2798 *Organometallics* 1991, *10*, 2798–2803

Stabilization of β Positive Charge by Silicon, Germanium, or Tin

Kiet A. Nguyen,[1a] Mark S. Gordon,*[,1a] Gen-tai Wang,[1b] and Joseph B. Lambert*[,1b]

Departments of Chemistry, North Dakota State University, Fargo, North Dakota 58105, and Northwestern University, Evanston, Illinois 60208-3113

Received March 26, 1991

Ab initio molecular orbital theory is used to study the β effect of carbon, silicon, germanium, or tin on the carbenium ions in $H_2R'MCH_2CHR^+$ ($R' = H$; $R = H, CH_3$). The relative stabilization energies of carbenium ions provided by M ($M = C, Si, Ge, Sn$) were determined by calculating the energy change in an isodesmic reaction using MP2/3-21G(d) (at SCF/3-21G* geometries) and MP2/6-31G(d) (at SCF/6-31G(d) geometries) wave functions. The magnitude of the β effect is predicted to increase in the order C < Si < Ge < Sn. For R = H, the nonvertical cyclic structure is favored for the cations, whereas methyl substitution appears to stabilize the vertical acyclic arrangement.

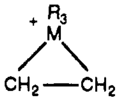
Introduction

In either the liquid or gas phase, a C–Si bond provides a strongly stabilizing interaction with a developing or fully formed empty p orbital at the β position to silicon ($SiCC^+$).[2-5] The overall reaction is an E1 elimination (eq 1) (formation of a carbocation by rate-determining loss of

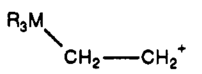
$$R_3SiCH_2CH_2X \rightarrow R_3SiCH_2CH_2^+ \rightarrow CH_2{=}CH_2 + R_3SiX \quad (1)$$

the nucleofuge X). Several alternative mechanisms either have been proved to be absent or can be removed from the reaction pathway by suitable choice of conditions. Rate-determining loss of the electrofuge through the Si–C bond cleavage (E_1cb) has not been supported by solvent studies. Rate-determining nucleophilic attack of the solvent or a base on silicon (analogous to an E2 mechanism) or on the C–X bond (S_N2) likewise has been eliminated as a viable alternative because the reaction is independent of solvent nucleophilicity.[5,6]

The β effect of silicon thus is manifested primarily in an E1-like mechanism, in which departure of the nucleofuge is rate determining (eq 1). The effect arises because the high polarizability and electropositivity of silicon enable it to stabilize the electron-deficient intermediate. Two modes of stabilization, differing in the geometry of the intermediate, have been considered: (1) The silicon atom moves toward the positive charge and forms a full C–Si bond to the carbon atom from which the nucleofuge departed. The movement may be in concert with this departure, so that the reaction is analogous to neighboring group participation or epoxide formation. The result is the formation of a bridged ion such as **1** (M = Si). This pathway has been termed *nonvertical* because of the movement of the silicon atom. (2) Full charge develops on carbon, and stabilization of this electron deficiency occurs by hyperconjugation between the highly polarizable C–M bond (M = Si) and the empty p orbital (**2**). This unbridged pathway has been termed *vertical* because stabilization requires little movement of the silicon atom.[7]



1



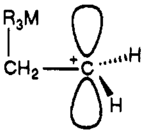
2

Both bridged and unbridged models are consistent with the preponderance of evidence.[5] The optimal stereochemistry for nonvertical participation involves a 180° dihedral angle between electrofuge and nucleofuge; i.e., the SiCCX unit has the antiperiplanar arrangement. This stereochemistry is required in order to place the internal nucleophile (silicon) backside to the breaking C–X bond during formation of the three-membered ring (**1**). Likewise, the antiperiplanar geometry is optimal for σ–π conjugation in the nonbridged cation **2**, since all the orbitals lie in the same plane and have the optimal relative phases.

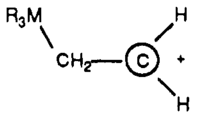
Earlier calculations attempted to compare the bridged with the open forms[8] and the β-silyl with the α-silyl system.[9] Jorgensen and co-workers[10] carried out calculations on the primary system for three geometries: the bridged form **1** and two versions of the open form **2**. In one open form (**3**) the empty p orbital is parallel to the beta M–C bond (M = Si), and in the other (**4**) these two orbitals are orthogonal. It is expected that full hyperconjugation could occur in **3** but not in **4**. The β effect was assessed by calculation of the energy change of the isodesmic reaction (eq 2, M = Si) at the MP3/6-31G(d)//SCF/3-21G* level

$$CH_4 + H_3MCH_2CH_2^+ \rightarrow H_3MCH_2CH_3 + CH_3^+ \quad (2)$$

for the three geometries. The cyclic form (**1**, R = H) had the largest stabilization in this comparison to CH_3^+ (74.4 kcal mol^{-1}), followed closely by the parallel structure **3** (72.0 kcal mol^{-1}) and distantly by the orthogonal form **4** (42.4 kcal mol^{-1}). The parallel open form was not a minimum but was transformed into the slightly more stable bridged form on geometry optimization. Hyperconjugative overlap in the parallel open form **3** is improved by geometric distortions from the neutral parent or from the orthogonal form. The C–C bond is shorter in **3** (1.360 Å) than that in **4** (1.443 Å), and the Si–C–C angle is smaller (94.3° vs 119.6°). Thus, the Si leans toward the empty p orbital.



3



4

---

[1] (a) North Dakota State University. (b) Northwestern University.

[2] Ushakov, S. N.; Itenberg, A. M. *Zh. Obshch. Khim.* **1937**, *7*, 2495.

[3] Sommer, L. H.; Whitemore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 485.

[4] Sommer, L. H.; Dorfman, E.; Goldberg, G. M.; Whitmore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 488.

[5] For a comprehensive review, see: Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.

[6] Lambert, J. B.; Wang, G.-t.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838.

[7] Hanstein, W.; Berwin, H. J.; Traylor, T. G. *J. Am. Chem. Soc.* **1970**, *92*, 829.

[8] Eaborn, C.; Feichtmayr, F.; Horn, M.; Murrell, J. N. *J. Organomet. Chem.* **1974**, *77*, 39.

[9] Apeloig, Y.; Karni, M.; Stanger, A.; Schwarz, H.; Drewello, R.; Czekay, G. *J. Chem. Soc., Chem. Commun.* **1987**, 989.

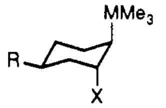
[10] Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496.

0276-7333/91/2310-2798$02.50/0

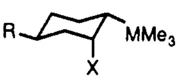
A measure of the β effect was obtained by comparing the energy of $H_3SiCH_2CH_2^+$ with that of $HCH_2CH_2^+$. For the parallel geometry, the silicon system is 38 kcal mol^{-1} more stable (a measure of all interactions), and for the orthogonal geometry, the silicon system is only 8.9 kcal mol^{-1} more stable (a measure of angle-independent contributions such as induction).

Ibrahim and Jorgensen[11] carried out similar calculations at the MP2/6-31G(d)//SCF/6-31G(d) level for secondary and tertiary systems, in order to assess the effect of substitution at carbon. The secondary β effect was estimated by comparison of $SiH_3CH_2C^+HCH_3$ with $HCH_2C^+HCH_3$. The open parallel form analogous to **3** was found to have a β effect of 22.1 kcal mol^{-1} compared with 18.2 kcal mol^{-1} for the bridged form and 38 kcal mol^{-1} for the parallel primary system. The primary system has higher electron demand, so that stabilization is greater. Furthermore, in the secondary case the bridged form is not an energy minimum but relaxes to the open form. However, force constant matrices were not diagonalized in refs 10 or 11 to verify the existence of minima.

No calculations have previously been carried out for the β effect in germanium or tin systems, but a few experimental results have been reported.[12,13] The cyclohexane framework offers two stereochemical relationships between the electrofugal metal (M) and the nucleofuge (X). The diaxial arrangement in the 1,2-trans isomer **5** is antiperiplanar and hence is optimal for either vertical or nonvertical participation.



5



6

The cis isomer **6** offers the gauche arrangement between groups, in which only a diminished vertical participation is possible. Experimental measurements of the rates of solvolysis of these compounds for silicon (R = H), germanium (R = H), and tin (R = H for cis and trans but also R = *tert*-butyl for trans) were carried out by Lambert et al.[12,13] Rate ratios were calculated for the trifluoroacetate in 97% trifluoroethanol at 25.0 °C, compared with 1.0 for cyclohexyl. In the cis series (R = H), the rate acceleration was observed to be 3.3×10^4 for Si, 4.6×10^5 for Ge, and 1.3×10^{11} for Sn. In the trans series (R = H), the rate accelerations were 5.7×10^9 for Si, 1.0×10^{11} for Ge, and $\gg 10^{14}$ for Sn.

In the present study, calculations of geometries and energies of carbocations carrying β germanium or tin, as well as carbon and silicon ($H_2R'MCH_2CHR^+$: R = H, CH_3), are carried out in order to assess these very substantial differences within the group 4 series. Two questions are of prime interest in this study: (1) How is the stabilization of positive charge affected as M varies from C to Sn? (2) How does the presence of bulky substituents (in this case methyl groups) affect the relative stabilities of **1** vs **2**?

Computational Methods

All structures were optimized with the use of analytical energy gradients with the 3-21G* basis set[14] at the SCF level of theory[15] (SCF/3-21G*). For M = C and Si, the larger 6-31G(d) basis set[16] was also incorporated when locating optimal structures for these compounds. This level of theory has been shown to give good agreement with experiment for complex species, such as pentastanna[1.1.1]propellane.[17] Single-point correlation corrections were done with the 6-31G(d) basis for C and Si and 3-21G(d) for Ge and Sn, using the second (MP2) order many-body perturbation theory formulated by Pople and co-workers.[18] The 3-21G(d) basis set adds a set of d functions to each C, whereas 3-21G* omits these functions. For M = C and Si, only valence electrons were correlated. MP2 single-point corrections were also carried out with the 6-31G(d) basis set at SCF/6-31G(d)-optimized geometries (MP2/6-31G(d)//SCF/6-31G(d)) for M = C and Si. Minima were identified by diagonalizing the force constant matrices (Hessians) to verify that they are positive definite. The energy change (ΔE) for the isodesmic reaction[19] (eq 2; M = C, Si, Ge, Sn) was used to assess the β effect for both the bridged (**1**) form (nonvertical pathway) and two open (vertical pathway) forms (**3** and **4**). Stabilization energies upon methyl substitution were also determined by the isodesmic reactions 3 and 4 for M = C and Si. Ab initio electronic structure calculations were performed with use of the GAMESS[20] and GAUSSIAN86[21] quantum chemistry programs.

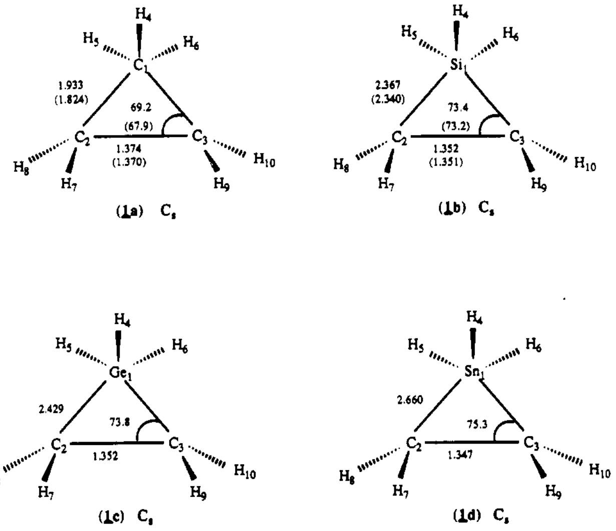


Figure 1. SCF/3-21G* structures of bridged $H_3MCH_2CH_2^+$ (**1**) (M = C, Si, Ge, Sn). SCF/6-31G(d) values are in parentheses; bond lengths are in angstroms; angles are in degrees.

$$CH_4 + H_3MCH_2CH^+Me \rightarrow H_3MCH_2CH_2Me + CH_3^+ \quad (3)$$

$$CH_3CH_2CH_3 + H_3MCH_2CH^+Me \rightarrow H_3MCH_2CH_2Me + CH_3CH^+CH_3 \quad (4)$$

---

[11] Ibrahim, M. R.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 819.

[12] Lambert, J. B.; Wang, G.-t. *Tetrahedron Lett.* **1988**, *29*, 2551.

[13] Lambert, J. B; Wang, G.-t.; Teramura, D. H. *J. Org. Chem.* **1988**, *53*, 5422.

[14] Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

[15] Roothan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.

[16] (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, J. D.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

[17] Gordon, M. S.; Nguyen, K. A.; Carroll, M. T. *Polyhedron*, in press.

[18] (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1. (c) Pople, J. A.; Seeger, R.; Krishnan, R. *Int. J. Quantum Chem. Symp.* **1977**, *11*, 149. (d) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91. (e) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

[19] Hehre, W. J.; Ditchfield, R.; Random, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

[20] (a) Dupuis, M.; Spangler, D.; Wendoloski, J. J. *National Resource for Computational in Chemistry Software Catalog*; University California: Berkley, CA, 1980; Prog. QG01. (b) Schmidt, M. W.; Boatz, J. A.; Baldridge, K. K.; Koseki, S.; Gordon, M. S.; Elbert, S. T.; Lam, B. *QCPE Bull.* **1978**, *7*, 115.

[21] GAUSSIAN86: M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, L. R. Kahn, D. J. DeFrees, R. Seeger, R. A. Whiteshide, C. M. Rohlfing, D. J. Fox, E. M. Fleuder, and J. A. Pople, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1984.

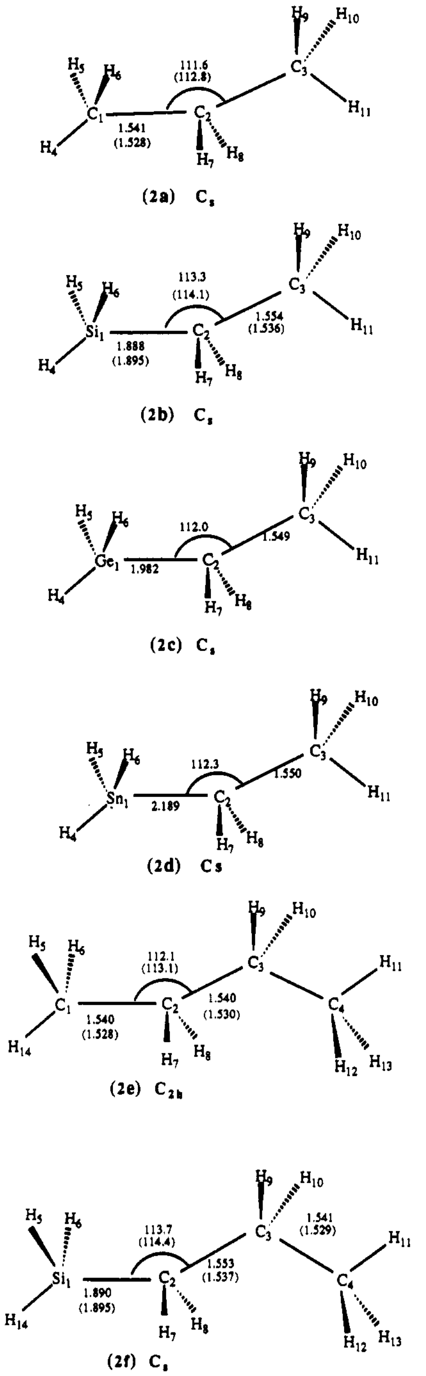


Figure 2. SCF/3-21G* structures of neutral species. SCF/6-31G(d) values are in parentheses; bond lengths are in angstroms; angles are in degrees.

Results and Discussion

The structures of $H_3MCH_2CHR^+$ cations and their neutral counterparts are shown in Figures 1–4. Three geometrical systems, bridged form 1, open form 3 (empty p orbital is parallel to the β M–C bond), and open form 4 (orbitals are orthogonal), were fully optimized for R = H and M = C, Si, Ge, and Sn at the SCF/3-21G* level of theory. The results are shown in Figures 1, 3, and 4. The structures of an open form with C_s symmetry and an unrestricted C_1 form for R = CH_3 and M = C and Si are given in Figures 5 and 6.

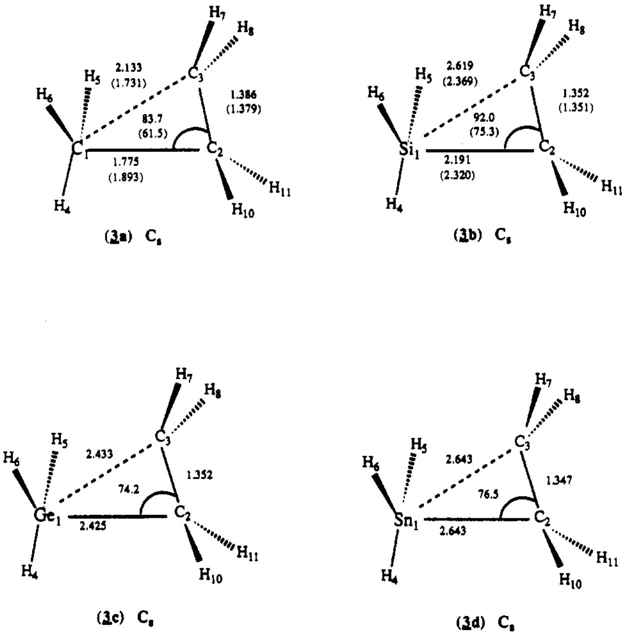


Figure 3. SCF/3-21G* structures of parallel $H_3MCH_2CH_2^+$ (3) (M = C, Si, Ge, Sn). Bond lengths are in angstroms; angles are in degrees; SCF/6-31G(d) values are in parentheses.

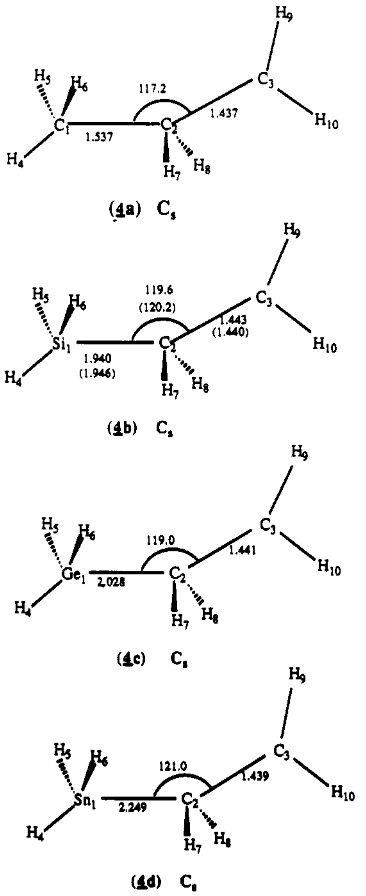


Figure 4. SCF/3-21G* structures of orthogonal $H_3MCH_2CH_2^+$ (4) (M = C, Si, Ge, Sn). Bond lengths are in angstroms; angles are in degrees; SCF/6-31G(d) values are in parentheses.

Consider first the predicted structures for the species $H_3MCH_2CH_2^+$ (M = C, Si, Ge, Sn). If a nonvertical pathway is defined as one having a C–Si bond formation to stabilize the electron-deficient intermediate, these can occur via the bridged and parallel structures in Figures 1 and 3. In all cases, both parallel (3) and bridged (1) structures are almost identical in energy (see Tables I and II). Geometrically, both 1 and 3 consist of a cyclic complex between MH_3^+ (M = C, Si, Ge, Sn) and ethylene. At the SCF/3-21G* level of theory, parallel (3) forms of M = C

Table I. Total Energies (au)

(a) $H_3MCH_2CH_2^+$, CH_3^+, $H_3MCH_2CH_3$, and CH_4 (M = C, Si, Ge, Sn)

molecule	SCF/3-21G*//SCF/3-21G*	MP2/3-21G(d)//SCF/3-21G*	zero-point energy[d]
$H_3CCH_2CH_2^+$ (**1a**)	−116.705 35	−117.179 36	60.7
$H_3CCH_2CH_2^+$ (**3a**)	−116.705 33	−117.175 13	60.7[b]
$H_3CCH_2CH_2^+$ (**4a**)	−116.697 31	−117.159 63	59.3
$H_3SiCH_2CH_2^+$ (**1b**)	−366.549 43	−366.942 72	52.7[a]
$H_3SiCH_2CH_2^+$ (**3b**)	−366.549 93	−366.939 68	52.7[b]
$H_3SiCH_2CH_2^+$ (**4b**)	−366.511 44	−366.889 00	50.3
$H_3GeCH_2CH_2^+$ (**1c**)	−2144.602 38	−2145.011 38	51.7[b]
$H_3GeCH_2CH_2^+$ (**3c**)	−2144.602 27	−2145.011 18	51.6
$H_3GeCH_2CH_2^+$ (**4c**)	−2144.548 99	−2144.944 88	48.8
$H_3SnCH_2CH_2^+$ (**1d**)	−6075.840 07	−6076.260 42	49.3[b]
$H_3SnCH_2CH_2^+$ (**3d**)	−6075.840 02	−6076.260 42	49.3
$H_3SnCH_2CH_2^+$ (**4d**)	−6075.770 81	−6076.179 16	46.2[c]
CH_3^+	−39.009 13	−39.137 71	20.8[b]
$H_3CCH_2CH_3$ (**2a**)	−117.613 30	−118.103 62	69.6[b]
$H_3SiCH_2CH_3$ (**2b**)	−367.430 59	−367.836 05	60.5[b]
$H_3GeCH_2CH_3$ (**2c**)	−2145.466 12	−2145.890 46	59.0[b]
$H_3SnCH_2CH_3$ (**2d**)	−6076.684 13	−6077.120 61	56.7[b]
CH_4	−39.976 88	−40.143 19	30.1[b]

(b) $H_3MCH_2CH_2^+$, $H_3MCH_2CH_3$ (M = C, Si), CH_3^+, and CH_4 Optimized at SCF/6-31G(d)

molecule	SCF/6-31G(d)//SCF/6-31G(d)	MP2/6-31G(d)//SCF/6-31G(d)	zero-point energy[e]
$H_3CCH_2CH_2^+$ (**1a**)	−117.359 17	−117.737 38	61.2
$H_3CCH_2CH_2^+$ (**3a**)	−117.359 41	−117.737 56	61.3[b]
$H_3SiCH_2CH_2^+$ (**1b**)	−368.428 00	−368.752 95	52.9[b]
$H_3SiCH_2CH_2^+$ (**3b**)	−368.427 82	−368.752 64	52.8
$H_3CCH_2CH_3$ (**2a**)	−118.263 65	−118.659 97	69.4[b]
$H_3SiCH_2CH_3$ (**2b**)	−369.302 09	−369.646 72	60.3[b]
CH_3^+	−39.230 64	−39.325 15	21.2[b]
CH_4	−40.195 17	−40.332 45	30.0[b]

(c) $H_3MCH_2CH^+Me$, $H_3MCH_2CH_2Me$ (M = C, Si), and $CH_3CH^+CH_3$ Optimized at SCF/3-21G*

molecule	SCF/3-21G*//SCF/3-21G*	MP2/3-21G(d)//SCF/3-21G*	zero-point energy[d]
$H_3CCH_2CH^+Me$ (**5a**)	−155.549 16	−156.176 87	78.6
$H_3CCH_2CH^+Me$ (**5b**)	−155.553 02	−156.181 41	79.6[b]
$H_3SiCH_2CH^+Me$ (**5c**)	−405.363 12	−405.906 38	69.4
$H_3SiCH_2CH^+Me$ (**5d**)	−405.390 63	−405.941 40	71.5
$H_2MeCCH_2CH_2^+$ (**6a**)	−155.531 23	−155.888 73	80.1[b]
$H_2MeSiCH_2CH_2^+$ (**6b**)	−405.398 59	−405.743 05	72.3
$H_3CCH_2CH_2Me$ (**1e**)	−156.432 47	−157.085 78	88.8[b]
$H_3SiCH_2CH_2Me$ (**1f**)	−406.250 18	−406.819 05	79.7[b]
$CH_3CH^+CH_3$	−116.726 44	−117.191 91	59.6[b]

(d) $H_3MCH_2CH^+Me$, $H_3MCH_2CH_2Me$ (M = C, Si), and $CH_3CH^+CH_3$ Optimized at SCF/6-31G(d)

molecule	SCF/6-31G(d)//SCF/6-31G(d)	MP2/6-31G(d)//SCF/6-31G(d)	zero-point energy[e]
$H_3CCH_2CH^+Me$ (**5a**)	−156.419 12	−156.913 56	78.5
$H_3CCH_2CH^+Me$ (**5b**)	−156.420 62	−156.917 76	79.6[b]
$H_3SiCH_2CH^+Me$ (**5c**)	−407.455 35	−407.897 84	69.3
$H_3SiCH_2CH^+Me$ (**5d**)	−407.481 27	−407.934 06	71.4[b]
$H_2MeCCH_2CH_2^+$ (**6a**)	−156.398 53	−156.908 11	80.5
$H_2MeSiCH_2CH_2^+$ (**6b**)	−407.472 59	−407.888 95	72.5
$H_3CCH_2CH_2Me$ (**1e**)	−157.298 41	−157.825 53	88.6[b]
$H_3SiCH_2CH_2Me$ (**1f**)	−408.337 17	−408.813 01	79.5[b]
$CH_3CH^+CH_3$	−117.381 16	−117.745 50	59.6[b]

[a] Becomes positive definite at the SCF/6-31G(d) level of theory. [b] Positive definite force field; others have one imaginary frequency. [c] Two imaginary frequencies. [d] Zero-point energies (kcal mol^{-1}) calculated at the SCF/3-21G*//SCF/3-21G* level. [e] Zero-point energies (kcal mol^{-1}) calculated at the SCF/6-31G(d)//SCF/6-31G(d) level.

and Si are verified minima. The larger basis set 6-31G(d), however, predicts the bridged form to be the minimum structure for M = Si. The bridged forms are the most favorable SCF/3-21G* configurations for Ge and Sn.

The calculated total energies and zero-point vibrational energies of all species are given in Table I. For both vertical and nonvertical pathways, MP2/3-21G(d)//SCF/3-21G* and SCF/3-21G*//SCF/3-21G* stabilization energies of the $H_3MCH_2CH_2^+$ (M = C, Si, Ge, Sn) cations compared to CH_3^+ in the isodesmic reaction (eq 2) are provided in Table IIa; the MP2/6-31G(d)//SCF/6-31G(d) and SCF/6-31G(d)//6-31G(d) values are in Table IIb (M = C, Si). The stabilization energies of methyl-substituted $H_3MCH_2CH^+Me$ cations, obtained from reactions 3 and 4, are reported in Table IIIa,b. A larger value for ΔE indicates a greater stabilization energy: The corresponding substituent is better able to stabilize the positive charge. These stabilization energies increase substantially upon the addition of correlation corrections, except for the high-lying orthogonal structures.

Turning to the energetics for reaction 2, the MP2/3-21G(d)//SCF/3-21G* stabilization energies (Table IIa) increase from 48 to 69 to 77 to 89 kcal mol^{-1}, upon proceeding vertically in group 4 from C to Sn, where the most stable structure is used as reference in each case. For C and Si, increasing the basis set to 6-31G(d) has little effect on the relative stabilization energies (see Table IIb), or on the relative energies of the open and bridged forms.

Table II. Energy Differences (kcal mol^{-1}, Zero-Point Correction Included) for Isodesmic Reaction 2

(a) M = C, Si, Ge, and Sn

molecule	SCF/3-21G*//SCF/3-21G*	MP2/3-21G(d)//SCF/3-21G*	no. of imag freq
$H_3CCH_2CH_2^+$ (**1a**)	37.1	50.6	1
$H_3CCH_2CH_2^+$ (**3a**)	37.1	47.9	0
$H_3CCH_2CH_2^+$ (**4a**)	33.5	39.6	1
$H_3SiCH_2CH_2^+$ (**1b**)	52.8	68.9[a]	1
$H_3SiCH_2CH_2^+$ (**3b**)	53.1	67.0	0
$H_3SiCH_2CH_2^+$ (**4b**)	31.4	37.9	1
$H_3GeCH_2CH_2^+$ (**1c**)	63.3	77.3	0
$H_3GeCH_2CH_2^+$ (**3c**)	63.3	77.3	1
$H_3GeCH_2CH_2^+$ (**4c**)	32.7	38.5	1
$H_3SnCH_2CH_2^+$ (**1d**)	75.7	89.3	0
$H_3SnCH_2CH_2^+$ (**3d**)	75.7	89.3	1
$H_3SnCH_2CH_2^+$ (**4d**)	35.4	41.4	2

(b) M = C and Si

molecule	SCF/6-31G(d)//SCF/6-31G(d)	MP2/6-31G(d)//SCF/6-31G(d)	no. of imag freq
$H_3CCH_2CH_2^+$ (**1a**)	37.1	52.6	1
$H_3CCH_2CH_2^+$ (**3a**)	37.1	52.6	0
$H_3SiCH_2CH_2^+$ (**1b**)	53.3	69.9	0
$H_3SiCH_2CH_2^+$ (**3b**)	53.3	69.8	1

[a] Becomes positive definite at the SCF/6-31G(d) level of theory.

Table III. Energy Differences (kcal mol^{-1}, Zero-Point Correction Included)

(a) Isodesmic Reaction 3 (M = C, Si)

	SCF		MP2	
molecule	3-21G*//SCF/3-21G*	6-31G(d)//SCF/6-31G(d)	3-21G(d)//SCF/3-21G*	6-31G(d)//SCF/6-31G(d)
$H_3CCH_2CH^+Me$ (**5a**)	53.9	61.5	54.8	61.1
$H_3CCH_2CH^+Me$ (**5b**)	55.3	63.3[a]	54.6[a]	62.7[a]
$H_3SiCH_2CH^+Me$ (**5c**)	51.6	59.2	53.3	59.3
$H_3SiCH_2CH^+Me$ (**5d**)	66.8	79.1[a]	67.4[a]	79.8[a]

(b) Isodesmic Reaction 4 (M = C, Si)

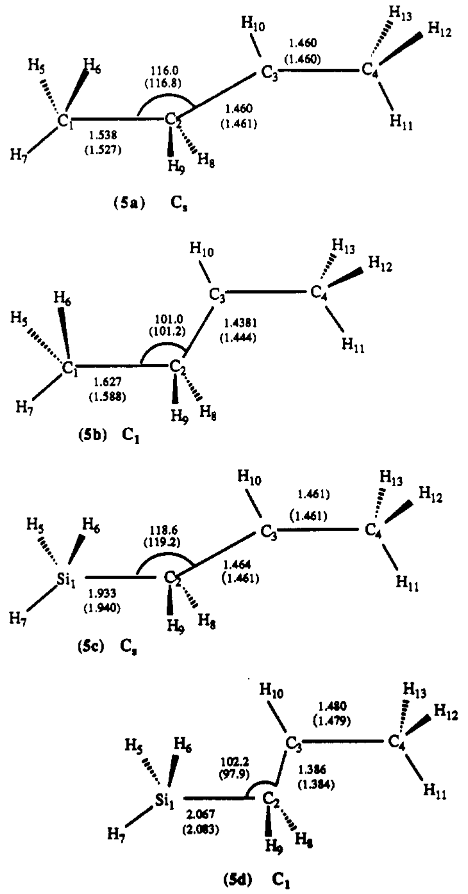
	SCF		MP2	
molecule	3-21G*//SCF/3-21G*	6-31G(d)//SCF/6-31G(d)	3-21G(d)//SCF/3-21G*	6-31G(d)//SCF/6-31G(d)
$H_3CCH_2CH^+Me$ (**5a**)	2.4	2.3	2.0	1.9
$H_3CCH_2CH^+Me$ (**5b**)	3.8	2.1[a]	3.9[a]	3.4[a]
$H_3SiCH_2CH^+Me$ (**5c**)	0.2	1.1	−0.3	0.3
$H_3SiCH_2CH^+Me$ (**5d**)	15.3	15.0[a]	19.6[a]	20.6[a]

[a] Positive definite force field; others have one imaginary frequency.

Jorgensen and co-workers,[10] with SCF calculations on the $H_3MCH_2CH_2^+$ (M = C, Si) systems with the 3-21G* basis set (Si d exponent = 0.45) reported the following: (a) for M = C, the parallel form **3** is lower in energy compared to the orthogonal form **4**; (b) for M = Si, the bridged form **1** and the parallel form **3** were almost identical in energy; however, single-point MP2/6-31G(d)//SCF/3-21G* calculations favored the bridged structure by 2.4 kcal mol^{-1}. MP2/6-31G(d)//SCF/3-21G* stabilization energies of 49.0 and 70.0 kcal mol^{-1}, obtained from reaction 2 were predicted for the parallel form **3** of C and the bridged form **1** for Si. These findings are in agreement with the results given in Table IIb.

Placing the methyl group on the positively charged carbon could preferentially stabilize the acyclic structure due to steric hinderance. For M = C (Figure 5), the acyclic structure with C_1 symmetry (**5b**) is the lowest in energy on both the SCF/3-21G* and the SCF/6-31G(d) potential energy surfaces. In this C_1 structure, one CH_3^+–C bond lengthens by 0.45 Å and the other shortens by 0.1 Å when the methyl group is added (cf. Figure 3 (**3a**)), as predicted at the SCF/6-31G(d) level of theory. Compared to the planar C_s structure, the C_1 structure is 1.5 kcal mol^{-1} lower at the MP2/6-31G(d)//6-31G(d) level (cf. Table IIIa). For M = Si, the SCF/6-31G(d) distance between the positively charged carbon and silicon increases by 0.32 Å when the methyl group is added (cf. Figures 5 (**5d**) and 3 (**3b**)) to form the C_1 structure. This C_1 configuration (**5d**) is 17.2 kcal mol^{-1} (19.9 kcal mol^{-1}) lower than C_s configuration (**5c**) at the MP2/6-31G(d)//SCF/6-31G(d) (MP2/3-21G(d)//SCF/3-21G*) level of theory (see Table IIIa). The stabilization energies of the C_1 configurations of $H_3MCH_2CH^+Me$ (M = C, Si) (**5b** and **5d**) compared to CH_3^+, using reaction 3, increase to 63 kcal mol^{-1} for C and to 80 kcal mol^{-1} for Si at the MP2/6-31G(d)//SCF/6-31G(d) level of theory, so both stabilization energies increase about 10 kcal mol^{-1} upon methyl substitution. Thus, methyl substitution at the positively charged carbon provides a constant stabilization energy while the β effect increases in energy upon going from C to Si. A comparison of the C_1 configuration of $H_3MCH_2CH^+Me$ (M = C, Si) energetics with a secondary cation $CH_3CH^+CH_3$ in eq 4 using the MP2/6-31G(d)//SCF/6-31G(d) wave function, also gives a 17 kcal mol^{-1} increase in stability upon going from C (3.4 kcal mol^{-1}) to Si (20.6 kcal mol^{-1}) (see Table IIIb).

Calculations of the bridged structures with a methyl group replacing a hydrogen at the M position were also



(5a) C_s

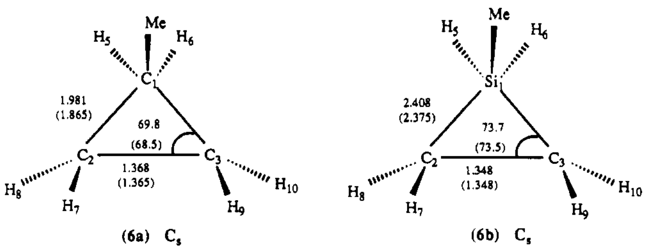
(5b) C_1

(5c) C_s

(5d) C_1

Figure 5. SCF/3-21G* structures of $H_3MCH_2CH^+CH_3$ (M = C, Si). SCF/6-31G(d) values are in parentheses; bond lengths are in angstroms; angles are in degrees. (c) $R(1,3)$ = 2.368 (2.345); (d) $R(1,3)$ = 2.722 (2.655).

carried out using both SCF/3-21G* and SCF/6-31G(d) wave functions. For M = Si, this cyclic structure (Figure 6 (**6b**)) is a minimum on the potential energy surface. Energetically, **6b** is 28.3 kcal mol^{-1} above the C_1 structure (**5d**) at the MP2/6-31G(d)//SCF/6-31G(d) level. Thus, methyl substitution substantially stabilizes the open (vertical) structure relative to the unsubstituted parent compound. For M = C, the cyclic form is a transition state at both 6-31G(d) and 3-21G* levels, with imaginary frequencies of 91.8*i* and 98.7*i* cm^{-1}, respectively. Germanium and tin are expected to behave in a manner similar to that



(6a) C_s

(6b) C_s

Figure 6. SCF/3-21G* structures of bridged $MeH_2MCH_2CH_2^+$ (1) (M = C, Si). SCF/6-31G(d) values are in parentheses; bond lengths are in angstroms; angles are in degrees.

of silicon. These calculations were omitted in the interest of conserving computational resources.

Conclusion

An investigation of the β effect of group 4 elements, including the first such calculations on germanium and tin, on the carbenium ion $H_3MCH_2CHR^+$ (R = H, CH_3) has shown that the thermodynamics of this effect are consistent with the observed kinetics, although the trend is not as dramatic. This suggests that the nature of the transition state(s) for reaction 1 as a function of M also plays an important role. The magnitude of the β effect is predicted to increase steadily upon going from C to Sn in group 4. The nonvertical cyclic configuration (1) with C_s symmetry is the most favorable one for R = H. Methyl substitution, however, appears to stabilize the vertical acyclic form with C_1 symmetry, and one expects other hydrocarbon substituents to behave in a manner similar to that of methyl. For carbon and silicon, increasing the basis set from 3-21G* to 6-31G(d), has little effect on the relative stabilization energies but correlation corrections have a considerable effect.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHEM-8910841 to Northwestern University and Grant No. CHEM89-11911 to North Dakota State University), by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the Air Force Office of Scientific Research (90-0050). These calculations were performed in part on the North Dakota State University IBM 3090 (aided by a joint study agreement with IBM) and on the NDSU Quantum Chemistry VAX 8530 (funded by a grant from the Air Force Office of Scientific Research).