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* (CH_6^{2+}) and 3-21G[5] ($C_2H_4^{2+}$, $C_2H_6^{2+}$, and $C_2H_8^{2+}$) 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 scaling[8] included as our final adjustment in all subsequent reaction energies given at the MP3/6-31G** level (Scheme I).

The methane dication, CH_4^{2+}, is trivalent and tetracoordinate with a planar (D_{4h} symmetry) geometry.[9] Interaction of molecular hydrogen with the empty p_z orbital of CH_4^{2+} results in CH_6^{2+}. Diprotonated methane is *hexacoordinate*. The minimum-energy equilibrium structure **1** (Chart I) calculated for CH_6^{2+} (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 CH_4^{2+} amounts to 79.4 kcal/mol. Intuitively one expects carbodications to be highly unstable because of electrostatic repulsion. Indeed CH_6^{2+} has a high exothermicity of 63.1 kcal/mol for proton loss and of 126.8 kcal/mol toward dissociation to CH_3^+ and H_3^+. However, our studies indicate a barrier of 40 kcal/mol (MP3/6-31G**) for the deprotonation and suggest even more for loss of H_3^+. Since CH^{2+}, CH_2^{2+}, CH_3^{2+}, and CH_4^{2+} have already been reported in a gas-phase study,[10] CH_6^{2+} may be also a viable species. The calculated heat of formation of 651 ± 3 kcal/mol is actually the lowest of the C_1 dications.

In diprotonated ethane, $C_2H_8^{2+}$, *each carbon is pentacoordinate*. We may regard $C_2H_8^{2+}$ as hydrogenated ethane dication, $C_2H_6^{2+}$ (see later). Even better, $C_2H_8^{2+}$ can be considered as doubly hydrogenated ethylene dication, $C_2H_4^{2+}$, 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 C_2 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 $C_2H_4^{2+}$ to give diprotonated ethane is 79.8 kcal/mol. The most likely dissociation of $C_2H_8^{2+}$ is toward CH_5^+ and CH_3^+ 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 recently[11] 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 $C_2H_6^{2+}$ as hydrogenated $C_2H_4^{2+}$. 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 $C_2H_6^{2+}$, with the carbonium center involved in a 3c-2e interaction as in **8** (C_s symmetry). This is indeed confirmed by our calculations on a reinvestigation of $C_2H_6^{2+}$. 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 $C_2H_4^{2+}$ combined with the reported barrier for dissociation of $C_2H_6^{2+}$,[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, CH_6^{2+}, $C_2H_8^{2+}$, and $C_2H_6^{2+}$, 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 carbodication precursors, obtained by the mass spectroscopic charge-stripping technique in the presence of hydrogen in the neutral gas.

Acknowledgment. The cooperation of the USC computer center greatly facilitated the present investigation. M.B. thanks the Italian Consiglio Nationale delle Ricerche for the award of a National Scholarship for research abroad.

Registry No. CH_6^{2+}, 83561-00-6; $C_2H_8^{2+}$, 83561-01-7; CH_4^{2+}, 34557-54-5; $C_2H_4^{2+}$, 54509-73-8.

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Bimolecular Substitution at Carbon in Neopentyl-Like Silylcarbinyl 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 $(CH_3)_3SiCH_2X$ (X = Br, Cl) was observed in aqueous solvents at 70 °C.[3] Furthermore, $PhCMe(SiMe_3)Br$ reacts slower than $PhC(CH_3)_2Br$, as does $(CH_3)_3SiC(CH_3)_2Br$ compared to $(CH_3)_3CC(CH_3)_2Br$.[4]

The effect of silicon substitution at the reaction center on a bimolecular displacement at carbon is even less well understood. Thus, while $(CH_3)_3SiCH_2Br$ reacts 2600 times more rapidly with ethoxide in ethanol than does $(CH_3)_3CCH_2Br$,[5] $(CH_3)_3SiCH_2Cl$ reacts slower than CH_3CH_2Cl with I^- in aqueous ethanol and faster than CH_3CH_2Cl with I^- in acetone.[3]

The solvolysis reaction of neopentyl-X compounds proceeds with considerable k_Δ 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}	$\Delta S^{\ddagger}$, eu
1a	25.0	60E	1.44×10^{-6}[d]				
		80E	8.81×10^{-7}[d]				
	65.04 ± 0.02	60E	$(8.43 \pm 0.01) \times 10^{-5}$				
	75.32 ± 0.05	60E	$(2.02 \pm 0.01) \times 10^{-4}$	0.23	0.19	20.5	−18.8
		70E	$(1.574 \pm 0.005) \times 10^{-4}$				
		80E	$(1.24 \pm 0.04) \times 10^{-4}$				
	94.7 ± 0.15	97T	$(2.249 \pm 0.002) \times 10^{-5}$				
1b	25.0	60E	0.214[d]				
		80E	9.59×10^{-2}[d]				
		97T	7.38×10^{-5}[d]				
	−20.3 ± 0.1	90E	$(5.05 \pm 0.03) \times 10^{-4}$	0.34	0.31		
		95E	$(3.40 \pm 0.06) \times 10^{-4}$				
		100E	$(2.02 \pm 0.09) \times 10^{-4}$				
	−10.2 ± 0.1	95E	$(1.12 \pm 0.06) \times 10^{-3}$			15.8	−13.7
		100E	$(5.70 \pm 0.06) \times 10^{-4}$			13.7	−23.0
	34.97 ± 0.01	97T	$(1.83 \pm 0.04) \times 10^{-4}$			16.4	−24.4
	14.9 ± 0.1		$(2.84 \pm 0.01) \times 10^{-5}$				
2a	25.0	60E	7.87×10^{-10}[e]				
		80E	2.05×10^{-9}[e]				
	75.0	100E	2.7×10^{-8}[e]	0.58	0.52	26.7	−18.3
		90E	9.6×10^{-8}[e]			29.2	−8.9
		80E	2.6×10^{-7}[e]			29.0	−7.5
	100.0	100E	3.6×10^{-7}[e]				
		90E	1.6×10^{-6}[e]				
		80E	4.3×10^{-6}[e]				
	94.7 ± 0.15	97T	$(2.35 \pm 0.05) \times 10^{-5}$				
2b	25.01 ± 0.01	60E	2.235×10^{-4}				
		70E	$(1.39 \pm 0.06) \times 10^{-4}$				
		80E	$(8.19 \pm 0.06) \times 10^{-5}$	0.49	0.39	19.4	−14.1
		97T	1.375×10^{-4}				
	35.72 ± 0.02	80E	2.552×10^{-4}				
	34.97 ± 0.03	97T	$(4.35 \pm 0.05) \times 10^{-4}$			21.0	−7.8
	14.9 ± 0.1		$(4.004 \pm 0.002) \times 10^{-5}$				

[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 concluded[13] that in the gas phase $H_3SiCH_2^+$ is less stable than $CH_3SiH_2^+$ by 49.1 kcal·mol^{-1} and $(CH_3)_3SiC^+(CH_3)_2$ is calculated to be less stable than $(CH_3)_3CSi^+(CH_3)_2$ by about 23 kcal·mol^{-1}.[14] Clearly these data imply a substantial driving force associated with the rearrangement $(CH_3)_3SiCH_2^+ \rightarrow (CH_3)_2Si^+CH_2CH_3$.

Therefore we chose to investigate the solvolysis of the silyl analogues **1** ($(CH_3)_3SiCH_2X$, **a**, X = p-$OSO_2C_6H_4CH_3$; **b**, X = OSO_2CF_3) of the neopentyl carbon skeleton **2** ($(CH_3)_3CCH_2X$, **a**, X = p-$OSO_2C_6H_4CH_3$; **b**, X = OSO_2CF_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 $(CH_3)_3SiCH_2OCH_2CH_3$ 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 $(CH_3)_3SiCH_2^+$ 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. $Y_{t\text{-BuCl}}$.

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 S_N1 vs. S_N2 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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(16) log k vs. $Y_{2\text{-AdOTs}}$ from the following: Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667–7674.

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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 $H_3SiCH_2^+$ by 13.2 kcal·mol^{-1} (eq 1).[5,20] An α-H_3Si substituent is, however, more stabilizing than

$$H_3SiCH_2^+ + CH_3CH_3 \rightarrow H_3SiCH_3 + CH_3CH_2^+ \quad (1)$$

$$(CH_3)_3SiCH_2^+ + (CH_3)_4C \rightarrow (CH_3)_4Si + (CH_3)_3CCH_2^+ \quad (2)$$

hydrogen by 16.1 kcal·mol^{-1} (6-31G*//3-21G). β-Methyl substitution stabilizes $H_3SiCH_2^+$ somewhat more effectively than it stabilizes $CH_3CH_2^+$ so that $(CH_3)_3SiCH_2^+$ is less stable than $(CH_3)_3CCH_2^+$ 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 $(CH_3)_3Si$ is a stronger σ donor than *t*-Bu (σ_I 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 alcohols[25]) are relatively small (eq 3a and 3b[26]). Equation 4b, which models the S_N1 reactivities of **1** and **2** more closely than eq 2,[25,26] is therefore also highly exothermic.

$$R_3SiCH_2OH + R_3CCH_3 \rightarrow R_3SiCH_3 + R_3CCH_2OH$$

$$R = H \quad \Delta E = -7.6 \text{ kcal·mol}^{-1} \quad 6\text{-}31G^*//3\text{-}21G \quad (3a)$$

$$R = CH_3 \quad \Delta E = -5.9 \text{ kcal·mol}^{-1} \quad 3\text{-}21G//3\text{-}21G \quad (3b)^{22}$$

$$R_3SiCH_2^+ + R_3CCH_2OH \rightarrow R_3SiCH_2OH + R_3CCH_2^+$$

$$R = H \quad \Delta E = -5.6 \text{ kcal·mol}^{-1} \quad 6\text{-}31G^*//3\text{-}21G \quad (4a)$$

$$R = CH_3 \quad \Delta E = -3.8 \text{ kcal·mol}^{-1} \quad 3\text{-}21G//3\text{-}21G \quad (4b)^{22}$$

We conclude that the S_N1 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 S_N2 reactivity is even more dramatic. The calculated barriers for the S_N2 hydride exchange reactions[27] 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).

$$H^- + CH_3R \rightarrow [H\cdots CH_2R\cdots H]^- \rightarrow H^- + CH_3R$$

$$R = H\ (5a) \quad R = CH_3\ (5b) \quad R = H_3Si\ (5c)$$

$$R = (CH_3)_3C\ (5d) \quad R = (CH_3)_3Si\ (5e)$$

The dramatic lowering of the S_N2 barrier by R = H_3Si 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 S_N2 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 $(CH_3)_3SiCH_3$ is 33.0 kcal·mol^{-1} (eq 5e, 3-21G//3-21G),[29] *20 kcal·mol^{-1} lower* than for $(CH_3)_3CCH_3$.[30]

In conclusion, both calculations and experimental data indicate that *silylcarbinyl sulfonates, **1**, react slower than their neopentyl analogues, **2**, via the S_N1 mechanism, but faster than **2** via the S_N2 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.

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(21) This applies to the classical structures. At 3-21G $(CH_3)_3SiCH_2^+$ does not collapse to $(CH_3)_2Si^+CH_2CH_3$.[15]

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(26) ΔE of eq 3b for the sulfonates is probably even less exothermic due to F strain between the sulfonate and the $(CH_3)_3C$ substituent.

(27) Given by the energy difference between the reactants and the transition state which was assumed to possess C_s (D_{3h} in CH_5^-) symmetry. The symmetry plane is defined by the central carbon and the two apical hydrogens.

(28) The calculated proton affinity of $H_3SiCH_2^-$ is 33.0 kcal·mol^{-1} lower than that of $CH_3CH_2^-$.[20a]

(29) Thus, methyl substitution reduces the S_N2 barrier by 2.3 kcal·mol^{-1}, probably due to the better charge dispersal in the negatively charged transition state by the larger $(CH_3)_3Si$ 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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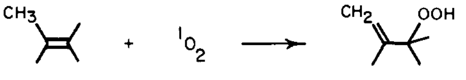
The chemistry of singlet oxygen ($^1\Delta_g$, $^1O_2$) has been extensively studied and is of continuing interest.[1] The "ene" reaction of $^1O_2$ with olefins containing an allylic hydrogen is a synthetically useful route to allylic hydroperoxides[2] (eq 1). Proposed mechanisms for this conversion include a concerted reaction[3] and stepwise sequences proceeding through a biradical (**1**, Chart I),[4] a zwitterion



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