Silanes/Oxygen/(Water): Green High-Energy-Density Materials

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Design of green high-energy-density materials as powerful as the well-known H_2/O_2 and N_2H_4/O_2 systems is a never-ending goal. Here, we study the energetic properties of reactions of silanes with oxygen (and gaseous water) by the bond energy procedure and high-level quantum chemistry calculations. The silanes/oxygen/(water) reactions finally lead to the green products, namely silica and water or silicic acids that exist in nature. The energy densities of these systems with respect to silica and water are higher than those of the conventional H_2/O_2 and N_2H_4/O_2 systems. Their energy densities with respect to silicic acids are also higher than or comparable to that of the N_2H_4/O_2 system. We propose that silanes/oxygen/(water) could be powerful green high-energy-density materials.

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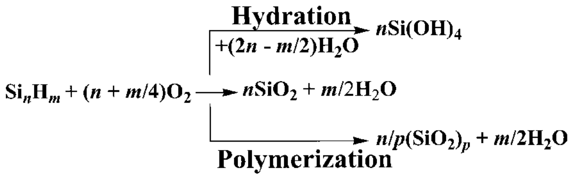
Introduction

Recently, high-energy-density materials (HEDM) have received considerable attention as energetic carriers and fuels in various fields.[1] On the other hand, green chemistry is actively seeking ways to produce materials benign to human health and the environment.[2] We proposed[3] green high-energy-density materials (green HEDM), which should satisfy four conditions: (i) they should have high energy densities; (ii) they should have considerable kinetic stability; (iii) the predominant products of the reactions should be green compounds, i.e., species benign to human health and environment, especially ones, e.g., N_2, H_2O, silica, etc., which exist in nature; and (iv) the possibility to actually synthesize them for practical use should be high. We previously designed seven N_2H_2O isomers as potential "green HEDMs" that might produce the green exhausts N_2 and H_2O.[3] In fact, the greenness of energetic materials has received recent attention.[4,5]

The bimolecular H_2/O_2 and N_2H_4/O_2 systems are conventional HEDMs, which can produce green exhausts (H_2O and N_2) from the reactions $H_2 + ½\, O_2 \rightarrow H_2O$ and $N_2H_4 + O_2 \rightarrow N_2 + 2\, H_2O$. Here we report a new type of bi- or termolecular green HEDMs: silanes/oxygen/(water) systems. By means of the bond energy procedure and high-level theoretical computations, we find that the energy densities of all the systems are higher than or comparable to those of the conventional H_2/O_2 and N_2H_4/O_2 systems. To the best of our knowledge, this represents the first consideration of the silanes as "**green HEDMs**", although the self-ignition and explosiveness of monosilane (SiH_4) in air has long been known, and SiH_4 has been widely used in the semiconductor industries.[6,7]

Results and Discussion

In the present work, we investigate the energetic properties of the reactions (Scheme 1) of silanes (Si_nH_m) (Figure 1) including acyclic silanes (1 Si_nH_{2n+2}), cyclic silanes (2 Si_nH_{2n}), ladder silanes (3 $Si_{2n}H_{2n+4}$), and cage silanes (4 $Si_{2n}H_{2n}$).



Scheme 1.

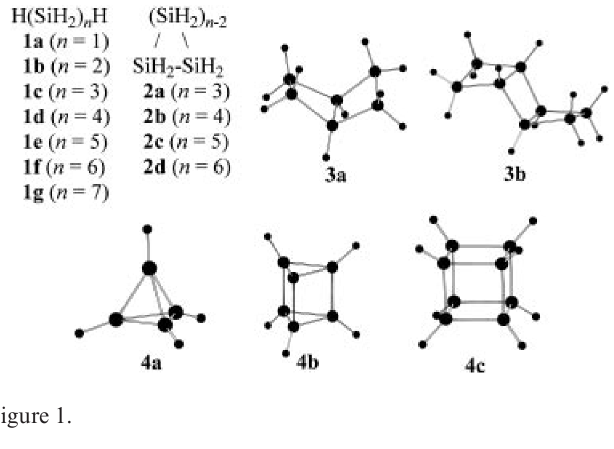


Figure 1.

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The combustion of SiH_4 ($SiH_4 + 2\ O_2 \rightarrow SiO_2 + 2\ H_2O$) releases energy (190.31 kcal/mol at the CBS-QB3 level). The energy density (ED in cal/g) for a reaction system is defined as the released energy (ΔE in cal/mol) divided by the mollar mass (M in g/mol). The molar masses of the elements H, N, O and Si are taken as 1, 14, 16 and 28 g/mol, respectively. The energy density of the SiH_4/O_2 system was calculated to be 1982 cal/g with respect to the products SiO_2 and H_2O. This value is close to that (2191 cal/g) of the known N_2H_4/O_2 system with respect to N_2 and H_2O. Yet, it is still lower than that (3108 cal/g) of the H_2/O_2 system with respect to H_2O. The products SiO_2 and H_2O can further undergo a hydration reaction and increase the energy density of the SiH_4/O_2 system. Two H_2O molecules were found to undergo a stepwise, barrierless addition to the Si=O double bonds of SiO_2, producing monosilicic acid $Si(OH)_4$.[8] The heat of the hydration, $SiO_2 + 2\ H_2O \rightarrow Si(OH)_4$, is 135.73 kcal/mol. The total released energy for $SiH_4 + 2\ O_2 \rightarrow Si(OH)_4$ is thus 326.04 kcal/mol (190.31 + 135.73). The hydration increases the energy density by 1414 cal/g ($135.73 \times 1000/96$). The energy density of the SiH_4/O_2 system with respect to the product $Si(OH)_4$ was calculated to be surprisingly high (3396 cal/g), as high as that (3108 cal/g) of the H_2/O_2 system and much higher than that (2191 cal/g) of the N_2H_4/O_2 system.

Higher silanes need water to be fully converted to $Si(OH)_4$ (see Scheme 1, $n \geq 2$). As listed in Table 1, the energy densities of the seven acyclic silane (Si_nH_{2n+2})/O_2/H_2O systems with respect to $Si(OH)_4$ lie between 3396 ($n = 1$) and 2904 cal/g ($n = 7$) at the CBS-QB3 level. For the four cyclic silane (Si_nH_{2n})/O_2/H_2O systems, the energy densities are between 2944 ($n = 3$) and 2819 cal/g ($n = 6$). The two ladder silane ($Si_{2n}H_{2n+4}$)/O_2/H_2O systems have the energy densities 2760 ($n = 3$) and 2709 cal/g ($n = 4$). The three cage silanes ($Si_{2n}H_{2n}$)/O_2/H_2O have the energy densities 2826, 2672 and 2606 cal/g for $n = 2$–4, respectively. The silanes/oxygen/water examined here by the high-level CBS-QB3 calculations are as powerful HEDMs as the H_2/O_2 or N_2H_4/O_2 systems. The energy densities of SiH_4/O_2 and $Si_2H_6/O_2/H_2O$ are even higher than that of H_2/O_2.

The high-level CBS-QB3 calculations are rather expensive for much larger silanes/oxygen/(water) systems. We employed a semiquantitative bond energy procedure on the assumption of the locality of chemical bonds. The bond energy (BE) is usually defined as the energy required to break a covalent bond in a gaseous substance. Computationally, for a diatomic molecule AB, the A–B bond energy is defined as $BE(A–B) = E(AB) - E(A) - E(B)$, in which $E(X)$ means the total energy of an atom or a molecule X. Then, the bond energy differences between the reactants and products in a chemical reaction are used to estimate the reaction heat. In more detail, for a typical reaction between two diatomic molecules: $A–A + B–B \rightarrow 2\ A–B$, the reaction heat is described as $\Delta E = 2BE(A–B) - BE(A–A) - BE(B–B)$. At the CBS-QB3 level, the bond energies are calculated to be 109.87 (O–H), 118.71 (O=O), 76.43 (Si–H), 107.42 (Si–O), 146.98 (Si=O), and 45.49 (Si–Si) kcal/mol.[9] The reaction heats (ΔE in kcal/mol) and energy densities (ED in cal/g) of the $Si_nH_m/O_2/H_2O$ systems with respect to $Si(OH)_4$ can be expressed[10,11] by Equation (1)

$$\Delta E = 219.99n + 26.507m \qquad (1)$$

and Equation (2)

$$ED = 2291.563 + 276.115/(n/m) \qquad (2)$$

As shown in Table 1, the energy densities of the 16 silane (Si_nH_m)/O_2/H_2O systems with respect to $Si(OH)_4$ estimated from the bond energies are very close to the values predicted by the fully geometry-optimized CBS-QB3 calculations. The relatively large errors (100, 258 and 104 cal/g for **1a**, **4a** and **4b**) are caused by the high strain of the three-membered rings. The generally good agreement of the energy densities between the bond energy procedure and high-

Table 1. The energy density (in cal/g) of silanes (Si_nH_m)/oxygen/(water) with respect to silic acid based on the CSB-QB3 (ED1//CBS-QB3) and bond energy (ED1//bond energy) calculations, and with respect to silica based on bond energy (ED2//bond energy) calculations.

Si_nH_m Species	ED1//CBS-QB3	ED1//Bond energy	ED2//Bond energy
SiH_4 (**1a**)	3396	3396	3396
Si_2H_6 (**1b**)	3120	3120	3443
Si_3H_8 (**1c**)	3020	3028	3460
Si_4H_{10} (**1d**)	2970	2982	3470
Si_5H_{12} (**1e**)	2939	2954	3476
Si_6H_{14} (**1f**)	2918	2936	3480
Si_7H_{16} (**1g**)	2904	2923	3482
Si_3H_6 (**2a**)	2944	2844	3500
Si_4H_8 (**2b**)	2858	2844	3500
Si_5H_{10} (**2c**)	2828	2844	3500
Si_6H_{12} (**2d**)	2819	2844	3500
Si_6H_{10} (**3a**)	2760	2752	3522
Si_8H_{12} (**3b**)	2709	2706	3534
Si_4H_4 (**4a**)	2826	2568	3572
Si_6H_6 (**4b**)	2672	2568	3572
Si_8H_8 (**4c**)	2606	2568	3572

level CBS-QB3 calculations suggests the reliability and usefulness of the bond energy procedure.

Gaseous silicon dioxide can also polymerize to silica $(SiO_2)_p$ to increase the energy density of the Si_nH_m/O_2 systems. Similar accurate evaluation of the reaction heats and energy densities with respect to silica is surely impossible because of the infinite structure of silica. We applied the bond energy procedure. The heat of the reaction: $SiO_2 \rightarrow 1/p(SiO_2)_p$ is calculated from the bond energies to be 135.72 kcal/mol (107.42×4 – 146.98×2).[12] This is the same value as that estimated for the hydration because the same numbers of each kind of bonds are broken or formed in the polymerization and the hydration. The reaction heats and energy densities of the $(Si_nH_m)/O_2$ systems with respect to silica and water can be generally expressed by Equation (3)[12,13]

$$\Delta E = 219.99n + 26.507m \quad (3)$$

and Equation (4)

$$ED = 3666.500 - 108.192/(n/m + 0.15) \quad (4)$$

The heat (326.02 kcal/mol) of the reaction $SiH_4 + 2\ O_2 \rightarrow$ silica$[1/p(SiO_2)_p] + 2\ H_2O$ estimated from the bond energy procedure is in excellent agreement with the experimental value of 325.2 ± 1.2 kcal/mol.[14] The estimated reaction heats for the transformation of other silanes (599.02 for Si_2H_6, 872.03 for Si_3H_8, and 1145.03 kcal/mol for Si_4H_{10}) in the gas phase to silica are a little larger than those (573.3, 835.1 ± 0.7 and 1092.4 kcal/mol, respectively[14]) observed for liquid Si_2H_6, Si_3H_8 and Si_4H_{10}; this discrepancy is due to the latent heat of vaporization. With respect to the products silica and water, all of the 16 silanes have energy densities equal to or higher than that (3396 cal/g) of SiH_4 (Table 1), which is higher than that of the H_2/O_2 system. When the increment caused by strain is taken into account, the energy densities of Si_3H_6, Si_4H_4, and $Si_6H_6/O_2/H_2O$ with respect to silica and water are expected to be as high as 3600, 3830, and 3676 cal/g, respectively.

The bond energy procedure shows that the energy densities of the $Si_nH_m/O_2/H_2O$ systems depend on the Si/H ratio (n/m). The energy density with respect to silicic acid increases as the Si/H ratio decreases: 2292 ($n/m \rightarrow \infty$) < ED ≤ 3396 ($n/m = 1/4$), while that with respect to silica and water increases with the Si/H ratio: 3396 ($n/m = 1/4$) ≤ ED ≤ 3667 ($n/m \rightarrow \infty$). The upper limit (3396 cal/g) of the energy density with respect to silicic acid is identical to the lower limit with respect to silica and water. This clearly shows that the polymerization is preferable to the hydration because stable water is needed to complete the hydration. A high Si/H ratio is unfavorable for the energy density with respect to silicic acid, yet it is desirable for the energy density with respect to silica and water. The largest energy density (3667 cal/g) is expected for the combustion of the silane Si_nH_m ($n/m \rightarrow \infty$) followed by the polymerization to silica. The limit "$n/m \rightarrow \infty$" means pure silicon. The bond energy procedure also shows that the silanes with the same Si/H ratio (n/m) have the same energy densities. The cage silanes $(Si_{2n}H_{2n})/O_2/H_2O$ ($n/m = 1$) have higher energy densities than the cyclic silanes $(Si_nH_{2n})/O_2/H_2O$ ($n/m = 0.5$) with respect to silica and water, while the opposite is the case with the energy with respect to silicic acid.

The final products of the silane/oxygen/(water) systems, i.e., monosilicic acid $Si(OH)_4$, silica and water, all exist in nature and do no harm to the environment or humans. Monosilicic acid $Si(OH)_4$ is known to be "the dominant form of silicon in natural waters."[15] Silica is abundant[16] and "green"! Monosilane (**1a**) and disilane (**1b**) are now readily available commercially. The acyclic (**1c**,[17] **1d**[17] and **1e**[18]) and cyclic (**2c**[19] and **2d**[20]) silanes have already been synthesized in laboratory. The substituted species of cyclic (**2a**[21] and **2b**[22]), ladder (**3a**[23] and **3b**[24]), and cage (**4a**,[25] **4b**[26] and **4c**[27]) silanes have also been synthesized. Surely, here we only present a limited number of silanes (**1**–**4**) as examples. Given the molecular formula Si_mH_n, silanes could have various structural forms ranging from chainlike, cyclic, ladder, and even cage-type species. The green HEDMs with higher Si/H ratios have larger power. From a synthetic viewpoint, silyl (Si_pH_{2p+1}) derivatives of cyclic and cage silanes are also expected to be promising as green HEDMs.[28] Thus, silanes satisfy the green HEDM conditions (ii) considerable kinetic stability and (iv) high possibility of synthesis.

We are aware that the simplest SiH_4/O_2 system has already been utilized in a microengine for explosive combustion.[6] From the preceding discussions, we know that with respect to the green products $SiO_2 + H_2O$, the power of Si_nH_m/O_2 is between 3396 ($n/m = 1/4$) ≤ ED ≤ 3667 ($n/m \rightarrow \infty$). Surely, the power of SiH_4/O_2 is just the lower limit. So there is great hope to design various types of silane systems more powerful than the SiH_4/O_2 system. We optimistically hope that many kinds of interesting and powerful silanes could be synthesized in future as green HEDMs because only the Si/H ratio and strain determines the power. The systems are not only powerful but also "green". We also know that alkenyl silanes such as tetraallylsilane[29] and triallylsilane[30] and alkynyl silanes have been used as igniters. But such systems are surely much less powerful than our designed Si_nH_m systems because they have much lower Si/H ratios.

Conclusion

In summary, silanes/oxygen/(water) systems are green HEDMs. The energy densities of these systems are higher than or comparable to the conventional H_2/O_2 and N_2H_4/O_2 systems. The Si/H ratio together with ring strain is important for the HEDM power of silanes.

Computational Section

For the small and medium-sized silanes/oxygen/(water) systems producing silicic acid, ab initio calculations are performed to obtain the heat of reaction using the composite CBS-QB3 method that is incorporated in the Gaussian program package.[32] This method follows the complete basis set, CBS-Q, model chemistry

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using B3LYP hybrid density functional geometries and frequencies, and has been demonstrated to have high accuracy on a variety of thermochemical properties.[33]

We apply the bond energy procedure for the larger reaction systems producing silicic acid and all the reaction systems producing silica. The bond energies are calculated by the CBS-QB3 method, which is known to give the atomic energies through inclusion of the atomic spin-orbit interactions (readily available from experiment) consistent with the experimental heats of formation of the atoms, although no relativistic corrections are made.[33]

The less computationally expensive B3LYP method underestimates the energy density of the silanes/oxygen/(water) systems. In fact, the energy densities of the SiH_4, Si_2H_6, Si_3H_8, and $Si_7H_{16}/O_2/(H_2O)$ reaction systems with respect to $Si(OH)_4$ are 2782, 2591, 2524, and 2446 cal/g,[31] which are significantly lower than the CBS-QB3 values (3396, 3120, 3020, and 2904 cal/g, respectively).

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[8] All the intermediates and transition states involved in the addition reaction of two H_2O molecules to SiO_2 lie energetically lower than $SiO_2 + 2H_2O$.
[9] The following reactions: $H_2O \rightarrow 2H + {}^3O$, ${}^3O_2 \rightarrow 2\,{}^3O$, $SiH_4 \rightarrow {}^3Si + 4H$, $Si(OH)_4 \rightarrow {}^3Si + 4\,{}^3O + 4H$, $SiO_2 \rightarrow {}^3Si + 2\,{}^3O$ and $Si_2H_6 \rightarrow 2\,{}^3Si + 6H$ are used to calculate the bond energies of the O–H, O=O, Si–H, Si–O, Si=O, and Si–Si bonds that are involved in the reaction systems. Take the reaction $H_2O \rightarrow 2H + {}^3O$ as an example. The CBS-QB3 total energies of H_2O, H, and ${}^3O$ are –76.337462, –0.499818, and –74.987638 a. u., respectively. The energy required to break all the bonds of H_2O is $\Delta E = |2\times(-0.499818) + (-74.987638) - (-76.337462)|$ a. u. = 219.746 kcal/mol. Then the average O–H bond energy is BE(O–H) = 219.746/2 = 109.87 kcal/mol.
[10] In silanes, each Si atom is bonded to four Si or H atoms and each H atom to one Si atom. So there are $(4n - m)/2$ Si–Si and m Si–H bonds in one Si_nH_m.
[11] The calculation details of the reaction heats (ΔE) and energy densities (ED) of $Si_nH_m + (n + m/4)\,O_2 + (2n - m/2)H_2O \rightarrow n\,Si(OH)_4$ are as follows: $\Delta E = [4n\times BE(Si–O) + 4n\times BE(O–H)] - [(4n - m)/2\times BE(Si–Si) + m\times BE(Si–H) + (n + m/4)\times BE(O{=}O) + (2n - m/2)\times 2\times BE(O–H)] = [4\times BE(Si–O) - 2\times BE(Si–Si) - BE(O{=}O)]n + [½\times BE(Si–Si) - BE(Si–H) - ¼\times BE(O{=}O) + BE(O–H)]m = 219.99n + 26.507m$ kcal/mol. The molar mass of $n\,Si(OH)_4$ is $M = 96n$ g/mol. So $ED = 1000\times\Delta E/M = 2291.563 + 276.115/(n/m)$.
[12] Suppose the polymerization: $SiO_2 \rightarrow 1/p(SiO_2)_p$. In silica $[1/p(SiO_2)_p]$, each Si atom in the center of a tetrahedron is bonded to four O atoms. Each O-atom is bonded to two Si atoms. There are 2×2 Si–O bonds around the two O atoms. The total Si–O number is 8 $(4 + 2\times 2)$. Because each bond is shared by two atoms, the exact number of the Si–O bonds in $1/p(SiO_2)_p$ is 8/2 = 4. As a result, in the polymerization process, two Si=O bonds in each SiO_2 molecule are transformed into four Si–O bonds in silica.
[13] For the $Si_nH_m + (n + m/4)\,O_2 \rightarrow n/p(SiO_2)_p + m/2H_2O$ process, the reaction heats are $\Delta E = 219.99\,n + 26.507m$ kcal/mol, the same as those for the $Si_nH_m + (n + m/4)O_2 + (2n - m/2)H_2O \rightarrow n\,Si(OH)_4$ process. The molar mass of $n/p(SiO_2)_p + m/2H_2O$ is $M = 60n + 9m$ g/mol. So $ED = 1000\times\Delta E/M = 3666.500 - 108.192/(n/m + 0.15)$ cal/g.
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