

Comparison of steric hindrance in silylenium and carbenium cations and their complexes

Natural steric analysis

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Abstract

Steric effect in the complexes of tri-coordinate silylenium and carbenium ions with model nucleophiles is discussed based on calculated energies of complex formation and on natural steric analysis (a part of the NBO theory). While the energies of complexation of CH_3^+ are greater than those of SiH_3^+ , for trimethyl-substituted cations the order is reversed. This observation is interpreted in terms of smaller steric hindrance of trimethylsilyl cation compared to *t*-butyl cation. Natural steric analysis points to the potentials and difficulties in separate treatment of steric and electron delocalization effects on stabilization of these species.

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1. Introduction

Three-coordinate silyl cations (known under the names: silylium, silylenium and silicenium) were the elusive species until very recently, when the first evidence for such species was provided [1]. Crystal structure of $\text{Mes}_3\text{Si}^+\text{HCB}_{11}\text{Me}_5\text{Br}_6^-(\text{C}_6\text{H}_6)$ (where Mes = 2,4,6-trimethylphenyl) shows planar, tri-coordinated center, well separated from carborane anions and benzene solvate molecules. The ^{29}Si -NMR chemical shift in the solid state is almost identical to that in benzene solution [2] and in gas-phase calculations [3,4] indicating that the cationic character of silicon is preserved in all phases.

Silylenium ions, despite their greater thermodynamic stability compared with carbenium ions, confirmed by the gas-phase studies reviewed in Ref. [5] and by theoretical calculations reviewed in Refs. [6–8], in condensed phases are much more reactive than their carbon analogues. Larger size of silicon atom and longer bonds to substituents make Si more accessible to the approach of a reactant, as compared with carbon. Thus,

reactions at silicon are generally less sensitive to steric hindrance, as it was shown, for example, in the kinetic study of the hydride transfer reaction [9]. Silicon is also more electropositive than carbon and the positive charge in $\equiv\text{Si}^+$ is highly localized on silicon, while in $\equiv\text{C}^+$ it is largely dispersed over the substituents. This results in stronger electrostatic attraction forces between silylenium cation and electron-rich species [10].

Therefore, silyl cations react very rapidly with any nucleophile and are strongly solvated even in weakly nucleophilic solvents. The degree of bonding in such complexes may be greater than in similar carbenium ion systems [10,11]. Possibility of synthesizing of stable, “free” silylenium ions in condensed phases has been a subject of long dispute [2,7]. Factors leading to silylenium ion stabilization, including electron delocalization (inductive, conjugative and hyperconjugative) and steric effects are comprehensively reviewed in Ref. [7]. The general conclusion is that both types of stabilization are required to obtain relatively unreactive, long-living silylenium ions [7,8]. However, the efficient protection of the silylenium center requires very large steric hindrance, as this is the case for mesityl substituents used by Lambert and coworkers [1,2].

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Electron delocalization effects in silylenium and carbenium ions were extensively studied by theoretical methods [6,7,12], while steric effect focused less attention. For understanding the reaction mechanisms, it would be helpful to be able to estimate the role of each effect more precisely. However, the separation of the effects is very difficult. Every structural change in a molecule induces changes in electron delocalization as well as in steric repulsion. The overall energy change involves all co-operating and co-dependent effects. Recent development of the natural bond orbital (NBO) theory offers the possibility of quantitative estimation of the steric repulsion in a molecule and between the molecular units in the complex [13–15] and to analyze delocalization and repulsion interactions separately, as it was nicely shown in the study of the internal rotation barriers about single bonds in organic molecules [16].

The idea of this work is to estimate the change in the steric repulsion with increase in the size of substituents in a series of simple silylenium cation–nucleophile complexes in comparison with the analogous carbenium ion complexes, using the NBO method. Natural steric analysis is a relatively recent method and its scope of functionality is not fully recognized. Therefore, it would be interesting to examine its applicability to the charged complexes containing silicon.

2. Theoretical methods

Geometry optimizations, harmonic frequencies and zero-point energies were calculated using the GAUSSIAN 98 package [17], with the hybrid density functional B3LYP/6-31G* method [18]. Stationary points were confirmed by vibrational analysis. Final single-point electronic energies were calculated at the B3LYP/6-311+G(2d,p) level. Vibrational components of the thermal energy were scaled by 0.98. Enthalpies of complex formation were calculated at 298 K using corrections obtained from frequency analysis, including rotational and translational terms. Energies and enthalpies of complex formation were corrected for the basis set superposition error (BSSE) [19] using the counterpoise option built in the GAUSSIAN program. At this level of theory, these corrections were in the range 0.4–1.0 kcal mol⁻¹. Orbital population and Wiberg bond orders [20] were calculated with the NBO 3.0 program implemented in GAUSSIAN 98. Natural steric analysis [13,14] was performed at the HF/6-311+G(2d,p) level using the NBO 5.0 program [15] which applied the wavefunction information file generated by the earlier version of NBO (3.0) implemented in GAUSSIAN 98.

Natural steric analysis expresses total steric exchange repulsion in a molecule as the energy difference due to orbital orthogonalization [15]. The intermolecular steric

exchange energy between R₃X⁺ and a nucleophile was calculated as the difference between the steric exchange energy for the R₃X⁺⋯Nu complex and the steric exchange energy for the system consisting of the R₃X⁺ and Nu units (in the same geometry as in the complex) separated by a large distance (the distance of 12 Å was applied, as it is assumed that the repulsive energy between molecular units is 0 at this distance). Indeed, calculations performed for various distances between molecular units showed that further increase of separation did not change the calculated steric energy. The relatively high level of calculations was required to achieve reliable results of steric analysis, since the silicon ionic species appeared to be very sensitive to basis set quality. We have tested the system at the Hartree-Fock level with different basis sets: Pople's sets up to 6-311+G(3df,2pd) and Dunning's correlation consistent basis sets up to cc-pVTZ. The results are presented in Table 1. Although the convergence was not reached, the results obtaining with basis sets of triple zeta quality were fairly consistent within a series of homologue compounds. B3LYP/6-311+G(2d,p) calculations for several CH₃⁺ and SiH₃⁺ complexes gave similar results to the HF/6-311+G(2d,p) method. The example results for CH₃–NH₃⁺ and SiH₃–NH₃⁺ complexes are also given in Table 1. Since DFT calculations were more time-consuming than those at the Hartree-Fock level, the HF/6-311+G(2d,p) method was chosen as a compromise between accuracy and the computing time.

Pauling bond order was calculated according to Eq. (1) [21]:

$$D(n) = D(1) - 0.60 \log n \quad (1)$$

where $D(1)$ is the “normal” bond length for a bond of order 1.0 and $D(n)$ the calculated bond length for a bond of order n . The following “normal” bond distances $D(1)$ were assumed [22]: $r(\text{Si}-\text{C}-\text{sp}^3) = 1.860 \text{ \AA}$;

Table 1

The steric repulsion energy between H₃X⁺ and NH₃ units, measured as the difference between the steric exchange energies in the complex and in the system of molecular units H₃X⁺ and NH₃ separated by 12 Å

Method	CH ₃ ⁺ –NH ₃	SiH ₃ ⁺ –NH ₃
HF/6-31G*	79.0	71.4
HF/6-311+G(2d,p)	59.3	30.1
HF/6-311+G(2df,2p)	46.7	32.9
HF/6-311++G(3df,2pd)	41.7	19.3
HF/cc-pVDZ	81.7	55.6
HF/cc-pVTZ	47.5	32.5
B3LYP/6-311+G(2d,p)	44.8	25.6
B3LYP/6-311++G(3df,2pd)	40.5	20.3

$\Delta E_{\text{st}} = E_{\text{st}}(\text{complex}) - E_{\text{st}}(r(\text{X}^+ \cdots \text{Nu}) = 12 \text{ \AA})$ calculated by the NBO 5.0 program.

$r(\text{Si}-\text{C}-\text{ar}) = 1.870 \text{ \AA}$; $r(\text{Si}-\text{O}(\text{C})) = 1.645 \text{ \AA}$; $r(\text{Si}-\text{N}) = 1.750 \text{ \AA}$; $r(\text{Si}-\text{Cl}) = 2.070 \text{ \AA}$; $r(\text{Si}-\text{S}) = 2.145 \text{ \AA}$.

All calculations were performed for the gas-phase conditions.

3. Results and discussion

The important difference between C and Si is that silicon, in contrast to carbon, relatively easily forms intermediates with expanded coordination at Si (five- and six-coordinate). This behavior arises from both electronic and steric reasons and has important consequences for the problem studied here, as the silylenium cation may be stabilized by two molecules of a nucleophile, located preferably in axial arrangement [23,24]. Both tetra- and penta-coordinate complexes of silylenium ions with nucleophiles are known. The domination of a particular form depends on various factors, such as the electronic nature of a nucleophile, of the leaving group and of the ligands at silicon, as well as their steric hindrance (for review, see Refs. [25,26]). For example, expansion of coordination at silicon is favored for hydrogen-substituted silicon species [27,28]. For larger non-polar substituents, both forms may exist in equilibrium [24,28]. The tetra-coordinate form may eventually dominate, as it is in alkylnitriles solution, where silylenium ions were reported to form 1:1 complexes with a solvent [29]. X-ray analyses also provide evidence for tetra-coordinate silylenium ion complexes in the solid state [30].

Taking this into account, we focused here mainly on tetra-coordinate (1:1) complexes of silylenium cations to make possible a direct comparison of the steric effect in silylenium and carbenium ion complexes. However, the steric effects in the example penta-coordinate (2:1) complexes, $\text{H}_3\text{N} \cdots \text{SiX}_3^+ \cdots \text{NH}_3$ and $\text{H}_3\text{N} \cdots \text{CX}_3^+ \cdots \text{NH}_3$ ($\text{X} = \text{H}, \text{Me}$), were also calculated and compared with those in the corresponding 1:1 complexes.

The criteria used for estimating the degree of “freedom” of the carbenium or silylenium cation in the presence of a nucleophile are: geometry (deviation from planarity, the distance between C^+ or Si^+ and Nu, and the related bond index), the energy of interaction with nucleophile and the NMR chemical shift [7,8]. All model complexes are analyzed with respect to the above criteria except NMR and in relation to the calculated steric repulsion between the cation moiety and a nucleophile.

3.1. Geometries

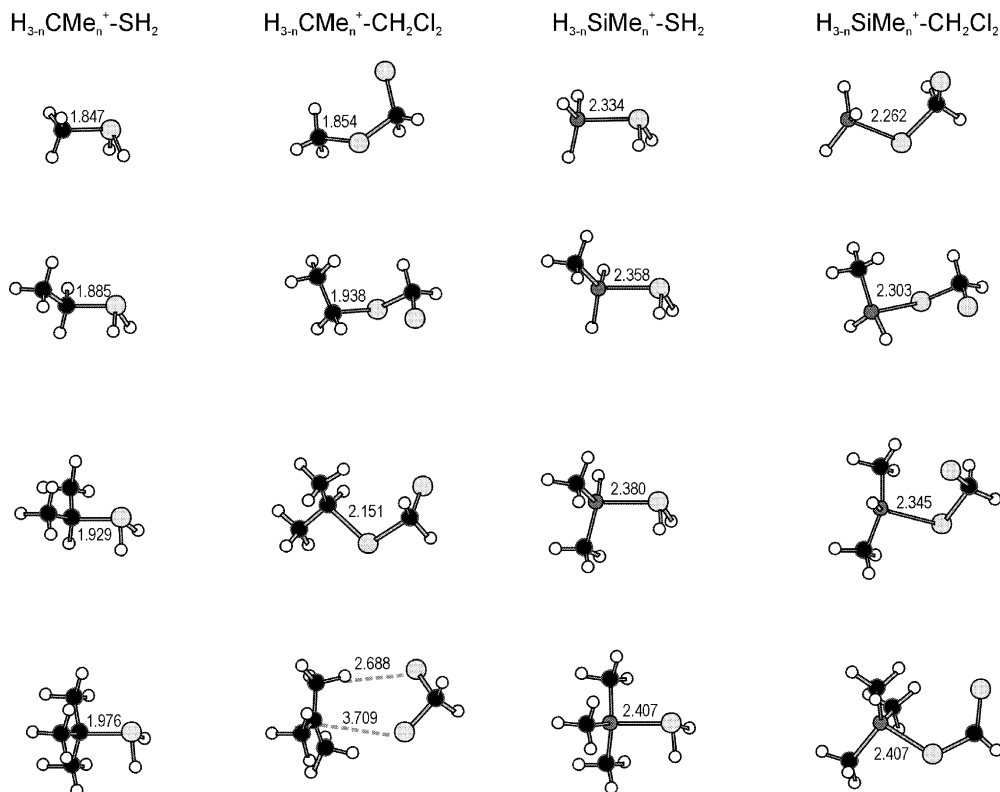
A series of complexes of simple silylenium and carbenium ions, $\text{H}_{3-n}\text{SiMe}_n^+$, $\text{H}_{3-n}\text{CMe}_n^+$, with model nucleophiles, H_2O , H_2S , H_3N , CH_2O , CH_3CN , CH_2Cl_2 , and C_6H_6 , and complexes of Et_3Si^+ and Et_3C^+ with

H_2O and H_3N were studied using the hybrid density functional method, B3LYP/6-31G*. These substituents are too small to assure the “free” character of the silylenium cation, but such simple models make possible to study the trends of change in the steric effect with the increasing size of substituents at C and Si at a moderate computational cost. Some of these complexes were investigated previously with a variety of theoretical methods [6–8,11,12]. Therefore, their geometries are discussed here very briefly. Only the structures of the 1:1 complexes calculated for the first time (to our knowledge) are shown in Schemes 1 and 2. Structures of the 2:1 complexes with NH_3 are shown in Scheme 3. Geometries of $\text{H}_3\text{N} \cdots \text{CH}_3^+ \cdots \text{NH}_3$ and $\text{H}_3\text{N} \cdots \text{SiH}_3^+ \cdots \text{NH}_3$ complexes were calculated previously at different levels of theory [8,11]. In Schemes 1–3, the color for carbon atoms is black, silicon is dark grey, heteroatoms is light grey, and hydrogen is white. The distances in \AA between central atoms in the cation and the nucleophile are shown. Full structural and energetic data are available as the supplementary information.

All cations possess a planar structure, as it was found previously [6,7], except CH_3CH_2^+ , which has a “non-classical” C_{2v} geometry with a hydrogen atom bridging two carbons (Scheme 4) [12].

B3LYP/6-31G* geometries of complexes with nucleophiles such as H_2O , NH_3 , CH_2O , and CH_3CN are similar to those reported previously using different levels of theory [11,12]. Carbenium ion–benzene complexes are σ -type Wheland species, while the geometries of $\text{R}_3\text{Si}^+ - \text{C}_6\text{H}_6$ complexes indicate the hybrid π – σ interaction with the angle between the Si–C linkage and the ring plane being in the range 102 – 107.5° [7,30,31]. Interestingly, although geometries of complexes point to the interaction of the cation with one carbon in the ring (*ipso*-carbon), the interactions with the two neighboring *ortho*-carbons are also non-negligible (Wiberg bond indices of these interactions are ca. 0.03 for C^+ and 0.05 for Si^+).

In addition to these model nucleophilic solvents, the structures of the complexes with H_2S and CH_2Cl_2 were calculated. H_2S is the representative of a soft nucleophile and it is known that its bond to Si shows more covalent character, compared to hard donors [24]. Dichloromethane is a common solvent routinely applied in ionic reactions. It has been assumed to be relatively inert in ionic systems. However, calculations showed that it interacts with carbenium and silylenium cations via the lone pair of a chlorine atom. In the case of *t*-butyl cation, the interaction is very weak (Wiberg bond order < 0.01) and the enthalpy of complex formation of ca. -5 kcal mol^{-1} is mostly due to the interaction of the methyl hydrogen (which bears a partial positive charge) with the other chlorine atom (Scheme 1). Planar geometry of the cation confirms that there is almost

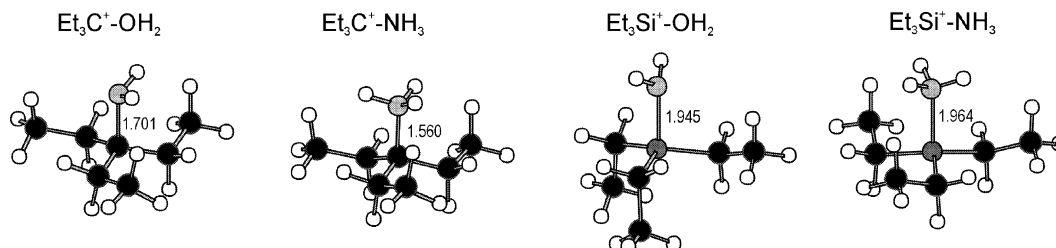


Scheme 1.

no interaction with the carbenium center. All other 1:1 complexes studied here reveal a considerable deviation from planarity (Schemes 1 and 2).

The bipyramidal penta-coordinate species resulted from interaction of $CX_3^+-NH_3$ with the second $N'H_3$ molecule, $X = H$ (D_{3h} symmetry) and Me (C_{3h} symmetry), are the transition states. The structure of minimal energy (C_{3v} symmetry) involves a weak interaction ($\Delta H^{298} = -7.0$ kcal mol $^{-1}$) between the $CH_3^+-NH_3$ complex and $N'H_3$ ($r(C-N') = 2.936$ Å). The corresponding distance and enthalpy of interaction for the $H_3N-Me_3C^+\cdots N'H_3$ complex (C_{3v} symmetry) are $r(C-N') = 3.784$ Å and $\Delta H^{298} = -8.4$ kcal mol $^{-1}$ (Scheme 3).

The symmetrical penta-coordinate species $H_3N-SiH_3^+-NH_3$ (D_{3h}) and $H_3N-SiMe_3^+-NH_3$ (C_{3h}) are the energy minima on the potential energy surface, as was found previously at different levels of theory [8,11].

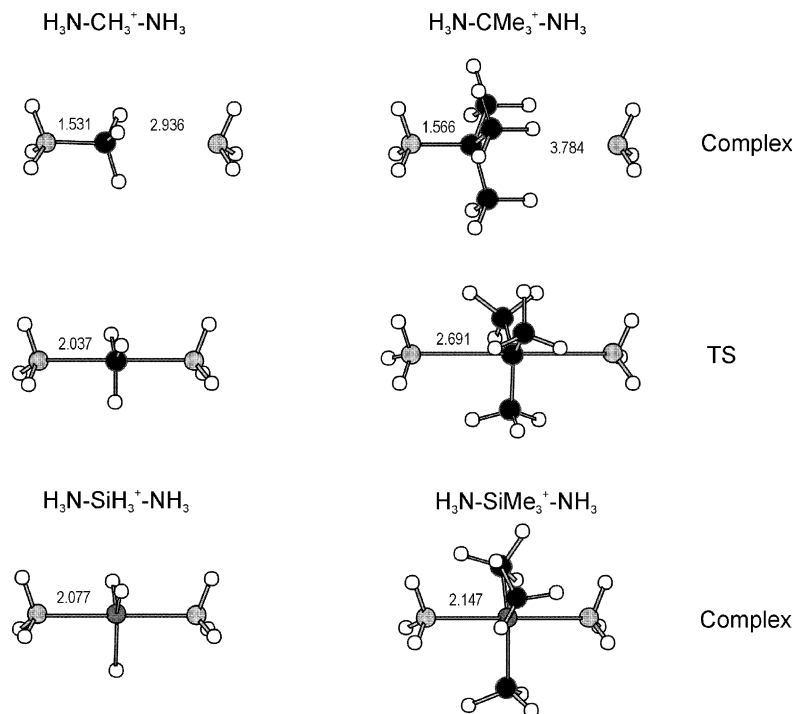


Scheme 2.

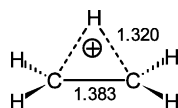
3.2. Bond orders of cation–nucleophile interactions

Distances between central atoms in the cation and the interacting nucleophile and the corresponding Wiberg bond orders are also shown in Tables 2 and 3. The Wiberg bond order corresponding to the overlap between electrophilic and nucleophilic centers is approximately inversely proportional to the bond distance. It can be used as an approximate measure of the degree of bonding and should be proportional to the energy of interaction. Wiberg bond orders correlate with Pauling ones, although the values are somewhat different. The accuracy of Pauling orders is limited, since they depend to some extent on the assumed values of the “normal” bond lengths (Eq. (1)).

In the series of homologue complexes, the bond distance is proportional to the number of methyl substituents at the cationic center, which means that



Scheme 3.



Scheme 4.

the effect of methyl groups on the cation–nucleophile bonding is additive. In all complexes but $t\text{-Bu}^+-\text{CH}_2\text{Cl}_2$, the Wiberg bond order is >0.5 for $\equiv\text{C}^+$ and >0.3 for $\equiv\text{Si}^+$. The cation–nucleophile increase and the bond order decrease in carbenium complexes are larger than in silylenium complexes. The bond orders for $\equiv\text{Si}^+$ are generally lower than for $\equiv\text{C}^+$ complexes, which may suggest weaker interactions with Si^+ . However, these numbers may not be compared directly, because due to the more diffuse orbitals at silicon the effective bonding to Si extends over a longer distance. For example, bond orders for complexes with Me_3Si^+ are generally lower than those for Me_3C^+ , while the enthalpies of complexation are higher. Thus, both quantities, bond order and the enthalpy of interaction, must be taken into consideration.

3.3. Enthalpies of complex formation

Tables 2 and 3 present the calculated energies at 0 K (not corrected for zero-point energy, ZPE) and enthalpies of complex formation at 298 K. All values are corrected for BSSE, which is in the range 0.4–1 kcal mol⁻¹ at the B3LYP/6-311+G(2d,p) level used here for energy calculations. The agreement between calculated

enthalpies of complex formation and scarce experimental data collected in Ref. [12] is very good (Tables 2 and 3), which allows us to believe that the method used here for thermodynamic calculations is sufficiently accurate. The results for $\text{X}_3\text{Si}^+-\text{Nu}$ ($\text{X} = \text{H}, \text{Me}$; $\text{Nu} = \text{H}_2\text{O}, \text{NH}_3, \text{MeCN}$) are also consistent with the previous calculations at lower level of theory [11]. Comparison of complex formation energies shows some general trends. As expected, the energy of complexation decreases with increasing number of methyl groups at the cationic center, which has both steric and hyperconjugative sources. In a series of nucleophiles, the strength of interaction with H_3C^+ decreases in order: $\text{NH}_3 > \text{CH}_3\text{CN} > \text{C}_6\text{H}_6 > \text{H}_2\text{S} > \text{H}_2\text{CO} > \text{H}_2\text{O} > \text{CH}_2\text{Cl}_2$. For Me_3C^+ , it changes to $\text{NH}_3 > \text{CH}_3\text{CN} > \text{H}_2\text{CO} \approx \text{H}_2\text{S} > \text{H}_2\text{O} > \text{CH}_2\text{Cl}_2 > \text{C}_6\text{H}_6$. The corresponding order for interaction with H_3Si^+ is slightly different: $\text{NH}_3 \approx \text{CH}_3\text{CN} > \text{H}_2\text{CO} > \text{H}_2\text{O} > \text{C}_6\text{H}_6 > \text{H}_2\text{S} > \text{CH}_2\text{Cl}_2$ and for Me_3Si^+ it slightly changes to $\text{NH}_3 \approx \text{CH}_3\text{CN} > \text{H}_2\text{CO} > \text{H}_2\text{O} > \text{H}_2\text{S} > \text{C}_6\text{H}_6 > \text{CH}_2\text{Cl}_2$.

The strongest interactions are those with nitrogen nucleophiles, while the weakest are the interactions with CH_2Cl_2 . Surprisingly strong is the interaction of CH_3^+ with benzene ($\Delta H^{298} = -81.2$ kcal mol⁻¹). The energy of complex formation rapidly decreases with methyl substitution at $\equiv\text{C}^+$ and becomes close to zero for $t\text{-butyl}$ cation. However, a high value of Wiberg bond index and a large deviation of the Me_3C fragment from planarity suggest that still a significant interaction of $t\text{-Bu}^+$ with C_6H_6 occurs. In general, for trimethyl-substituted carbenium and silylenium ions the interac-

Table 2

B3LYP/6-311+G(2d,p)//B3LYP/6-31G* electronic energies, $\Delta E_{\text{compl}}^0$ (at 0 K, ZPE not included), and enthalpies, $\Delta H_{\text{compl}}^{298}$ (at 298 K), both corrected for BSSE, of complex formation by carbenium ions with nucleophiles, and total steric exchange energies, ΔE_{steric} (NBO, HF/6-311+G(2d,p)//B3LYP/6-31G*), between molecular units in the complex

	$r(\text{C}-\text{Nu})$ (Å)	Wiberg bond order	Pauling bond order	$\Delta E_{\text{compl}}^0$ (kcal mol ⁻¹)	$\Delta H_{\text{compl}}^{298}$ (kcal mol ⁻¹)	$\Delta H_{\text{exp}}^{298}$ [12]	$\Delta E_{\text{steric}}^a$ (kcal mol ⁻¹)
CH ₃ ⁺ -C ₆ H ₆	1.574	0.958	0.848	-85.0	-81.2		64.7
CH ₃ ⁺ -NCCH ₃	1.435	0.922	1.144	-100.8	-96.7	-98.0	31.6
CH ₃ ⁺ -O=CH ₂	1.488	0.747	0.788	-77.4	-72.9		40.4
CH ₃ ⁺ -OH ₂	1.521	0.712	0.694	-69.7	-64.4	-68.5	15.3
CH ₃ ⁺ -NH ₃	1.517	0.897	0.835	-108.8	-102.4	-105.2	59.4
CH ₃ ⁺ -SH ₂	1.847	1.011	0.891	-83.9	-79.3		31.8
CH ₃ ⁺ -CH ₂ Cl ₂	1.854	0.913	0.716	-62.1	-58.9		10.8
CH ₃ CH ₂ ⁺ -C ₆ H ₆	1.607	0.924	0.747	-43.2	-39.5		108.0
CH ₃ CH ₂ ⁺ -NCCH ₃	1.451	0.895	1.076	-62.6	-58.3		82.8
CH ₃ CH ₂ ⁺ -O=CH ₂	1.526	0.695	0.681	-42.8	-37.9		90.5
CH ₃ CH ₂ ⁺ -OH ₂	1.567	0.653	0.582	-36.3	-31.3		51.9
CH ₃ CH ₂ ⁺ -NH ₃	1.534	0.871	0.782	-71.4	-65.1		98.9
CH ₃ CH ₂ ⁺ -SH ₂	1.885	0.970	0.750	-45.9	-41.2		72.4
CH ₃ CH ₂ ⁺ -CH ₂ Cl ₂	1.938	0.816	0.663	-26.6	-23.5		32.1
(CH ₃) ₂ CH ⁺ -C ₆ H ₆	1.655	0.879	0.621	-20.0	-16.2		126.2
(CH ₃) ₂ CH ⁺ -	1.466	0.904	1.015	-43.6	-39.3		88.4
NCCH ₃							
(CH ₃) ₂ CH ⁺ -O=	1.570	0.639	0.575	-27.1	-22.3		104.7
CH ₂							
(CH ₃) ₂ CH ⁺ -OH ₂	1.619	0.589	0.477	-21.6	-16.8		77.7
(CH ₃) ₂ CH ⁺ -NH ₃	1.548	0.847	0.741	-53.2	-47.0		127.8
(CH ₃) ₂ CH ⁺ -SH ₂	1.929	0.917	0.633	-27.4	-27.8		102.2
(CH ₃) ₂ CH ⁺ -	2.151	0.573	0.229	-11.1	-8.3		44.2
CH ₂ Cl ₂							
(CH ₃) ₃ C ⁺ -C ₆ H ₆	1.695	0.838	0.533	-2.5	0.8		166.1
(CH ₃) ₃ C ⁺ -NCCH ₃	1.482	0.840	0.962	-28.7	-24.9		118.2
(CH ₃) ₃ C ⁺ -O=CH ₂	1.649	0.553	0.425	-14.4	-10.3	-11.0	120.7
(CH ₃) ₃ C ⁺ -OH ₂	1.686	0.526	0.369	-10.5	-6.5		101.3
(CH ₃) ₃ C ⁺ -NH ₃	1.562	0.820	0.703	-39.1	-35.1	-40	172.0
(CH ₃) ₃ C ⁺ -SH ₂	1.976	0.864	0.543	-13.0	-9.0		125.0
(CH ₃) ₃ C ⁺ -CH ₂ Cl ₂	3.709	0.005	0.0006	-6.0	-4.8		-4.1
Et ₃ C ⁺ -OH ₂	1.701	0.498		-4.3	0		
Et ₃ C ⁺ -NH ₃	1.560	0.816		-31.6	-25.8		
CH ₃ ⁺ (NH ₃) ₂	1.531, 2.936	0.873, 0.005		-8.3 ^b , -118.2 ^c	-7.0 ^b , -109.4 ^c		3.2 ^b , 59.0 ^c
CH ₃ ⁺ (NH ₃) ₂ , TS	2.037	0.371					32.0 ^b
Me ₃ C ⁺ (NH ₃) ₂	1.566, 3.784	0.813, 0.000		-10.0 ^b , -47.2 ^c	-8.4 ^b , -38.8 ^c		3.2 ^b , 165.0 ^c
Me ₃ C ⁺ (NH ₃) ₂ , TS	2.691	0.078					30.8

^a Details of calculations are described in Section 2.

^b Calculated according to Eq. (2).

^c Calculated according to Eq. (3).

tions with benzene become relatively weaker compared to other nucleophiles. This suggests the role of steric hindrance, as C₆H₆ is more sterically demanding than the other nucleophiles.

Long Si–O distance and relatively weak interaction in ≡Si–OH₂⁺ complexes is somewhat surprising, taking into account the strength of a regular Si–O bond. It may be concluded that the Si–OH bond in silanols is significantly weakened upon protonation. This explains, at least partially, a high reactivity of silanols under acidic conditions.

The interactions of H₂S with carbenium ions are stronger compared to H₂O, which is in accord with a

hard and soft acid–base principle. The interactions of H₂S with silylenium ions are also relatively strong, only slightly weaker than those with H₂O.

The weakest interaction in terms of the bond index occurs between *t*-butyl cation and dichloromethane. As it was already mentioned, the interaction of H in methyl group of Me₃C with a chlorine atom is responsible for the non-zero enthalpy of complexation (Scheme 1).

While the energies of complexation for CH₃⁺ are greater than for SiH₃⁺, for trimethyl- and triethyl-substituted cations the order is reversed (Fig. 1). This observation was interpreted in terms of stronger hyperconjugative interactions in the Me₃C⁺ cation compared

Table 3

B3LYP/6-311+G(2d,p)//B3LYP/6-31G* electronic energies, $\Delta E_{\text{compl}}^0$ (at 0 K, ZPE not included), and enthalpies, $\Delta H_{\text{compl}}^{298}$ (at 298 K), both corrected for BSSE, of complex formation between silylenium ions and nucleophiles, and total steric exchange energies, ΔE_{steric} (NBO, HF/6-311+G(2d,p)//B3LYP/6-31G*) between molecular units in the complex

	$r(\text{Si}-\text{Nu})$ (Å)	Wiberg bond order	Pauling bond order	$\Delta E_{\text{compl}}^0$ (kcal mol ⁻¹)	$\Delta H_{\text{compl}}^{298}$ (kcal mol ⁻¹)	$\Delta H_{\text{exp}}^{298}$ [12]	$\Delta E_{\text{steric}}^a$ (kcal mol ⁻¹)
SiH ₃ ⁺ -C ₆ H ₆	2.083	0.459	0.442	-51.8	-49.5		28.9
SiH ₃ ⁺ -NCCH ₃	1.844	0.482	0.697	-74.1	-71.8		12.5
SiH ₃ ⁺ -O=CH ₂	1.843	0.378	0.468	-57.2	-54.1		23.9
SiH ₃ ⁺ -OH ₂	1.868	0.351	0.425	-53.7	-50.8		0.4
SiH ₃ ⁺ -NH ₃	1.929	0.490	0.503	-75.2	-71.5		30.1
SiH ₃ ⁺ -SH ₂	2.334	0.679	0.484	-50.9	-48.1		-2.8
SiH ₃ ⁺ -SiH ₂ Cl ₂	2.262	0.558	0.479	-39.8	-38.0		-11.7
CH ₃ SiH ₂ ⁺ -C ₆ H ₆	2.124	0.416	0.377	-39.8	-37.4		42.5
CH ₃ SiH ₂ ⁺ -NCCH ₃	1.862	0.464	0.651	-63.5	-61.1		23.9
CH ₃ SiH ₂ ⁺ -O=CH ₂	1.863	0.363	0.433	-48.6	-45.5		38.2
CH ₃ SiH ₂ ⁺ -OH ₂	1.891	0.337	0.389	-45.4	-42.5		8.9
CH ₃ SiH ₂ ⁺ -NH ₃	1.941	0.471	0.480	-65.1	-61.3		40.9
CH ₃ SiH ₂ ⁺ -SH ₂	2.358	0.643	0.442	-41.4	-38.5		17.0
CH ₃ SiH ₂ ⁺ -CH ₂ Cl ₂	2.303	0.514	0.409	-30.5	-28.5		1.9
(CH ₃) ₂ SiH ⁺ -C ₆ H ₆	2.168	0.376	0.319	-29.4	-27.1		39.0
(CH ₃) ₂ SiH ⁺ - NCCH ₃	1.877	0.446	0.614	-54.6	-52.2		28.4
(CH ₃) ₂ SiH ⁺ -O= CH ₂	1.880	0.347	0.406	-41.3	-38.3		43.9
(CH ₃) ₂ SiH ⁺ -OH ₂	1.911	0.322	0.360	-38.2	-35.4		14.4
(CH ₃) ₂ SiH ⁺ -NH ₃	1.953	0.454	0.459	-56.5	-52.8		49.4
(CH ₃) ₂ SiH ⁺ -SH ₂	2.380	0.612	0.406	-33.1	-30.3		26.0
(CH ₃) ₂ SiH ⁺ - CH ₂ Cl ₂	2.345	0.471	0.348	-23.1	-21.2		5.0
(CH ₃) ₃ Si ⁺ -C ₆ H ₆	2.229	0.335	0.252	-20.4	-18.7	-23.9	47.0
(CH ₃) ₃ Si ⁺ -NCCH ₃	1.893	0.426	0.578	-47.6	-45.2		35.9
(CH ₃) ₃ Si ⁺ -O=CH ₂	1.902	0.330	0.373	-34.4	-31.6		53.2
(CH ₃) ₃ Si ⁺ -OH ₂	1.930	0.308	0.442	-32.6	-30.0	-31	22.4
(CH ₃) ₃ Si ⁺ -NH ₃	1.963	0.435	0.366	-49.8	-46.3	-45 to - 50	59.1
(CH ₃) ₃ Si ⁺ -SH ₂	2.407	0.577	0.274	-26.9	-24.2		36.8
(CH ₃) ₃ Si ⁺ -CH ₂ Cl ₂	2.407	0.422		-17.2	-15.4		15.7
Et ₃ Si ⁺ -OH ₂	1.945	0.302		-28.6	-24.7		44.1
Et ₃ Si ⁺ -NH ₃	1.964	0.427		-45.8	-42.3		76.0
SiH ₃ ⁺ (NH ₃) ₂	2.077	0.344		-29.8 ^b , -105.6 ^c	-27.0 ^b , -100.0 ^c		58.2 ^b , 78.0 ^c
Me ₃ Si ⁺ (NH ₃) ₂	2.147	0.303		-10.5 ^b , -62.1 ^c	-8.1 ^b , -55.2 ^c		83.1 ^b , 125.4 ^c

^a Details of calculations are described in Section 2.

^b Calculated according to Eq. (2).

^c Calculated according to Eq. (3).

to Me₃Si⁺ [12], but it seems to be only partly true. Complexation results in an almost complete loss of CH₃→X⁺ hyperconjugation energy, which should be little dependent on the nucleophile. The decrease in energy of complex formation is different for various nucleophiles and reflects the difference in steric repulsion energy between the nucleophile and the cation. Comparing the plots of complexation energy vs. number of methyl substitution for various nucleophiles and the chosen cation, which may be considered a “probe”, we can estimate the relative steric hindrance of a nucleophile. For example, the difference in bonding energy between H₃C⁺-NCMe and Me₃C⁺-NCMe is 71.8 kcal mol⁻¹, while the corresponding difference for C₆H₆ is 82 kcal mol⁻¹, due to the smaller hindrance

of the linear N≡C- group compared to C₆H₆ (Fig. 2). The corresponding differences in bonding energy are much smaller for silylenium ions (26.6 and 30.8 kcal mol⁻¹ for MeCN and C₆H₆, respectively), because the steric effect in ≡Si⁺ is generally smaller than that in ≡C⁺.

It should be mentioned that the above analysis is simplified. We neglect small variations in hyperconjugation energy depending on the type of interacting nucleophile, which implies different efficiency of orbital overlap (i.e. bond strength and degree of ionic character of the bond to a cation).

Substitution of methyl by ethyl in the cationic center leads to further decrease in bonding energy, as expected. The decrease is more distinct for carbenium ions than

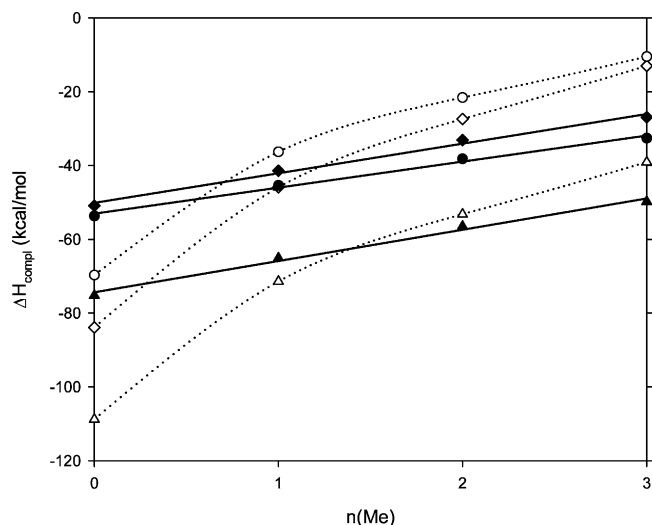


Fig. 1. Dependences of enthalpies of complex formation on number of methyl groups in $H_{3-n}Me_nX^+-Nu$, $X = C, Si$; (○): $H_{3-n}Me_nC^+-OH_2$, (●): $H_{3-n}Me_nSi^+-OH_2$, (◇): $H_{3-n}Me_nC^+-SH_2$, (◆): $H_{3-n}Me_nSi^+-SH_2$, (△): $H_{3-n}Me_nC^+-NH_3$, (▲): $H_{3-n}Me_nSi^+-NH_3$.

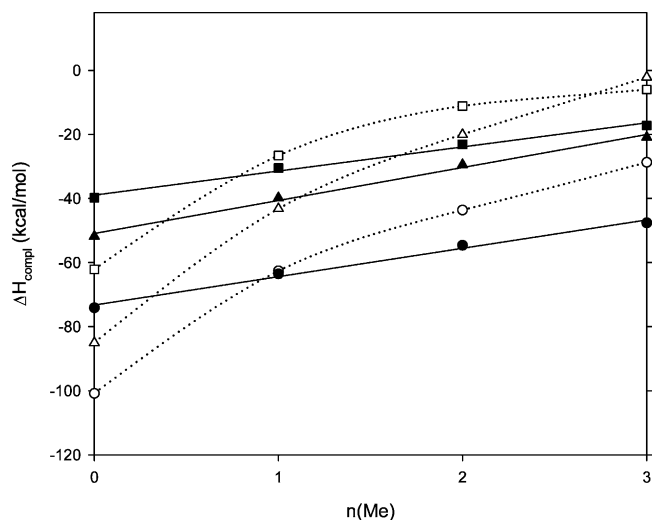
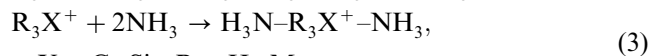


Fig. 2. Dependences of enthalpies of complex formation on number of methyl groups in $H_{3-n}Me_nX^+-Nu$ ($X = C, Si$); (○) $H_{3-n}Me_nC^+-NCMe$, (●) $H_{3-n}Me_nSi^+-NCMe$, (△) $H_{3-n}Me_nC^+-C_6H_6$, (▲) $H_{3-n}Me_nSi^+-C_6H_6$, (□) $H_{3-n}Me_nC^+-CH_2Cl_2$, (■) $H_{3-n}Me_nSi^+-CH_2Cl_2$.

for silylenium ions and, for example, on change from $t-Bu^+-NH_3$ to $Et_3C^+-NH_3$ the bonding energy drops by 10 kcal mol⁻¹ (Table 2). For $Et_3C^+-OH_2$, the energy of complex formation was calculated to be about zero; however, it seems underestimated, since the C–O distance of 1.701 Å and the Wiberg bond index of 0.5 indicate that a significant interaction exists. In the case of silylenium ions, the decrease in complexation energy between Me_3Si^+-Nu and Et_3Si^+-Nu , $Nu = H_2O, NH_3$, is only ca. 4–5 kcal mol⁻¹. Thus, steric hindrance of ethyl groups effectively weakens the interaction of

carbenium cation with the nucleophiles, but is not sufficient to prevent coordination of nucleophiles to silylenium ions, in accord with experimental observations [30].

Complexation enthalpies in 2:1 complexes were calculated using Eqs. (2) and (3). For methyl and *t*-butyl carbenium complexes, the enthalpies of bonding of the second NH_3 molecule, calculated according to Eq. (2), are almost the same, 7–8 kcal mol⁻¹. The interaction of the second donor molecule only slightly affects the bonding to the first one, as the total complexation enthalpies, calculated from Eq. (3), are approximately equal to the sum of the complexation enthalpy for the 1:1 complex and the enthalpy of bonding to the second NH_3 molecule, found from Eq. (2) (Table 2). Activation enthalpies, ΔH^\ddagger , for the reaction of nucleophile exchange at the carbenium center, deduced from the enthalpies of the transition states, are 16.4 and 24.1 kcal mol⁻¹ for $CH_3^+(NH_3)_2$ and $CMe_3^+(NH_3)_2$, respectively. Total complexation enthalpies for 2:1 silylenium complexes (Eq. (3)) are greater than those for 1:1 complexes by 29 and 10 kcal mol⁻¹ for SiH_3^+ and $SiMe_3^+$, respectively. This means, however, that the Si–N bond in 2:1 complex is by ca. 20 kcal mol⁻¹ weaker than that in the 1:1 complex (Table 3).



3.4. Natural steric analysis

The qualitative concept of “steric repulsion” is commonly used in chemistry, but the quantitative ab initio characterization of this concept is still incomplete. From the theoretical standpoint, steric repulsions arise from the Pauli’s exclusion principle and can be viewed as the “quantum pressure” that resists crowding too many electrons into the same special region. In natural steric analysis, the steric repulsions are formulated in terms of the energy difference between filled NBOs and the corresponding non-orthogonal “pre-NBOs” (PNBOs). It should be stressed that all occupied NLMOs make significant contributions to the total steric effect because all are involved in the mutual orthogonality associated with full N-electron antisymmetry [13–15].

The estimation of the steric repulsion between two fragments (nucleophilic and electrophilic) of a complex involves calculation of the total steric exchange energy for a given complex and for the system with two molecular units separated by a large distance (a distance of 12 Å was assumed, which guarantees that the inter-unit repulsions may be neglected). Subtraction of these

two values gives an estimate of the repulsion energy between both molecular fragments in the complex.

The results of calculations of the steric exchange energy for Si^+ are very sensitive to the quality of basis set. The orthogonalization effect leads to higher kinetic energy (and positive steric exchange energy). But there may be also a potential energy change, if the orthogonalized orbital is made bigger or smaller than the starting pre-orthogonal orbital and this “inner” change may be particularly dramatic for a species with a net charge, due to strong electrostatic interactions. The proper representation of this effect is more challenging in Si, because there are two inner core levels, strongly coupled through the screening effect. Indeed, contributions dE from inner core shells of heavier elements (Si, Cl) to total steric exchange energy are by an order of magnitude greater than contributions of valence orbitals. The error in estimation of those core coupling energies largely affects total steric energy. Silyl ions demonstrate the extreme basis sensitivity of describing these “inner” exchange effects consistently [32]. The estimated total steric energies of repulsion between cations and nucleophiles are collected in Tables 2 and 3.

In accord with expectations, steric exchange energy of repulsion between molecular fragments increases with the increasing size of substituents at the ionic center (Fig. 3). The only exception from this rule is the $t\text{-Bu}^+ - \text{CH}_2\text{Cl}_2$ complex, where the steric exchange energy is lower than in the $i\text{-Pr}^+ - \text{CH}_2\text{Cl}_2$ complex. This reflects the change in intermolecular interaction, as discussed above (Scheme 1) and points to the strong anisotropy of the steric effect.

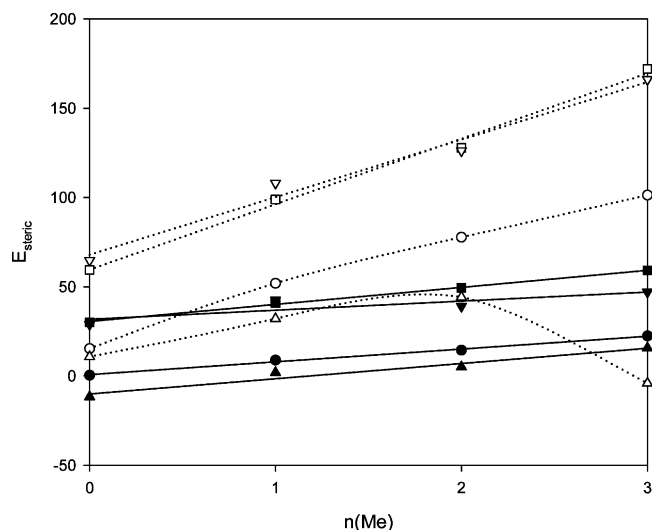


Fig. 3. Dependences of steric exchange energies between cationic and nucleophilic fragments on number of methyl groups in the complexes: (○) $\text{H}_{3-n}\text{Me}_n\text{C}^+ - \text{OH}_2$, (●) $\text{H}_{3-n}\text{Me}_n\text{Si}^+ - \text{OH}_2$, (□) $\text{H}_{3-n}\text{Me}_n\text{C}^+ - \text{NH}_3$, (■) $\text{H}_{3-n}\text{Me}_n\text{Si}^+ - \text{NH}_3$, (△) $\text{H}_{3-n}\text{Me}_n\text{C}^+ - \text{CH}_2\text{Cl}_2$, (▲) $\text{H}_{3-n}\text{Me}_n\text{Si}^+ - \text{CH}_2\text{Cl}_2$, (▽) $\text{H}_{3-n}\text{Me}_n\text{C}^+ - \text{C}_6\text{H}_6$, (▼) $\text{H}_{3-n}\text{Me}_n\text{Si}^+ - \text{C}_6\text{H}_6$.

The increase is less distinct for silylenium ions than for carbenium ones, and it is less sensitive to the size of substituents, which was also expected (Tables 2 and 3). The complexation energy is inversely proportional to the total steric energy. In the case of silylenium ions, the correlation is approximately linear (Fig. 4).

Steric exchange energies in 2:1 complexes were calculated in two ways: (i) as an increase of steric exchange energy compared to 1:1 complex due to the interaction with additional molecule of nucleophile; (ii) as the steric exchange energy due to the interactions of both donor molecules with the cation. For methyl and t -butyl carbenium complexes, the steric energies obtained according to the first method are very small, ca. 3 kcal mol^{-1} , and the corresponding C–N distance are as long as 2.936 and 3.784 Å in methyl and t -butyl complexes, respectively. The total steric repulsion, according to method (ii) is approximately the same as in the corresponding 1:1 complexes. The steric exchange energy between carbenium ion and NH_3 molecules in the transition state is largely released (Table 2). For silylenium 2:1 complexes, the steric exchange energies are significantly larger than those for 1:1 complexes (Table 3), which indicates that electronic attractive forces associating with the formation of the additional bond overcome the steric repulsion.

4. Concluding remarks

Calculations of steric effect according to the NBO theory reveal the potential as well as the limitations of the method. Separation of electronic delocalization and spatial repulsion effects is ambiguous and difficult to

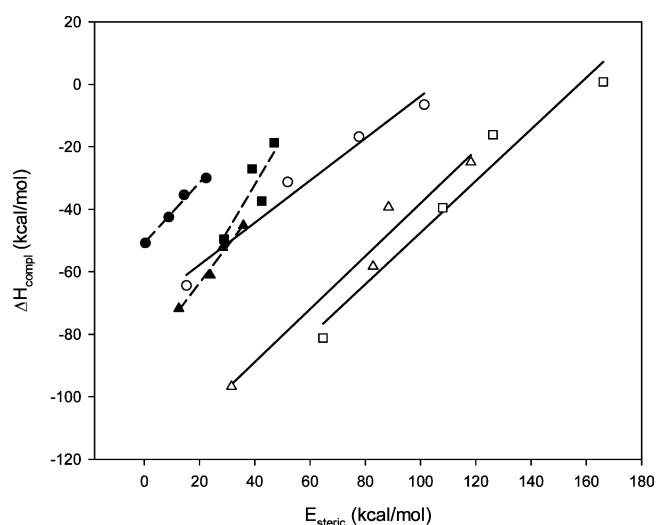


Fig. 4. Dependences of energies of complex formation on steric exchange energies between cationic and nucleophilic fragments in the complexes: (○) $\text{H}_{3-n}\text{Me}_n\text{C}^+ - \text{OH}_2$, (●) $\text{H}_{3-n}\text{Me}_n\text{Si}^+ - \text{OH}_2$, (△) $\text{H}_{3-n}\text{Me}_n\text{C}^+ - \text{NCMe}$, (▲) $\text{H}_{3-n}\text{Me}_n\text{Si}^+ - \text{NCMe}$, (□) $\text{H}_{3-n}\text{Me}_n\text{C}^+ - \text{C}_6\text{H}_6$, (■) $\text{H}_{3-n}\text{Me}_n\text{Si}^+ - \text{C}_6\text{H}_6$.

perform, although it may be very instructive and helpful in understanding of reaction mechanisms. The observed numerical instability at smaller basis sets may indicate difficulties in description of inner shell interactions in heavy atoms, especially those bearing an electric charge. These effects may strongly depend on the long-range ion dipole and ion-induced dipole interactions and on the polarizability of the given atom. These difficulties point also to the limitations of the commonly used frozen-core basis sets in description of charged heavy atoms [32]. Natural steric analysis requires very large basis sets to satisfactorily reproduce the orbital repulsions and should rather be used for comparisons of very similar systems. Although the numbers should be treated with great care, the clear trends relating the increasing size of substituents with the increase of steric repulsion and with the decrease of complex formation energy suggest that natural steric analysis may become helpful in predictions of the influence of steric hindrance on the reaction mechanisms.

Concerning the “long-living” question of the existence of “free” silylenium ions in condensed phases, the answer is that there are no perfectly free ions under such conditions. This is in fact the question about the criterion, which interactions are weak enough to be considered negligible. According to Pauling [21], the interaction associated with the bond order as low as 0.1 still must be regarded as significant. In line with this statement, all silylenium ions discussed here may not be considered free, even in solvents of such low nucleophilicity as CH_2Cl_2 . On the other hand, *t*-butyl and, probably, triethylmethyl cations in CH_2Cl_2 and in C_6H_6 are essentially free, because the steric hindrance is large enough to prevent strong interaction with these solvents.

It should be stressed, however, that presented calculations concern the gas-phase conditions. In solution, particularly in polar solvents, the solvation may convolute steric effects in the way that would be very difficult to analyze.

5. Supplementary information

B3LYP/6-31G*-optimized structures of silylenium and carbenium ions and of their complexes with nucleophiles as well as the calculated electronic energies are available on demand upon writing to mcypryk@bilbo.cbmm.lodz.pl.

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