

The Free Tricoordinated Silyl Cation Problem

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As the importance and abundance of silicon in our environment is large, it has been thought that silicon might take the place of carbon in forming a host of similar compounds and silicon-based life. However, until today there is no experimental evidence for such a hypothesis and carbon is still unique among the elements in the vast number and variety of compounds it can form. Also, the corresponding derivatives of the two elements show considerable differences in their chemical properties.

The essential debate concerning organosilicon chemistry relates to the existence of the free planar tricoordinated silyl cations in condensed phase (R_3Si^+), in analogy to carbocations (R_3C^+) which have been known and characterized as free species. Although silyl cations are thermodynamically more stable than their carbon analogs, they are very reactive due to their high inherent electrophilicity and the ability of hypervalent coordination. On the other hand, stabilization by inductive and hyperconjugative effects and larger steric effects of carbocations make them less sensitive to solvation or other environmental effects than silyl cations. Hence, observation of free silyl cations in the condensed phase proved extremely difficult and the actual problem is the question of the degree of the (remaining) silyl cation character.

The first free silyl cation, trimesitylsilyl cation, and in analogy with it tridurylsilyl cation, were synthesized by Lambert *et al.* Free silyl cations based on analogy to aromatic ions (homocyclopropenylum and tropylium) have also been prepared. However, in these silyl cations the cationic character is reduced by internal π -conjugation. Čičak *et al.* prepared some silyl-cationic intermediates ($Me_3Si-CH\equiv CR$)⁺ in solid state. With the help of quantum-mechanical calculations it was concluded that these adducts have much more silyl cation than carbocation character.

Key words: Silicon, organosilicon compounds, silyl cations, carbocations, β -silyl effect, degree of silyl cation character

Introduction – Why is silicon interesting?

Silicon makes up 26 % of the earth's crust by mass, and is the second most abundant element, exceeded only by oxygen (49 %). Silicon has not been found free in nature. It occurs mostly as oxide (sand, quartz, rock crystal, amethyst, agate, flint, jasper, opal, etc.) or silicate (granite, asbestos, clay, mica, etc.). These numerous silicon minerals are the most abundant minerals in the earth's crust (95 %). Silicon is also present in the Sun, stars and some meteorites.

Silicon is one of man's most useful elements.¹ In the form of sand and clay it is an ingredient of concrete and bricks, it is a useful refractory material for high-temperature works, and in the form of silicate it is used in making enamels, pottery, etc. Silicon, as silicon dioxide, is a principal ingredient of glass, one of the most inexpensive materials with excellent mechanical, optical, thermal, and electrical properties. Glass can be made in a variety of shapes, and is used for

containers, window glass, insulators, and thousands of other uses.

Hyperpure silicon can be doped with boron, gallium, phosphorus, or arsenic for use in transistors, solar cells, rectifiers, and other solid-state devices which are used extensively in electronics.

Silicon is an important ingredient of steel. Silicon carbide is one of the most important abrasives and has been used in lasers. Hydrogenated amorphous silicon has shown promise in producing economical cells for converting solar energy into electricity.

Silicones are important products of silicon with many useful properties. They may be prepared by hydrolyzing a silicon organic chloride, such as dimethylsilicon chloride.

Silicon is also important to plant, animal and even human life. It is present in cell walls of some higher plants, but also in the human and animal skeleton and organs (there are about 18 g of silicon in a man weighing 70 kg).

Silicon is not particularly toxic but siliceous dust can cause a serious lung disease known as silicosis (such as asbestosis from asbestos), especially for long time exposed people.

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Comparison of the carbon and silicon

As the importance and abundance of silicon in our environment is large, it has been thought that silicon might take the place of carbon in forming a host of similar compounds and silicon-based life. That assumption was supported by the positions of two elements in the periodic table: silicon and carbon are placed in the same group of the periodic table (14th, usually named as the carbon group), silicon being one period below the carbon (3rd and 2nd, respectively). However, they belong to different classes of elements: silicon is metalloid and carbon is nonmetal. Still, until today there is no experimental evidence for such a hypothesis and carbon is still unique among the elements in the vast number and variety of the compounds that it can form.

At the beginning of the 20th century F. S. Kipping, who laid the foundations for development of organosilicon chemistry, wrote: "Even after a very short experience, it was evident that the corresponding derivatives of the two elements showed very considerable differences in their chemical properties ...".²

However, silicon and organosilicon compounds still receive intensive attention and research and it is common practice to compare them with analogous carbon compounds.

In this review the detailed comparison will continue with the fundamental properties of carbon and silicon atoms (Table 1).^{3,4}

The following differences between carbon and silicon are evident: (1) the silicon atom is significantly larger and more polarizable, (2) the valence atomic orbitals of silicon are larger and more diffuse, (3) silicon has d-orbitals which may participate in bonding, (4) silicon electron affinity is higher, but electronegativity is lower (electronegativity is not strictly an atomic property, but rather a property of an atom in a molecule), (5) silicon ionization energies are lower.

It is evident that the shown properties of silicon and carbon atoms can cause substantial differences in their chemical reactions and character of corresponding compounds. Several obvious examples are the existence of stable hypervalent compounds for silicon but not for carbon, the difficulties in forming multiple bonds to silicon but not to carbon, and different geometries and other physical properties of analogous silicon and carbon compounds.

The lower electronegativity of the Si-atom than C-atom causes partial ionic character of C–Si single bond in organosilicon compounds of about 12 %. It results in allocation of negative and positive charge as shown: C^{δ-}–Si^{δ+}. Quantum-mechanical calculations at all levels predict that the C=Si double bond is even more polarized.³

C–Si bonds are in average 26 % and Si–Si 57 % longer than analogous C–C bonds (Table 2).³

Since C–Si π bonds are longer than C–C, it has been thought that organosilicon compounds with double bonds have weaker p-orbitals overlap and hence lower π -bonding character. However, bond polarization expands carbon p-orbitals, and contracts silicon p-orbitals resulting in relative efficient π -overlap (Fig. 1).³

Table 1 – Some fundamental properties of C and Si atoms
T a b l i c a 1 – Neka fundamentalna svojstva atoma C i Si

Property Svojstvo		⁶ C	¹⁴ Si
atomic number atomski broj		6	14
relative atomic mass relativna atomska masa		12.0110	28.0855
atomic radius (Bragg-Slater)/pm atomski polumjer (Bragg-Slater)/pm		70	110
covalent radius/pm kovalentni polumjer/pm		77.2	116.9
ionic radius/pm ionski polumjer/pm		16 (+4), 260 (–4)	41 (+4), 271 (–4)
	(oxidation states) (oksidacijska stanja)		
van der Waals radius/pm	Pauling Glidewell	170 125	217 155
van der Waalsov polumjer / pm			
electronegativity elektronegativnost	Pauling (1932) Mulliken (1934) Allred-Rochow (1958) Voronkov-Kovalev (1965) Mande-Deshmukh (1977) Sanderson (1983)	2.50 2.63 2.60 2.46 2.73 2.75	1.80 2.44 1.90 1.89 1.87 2.14
ionization energies/eV ^a ionizacijske energije / eV ^a	E_1 E_2 E_3	11.26 24.38 47.89	8.15 16.34 34.49
electron affinity/eV ^a elektronski afinitet / eV ^a		1.12	1.39
dipole polarizability/a. u. ^b dipolna polarizabilnost / a.u. ^b		11.8	36.3
radii of the principal maxima of outer orbital/pm polumjeri glavnih maksimuma vanjske orbitale/ pm		62.0 (2s) 59.6 (2p)	90.4 (3s) 106.8 (3p)
electron configuration elektronska konfiguracija		[He] 2s ² 2p ²	[Ne] 3s ² 3p ² 3d ⁰

^a 1 eV = 1.60219 10⁻¹⁹ J. ^b 1 a. u. = 1.48185 10⁻³¹ m³ = 1.482 10⁻⁴ nm³.

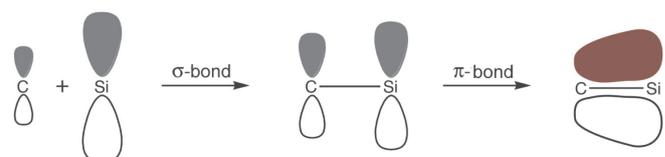


Fig. 1 – Schematic representation of C–Si single and double bond forming

Slika 1 – Shematski prikaz stvaranja jednostruke i dvostruke veze C–Si

Table 2 – Experimental C–C, C–Si and Si–Si single and double bond lengths and relative bond strengths (in H_3XXH_3 and $H_2X=XH_2$, $X=C, Si$, except * $H_2X=X(CH_3)_2$)

Tablica 2 – Eksperimentalne duljine i relativne jakosti jednostrukih i dvostrukih veza C–C, C–Si i Si–Si (u H_3XXH_3 i $H_2X=XH_2$, $X=C, Si$, osim * $H_2X=X(CH_3)_2$)

	C–C	C–Si	Si–Si
single bond length/ $10^{-10}m$ duljina jednostruke veze/ $10^{-10}m$	1.534	1.889	2.342
double bond length/ $10^{-10}m$ duljina dvostruke veze/ $10^{-10}m$	1.315	1.695	2.116
relative single bond strength/ $kJ mol^{-1}$ relativna jakost jednostruke veze/ $kJ mol^{-1}$	68.7	48.1	0.0
relative double bond strength*/ $kJ mol^{-1}$ relativna jakost dvostrukih veze*/ $kJ mol^{-1}$	180	67	0

The knowledge of bond strengths is central to chemistry. Unfortunately, experimental thermodynamic data for silicon compounds are limited and only a few bond energies are known. Single bond strengths decrease in the sequence of the increasing of bond lengths: C–C, C–Si and Si–Si (Table 2). For example, the C–C bond in H_3C-CH_3 is by 20.6 $kJ mol^{-1}$ stronger than the C–Si bond in H_3C-SiH_3 , and H_3C-SiH_3 stronger than $H_3Si-SiH_3$ by 48.1 $kJ mol^{-1}$. The strengths of the π -bond in $H_2C=SiH_2$ and $H_2C=CH_2$ have been estimated by quantum-mechanical calculations that C=Si bond is less stable than C=C bond by more than 146 $kJ mol^{-1}$. Experimental double bond strength of $H_2C=C(CH_3)_2$ relative to the $H_2C=Si(CH_3)_2$ is 113 $kJ mol^{-1}$ and of $H_2C=Si(CH_3)_2$ relative to the $H_2Si=Si(CH_3)_2$ is 67 $kJ mol^{-1}$ (Table 2).

And what about C–H and Si–H bonds? The electronegativity of the hydrogen atom is in between carbon and silicon (2.2 on Pauling scale). Therefore, the polarity of C–H bond ($C^{\delta-}-H^{\delta+}$) is opposite to the polarity of Si–H bond ($Si^{\delta+}-H^{\delta-}$) (see charges in Table 3).³

Table 3 – C–H and Si–H single bond lengths (experimental and HF/3–21G(d)), relative bond energies (MP4/6–31G(d)) and charges (Mulliken, HF/3–21G(d)) in CH_4 and SiH_4 structures

Tablica 3 – Duljine (eksperimentalne i HF/3–21G(d)) i relativne energije (MP4/6–31G(d)) jednostrukih veza C–H i Si–H te naboji (Mulliken, HF/3–21G(d)) u strukturama CH_4 i SiH_4

Structure, bond Struktura, veza	$d(\text{exp})/10^{-10}m$	$d(\text{calc})/10^{-10}m$	$q(\text{Si, C})/e^a$	$q(\text{H})/e^a$	Relative bond energy/ $kJ mol^{-1}$ Relativna energija veze / $kJ mol^{-1}$
SiH_4 , Si–H	1.481	1.475	+0.52	–0.13	0.0
CH_4 , C–H	1.091	1.080	–0.80	+0.20	60.7

^a Elementary charge, $e = 1.60218 \cdot 10^{-19} C$
Elementarni naboj, $e = 1.60218 \cdot 10^{-19} C$

Si–H bond in SiH_4 is 36 % longer than C–H bond in CH_4 , while C–H bond in CH_4 is by 60.7 $kJ mol^{-1}$ stronger than the Si–H bond in SiH_4 .

By similar analysis the other Si–Y bonds can be described. If Y is a more electronegative element, for example F, Cl or O in OH group, Si–Y bond is much stronger compared to the C–Y bond (by 159, 84 and 113 $kJ mol^{-1}$, respectively), due to a larger electronegativity difference between Si and Y than C and Y.^{3,4} Hence, in this case the bond is stronger and contribution of ionic structure $[R_3(Si, C)^+Y^-]$ to the bonding larger for Si-compounds than for C-compounds. These huge differences in bond energies are expected to play a major role in comparisons of substitution reactions at silicon and carbon, when these groups are used as the leaving groups or nucleophiles.

It has also been determined that d- π conjugation has minor influence on the strength of certain Si–Y bonds, even with good π donors such as OH or NH_2 groups possessing lone-pair electrons. In other words, the resonance structure with negative charge on silicon has small contribution (Fig. 2).

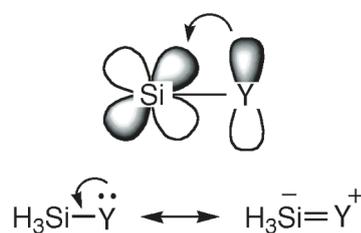


Fig. 2 – d- π conjugation
Slika 2 – d- π konjugacija

If Y is a metal, only elements with extremely small electronegativity will form stronger Si–Y bonds compared with C–Y bonds because of larger contribution from R_3Si-Y^+ type structure (for example Li or Na, see Table 4).^{3,4} The substituents with electronegativities closer to silicon have stronger bonds to carbon than to silicon due to higher ionic character of the C–Y bond (for example metals Mg, Al, Be or nonmetals B, P, see Table 4).

Calculated X–Y bond energies in Table 4 provide very useful information. The bond strengths correlate very nicely with the electronegativity of Y, suggesting that it is the major factor which determines the strengths of single bond to silicon. As the electronegativity of Y increases, so does the Si–Y bond strength.

Since H_3Si -group supports both negative and positive charge better than H_3C -group, it could be said that H_3Si has an ambielectronic character.

Comparison of silyl cations and carbocations

The main debate in organosilicon chemistry concerns the existence of the free planar tricoordinated R_3Si^+ cations (where R is an alkyl or aryl group) in condensed phase in analogy to carbocations, R_3C^+ , which have been known and characterized as free species.^{3–18} Cationic species R_3Si^+ are called either silicenium or silylenium (in analogy to carbenium ions which are tricoordinated carbocations), or silyl, silicon or silylium ions. In the gas phase, silyl cations have been known and studied for over 40 years. Although silyl cations are thermodynamically more stable than their

Table 4 – Si–Y and C–Y bond energies calculated by equation $H_3Si-Y + \cdot CH_3 \rightarrow H_3C-Y + \cdot SiH_3$ at MP4/6–31G(d) level of theory (Horizontal lines divide first, second and third-row elements)

Tablica 4 – Energije veza Si–Y i C–Y računane pomoću jednadžbe $H_3Si-Y + \cdot CH_3 \rightarrow H_3C-Y + \cdot SiH_3$ na MP4/6–31G(d) razini teorije (Vodoravne linije dijele elemente prve, druge i treće periode)

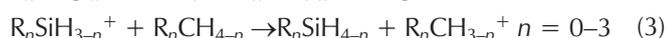
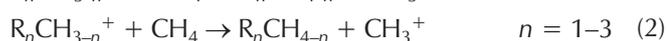
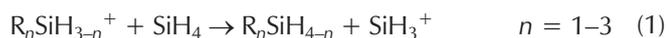
Y	Electronegativity Elektronegativnost	Bond energy*/kJ mol ⁻¹ Energija veze*/kJ mol ⁻¹
H	2.2	60.7
Li	1.0	26.0
BeH	1.5	62.0
BH ₂	2.0	82.1
CH₃	2.5	20.5
NH ₂	3.1	57.8
OH	3.5	111.4
F	4.1	158.7
Na	1.0	34.8
MgH	1.2	6.7
AlH ₂	1.5	44.8
SiH₃	1.8	48.1
PH ₂	2.1	10.5
SH	2.4	38.1
Cl	2.8	85.0

* Negative sign means that C–Y bond is stronger, and positive that Si–Y bond is stronger

* Negativne vrijednosti znače da je jača veza C–Y, a pozitivne da je jača veza Si–Y

carbon analogs, they are extremely reactive due to their high inherent electrophilicity. In the condensed phase, silyl cations have been sought for more than 60 years and the main problem comes from their interactions with a wide variety of both π - and σ -electron donating compounds or groups (solvent molecules, counterions, neighboring groups) forming tetra- or even higher-coordinated Si compounds.

Relative stability of methyl-substituted silyl cations was studied experimentally (by ion cyclotron resonance spectroscopy) and by quantum-mechanical calculations (using isodesmic reactions (1)–(3)).^{3,4}



From the eq. (1) one can assess the relative stability of R-substituted silyl cations vs. parent SiH_3^+ and from the eq. (2) the relative stability of R-substituted carbocations vs. parent CH_3^+ . The eq. (3) compares stabilities of analogous silyl cation and carbocation. Parent SiH_3^+ is more stable than CH_3^+ by 240.3 kJ mol⁻¹ at MP2(fc)/6–31G(d)//MP2(fc)/6–31G(d) level of theory.

Table 5 – Effect of successive methyl substitution on the stability of $Me_nCH_{3-n}^+$ and $Me_nSiH_{3-n}^+$ ions (kJ mol⁻¹)

Tablica 5 – Utjecaj višestruke metilne supstitucije na stabilnost iona $Me_nCH_{3-n}^+$ i $Me_nSiH_{3-n}^+$ (kJ mol⁻¹)

Ion	eq. (1) jedn. (1)		eq. (2) jedn. (2)		eq. (3) jedn. (3)	
	calc ^a izrač. ^a	exp ^c eksp. ^c	calc ^a izrač. ^a	exp ^c eksp. ^c	calc ^a izrač. ^a	exp ^c eksp. ^c
$n = 1$	63.2 (63.2) ^b	64.9	170.0	183.8	133.1 (114.7) ^b	103.8
$n = 2$	116.8 (117.2) ^b	131.0	245.8	263.3	111.4 (72.9) ^b	91.3
$n = 3$	160.8 (161.6) ^b	171.2	313.2	338.3	87.9 (54.0) ^b	54.0

^a MP2(fc)/6–31G(d)//MP2(fc)/6–31G(d)

^b MP3/6–31G(d)//HF/6–31G(d)

^c Ref. 19

From Table 5, it can be seen that stabilization per methyl is reduced upon multiple substitution for both parents, SiH_3^+ and CH_3^+ .

The data obtained by eq. (3) show that trimethylsilyl cation, $(CH_3)_3Si^+$, is more stable than *tert*-butyl cation, $(CH_3)_3C^+$, by only 87.9 kJ mol⁻¹ (at MP2(fc)/6–31G(d)//MP2(fc)/6–31G(d)), which is much less than their parents stability difference (152.4 kJ mol⁻¹). $(CH_3)_3Si^+$ is more stable than SiH_3^+ by 160.8 kJ mol⁻¹ (at MP2(fc)/6–31G(d)//MP2(fc)/6–31G(d)).

It is determined that all the alkyl-substituted tertiary silyl cations are more stable than the analogous tertiary carbocations and the stabilization effect is increasing in order Me, Et, *t*-Bu, *i*-Pr. Factors that are responsible for the difference in stabilities of the alkyl-substituted tertiary silyl cations and tertiary carbocations are hyperconjugative, inductive and steric effects.^{11,18}

Hyperconjugative effects, which are σ - π conjugations, lead to a transfer of negative charge to the cationic atom and reduce its electrophilic character.^{5,11} These stabilizations are less effective in silyl cations than in carbocations because of the longer C–Si compared to the C–C bonds and poorer orbital overlap (Fig. 3).

The difference in electronegativity between silicon and carbon leads to electron withdrawal from the silicon atom in $(CH_3)_3Si^+$ (inductive effect), and also adds to the relatively large positive charge at silicon. In $(CH_3)_3C^+$ cationic carbon withdraws electron density from the methyl groups both via the π -orbital (hyperconjugatively) and σ -orbitals (inductively) thus reducing its positive charge. Therefore, the need for $(CH_3)_3C^+$ solvation is much smaller.

For comparison, the partial charge at carbon in $(CH_3)_3C^+$ is 0.225 e while that at silicon in $(CH_3)_3Si^+$ is 0.947 e. The corresponding partial charges for CH_3^+ and SiH_3^+ are 0.414 and 0.967 e, respectively (Mulliken charges calculated with basis set [7s6p2d/5s4p1d/3s1p]).¹¹

Steric effects hinder solvation of the cations. Again, silyl cations are less sensitive to steric effects because of the larger size of silicon.

Apeloig and coworkers carried out systematic studies on substituted silyl cations $RSiH_2^+$ in the gas phase, where R

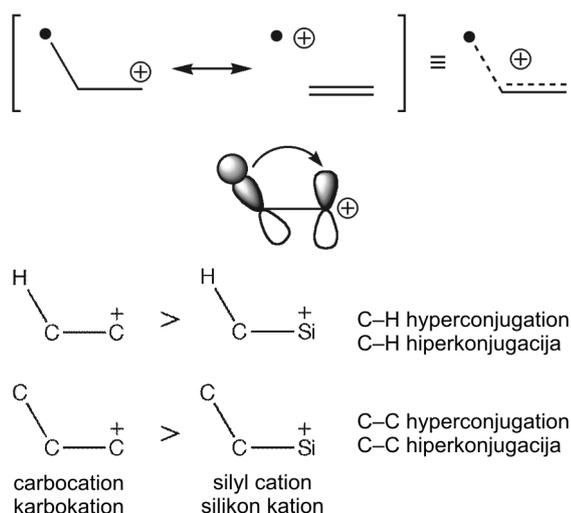


Fig. 3 – Hyperconjugative effects in carbocationic and silyl-cationic species

Slika 3 – Hiperkonjugacijski učinci u karbokationskim i silyl-kationskim vrstama

was varied along the standard second-row (i. e. Li to F) and third-row (i. e. Na to Cl) substituents, using isodesmic reactions (1) and (2) with $n = 1$.³ Although these calculations used inadequately small basis sets (STO-3G and 3-21G), their conclusions are probably qualitatively correct. They found that all the examined substituents stabilize RSiH_2^+ relative to the parent SiH_3^+ , and multiple substitution provides higher stabilizations (even by extremely electropositive substituents such as Li and BeH). However, these stabilizations are less effective in silyl cations than in carbocations. This is most pronounced for substituents which are good π donors such as OH or NH_2 probably because of poorer orbital overlap for silicon than for carbon, but those substituents are still more stabilizing than, for example, methyl. Cremer and coworkers also found that electropositive substituent dimethylboryl, $\text{B}(\text{CH}_3)_2$, is more stabilizing than methyl; $[(\text{CH}_3)_2\text{B}]_3\text{Si}^+$ is more stable than $(\text{CH}_3)_3\text{Si}^+$ by 78.3 kJ mol^{-1} at B3LYP/6-31G(d) level of theory.^{5,16}

Conjugating organic substituents such as vinyl ($\text{CH}=\text{CH}_2$) and phenyl (C_6H_5) were found, as OH or NH_2 , to be less effective in stabilizing silyl ions than carbocations. Electron-withdrawing substituents (CHO, CN and CF_3) destabilize silyl cation while $\text{C}\equiv\text{CH}$ is weakly stabilizing relative to the parent SiH_3^+ .³

Silyl-substituted carbocations

Silyl-substituted carbocations were studied by many research groups, experimentally (gas phase and solvolytic studies) and by quantum-mechanical calculations.^{3,20–28}

According to the *ab initio* calculations, an α -silyl-substituent ($\text{R} = \text{SiH}_3$) stabilizes alkyl cation (RCH_2^+) compared with hydrogen ($\text{R} = \text{H}$), but destabilizes it compared with a methyl substituent ($\text{R} = \text{CH}_3$).^{3,20} For vinyl cations ($\text{RC}^+ = \text{CH}_2$) the situation is slightly different. It is found that α -silyl and α -methyl substituents stabilize the vinyl cation nearly to the same extent.^{3,20}

The destabilizing effect of α -silyl group compared with a methyl group in alkyl carbocation was explained by the weaker Si–H hyperconjugation relative to the C–H and by electrostatic repulsion between the adjacent cationic carbon and the electropositive silicon.^{3,20} In the vinyl cation $\text{C}-\text{H}_{\text{vinyl}}$ hyperconjugation is stronger and diminishes the demand for hyperconjugative stabilization from the α -substituent. In addition, the vinyl cation is more sensitive to the σ -effects than an alkyl cation and the stabilizing σ -donation by the electropositive silyl group is therefore more important for the vinyl than for the tricoordinated carbocation.^{3,20}

All experimental and quantum-mechanical gas phase studies of α -silyl-substituted carbocations have shown that these intermediates exist only in a very flat potential well and undergo fast rearrangements producing the more stable silyl or β -silyl-substituted carbocations.²⁰

β -silyl-substitution is predicted to be far more stabilizing than β -alkyl-substitution (C–Si hyperconjugation > C–C hyperconjugation).^{3,20–23} Such a stabilization, known as the β -silyl effect (or β -silicon effect), depends on the electron demand of the electron-deficient carbon. Thus, the hyperconjugative stabilization is larger for the primary alkyl (a) and even more for the vinyl cations (b) than for secondary (c) or tertiary cations (d) shown in Fig. 4.

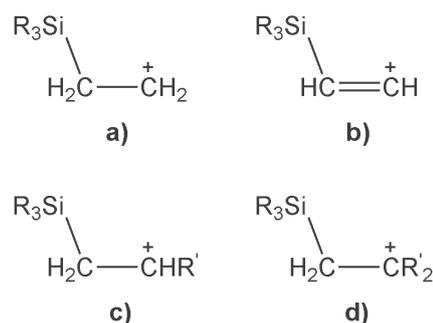


Fig. 4 – Some of the β -silyl-substituted carbocations

Slika 4 – Neki β -silyl-supstituirani karbokationi

Furthermore, the stabilizing effect, and thus the cationic character of silicon, of the β - Me_3Si group is larger than β - H_3Si group.

The hyperconjugative interaction between the σ -C–Si bond and the formally empty $2p(\text{C})$ orbital (σ - π conjugation) results in changes of bond distances and angles. The degree of bridging (taking the $\text{SiC}_\beta\text{C}^+$ bond angle as a measure) was found to increase with increasing hyperconjugative effect.^{3,21} Three possible types of bridging are given in Fig. 5: open (a), asymmetrically bridged (b) and symmetrically bridged (c) structures.

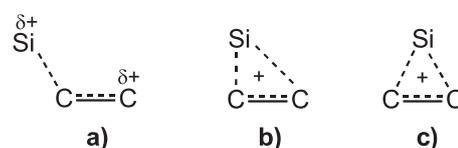
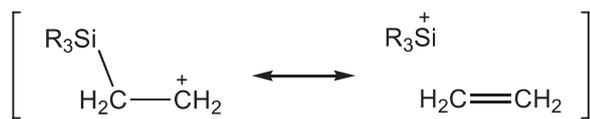


Fig. 5 – Degree of bridging in cationic structures

Slika 5 – Stupanj premoštenja u kationskim strukturama

The term hyperconjugativity is suggested to represent the relative contribution of resonance structure with positive charge at Si-atom compared to the resonance structure with positive charge at C-atom (Scheme 1).²¹ If there is no hyperconjugation (the first resonance structure is dominating), hyperconjugativity is 0.00 and for complete hyperconjugation (the second resonance structure is dominating), hyperconjugativity is 1.00.



Scheme 1
Shema 1

Hyperconjugativity can be calculated as $1-p(\text{Si}-\text{C})$, where p is bond order.²⁶ Larger hyperconjugativity usually results with a larger degree of bridging.

Silyl effects beyond the β -position were also examined (Scheme 2): γ (homohyperconjugation or σ - σ conjugation), δ (double hyperconjugation or σ - π/σ - π conjugation), ε (hyperconjugation/homohyperconjugation or σ - π/σ - σ and σ - σ/σ - π conjugation) and ζ (triple hyperconjugation or σ - π/σ - π/σ - π conjugation).^{3,21}

These various forms of conjugation, of which the β -effect may be thought of as the parent, give rise to observable but diminishing stabilization as the donor atom moves further from the cationic carbon. Thus, ζ -effect has not been observed at all.

Although the stability of silyl cations in the gas phase is higher than that of carbocations, observation of free silyl cations in the condensed phase proved extremely difficult. Several reasons, which have already been mentioned, were given: (1) stabilization by substituents is less effective for silyl cations than for carbocations due to the larger Si atom, longer Si-R bonds and lower tendency of silicon to conjugate, (2) high "apetite" of silyl cations for nucleophiles, including leaving groups, counterions and solvent molecules; calculations have shown that silyl cations can complex even

with rare gases, (3) the possibility for hypervalent coordination. On the other hand, internal stabilization of carbocations is responsible for the similarity of their properties in the gas and condensed phases.

Determination of the degree of silyl cation character

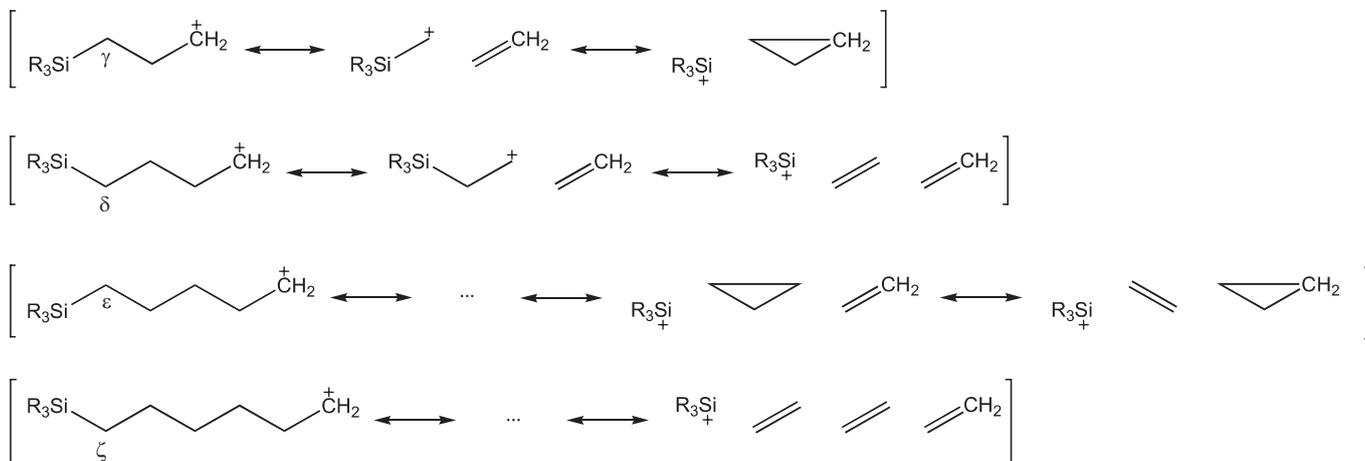
From the presented results one can conclude that the difference between silyl cations and carbocations results from internal stabilization by inductive and hyperconjugative effects and also steric effects making carbocations less sensitive to solvation or other environmental effects than silyl cations. Hence, one could get the impression that a completely free silyl cation in condensed phase is an illusion that can never be realized. Therefore, the actual problem seems to be just the question of the degree of the (remaining) silyl cation character.

In literature, several criteria for determination of the degree of silyl cation character were used.^{3-18,20-29} These are: (1) structural quantities (bond distances and orders, especially to the nearest nucleophile, pyramidalization angle (or planarization), sum of all the three bond angles in R_3Si -fragment involved by Si, etc.), (2) complexation (or binding or association) energy (with nucleophile), (3) ^{29}Si NMR chemical shift, (4) partial charges and (5) population of the LUMO of the silyl cation, which is dominated by the $3p_\pi(\text{Si})$ AO. Using these criteria, the silyl cation character can be examined by different experimental and quantum-mechanical methods shown in Table 6.

It is obvious that the degree of silyl cation character will be higher if the distance to the nucleophile is greater than the appropriate covalent bond, but there is no exact limit for "how far is far enough". On the other hand, bond order and pyramidalization angle are more precise criteria, hence their values tend to be zero for completely free silyl cation.

The degree of silyl cation character will also be high if the sum of the Si bonds' angles approaches 360° .

Furthermore, weaker interaction of silyl cation with nucleophile (e. g. solvent) will result in smaller complexation energy, which can be calculated by eq. (5).²⁹



Scheme 2
Shema 2



$$\Delta E = \{[R_3Si^+] + E[\text{solvent}]\} - E[(R_3Si\text{-solvent})^+] \quad (5)$$

^{29}Si NMR chemical shift will be larger for “more free” silyl cation and degree of silyl cation character can be estimated from the ranges established by Cremer and coworkers, shown in Table 7.¹¹

Table 6 – The criteria and methods for determination of the degree of silyl cation character^a

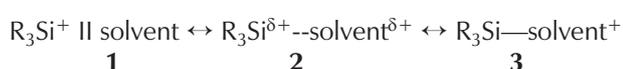
Tablica 6 – Kriteriji i metode za utvrđivanje stupnja sililkationskog karaktera^a

Criteria Kriterij	Experimental method Eksperimentalna metoda	Quantum- mechanical method (g, l) Kvantno-mehanička metoda (g, l)
structural parameters strukturni parametri	X-ray crystallography (s) Rendgenska kristalografija (s)	geometry optimization geometrijska optimizacija
complexation energy energija kompleksiranja	combined methods with mass spectrometry (g) kombinirane metode sa spektrometrijom masa (g)	vibration analysis vibracijska analiza
^{29}Si NMR chemical shift kemijski pomak ^{29}Si NMR	^{29}Si NMR (l)	NMR analysis analiza NMR
LUMO population and charges LUMO populacija i naboji	—	population analysis populacijska analiza

^a In parenthesis are given aggregate states

^a U zagradama su naznačena agregatna stanja

^{29}Si NMR chemical shifts of silyl cations R_3Si^+ with $R = \text{Me}$, Et , etc. are 400 ± 20 ppm in the gas phase, and are slightly reduced in noncoordinating solvents (by 10–20 ppm; structure **1** in Scheme 3; solvation is labeled as “II”). In weakly interacting solvents values are reduced to 200–390 ppm because of charge transfer to the electrophilic silicon atom and partial loss of silyl cation character (structure **2**, non-bonding interaction is labeled as “--”). Silyl cation character is totally lost in coordinating (nucleophilic) solvents, which form covalent complexes with silyl cations (structure **3**, bonding interaction is labeled as “—”). ^{29}Si NMR chemical shifts for those coordination complexes are typically between –50 and 200 ppm.



Scheme 3
Shema 3

Table 7 – Estimated ranges of ^{29}Si /ppm values for silyl cations in the gas phase and in solution^a

Tablica 7 – Procijenjeni rasponi ^{29}Si /ppm vrijednosti za sililne katione u plinskoj fazi i otapalu^a

R_3Si^+	Gas phase Plino- vita faza	Noncoo- ordinating solvents Nekoordi- nirajuća otapala ($0 < \epsilon$ ≤ 80)	Weakly interacting solvents Slabo među- djelujuća otapala ($0 < DN$ ≤ 1)	Weakly coordinating solvents Slabo koordinirajuća otapala ($1 < DN$ ≤ 10)	Strongly coordinating solvents Snažno koordinirajuća otapala ($DN > 10$)
$R = \text{H}$	300	290–300	120–290	10–110	–130 do 10
$R = \text{Me}$	385	370–385	200–370	90–190	–50 do 90
$R = \text{Et}$	410	390–410	220–390	110–210	–30 do 110
Si–solvent interaction među- djelovanje Si–otapala		solvation ^b solvatacija ^b	van der Waals ^c	weak bonding slabo vezanje	stronger bonding jače vezanje
cation character kationski karakter		free silyl cation slobodni sililni kation	partial loss of silyl cation character djelomični gubitak sililkationskog karaktera	total loss of silyl cation character potpuni gubitak sililkationskog karaktera	

^a Solvent is characterized by dielectric ϵ and electron-pair donor number (or donicity) DN . ϵ is scalar and DN is defined in the non-SI unit kcal mol^{-1} ($1 \text{ kcal mol}^{-1} = 4.1868 \text{ kJ mol}^{-1}$)

^a Otapalo je karakterizirano dielektričnošću i donorskim brojem elektronskog para (ili donorstvom) DN . ϵ je skalarni i DN je definiran jedinicom kcal mol^{-1} ($1 \text{ kcal mol}^{-1} = 4.1868 \text{ kJ mol}^{-1}$) izvan sustava SI

^b Solvation without any charge transfer from solvent to R_3Si^+

^b Solvatacija bez ikakvog prijenosa naboja s otapala na R_3Si^+

^c Van der Waals interactions imply here already some charge transfer

^c Van der Waalsova međudjelovanja ovdje već ukazuju na neke prijenose naboja

Alternatively, one can simply calculate the shift difference between the gas (calculated value) and solution phase (measured value) indicating the degree of interaction between silyl cation and solvent molecules according to eq. (6), or define the percentual silyl cation character – eq. (7):^{5,29}

$$\Delta(\delta^{29}\text{Si}) = \delta^{29}\text{Si}[R_3Si^+]_{\text{gas}} - \delta^{29}\text{Si}[(R_3Si\text{-solvent})^+]_{\text{solution}} \quad (6)$$

$$\%[R_3Si^+] = \frac{\delta^{29}\text{Si}[R_3SiH]_{\text{gas}} - \delta^{29}\text{Si}[(R_3Si\text{-solvent})^+]_{\text{solution}}}{\delta^{29}\text{Si}[R_3SiH]_{\text{gas}} - \delta^{29}\text{Si}[R_3Si^+]_{\text{gas}}} \cdot 100 \quad (7)$$

The LUMO of SiH_3^+ cation in the gas phase is identical to an empty $3p_\pi(\text{Si})$ orbital.⁵ As soon as the hydrogen atoms are replaced by alkyl groups the $3p_\pi(\text{Si})$ orbital mixes with some of the occupied molecular orbitals and, therefore, becomes partially occupied (see Table 8).

Table 8 – $3p_{\pi}(\text{Si})$ atomic orbital populations and silicon charges of methylated silyl cations^a

Tablica 8 – Popunjenost atomske orbitale $3p_{\pi}(\text{Si})$ i naboj na siliciju u metiliranim sililnim kationima^a

Cation Kation	$3p_{\pi}(\text{Si})/\text{me}$	$+q(\text{Si})/\text{me}$
H_3Si^+	0	760
MeH_2Si^+	116	790
Me_2HSi^+	132	835
Me_3Si^+	196	885

^a Geometries and Mulliken charges were obtained at B3LYP/6–31G(d) level of theory

^a Geometrije i Mullikenovi naboji dobiveni su na razini teorije B3LYP/6–31G(d)

However, for all alkyl-substituted silyl cations the LUMO is still dominated by the $3p_{\pi}(\text{Si})$ orbital. In this respect, the availability of the $3p_{\pi}(\text{Si})$ orbital for nucleophilic interaction partners is of central importance and the population of this AO is a natural measure for the degree of silyl cation character.

One might argue that the charge at the central silicon atom is also a suitable measure for the silyl cation character. However, the positive charge at silicon does not always parallel the occupation of the $3p_{\pi}(\text{Si})$ orbital because changing of positive charge is the result of not only π -electron transfers (conjugative effects), but also σ -electron transfers (inductive effects). For example, strongly σ -electron donating substituents attached to silicon reduce the positive charge, but do not change the population of the $3p_{\pi}(\text{Si})$ orbital.

Thus, the silyl cation character is best assessed by the availability and population of the $3p_{\pi}(\text{Si})$ orbital and it is established that silyl cation is free if the electron population of the $3p_{\pi}(\text{Si})$ orbital is less than 30 %.

Calculations at B3LYP/6–311G(d) level of theory have shown that populations of LUMO in Me_3Si^+ and $i\text{-Pr}_3\text{Si}^+$ are 0.146 and 0.104 e, respectively, with 100 % p-orbital character.²⁹ In Figs. 6 and 7, LUMOs with characteristic bond lengths are shown. It is obvious that C–H hyperconjugation exists in Me_3Si^+ cation, while only C–C hyperconjugation exists in $i\text{-Pr}_3\text{Si}^+$ cation.

The silyl cation character could be estimated qualitatively by calculating an electrostatic potential map.²⁹ The first step is to define a set of points (isodensity surface) where the electrostatic potential (ESP) will be calculated, and the second step is to calculate the ESP at these points. The ESP at a point (x, y, z) is given by the electrostatic potential energy between an imaginary positively charged (+1) point charge located at (x, y, z) and the molecule. Since the point charge is positive it will be attracted to electron-rich regions of the molecule and repelled by electron-poor regions. Thus, electron-rich regions have negative ESPs and electron-poor regions have positive ESPs. Variation in ESP is represented by colour: negative ESP regions are coloured red, and positive ESP blue. If ESP is zero, the colour is green.

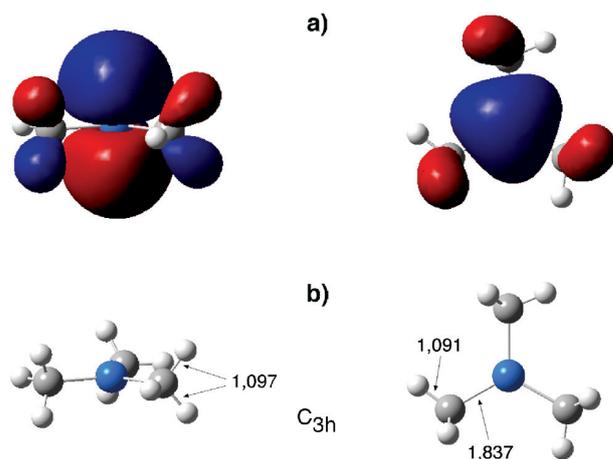


Fig. 6 – a) LUMO (isovalue = 0.025 a. u.) and b) geometry of Me_3Si^+ (bond lengths in 10^{-10} m) at B3LYP/6–311G(d) level of theory ($1 \text{ a. u.} = 1 e a_0^{-3}$; $1 a_0 = 5.291772 \cdot 10^{-11} \text{ m}$)

Slika 6 – a) LUMO (konturna razina = 0,025 a. u.) i b) geometrija (duljine veza u 10^{-10} m) Me_3Si^+ kationa na B3LYP/6–311G(d) razini teorije

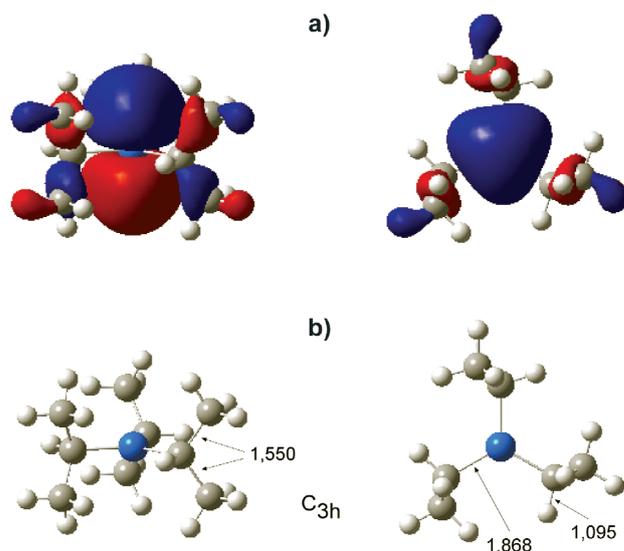


Fig. 7 – a) LUMO (isovalue = 0.025 a. u.) and b) geometry of $i\text{-Pr}_3\text{Si}^+$ (bond lengths in 10^{-10} m) at B3LYP/6–311G(d) level of theory

Slika 7 – a) LUMO (konturna razina = 0,025 a. u.) i b) geometrija (duljine veza u 10^{-10} m) $i\text{-Pr}_3\text{Si}^+$ kationa na B3LYP/6–311G(d) razini teorije

Electrostatic potential maps of Me_3Si^+ and $i\text{-Pr}_3\text{Si}^+$ cations are presented in Fig. 8. The maps show larger localization of positive ESP (blue) at silicon atom in $i\text{-Pr}_3\text{Si}^+$ than in Me_3Si^+ . However, the extent of the ESP can be visually estimated only approximately by the intensity of the blue colour.

Approaching a free silyl cation in condensed phase

In the sense of previous discussions, the goal of generating a free silyl cation in condensed phase can only be realized if the following requirements are achieved:

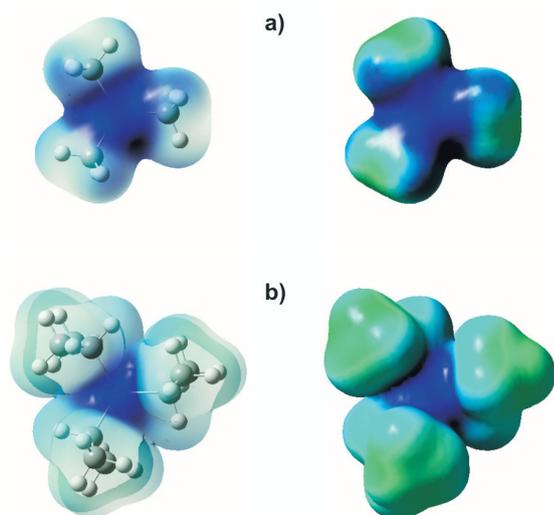


Fig. 8 – Electrostatic potential maps (transparent and solid) of Me_3Si^+ (a) and $i\text{-Pr}_3\text{Si}^+$ (b) (isovalue = 0.004 a. u., ESP range = 0.00 do 0.22 kJ e^{-1}) at B3LYP/6–311G(d) level of theory

Slika 8 – Mape elektrostatskog potencijala (transparent i solid) Me_3Si^+ (a) i $i\text{-Pr}_3\text{Si}^+$ (b) (konturna razina = 0,004 a. u., raspon ESP = 0,00 do 0,22 kJ e^{-1}) na B3LYP/6–311G(d) razini teorije

(1) The silyl cation has to be internally stabilized by inductive or hyperconjugative effects and access to positive centre sterically blocked by bulky substituents. Except alkyl substituents already mentioned, trimethylsilyl (Me_3Si), mesityl (2,4,6-trimethylphenyl, Mes), dialkylboryl (R_2B) and some other substituents have shown eligible characteristics (Fig. 9).^{5,14,16,30,31}

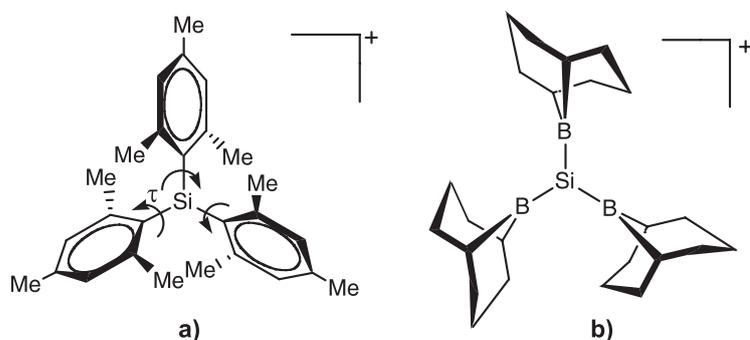


Fig. 9 – a) Mesityl ($\tau \approx 49^\circ$) and b) dialkylboryl substituents

Slika 9 – a) Mezištilni ($\tau \approx 49^\circ$) i b) dialkilborilni supstituenti

(2) The coordination ability of solvent has to be minimized by using weakly nucleophilic solvents, such as CH_2Cl_2 , aromatic compounds or alkanes.^{9,14,17,30,31}

(3) Weakly coordinating counterions should have either delocalized negative charge and/or be sterically demanding to make the attack to a silyl cation more difficult. More recently, anions such as ones shown in Fig. 10 were designed, synthesised and some of them were used in silyl cation chemistry.^{5,8–13,15–17,30–32}

(4) Alternatively, the idea of “intra-solvation” was created.^{5,15} The general structure of bidentated molecular tem-

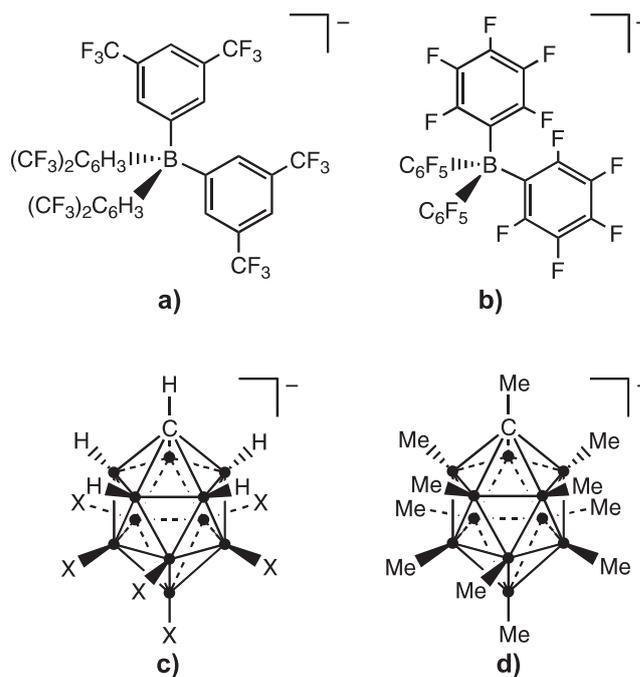


Fig. 10 – Anions: a) = tetrakis(2,4-difluoromethylphenyl)borate, b) = tetrakis(pentafluorophenyl)borate (TPFPB⁻, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$), c) = hexahalocarborene ($[\text{CB}_{11}\text{H}_6\text{X}_6]^-$, X = Br, Cl), d) = dodecamethylcarba-closo-dodecaborate (● = B)

Slika 10 – Anioni: a) = tetrakis(2,4-difluormetilfenil)borat, b) = tetrakis(pentafluorofenil)borat (TPFPB⁻, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$), c) = heksahalo-karboran ($[\text{CB}_{11}\text{H}_6\text{X}_6]^-$, X = Br, Cl), d) = dodekametilkarba-closo-dodekaborat (● = B)

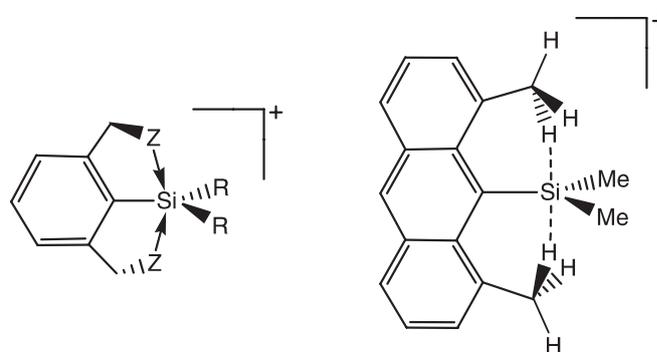


Fig. 11 – Intramolecularly “solvated” silyl cations: a) general structure, b) example with the largest silyl cation character

Slika 11 – Intramolekulski “solvatirani” sililni kationi: a) opća strukturna formula, b) primjer s najvećim sililkationskim karakterom toga tipa

plate with intramolecular nucleophilic “solvent” $-\text{CH}_2-\text{Z}$ was originally developed by van Koten and coworkers (Fig. 11.a). In Fig. 11.b intramolecularly solvated silyl cation with electrostatic $\text{Si} \cdots \text{H}$ interactions is shown, with estimated silyl cation character of 60 % (by eq. 7).

Silyl cations in solution

Two groups, of Lambert and Reed, tried hard to generate free silyl cation in solution.⁵ Lambert claimed that he had generated R_3Si^+ cations (R = Me, Et, *i*-Pr, Me_3Si) with

TPFPB⁻ as counterion in aromatic solvents such as benzene and toluene. These conclusions were based on experimental results, such as ²⁹Si NMR chemical shift and structural quantities (bond distances, pyramidalization, etc). Lambert's results seemed to find further support by parallel work published by Reed, who also studied R₃Si⁺ cations (R = *i*-Pr, *t*-Bu) in aromatic solvents, but with hexahalocarboranes [CB₁₁H₆X₆]⁻, X = Br, Cl, as counterions.

Within relatively short time, Pauling and other three independent groups who carried out elaborate quantum-mechanical calculations (Olsson and Cremer, Schleyer, Apeiloig and coworkers, and Olah and coworkers) criticized Lambert's and Reed's interpretations on the nature of silyl cations in aromatic solvents.^{5,8,9,11} Their investigations showed that silyl cation in aromatic solvents forms a Wheland σ -complex (interaction of Si and C_{Ar} is covalent) with more carbocation than silyl cation character (Fig. 12).

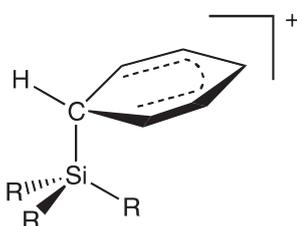
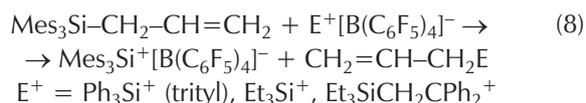


Fig. 12 – Wheland σ -complex
Slika 12 – Whelandov σ -kompleks

All these results suggested that Lambert and Reed had too little information from their experimental work, and the experimental measurements had to be combined with quantum-mechanical calculations to ensure the reliable description of silyl cation character.

Ottosson and coworkers also investigated bulky boryl substituted silyl cation (9-BBN)₃Si⁺ (see Figure 4.b, 9-BBN = 9-borabicyclo[3.3.1]nonyl) because it had lower electrophilicity than those previously investigated.⁵ However, they established weak interactions between (9-BBN)₃Si⁺ cation and aromatic solvent molecule and described it as the weakest Wheland σ -complex ever known, with silyl cationic character of about 40 %.

In spite of the difficulties, Lambert continued in trying to solve the silyl cation problem. Finally, Lambert and Zhao synthesised a trimesitylsilyl cation, Mes₃Si⁺ (given in Fig. 9.a) with TFPBPB⁻ as counterion, by remote attack of a strong electrophile on the allyltrimesityl silane in dry benzene (eq. 8).^{30,31}



Mes₃Si⁺---C₆H₆ represents a weak van der Waals' complex as indicated by the calculated complexation energy of 7.54 kJ mol⁻¹ and the calculated distance of 5.87 Å between the Si atom and the nearest C, which is much larger than Si---C van der Waals' distance of 3.85 Å. Calculated ²⁹Si NMR chemical shift values of "solvated" and nonsolvated Mes₃Si⁺ of δ = 227.6 and 226.3 ppm, respectively, agree with the measured value of δ = 225.5 ppm.³³

However, the problem with that study was considerable π -conjugation between 3p _{π} (Si) orbital and the three aromatic rings. Although that internal π -conjugation stabilizes silyl cation, it reduces the silyl cation character by increasing 3p _{π} (Si) orbital population and spreading positive charge over the aromatic C framework. Cramer and coworkers assessed that π -conjugation in Mes₃Si⁺ is mostly retained (degree of electron delocalization is about 70 %) even though orbitals' overlaps are not maximal because in equilibrium form the mesityl groups have a propeller-like arrangement around the Si atom with twist angles of 47.3 to 49° (depending on the calculation method) or 49.2° (average experimental value) out of the SiC₃ reference plane (see Figs 9.a and 13). However, LUMO τ of Mes₃Si⁺ is dominated by 3p _{π} (Si) orbital, but it is filled up 40 % (10 % more than the upper limit for totally free silyl cation). Therefore, one can speak of the first free silyl cation but with substantial positive charge delocalization.³⁵ However, silicon is significantly larger than carbon and, even though it is considerably more electropositive, its cation is less easily stabilized by π -conjugation (or hyperconjugation) and delocalization of charge is smaller than in carbocation.

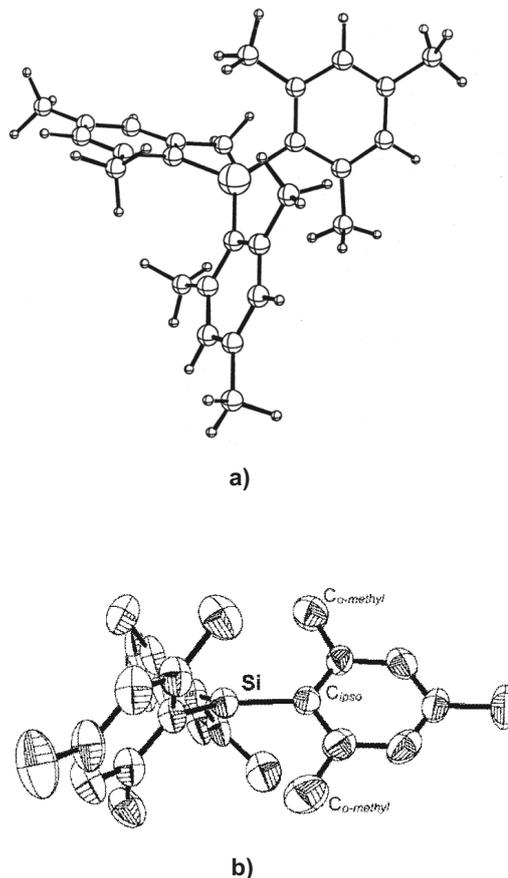


Fig. 13 – Trimesitylsilyl cation: a) calculated B3LYP/6–31G(d) structure, b) crystal structure³⁴

Slika 13 – Trimezitilsililni kation: a) računski B3LYP/6–31G(d) struktura, b) kristalna struktura

In analogy with trimesitylsilyl cation, Lambert and Lin synthesised tridurylsilyl cation, (duryl is 2,3,5,6-tetramethylphenyl) by remote attack of a strong electrophile on the allyltriduryl silane.³⁶

Free silyl cations based on analogy to aromatic ions (homocyclopropenylum and tropylium) rather than to trialkyl or triaryl carbenium ions have also been prepared.³⁷

Silyl cations in solid state

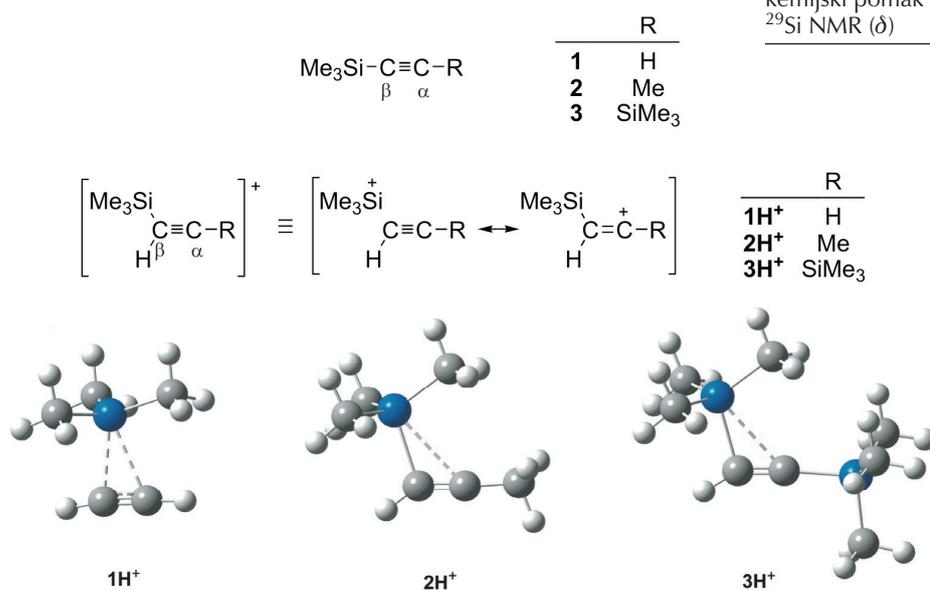
Čičak *et al.* reported results and discussion of possible silyl-cationic intermediates in reactions of some trimethylsilylacetylenes with superacid SbF_5/HF in solid state.²⁹ These reactions were studied by the matrix isolation technique and IR spectroscopy (matrix isolation spectroscopy) in combination with high-level quantum-mechanical calculations.

They selected solid state with the intention to avoid coordination of silyl cation with neighbouring molecules, and low temperatures to slow down the reactions.

The cationic adducts 1H^+ , 2H^+ and 3H^+ , which could be formed by protonation of trimethylsilylacetylenes **1**, **2** and **3** (Scheme 4), were examined at the B3LYP/6–311G(d, p) level of theory. It is well known that these species are stabilized by the β -silicon effect, which has already been commented.

In order to estimate the degree of the silyl cation character of protonated trimethylsilylacetylenes 1H^+ – 3H^+ several molecular properties such as structural features, electron distributions, intramolecular interaction energies and NMR chemical shifts are determined by adequate quantum-mechanical techniques and by comparing cationic adducts with unprotonated trimethylsilylacetylenes (**1** – **3**) and free trimethylsilyl cation. All of these criteria have shown that cationic adduct 1H^+ has a larger degree of silyl cation character than the other two, 2H^+ and 3H^+ . All the examined criteria and estimated silyl cation character of 1H^+ are presented in Table 9.

The criteria used did not give the same evaluation of the degree of the silyl cation character of protonated trimethylsily-



Scheme 4
Shema 4

Table 9 – Results of quantum-mechanical calculations and estimation of silyl cation character for the adduct 1H^+ (B3LYP/6–311G(d, p))

Tablica 9 – Rezultati kvantno-mehaničkih računa i procjena silyl-kationskog karaktera za adukt 1H^+ (B3LYP/6–311G(d, p))

Criterion Kriterij	1	1H^+	Me_3Si^+	Interaction (Si-cation character) Međudjelovanje (Si-kationski karakter)
Si–C β bond distance	0.185 nm	0.237 nm	–	weak slabo
Si–C β bond order	0.812	0.231	0.000	(72 %)
Si–C β red veze				
C–Si hyperconjugativity	0.188	0.769	–	
C–Si hiperkonjugativnost				
pyramidalization angle	18.3°	11.4°	0.0°	(38 %)
piramidalizacijski kut				
sum of the angles around Si	331.8°	348.6°	360.0°	(60 %)
zbroj kuteva oko Si				
interaction energy	–	–61.13 kJ mol ^{–1}	–	not strong ne jako
međudjelovanja				
Si charge	1.558 e	1.752 e	1.944 e	(50 %)
naboj Si				
R ₃ Si charge	0.439 e	0.769 e	1.000 e	(59 %)
naboj R ₃ Si				
LUMO population	–	0.303 e	0.148 e	(free silylium ion) (slobodni sililni ion)
populacija LUMO				
²⁹ Si NMR chemical shift (δ)	–33.7 ppm	118.0 ppm	404.6 ppm	weak (34 %) slabo (34 %)
kemijski pomak				
²⁹ Si NMR (δ)				

lacetylene 1H^+ , and Si–C β interaction could be characterized from weak to considerable.

LUMOs of cationic adducts, which in all cases are dominated by the $3p_\pi(\text{Si})$ orbital, are shown in Fig. 14. The LUMO orbital of 1H^+ adduct is filled up 30 %, which, according to those criteria makes it the true silyl cation. The population of the LUMO orbital in free Me_3Si^+ is 0.148 e due to the C–H hyperconjugative effect, 0.155 e less than in 1H^+ . It means that there is an interaction of trimethylsilyl-group with the acetylene part donating electrons to the LUMO at an extent equal to C–H hyperconjugation.

The LUMO orbitals of 2H^+ and 3H^+ adducts are filled up 36 and 37 %, respectively.

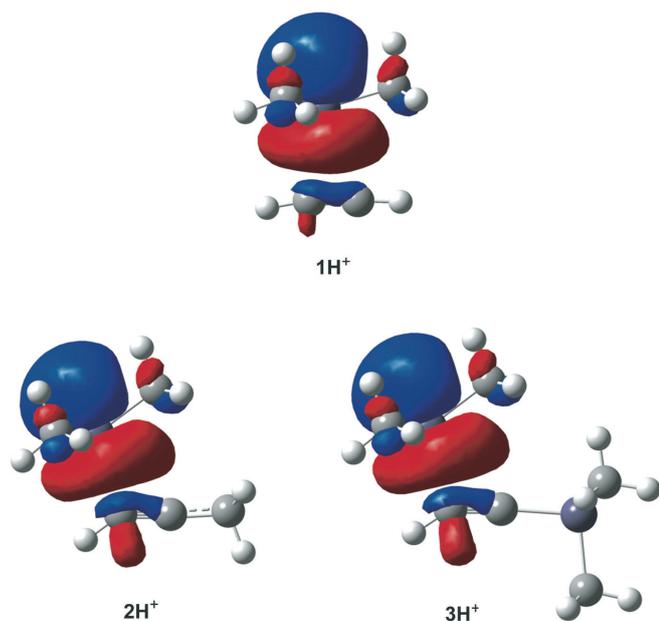


Fig. 14 – LUMOs of the cationic adducts $1H^+$ – $3H^+$ (isovalue = 0.025 a. u.)

Slika 14 – LUMO kationskih adukata $1H^+$ – $3H^+$ (konturna razina = 0,025 a. u.)

Electrostatic potential maps are given in Fig. 15. It can be seen that the Si-atom in $1H^+$ adduct has a substantial amount of positive ESP.

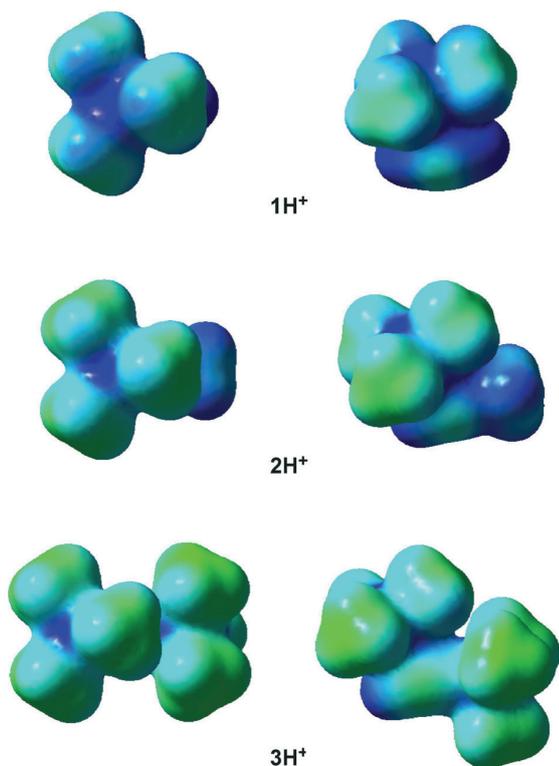


Fig. 15 – Electrostatic potential maps of cationic adducts $1H^+$ – $3H^+$ (isovalue = 0.004 a. u., ESP range = 0.00 to 0.22 kJ e⁻¹)

Slika 15 – Mape elektrostatskog potencijala kationskih adukata $1H^+$ – $3H^+$ (konturna razina = 0,004 a. u., ESP raspon = 0,00 do 0,22 kJ e⁻¹)

However, it was concluded that protonated trimethylsilylacetylenes $1H^+$ (even $2H^+$ and $3H^+$) have much more silyl cation than carbocation character. Therefore, it is not quite correct to call them β -silyl substituted vinyl cations, as usual, but silyl cations weakly coordinated with acetylenes.

Concluding remarks

Silicon and carbon compounds show considerable differences in their chemical properties, which originate from their fundamental atom characteristics.

Although preparations of free silyl cations in condensed phase are extremely difficult (with some successful attempts), the degree of the silyl cation character still remains the main question. The major problem comes from the interactions with a wide variety of π - and σ -electron donating compounds or groups – solvent molecules, counterions, neighbouring groups – forming tetra- or higher-coordinated Si compounds.

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References:

Literatura:

1. P. Atkins, T. Overton, J. Rourke, M. Weller, F. Armstrong, *Inorganic Chemistry*, Oxford University Press, Oxford New York, 2006.
2. C. Eaborn, *Organosilicon Compounds*, Butterworths Scientific Publications, London, 1960.
3. Y. Apeloig, *Theoretical Aspects of Organosilicon Compounds* (Chapter 2); In: *The Chemistry of Organic Silicon Compounds*, Ed. S. Patai and Z. Rappoport, John Wiley & Sons, 1989, p. 57–225.
4. M. Karni, Y. Apeloig, J. Kapp, P. v. R. Schleyer, *Theoretical Aspects of Compounds Containing Si, Ge, Sn and Pb* (Chapter 1), In: *The Chemistry of Organic Silicon Compounds*, Vol. 3, Ed. Z. Rappoport and Y. Apeloig, John Wiley & Sons, 2001, p. 1–163.
5. C.–H. Ottosson, E. Kraka, D. Cremer, *Theory as a Viable Partner for Experiment – The Quest for Trivalent Silylium Ions in Solution*; In: *Pauling's Legacy: Modern Modelling of the Chemical Bond*, Ed. Z. B. Maksić and W. J. Orville-Thomas, *Theoretical and Computational Chemistry*, Vol. 6, Elsevier Science B. V., 1999, p. 231–301.
6. G. K. S. Prakash, S. Keyaniyan, R. Aniszfeld, L. Heiliger, G. A. Olah, R. C. Stevens, H.–K. Choi, R. Bau, *J. Am. Chem. Soc.* **109** (1987) 5123.
7. G. A. Olah, G. Rasul, L. Heiliger, J. Bausch, G. K. S. Prakash, *J. Am. Chem. Soc.* **114** (1992) 7737.
8. P. v. R. Schleyer, P. Buzek, T. Müller, Y. Apeloig, H.–U. Siehl, *Angew. Chem. Int. Ed. Engl.* **32** (10) (1993) 1471.
9. L. Olsson, D. Cremer, *Chem. Phys. Lett.* **215** (5) (1993) 433.
10. J. B. Lambert, L. Kania, S. Zhang, *Chem. Rev.* **95** (1995) 1191.
11. L. Olsson, C.–H. Ottosson, D. Cremer, *J. Am. Chem. Soc.* **117** (1995) 7460.
12. M. Arshadi, D. Johnels, U. Edlund, C.–H. Ottosson, D. Cremer, *J. Am. Chem. Soc.* **118** (1996) 5120.

13. Z. Xie, J. Manning, R. W. Reed, R. Mathur, P. D. W. Boyd, A. Benesi, C. A. Reed, *J. Am. Chem. Soc.* **118** (1996) 2922.
14. C.–H. Ottosson, D. Cremer, *Organometallics* **15** (26) (1996) 5495.
15. J. Belzner, *Angew. Chem. Int. Ed. Engl.* **36** (12) (1997) 1277.
16. C.–H. Ottosson, K. J. Szabó, D. Cremer, *Organometallics* **16** (11) (1997) 2377.
17. C. A. Reed, *Acc. Chem. Res.* **31** (6) (1998) 325.
18. Z. Xie, R. Bau, A. Benesi, C. A. Reed, *Organometallics* **14** (8) (1995) 3933.
19. S. K. Shin, J. L. Beauchamp, *J. Am. Chem. Soc.* **111** (1989) 900.
20. H.–U. Siehl, T. Müller, Silyl-substituted Carbocations (Chapter 12), In: *The Chemistry of Organic Silicon Compounds*, Vol. 2, Ed. Z. Rappoport and Y. Apeloig, John Wiley & Sons, 1998, p. 595–701.
21. J. B. Lambert, Y. Zhao, R. W. Emblidge, L. A. Salvador, X. Liu, J.–H. So, E. C. Chelius, *Acc. Chem. Res.* **32** (1999) 183.
22. H.–U. Siehl, F.–P. Kaufmann, *J. Am. Chem. Soc.* **114** (1992) 4937.
23. H.–U. Siehl, F.–P. Kaufmann, K. Hori, *J. Am. Chem. Soc.* **114** (1992) 9343.
24. H.–U. Siehl, F.–P. Kaufmann, Y. Apeloig, V. Braude, D. Danovich, A. Berndt, N. Stamatidis, *Angew. Chem. Int. Ed. Engl.* **30** (11) (1991) 1479.
25. T. Müller, R. Meyer, D. Lennartz, H.–U. Siehl, *Angew. Chem. Int. Ed. Engl.* **39** (17) (2000) 3074.
26. J. B. Lambert, Y. Zhao, H. Wu, *J. Org. Chem.* **64** (1999) 2729.
27. J. B. Lambert, Y. Zhao, *J. Am. Chem. Soc.* **118** (1996) 7867.
28. X. Li, J. A. Stone, *J. Am. Chem. Soc.* **111** (1989) 5586.
29. H. Čičak, Doctoral Thesis, Zagreb, 2006.
30. J. B. Lambert, Y. Zhao, *Angew. Chem. Int. Ed. Engl.* **36** (1977) 400.
31. J. B. Lambert, Y. Zhao, H. Wu, W. C. Tse, B. Kuhlmann, *J. Am. Chem. Soc.* **121** (1999) 5001.
32. C. A. Reed, *Acc. Chem. Res.* **31** (1998) 133.
33. E. Kraka, C. P. Sosa, J. Gräfenstein, D. Cremer, *Chem. Phys. Lett.* **279** (1997) 9.
34. K.–C. Kim, C. A. Reed, D. W. Elliott, L. J. Mueller, F. Thaim, L. Lin, J. B. Lambert, *Science* **297** (2002) 825.
35. P. P. Gaspar, *Science* **297** (2002) 785.
36. J. B. Lambert, L. Lin, *J. Org. Chem.* **66** (25) (2001) 8537.
37. J. B. Lambert, Y. Zhao, S. M. Zhang, *J. Phys. Org. Chem.* **14** (2001) 370.

List of symbols

Popis simbola

- a_0 – Bohr radius, $5.291772 \cdot 10^{-11}$ m
– Bohrov radijus, $5.291772 \cdot 10^{-11}$ m
- a. u. – atomic unit
– of dipole polarizability, $1.482 \cdot 10^{-31}$ m³
– of isosurface value (isovalue), $e a_0^{-3}$
– atomska jedinica
– dipolne polarizabilnosti, $1,482 \cdot 10^{-31}$ m³
– konturne razine, $e a_0^{-3}$
- d – bond length, m, nm
– duljina veze, m, nm
- DN – donor number, kcal mol⁻¹, kJ mol⁻¹
– donorski broj, kcal mol⁻¹, kJ mol⁻¹
- E – energy, eV, J, kJ mol⁻¹
– energija, eV, J, kJ mol⁻¹
- e – elementary charge, $1.60218 \cdot 10^{-19}$ C
– elementarni naboj, $1,60218 \cdot 10^{-19}$ C

- ESP – electrostatic potential range, kJ e⁻¹
range – raspon elektrostatskog potencijala, kJ e⁻¹
- g – gas phase
– plinska faza
- l – liquid phase
– tekuća faza
- n – whole number
– cijeli broj
- q – electrostatic charge, C
– elektrostatski naboj, C
- s – solid phase
– čvrsta faza
- δ^- – partial negative charge, C
– parcijalni negativni naboj, C
- δ^+ – partial positive charge, C
– parcijalni pozitivni naboj, C
- δ – chemical shift, ppm
– kemijski pomak, ppm
- ϵ – dielectric
– dielektričnost
- π – bond
– veza
- σ – bond
– veza
- τ – dihedral angle, °
– diedarski kut, °

Abbreviations

Popis kratica

- [7s6p2d/5s4p1d/3s1p]
– Kutzelnigg's basis set of triple-zeta (TZ) quality
– Kutzelniggov osnovni skup kvalitete triple-zeta (TZ)
- 6–31G(d), 3–21G
– Pople's split-valence basis sets of double-zeta (DZ) quality
– Popleovi split-valence osnovni skupovi kvalitete double-zeta (DZ)
- B3LYP – Becke's 3-parameter exchange functional and Lee, Young and Parr's correlation functional
– Beckeov tročlani funkcional za izmjenu i Lee, Young i Parrov funkcional za korelaciju
- DFT – density functional theory
– teorija funkcionala gustoće
- ESP – electrostatic potential
– elektrostatski potencijal
- fc – "frozen core" calculation method
– metoda računanja "frozen core"
- HF – Hartree-Fock method
– metoda Hartree-Fock
- LUMO – lowest unoccupied molecular orbital
– najniža nepopunjena molekulska orbitala
- MP n – Møller-Plesset perturbation method of the n th order
– Møller-Plessetova perturbacijska metoda n -tog reda
- STO–3G – Slater type orbitals simulated by 3 Gaussians (minimal basis set)
– orbitale Slaterovog tipa opisane pomoću 3 Gaussiana (najmanji osnovni skup)

SAŽETAK

Problem slobodnog trikoordiniranog sililnog kationa

H. Čičak

Silicij je, zbog svoje velike zastupljenosti u našoj okolini, kao i zbog široke primjenljivosti kako u elementarnom obliku tako i u spojevima, jedan od najkorisnijih elemenata. Zbog nekih sličnih svojstava elemenata silicija i ugljika (tablica 1), kao i analognih spojeva koje tvore, pojavilo se pitanje o mogućnosti postojanja života temeljenog na siliciju. Ipak, razlike u svojstvima koje postoje između tih dvaju elemenata utječu na tvorbu niza strukturno različitih spojeva i različito ponašanje u kemijskim reakcijama. Osnovne razlike mogu se svesti na veću veličinu i polarizabilnost silicijeva atoma, difuznije valentne orbitale, postojanje d orbitala koje također mogu sudjelovati u vezanju te manju elektronegativnost. Zbog tih se razlika pokazalo da silicij teže stvara spojeve s višestrukim vezama i ne može tvoriti tako velik broj raznih vrsta spojeva kao što to može ugljik, ali može tvoriti stabilne hipervalentne spojeve. Utjecaj tih razlika na duljine i jakosti veza, kao i parcijalne naboje na atomima u nekim molekulama prikazane su u tablicama 2, 3 i 4. Uloga p i d orbitala silicija u stvaranju π veza prikazana je na slikama 1 i 2.

Glavna rasprava na području organosilicijeve kemije vodi se oko pitanja postojanja planarnih trikoordiniranih kationa u kondenziranoj fazi (R_3Si^+ , R = alkil, aril), analognih karbokationima (R_3C^+), koji su poznati i opisani kao slobodne vrste. Iako su sililni kationi termodinamički stabilniji od ugljikovih analoga (tablica 5 i izodezmičke reakcije (1) – (3)), oni su vrlo reaktivni zbog velike elektrofilnosti i mogućnosti hipervalentne koordinacije. S druge strane, stabilizacija pomoću inductivnih i hiperkonjugacijskih učinaka (slika 3) te veći sterički učinci čine karbokatione manje osjetljivima od sililnih kationa na solvataciju i druge vanjske utjecaje.

Također su intenzivno proučavani silil-supstituirani karbokationi. Pokazalo se da su kationske vrste koje imaju silicij u β -položaju (slika 4) stabilizirane β -sililnim učinkom (shema 1), koji je izravno povezan sa stupnjem premoštenja (slika 5). Veličina β -sililnog učinka može se izraziti pomoću veličine nazvane hiperkonjugativnost. Silil-supstituirani karbokationi sa silicijem u α -odnosno dalje od β -položaja nisu dodatno stabilizirani u odnosu na katione s ugljikom na mjestu silicija (shema 2). Stoviše, α -silil-supstituirani karbokationi su destabilizirani.

Priprava slobodnih sililnih kationa u kondenziranoj fazi izrazito je teška jer nastaju kationske vrste s većim ili manjim stupnjem sililkationskog karaktera. U Tablici 6 je navedeno više eksperimentalnih i teorijskih kriterija za utvrđivanje stupnja sililkationskog karaktera koji su primijenjeni u literaturi, kao što su: strukturne veličine, energija kompleksiranja (jednadžbe (4) i (5)), ^{29}Si NMR kemijski pomak (tablica 7, shema 3 i jednadžbe (6) i (7)), parcijalni naboji i popunjenost LUMO sililnog kationa kojom dominira $3p_{\pi}(Si)$ AO (primjeri jednostavnih sililnih kationa dani su u tablici 8 i na slikama 6 i 7). Popunjenost LUMO sililnog kationa procijenjena je jednim od najkvalitetnijih kriterija te je postavljena gornja granica od 30 % popunjenosti da bi se sililni kation mogao nazvati slobodnim. Sililkationski karakter može se procijeniti i vizualno pomoću mapa elektrostatskog potencijala (slika 8).

Kako bi se pripravio sililni kation sa što većim sililkationskim karakterom, potrebno ga je interno stabilizirati pomoću odgovarajućih supstituenata (neki primjeri dani su na slici 9) te upotrijebiti nenukleofilna otapala i slabo koordinirajuće anione (slika 10). Jedan od načina je i intramolekulska "solvatacija" prikazana na slici 11. I uz te poznate činjenice malo je uspješnih pokušaja pripreme sililnih kationa. Jedan od neuspjelih je sinteza nekoliko Whelandovih σ -kompleksâ (slika 12), koje su pripravili Lambert i Reed sa svojim istraživačkim skupinama, za koje su prvobitno smatrali da se radi o slobodnim sililnim kationima.

Prvi slobodni sililni kation, trimezitsililni kation (slika 13) i, analogno njemu, tridurilsililni kation pripravili su Lambert i sur. Također su izolirani slobodni sililni kationi analogni aromatičnim ionima (homociklopropenilni i tropilij). Međutim u tim je sililnim kationima smanjen sililkationski karakter internom π -konjugacijom. Čičak i sur. pripravili su neke sililkationske međuprodukte ($Me_3Si-CH\equiv CR$)⁺ u čvrstom stanju (shema 4). Na temelju provedenih kvantno-mehaničkih računa zaključili su da ti adukti imaju znatno veći sililkationski nego karbokationski karakter, od kojih je najveći za R=H (tablica 9, slike 14 i 15).

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