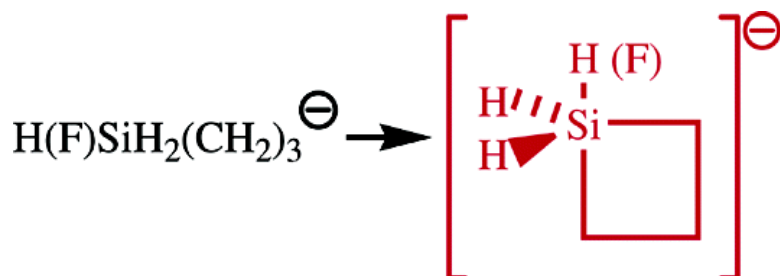


Electron, Hydride, and Fluoride Affinities of Silicon-Containing Species: Computational Studies

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Electron, Hydride, and Fluoride Affinities of Silicon-Containing Species: Computational Studies

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Abstract: The distance dependence of silicon substitution on the electron affinity (EA) of carbon radicals has been studied using computational methods in $\text{SiH}_3(\text{CH}_2)_n\text{CH}_2$ (**A**) and $\text{SiH}_2\text{F}(\text{CH}_2)_n\text{CH}_2$ (**B**). Large EAs result when $n = 0$ for both **A** and **B**. The result for **A** is compared with the experimental EA value of $(\text{CH}_3)_3\text{SiCH}_2$. Similar comparisons with known EAs (CH_3 and SiH_3) establish the validity of the computational approach. Fluorine substitution in SiH_2FCH_2 is consistent with other fluorine substitution effects. When $n > 1$, the anions of both **A** and **B** cyclize to pentacoordinate structures in which silicon has trigonal bipyramidal geometry. The corresponding EA values raise important questions about computed EAs that result from profound geometry changes between radicals and anions. Anions that have not cyclized give rise to EA values more easily interpreted. Such results, combined with computations of vertical attachment energies, indicate that the EA values of **A** and **B** attenuate rapidly for $n > 1$, quickly approaching that of CH_3 . Pentacoordination effects of silicon anions were also studied for SiH_4 , $(\text{CH}_3)_2\text{SiH}_2$, 1-silacyclopropane, 1-silacyclobutane, and 1-silacyclopentane.

Introduction

Electron affinities (EA) are fundamentally important in all areas of chemistry, not least in gas-phase ion studies where they can serve as links to important properties in thermodynamic cycles.^{1–5} Gas-phase acidities [$\Delta G_{\text{acid}}(\text{HA})$] and heats of formation of anions [$\Delta H_f^\circ(\text{A}^-)$] are important among these. For example, the EA of **A** is linked to the gas-phase acidity of HA [$\Delta G_{\text{acid}}(\text{HA})$], the bond dissociation energy (BDE) of HA, and the ionization energy of H (which is well-known) in one such cycle; knowing any three of these quantities allows estimation of the fourth.^{6–8} Because direct, accurate measurements of EAs now are relatively easily made, a large body of knowledge exists about the stability of anions.⁹ Added to this are the continuing advances in computational chemistry that make the computation of accurate EAs practical, even for fairly large molecules.^{8,10–13}

Simple alkyl anions are either unstable with respect to electron loss (negative EAs) or are barely stable like CH_3^- (EA of $\text{CH}_3 = 1.8 \pm 0.7$ kcal/mol).^{14–22} Closely related unsubstituted and alkyl-substituted silicon anions such as SiH_3^- and $\text{R}_n\text{SiH}_{3-n}^-$ are considerably more stable (EA of $\text{SiH}_3 = 32.4 \pm 0.3$ kcal/mol).^{23,24} The α -silyl-substituted carbanion, $(\text{CH}_3)_3\text{SiCH}_2^-$, is stable (EA of $(\text{CH}_3)_3\text{SiCH}_2 = 21.9$ kcal/mol), while its carbon analogue, $(\text{CH}_3)_3\text{CCH}_2^-$, is barely so (EA of $(\text{CH}_3)_3\text{CCH}_2 = 4.8$ kcal/mol).^{15,19,25,26} These few examples make clear that silicon, whether directly bearing the formal negative charge or located α to a carbanionic center, strongly stabilizes anions to electron loss. That these effects are “molecular” ones is clear, since atomic carbon and silicon have reasonably similar EAs of $1.262\ 119 \pm 0.000\ 020$ eV and $1.389\ 521 \pm 0.000\ 020$ eV (about a 3 kcal/mol difference).⁸

- (1) NIST has an excellent Gas-Phase Ion tutorial at <http://webbook.nist.gov/chemistry/ion/#A>.
- (2) The NIST Standard Reference Database is at <http://webbook.nist.gov/chemistry>.
- (3) Bowers, M. T., Ed. *Gas-Phase Ion Chemistry*; Academic Press: New York, 1979; Vol. 1.
- (4) Bowers, M. T., Ed. *Gas-Phase Ion Chemistry*; Academic Press: New York, 1979; Vol. 2.
- (5) Bowers, M. T., Ed. *Gas-Phase Ion Chemistry*; Academic Press: New York, 1984; Vol. 3.
- (6) See refs 1 and 2.
- (7) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744–2765.
- (8) Rienstra-Kiracofe, J. C.; Tschumper, G. S.; Schaefer, H. F., III.; Nandi, S.; Ellison, G. B. *Chem. Rev.* **2002**, *102*, 231–282.
- (9) The EAs herein are expressed for radical species. A positive EA corresponds to a positive ΔE value for the reaction of $\text{R}^- \rightarrow \text{R}$, thus indicating that the corresponding anion is stable with respect to electron loss. A negative EA means that the anion is unstable.
- (10) Cramer, C. J. *Essentials of Computational Chemistry: Theories and Models*; John Wiley and Sons: LTD: Chichester, 2002.
- (11) Leach, A. R. *Molecular Modeling: Principles and Applications*, 2nd ed.; Prentice Hall: Harlow, U.K., 2001.

- (12) Li, Q.-S.; Zhao, J.-F.; Xie, Y.; Schaefer, H. F., III. *Mol. Phys.* **2002**, *100*, 3615–3648.
- (13) Li, Q.; Lü, S.; Xu, W.; Xie, Y.; Schaefer, H. F., III. *J. Phys. Chem. A* **2002**, *106*, 12324–12330.
- (14) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051–4053.
- (15) DePuy, C. H.; Gronert, S.; Barlow, S. E.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1989**, *111*, 1968–1973.
- (16) Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556–2558.
- (17) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 607–608.
- (18) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 892–899.
- (19) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2506–2516.
- (20) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2517–2529.
- (21) Damrauer, R. In *Selective Hydrocarbon Activation: Principles and Progress*; Davies, J. A., Watson, P. L., Greenburg, A., Liebman, J. F., Eds.; VCH Publishers: New York, 1990; pp 535–556.
- (22) Damrauer, R.; Hankin, J. A. *Chem. Rev.* **1995**, *95*, 1137–1160.
- (23) Nimlos, M. R.; Ellison, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 6522–6529.
- (24) Wetzel, D. M.; Salomon, K. E.; Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 3835–3841.
- (25) Wetzel, D. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1988**, *110*, 8333–8336.
- (26) Damrauer, R.; Kass, S. R.; DePuy, C. H. *Organometallics* **1988**, *7*, 637–640.

Brauman and co-workers have examined various substituent effects on and of silicon in ion cyclotron resonance spectroscopy studies.^{24,25,27,28} All of the substitution patterns of silyl anions reveal large EAs, with methyl-substitution on silicon slightly decreasing the stability of silyl anions (EAs of SiH_3 , CH_3SiH_2 , $(\text{CH}_3)_2\text{SiH}$, and $(\text{CH}_3)_3\text{Si}$: 32.4, 27.5, 24.7, and 22.4 kcal/mol) and phenyl substitution having practically no effect (EAs of $\text{C}_6\text{H}_5\text{SiH}_2$ and $\text{C}_6\text{H}_5(\text{CH}_3)\text{SiH}$: 33.1 and 30.7 kcal/mol).²⁴ The effect of trimethylsilyl substitution on either a carbanionic or silicon anionic center is very large. The EAs of $(\text{CH}_3)_3\text{SiCH}_2$ and $((\text{CH}_3)_3\text{Si})_2\text{CH}$ are 21.9 and 36.0 kcal/mol, while those of $((\text{CH}_3)_3\text{Si})_2\text{SiH}$ and $((\text{CH}_3)_3\text{Si})_3\text{Si}$ are 44.7 and 46.8 kcal/mol.^{25,27} Thus, silyl anions are quite stable to electron loss with (1) methyl-substitution reducing stability a few kcal/mol per substitution and (2) phenyl-substitution having virtually no effect. α -Trimethylsilyl substitution of carbanions has a larger effect, between 14 and 20 kcal/mol. α -Trimethylsilyl and α -dimethylsilyl substitution of silyl anions also have an anion stabilizing effect but one that is smaller than silyl substitution of carbanions.²⁷

There have been several explanations for such effects. The large electron affinities of silyl anions are thought to be due to the enhanced s-character of the orbitals in which the nonbonding electrons “reside” in these anions. Not only are structures of such anions known to have R–Si–H bond angles approaching 90° , but photodetachment cross sections indicate that the nonbonding electrons of the silyl anions are removed from an orbital with “substantial s-character”.²⁴ The small methyl-substitution effects, which destabilize the anions to electron loss, are believed to result from methyl electron donation into a π -type silicon orbital.²⁴ Computational studies of $\text{H}_3\text{SiSiH}_2^-$, $(\text{H}_3\text{Si})_2\text{SiH}^-$, and $(\text{H}_3\text{Si})_3\text{Si}^-$ compared with H_3SiSiH_3 , $(\text{H}_3\text{Si})_2\text{SiH}_2$, and $(\text{H}_3\text{Si})_3\text{SiH}$ show slight Si–Si bond lengthening of the anions, suggesting that hyperconjugative effects are not important for silicon-substituted silyl anions.²⁷ Decreases in the bond angles about the central silicon in the silyl anions (to near 90°) indicate, as above, that the “anionic electrons” occupy orbitals of increased s-character.

The substantial anion stabilization resulting from α -silyl substitution in $(\text{CH}_3)_3\text{SiCH}_2^-$ and $((\text{CH}_3)_3\text{Si})_2\text{CH}^-$ is suggested to result from negative hyperconjugative effects in which a carbanion donates electron density from its highest occupied molecular orbital to a suitable low energy unoccupied silicon orbital.²⁵ Computational studies of simpler systems that have been examined experimentally support this suggestion where shortened bond lengths for C–Si bonds and increased H–C–Si bond angles are reported in the anions $\text{H}_3\text{SiCH}_2^-$ and $(\text{H}_3\text{Si})_2\text{CH}^-$ compared with H_3SiCH_3 and $(\text{H}_3\text{Si})_2\text{CH}_2$.²⁷ Such computations suggest that silicon d-orbital contributions to carbanion stability are of no consequence,^{25,29} although this remains a controversial topic.³⁰ Related silyl-substituted carbon radicals are not similarly stabilized, likely because the radical and adjacent silicon orbitals cannot interact in an energetically favorable way.²⁵

A different silicon substitution effect is examined in this study, namely, the distance dependence of silicon-substitution on carbanion stability. Computational methodology is used to examine this question and some surprising results are uncovered that will lead to new experimentation. The computational results raise interesting questions about the stability of various penta-coordinate silicon anions (siliconates). As a result, the hydride and fluoride affinities of several relevant silicon species have been studied as well. In addition, various features that affect the stability of siliconates have been examined.

Computational Methods

Optimized molecular structures were computed mostly without symmetry constraints using Møller–Plesset second-order perturbation theory (MP2)³¹ with a 6-31++G(d) basis set. Numerical Hessians (matrix of energy second derivatives) of the optimized structures were obtained from finite double differences of analytical derivatives and used to determine the nature of such structures (minima = positive definite Hessian; nth-order saddle point = n negative eigenvalues). The structures discussed herein all are minima. Single point energies were computed using several techniques. Most of the electron affinity computations consisted of single point energy computations using density functional theory (DFT) with a 6-311+G(3df,2p) basis set and the B3LYP exchange-correlation functional.^{8,32–34} Quite similar methodology has been used by Curtiss, Redfern, Raghavachari, and Pople (CRRP) in demonstrating its efficacy in computing ionization potentials and EAs for a diverse test group of 146 species (in the 0.1 to 0.2 eV range compared with experimental values).³⁴ The energies obtained here were corrected for zero point energy contributions (ZPC) using the vibrational analysis of the optimized structures. These data are reported as energies at 0 K and have not been corrected for temperature effects.

The EA computations were carried out by this three-step procedure (optimization, frequency, single point) except for a few in which the single point energies were computed using either (1) density functional theory (DFT) with the B3LYP exchange-correlation functional and the Dunning aug-cc-pVTZ basis set or (2) Møller–Plesset second-order perturbation theory (MP2) with the aug-cc-pVTZ basis.^{31,35–38} Vertical attachment energy (VAE) computations were performed using single point energy computations using density functional theory (DFT) with a 6-311+G(3df,2p) basis set and the B3LYP exchange-correlation functional. In these cases, MP2/6-31++G(d) optimized structures were obtained for the neutral radicals and these structures were used for both the radical and corresponding anion single point energies. The resulting VAEs are not zero point energy corrected.⁸ The hydride and fluoride affinity computations were carried out by optimization of the relevant structures at the MP2/6-31++G(d) level followed by frequency computations of the optimized structures. Energies were determined by single point MP2/aug-cc-pVTZ computations, which subsequently were corrected for zero point energy contributions (ZPC) using the vibrational analysis of the optimized structures.³⁹ All computations were

(31) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618–622.

(32) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(33) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785–789.

(34) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 42–55.

(35) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(36) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(37) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(38) Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, V., as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.

(39) These computations were carried out with a different basis than the EA computations to better describe hydride.

(27) Brinkman, E. A.; Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1994**, *116*, 8304–8310.

(28) Römer, B.; Gatev, G. G.; Zhong, M.; Brauman, J. I. *J. Am. Chem. Soc.* **1998**, *120*, 2919–2924.

(29) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467–6475.

(30) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley-Interscience: New York, 2000.

carried out using the GAMESS suite of programs.⁴⁰ MacMolPlot has been used to visualize the molecular structures.⁴¹

Results and Discussion

In an important recent review of the experimental and computational aspects of determining atomic and molecular EAs by Rienstra–Kiracofe, Tschumper, Schaefer, Nandi, and Ellison (RTSNE), various computational recipes have been described that provide accurate molecular EAs (± 0.1 – 0.2 eV).⁸ The “theroretical” electron affinity, sometimes called the adiabatic electron affinity, is defined for computational purposes as the “difference between the total energies of the neutral and anion at their respective equilibrium nuclear configurations” and is designated as EA herein. A related “EA transition”, the vertical attachment energy (VAE) is important for anions with very short lifetimes with respect to electron loss (near zero EAs), since such species can often be probed by techniques such as transmission electron spectroscopy.^{42,43}

The most popular and inexpensive computations of EAs employ density functional theory (DFT). By using diffuse function basis sets with functionals such as B3LYP that combine exchange and correlation, accurate EAs can be computed on molecular systems of reasonable size.^{8,12,13,44} To decide what computational protocol for EAs would best provide suitable accuracy at reasonable cost, several approaches have been examined. Optimized geometries and vibrational analyses for CH_3^- , CH_3 , SiH_3^- , and SiH_3 were obtained using Möller–Plesset second-order perturbation theory (MP2) with various basis sets. These species were chosen for pilot study because the EAs of CH_3 and SiH_3 have been accurately measured (2 and 32.4 kcal/mol).⁸ Various optimized structures were used as input for single point energy calculations using the B3LYP exchange–correlation functional with a 6-311+G(3df,2p) basis (see Computational Methods section for further comments).^{8,34} The energies so obtained were corrected using the zero point energy contributions obtained from vibrational analyses of the optimized structures. The EA results for CH_3 and SiH_3 show some variation with optimization basis set (Table 1). Optimizations using MP2/6-31++G(d) provide acceptable results at acceptable cost; using this protocol, the EA of methyl and silyl are 0.146 and 30.1 kcal/mol. The single point energies of CH_3^- , CH_3 , SiH_3^- , and SiH_3 also were computed using the Dunning basis aug-cc-pVTZ: with this basis, the EAs of methyl and silyl are 1.00 and 30.5 kcal/mol with the B3LYP exchange–correlation functional and 2.40 kcal/mol and 27.8 kcal with Möller–Plesset second-order perturbation theory (MP2). The VAEs of CH_3 and SiH_3 are -3.43 and 19.5 kcal/mol.

The EAs of both CH_2F and SiH_2F are unknown, although CH_2F^- has been observed and the EA of CH_2F is said to be greater than that of CH_3 .^{8,19,20} These EAs have been determined computationally to be 3.97 and 33.1 kcal/mol (the corresponding VAEs are -8.13 and 20.4 kcal/mol) (Table 1) and are 3–4 kcal/mol larger than those of CH_3 and SiH_3 , verifying a small

Table 1. Computed Electron Affinities of Silicon and Carbon Radicals

radical species	computed electron affinity ^a (kcal/mol)	computed vertical attachment energy ^b (kcal/mol)	experimental electron affinity (kcal/mol)
CH_3	0.146 ^c (1.00) ^d (2.40) ^e	-3.43	2 ^f
SiH_3	30.1 ^g (30.5) ^d (27.8) ^e	19.5	32.4 ^f
H_3SiCH_2	27.8 ^h	13.5	21.9 ⁱ
$\text{H}_3\text{SiCH}_2\text{CH}_2$	-1.45 (acyclic) ^j -15.6 (cyclic) (-15.5) ^d (-11.6) ^e	-1.92	
$\text{H}_3\text{SiCH}_2\text{CH}_2\text{CH}_2$	-0.175 (acyclic) 7.09 (cyclic)	-2.66 (low E) -3.60 (W-shape)	
$\text{H}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$	9.63 (acyclic) 27.1 (cyclic)	-3.86 (low E) -2.63 (W-shape)	
CH_2F	3.97	-8.13	
SiH_2F	33.1	20.4	
SiH_2FCH_2	31.5	27.0	
$\text{SiH}_2\text{FCH}_2\text{CH}_2$	3.94 (acyclic) 21.7 (cyclic) (18.1) ^d (26.6) ^e	-0.0956	
$\text{SiH}_2\text{FCH}_2\text{CH}_2\text{CH}_2$	7.84 (acyclic) 41.1 (cyclic)	-1.30 (low E) -2.79 (W-shape)	
$\text{SiH}_2\text{FCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$	-1.48 (acyclic) 9.56 (cyclic)	-1.70 (low E) -0.892 (W-shape)	

^a Optimizations and vibrational analyses were carried out at MP2/6-31++G(d). These were followed by single point energy determinations at B3LYP/6-311+G(3df,2p). The energies were corrected for zero point contributions from the vibrational analyses. The reported EA is the zero point corrected energy of the radical minus that of the corresponding anion.

^b Vertical attachment energies were determined from the difference in single point energy between the radical and anion at the optimized geometry of the radical (the optimizations were performed at MP2/6-31++G(d) and the energies determined at B3LYP/6-311+G(3df,2p)). ^c Using the protocol outlined in footnote a and in the methods section, but with a 6-31+G(d) basis in the optimization step, a value of 0.11 kcal/mol was obtained. With a 6-31G(d) basis in the optimization step, a value of -1.4 kcal/mol was obtained. ^d Optimizations and vibrational analyses were carried out at MP2/6-31++G(d). These were followed by single point energy determinations at B3LYP/aug-cc-pVTZ. The energies were corrected for zero point contributions from the vibrational analyses. The reported EA is the zero point corrected energy of the radical minus that of the corresponding anion.

^e Optimizations and vibrational analyses were carried out at MP2/6-31++G(d). These were followed by single point energy determinations at MP2/aug-cc-pVTZ. The energies were corrected for zero point contributions from the vibrational analyses. The reported EA is the zero point corrected energy of the radical minus that of the corresponding anion. ^f These experimental values are obtained from the compilation in ref 8. ^g Using the protocol outlined in footnote a and in the methods section, but with a 6-31+G(d) basis in the optimization step, a value of 30.0 kcal/mol was obtained. With a 6-31G(d) basis in the optimization step, a value of 30.1 kcal/mol was obtained. ^h Using the protocol outlined in footnote a and in the methods section, but with a 6-31+G(d) basis in the optimization step, a value of 28.3 kcal/mol was obtained. With a 6-31G(d) basis in the optimization step, a value of 27.5 kcal/mol was obtained. ⁱ This experimental value is for $(\text{CH}_3)_3\text{SiCH}_2$ reported in ref 23; see text for discussion. ^j The optimized geometry from the lowest energy acyclic anion obtained at 6-31++G(d,p) was submitted to single point energy determination at B3LYP/6-311+G(3df,2p). The zero point energy correction was obtained from the vibrational analysis of the optimized anion.

carbanion stabilizing effect by fluorine and suggesting a similar effect for silyl anions. The CH_2F^- is nearly pyramidal, but SiH_2F^- has bond angles near 90° like other silyl anions.²⁴ Previous computational studies by Hopkinson and co-workers of CH_3 and CH_2F as well as SiH_3 and SiH_2F at MP4SDTQ/6-311++G(2df,p) gave EAs of 1.38, 6.23, 32.1, and 35.3 kcal/mol.^{45,46}

(40) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347–1363.

(41) Bode, B. M.; Gordon, M. S. *J. Mol. Graphics Modell.* **1998**, *16*, 133–138.

(42) Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341–348.

(43) Jordan, K. D.; Burrow, P. D. *Chem. Rev.* **1987**, *87*, 557–588.

(44) Rienstra–Kiracofe, J. C.; Barden, C. J.; Brown, S. T.; Schaefer, H. F., III *J. Phys. Chem. A* **2001**, *105*, 524–528.

(45) Rodriguez, C. F.; Sirois, S.; Hopkinson, A. C. *J. Org. Chem.* **1992**, *57*, 4869–4876.

(46) Rodriguez, C. F.; Hopkinson, A. C. *Can. J. Chem.* **1992**, *70*, 2234–2240.

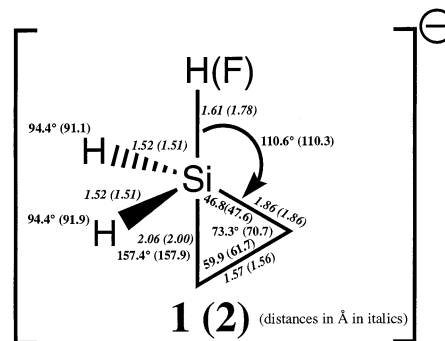
Given the large effects of silicon substitution on the EAs of carbon radicals as well as the heightened reactivity of silicon compared with carbon, particularly under anionic conditions, a study of the distance dependence of silicon substitution on the EAs of carbon radicals seemed likely to provide important avenues to explore.^{22,30} The homologues, $\text{SiH}_3(\text{CH}_2)_n\text{CH}_2$, where n varies from 0 to 3, and related systems, where a hydrogen atom on silicon is replaced by fluorine, have been studied as have the fluoride and hydride affinities of a number of silanes.

SiH_3CH_2 and SiH_2FCH_2 . The energies of the optimized structures of the SiH_3CH_2 radical and its corresponding anion yield an EA value of 27.8 kcal/mol (Table 1). Although there are no experimental data for this species, the closely related $(\text{CH}_3)_3\text{SiCH}_2$ has an EA of 21.9 kcal/mol.²⁶ The computational result is consistent with estimations that can be made from earlier studies. In these, a small difference between the C–H acidity of $\text{SiH}_3\text{CH}_2\text{--H}$ and $\text{CH}_3\text{SiH}_2\text{CH}_2\text{--H}$ was reported. Assuming that the C–H BDE does not vary dramatically with methyl-substitution on silicon,⁴⁷ we find the EA of $\text{CH}_3\text{SiH}_2\text{CH}_2$ is 3 kcal/mol smaller than that of H_3SiCH_2 , suggesting that trimethyl substitution on the α -silicon would reduce the EA of $(\text{CH}_3)_3\text{SiCH}_2$ below that of SiH_3CH_2 . The geometries of SiH_3CH_2 and $\text{SiH}_3\text{CH}_2^-$ indicate that negative hyperconjugation plays an important role in the anion; this will be addressed subsequently in discussing SiH_2FCH_2 .

The fluorine-for-hydrogen substitution in SiH_2FCH_2 leads to an EA value of 31.5 kcal/mol, which is about the same effect as fluorine substitution in SiH_3 and SiH_2F . The structural features of SiH_2FCH_2 and SiH_3CH_2 and their anions indicate the importance of negative hyperconjugation.⁴⁸ The SiH_2FCH_2 radical has equilibrium Si–C, Si–H, and Si–F bond lengths of 1.85, 1.48, and 1.65 Å; in the anion, the Si–C bond shortens, and the Si–H and Si–F bonds lengthen to 1.77, 1.51, and 1.72 Å. The Si–F bond is anti to the “lone pair” on the carbanionic center, which is nonplanar (*vide infra*). SiH_3CH_2 and its anion display similar changes in bond lengths: the radical has equilibrium Si–C and Si–H bond lengths of 1.86 and 1.49 Å; in the anion, the Si–C bond shortens to 1.80, and the Si–H lengthens to 1.55 and 1.52 Å. There is a clear angle dependence for the Si–H bond lengthening in $\text{SiH}_3\text{CH}_2^-$ as well, with the H atom anti to the lone pair lengthening more than the gauche H atoms. The geometry about the carbon atom in $\text{SiH}_2\text{FCH}_2^-$ approaches trigonal planar (average bond angle = 118.5°) and is similar to that of $\text{SiH}_3\text{CH}_2^-$ (average bond angle = 116.7°). Combined, such structural features suggest that negative hyperconjugative effects are important in both the $\text{SiH}_2\text{FCH}_2^-$ and $\text{SiH}_3\text{CH}_2^-$ while the two radicals are unaffected; these data also suggest that negative hyperconjugation contributes somewhat more in $\text{SiH}_2\text{FCH}_2^-$.⁴⁸

$\text{SiH}_3\text{CH}_2\text{CH}_2$ and $\text{SiH}_2\text{FCH}_2\text{CH}_2$. $\text{SiH}_3\text{CH}_2\text{CH}_2^-$ optimizes at the MP2 level to cyclic structure **1** in which silicon is pentacoordinate. It is well-known that pentacoordinate silicon anions are stable and readily made.^{22,49–54} All attempts to find an acyclic optimized anion at the MP2 level failed, although

all radicals optimized at the MP2 level are acyclic. Optimizations of the anion using the RHF/6-31++G(d) basis only gave several acyclic anions, but three-membered ring formation “occurred” when some structures so obtained were optimized using MP2 theory. One attempt to “ring-open” **1** without MP2 failed. The



pentacoordinate silicon in the cyclic anion has a distorted trigonal bipyramidal geometry with internal ring angles of 46.8°, 73.3° and 59.9°. The external angles about silicon approach trigonal bipyramidal geometry; thus, the axial hydrogen atom makes a 94.4° angle with both equatorial hydrogen atoms, a 110.6° angle with the axial carbon, and a 157.4° with the equatorial carbon. In addition, the angle between the equatorial hydrogen atoms is 118.7°.

The EA, which is –15.6 kcal/mol, as defined by the difference between the total energies of the neutral and anion at their equilibrium nuclear configurations (Table 1) corresponds to what is described as a “pathological case” by RTSNE, since the equilibrium geometry of the cyclic anion and the acyclic radical are so dramatically different.⁸ To verify that this large negative value is not a basis set or DFT artifact, the Dunning aug-cc-pVTZ basis with the B3LYP exchange-correlation functional gave a similarly negative EA value of –15.5 kcal/mol. Likewise, a –11.6 kcal/mol value was obtained with Möller–Plesset second-order perturbation theory (MP2) using the aug-cc-pVTZ basis. To force a determination of “an acyclic EA”, the geometry of the lowest energy acyclic anion optimized at the RHF/6-31++G(d) level has been used as input for a B3LYP/6-31++G(3df,2p) single point computation. The resulting EA of –1.45 kcal/mol (VAE = –1.92 kcal/mol) indicates that the large negative value for the cyclic system results from ring formation (pentacoordination). Such “acyclic values” reveal that the substituent effect of silicon one further atom removed from a carbon radical center begins to approach that of methyl.

The strikingly different geometries of anions and radicals in those species that can form pentacoordinate rings (**1**) (and later, **3** and **5**) as well as the very small EA and VAE of the two-carbon acyclic species (and the three- and four-carbon homologues later) emphasize the need for experimental EA measurements. Although electron detachment determinations of stable anions are possible, it is an open question whether and

(47) Only the C–H BDE of $(\text{CH}_3)_3\text{Si}$ is well-known in the methylsilane series. Its reported value is 99.2 kcal/mol, but in light of a recent modification of the activation energy for the reaction of $\text{H} + \text{HI}$, the C–H BDE might be 1 kcal/mol or so higher. Personal communication: Robin Walsh, August, 2002.

(48) Schleyer, P. v. R.; Kost, D. *Tetrahedron* **1983**, *39*, 1141–1150.

(49) Chuit, C.; Corriu, J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371–1448.

(50) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Functional Groups*; Patai, S., Rappaport, Z., Eds.; John Wiley and Sons: New York, 1989; Vol. 1, pp 1241–1288.

(51) Damrauer, R.; Danahey, S. E. *Organometallics* **1986**, *5*, 1490–1494.

(52) Damrauer, R.; Burggraf, L. W.; Davis, L. P.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 6601–6606.

(53) Damrauer, R.; O’Connell, B.; Danahey, S. E. *Organometallics* **1989**, *8*, 1167–1171.

(54) Gordon, M. S.; Davis, L. P.; Burggraf, L. W.; Damrauer, R. *J. Am. Chem. Soc.* **1986**, *108*, 7889–7893.

which cyclic and acyclic anions in this system and its homologues discussed subsequently can be prepared.⁵⁵ It is very unlikely that electron transmission spectroscopy (ETS) studies of radicals can be carried out.^{8,43} As indicated earlier, the ETS method has been important in determining the vertical attachment energies (VAE) of many short-lived radical anions; its results are often compared with computational VAE results. Assuming the radicals can be prepared, it is unlikely that their concentration will be sufficiently high to produce anions of usable concentrations for ETS.⁵⁶ Nevertheless, a measure of the results of such experiments may be told by VAE computations such as those given in Table 1. It needs to be emphasized that VAE computations do not include zero point corrections (see ref 8). Although this is standard practice, differences in zero point energies for species whose geometries are different can be fairly large. These clearly show values between about 0 and -4 kcal/mol (1) whether the radical geometries are for the lowest energy radical (usually one where the carbon radical center and silicon are nearer each other than in the W-shaped structures) or ones whose carbon radical centers are more distant from silicon (W-shaped) and (2) whether the radicals are fluorinated or not.

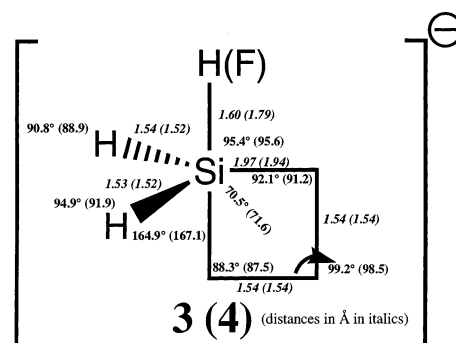
Quite different EA results are found for the $\text{SiH}_2\text{FCH}_2\text{CH}_2$ system. Both cyclic **2** and acyclic anions are obtained with MP2/6-31++G(d) optimization. Single point energy computations lead to EAs of 21.7 and 3.94 (VAE = -0.096 kcal/mol) kcal/mol for the cyclic and acyclic cases. The EA corresponding to the fluorine-containing cyclic anion **2** is about 37 kcal/mol larger than that of $\text{SiH}_3\text{CH}_2\text{CH}_2$ (34 kcal/mol using the B3LYP/aug-cc-pVTZ and 38 kcal/mol with MP2/aug-cc-pVTZ)(Table 1). This is far larger than the 3–4 kcal/mol fluorine substitution effect for either SiH_2FCH_2 or SiH_2F .

Such a large difference in the EAs of **1** and **2** might be expected to manifest itself in recognizable structural characteristics or charge distributions among the radicals and cyclic anions, but this is not obviously the case. Analysis of the structures of the acyclic radicals, $\text{SiH}_3\text{CH}_2\text{CH}_2$ and $\text{SiH}_2\text{FCH}_2\text{CH}_2$, show no remarkable differences in bond lengths or angles, certainly none that would serve to explain such a large EA difference. Strikingly, the corresponding cyclic anions **1** and **2** have very similar structures, again ones that seem not to differ enough to explain the large EA difference (structure **2** values are in parentheses). Examination of both the exocyclic bond angles and the bond distances of the anions and radicals reveal no surprising differences. In addition, analyses of the differences between bond lengths on going from the radical to the anion indicate no unusual effects, although, as expected, there are noticeable pentacoordination effects. Both of the cyclic anions are distorted trigonal bipyramidal structures in which the axial Si–H or Si–F bond is lengthened considerably. Such lengthening is not, however, any different from that found in acyclic pentacoordinate anions. Both $[\text{SiH}_5]^-$ (**7**) and $[\text{SiH}_4\text{F}]^-$ (**8**) have been optimized at the MP2/6-31++G(d) level and have axial Si–H and Si–F bond distances of 1.62 and 1.81 Å, which are nearly identical to the axial Si–H and Si–F bond distances of 1.61 and 1.78 Å in the three-membered cyclic anions **1** and **2**.

Examination of charges in **1** and **2** sheds no light either. The distribution of charge using Mulliken, Löwdin, and Natural Population analyses¹⁰ in going from the radicals to the anions is unremarkable for the B3LYP/6-311+G(3df,2p) structures and for the B3LYP/aug-cc-pVTZ structures using Mulliken and Löwdin charges.

That the cyclic anion **1** is some 14 kcal/mol less stable in energy than its corresponding acyclic radical and that the cyclic anion **2** is more stable than its corresponding radical seem clearly to be the result of some very subtle geometric or bonding effects.^{22,49–54} The dominant factors determining EA values in this series in which the cyclic pentacoordinate anion **1** and **2** form might be thought to be how closely ideal trigonal bipyramidal geometry is approached; however, making definitive statements about the EA values and their corresponding *raison d'être* is very uncertain, particularly in the case where the geometries of the cyclic anions and acyclic radicals are correspondingly so similar.

$\text{SiH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ and $\text{SiH}_2\text{FCH}_2\text{CH}_2\text{CH}_2$. A number of minima have been computed for both $\text{SiH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ and the corresponding anion at the MP2 level. The radical species all are acyclic, while both cyclic **3** and acyclic anions have been located. The EAs obtained from (1) the lowest energy acyclic radical and cyclic anion **3** and (2) the lowest energy acyclic radical and acyclic anion are 7.09 and -0.175 (VAE = $-2.66/-3.60$ kcal/mol depending on geometry) kcal/mol (Table 1).



Silicon in the cyclic anion **3** is a distorted trigonal bipyramid with the angles shown, but it is far less distorted than the three-membered anion **1**. In addition to the angles shown, the HSiH angle is 111.2° and the HSiC angles are 135.8° and 112.8° .

The EA value corresponding to cyclic **3** is consistent with the “closer to trigonal bipyramidal” geometry of **3**. The lowest energy acyclic anion, on the other hand, not only is unable to gain the favorable energetic boost of silicate formation but also has no particularly favorable geometric stabilization; thus, its energy and that of the lowest energy radical are nearly the same, which leads to quite small EA and VAE values. Anion **1** is more highly distorted than the four-membered anion **3**, particularly in its endocyclic bond angles. This indicates that the three-membered anion **1** is destabilized with respect to its corresponding lowest energy radical, thus giving an EA (defined as it is)⁸ that is negative. These qualitative features call attention to the importance of large geometric changes in these systems.

In the $\text{SiH}_2\text{FCH}_2\text{CH}_2\text{CH}_2$ system, the results are similar to $\text{SiH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ in that at the MP2 level all the radical species found are acyclic and both cyclic anion **4** and acyclic anions have been located. The EAs obtained from (1) the lowest energy acyclic radical and cyclic anion and (2) the lowest energy acyclic

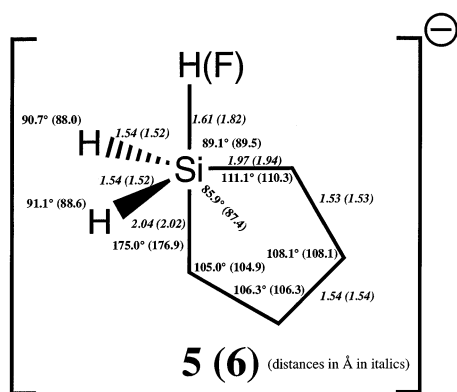
(55) Attempts to prepare these ions for photodetachment studies are currently underway. Personal communication: Professor Paul G. Wenthold, Spring, 2003.

(56) Insights into these matters were provided in discussions with G. Barney Ellison, Spring, 2003.

radical and acyclic anion **4** are 41.1 and 7.8 (VAE = $-1.30/-2.79$ kcal/mol depending on geometry) kcal/mol (Table 1). These values show that (1) the EAs “leading to” the cyclic anions have increased with ring size (**2** to **4**) and (2) the EA difference between the cyclic anions **3** and **4** is large, 34.0 kcal/mol in this case. The acyclic EA seems too large compared to methyl, but the VAEs are very small.

Anion **4** is a distorted trigonal bipyramid, quite similar to its analogue **3**. Its more important bond angles are shown. The HSiH and HSiC angles (116.2° , 128.3° , and 115.1°) deviate to a greater extent in the two structures.

SiH₃CH₂CH₂CH₂CH₂ and **SiH₂FCH₂CH₂CH₂CH₂**. The SiH₃CH₂CH₂CH₂CH₂ system is similar to SiH₃CH₂CH₂CH₂ since both cyclic (**5**) and acyclic anions are obtained at the MP2 level. The corresponding EAs are 27.1 and 9.63 (VAE = $-3.86/-2.63$ kcal/mol depending on geometry) kcal/mol. The five-membered anion **5** is closer still to ideal trigonal bipyramidal geometry than **3** as shown.



The cyclic anion **5** is some 17 kcal/mol lower in energy than the acyclic radical. This is certainly a manifestation of the nearly trigonal bipyramidal geometry of **5**.^{22,49–54} Although all the four-carbon radicals are considerably higher in energy than the lowest energy acyclic anion, no matter the radical geometry, the VAE values of the acyclic radical are nearly identical to that of methyl, which suggests that this radical cannot favorably bind an electron (Table 1).

The SiH₂FCH₂CH₂CH₂CH₂ system leads to both a cyclic (**6**) and acyclic anions. The corresponding EAs are 9.6 and -1.5 (VAE = $-1.70/-0.892$ kcal/mol depending on geometry) kcal/mol. The EA value leading to cyclic **6** is much smaller than that for **2** and **4**, particularly considering the geometrical similarity of unfluorinated **5** and the “close to” trigonal pyramidal geometry of **6**. The cyclic value is again an indicator of the caution that needs to be used in interpreting EAs where profound geometry changes occur. The negative acyclic EA and the VAE values certainly suggest that the radical carbon and silicon centers are far enough removed so that SiH₂FCH₂CH₂CH₂CH₂ is much like the methyl radical.

The geometry of **6** is similar to that of **5**; all of these angles are within 3° of the corresponding ones in **5**.

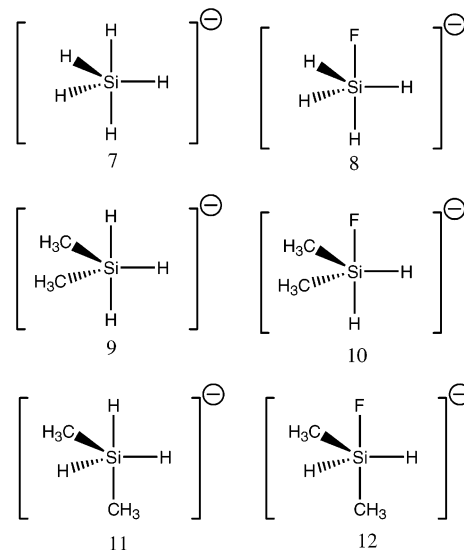
Additional Studies and Comments

The studies presented above reveal the large differences between the EAs of cyclic fluorine- and nonfluorine-containing species: 37 kcal/mol for the two carbon system **1/2**, and 34 kcal/mol for the three carbon one **3/4**, and the reversed and

smaller difference (-17 kcal/mol) in **5/6**. With much smaller differences occurring in the acyclic analogues (EA differences of $\sim 5-10$ kcal/mol and even smaller VAE differences), the large cyclic species differences are a manifestation of the profound and subtle changes in geometry between the acyclic radicals and the cyclic anions but likely depend on silicon pentacoordination effects. To begin to probe the later effects, various pentacoordinate silicon anions have been studied by computing the hydride and fluoride affinity of SiH₄, (CH₃)₂SiH₂, 1-silacyclopropane, 1-silacyclobutane, and 1-silacyclopentane (siliconates **1–12**). In each case, the relevant structures have been optimized at the MP2/6-31++G(d) level, after which energies were determined by single point MP2/aug-cc-pVTZ computation and corrected for zero point contributions as described earlier. The hydride and fluoride affinities of these species can be understood with reference to eqs 1 and 2 for SiH₄. The hydride



affinity can be defined as $\Delta H_{\text{eq}} 1$. A positive anion affinity for SiH₄ indicates that the siliconate is stable with respect to anion loss. Table 2 lists the computed hydride and fluoride affinities of SiH₄ (**7** and **8**), (CH₃)₂SiH₂ (**9–12**), 1-silacyclopropane (**1** and **2**), 1-silacyclobutane (**3** and **4**), and 1-silacyclopentane (**5** and **6**).



It has been shown in previous studies at the MP2/6-31++G-(d,p)//6-31G(d) level that comparable fluoride affinities are larger than hydride affinities for second row elements with trigonal bipyramidal geometries.^{52,54,57} Thus, the fluoride and hydride affinities of [H₃SiZ], where Z = OH, CH₃, and F, are 39.5/31.6 kcal/mol, 29.0/18.2 kcal/mol, and 49.4/42.2 kcal/mol. When Z = Cl, however, the fluoride and hydride affinities are nearly equal. The fluoride (32.0 kcal/mol) and hydride (17.0 kcal/mol) affinities of SiH₄ in Table 2 are similar to the 29.1 and 16.7 kcal/mol values previously reported at the MP2/6-31++G(d,p)//6-31G(d) level.⁵²

The difference between fluoride and hydride affinities is also reported in Table 2. The most striking result is that of the

Table 2. Computed Hydride and Fluoride Affinities of Selected Silanes^a

silane	hydride affinity ^b (kcal/mol)	fluoride affinity ^c (kcal/mol)	difference between fluoride and hydride affinity (kcal/mol)
SiH ₄	17.0	32.0	15.0
(CH ₃) ₂ SiH ₂ (ee) ^d	26.0	42.2	16.2
(CH ₃) ₂ SiH ₂ (ea) ^e	37.7	47.5	9.8
(CH ₂) ₂ SiH ₂	32.2	64.7	32.5
(CH ₂) ₃ SiH ₂	37.1	50.8	13.7
(CH ₂) ₄ SiH ₂	37.5	45.0	7.5

^a Optimizations and vibrational analyses were carried out at MP2/6-31++G(d). These were followed by single point energy determinations at MP2/aug-cc-pVTZ. The energies were corrected for zero point contributions from the vibrational analyses. ^b The hydride affinity was computed from the sum of the energies of hydride and the silane minus the energy of the silicate. ^c The fluoride affinity was computed from the sum of the energies of fluoride and the silane minus the energy of the silicate. ^d Both methyl groups were equatorial in a trigonal bipyramidal geometry. ^e One methyl group was equatorial, and the other, axial, in a trigonal bipyramidal geometry.

Table 3. Computed Electron Affinities of Silicon and Carbon Radicals: The Effect of Geometric Distortion

silane	hydride affinity ^b (kcal/mol)	fluoride affinity ^c (kcal/mol)	difference between fluoride and hydride affinity (kcal/mol)
SiH ₄ (TBP) ^a	17.0	32.0	15.0
SiH ₄ (ee 45°) ^b	-32.4	-26.8	5.6
SiH ₄ (ea 45°) ^c	-33.1	-16.2	16.8
SiH ₄ (cyclo long) ^d	-36.6	-25.5	11.1
SiH ₄ (cyclo short) ^e	-33.3	-12.4	20.8

^a TBP = trigonal bipyramidal geometry. ^b The angle between two equatorial H atoms is 45°. ^c The angle between an equatorial and axial H atom is 45°. ^d The CH₂ groups in optimized **1** are replaced by H atoms. ^e The longer Si-H distances from the replacement in SiH₄ (cyclo long) are adjusted to normal Si-H distances.

silacyclopentyl siliconates **1** and **2**, where this difference is more than twice the others suggesting that an additional factor be examined in this study, namely the effect of geometrical distortions on hydride and fluoride affinities. Four examples of geometric distortions to [SiH₅]⁻ and [SiH₄F]⁻ have been studied. All of the distortions studied lead to enormous variations in anion affinities, to cases in which the anion is unbound (Table 3). If the angle between two equatorial H atoms is narrowed from 120° to 45° (roughly the C-Si-C angle in **1** and **2**), the corresponding hydride and fluoride affinities change from 17.0 and 32.0 kcal/mol to -32.4 and -26.8 kcal/mol. Narrowing the angle between an equatorial and axial H atom to 45° gives a -33.1 and -16.2 kcal/mol hydride and fluoride affinity. If the CH₂ groups in optimized **1** are replaced by H atoms, the corresponding [SiH₅]⁻ and [SiH₄F]⁻ have elongated Si-H bonds at the replacement positions. This geometry is called “cyclo long” in Table 3 and leads to hydride and fluoride affinities of -36.6 and -25.5 kcal/mol. When these replacements are changed to normal Si-H bond lengths (termed “cyclo short”), the hydride and fluoride affinities are -33.3 and -13.4 kcal/mol. The entries in Table 3 demonstrate (1) how acutely sensitive the hydride and fluoride affinities are to geometric

changes and (2) that corresponding fluoride affinities are always larger than hydride affinities. No matter how much “strain” is introduced into [SiH₅]⁻ and [SiH₄F]⁻, the affinity values are strongly negative and the difference between them remains large. The most realistic geometric comparison is between [SiH₅]⁻/[SiH₄F]⁻ and **1/2** and is given in the “cyclo short” entries in Table 3. Here the difference between fluoride and hydride affinity is the largest, larger than any corresponding entry in Table 2 except that for **1** and **2**.

Di-carbon substitution on silicon substantially increases both the hydride and fluoride affinity (Table 2). The siliconates of dimethylsilane (both diequatorial and equatorial-axial), 1-silacyclopropane, 1-silacyclobutane, and 1-silacyclopentane have hydride affinities between ~26–38 kcal/mol. Except for 1-silacyclopropane with a fluoride affinity of ~65 kcal/mol, the fluoride affinities of the other dicarbon-substituted species are between ~42–50 kcal/mol. The difference between the hydride and fluoride affinities for second row attachments to silicon in this and previous work is in the range of ~8–16 kcal/mol with one exception, that of 1-silacyclopropane, where this difference is 32.5 kcal/mol (Table 2).⁵² The 32.5 kcal/mol difference for 1-silacyclopropane indicates that the fluoro-silicate **2** is unusually stable relative to silicate **1**, although there are no obvious structural or charge differences (*vide supra*).

Table 2 has another surprising result, namely that the hydride and fluoride affinities of dimethylsilane are larger for the equatorial-axial (ea) than the equatorial-equatorial (ee) regioisomers. These results suggest that the ea isomer is more stable, a result that seems counter-intuitive on steric grounds, but not so if the more electronegative methyl substituent prefers the axial position as would be expected.⁵⁸ The energy difference between the [(CH₃)₂SiH₃]⁻ isomers is 11.6 kcal/mol, while that between the [(CH₃)₂SiH₂F]⁻ isomers is 5.2 kcal/mol, where in each case the ea isomer is more stable. Examination of the structures of these dimethyl siliconates indicates that there are significant geometric distortions for several isomers. Thus, ee-[(CH₃)₂SiH₃]⁻ has an H_a-Si-H_a angle of 174°, while the C_a-Si-H_a angle of ea-[(CH₃)₂SiH₃]⁻ is 179°. Other geometric indicators clearly show that ee-[(CH₃)₂SiH₃]⁻ is the more distorted isomer. The ee- and ea-[(CH₃)₂SiH₂F]⁻ geometries are more similar, but the ea isomer is slightly more distorted from trigonal bipyramidal geometry despite the energy differences found. Comparison of bond lengths, however, gives an indication of why the ea isomer is lower in energy, since the distances between Si and comparable F and C atoms are shorter in the ea isomer. The corresponding Si-H bonds are slightly lengthened in the ea isomer, but in all cases, the differences are small, suggesting the subtlety of geometric effects.

Conclusions

A number of computations of silicon-containing species have been carried out to probe silicon substituent effects on carbon radicals and anions. These have proved to be provocative in raising issues about “pathological” changes in geometry in computing EAs, the differences between EA and VAE computations and experiments, and the importance of zero point correction in VAE computations. Although there is no doubt that the strongly stabilizing substituent effect of silicon in α -silyl

(57) Gordon, M. S.; Davis, L. P.; Burggraf, L. W. *Adv. Gas Phase Ion Chem.* **1992**, *1*, 203–223.

(58) A referee (thanks) has suggested that the methyl in the axial position is expected because it has greater electronegativity than hydrogen.

carbanions is attenuated rapidly with homologation, the profound geometry changes leading to the two-, three-, and four-carbon pentacoordinate anions raise difficult questions regarding substituent effects. Some of these questions may be resolved by experimental studies.⁵⁵

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versations with Professors Larry Burggraf, Charles H. DePuy, G. Barney Ellison, Mark S. Gordon, and Paul Wenthold.

Supporting Information Available: Tables containing the absolute and relative energies for the species reported as well as optimized Cartesian coordinates for these structures can be found in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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