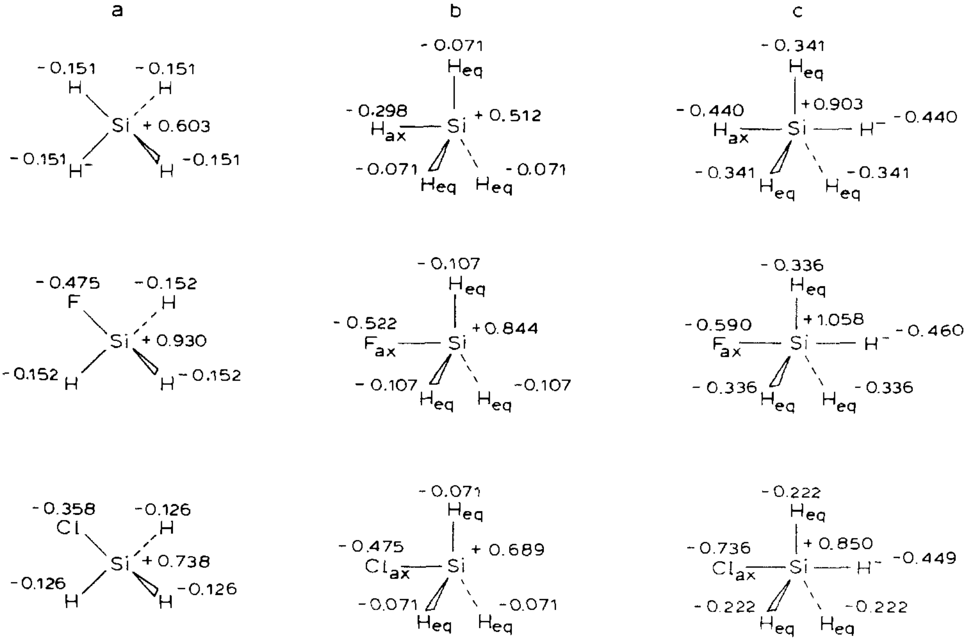


Fig. 2. Charge distribution in individual $XSiH_3$ molecules and complex anions I for equilibrium Si...H^- distances, e.

nate $XSiH_3$, is +0.303, +0.128 and +0.112 e for X = H, F and Cl, respectively. The charge is almost completely transferred from H^- to the equatorial and axial atoms surrounding silicon. The amplitude of change in the positive charge on the equatorial hydrogen atoms increases in the following order: Cl < F < H. The corresponding changes with respect to $XSi_{sp^3}H_3$ are −0.189, −0.184, −0.096 and 0.096 for X = H, F and Cl, respectively (Fig. 2c). When the $XSiH_4^-$ complex is formed, the negative charge on the axial hydrogen atoms increases in the series H < F < Cl, opposite to that for equatorial hydrogens. The change in the charge on X_{ax} relative to $XSi_{sp^3}H_3$ is −0.378, −0.289 and −0.115e for X = Cl, H and F, respectively. Taking into account that with shortening the Si...H^- distance, the longest Si–Hal bond is observed with X = Cl, it may be concluded that with increasing the substituent polarizability the ionic character of the Si–X_{ax} bond becomes more pronounced (F < Cl).

Since the coordination process is associated with a change in the central silicon atom hybridization and a parallel transfer of the negative charge from H^- to SiH_3X, we decided to consider the electron density redistribution with changing the valence angles of the $XSiH_3$ fragment in the isolated state. Fig. 2,b shows that SiH_3 fragment flattening leads not to an increase, as we assumed previously [3], but to a 0.05–0.09 e decrease of the positive charge on the silicon atom, which is accompanied by increasing the negative charge on the equatorial hydrogen atoms within 0.05–0.08 e and increasing the electron density on the axial substituent. The change in the latter follows an order of F (−0.047) < Cl (−0.117) < H (−0.147).

By summation of the charge redistribution pattern in the pentacoordination, it may be concluded that the increase in the positive charge on the central coordinative

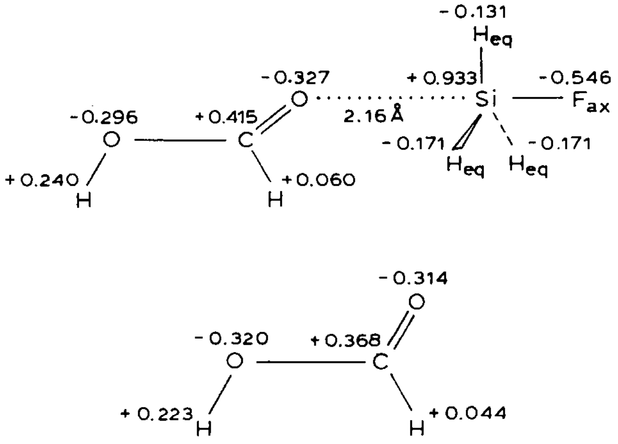


Fig. 3. Equilibrium charge distribution in complex II and individual O=CH–OH molecule, e.

silicon atom and of the negative charge on H_{eq} is due exclusively to $H^- \rightarrow XSi_{ps^2}H_3$ coordination. At the same time, the change in the effective negative charge on substituent X_{ax} is determined by the sum of rehybridization and $Si \leftarrow H^-$ bond coordination.

Calculation for the molecular complex $F_{ax}(H_3)_{eq}Si\ldots O{=}CH{-}OH$

The investigation of this system is of interest for a better understanding of the coordinate bond in molecular complexes, especially, in (aroyloxymethyl)trifluorosilanes [16]. The calculation has shown that when the reaction energy and the charge redistribution are considered the difference in the formation of the $FSiH_4^-$ anion and molecular complex II is only quantitative, and determined by weaker perturbation of the $FSiH_3$ molecule under the effect of the O=CH–OH ligand (changes of the calculated F_{ax}–Si bond lengths are given in Table 2, changes of equilibrium charges in Fig. 3). The potential coordination curve of II, corresponding to the approach of the O=CH–OH molecule to the silicon atom to form the Si ← O= bond, is less steep than that of the $FSiH_4^-$ anion. The energy of stabilization for complex II (−17.4 kJ/mol) is considerably lower than that for $FSiH_4^-$. On the potential curve a total energy minimum corresponds to the equilibrium distance, 2.16 Å, which is in agreement with the experimental value 2.03 Å for (4*F*-benzoyloxymethyl)trifluorosilane [16]. Despite the existance of the minimum, the formation of the complex considered is energetically disadvantageous which is indicated by the positive value of complexation energy (Table 1). Analogous results have been obtained in empirical calculations for the $H_4Si \leftarrow NH_3$ complex on an expanded STO-4LGF basis [17].

The change in charges within a Si...O=C distance range of 2.2–2.7 Å is considerably smaller than in the case of $FSiH_4^-$ formation (Fig. 3). The comparison of charge distribution in the molecular complex II with that in $FSiH_4$ (Figs. 2 and 3) for equilibrium distances show a decrease of 0.13 e for the effective positive charge on the silicon atom. Consequently, the positive charge value is governed not only by the axial substituent, but also by the charge on the coordinative electron-donor atom Y.

The higher positive charge on the silicon atom which acts, as seen from model calculations, as a conducting bridge, is unexpected. As a possible explanation for the $+q(\mathrm{Si})$ increase it may be assumed that the electrostatic effect of the resulting dipole of the nucleophilic group involved in coordination ($-NC_3$ in silatranes and O=C in (aroyloxymethyl)trifluorosilanes and model molecular structure), included bond dipoles and the lone electron pair. The high polarization of the O=CH–OH molecule approaching the fluorosilane molecule gives good support for this assumption (Fig. 3).

Calculation procedure

The calculation has been carried out in a semi-empirical MNDO approximation [18].

Full optimization of the $XSiH_3$ molecular geometry with a tetracoordinate silicon atom and partial optimization (X_{ax}–Si and =C–O– bond lengths) for other systems were performed. In calculating the complexation in I and II a fixed trigonal-bipyramidal orientation of the $XSiH_3$ fragment bonds were used. The geometry parameters are listed in Table 2. All the calculations were done on an ES-1033 computer.

Acknowledgment

The authors wish to express their deep gratitude to Drs. N.M. Vitkovskaya, V.G. Zakzhevskii and F.S. Lurye of the Computing Center of the Irkutsk University for their assistance in quantum-chemical calculations.

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