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Ab initio structures and energetics of selected hydrogenated silicon clusters containing six to ten silicon atoms

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Abstract

The structures and energies of eight fully saturated polycyclic polysilanes (Si_6H_8, Si_6H_{10}, Si_7H_8, Si_7H_{10}, Si_8H_{12}, Si_9H_{14}, $Si_{10}H_{14}$, and $Si_{10}H_{16}$) were investigated using ab initio molecular orbital calculations. Structures and vibrational frequencies were computed at the HF/3-21G(d) level. A complete basis set extrapolation method (CBS-4) was used to calculate the energies of the structures. Heats of formation were evaluated based on homodesmotic reactions involving disilane, trisilane, and isotetrasilane. The calculations predict a negative free energy of reaction for cluster formation from silane (with H_2 as a by-product) for conditions typically used in chemical vapor deposition of silicon from silane. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Homogeneous nucleation of particles during chemical vapor deposition (CVD) of thin films is an important problem in microelectronics manufacturing, where particle contamination is a substantial source of yield loss. Nucleation of hydrogenated silicon particles during thermal CVD of silicon from silane is a prototypical case. As part of a larger study of the thermochemistry and chemical kinetics of particle nucleation during silane thermal decomposition [1], we have used ab initio methods to calculate the structures and energetics of several hydrogenated silicon clusters containing six to ten silicon atoms. The particular clusters investigated are those that, in a preliminary kinetic and thermodynamic model [1], were predicted to play the most important role in particle nucleation from silane. Accurate determination of the enthalpy and entropy of these clusters is necessary if we are to model and understand the particle nucleation process in which they participate.

For a nucleation process involving condensation of a supersaturated vapor, we would expect the overall free energy change in going from monomers to a cluster to increase with cluster size, reach a maximum, and then decrease with cluster size for all larger clusters. When that is the case, the cluster size where the free energy change reaches its maximum can be identified as a ‘critical cluster size’, and all clusters larger than that size are expected to grow irreversibly into particles. For a chemical nucleation process like the one that leads to silicon hydride particle formation, it is not clear that the overall free energy change should have such a simple dependence on cluster size. The free energy change may

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go through multiple local maxima that can individually act as bottlenecks in the cluster growth process. In addition, the free energy change in this system depends both on the size of the cluster (number of Si atoms) and its degree of hydrogenation (number of H atoms).

Smaller silicon hydride molecules have been investigated in numerous studies that will not be reviewed here. A large number of small to medium-sized silicon hydride molecules were investigated by Katzer et al. [2] using an empirically corrected ab initio scheme. Theoretical studies of strained, polycyclic silicon hydrides were presented by Zhao and Gimarc [3], and by Nagase and co-workers [4,5]. To our knowledge, the somewhat larger and less-strained molecules considered here have not previously been studied.

2. Methodology

The GAUSSIAN94 [6] suite of programs was used for the calculations presented here. The CBS-4 complete basis set method [7] was used for the energy calculations. This is the least expensive of the complete basis set methods presented by Ochterski and co-workers [7]. In benchmark tests that they presented, this method predicted the atomization energies of the 55 molecules in the G2 test set with a mean absolute error of 7.1 kJ mol^{-1}. The geometry optimization and frequency calculation in this method are done at the HF/3-21G(d) level, and the structures obtained at that level are presented here. The total energy is computed in a multistep procedure that uses progressively smaller basis sets for higher order calculations of the correlation energy. Using the CBS-4 energies, the heats of formation of these structures were computed based on the homodesmotic reaction

$$Si_{m+n}H_{2m+n} + (m + 3/2n)\,Si_2H_6 \rightarrow m\,Si_3H_8 + n\,iso\text{-}Si_4H_{10}\,. \qquad (1)$$

In Eq. (1), m is the number of SiH_2 units in the cluster, and n is the number of SiH units in the cluster. The heats of formation of Si_2H_6, Si_3H_8, and *iso*-Si_4H_{10} were taken from the work of Katzer et al. [2].

3. Results

The structures of the eight compounds studied are shown in Fig. 1. Geometric parameters for the structures are given in Table 1. The silicon–hydrogen bond lengths (not listed in Table 1) were all 1.48 ± 0.01 Å, which is the same as their value in the smaller silanes. The silicon–silicon bond lengths are also close to their values in the smaller silanes (2.34 Å in disilane at this level of theory). Most of the Si–Si bond lengths computed here are longer than the corresponding bond in disilane. Silicon–silicon bonds appear to be lengthened by silyl substitution for hydrogen and appear to be shortened when they are part of a highly strained ring. The Si–Si–Si bond angles are tightly constrained by the polycyclic geometry and many of them are far from the ideal tetrahedral angle (about 110°). The H–Si–Si bond angles come as close to the tetrahedral angle as possible, given the positions of the silicon atoms.

Table 2 summarizes the calculated thermochemical properties of the species. The heat of formation per silicon atom is about 40 kJ mol^{-1} for acyclic polysilanes. The highly strained clusters containing six or seven silicon atoms have much higher heats of formation per silicon atom, due to the ring strain. One reasonable measure of the total strain energy of a cluster is the energy released when the cluster is converted to acyclic molecules via reaction (1). This energy is given in the last column of Table 2. From calculations on the monocyclic polysilanes [3,8], the strain energies for three-, four-, five-, and six-membered rings are expected to be about 160, 70, 23, and 0 kJ mol^{-1}, respectively. The strain energies calculated here are substantially smaller than what would be predicted by addition of those individual ring strain energies, particularly for the six- and seven-silicon containing clusters that are made up of highly strained three- and four-membered rings. This is

Fig. 1. Structures of the hydrogenated silicon clusters studied in this work. Atom numbering corresponds to geometric parameters in Table 1. Atoms with the same number are identical (interchangeable by symmetry operations).

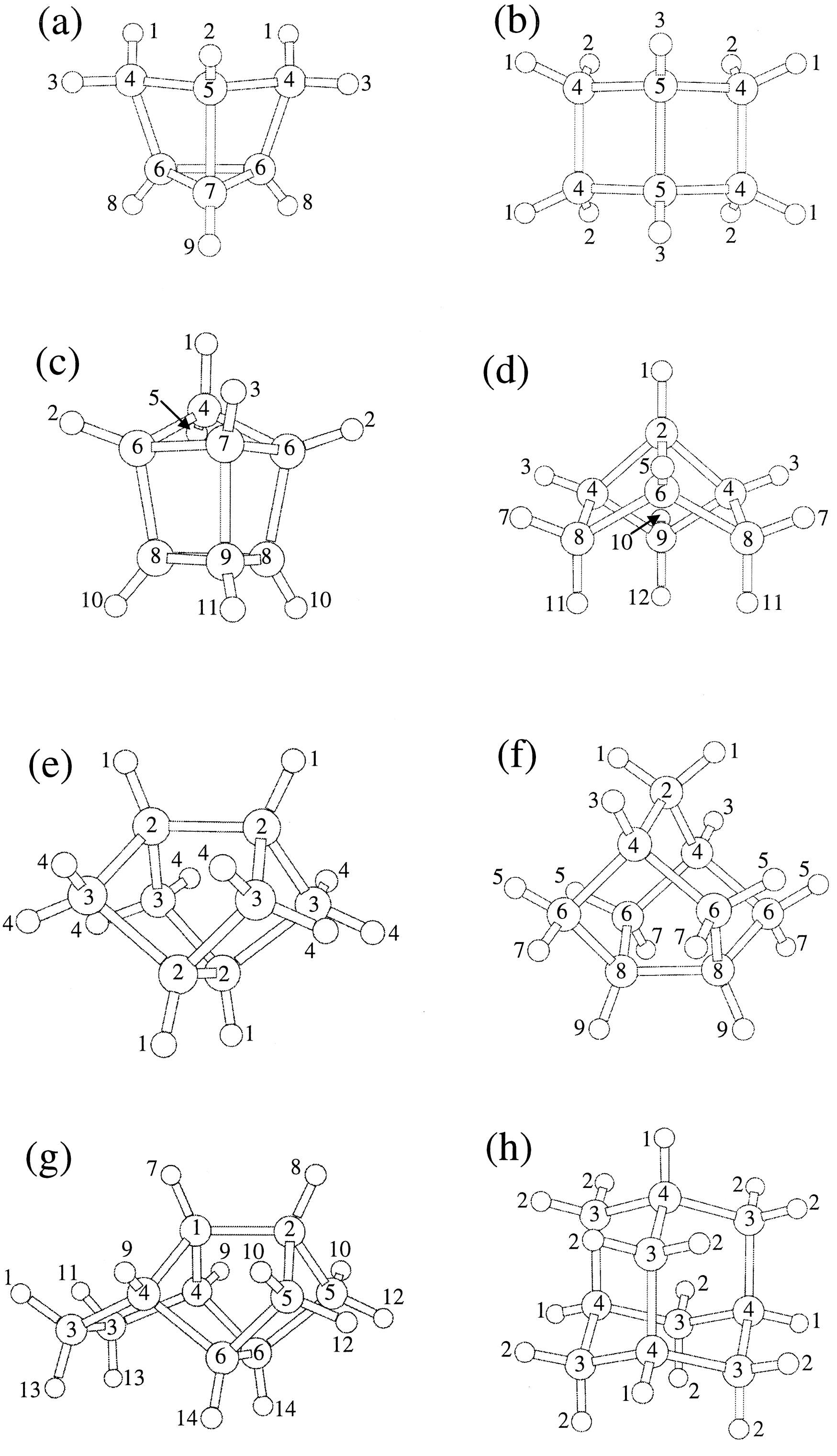
(a)
1 2 1
3 4 5 4 3
6 6
8 7 8
9
(b)
3
2 2
1 4 5 4 1
1 4 5 4 1
2 2
3
(c)
1
5 4 3
2 6 7 6 2
8 9 8
10 11 10
(d)
1
2
3 5 3
4 6 4
7 8 9 8 7
10
11 12 11
(e)
1 1
2 2
4 4 4 4
3 3 3 3
4 4 4 4
2 2
1 1
(f)
1 1
3 2 3
4 4
5 5 5 5
6 6 6 6
7 7 7 7
8 8
9 9
(g)
7 8
1 2
9 9 10 10
11 11 4 4 5 5 12
3 3 12
13 13 6 6
14 14
(h)
1
2 2 4 2 2
3 3
2 3 2
2
1 4 3 4 1
2 3 4 3 2
1 2
2 2

Table 1
Geometric parameters[a]

Si_6H_8		Si_6H_{10}		Si_7H_8		Si_7H_{10}		Si_8H_{12}		Si_9H_{14}		$Si_{10}H_{14}$		$Si_{10}H_{16}$	
Si–Si bond lengths (Å)															
$R_{4,5}$	2.36	$R_{4,5}$	2.37	$R_{6,4}$	2.36	$R_{2,4}$	2.39	$R_{2,2}$	2.41	$R_{2,4}$	2.36	$R_{1,2}$	2.39	$R_{3,4}$	2.35
$R_{4,6}$	2.33	$R_{5,5}$	2.39	$R_{6,7}$	2.39	$R_{2,6}$	2.39	$R_{2,3}$	2.37	$R_{4,6}$	2.35	$R_{1,4}$	2.37		
$R_{5,7}$	2.38	$R_{4,4}$	2.37	$R_{6,8}$	2.35	$R_{8,4}$	2.36			$R_{6,8}$	2.36	$R_{3,4}$	2.35		
$R_{6,7}$	2.32			$R_{9,7}$	2.37	$R_{8,6}$	2.36			$R_{8,8}$	2.38	$R_{3,3}$	2.36		
$R_{6,6}$	2.36			$R_{8,9}$	2.33	$R_{9,4}$	2.36					$R_{6,4}$	2.36		
				$R_{8,8}$	2.37							$R_{6,6}$	2.40		
												$R_{5,6}$	2.36		
												$R_{2,5}$	2.36		
Bond angles (degrees)															
$\angle 1,4,5$	117	$\angle 1,4,5$	114	$\angle 1,4,6$	111	$\angle 1,2,6$	126	$\angle 1,2,2$	115	$\angle 1,2,4$	109	$\angle 7,1,2$	116	$\angle 1,4,3$	110
$\angle 3,4,5$	113	$\angle 2,4,5$	115	$\angle 5,4,6$	119	$\angle 4,2,6$	89	$\angle 3,2,2$	103	$\angle 4,2,4$	112	$\angle 4,1,2$	105	$\angle 3,4,3$	109
$\angle 6,4,5$	85	$\angle 4,4,5$	90	$\angle 4,6,7$	90	$\angle 2,4,8$	90	$\angle 4,3,2$	115	$\angle 3,4,6$	114	$\angle 8,2,1$	115	$\angle 4,3,4$	110
$\angle 2,5,4$	121	$\angle 3,5,4$	118	$\angle 2,6,7$	126	$\angle 3,4,8$	118	$\angle 2,3,2$	93	$\angle 2,4,6$	109	$\angle 5,2,1$	103	$\angle 2,3,4$	110
$\angle 7,5,4$	90	$\angle 5,5,4$	90	$\angle 8,6,7$	84	$\angle 9,4,8$	110			$\angle 6,4,6$	100	$\angle 9,4,1$	116		
$\angle 4,5,4$	103	$\angle 4,5,4$	109	$\angle 3,7,6$	125	$\angle 7,8,4$	111			$\angle 5,6,4$	113	$\angle 3,4,1$	108		
$\angle 4,6,7$	92			$\angle 9,7,6$	93	$\angle 11,8,4$	117			$\angle 7,6,4$	110	$\angle 6,4,1$	92		
$\angle 8,6,7$	129			$\angle 6,7,6$	84	$\angle 6,8,4$	90			$\angle 8,6,4$	101	$\angle 3,3,4$	103		
$\angle 6,6,7$	59			$\angle 6,8,9$	95	$\angle 5,6,2$	126			$\angle 9,8,6$	114	$\angle 11,3,4$	111		
$\angle 9,7,6$	135			$\angle 10,8,9$	130	$\angle 8,6,2$	90			$\angle 8,8,6$	105	$\angle 13,3,4$	111		
$\angle 5,7,6$	84			$\angle 8,8,9$	59	$\angle 10,9,4$	111			$\angle 6,8,6$	105	$\angle 14,6,4$	118		
$\angle 6,7,6$	61			$\angle 7,9,8$	85	$\angle 12,9,4$	117					$\angle 6,6,4$	103		
				$\angle 8,9,8$	61	$\angle 4,9,4$	90					$\angle 5,6,4$	97		
				$\angle 11,9,8$	134							$\angle 2,5,6$	93		
												$\angle 10.5.6$	112		
												$\angle 12,5,6$	115		

[a] Geometries at the HF/3-21G(d) level. Atom numbering is shown in Fig. 1. Silicon–hydrogen bond lengths (not shown) were 1.48 ± 0.01 Å. This is the same as their length in the smaller silanes. Vibrational frequencies and more detailed structural information at this level are available upon request from the authors.

Table 2
CBS-4 thermochemistry

Species	CBS-4 enthalpy (hartrees)	Entropy (J mol^{-1} K^{-1})	Heat of formation (kJ mol^{-1})	Total strain energy (kJ mol^{-1})
$Si_2H_6^a$	−581.682739	283.2[b]	79.9[b]	0.0[c]
$Si_3H_8^a$	−871.938607	347.0[b]	120.6[b]	0.0[c]
$Si_4H_{10}^a$	−1162.197364	408.9[b]	156.8[b]	0.0[c]
Si_6H_8	−1739.124352	402.5	440.3	211.1[d]
Si_6H_{10}	−1740.327290	439.0	348.8	112.1[d]
Si_7H_8	−2028.200727	420.9	511.0	248.6[d]
Si_7H_{10}	−2029.411805	449.1	398.1	128.2[d]
Si_8H_{12}	−2319.701679	462.7	349.5	38.9[d]
Si_9H_{14}	−2609.974839	521.9	344.8	−6.5[d]
$Si_{10}H_{14}$	−2899.054941	544.4	405.7	21.2[d]
$Si_{10}H_{16}$	−2900.240615	565.4	359.5	−32.5[d]

[a] These molecules were used as reference compounds for calculating the heats of formation using the homodesmotic reaction (1) given in the text.
[b] From Ref. [2].
[c] Taken to be zero by definition.
[d] Enthalpy change for the homodesmotic reaction $Si_{m+n}H_{2m+n} + (m + 3/2n)Si_2H_6 \rightarrow mSi_3H_8 + n\textit{iso}\text{-}Si_4H_{10}$.

consistent with the calculations of Nagase [5], who concluded that strained rings were substantially stabilized by silyl substitution for hydrogen.

The overall thermodynamics for the formation of these silicon hydride clusters from silane are summarized in Table 3. Results for species containing five or fewer silicon atoms are based on the calculations of Katzer et al. [2]. Note that the reaction enthalpies and entropies are given per mole of SiH_4. Formation of the highly strained clusters containing six or seven silicon atoms is substantially endothermic, while formation of acyclic polysilanes and the less-strained clusters (Si_5H_{10} and the clusters with eight or more Si atoms) is roughly thermoneutral. At the temperatures where significant silane dissociation occurs ($>$ 700 K) the clustering process is entropically driven. The entropy of reaction for forming any cluster that contains at least one ring is positive, simply because there is an increase in the number of moles of gas-phase species. Production of the more highly strained clusters that contain more rings also produces more H_2 as a by-product. This results in higher entropies of reaction for formation of the highly strained clusters. So, increasing temperature favors clustering in general, and particularly favors formation of the strained but less hydrogenated clusters containing six or seven silicon atoms. At 1000 K and 1 bar, the free energy of reaction for cluster formation is positive for all the clusters in Table 3 with six or fewer silicon atoms except for cyclopentasilane, Si_5H_{10}, and is negative for all clusters in Table 3 that contain seven or more silicon atoms. The free energy of reaction at this temperature does not vary smoothly with increasing cluster size, but has a maximum at four silicon atoms, a minimum at five silicon atoms, a maximum at six silicon atoms, and then decreases for larger sizes. In addition, there are energetic barriers to conversion from one structure to another that are not considered in this analysis. The free energy profile changes with temperature, and this can move the positions of these maxima and minima, but the data given in Table 3 allow approximate calculation of the free energy profile for arbitrary conditions.

Table 3
Overall thermodynamics of clustering[a]

Molecules produced	Enthalpy of reaction ($kJ\ mol^{-1}$)	Entropy of reaction ($J\ mol^{-1}\ K^{-1}$)
$1/2\ (Si_2H_6 + H_2)$[b]	5.6	2.4
$1/3\ (Si_3H_6 + 3H_2)$[b]	59.5	26.8
$1/3\ (Si_3H_8 + 2H_2)$[b]	5.8	−1.7
$1/4\ (Si_4H_8 + 4H_2)$[b]	23.5	14.0
$1/4\ (Si_4H_{10} + 3H_2)$[b]	4.8	−4.3
$1/5\ (Si_5H_8 + 6H_2)$[b]	34.8	24.0
$1/5\ (Si_5H_{10} + 5H_2)$[b]	9.9	11.2
$1/6\ (Si_6H_8 + 8H_2)$[c]	39.0	36.8
$1/6\ (Si_6H_{10} + 7H_2)$[c]	23.7	21.1
$1/7\ (Si_7H_8 + 10H_2)$[c]	38.6	42.3
$1/7\ (Si_7H_{10} + 9H_2)$[c]	22.5	27.7
$1/8\ (Si_8H_{12} + 10H_2)$[c]	9.3	16.7
$1/9\ (Si_9H_{14} + 11H_2)$[c]	3.9	13.2
$1/10\ (Si_{10}H_{14} + 13H_2)$[c]	6.2	19.9
$1/10\ (Si_{10}H_{16} + 12H_2)$[c]	1.5	8.9

[a] Enthalpies and entropies of reaction are for conversion of SiH_4 to the products listed, at 298 K and 1 bar.
[b] Based on Ref. [2].
[c] Based on this work.

4. Conclusions

Structures, enthalpies of formation, and standard entropies for eight selected silicon hydride clusters with six to ten silicon atoms were calculated using ab initio methods. Ring strain in these polycyclic compounds, particularly those with highly strained three- and four-membered rings, was found to be substantially smaller than would be predicted by additivity of ring strain energies of the unsubstituted monocyclic polysilanes. Formation from silane of clusters containing seven or more silicon atoms was found to be thermodynamically favorable at conditions typical of silicon CVD. The free energy for cluster formation did not vary smoothly with cluster size.

Acknowledgements

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