

An assessment of DFT methods for predicting the thermochemistry of ion-molecule reactions of group 14 elements (Si, Ge, Sn)

Igor S. Ignatyev · Manuel Montejo ·
Juan Jesús López González

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Abstract Experimental mass-spectrometry data on thermochemistry of methide transfer reactions $(\text{CH}_3)_3\text{M}^+ + \text{M}'(\text{CH}_3)_4 \leftrightarrow \text{M}(\text{CH}_3)_4 + (\text{CH}_3)_3\text{M}'^+$ ($\text{M}, \text{M}' = \text{Si}, \text{Ge}$ or Sn) and the formation energy of the $[(\text{CH}_3)_3\text{Si}-\text{CH}_3-\text{Si}(\text{CH}_3)_3]^+$ complex are used as benchmarks for DFT methods (B3LYP, BMK, M06L, and ωB97XD). G2 and G3 theory methods are also used for the prediction of thermochemical data. BMK, M06L, and ωB97XD methods give the best fit to experimental data (close to chemical accuracy) as well as to G2 and G3 results, while B3LYP demonstrates poor performance. From the first three methods M06L gives the best overall result. Structures and formation energies of intermediate “mixed” $[(\text{CH}_3)_3\text{M}-\text{CH}_3-\text{M}'(\text{CH}_3)_3]^+$ complexes not observed in experiment are predicted. Their structures, better described as $\text{M}(\text{CH}_3)_4 [\text{M}'(\text{CH}_3)_3]^+$ complexes, explain their fast decompositions.

Keywords DFT · Group 14 elements · Ion-molecule reactions · Thermochemistry

Introduction

Trimethylsilyl cations $(\text{CH}_3)_3\text{Si}^+$ are the most abundant products of the electron impact ionization of $(\text{CH}_3)_4\text{Si}$ [1]. This ion associates with the parent tetramethylsilane molecule to produce the $(\text{CH}_3)_7\text{Si}^+$ ion [2], that was also observed in the chemical ionization studies of pure tetramethylsilane [3–5]. Albeit the structure of this ion was proposed to contain a Si-Si

bond with one silicon atom being pentacoordinated [3], the analysis of experimental data and the quantum chemical study of the $(\text{CH}_3)_7\text{Si}^+$ ion [6] allowed authors to suggest a structure corresponding to a C_{3h} point group in which a planar methyl group is symmetrically bonded to two $-\text{Si}(\text{CH}_3)_3$ moieties. This structure was found to be a minimum at both B3LYP/6-311+G(3df,2pd) and QCISD/6-311+G(d,p) levels of theory [6]. The latter level predicts ΔH^0 of the ion association to be $-23.2 \text{ kcal mol}^{-1}$ in good agreement with the experimental value of $-22.3 \pm 0.4 \text{ kcal mol}^{-1}$ [5]. Similar structure (although with nonplanar central methyl moiety) was found earlier as an intermediate in the potential energy surface of the hydrogen transfer reaction between the SiH_3^+ ion and GeH_4 [7].

Fernández, Uggerud, and Frenking [8] obtained equilibrium structures for the $[\text{H}_3\text{M}-\text{CH}_3-\text{MH}_3]^+$ ions, where M are Group 1, 2, 13 or 14 (Si, Ge, Sn and Pb) elements. Nevertheless, among structures with methyl groups at M, i.e., $[(\text{CH}_3)_3\text{M}-\text{CH}_3-\text{M}'(\text{CH}_3)_3]^+$, only the equilibrium structure of the “symmetric” $[(\text{CH}_3)_3\text{Si}-\text{CH}_3-\text{Si}(\text{CH}_3)_3]^+$ molecule was obtained by quantum chemical methods [6]. Analogous nonsymmetric (“mixed”) structures (M, M' = Si, Ge, and Sn) were not observed by mass spectrometry. Thus, one of the aims of this work is to predict their structures and to get an insight into the factors that prevent them from experimental identification. Despite the lack of information about the intermediates, there exist thermodynamic experimental data of the $(\text{CH}_3)_3\text{M}^+ + \text{M}'(\text{CH}_3)_4 \leftrightarrow \text{M}(\text{CH}_3)_4 + (\text{CH}_3)_3\text{M}'^+$ reactions (M, M' = Si, Ge and Sn), that can be used as experimental benchmarks for the quantum chemical calculations of ion-molecule reactions of group 14 elements. Due to the significant size of the systems, which include methyl derivatives, DFT methods are a reasonable choice for this task.

Resembling other commonly used semilocal and hybrid density functionals, which cannot provide the correct dependence of the dispersion interaction energy on the interatomic distance, the widespread B3LYP method yields large errors in

I. S. Ignatyev
Department of Chemistry, Radiochemistry Laboratory, St. Petersburg State University, St. Petersburg 199034, Russia

M. Montejo · J. J. López González (✉)
Department of Physical and Analytical Chemistry, University of Jaén, Campus “Las Lagunillas”, 23071 Jaén, Spain
e-mail: jjlopez@ujaen.es

predicting thermochemical parameters for molecular systems with noncovalent interactions [9–21].

For this reason, we used some of the DFT methods recently developed, such as Thrular's M06L (reported to have the best overall performance of any functional for the study of organometallic thermochemistry [22–28]), the hybrid meta-GGA BMK functional which was reported to be superior to B3LYP and other hybrid functionals for equilibrium properties [29–33] as well as the ω B97XD functional that includes dispersion corrections. Further, G2 and G3 methods, which

provide the most accurate predictions of thermochemical parameters, have also been implemented for comparison.

Computational methods

Geometries of stationary points have been fully optimized and characterized by harmonic vibrational frequency calculations using the following DFT methods: (i) the hybrid meta-GGA B3LYP functional [34, 35], (ii) Thrular's pure M06L functional [36], (iii) Boese and Martin's BMK functional [13], and (iv) the long-range corrected (LC) hybrid density functional by Chai and Head-Gordon, with empirical atom–atom dispersion corrections, denominated ω B97X-D [37].

The Dunning correlation-consistent sets [38] were employed for H, C, Si, and Ge atoms. For Sn, a valence double- ζ set with an ECP and relativistic corrections, denominated LANL2DZ [39–41], was used.

G2 [42] and G3 [43] methods were also used for the high-level predictions in cases where experimental thermochemical data were absent.

All the methods and basis sets were used as implemented in the Gaussian09 program [44]. In the DFT methods, the integration was carried out with the Int=Ultrafine option and, for all the methods employed, the geometry optimization criterion used was that corresponding to the Opt=Tight option. Natural bond orbital (NBO) analysis [45, 46] and the counterpoise method [47] for the estimation of basis set superposition errors (BSSE) were also used as implemented in Gaussian09.

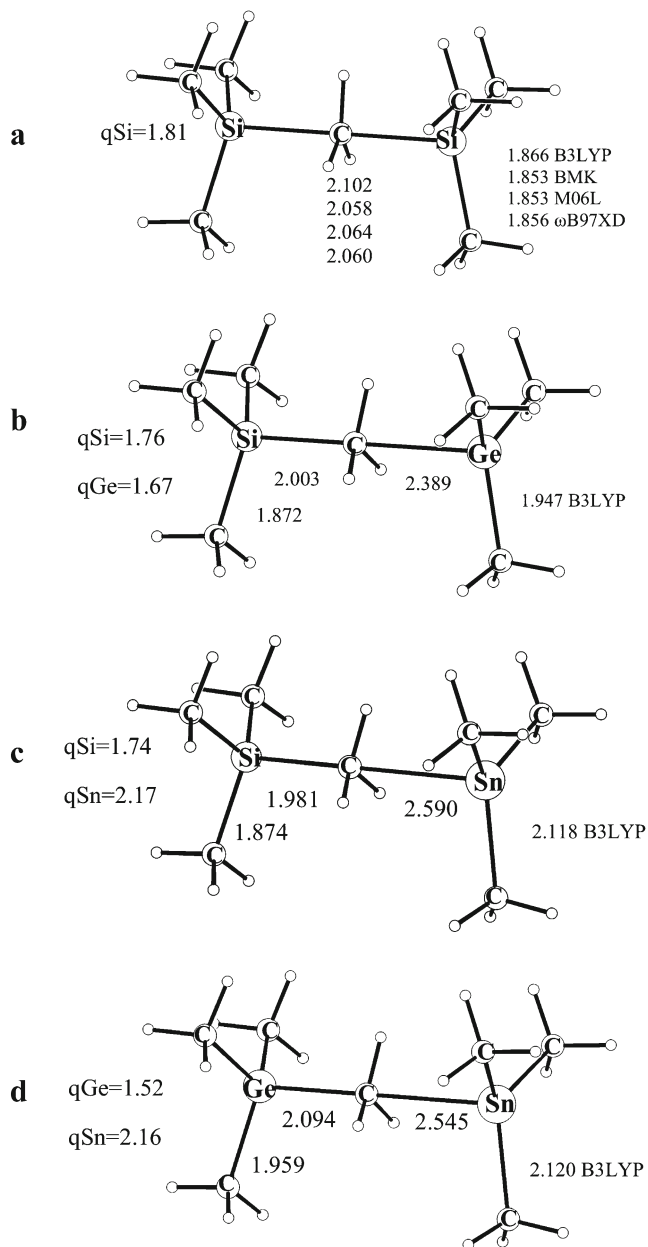


Fig. 1 Structure (bond lengths in Å) of the $(\text{CH}_3)_7\text{Si}^+$ ion (**a**) and of the intermediates in the methide transfer reactions: $(\text{CH}_3)_3\text{M}^+ + \text{M}'(\text{CH}_3)_4 \leftrightarrow (\text{CH}_3)_4\text{M}' + (\text{CH}_3)_3\text{M}^+$, where M and M' denote Si, Ge, and Sn and $\text{M} \neq \text{M}'$ (**b**, **c**, **d**)

Table 1 Theoretical and experimental association energies (ΔH^0 in kcal mol $^{-1}$) of the $[(\text{CH}_3)_3\text{Si}-\text{CH}_3-\text{Si}(\text{CH}_3)_3]^+$ complex

	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ	aug-cc-pVTZ ^a	BSSE ^b
B3LYP	-17.5	-17.4	-16.5	-16.5		0.3
BMK	-20.8	-21.3	-23.3	-21.4	-20.5	0.5
M06L	-22.6	-23.2	-22.3	-22.0	-22.3	0.7
ω B97XD	-23.9	-24.6	-23.5	-23.4	-23.2	0.3
G2	-23.7					
G2(MP2)	-23.8					
G3	-25.7					
G3(MP2)	-25.4					
Experiment ^c	-22.3 \pm 0.4					

^a Single-point calculation at the B3LYP/aug-cc-pVTZ optimized geometries with thermal correction to enthalpy with the B3LYP method

^b Basis set superposition error (kcal mol $^{-1}$) calculated by counterpoise method for B3LYP/aug-cc-pVTZ optimized geometries

^c Taken from ref [5]

Table 2 Theoretical and experimental enthalpies (ΔH^0 in kcal mol⁻¹) of the (CH₃)₃Si⁺ + (CH₃)₄Ge ↔ (CH₃)₄Si⁺ + (CH₃)₃Ge⁺ reaction

	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ	aug-cc-pVTZ ^a
B3LYP	-7.9	-7.9	-8.3	-8.2	
BMK	-10.0	-10.1	-10.1	-9.9	-10.3
M06L	-9.5	-9.4	-9.6	-9.6	-9.9
ωB97XD	-8.1	-8.1	-8.6	-8.3	-8.3
G2	-9.4				
G2(MP2)	-9.5				
G3	-9.9				
G3(MP2)	-9.3				
Experiment ^b	-10.2±0.6				

^a Single-point calculation at the B3LYP/aug-cc-pVTZ optimized geometries with thermal correction to enthalpy at the B3LYP level

^b Taken from ref [5]

Results and discussion

Structure of the intermediate and thermochemistry of the interaction of (CH₃)₃Si⁺ with (CH₃)₄Si

The structure of the adduct formed by the interaction of the trimethylsilylium cation with tetramethylsilane is depicted in Fig. 1(a). In accordance with previous optimizations [6], it possesses *C*_{3h} symmetry. As shown in Fig. 1a, the equilibrium SiC bond distance obtained with aug-cc-pVTZ basis set increases from 2.058 Å (BMK) to 2.102 Å (B3LYP). The highest level QCISD/6-311+G(d,p) equilibrium bond length of 2.071 Å [6] lies in the middle of the range of these values.

Along with the reduction of equilibrium bond lengths, the association energies increase from B3LYP to ωB97XD. The B3LYP values are far from experimental values for all the basis sets employed (see Table 1). Other DFT values provide a good agreement with experimental values as well as with the highest level QCISD estimate (-23.2 kcal mol⁻¹) [6]. The G2 result matches this last value, but is slightly lower than the G3 value (Table 1). Basis set superposition error calculated by the counterpoise method with aug-cc-pVTZ method is small for B3LYP and ωB97XD (0.3 kcal mol⁻¹) and slightly higher for BMK and M06L (0.5 and 0.7 kcal mol⁻¹). Thus, the BSSE-corrected association energy calculated by ωB97XD (-23.1 kcal mol⁻¹) is the closest one to the experimental value (-22.3 kcal mol⁻¹), although the M06L value

(-21.6 kcal mol⁻¹) is also close (±1 kcal mol⁻¹) to the experimental result. Note, that B3LYP values demonstrate a small decrease of association energies with the basis set size, while for the other DFT methods the values depend on the basis set to a lesser extent. In Table 1, we also compared the difference of enthalpies calculated with the largest aug-cc-pVTZ set at the optimized geometry obtained by the same method and at geometries of B3LYP. These differences within M06L and ωB97XD are very small (they are slightly larger for BMK). Due to the convergence problems in optimizing the geometries of lower symmetry structures with this extended basis set in the subsequent calculations of “mixed” intermediate complexes we used energy values estimated at the B3LYP/aug-cc-pVTZ geometry.

Thermochemistry of the (CH₃)₃M⁺ + M'(CH₃)₄ ↔ (CH₃)₄M' + (CH₃)₃M⁺ methide transfer reaction

Since tricoordinated germanium cations are more stable than their silicon analogues [34], reactions (CH₃)₃M⁺ + M'(CH₃)₄ ↔ (CH₃)₄M' + (CH₃)₃M⁺, with M' lying lower down the group than M, are exothermic. The accurate values of their enthalpies, obtained by mass-spectrometry [5], may be a benchmark for DFT methods.

The values predicted for the enthalpy of the (CH₃)₃Si⁺ + (CH₃)₄Ge ↔ (CH₃)₄Si⁺ + (CH₃)₃Ge⁺ reaction by the four DFT methods and the aug-cc-pVTZ basis set are ca. 2 kcal mol⁻¹

Table 3 Theoretical and experimental enthalpies (ΔH^0 in kcal mol⁻¹) of the (CH₃)₃Ge⁺ + (CH₃)₄Sn ↔ (CH₃)₄Ge + (CH₃)₃Sn⁺ reaction

	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ	aug-cc-pVTZ ^a
B3LYP	-5.7	-8.2	-7.9	-7.8	
BMK	-7.2	-9.6	-8.0	-9.4	-9.2
M06L	-5.5	-7.9	-6.6	-7.8	-7.9
ωB97XD	-6.5	-9.2	-8.5	-9.4	-9.2
Experiment ^b	-8.1±0.5				

^a Single-point calculation at the B3LYP/aug-cc-pVTZ optimized geometries with thermal correction to enthalpy at the B3LYP level

^b Taken from ref [5]

Table 4 Theoretical and experimental enthalpies (ΔH^0 in kcal mol⁻¹) of the $(\text{CH}_3)_3\text{Si}^+ + (\text{CH}_3)_4\text{Sn} \leftrightarrow (\text{CH}_3)_4\text{Si} + (\text{CH}_3)_3\text{Sn}^+$ reaction

	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ	aug-cc-pVTZ ^a
B3LYP	-13.7	-16.1	-15.6	-16.0	
BMK	-17.2	-19.6	-18.1	-19.3	-19.5
M06L	-15.0	-17.3	-16.2	-17.4	-17.8
ω B97XD	-14.6	-17.2	-17.1	-17.7	-17.2
Experiment ^b	-18.4				

^a Single-point calculation at the B3LYP/aug-cc-pVTZ optimized geometries with thermal correction to enthalpy at the B3LYP level

^b Taken from ref [5]

deviated from experimental values and from those obtained using quantum chemistry composite methods (G2 and G3), as shown in Table 2. Remarkably, M06L and BMK values show an excellent agreement with experiment.

Also considering the results obtained with the aug-cc-pVTZ basis set, for the $(\text{CH}_3)_3\text{Ge}^+ + (\text{CH}_3)_4\text{Sn} \leftrightarrow (\text{CH}_3)_4\text{Ge} + (\text{CH}_3)_3\text{Sn}^+$ reaction both B3LYP and M06L predictions agree well with experiment (G-theory is unavailable for tin), while BMK and ω B97XD slightly overestimate reaction enthalpies as reported in Table 3. Nevertheless, as in the $(\text{CH}_3)_3\text{Si}^+ + (\text{CH}_3)_4\text{Ge} \leftrightarrow (\text{CH}_3)_4\text{Si} + (\text{CH}_3)_3\text{Ge}^+$ reaction, all methods are ca. 2 kcal mol⁻¹ deviated from experiment.

As concerns the $(\text{CH}_3)_3\text{Si}^+ + (\text{CH}_3)_4\text{Sn} \leftrightarrow (\text{CH}_3)_4\text{Si} + (\text{CH}_3)_3\text{Sn}^+$ reaction, it has the highest value of ΔH^0 for the studied methide transfer process, i.e., -18.4 kcal mol⁻¹ [5]. Again, M06L, BMK and ω B97XD values are in good agreement with experiment (deviations of ca. 2 kcal mol⁻¹ from experiment, when using aug-cc-pVTZ basis set), while the

B3LYP value is underestimated (2.4 kcal mol⁻¹ far from the experimental value), as shown in Table 4.

Structure and thermochemistry of the intermediates of the methide transfer reactions

Intermediate “mixed” complexes of these methide transfer reactions were not observed in mass-spectrometry experiments, probably due to the fact that fast exothermic dissociation precludes collisional stabilization [5].

Their predicted structures using quantum chemical methods, firstly reported here, are depicted in Fig. 1 (b-d). All three complexes exist as minima (no imaginary frequencies were calculated for them) on the potential energy surfaces of the methide transfer reactions and belong to the C_{3v} point group.

Contrasting the “symmetric” $[(\text{CH}_3)_3\text{Si}-\text{CH}_3-\text{Si}(\text{CH}_3)_3]^+$ complex (Fig. 1a), the central methyl group in $[(\text{CH}_3)_3\text{M}-\text{CH}_3-\text{M}'(\text{CH}_3)_3]^+$ is not planar and the H-C-H angle in it

Table 5 Theoretical association energies (ΔH^0 in kcal mol⁻¹) of the $[(\text{CH}_3)_3\text{M}-\text{CH}_3-\text{M}'(\text{CH}_3)_3]^+$ complexes (M, M' = Si, Ge, Sn)

	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ ^a	BSSE ^b
$[(\text{CH}_3)_3\text{Si}-\text{CH}_3-\text{Ge}(\text{CH}_3)_3]^+$					
B3LYP	-22.4	-22.9	-21.7		0.3
BMK	-25.0	-25.6	-25.1	-25.5	0.4
M06L	-27.6	-28.4	-27.4	-27.3	0.6
ω B97XD	-27.6	-28.0	-28.0	-27.3	0.3
G2(MP2)	-28.6				
G3(MP2)	-28.5				
$[(\text{CH}_3)_3\text{Si}-\text{CH}_3-\text{Sn}(\text{CH}_3)_3]^+$					
B3LYP	-28.7	-30.7	-29.6	-30.1	0.5
BMK	-33.2	-36.0	-34.3	-35.7	0.6
M06L	-35.1	-37.6	-35.7	-36.2	0.7
ω B97XD	-35.3	-37.8	-37.1	-37.5	0.5
$[(\text{CH}_3)_3\text{Ge}-\text{CH}_3-\text{Sn}(\text{CH}_3)_3]^+$					
B3LYP	-22.8	-24.4	-23.2	-23.8	0.5
BMK	-25.1	-27.5	-26.3	-27.5	0.6
M06L	-27.5	-29.9	-27.5	-27.9	0.7
ω B97XD	-28.4	-30.6	-30.0	-30.5	0.5

^a Single-point calculation at the B3LYP/aug-cc-pVTZ optimized geometries with thermal correction to enthalpy at the B3LYP level

^b Basis set superposition error (kcal mol⁻¹) calculated by a counterpoise method at B3LYP/aug-cc-pVTZ optimized geometries

deviates from 120° , for the M, M'=Si complex, to 116.6° for M=Si, M'=Ge, 114.8° for M=Si, M'=Sn, and 116.2° for M=Ge, M'=Sn. Correspondingly, the NBO charge on M decreases and that on M' increases along with the planarity of the M'(CH₃)₃ group. Thus, in “mixed” (CH₃)₃M-CH₃-M'(CH₃)₃ intermediates, the structure may be presented as a complex between the M(CH)₄ molecule and the [M'(CH₃)₃]⁺ ion. This fact favors the detachment of [M'(CH₃)₃]⁺ ions and may be the reason for the fast dissociation of these ions.

Taking into account the comparison of the association energy, i.e., enthalpy of formation, of the [(CH₃)₃Si-CH₃-Si(CH₃)₃]⁺ ion with the experimental value we may predict similar energies for “mixed” ions. For the “symmetric” ion, the closest results were given by BSSE-corrected ω B97XD and M06L methods. For M, M' = Si, Ge these methods give, respectively, -27.0 and -26.7 kcal mol⁻¹, for M, M' = Si, Sn -37 and -35.5 kcal mol⁻¹, and for M, M' = Ge, Sn -30.0 and -27.2 kcal mol⁻¹ (Table 5).

Conclusions

1. The binding energy of trimethylsilylium ion with tetramethylsilane estimated by density functionals BMK, M06L, and ω B97XD are in a good agreement with the experimental value and the G2 theoretical estimation. Popular B3LYP substantially underestimates the reaction enthalpy. Basis set superposition error (BSSE) is small for B3LYP and ω B97XD, but substantially larger for the other two DFT methods employed. The BSSE corrected M06L (-21.6 kcal mol⁻¹) and ω B97XD (-22.9 kcal mol⁻¹) closely bracket the experimental value (-22.3 ± 0.4 kcal mol⁻¹), while G2 and G3 values overestimate it.
2. For the (CH₃)₃Si⁺ + (CH₃)₄Ge \leftrightarrow (CH₃)₄Si + (CH₃)₃Ge⁺ methide transfer reaction, the M06L method along with BMK provide the best fit to G2, G3 and experimental enthalpies.
3. For the reactions with M' = Sn, three methods (with the exclusion of B3LYP) give results within the chemical accuracy criterion (± 1 kcal mol⁻¹).
4. Structures of the “mixed” [(CH₃)₃M-CH₃-M'(CH₃)₃]⁺ (M \neq M') methide reaction intermediates of C_{3v} symmetry correspond to energy minima at potential energy surfaces. Their equilibrium structures indicate that they may be better described as M(CH)₄-[M'(CH₃)₃]⁺ complexes. These structures provide their fast decomposition and preclude their observation in experiment. Predicted complexation energies (BSSE corrected M06L/aug-cc-pVTZ values) are -26.7 kcal mol⁻¹ for M=Si, M' = Ge, -35.5 kcal mol⁻¹ for M=Si, M' = Sn, and -27.2 kcal mol⁻¹ for M=Ge, M' = Sn.

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