Theoretical Gas-Phase Stabilities of α-Trimethylsilyl-Substituted Tertiary Carbenium Ions

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Theoretical hydride ion affinities in the gas phase are presented for α-$SiMe_3$-substituted tertiary carbenium ions. Thermodynamic stabilization of the "nascent" ions by a single trimethylsilyl group is weaker than by a *tert*-butyl group but comparable to the effect of a methyl group. In the case of the cyclopropenylium cation, the stabilization by a trimethylsilyl group even exceeds the effectiveness of a *tert*-butyl group. Compliance constants are used to quantify the chemical concept of hyperconjugation.

Introduction

The effect of silicon on the stability of carbenium ions has been intensively investigated.[1,2] It is well known, from solvolytic and theoretical studies, that carbenium ions are stabilized more by β-silyl groups than by the corresponding β-alkyl groups and this β-silicon effect has been used in a variety of synthetic applications.[1] In contrast, the results obtained from α-silyl carbenium ions were less clear-cut. Ab-initio calculations by Apeloig,[3] Jorgensen[4] and others[1,5] showed that an α-SiH_3 group stabilizes the carbenium ion by 17.8 kcal mol^{-1} more than H, but 12.2 kcal mol^{-1} less than an α-CH_3 group. Discrepancies were observed particularly during solvolytic studies. Whereas Shimizu[6] reported a marked rate reduction by a factor of $1.6-3\cdot10^4$ by an α-$SiMe_3$ group relative to CH_3 and a similar rate for α-$SiMe_3$ compared with *t*Bu in benzyl solvolysis, Apeloig and Stanger[7] found the following relative reaction rates in 2-adamantyl solvolysis: k(α-$SiMe_3$)/k(α-Me)/k(α-*t*Bu) = 0.5:1:10^5. The differences were ascribed to steric effects.[6,8,9] Gas-phase experiments by Schwarz showed that α-silyl carbenium ions easily undergo 1,2-methyl and 1,2-H shifts to the β-silylcarbenium ions,[10,11] a fact which further complicates the situation. In theoretical studies, the $SiMe_3$ group effect is often extrapolated from the simple SiH_3 model calculations, while the influence of several silyl groups on the stability of an adjacent tertiary carbenium ion has not been explored so far.[12] In order to separate the different aspects of the α-silylcarbenium ion stability and reactivity we therefore, in a first step, performed a systematic quantum mechanical study of the gas-phase hydride ion affinities of the "nascent" $SiMe_3$-substituted tertiary carbenium ions.

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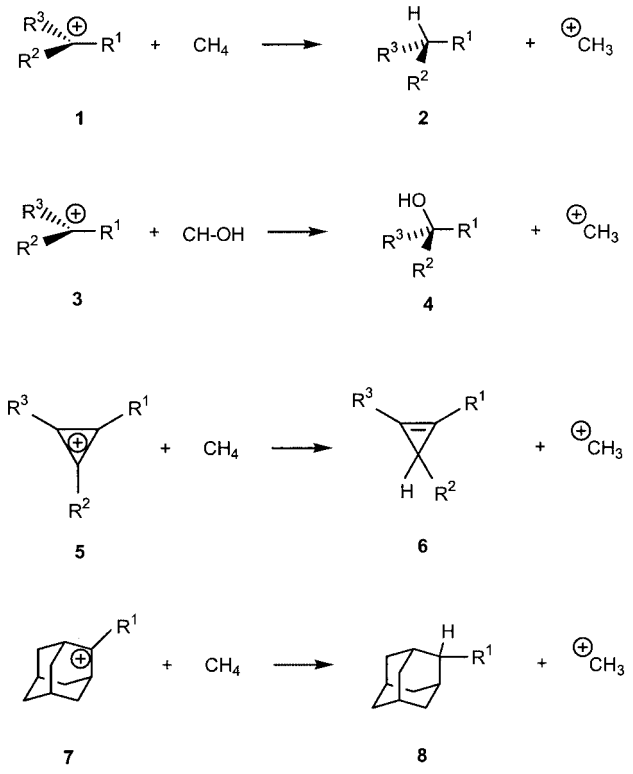
Computational Methods

As shown in Scheme 1, isodesmic hydride and hydroxide transfer reactions of three different carbenium ion systems were calculated as a measure of their relative thermodynamic stabilities. All calculations were carried out using the B3LYP hybrid density functional[14] and a double zeta standard basis set augmented with diffuse basis functions on heavy atoms [6-31+G(d)]. Since we were dealing with many nonbonded H···H interactions, we first checked the ability of our theoretical model to describe the correlated $SiMe_3$ rotation as a test case for sterically overcrowded silanes. In a combined low-temperature NMR, X-ray diffraction and Molecular Mechanics (MMX force field) study of tris(trimethylsilyl)methane, Casarini et al. found a barrier of 3.9 kcal/mol^{-1} for the correlated conrotatory $SiMe_3$ motion, starting from the C_3-symmetric global minimum.[13] Our calculations at the B3LYP/6-31+G(d) level of theory predicted a barrier of 3.4 kcal/mol^{-1} for this process, pointing to a realistic description of the studied $SiMe_3$-substituted systems, especially if we take into account the error cancellation due to approximately the same error on both sides of the isodesmic equation in Scheme 1. Preliminary calculations of the isodesmic reactions **1f** → **2f** and **1d** → **2d** with a 6-311G(d,p)-polarized triple-zeta basis set yielded energy differences of less than 1 kcal mol^{-1}, compared with the 6-31+G(d) basis. As a compromise between computing time and accuracy, further studies were carried out using the polarized double zeta basis augmented with diffuse functions instead of using a triple zeta 6-311G(d,p) basis



Scheme 1

set. For each carbenium ion, the search for stationary points on the potential energy surface started at the global minimum geometry of the alkane/alcohol precursors without any symmetry restraints, leading us to the "nascent" ions. All optimized structures were characterized as minima on the potential surface by analytical frequency calculations.[15] B3LYP/6-31+G(d) total energies (zero point corrected) of the optimized structures and the reaction energies of the isodesmic equations are summarized in Tables 1, 2, 3, and 4.

Results

Upon successive replacement of the α-substituent R^1 in the tertiary cation **1** while keeping the remaining substituents constant ($R^2 = R^3 = Me$), the following gas phase stabilities of the cations **1a**−**j** were obtained from their hydride ion affinities:

*t*Bu > $SiMe_3$ ≥ Me > SiH_3 >> H (Table 1)

According to our calculations, the methyl group stabilizes the adjacent carbenium ion (**1c**) by 16.9 kcal mol^{-1} in comparison with hydrogen (**1b**), which is consistent with experimental gas-phase hydride ion affinities for the *tert*-butyl ion (230.0 kcal mol^{-1}) and the isopropyl ion (246.8 kcal mol^{-1}).[16] The *t*Bu substituent in **1d** stabilizes the carbenium ion by a further 7.0 kcal mol^{-1} in comparison with a methyl substituent (**1c**). Replacement of R^1 by a silyl group gave mixed results, depending on the type of silyl group considered. The SiH_3-substituted carbenium ion **1e** is 9.8 kcal mol^{-1} less stable than the methyl-substituted cation **1c**. In contrast, $SiMe_3$ *stabilizes* the cation **1f** by 2.1 kcal mol^{-1} compared with a methyl group (**1c**). Whereas the destabilization caused by α-SiH_3 relative to α-Me agrees well with earlier calculations by Apeloig and Stanger, these authors deduced a significant destabilization for α-$SiMe_3$ (6−8 kcal mol^{-1}) on the basis of Hartree-Fock [6-31G(d)//3-21G] calculations on model systems in combination with essentially the same solvolysis rates for 2-(trimethylsilyl)-2-adamantyl *p*-nitrobenzoate and 2-methyl-2-adamamtyl *p*-nitrobenzoate.[7]

Nevertheless, the gas-phase stability order

*t*Bu > $SiMe_3$ ≥ Me > SiH_3 >> H

is maintained using hydroxide exchange instead of the hydride ion (Table 2) as well as in our direct calculations of the 2-adamantyl cation (**7**) gas-phase stabilities (Table 4).

The different behavior of SiH_3 and $SiMe_3$ with respect to carbenium ions **1** is even more pronounced when two or three of the substituents R^1, R^2, R^3 in **1** and **2** were replaced by silyl groups (Entries 7−10). Cation **1g** bearing two SiH_3

Table 1. Zero point corrected total energies E_{total} (B3LYP/6-31+G*) [Hartree] of the calculated structures **1** and **2** and reaction energies ΔE_{iso} [kcal mol^{-1}] of the corresponding isodesmic equation shown in Scheme 1

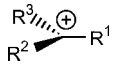
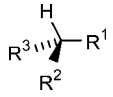
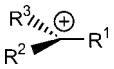
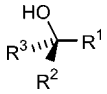
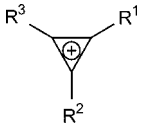
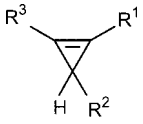
										
Entry	R^1	R^2	R^3	Cation	Symmetry	E_{total}	Alkane	Symmetry	E_{total}	ΔE_{iso}
1	H	H	H	**1a**	D_{3h}	−39.44878	**2a**	T_d	−40.47559	0
2	H	Me	Me	**1b**	C_2	−118.12410	**2b**	C_{2v}	−119.04472	66.6
3	Me	Me	Me	**1c**	C_3	−157.43856	**2c**	C_{3v}	−158.33220	83.5
4	*t*Bu	Me	Me	**1d**	C_1	−275.30146	**2d**	C_S	−276.18411	90.5
5	SiH_3	Me	Me	**1e**	C_1	−408.80995	**2e**	C_S	−409.71932	73.7
6	$SiMe_3$	Me	Me	**1f**	C_1	−526.72526	**2f**	C_S	−527.61613	85.6
7	SiH_3	SiH_3	Me	**1g**	C_1	−660.18240	**2g**	C_S	−661.11265	60.6
8	$SiMe_3$	$SiMe_3$	Me	**1h**	C_1	−896.00725	**2h**	C_1	−896.90391	81.6
9	SiH_3	SiH_3	SiH_3	**1i**	C_S	−911.55980	**2i**	C_3	−912.51353	45.8
10	$SiMe_3$	$SiMe_3$	$SiMe_3$	**1j**	C_3	−1265.28442	**2j**	C_3	−1266.19617	72.6

Table 2. Zero point corrected total energies E_{total} (B3LYP/6-31+G*) [Hartree] of the calculated structures **3** and **4** and reaction energies ΔE_{iso} [kcal mol^{-1}] of the corresponding isodesmic equation shown in Scheme 1

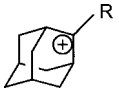
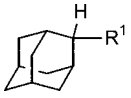
Entry	R^1	R^2	R^3	Cation	Symmetry	E_{total}	Alcohol	Symmetry	E_{total}	ΔE_{iso}
1	H	H	H	**3a**	C_1	−39.44878	**4a**	C_s	−115.67389	0
2	H	Me	Me	**3b**	C_2	−118.12410	**4b**	C_s	−194.25717	57.7
3	SiH_3	Me	Me	**3c**	C_1	−408.80995	**4c**	C_s	−484.92899	66.6
4	Me	Me	Me	**3d**	C_3	−157.43856	**4d**	C_s	−233.54811	72.5
5	$SiMe_3$	Me	Me	**3e**	C_1	−526.72526	**4e**	C_s	−602.82761	77.0
6	*t*Bu	Me	Me	**3f**	C_1	−275.30146	**4f**	C_s	−351.39757	80.9

Table 3. Zero point corrected total energies E_{total} (B3LYP/6-31+G*) [Hartree] of the calculated structures **5** and **6** and reaction energies ΔE_{iso} [kcal mol^{-1}] of the corresponding isodesmic equation shown in Scheme 1

Entry	R^1	R^2	R^3	Cation	Symmetry	E_{total}	Alkane	Symmetry	E_{total}	ΔE_{iso}
1	H	H	H	**5a**	D_{3h}	−115.68923	**6a**	C_{2v}	−116.56885	92.4
2	Me	Me	Me	**5b**	C_s	−233.62986	**6b**	C_s	−234.45273	128.0
3	SiH_3	SiH_3	SiH_3	**5c**	C_s	−987.79032	**6c**	C_s	−988.63090	116.9
4	*t*Bu	*t*Bu	*t*Bu	**5d**	C_s	−587.21876	**6d**	C_s	−588.02654	137.4
5	$SiMe_3$	$SiMe_3$	$SiMe_3$	**5e**	C_s	−1341.52667	**6e**	C_s	−1342.33075	139.8
6	Me	Me	*t*Bu	**5f**	C_s	−351.49461	**6f**	C_s	−352.31209	131.3
7	Me	Me	$SiMe_3$	**5g**	C_s	−587.21876	**6g**	C_s	−588.02654	136.8

Table 4. Zero point corrected total energies E_{total} (B3LYP/6-31+G*) [Hartree] of the calculated structures **7** and **8** and reaction energies ΔE_{iso} [kcal mol^{-1}] of the corresponding isodesmic equation shown in Scheme 1

Entry	R	Cation	Symmetry	E_{total}	Alkane	Symmetry	E_{total}	ΔE_{iso}
1	H	**7a**	C_s	−389.59321	**8a**	T_d	−390.48898	82.2
2	Me	**7b**	C_s	−428.90336	**8b**	C_s	−429.77389	98.1
3	SiH_3	**7c**	C_s	−680.27691	**8c**	C_s	−681.16161	89.2
4	*t*Bu	**7d**	C_s	−546.76086	**8d**	C_s	−547.61827	106.3
5	$SiMe_3$	**7e**	C_s	−798.18741	**8e**	C_s	−799.05590	99.3

groups was found to be 22.9 kcal mol^{-1} less stable than the corresponding cation **1c**. However, cation **1h** with two $SiMe_3$ groups was only slightly destabilized (1.9 kcal mol^{-1}) when compared with the methyl analogue **1c**. Replacement of all three substituents by silyl groups resulted in significant destabilization in both cases (**1i**: 3 × SiH_3, 37.7 kcal mol^{-1}; **1k**: 3 × $SiMe_3$, 10.9 kcal mol^{-1}) when compared with the *tert*-butyl cation **1c**.

In order to estimate different contributions in terms of concepts such as "inductive" or "hyperconjugative" effects, we analyzed the B3LYP 6-31+G(d) compliance matrices[17] for the systems **2f/1f** and **2d/1d**. Figure 1 shows a comparison of the relevant B3LYP/6-31+G(d) compliance constants for the C−Si (C−C) stretching force constant and the C−Si (C−C) torsional force constant. Since compliance constants (unit: Å mdyn^{-1}) measure the displacement of a specific bond under a unit force, a lower numerical value corresponds to a stronger bond. In the case of **1d**, hydride elimination leads to the well-known hyperconjugative stabilization of the 1,1,2,2-tetramethylpropylium ion (**2d**). After H^- ion elimination, the α-C−C bond length becomes shorter (from 1.53 to 1.47 Å) and stronger (from 0.306 to 0.254 Å mdyn^{-1}),[18] while the "donating" C−Me bond becomes weaker (from 0.268 to 0.458 Å mdyn^{-1}). The

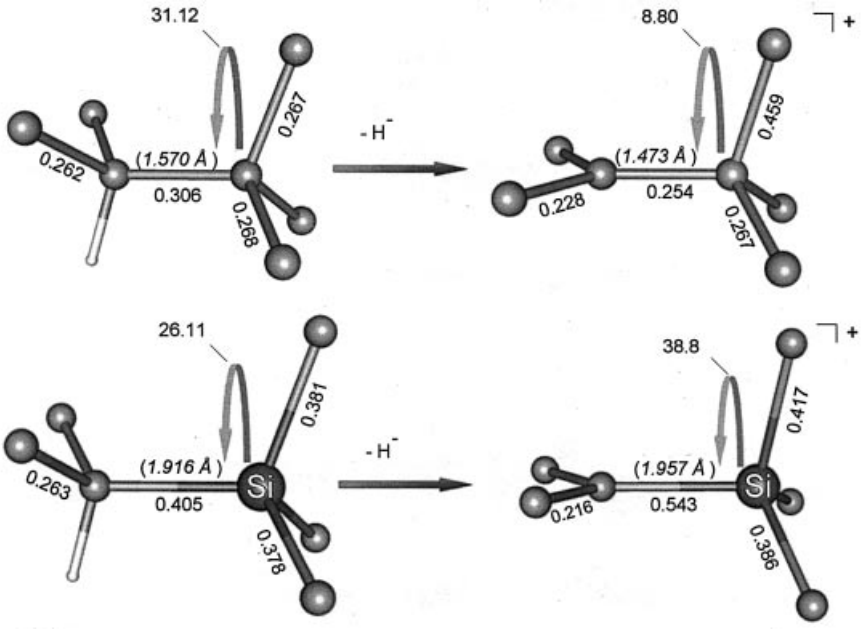


Figure 1. C−C (C−Si) stretching and C−CMe_3 (C−$SiMe_3$) rotational compliance constants at the B3LYP/6-31+G(d) level of theory for structures **2f/1f** and **2d/1d** (methyl hydrogenn atoms omitted); a lower numerical value of the compliance constant is connected with a stronger bond

C−CMe_3 rotational compliance constant showed a pronounced rigidity after H^- ion elimination pointing to a partial double-bond character of the α-C−C bond. Both effects are in agreement with the concept of hyperconjugation. Turning attention to the $SiMe_3$-substituted system **1f/2f** we found quite the opposite trend. Hydride ion elimination led to a *lengthening* (from 1.916 to 1.957 Å) and a *weakening* (from 0.405 to 0.543 Å $mdyn^{-1}$) of the C−Si bond, while the C−$SiMe_3$ rotational compliance constant points to a flattening of the energy surface for the carbenium ion, excluding hyperconjugation. A pronounced +I effect in combination with the absence of hyperconjugation should make the $SiMe_3$ group an ideal candidate for the stabilization of aromatic carbenium ions. Indeed, the first crystal structure of an α-trialkylsilyl-substituted carbenium ion was the tris-(trimethylsilyl)cyclopropenylium cation.[5] We therefore computed the hydride ion affinities for selected cyclopropenylium systems, which are summarized in Table 3. Stabilization of the carbenium ion by an $SiMe_3$ group is even more effective than a *tert*-butyl group where, in this case, hyperconjugation led to a perturbation of the aromatic system (Entries 6 and 7 in Table 3).

Conclusions

The major findings of our study are as follows: 1) Due to gas-phase calculations, the stabilization of a "nascent" tertiary carbenium ion by an α-$SiMe_3$ group is 4.9 kcal mol^{-1} smaller than by an α-*t*Bu substituent. The effects of α-$SiMe_3$ and α-Me are comparable and significantly larger than those observed for α-SiH_3. This stabilization effect of carbenium ions does not follow a simple additive scheme. If several silyl groups are placed around the cationic center, a pronounced destabilization can be observed. 2) The stabilizing ability of a single α-$SiMe_3$ group is caused by a positive inductive effect of the silicon atom and its methyl substituents, while hyperconjugation is absent. 3) Theoretical compliance constants offer a unique tool for studying and quantifying chemical concepts such as "hyperconjugation" or "inductive effects".

Acknowledgments

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[18] For comparison: Using a B3LYP compliance matrix, the strength of the "real" C=C double bond in ethylene is 0.102 Å mdyn^{-1} and 0.104 Å mdyn^{-1} with a double and a triple zeta basis, respectively. See: J. Grunenberg, N. Goldberg, *J. Am. Chem. Soc.* **2000**, *122*, 6046.

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