

31G**) for all data and used these throughout the text (see Table I). All species reported are considered to be equilibrium structures, since the force-constant matrix obtained from the 6-31G* (CH₆²⁺) and 3-21G^s (C₂H₄²⁺, C₂H₆²⁺, and C₂H₈²⁺) optimized geometries have no negative eigenvalues, except **2**, which has one. The zero-point vibrational energies deduced from these force constants (see Table I) are after scaling⁸ included as our final adjustment in all subsequent reaction energies given at the MP3/6-31G** level (Scheme I).

The methane dication, CH₄²⁺, is trivalent and tetracoordinate with a planar (*D*_{4h} symmetry) geometry.⁹ Interaction of molecular hydrogen with the empty p_z orbital of CH₄²⁺ results in CH₆²⁺. Diprotonated methane is *hexacoordinate*. The minimum-energy equilibrium structure **1** (Chart I) calculated for CH₆²⁺ (see Table I) has two orthogonal 3c-2e interactions (*C*_{2v} symmetry), emphasizing the importance of this effect. The structure **2** with only one such interaction may be regarded as the transition for transfer of one 3c-2e interaction in **1** and is 2.6 kcal/mol higher in energy. The stabilization of **1** gained with respect to CH₄²⁺ amounts to 79.4 kcal/mol. Intuitively one expects carbocations to be highly unstable because of electrostatic repulsion. Indeed CH₆²⁺ has a high exothermicity of 63.1 kcal/mol for proton loss and of 126.8 kcal/mol toward dissociation to CH₃⁺ and H₃⁺. However, our studies indicate a barrier of 40 kcal/mol (MP3/6-31G**) for the deprotonation and suggest even more for loss of H₃⁺. Since CH²⁺, CH₂²⁺, CH₃²⁺, and CH₄²⁺ have already been reported in a gas-phase study,¹⁰ CH₆²⁺ may be also a viable species. The calculated heat of formation of 651 ± 3 kcal/mol is actually the lowest of the C₁ dications.

In diprotonated ethane, C₂H₆²⁺, each carbon is *pentacoordinate*. We may regard C₂H₈²⁺ as hydrogenated ethane dication, C₂H₆²⁺ (see later). Even better, C₂H₈²⁺ can be considered as doubly hydrogenated ethylene dication, C₂H₄²⁺, with each of the orthogonal vacant p_z orbitals in strong interaction with a hydrogen molecule. This view is confirmed through the calculations. For the equilibrium structure with minimum energy we find C₂ symmetry (**3**) with the two 3c-2e interactions at about a 90° dihedral angle. The Newman projection (Scheme I) shows that complexation of the two hydrogen molecules only slightly distorts the perpendicular ethylene dication skeleton **5** (*D*_{2d} symmetry). At the 6-31G** level **3** is 9.4 (HF) and 3.0 (MP3) kcal/mol more stable than the second equilibrium structure **4** (*D*_{4d} symmetry) and therefore underlines the importance of 3c-2e interactions. The heat of hydrogenation of C₂H₄²⁺ to give diprotonated ethane is 79.8 kcal/mol. The most likely dissociation of C₂H₈²⁺ is toward CH₅⁺ and CH₃⁺ and is exothermic by 100.1 kcal/mol. A significant barrier for dissociation is expected, however, because of the distinct reorganization of atoms needed in the transition state.

We reported recently¹¹ the structure of the ethane dication as the doubly bridged, diborane-like dication **6** (*D*_{2d} symmetry). Schleyer et al.¹² subsequently found the carbenium-carbonium structure **7** (*C*_{2v} symmetry) to be 9.0 kcal/mol more stable (MP4SDQ/6-31G**//6-31G*). The preference of **7** was explained by the reduced electrostatic repulsion for the hydrogens lying farther apart and the stronger C-C bonding through hyperconjugation.¹² Structure **7** has a *tri- and a tetravalent* carbon with *tri- and pentacoordination*, respectively. In the context of the present concept one might formulate C₂H₆²⁺ as hydrogenated

C₂H₄²⁺. Complexation of molecular hydrogen with a vacant orbital on one of the carbons of the ethylene dication **5** is then expected to result in the carbenium-carbonium dication C₂H₆²⁺, with the carbonium center involved in a 3c-2e interaction as in **8** (*C*_v symmetry). This is indeed confirmed by our calculations on a reinvestigation of C₂H₆²⁺. The equilibrium structure **8** is 3.5 kcal/mol (MP3/6-31G**) more stable than **7**, reported by Schleyer et al.¹² (see Table I). The Newman projection of **8** shows the orthogonality of the 3c-2e interaction and the vacant p orbital and also suggests a somewhat larger hyperconjugation as in **7**. The hydrogenation of the ethylene dication **5** is exothermic by 43.5 kcal/mol. The kinetic stability of C₂H₄²⁺ combined with the reported barrier for dissociation of C₂H₆²⁺,¹² now adjusted for **8**, of 30 kcal/mol may render the ethane dication feasible for experimental observation.

The calculations further suggest that all three hypercoordinate dications, CH₆²⁺, C₂H₈²⁺, and C₂H₆²⁺, with coordination numbers 6, 5-5, and 5-3, respectively, may be viable species. A possible route to experimental observation could be via hydrogenation of the appropriate carbocationic precursors, obtained by the mass spectroscopic charge-stripping technique in the presence of hydrogen in the neutral gas.

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Registry No. CH₆²⁺, 83561-00-6; C₂H₈²⁺, 83561-01-7; CH₄²⁺, 34557-54-5; C₂H₄²⁺, 54509-73-8.

Bimolecular Substitution at Carbon in Neopentyl-Like Silylcarbonyl Sulfonates

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There is considerable current synthetic and mechanistic interest in silicon chemistry. It has been reasonably well established that carbocations are stabilized by β-silicon substitution and largely by implication that they are destabilized by α-silicon substitution.^{1,2} For example, no detectable reaction of (CH₃)₃SiCH₂X (X = Br, Cl) was observed in aqueous solvents at 70 °C.³ Furthermore, PhCMe(SiMe₃)Br reacts slower than PhC(CH₃)₂Br, as does (CH₃)₃SiC(CH₃)₂Br compared to (CH₃)₃CC(CH₃)₂Br.⁴

The effect of silicon substitution at the reaction center on a bimolecular displacement at carbon is even less well understood. Thus, while (CH₃)₃SiCH₂Br reacts 2600 times more rapidly with ethoxide in ethanol than does (CH₃)₃CCH₂Br,⁵ (CH₃)₃SiCH₂Cl reacts slower than CH₃CH₂Cl with I⁻ in aqueous ethanol and faster than CH₃CH₂Cl with I⁻ in acetone.³

The solvolysis reaction of neopentyl-X compounds proceeds with considerable *k*_A character in many solvents, resulting in

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Table I. Solvolysis Rates and Parameters for 1 and 2

compd	temp, °C	solvent ^a	k , s ⁻¹	m_{OTs}^b	m_{Cl}^c	E_a , kcal·mol ⁻¹	ΔS^\ddagger , eu					
1a	25.0	60E	1.44×10^{-6d}	0.23	0.19	20.5	-18.8					
		80E	8.81×10^{-7d}									
	65.04 ± 0.02	60E	$(8.43 \pm 0.01) \times 10^{-5}$									
	75.32 ± 0.05	60E	$(2.02 \pm 0.01) \times 10^{-4}$									
		70E	$(1.574 \pm 0.005) \times 10^{-4}$									
		80E	$(1.24 \pm 0.04) \times 10^{-4}$									
1b	94.7 ± 0.15	97T	$(2.249 \pm 0.002) \times 10^{-5}$	0.34	0.31							
	25.0	60E	0.214 ^d									
		80E	9.59×10^{-2d}									
	-20.3 ± 0.1	97T	7.38×10^{-5d}									
		90E	$(5.05 \pm 0.03) \times 10^{-4}$									
	-10.2 ± 0.1	95E	$(3.40 \pm 0.06) \times 10^{-4}$									
		100E	$(2.02 \pm 0.09) \times 10^{-4}$									
	34.97 ± 0.01	95E	$(1.12 \pm 0.06) \times 10^{-3}$									
		100E	$(5.70 \pm 0.06) \times 10^{-4}$									
	14.9 ± 0.1	97T	$(1.83 \pm 0.04) \times 10^{-4}$									
25.0	97T	$(2.84 \pm 0.01) \times 10^{-5}$										
2a	25.0	60E	7.87×10^{-10e}	0.58	0.52	26.7	-18.3					
		80E	2.05×10^{-9e}									
	75.0	100E	2.7×10^{-8e}									
		90E	9.6×10^{-8e}									
	100.0	80E	2.6×10^{-7e}									
		100E	3.6×10^{-7e}									
	94.7 ± 0.15	90E	1.6×10^{-6e}									
		80E	4.3×10^{-6e}									
	2b	25.01 ± 0.01	97T					$(2.35 \pm 0.05) \times 10^{-5}$	0.49	0.39	19.4	-14.1
			60E					2.235×10^{-4}				
70E		$(1.39 \pm 0.06) \times 10^{-4}$										
80E		$(8.19 \pm 0.06) \times 10^{-5}$										
97T		1.375×10^{-4}										
80E		2.552×10^{-4}										
35.72 ± 0.02	97T	$(4.35 \pm 0.05) \times 10^{-4}$										
34.97 ± 0.03	97T	$(4.004 \pm 0.002) \times 10^{-5}$										
14.9 ± 0.1						21.0	-7.8					

^a 60E = 60:40 (v/v) ethanol:water; similarly 70E, 80E, 90E, 95E, 100E; 97T = 97:3 (w/w) 2,2,2-trifluoroethanol:water. ^b Solvent dependence based on $Y_2\text{-AdOTs}$ from ref 16. ^c Solvent dependence based on Y from ref 16. ^d Extrapolated. ^e Reference 17.

substantial rearrangement of the carbon skeleton.⁶⁻¹⁰ Furthermore, the greatly reduced rate of bimolecular displacement arising from β -alkyl substitution in this system is well documented.^{11,12} Moreover, it has been concluded¹³ that in the gas phase $\text{H}_3\text{SiCH}_2^+$ is less stable than $\text{CH}_3\text{SiH}_2^+$ by 49.1 kcal·mol⁻¹ and $(\text{CH}_3)_3\text{SiC}^+(\text{CH}_3)_2$ is calculated to be less stable than $(\text{CH}_3)_3\text{CSi}^+(\text{CH}_3)_2$ by about 23 kcal·mol⁻¹.¹⁴ Clearly these data imply a substantial driving force associated with the rearrangement $(\text{CH}_3)_3\text{SiCH}_2^+ \rightarrow (\text{CH}_3)_2\text{Si}^+\text{CH}_2\text{CH}_3$.

Therefore we chose to investigate the solvolysis of the silyl analogues **1** ($(\text{CH}_3)_3\text{SiCH}_2\text{X}$, **a**, $\text{X} = p\text{-OSO}_2\text{C}_6\text{H}_4\text{CH}_3$; **b**, $\text{X} = \text{OSO}_2\text{CF}_3$) of the neopentyl carbon skeleton **2** ($(\text{CH}_3)_3\text{CCH}_2\text{X}$, **a**, $\text{X} = p\text{-OSO}_2\text{C}_6\text{H}_4\text{CH}_3$; **b**, $\text{X} = \text{OSO}_2\text{CF}_3$).

We report that **1a** and **1b** undergo a facile substitution reaction without detectable rearrangement under the conditions described in Table I. These data indicate a dramatic change in the mechanism of the substitution reaction of the silyl analogues when compared to the neopentyl compounds.

First, unlike neopentyl-X compounds, the silyl analogue, **1b** solvolyzes in absolute ethanol at -20 °C without observable rearrangement, yielding $(\text{CH}_3)_3\text{SiCH}_2\text{OCH}_2\text{CH}_3$ exclusively. In

contrast, neopentyl tosylate affords 92% rearranged products and 8% neopentyl ethyl ether upon ethanolysis.^{7,8} This observation speaks against two possible mechanisms of reaction. A sulfur-oxygen cleavage mechanism would be expected to yield substantial amounts of the corresponding alcohol, and theoretical calculations indicate that formation of $(\text{CH}_3)_3\text{SiCH}_2^+$ should result in substantial amounts of rearranged products as well.¹⁵

Secondly, the change in m_{OTs} ¹⁶ from 0.49 for **2b** to 0.34 for **1b** implies an increased component of nucleophilic solvent participation in the solvolysis of **1b** that is not present in **2b**. A similar effect is noted for **2a** and **1a**, where m_{OTs} decreases from 0.58 to 0.23, respectively. Corresponding decreases are seen in plots of $\log k$ vs. $Y_{\text{t-BuCl}}$.

Perhaps the most striking demonstration of the bimolecular nature of the solvolysis reaction of **1** is seen in an examination of the relative rates of solvolysis in the less nucleophilic solvent 97% aqueous trifluoroethanol (97T). While the silyl analogue reacts 957 times faster than the carbon analogue (k_{1b}/k_{2b}) in 60E at 25 °C, a reversal of the rate ratio is observed in 97T at 25 °C, where $k_{1b}/k_{2b} = 0.54$. Similarly $k_{1a}/k_{2a} = 1830$ in 60E at 25 °C and 0.96 in 97T at 95 °C. We believe these data to be consistent only with a direct displacement by solvent in the case of the silyl "neopentyl-like" sulfonate esters.

We have pursued the question of $\text{S}_{\text{N}}1$ vs. $\text{S}_{\text{N}}2$ reactions of **1** and **2** from theory as well. Calculations were carried out with the GAUSSIAN 80 series of programs.¹⁸ The structures of all relevant species were fully optimized by using the split-valence

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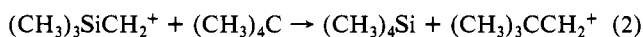
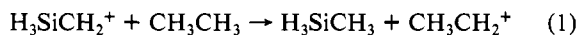
(15) At 3-21G//3-21G $(\text{CH}_3)_3\text{SiCH}_2^+$ is calculated to be less stable than $(\text{CH}_3)_2\text{Si}^+\text{CH}_2\text{CH}_3$ by ca. 48 kcal·mol⁻¹. Preliminary calculations indicate that the energy barrier for 1,2-methyl migration is small.

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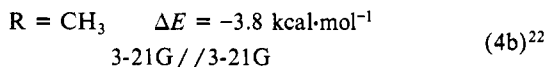
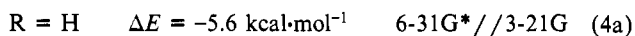
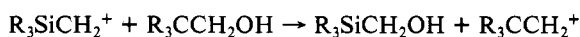
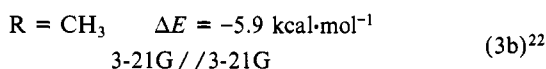
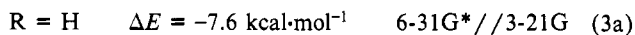
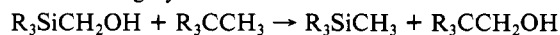
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3-21G basis set^{19a} (denoted as 3-21G//3-21G), and single-point calculations were then carried out at the 3-21G optimized geometries with the polarized 6-31G* basis set^{19b} (i.e., 6-31G*/3-21G). The calculations show that an α -silyl substituent is considerably less effective in stabilizing CH_3^+ than an α -methyl. At 6-31G*, CH_3CH_2^+ is more stable than $\text{H}_3\text{SiCH}_2^+$ by 13.2 kcal·mol⁻¹ (eq 1).^{5,20} An α -H₃Si substituent is, however, more stabilizing than



hydrogen by 16.1 kcal·mol⁻¹ (6-31G*/3-21G). β -Methyl substitution stabilizes $\text{H}_3\text{SiCH}_2^+$ somewhat more effectively than it stabilizes CH_3CH_2^+ so that $(\text{CH}_3)_3\text{SiCH}_2^+$ is less stable than $(\text{CH}_3)_3\text{CCH}_2^+$ by 11.0 kcal·mol⁻¹ (eq 2, 3-21G//3-21G).^{21,22} These results are surprising in light of the lower electronegativity of silicon compared to carbon (Pauling's electronegativities: Si, 1.8; C, 2.5^{23a}) and the fact that $(\text{CH}_3)_3\text{Si}$ is a stronger σ donor than *t*-Bu (σ_1 values are -0.11 and -0.01, respectively^{23b}). The calculations show that the destabilizing effect of silyl groups (relative to alkyl groups) results from a weaker hyperconjugation and from the electrostatic repulsion between the adjacent positively charged cationic carbon and silicon. Note, however, that α -alkyl and α -silyl substituents stabilize vinyl cations to a similar extent.²⁴

The energy differences between the ground states of **1** and **2** (modeled computationally by the corresponding alcohols²⁵) are relatively small (eq 3a and 3b²⁶). Equation 4b, which models the $\text{S}_{\text{N}}1$ reactivities of **1** and **2** more closely than eq 2,^{25,26} is therefore also highly exothermic.



We conclude that the $\text{S}_{\text{N}}1$ reactivity of neopentyl derivatives (**2**) is considerably higher than that of the corresponding silyl derivatives (**1**).

The effect of silyl substitution at carbon on the $\text{S}_{\text{N}}2$ reactivity is even more dramatic. The calculated barriers for the $\text{S}_{\text{N}}2$ hydride exchange reactions²⁷ 5a, 5b, and 5c are 47.4 (44.3), 50.1 (47.4), and 35.9 (35.3) kcal·mol⁻¹, respectively, at 6-31G*/3-21G (the values in parentheses are at 3-21G//3-21G).

(19) (a) First row: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939-947. Second row: Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *Ibid.* **1982**, *104*, 2797-2803. (b) First row: Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213-222. Second row: Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039-5048.

(20) (a) This result is in excellent agreement with the computations of the following: Hopkinson, A. C.; Lien, M. H. *J. Org. Chem.* **1981**, *46*, 998-1003.

(b) The minimal STO-3G basis set leads to erroneous results (see: Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 1291-1296, and ref 23), and it should be applied to molecules that contain silicon with great caution.

(21) This applies to the classical structures. At 3-21G $(\text{CH}_3)_3\text{SiCH}_2^+$ does not collapse to $(\text{CH}_3)_2\text{Si}^+\text{CH}_2\text{CH}_3$.¹⁵

(22) Our experience shows that the calculated energies of such isodesmic equations are practically identical at 6-31G*/3-21G and 3-21G//3-21G.

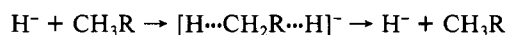
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(25) The validity of this approach is discussed in ref 24a.

(26) ΔE of eq 3b for the sulfonates is probably even less exothermic due to F strain between the sulfonate and the $(\text{CH}_3)_3\text{C}$ substituent.

(27) Given by the energy difference between the reactants and the transition state which was assumed to possess C_3 (D_{3h} in CH_3^-) symmetry. The symmetry plane is defined by the central carbon and the two apical hydrogens.



The dramatic lowering of the $\text{S}_{\text{N}}2$ barrier by $\text{R} = \text{H}_3\text{Si}$ results primarily from the fact that H_3Si is a better σ acceptor than CH_3 ²⁸ and therefore stabilizes the negatively charged transition state more effectively. The barrier in the $\text{S}_{\text{N}}2$ reaction for C_2H_6 is only 2.7 kcal·mol⁻¹ higher than for CH_4 , but for neopentane steric crowding in the transition state raises the barrier significantly to 52.0 kcal·mol⁻¹ (eq 5d, 3-21G//3-21G). Due to the long C-Si bonds, steric crowding in the transition state for eq 5e is much smaller than in the carbon analogue for eq 5d and the barrier for substitution at $(\text{CH}_3)_3\text{SiCH}_3$ is 33.0 kcal·mol⁻¹ (eq 5e, 3-21G//3-21G),²⁹ 20 kcal·mol⁻¹ lower than for $(\text{CH}_3)_3\text{CCH}_3$.³⁰

In conclusion, both calculations and experimental data indicate that *silylcarbinyl sulfonates*, **1**, react slower than their neopentyl analogues, **2**, via the $\text{S}_{\text{N}}1$ mechanism, but faster than **2** via the $\text{S}_{\text{N}}2$ mechanism.

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Registry No. **1a**, 59006-07-4; **1b**, 64035-64-9; **5a**, 74-82-8; **5b**, 74-84-0; **5c**, 992-94-9.

(28) The calculated proton affinity of $\text{H}_3\text{SiCH}_2^-$ is 33.0 kcal·mol⁻¹ lower than that of CH_3CH_2^- .^{20a}

(29) Thus, methyl substitution reduces the $\text{S}_{\text{N}}2$ barrier by 2.3 kcal·mol⁻¹, probably due to the better charge dispersal in the negatively charged transition state by the larger $(\text{CH}_3)_3\text{Si}$ substituent.

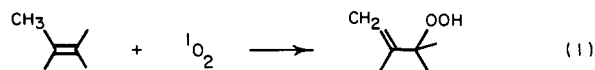
(30) Similar results are obtained for the analogous fluoride-exchange reactions.

Ene Reaction of Singlet Oxygen: An Entropy-Controlled Process Determines the Reaction Rate

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The chemistry of singlet oxygen ($^1\Delta_g$, $^1\text{O}_2$) has been extensively studied and is of continuing interest.¹ The "ene" reaction of $^1\text{O}_2$ with olefins containing an allylic hydrogen is a synthetically useful route to allylic hydroperoxides² (eq 1). Proposed mechanisms



for this conversion include a concerted reaction³ and stepwise sequences proceeding through a biradical (**1**, Chart I),⁴ a zwitterion

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