Predicted heats of formation for methylsilylene and dimethylsilylene

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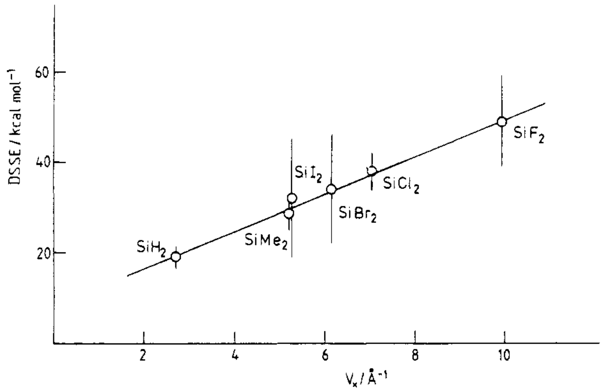

Figure 1. Plot of correlation between divalent state stabilization energies (DSSE) and substituent electronegativity (represented by unshielded core potential, V_x) for silylenes.

modern measure of electronegativity. Although there is some scatter in the data, there is clearly a reasonable correlation in which $SiMe_2$ fits reasonably close to the best fit line. If a value of $\Delta H_f^\circ(SiMe_2) = 31.6$ kcal mol^{-1} had been used, then the DSSE ($SiMe_2$) = 22.5 kcal mol^{-1}. The point for Me would then lie substantially away from the correlation line. It should be noted that if the more well-known Pauling electronegativities are used for this plot, this conclusion is not altered. [The electronegativity scale of Sanderson,[46] perhaps less well-known, does not support this correlation.] The existence of this correlation may be understood in terms of a *deshielding* effect.[44] The more electronegative the substituent, the more the bonding electrons are attracted further from the silicon nucleus, thus increasing the attraction of the nucleus for the (largely s-type) lone-pair electrons. Since carbon has a higher UCP than hydrogen, this means an increased stabilization energy for $SiMe_2$ compared with SiH_2.

Acknowledgment. I thank Mark Gordon, Ed O'Neal, and Morey Ring for valuable discussions.

Registry No. $Me_3SiSiMe_3$, 1450-14-2; Si_2H_6, 1590-87-0; $MeSiH_2SiH_3$, 13498-43-6; $Me_2SiHSiH_3$, 16342-86-2; $MeSiH_2SiH_2Me$, 870-26-8; Me_3SiSiH_3, 18365-32-7; $Me_2SiHSiH_2Me$, 814-74-4; Me_3SiSiH_2Me, 81633-92-3; $Me_2SiHSiHMe_2$, 814-98-2; $Me_3SiSiHMe_2$, 812-15-7; SiH_3Me, 992-94-9; SiH_2Me_2, 1111-74-6; $SiHMe_3$, 993-07-7; $SiMe_4$, 75-76-3; $SiMeCl_3$, 75-79-6; SiH_2MeCl, 993-00-0; $SiHMe_2Cl$, 1066-35-9; $SiMe_3Cl$, 75-77-4; $SiHMeCl_2$, 75-54-7; $SiMe_2Cl_2$, 75-78-5; SiF_4, 7783-61-1; $SiCl_4$, 10026-04-7; $SiBr_4$, 7789-66-4; SiI_4, 13465-84-4; SiF_2, 13966-66-0; $SiCl_2$, 13569-32-9; $SiBr_2$, 14877-32-8; SiI_2, 13465-83-3; $SiMe_2$, 6376-86-9; SiHMe, 55544-30-4.

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(45) Luo, Y.-R.; Benson, S. W. *J. Phys. Chem.* **1988**, *92*, 5255.

(46) Sanderson, T. T., *Chemical Bonds and Bond Energy*, 2nd ed.; Academic Press: New York, 1976.

Predicted Heats of Formation for Methylsilylene and Dimethylsilylene

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Ab initio calculations at the MP2/6-31G(d,p) level of computation, combined with a sequence of isodesmic reactions, have been used to predict the heats of formation of methylsilylene and dimethylsilylene to be 49.2 and 32–33 kcal/mol, respectively. These results are discussed in the light of recent experimental determinations in the accompanying experimental papers.

Introduction

The prediction of heats of formation is one of the prime goals of both ab initio and semiempirical electronic structure theory. For small molecules, Pople and coworkers[1] and Binkley and Melius[2] have demonstrated how large basis sets and fourth-order perturbation theory can be used to predict heats of formation to within 2–3 kcal/mol. For larger molecules, Dewar, Stewart, and coworkers[3] have parametrized semiempirical methods to predict this property.

Disch et al.[4] have shown that, if the heats of formation of key reference compounds are known either from experiment or from accurate electronic structure theory calculations, then the (previously unknown) heats of formation for compounds of moderate size can be predicted with a modest level of theory. The proposed procedure is to utilize the energetics of some chemical reaction which has two important features: (1) the heats of formation for all species in the reaction, except the compound of interest, are known and (2) the reaction is designed in such a way that the difference in the correlation error (implicit in the calculation at the Hartree–Fock level) for the reaction is minimized. Two such reactions may be referred to as isodesmic and homodesmic. The former is a reaction in which each formal bond type is conserved. This may be illustrated with the reaction of *n*-butane with methane to form ethane and propane:

$$CH_3CH_2CH_2CH_3 + CH_4 \rightarrow CH_3CH_3 + CH_3CH_2CH_3 \tag{1}$$

Here, both reactants and products have three CC single bonds and 14 CH bonds. Since the correlation error should be roughly constant for a given bond type, one can expect

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(1) Pople, J. A.; Luke, B. T.; Frisch, M. J.; Binkley, J. S. *J. Phys. Chem.* **1985**, *89*, 2198.

(2) Melius, C. F.; Binkley, J. S. *ACS Symp. Ser.* **1984**, *249*, 103.

(3) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) Stewart, J. J. P. MOPAC, Quantum Chemistry Program Exchange; Program 455, Department of Chemistry, Indiana University, Bloomington, IN 47405.

(4) Disch, R. L.; Schulman, J. M.; Sabio, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1904.

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that the energy difference for such a reaction may be reproduced with reasonable accuracy at a modest level of theory. Thus, if, for example, the heats of formation for methane, ethane, and propane were known and that for *n*-butane were not, the latter could be estimated from the calculated reaction energy, corrected for the zero-point vibrational energy (ZPE) difference, and the known heats of formation.

The restrictions in a homodesmic reaction are more stringent than those for an isodesmic reaction, since group types, not simply bond types, must be conserved. One may again use *n*-butane as an example:

$$CH_3CH_2CH_2CH_3 + CH_3CH_3 \rightarrow 2CH_3CH_2CH_3 \quad (2)$$

Here, both reactants and products have four CH_3 groups and two CH_2 groups. Since the variation in the nature of the chemical species being investigated is smaller in a homodesmic reaction, one would expect that the heat of formation predicted for *n*-butane would be even more reliable using reaction 2 than reaction 1. The results obtained by Disch and co-workers for cyclic and acyclic alkanes[4] and in this laboratory for cyclic and acyclic silanes[5] suggest that heats of formation obtained at an appropriate level of theory (typically second-order perturbation theory with a split valence plus polarization basis set) are accurate to within 2-3 kcal/mol with homodesmic reactions and 3–5 kcal/mol with isodesmic reactions.

Although homodesmic reactions are preferable, there are some compounds for which it is difficult to design such reactions. Examples are ionic species and compounds with reduced valence. In these cases, one must use isodesmic reactions and expect a slightly reduced accuracy in the predicted heats of formation. An important example of molecules with reduced valence are the silylenes. A great deal of experimental and theoretical effort has been expended to obtain the heat of formation of the parent prototype compound, SiH_2. The best estimate of this heat of formation now appears to be 65 ± 3 kcal/mol.[6] In the present work, isodesmic reactions are designed which relate silylene and saturated silanes whose heats of formation are well-known to substituted silylenes, so that the heats of formation of the latter may be estimated. In the accompanying papers,[12,13] the results of the calculations presented here are discussed in light of new experimentally determined heats of formation for dimethylsilylene.

Computational Methodology

The geometries for all compounds investigated in this work were optimized at the self-consistent field (SCF) level, using the 6-31G(d,p) basis set[7] and the analytical gradient techniques in GAUSSIAN86.[8] The structures so obtained were verified as minima on their respective potential energy surfaces by demonstrating that the matrices of their energy second derivatives, also obtained analytically, are positive definite. The energetics of the isodesmic reactions when then obtained with the same basis set and second-order many-body perturbation theory in the Møller–Plesset scheme,[9] as by Pople and co-workers.[10]

Table I. Molecular Structures[a]

molecule[b]	structure[c]
SiH_2 (C_{2v})	$R(SiH) = 1.514$, $(HSiH) = 93.4$
CH_3SiH (C_s)	$R(CSi) = 1.906$, $R(SiH) = 1.519$, $R(CH_i) = 1.084$, $R(CH_o) = 1.090$, $(CSiH) = 95.7$, $(H_iCSi) = 113.0$, $(H_oCSi) = 110.2$, $(H_iCH_o) = 108.5$
$(CH_3)_2Si$ (C_2)	$R(CSi) = 1.918$, $R(CH_a) = 1.085$, $R(CH_b) = 1.089$, $R(CH_c) = 1.092$, $(CSiC) = 98.5$, $(H_aCSi) = 112.1$, $(H_bCSi) = 112.6$, $(H_cCSi) = 108.4$, $(H_bCH_a) = 108.8$, $(H_cCH_a) = 107.6$, dihedral$(H_aCSiC) = 170.3$
SiH_4 (T_d)	$R(SiH) = 1.479$
CH_3SiH_3 (C_{3v})	$R(SiC) = 1.889$, $R(SiH) = 1.482$, $R(CH) = 1.086$, $(HCSi) = 110.9$, $(HSiC) = 110.6$
$(CH_3)_2SiH_2$ (C_{2v})	$R(SiC) = 1.890$, $R(SiH) = 1.485$, $R(CH_i) = 1.086$, $R(CH_o) = 1.086$, $(CSiC) = 111.4$, $(HSiC) = 109.5$, $(H_iCSi) = 111.1$, $(H_0CSi) = 111.1$, $(H_iCH_o) = 107.8$

[a] Bond lengths in Å, angles in deg. [b] Symmetry given in parentheses. [c] Subscripts i and o refer to in-plane and out-of-plane hydrogens, respectively.

Table II. Total Energies (hartree) and Zero-Point Energies (kcal/mol)

compd	E [MP2/6-31G(d,p)]	zero-point energy	$\Delta H_f°_{298}$
SiH_2	−290.085 12	7.8	65.3[a]
CH_3SiH	−329.281 01	27.9	see text
$(CH_3)_2Si$	−368.477 71	47.4	see text
SiH_4	−291.339 10	20.8	8.2[b]
CH_3SiH_3	−330.533 60	40.6	−6.96[b]
$(CH_3)_2SiH_2$	−369.728 63	59.9	−22.6[b]

[a] Frey, H. M.; Walsh, R.; Watts, I. M. *J. Chem. Soc., Chem. Commun.* 1986, 1189. [b] Doncaster, A. M.; Walsh, R. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 707.

For the monosubstituted methylsilylene, the following isodesmic reaction was used:

$$CH_3SiH + SiH_4 \rightarrow SiH_2 + CH_3SiH_3 \quad (3)$$

Four different isodesmic reactions were used to predict the heat of formation of dimethylsilylene:

$$(CH_3)_2Si + CH_3SiH_3 \rightarrow (CH_3)_2SiH_2 + CH_3SiH \quad (4)$$

$$(CH_3)_2Si + SiH_4 \rightarrow CH_3SiH_3 + CH_3SiH \quad (5)$$

$$(CH_3)_2Si + SiH_4 \rightarrow (CH_3)_2SiH_2 + SiH_2 \quad (6)$$

$$(CH_3)_2Si + SiH_2 \rightarrow 2\ CH_3SiH \quad (7)$$

For each reaction the ZPE differences were multiplied by 0.89 to correct for the overestimation of vibrational frequencies at the SCF level.[11]

Results and Discussion

The SCF/6-31G(d,p) geometries for all compounds considered in this paper are listed in Table I, and the corresponding vibrational zero-point energies, MP2/6-31G(d,p) total energies, and experimental heats of formation are listed in Table II. Using the values in Table II and reactions 3–7, one may obtain predicted heats of

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(5) (a) Boatz, J. A.; Gordon, M. S.; Hilderbrandt, R. L. *J. Am. Chem. Soc.* **1988**, *110*, 352. (b) Gordon, M. S.; Boatz, J. A.; Walsh, R. *J. Phys. Chem.* **1989**, *93*, 1584.

(6) Frey, H. M.; Walsh, R.; Watts, I. M. *J. Chem. Soc. Chem. Commun.* **1986**, 1189.

(7) (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1972**, *28*, 213. (b) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

(8) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Brobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Topiol. S.; Pople, J. A. Pople, GAUSSIAN86, Carnegie-Mellon Quantum Chemistry Publishing, Pittsburgh, PA 15213.

(9) Moller, C.; and Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(10) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

(11) Pople, J. A.; Schlegel, H. B. Krishnan, R.; Defrees, D. J. Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. J.; Hehre, W. J. *Int. J. Quantum Chem.* **1981**, *S15*, 269.

(12) Nares, K. E.; Harris, M. E.; Ring, M. A.; O'Neal, H. E. *Organometallics*, first of four papers in this issue.

formation for methylsilylene and dimethylsilylene. For CH_3SiH the calculated value at 298 K is 49.2 kcal/mol. Reactions 4-7 predict heats of formation of 32.8, 32.6, 33.1, and 32.0 kcal/mol, respectively, for dimethylsilylene. The agreement among these four reactions is encouraging, particularly since all but reaction 6 make use of the calculated value for methylsilylene. It is estimated that the average of these four values (32.6 kcal/mol) is accurate to 3-4 kcal/mol. The implications of these results are discussed in light of recent experimental results in the accompanying papers by Ring, O'Neal, and co-workers[12] and Walsh.[13]

Acknowledgment. This work was supported in part by grants from the National Science Foundation (CHE86-40771) and the Air Force Office of Scientific Research (87-0049). The computer time made available by the North Dakota State University Computer Center is gratefully acknowledged.

Registry No. SiH_2, 13825-90-6; CH_3SiH, 55544-30-4; $(CH_3)_2Si$, 6376-86-9; SiH_4, 7803-62-5; CH_3SiH_3, 992-94-9; $(CH_3)_2SiH_2$, 1111-74-6.

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[13] Walsh, R. *Organometallics*, third of four papers in this issue.

Stoichiometric and Catalytic Ring Opening of Hexaalkylcyclodisilazanes by Organoalkali Reagents

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The action of organoalkali reagents (RLi, RLi/Me_3CONa, RLi/Me_3COK) on cyclo-$(Me_2SiNMe)_2$ and cyclo-$(Me_2SiNPr^i)_2$ results in ring opening to give alkali-metal amides of the type $RMe_2SiNMeSiMe_2NMeM$ (M = Li, Na, K) which react with chlorosilanes, $R'Me_2SiCl$, to give the expected linear trisilazanes. Relatively unhindered lithium amides also open the cyclo-$(Me_2SiNMe)_2$ ring. The use of a catalytic amount of RLi or RLi/Me_3CONa (but not of RLi/Me_3COK) results in ring-opening polymerization of cyclo-$(Me_2SiNMe)_2$ but not of the more hindered cyclo-$(Me_2SiNPr^i)_2$.

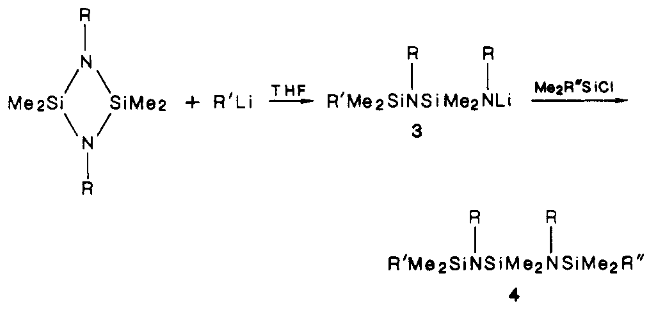
Introduction

Stoichiometric and catalytic ring opening of cyclotrisiloxanes by the action of strong nucleophilic reagents (OH^-, OR^-, $OSiMe_3^-$, RLi, etc.) is well-known,[1] and the catalytic processes are useful in the preparation of linear polysiloxanes. Applied to cyclopolysilazanes, cyclo-$(R^1R^2SiNR^3)_n$, such processes might be expected to result in formation of linear polysilazanes. However, none have been reported thus far.[2] Our interest in polysilazanes as precursors for silicon nitride and silicon carbonitride[3] led us to investigate the possibility of organoalkali reagent catalyzed ring-opening polymerization of cyclic polysilazanes.

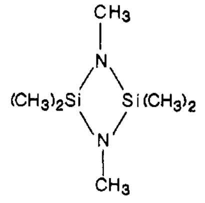
Results and Discussion

In the cyclopolysiloxane series, cyclo-$(R_2SiO)_n$, the four-membered ring is known only when R is an extremely bulky organic group,[4] and for the R = CH_3 series the cyclotrisiloxane is the smallest ring known. Hexamethylcyclotrisiloxane has enhanced reactivity, compared with the larger cyclics, and is readily cleaved by strong nucleophiles.[1] In the cyclopolysilazane series the four-membered cyclodisilazane ring system is very stable, and many examples of Si_2N_2 rings have been reported.[5]

Scheme I



Before investigating the possibility of the catalytic ring-opening polymerization of cyclodisilazanes, we have studied the stoichiometric opening of the cyclodisilazane ring by organoalkali reagents. The cyclodisilazanes chosen for study were 1 and 2. Both compounds are stable,



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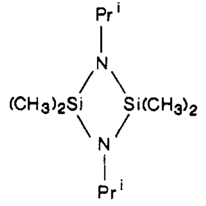

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distillable liquids. Hexamethylcyclodisilazane was found

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[1] Noll, W. *Chemistry and Technology of Silcones*; Academic Press: New York, 1968; Chapter 5.

[2] For a discussion of previous attempts to prepare linear polysilazanes containing R_2SiNR or R_2SiNH repeat units see: Aylett, B. J. *Organomet. Chem. Rev.* **1968**, *3*, 151.

[3] Seyferth, D. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360, American Chemical Society: Washington, DC, 1988; pp 143-155 and references cited therein.

[4] Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1986**, *5*, 531.

[5] For reviews on cyclodisilazanes see: (a) Fink, W. *Angew Chem., Int. Ed. Engl.* **1966**, *5*, 760. (b) Zhinkin, D. Ya.; Varezhkin, Yu. M.; Morgunova, M. M. *Russ. Chem. Rev. (Engl. Transl.)* **1980**, *49*, 1149. (c) Varezhkin, Yu. M.; Zhinkin, D. Ya; Morgunova, M. M. *Russ. Chem. Rev. (Engl. Transl.)* **1981**, *50*, 1158. (d) Klingebiel, U. *Nachr. Chem. Tech. Lab.* **1987**, *35*, 1042.

0276-7333/89/2308-1980$01.50/0