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Ab Initio Energetic Calculations of Elementary Reactions Relevant to Low-Temperature Silane Oxidation by Gaussian-2 Theory

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Ab initio G-2 calculations have been carried out for a number of elementary reactions relevant to low-temperature silane oxidation. The calculations have been made to identify the chain-branching process which enables the spontaneous ignition of silane at room temperature. Extensive calculations have also been made for the reactions of major intermediates with hydrogen atoms and water vapor.

Introduction

Silane is a feedstock gas for the semiconductor industry and advanced materials. Elucidation of the mechanism of silane oxidation is important to the understanding of the CVD process as well as from a safety point of view. In particular, understanding the phenomenon of spontaneous ignition is indispensable for treating this kind of material safely in laboratories and factories.[1−4] The combustion phenomenon of silane has been the subject of quite a number of investigations from both experimental and theoretical points of view.[5−21]

Since the ignition of this gas occurs in the air spontaneously at room temperature or even lower, elementary reactions active at low temperatures are of particular importance. According to Hartman et al.,[8] combustion of silane is initiated by production of SiH_3 radicals, followed by reaction of SiH_3 with $O_2(^3\Sigma_g^-)$ to give a vibrationally excited species of SiH_3O_2*,

$$SiH_3 + O_2(^3\Sigma_g^-) = SiH_3O_2^* \qquad (R1)$$

They have proposed that the subsequent reactions of SiH_3O_2* proceed through three different path ways.

$$SiH_3O_2^* = SiH_3O + O \qquad (R2)$$

$$SiH_3O_2^* = SiH_2O + OH \qquad (R3)$$

$$SiH_3O_2^* = OSiHOH + H \qquad (R4)$$

These reactions compete with a quenching reaction of SiH_3O_2*,

$$SiH_3O_2^* + M = SiH_3O_2 + M \qquad (R5)$$

If the former are faster than the latter, ignition occurs; otherwise it does not. Britten, Tong, and Westbrook[12] have presented a numerical model based on this mechanism in order to interpret the data of shock-tube ignition delay times[5] as well as the second explosion limit of mixtures containing silane and oxygen.[8]

On the other hand, we have shown in a previous paper[19,20] that the chemical stability of silane−oxygen−nitrogen mixtures depends on the concentration ratio of silane to oxygen. Namely, the mixture is unstable if the silane concentration relative to oxygen is higher than a certain threshold value, and it is stable otherwise. From this, it has been concluded that competition between the two reactions,

$$H + SiH_4 = H_2 + SiH_3 \qquad (R6)$$

and

$$H + O_2 + M = HO_2 + M \qquad (R7)$$

determines whether ignition occurs or not. If it is the case, the competition between reactions R2−R4 and reaction R5 must always favor ignition; namely, the decomposition reactions, (R2) + (R3) + (R4), must be faster than the quenching reaction (R5).

On the other hand, such radicals as $O(^3P)$, OH, H, and SiH_3 constitute the chain carriers in this reaction mechanism. The chain-branching reactions at room temperature are dominated by the one that produces $O(^3P)$ atoms, i.e., reaction R2, because $O(^3P)$ atoms can readily react with SiH_4 to produce two chain carriers of OH and SiH_3. The other carriers (H, OH, and SiH_3) can keep the chains active but do not increase the carrier number. Therefore, the competition discussed by Britten et al.[12] should actually be between reactions R2 and R5. In this way, the BTW model has successfully been modified to make simulation calculation of the spontaneous ignition itself and its concentration limit.[21]

At this stage, however, a large shortcoming of the model has been made clear, which is concerned with the adequacy of the chain-branching process itself. According to the energetic calculation made by Darling and Schlegel,[17,18] the reaction pathway to yield oxygen atoms through (R1) and (R2) must have an activation energy of at least 10.9 kcal/mol. If it is the case, the reaction rate cannot be fast enough to cause the spontaneous ignition at room temperature. Then, a new chain-branching process has to be identified in order to explain the spontaneous ignition phenomenon at room temperature.

Until now, ab initio MO calculations have been made for quite a number of Si−O−H molecules and relevant transition states.[17,18,22−24] However, there still seem to remain elementary reactions unidentified that may play an indispensable part in the low-temperature silane combustion. The objective of the present paper is to carry out accurate ab initio MO calculations of such reactions. Among these reactions, we may also have a

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chance to find out the true chain-branching process responsible for the spontaneous ignition.

Results and Discussion

The ab initio MO calculations have been carried out by using the GAUSSIAN 94 program[25] on a Cray computer at the Gaussian-2 level of theory.[26]

The geometry optimization has at first been made with the HF/6-31G(d) method. Then, optimization was remade with the MP2=FULL/6-31G(d) method. The optimized geometries obtained for various transition states with the MP2=FULL/6-31G(d) method are listed in Table 1, where the geometrical parameters are taken as illustrated in Figure 1. Unless otherwise stated, the systems with even electrons are in the singlet states, and ones with odd electrons are in the doublet states.

Table 2 shows the vibrational frequencies calculated with the HF/6-31G(d) method which is to be multiplied by a factor of 0.893 for the thermal correction calculation. For some of these systems, since the geometrical parameters obtained with the HF/6-31G(d) method are so different from the ones with the MP2=FULL/6-31G(d) method, the frequencies are also calculated with the MP2=FULL/6-31G(d) method. In this case, the results should be multiplied by a factor of 0.927.

The energetic calculations at the G-2 level of theory were made, and the results are summarized in Table 3. Table 4 shows the energies of the transition states relative to the reactants and products, respectively, of the reactions. The G-2 energies of molecular species other than HOSiOOH and $OSi(OH)_2$ are obtained from the literature.[17] The thermal corrections to energies have been made based either on the HF/6-31G(d) frequencies multiplied by a factor of 0.893 or on the MP2=FULL/6-31G(d) frequencies multiplied by a factor of 0.927.

(i) Main Reaction Route for Low-Temperature Combustion. As stated above, reaction R2 cannot be active at room temperature. Therefore, we may have to seek another $O(^3P)$ atom producing reaction. Considering the energetics of the various molecules relevant to the $SiH_3 + O_2$ system, $SiH_2OH + O(^3P)$ is the only one conceivable as the products. The energy sum of this system is 15.63 kcal/mol lower than $SiH_3 + O_2$. Unfortunately, however, we could not find out any reaction pathway directly connecting the two systems.

If it is not a reaction that produces oxygen atoms, the chain-branching process must be such that it produces more than one active carrier from a single carrier within a series of reactions. Since the spontaneous ignition limit is determined by a competition between reactions R6 and R7,[20] the chain-branching process must be contained in a series of reactions starting from reaction R1. The kinetic stoichiometry of the process may be one of the following equations:

$$SiH_3 + O_2 = OSiOH + 2H \quad (-18.80) \tag{R8}$$

$$SiH_3 + O_2 = OSiHO + 2H \quad (+16.34) \tag{R9}$$

$$SiH_3 + O_2 = SiH + 2OH \quad (+56.21) \tag{R10}$$

$$SiH_3 + O_2 = HSiO + H + OH \quad (+19.61) \tag{R11}$$

$$SiH_3 + O_2 = SiOH + H + OH \quad (+11.23) \tag{R12}$$

where numbers in parentheses are the energy differences (in kcal/mol) between the reactants and products. Among these, reaction R8 is the only one that has a negative energy change. All the other reactions have positive energy changes that are larger than 10 kcal/mol. The reaction route from $SiH_3 + O_2$ to OSiOH + 2H, if any, may consist of a few consecutive reactions. The question is how high are the energy barriers located along the reaction pathway connecting them.

Among the reactions that produce hydrogen atoms, the self-decomposition reaction of H_2SiOOH to HSiOOH + H is noticed, where the former is produced by isomerization of the vibrationally excited species of SiH_3O_2. As shown in Table 4 (reaction 24), the energy sum for HSiOOH + H is only 2.89 kcal/mol higher than that of the original reactants, $SiH_3 + O_2$, and the activation energy is no more than the energy difference between the reactants and products. The activation energy of this order of magnitude can be easily overcome even at room temperature.

The subsequent reactions to this are as follows. One is the direct decomposition of HSiOOH to HSiO + OH (reaction 10 in Table 4). Although the activation energy of this process is no more than the energy difference (16.73 kcal/mol), it is still a little too large for the reaction to be active at room temperature. Another possibility is the isomerization reaction to OSiHOH. This reaction is very much exothermic (110.84 kcal/mol). Therefore, the resulting OSiHOH could further undergo self-decomposition to yield H + OSiOH. The energy sum of the latter is 21.69 kcal/mol lower than that of HSiOOH, and the barrier height of the dissociation process is just the energy difference between the reactant and products (89.15 kcal/mol). In this case, the whole reaction route becomes as $SiH_3 + O_2 \rightarrow SiH_3O_2^* \rightarrow H_2SiOOH \rightarrow HSiOOH + H \rightarrow OSiHOH + H \rightarrow OSiOH + 2H$. According to Table 4, however, the barrier height of the isomerization from HSiOOH to OSiHOH is 21.67 kcal/mol (reaction 11 in Table 4). Since the system does not have any excess energy at this stage, this is a little too large to be overcome at room temperature. Thus, this route cannot be the chain-branching process for the spontaneous ignition either.

On the other hand, Murakami et al.[24] have recently found that there is a reaction pathway from $SiH_3O_2^*$ to *c*-$OSiH_2O$ + H (see Figure 2). They have made the energetic calculation with Gaussian-2(MP2) theory.[28] The geometry they have obtained by optimization with MP2=FULL/6-31G(d) for the transition state is a little different from the one obtained in the present study, although we do not know the reason. The barrier height of 28.93 kcal/mol calculated for this reaction (reaction 23 in Tables 4) is not small. However, the energy of the transition state is still 22.70 kcal/mol lower than the original reactants of $SiH_3 + O_2$.

The activation energy of isomerization from *c*-$OSiH_2O$ to HSiOOH is 61.88 kcal/mol (reaction 16 in Table 4). *c*-$OSiH_2O$ reacts with hydrogen atoms with an activation energy of only 3.52 kcal/mol (reaction 17 in Table 4), and the reaction may be active at room temperature. The resulting molecule of $OSiH_2OH$ can undergo self-decomposition to yield H + OSiHOH with the activation energy no more than the dissociation energy (reaction 25 in Table 4).

On the other hand, *c*-$OSiH_2O$ can undergo isomerization to yield OSiHOH. The transition state of this reaction has been identified by the HF/6-31G(d) method, but has not been found by the MP2=FULL/6-31G(d) method. CIS/6-31G(d) calculations at the HF/6-31G(d) optimized geometry have revealed that the energy of the first excited state which belongs to the same symmetry is fairly close to that of the ground state (1.05 eV). On the other hand, Murakami et al.[24] have calculated the same transition state with the CASSCF(6,6)/6-31G(d) method to obtain the barrier height of 6.4 kcal/mol. In this reaction, the resulting OSiHOH may further undergo isomerization to yield HOSiOH (reaction 18 in Table 4) or may undergo self-decomposition to yield SiO + H_2O (reaction 19 in Table 4). The HOSiOH molecule can also undergo self-decomposition,

TABLE 1: MP2=FULL/6-31G(d) Optimized Geometries of Transition States

Reaction	Geometrical parameters[c] (in A and degree)
(1) $SiH_3 + H_2O = H_2SiOH + H_2$	$SiO=1.8766, SiH_1=1.7744, SiH_2=1.4818, SiH_3=1.5079, OH_4=1.2052, OH_5=0.9788, aOSiH_1=70.91, aOSiH_2=102.71, aOSiH_3=93.58, aSiOH_4=74.18, aSiOH_5=113.98, bH_2SiOH_1=94.9, bH_3SiOH_1=-155.7, bH_4OSiH_1=0.4, bH_5OSiH_1=109.4, H_1H_4=1.0972$ (reactants)
(2) $SiOH = SiO + H$	$SiO=1.5325, OH=1.4066, aSiOH=132.15$ (reactant)
(3) $SiH_2O = HSiOH$	$SiO=1.6242, SiH_1=1.5191, OH_2=1.4983, aOSiH_1=119.66, aSiOH_2=59.02, bH_2OSiH_1=180, SiH_2=1.5420$ (product)
(4) $SiH_2O = H_2 + SiO$	$SiO=1.5615, SiH_1=1.4899, H_1H_2=1.3449, aOSiH_1=155.24, aSiH_1H_2=76.39, bH_2H_1SiO=0, SiH_2=1.7565$ (products)
(5) $SiH_2O + H_2O = HOSiH_2OH$	$SiO_1=1.5879, SiO_2=1.8875, SiH_1=1.4793, SiH_2=1.4855, O_2H_3=1.1258, O_2H_4=0.9779, aO_1SiO_2=84.92, aO_1SiH_1=122.66, aO_1SiH_2=122.36, aSiO_2H_3=72.34, aSiO_2H_4=115.75, bH_1SiO_1O_2=-104.6, bH_2SiO_1O_2=102.8, bH_3O_2SiO_1=1.3, bH_4O_2SiO_1=105.5, O_1H_3=1.4949$ (reactants)
(6) $SiH_2O + H_2O = OSiHOH + H_2$	$SiO_1=1.5385, SiO_2=1.8197, SiH_1=1.4734, SiH_2=1.6709, O_2H_3=0.9806, O_2H_4=1.2650, aO_1SiO_2=118.10, aO_1SiH_1=128.35, aO_1SiH_2=116.99, aSiO_2H_3=111.00, aSiO_2H_4=67.24, bH_1SiO_1O_2=-139.1, bH_2SiO_1O_2=88.6, bH_3O_2SiO_1=7.3, bH_4O_2SiO_1=111.4, H_2H_4=1.0477$ (reactants)
(7) $HSiOH = H_2 + SiO$	$SiO=1.6199, OH_1=1.3282, SiH_2=1.7817, aSiOH_1=69.22, aOSiH_2=81.20, bH_2SiOH_1=0, H_1H_2=1.0184$ (reactant)
(8) $SiO_2 + H_2O = OSi(OH)_2$[a]	$SiO_1=1.5772, SiO_2=1.8498, SiO_3=1.5296, O_2H_1=1.1492, O_2H_2=0.9773, aO_1SiO_2=84.42, aO_2SiO_3=122.18, aSiO_2H_1=72.77, aSiO_2H_2=120.15, bO_3SiO_2O_1=182.4, bH_1O_2SiO_1=4.7, bH_2O_2SiO_1=116.6, O_1H_1=1.4398$ (reactants)
(9) $H + OSiOH = OSiO + H_2$	$SiO_1=1.5598, SiO_2=1.6471, O_2H_1=0.9885, O_2H_2=2.4010, aO_1SiO_2=126.87, aSiO_2H_1=120.21, aSiO_2H_2=137.30, bH_1O_2SiO_1=0, bH_2O_2SiO_1=0, H_1H_2=1.4849$ (reactants)
(10) $HSiOOH = HSiO + OH$	$SiO_1=1.5479, O_1O_2=2.0729, O_2H_1=0.9852, SiH_2=1.5046, aSiO_1O_2=119.82, aO_1O_2H_1=85.05, aO_1SiH_2=121.09, bH_1O_2O_1Si=180, bH_2SiO_1O_2=0$ (reactant)
(11) $HSiOOH = OSiHOH$	$SiO_1=1.6392, SiO_2=1.9417, SiH_1=1.5270, O_2H_2=0.9851, aO_1SiO_2=61.06, aO_1SiH_1=109.85, aSiO_2H_2=106.17, bH_1SiO_1O_2=80.7, bH_2O_2SiO_1=64.6, O_1O_2=1.8376$ (product)
(12) $HSiOOH + H = SiOOH + H_2$	$SiO_1=1.6942, O_1O_2=1.4711, O_2H_1=0.9778, SiH_2=1.5548, H_2H_3=1.6146, aSiO_1O_2=114.51, aO_1O_2H_1=97.87 aO_1SiH_2=96.75, aSiH_2H_3=73.32, bH_1O_2O_1Si=183.9, bH_2SiO_1O_2=-7.3, bH_3H_2SiO_1=89.2, SiH_3=1.8930$ (reactants)
(13) $HSiOOH + H_2O = HSiOH + H_2O_2$	$SiO_1=1.9484, O_1O_2=1.4857, O_2H_1=0.9780, SiH_2=1.5175, SiO_3=1.8905, O_3H_3=1.2644, O_3H_4=0.9760, aSiO_1O_2=112.37, aO_1O_2H_1=97.71, aO_1SiH_2=93.97, aO_1SiO_3=73.56, aSiO_3H_3=76.11, aSiO_3H_4=113.91, bH_1O_2O_1Si=-150.9, bH_2SiO_1O_2=-1.3, bO_3SiO_1O_2=-94.8, bH_3O_3SiO_1=-1.4, bH_4O_3SiO_1=102.3, O_1H_3=1.2187$ (reactants)
(14) $HSiOOH + H_2O = HOSiOH + H_2O$	$SiO_1=1.7437, O_1O_2=1.6388, O_2H_1=0.9889, SiH_2=1.5534, SiO_3=1.7917, O_3H_3=1.5815, O_3H_4=0.9725, aSiO_1O_2=103.92, aO_1O_2H_1=69.41, aO_1SiH_2=69.41, aO_1SiO_3=86.13, aSiO_3H_3=87.88, aSiO_3H_4=111.52, bH_1O_2O_1Si=62.2, bH_2SiO_1O_2=165.6, bO_3SiO_1O_2=52.4, bH_3O_3SiO_1=-35.7, bH_4O_3SiO_1=203.9, O_2H_3=1.0555, O_1H_2=1.8838$ (reactants)
(15) $HSiOOH + H_2O = HOSiOOH$[b] $+ H_2$	$SiO_1=1.7418, O_1O_2=1.4902, O_2H_1=0.9783, SiH_2=1.7221, SiO_3=1.9102, O_3H_3=1.2902, O_3H_4=0.9796, aSiO_1O_2=97.66, aO_1O_2H_1=99.06, aO_1SiH_2=85.31, aO_1SiO_3=94.16, aSiO_3H_3=64.43, aSiO_3H_4=108.66, bH_1O_2O_1Si=112.3, bH_2SiO_1O_2=176.0, bO_3SiO_1O_2=102.6, bH_3O_3SiO_1=81.7, bH_4O_3SiO_1=-16.2, H_2H_3=1.0045,$ (reactants)
(16) cyc-$OSiH_2O = HSiOOH$	$SiO_1=1.9157, SiO_2=1.7271, SiH_1=1.5007, SiH_2=1.6379, aO_1SiO_2=48.75, aO_1SiH_1=107.68, aO_1SiH_2=42.50, bH_1SiO_1O_2=98.5, bH_2SiO_1O_2=-123.8, O_1O_2=1.5131, O_1H_2=1.3136$ (reactant)
(17) cyc-$OSiH_2O + H = OSiH_2OH$	$SiO_1=1.6537, SiO_2=1.6752, SiH_1=1.4721, SiH_2=1.4723, O_2H_3=1.5146, aO_1SiO_2=55.65, aO_1SiH_1=119.39, aO_1SiH_2=119.71, aSiO_2H_3=118.82, bH_1SiO_1O_2=106.3, bH_2SiO_1O_2=-105.2, bH_3O_2SiO_1=193.8, O_1O_2=1.5538$ (reactants)
(18) $OSiHOH = HOSiOH$	$SiO_1=1.6021, SiO_2=1.6493, O_2H_1=0.9777, O_1H_2=1.5491, aO_1SiO_2=123.51, aSiO_2H_1=116.04, aSiO_1H_2=58.61, bH_1O_2SiO_1=1.6, bH_2O_1SiO_2=147.7, SiH_2=1.5439$ (product)
(19) $OSiHOH = SiO + H_2O$	$SiO_1=1.5435, SiO_2=1.8258, O_2H_1=0.9900, O_2H_2=1.3603, aO_1SiO_2=120.22, aSiO_2H_1=119.94, aSiO_2H_2=60.31, bH_1O_2SiO_1=35.9, bH_2O_2SiO_1=147.3, SiH_2=1.6503$ (products)
(20) $HOSiOH = SiO + H_2O$	$SiO_1=1.9395, SiO_2=1.6015, O_2H_1=1.3441, O_1H_2=0.9769, aO_1SiO_2=79.97, aSiO_2H_1=80.08, aSiO_1H_2=120.13, bH_1O_2SiO_1=-2.3, bH_2O_1SiO_2=110.9, O_1H_1=1.1884$ (reactant)
(21) $HOSiOH = H + OSiOH$	$SiO_1=1.6500, SiO_2=1.5327, O_2H_1=2.3906, O_1H_2=0.9732, aO_1SiO_2=130.37, aSiO_2H_1=150.92, aSiO_1H_2=117.30 bH_1O_2SiO_1=0, bH_2O_1SiO_2=180$ (reactant)
(22) $HOSiOH + H = OSiOH + H_2$	$SiO_1=1.6622, SiO_2=1.5971, O_2H_1=1.2929, O_1H_2=0.9718, O_2H_3=2.1577, aO_1SiO_2=110.59, aSiO_2H_1=125.64, aSiO_1H_2=115.06, aSiO_2H_3=125.23, bH_1O_2SiO_1=0, bH_2O_1SiO_2=180, bH_3O_2SiO_1=0, H_1H_3=0.8649$ (reactants)
(23) $H_3SiOO =$ cyc-$OSiH_2O + H$	$SiO_1=1.7424, SiO_2=1.7339, SiH_1=1.4699, SiH_2=1.4743, SiH_3=1.6243, aO_1SiO_2=48.78, aO_1SiH_1=117.03, aO_1SiH_2=126.64, aO_1SiH_3=69.29, bH_1SiO_1O_2=-101.1, bH_2SiO_1O_2=79.2, bH_3SiO_1O_2=158.0, O_1O_2=1.4355$ (reactant)
(24) $H_2SiOOH = H + HSiOOH$	$SiO_1=1.6831, O_1O_2=1.4817, O_2H_1=0.9783, SiH_2=1.5194, SiH_3=2.6424, aSiO_1O_2=115.25, aO_1O_2H_1=97.50, aO_1SiH_2=97.33, aO_1SiH_3=104.44, bH_1O_2O_1Si=181.1, bH_2SiO_1O_2=-0.1, bH_3SiO_1O_2=-92.2$ (reactant)
(25) $OSiH_2OH = H + OSiHOH$	$SiO_1=1.5315, SiO_2=1.6374, SiH_1=1.4702, SiH_2=1.8580, O_2H_3=0.9734, aO_1SiO_2=127.54, aO_1SiH_1=127.83, aO_1SiH_2=66.58, aSiO_2H_3=115.64, bH_1SiO_1O_2=170.0, bH_2SiO_1O_2=-100.8, bH_3O_2SiO_1=-5.3$ (reactant)
(26) $HOSiHOH = H + HOSiOH$	$SiO_1=1.6607, SiO_2=1.6799, O_2H_1=0.9717, O_1H_2=0.9758, SiH_3=2.5141, aO_1SiO_2=98.51, aSiO_2H_1=114.64, aSiO_1H_2=114.66, aO_1SiH_3=101.31, bH_1O_2SiO_1=179.5, bH_2O_1SiO_2=0.2, bH_3SiO_1O_2=-106.6$ (reactant)
(27) $HOSiHOH + H = HOSiOH + H_2$	$SiO_1=1.6682, SiO_2=1.6802, O_2H_1=0.9708, O_1H_2=0.9718, SiH_3=1.4935, SiH_4=3.7513, aO_1SiO_2=107.94, aSiO_2H_1=114.71, aSiO_1H_2=114.67, aO_1SiH_3=103.21, aO_1SiH_4=91.35, bH_1O_2SiO_1=152.6, bH_2O_1SiO_2=-49.4, bH_3SiO_1O_2=-118.4, bH_4SiO_1O_2=-102.1, H_3H_4=2.4032$ (reactant)
(28) $HOSiH_2OH = H_2 + HOSiOH$	$SiO_1=1.6684, SiO_2=1.6804, O_2H_1=0.9701, O_1H_2=0.9716, SiH_3=1.5024, H_3H_4=1.1695, aO_1SiO_2=112.40, aSiO_2H_1=111.16, aSiO_1H_2=114.90, aO_1SiH_3=115.79, aSiH_3H_4=80.31, bH_1O_2SiO_1=117.5, bH_2O_1SiO_2=41.7, bH_3SiO_1O_2=-134.8, bH_4H_3SiO_1=70.0, SiH_4=1.7416$ (products)
(29) $HOSiOOH$[b] $= OSiOH + OH$	$SiO_1=1.6170, O_1O_2=1.8801, O_2H_1=0.9865, SiO_3=1.6561, O_3H_2=0.9761, aSiO_1O_2=69.94, aO_1O_2H_1=85.66, aO_1SiO_3=116.40, aSiO_3H_2=116.53, bH_1O_2O_1Si=121.9, bO_3SiO_1O_2=84.0, bH_2O_3SiO_1=-22.5$ (reactant)

a) MP2=FULL/6-31G(d) optimized geometry of $OSi(OH)_2$ is, $SiO_1=1.6322, SiO_2=1.6436, SiO_3=1.5295, O_2H_1=0.9722, O_1H_2=0.9720, aO_1SiO_2=104.99, aO_3SiO_1=127.49, aSiO_2H_1=114.41, aSiO_1H_2=114.96, bO_3SiO_1O_2=180, bH_1O_2SiO_1=180, bH_2O_1SiO_2=0$

b) MP2=FULL/6-31G(d) optimized geometry of HOSiOOH is, $SiO_1=1.7170, O_1O_2=1.4842, O_2H_1=0.9768, SiO_3=1.6545, O_3H_2=0.9788, aSiO_1O_2=113.59, aO_1O_2H_1=97.58, aO_1SiO_3=102.53, aSiO_3H_2=113.13, bH_1O_2O_1Si=141.1, bO_3SiO_1O_2=-2.9, bH_2O_3SiO_1=-0.6$

c) "(reactant)" means that the parameters are referred to the framework of the molecules in the reactant side of the reaction, and "(product)" means that the parameters are referred to the product side of the reaction. See Fig. 1.

yielding $SiO + H_2O$ (reaction 20 in Table 4). They have suggested that these reactions constitute the main route to yield SiO, which they observed in their experiments.[24]

On the other hand, it is remarkable that if these reactions are combined with the last stage of the above investigated reaction route, one may be able to complete a new reaction route from

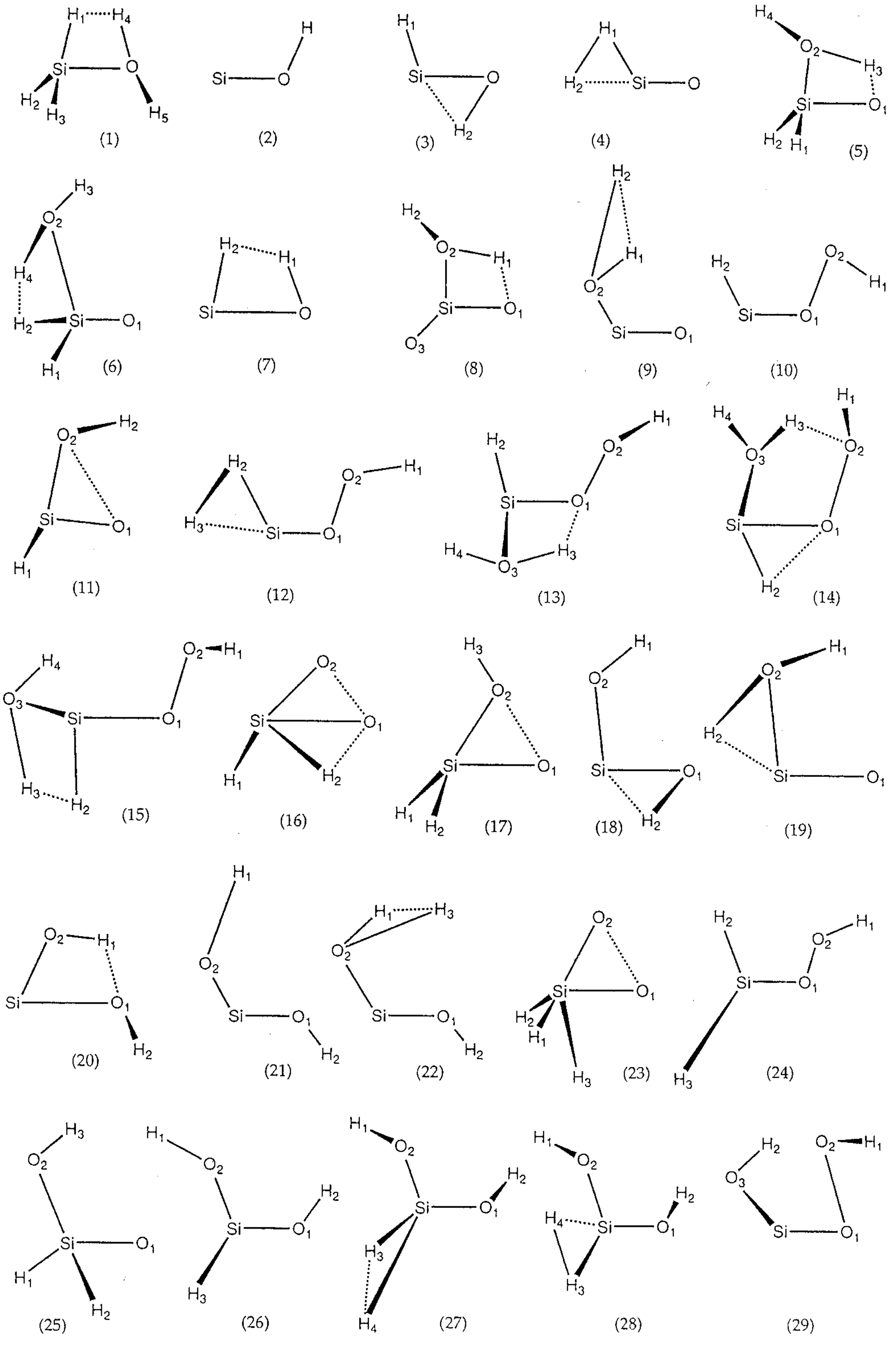

Figure 1. Geometrical configurations of the transition states of various elementary reactions relevant to low-temperature silane oxidation optimized at the level of MP2=FULL/6-31G(d).

SiH_3 + O_2 to OSiOH + 2H, i.e., $SiH_3 + O_2 \rightarrow SiH_3O_2^* \rightarrow$ *c*-$OSiH_2O$ + H → OSiHOH + H → OSiOH + 2H. The whole route is shown in Figure 2. At the last stage of this process, OSiHOH may also undergo isomerization to HOSiOH and further to H + OSiOH as well (reaction 21 in Table 4). In this reaction route, once produced, *c*-$OSiH_2O$ undergoes consecutive unimolecular processes to finally yield H + OSiOH. The energy sum of OSiOH + 2H is 6.69 kcal/mol higher than that of *c*-OSiH2O + H, but is still 18.80 kcal/mol lower than that of the original reactants, SiH_3 + O_2. Therefore, the whole process from SiH_3 + O_2 to OSiOH + 2H may proceed at a significant rate even at room temperature. In this case, we obtain two active radicals 2H starting from one SiH_3, which certainly makes a chain-branching process.

(ii) Reactions with Water Vapor. According to Hartman et al., there are several sets of explosion limits data for silane−oxygen system, which are quite divergent.[8] They have suggested that the divergence is due to the effect of water vapor; some of the data are suffering from the effect of water vapor and others are not. In this connection, reactions of water vapor with the major intermediates in silane oxidation are of much interest.

If the SiH_3 radical can easily react with water vapor, the effect of the reaction on the ignition behavior could be significant.

TABLE 2: HF/6-31G(d) Calculated Vibrational Frequencies of Transition States

Reaction	Frequencies (in cm-1)
(1) $SiH_3 + H_2O = H_2SiOH + H_2$	i2052, 417, 542, 637, 687, 721, 937, 978, 1056, 1442, 1644, 1921, 2225, 2398, 4049
(2) $SiOH = SiO + H$	i2477, 622, 1025
(3) $SiH_2O = HSiOH$	i2093, 308, 867, 1178, 2134, 2265
(4) $SiH_2O = H_2 + SiO$	i2396, 634, 699, 1272, 1433, 2380
(5) $SiH_2O + H_2O = HOSiH_2OH$	i1530, 516, 555, 593, 753, 775, 904, 987, 1109, 1212, 1487, 2231, 2408, 2444, 4076
(6) $SiH_2O + H_2O = OSiHOH + H_2$	i2069, 306, 521, 687, 741, 867, 879, 1017, 1165, 1349, 1528, 1872, 2047, 2485, 4034
(7) $HSiOH = H_2 + SiO$	i2545, 768, 1192, 1280, 1716, 2018
(8) $SiO_2 + H_2O = OSi(OH)_2$ a)	i1755, 325, 353, 501, 572, 834, 860, 1079, 1355, 1510, 2277, 4073
(9) $H + OSiOH = OSiO + H_2$	i700, 159, 244, 379, 462, 719, 926, 1207, 3204 (mp2=full)
(10) $HSiOOH = HSiO + OH$	i532, 13, 158, 426, 538, 685, 1063, 2191, 3622 (mp2=full)
(11) $HSiOOH = OSiHOH$	i1247, 487, 572, 674, 848, 885, 1092, 2192, 4113
(12) $HSiOOH + H = SiOOH + H_2$	i805, 145, 247, 332, 530, 712, 782, 860, 1168, 1575, 1887, 4096
(13) $HSiOOH + H_2O = HSiOH + H_2O_2$	i1657, 140, 242, 282, 497, 549, 627, 699, 756, 850, 1003, 1160, 1552, 1580, 2071, 2204, 4092, 4095
(14) $HSiOOH + H_2O = HOSiOH + H_2O$	i944, 220, 318, 421, 540, 597, 657, 714, 757, 796, 951, 1022, 1316, 1647, 1988, 2428, 3566, 3796 (mp2=full)
(15) $HSiOOH + H_2O = HOSiOOH$ b) $+ H_2$	i2130, 61, 220, 254, 344, 488, 627, 750, 766, 908, 953, 1166, 1553, 1557, 1765, 1953, 4053, 4099
(16) cyc-$OSiH_2O = HSiOOH$	i2012, 509, 577, 828, 845, 1038, 1098, 2080, 2366
(17) cyc-$OSiH_2O + H = OSiH_2OH$	i1986, 106, 373, 509, 733, 785, 801, 838, 1022, 1099, 2385, 2404 (mp2=full)
(18) $OSiHOH = HOSiOH$	i1875, 213, 345, 412, 815, 949, 1250, 2159, 4062
(19) $OSiHOH = SiO + H_2O$	i2109, 288, 403, 529, 704, 993, 1363, 1935, 3922
(20) $HOSiOH = SiO + H_2O$	i1836, 466, 509, 761, 778, 1190, 1438, 2115, 4087
(21) $HOSiOH = H + OSiOH$	i815, 146, 240, 290, 328, 795, 847, 1221, 3791 (mp2=full)
(22) $HOSiOH + H = OSiOH + H_2$	i3053, 210, 294, 443, 496, 851, 858, 915, 930, 986, 1641, 4125
(23) $H_3SiOO =$ cyc-$OSiH_2O + H$	i1373, 144, 626, 720, 743, 777, 812, 1005, 1034, 1095, 2445, 2482
(24) $H_2SiOOH = H + HSiOOH$	i74, 41, 68, 176, 348, 375, 793, 930, 1169, 1580, 2219, 4093
(25) $OSiH_2OH = H + OSiHOH$	i795, 252, 298, 369, 497, 688, 886, 972, 997, 1317, 2507, 4107
(26) $HOSiHOH = H + HOSiOH$	i322, 80, 117, 347, 483, 540, 868, 881, 933, 983, 4081, 4129
(27) $HOSiHOH + H = HOSiOH + H_2$	i721, 130, 155, 191, 235, 375, 749, 809, 829, 890, 938, 963, 2199, 3808, 3819 (mp2=full)
(28) $HOSiH_2OH = H_2 + HOSiOH$	i1891, 260, 303, 437, 664, 684, 870, 951, 965, 1062, 1094, 1463, 2347, 4112, 4143
(29) $HOSiOOH$ b) $= OSiOH + OH$	i1129, 246, 311, 425, 458, 613, 803, 886, 958, 1023, 4087, 4105

a) Vibrational frequencies of $OSi(OH)_2$ are obtained as, 338, 368, 382, 465, 509, 886, 919, 956, 1071, 1433, 4115, 4124

b) Vibrational frequencies of HOSiOOH are obtained as, 40, 186, 266, 451, 589, 742, 938, 971, 1157, 1555, 4087, 4112

TABLE 3: Energies of Transition States

reaction	transition state (in au)			ZPE (kcal/mol)	thermal (kcal/mol)
	MP2=FULL/6-31G(d)	G-1	G-2		
(1) $SiH_3 + H_2O = H_2SiOH + H_2$	−366.822 701	−367.047 093	−367.050 014	25.08	2.55
(2) $SiOH = SiO + H$	−364.507 956	−364.702 469	−364.700 008	2.10	1.93
(3) $SiH_2O = HSiOH$	−365.097 531	−365.289 499	−365.288 833	8.62	2.14
(4) $SiH_2O = H_2 + SiO$	−365.047 888	−365.253 503	−365.253 051	8.19	2.00
(5) $SiH_2O + H_2O = HOSiH_2OH$	−441.423 469	−441.731 174	−441.733 271	25.59	2.49
(6) $SiH_2O + H_2O = OSiHOH + H_2$	−441.379 431	−441.692 657	−441.694 892	24.89	2.57
(7) $HSiOH = H_2 + SiO$	−365.113 941	−365.314 825	−365.313 986	8.90	1.89
(8) $SiO_2 + H_2O = OSi\ (OH)_2{}^a$	−515.319 985	−515.714 525	−515.714 423	17.54	2.76
(9) $H + OSiOH = OSiO + H_2$	−440.140 477	−440.463 913	−440.463 412	9.68	3.05
(10) $HSiOOH = HSiO + OH$	−440.087 867	−440.403 295	−440.402 380	11.52	3.20
(11) $HSiOOH = OSiHOH$	−440.086 776	−440.383 493	−440.382 299	13.87	2.32
(12) $HSiOOH + H = SiOOH + H_2$	−440.612 521	−440.921 834	−440.921 648	15.75	3.19
(13) $HSiOOH + H_2O = HSiOH + H_2O_2$	−516.326 388	−516.737 581	−516.738 949	28.59	3.57
(14) $HSiOOH + H_2O = HOSiOH + H_2O$	−516.305 541	−516.731 092	−516.732 177	28.80	3.24
(15) $HSiOOH + H_2O = HOSiOOH^b + H_2$	−516.305 770	−516.726 345	−516.727 535	27.46	3.80
(16) *c*-$OSiH_2O = HSiOOH$	−440.070 128	−440.365 475	−440.363 337	11.92	2.25
(17) *c*-$OSiH_2O + H = OSiH_2OH$	−440.632 451	−440.956 193	−440.955 754	14.65	2.77
(18) $OSiHOH = HOSiOH$	−440.214 824	−440.511 207	−440.510 871	13.02	2.73
(19) $OSiHOH = SiO + H_2O$	−440.192 595	−440.485 561	−440.484 946	12.94	2.59
(20) $HOSiOH = SiO + H_2O$	−440.250 717	−440.541 268	−440.540 455	14.48	2.30
(21) $HOSiOH = H + OSiOH$	−440.131 790	−440.463 716	−440.462 969	11.13	2.63
(22) $HOSiOH + H = OSiOH + H_2$	−440.761 410	−441.083 299	−441.083 284	15.00	3.05
(23) $H_3SiOO =$ *c*-$OSiH_2O + H$	−440.642 078	−440.957 113	−440.956 821	15.17	2.71
(24) $H_2SiOOH = H + HSiOOH$	−440.619 340	−440.918 690	−440.918 024	14.68	3.61
(25) $OSiH_2OH = H + OSiHOH$	−440.788 457	−441.100 796	−441.102 525	17.18	2.56
(26) $HOSiHOH = H + HOSiOH$	−440.805 658	−441.105 877	−441.106 163	17.16	3.50
(27) $HOSiHOH + H = HOSiOH + H_2$	−441.312 773	−441.678 715	−441.680 762	21.32	3.87
(28) $HOSiH_2OH = H_2 + HOSiOH$	−441.359 441	−441.688 830	−441.690 377	24.71	2.98
(29) $HOSiOOH^b = OSiOH + OH$	−515.199 901	−515.606 074	−515.604 796	17.76	3.10

[a] Energy of $OSi(OH)_2$ is obtained as −515.402 121 (MP2=FULL/6-31G(d)), −515.796 958(G-1), and −515.797 529(G-2). [b] Energy of HOSiOOH is obtained as −515.247 525 (MP2=FULL/6-31G(d)), −515.641 408 (G-1), and −515.639 779 (G-2).

Calculation shows, however, that the activation energy for the reaction is 33.72 kcal/mol (reaction 1 in Table 4), which is fairly large.

On the other hand, according to the energy diagram reported by Darling and Schlegel,[18] SiH_2O is one of the major products from the $SiH_3 + O_2$ reaction. In fact, the branching ratio for its production has been reported to be about 25%.[16] Nagase et al.[22] have calculated by the MP3/6-31G(d) method that SiH_2O reacts with H_2O with no potential barrier to yield $HOSiH_2OH$. Figure 3 shows the G-2 energy diagram for the reaction between SiH_2O and a water molecule. The energy of $HOSiH_2OH$ is 66.54 kcal/mol lower than that of $SiH_2O + H_2O$ (reaction 5 in Table 4). In addition to this, SiH_2O resulting from the $SiH_3 + O_2$ reaction (exothermicity is 63.88 kcal/mol) is expected to have

TABLE 4: Transition States, Energy Differences, and Activation Energies at 298 K (in kcal/mol)[a]

	transition state			activation energy		
reaction	from reactants	from products	energy difference	this work	ref 23[b]	ref 24[c]
(1) $SiH_3 + H_2O = H_2SiOH + H_2$	33.72	49.36	−15.64	33.72		
(2) $SiOH = SiO + H$	38.52	9.70	28.82	38.52	40.2	
(3) $SiH_2O = HSiOH(t)$[d]	57.20	57.32	−0.12	57.20	52.8	
(4) $SiH_2O = H_2 + SiO$	79.52	80.29	−0.77	79.52	79.4	
(5) $SiH_2O + H_2O = HOSiH_2OH$	−14.75	51.79	−66.54	0.00		
(6) $SiH_2O + H_2O = OSiHOH + H_2$	9.41	39.52	−30.11	9.41	3.0	
(7) $HSiOH(c)$[d] $= H_2 + SiO$	41.29	41.94	−0.65	41.29	37.2	
(8) $SiO_2 + H_2O = OSi(OH)_2$	−14.48	53.17	−67.65	0.00		
(9) $H + OSiOH = OSiO + H_2$	−6.81	39.64	−46.45	0.00		
(10) $HSiOOH = HSiO + OH$	9.95	−6.78	16.73	16.73		
(11) $HSiOOH = OSiHOH$	21.67	132.51	−110.84	21.67		
(12) $HSiOOH + H = SiOOH + H_2$	−3.04	26.77	−29.81	0.00		
(13) $HSiOOH + H_2O = HSiOH + H_2O_2$	5.70	3.81	1.89	5.70		
(14) $HSiOOH + H_2O = HOSiOH + H_2O$	9.62	127.34	−117.72	9.62		
(15) $HSiOOH + H_2O = HOSiOOH + H_2$	13.09	48.11	−35.02	13.09		
(16) $c\text{-}OSiH_2O = HSiOOH$	61.88	33.50	28.38	61.88		
(17) $c\text{-}OSiH_2O + H = OSiH_2OH$	3.52	106.76	−103.24	3.52		
(18) $OSiHOH = HOSiOH$	52.24	59.12	−6.88	52.24	51.2	51.6
(19) $OSiHOH = SiO + H_2O$	68.36	39.04	29.32	68.36	66.9	67.6
(20) $HOSiOH = SiO + H_2O$	40.12	3.92	36.20	40.12	37.2	39.7
(21) $HOSiOH = H + OSiOH$	89.08	−6.95	96.03	96.03		
(22) $HOSiOH + H = OSiOH + H_2$	13.11	21.77	−8.66	13.11		
(23) $H_3SiOO = c\text{-}OSiH_2O + H$	28.93	2.79	26.14	28.93		31.5
(24) $H_2SiOOH = H + HSiOOH$	50.45	−0.35	50.80	50.80		
(25) $OSiH_2OH = H + OSiHOH$	14.45	−6.34	20.79	20.79		
(26) $HOSiHOH = H + HOSiOH$	37.43	−0.80	38.23	38.23		
(27) $HOSiHOH + H = HOSiOH + H_2$	−9.90	56.56	−66.46	0.00		
(28) $HOSiH_2OH = H_2 + HOSiOH$	79.20	49.64	29.56	79.20		
(29) $HOSiOOH = OSiOH + OH$	21.52	−5.77	27.29	27.29		

[a] Gaussian-2 energies of moleculer species are either calculated in this study or from ref 17. The thermal corrections to the energies are based on the HF/6-31G(d) frequencies multiplied by a factor of 0.893, or on the MP2=FULL/6-31G(d) frequencies multiplied by 0.927. [b] Calculated with BAC-MP4 at MP4/6-311G(2df,p)//MP2/6-31G(d). [c] Calculated with the Gaussian-2(MP2) method. [d] (t) means trans-form and (c) means cis-form.

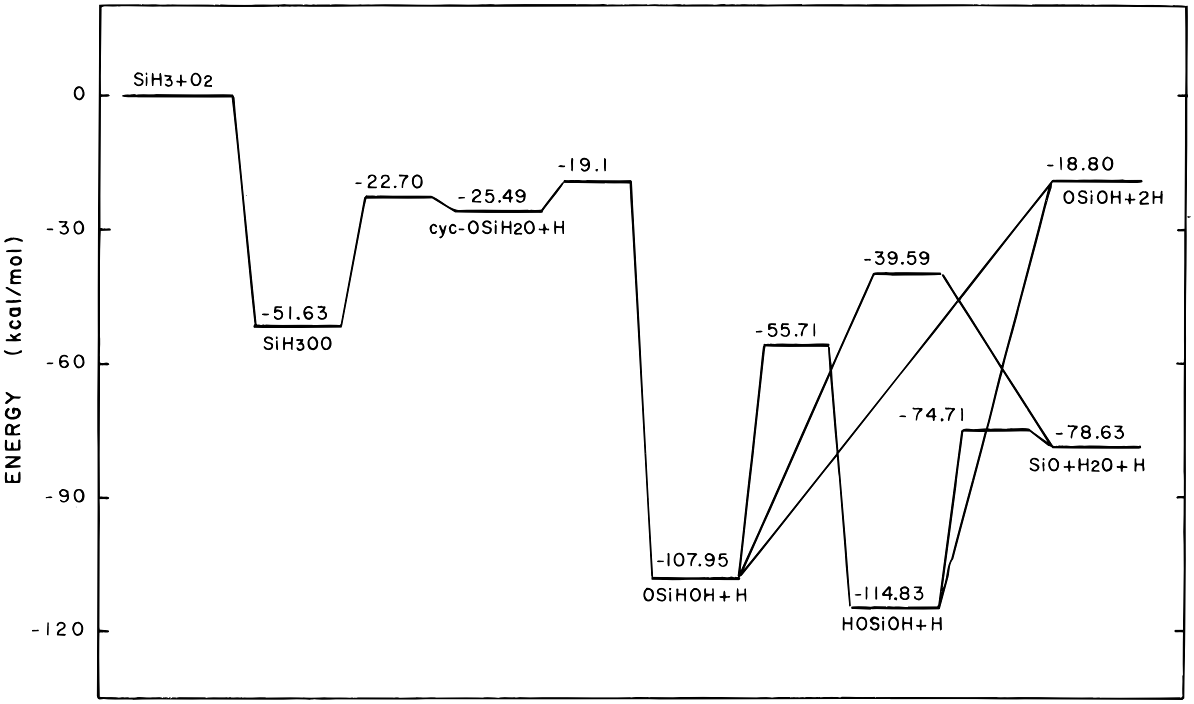

Figure 2. Energy diagram for the main route of $SiH_3 + O_2$ reaction calculated at the level of Gaussian-2 theory. The energy of the transition state between c-$OSiH_2O$ and OSiHOH is due to the CASSCF(6,6)/6-31G(d) method.[24]

a large amount of excess energy. Therefore, if it can react with H_2O before it loses the excess energy through collisions with other molecules (though this is difficult at the ordinary pressure), the resulting $HOSiH_2OH$ should have considerable excess energy, e.g. as much as 100 kcal/mol or more. In that case, the molecule may readily release a hydrogen atom to yield HOSiHOH + H, giving an additional active carrier. The barrier of this reaction has been found to be no more than the energy difference itself. $HOSiH_2OH$ can also release a hydrogen molecule to give H_2 + HOSiOH (reaction 28 in Table 4). In this case, the barrier height is 79.20 kcal/mol, and the energy difference between reactants and products is 29.56 kcal/mol. HOSiHOH can also release a hydrogen atom with barrier height no more than the energy difference (reaction

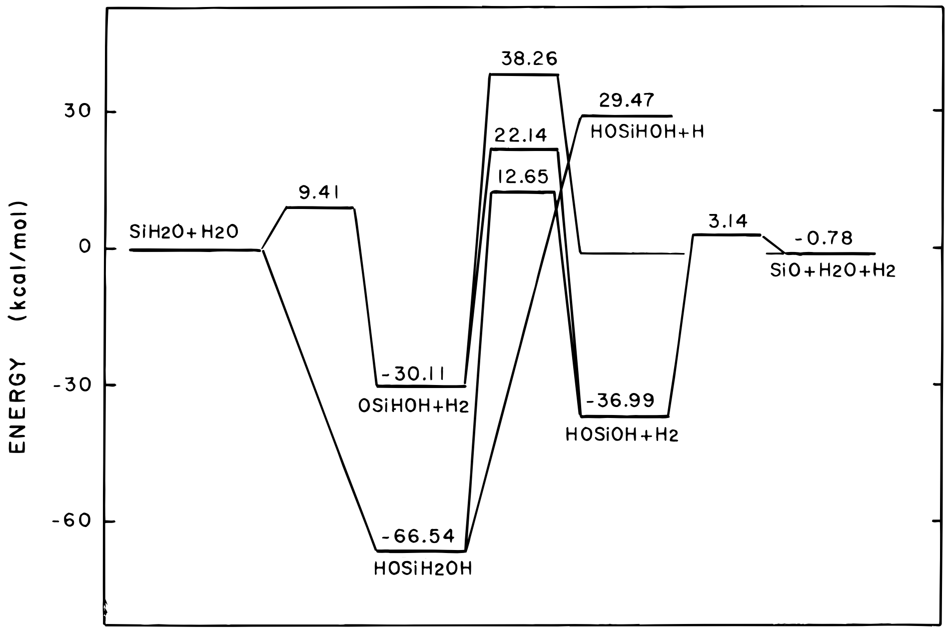

Figure 3. Energy diagram for the $SiH_2O + H_2O$ reaction calculated at the level of Gaussian-2 theory.

26 in Table 4). For the reaction of this molecule with a hydrogen atom to yield H_2 + HOSiOH, there is no energy barrier at all (reaction 27 in Table 4).

Figure 3 also shows that SiH_2O can react with H_2O in another way: $SiH_2O + H_2O = OSiHOH + H_2$. The activation energy is calculated to be 9.41 kcal/mol (reaction 6 in Table 4). In this case, there is no chance to yield an additional active carrier, but it will probably produce SiO + H_2O via HOSiOH.

Another interesting reaction of H_2O is the one with HSiOOH (reactions 13, 14, and 15 in Table 4). As seen in Figure 1, the oxygen atom in the water molecule tends to attack the Si atom in the other molecule. At the same time, a hydrogen atom in the water molecule attacks one of the neighboring atoms of the Si atom. In the reaction of HSiOOH + H_2O = HOSiOH + H_2O, a hydrogen atom in the water molecule attacks the oxygen atom next to the one adjacent to the silicon atom in HSiOOH. Since the energy difference between the reactant and product is very large (117.72 kcal/mol), the resulting HOSiOH may readily release a hydrogen atom to yield H + OSiOH. The total energy difference of the reaction, HSiOOH + H_2O = H + OSiOH + H_2O, is 21.69 kcal/mol. The barrier height of the former process is calculated to be 9.62 kcal/mol (reaction 14 in Table 4), while that of the latter is just the energy difference. Therefore, the effective barrier height for this process is also 9.62 kcal/mol.

As for reaction HSiOOH + H_2O = H_2 + HOSiOOH, the barrier height has been calculated to be 13.09 kcal/mol (reaction 15 in Table 4). HOSiOOH can undergo self-decomposition, yielding OSiOH + OH. The barrier height for this reaction is also just the energy difference between the reactant and products, which is calculated to be 27.29 kcal/mol (reaction 29 in Table 4). In this case, the total energy difference of the reaction, HSiOOH + H_2O = H_2 + OSiOH + OH, is calculated to be −7.73 kcal/mol, while the barrier height 13.09 kcal/mol.

For the reaction of HSiOOH + H_2O = HSiOH + H_2O_2, the energy difference is calculated to be 1.89 kcal/mol and the barrier height to be 5.70 kcal/mol (reaction 13 in Table 4).

One more interesting reaction of water vapor is the one with SiO: SiO + H_2O = HOSiOH. The reverse of this reaction (reaction 20 in Table 4) has already been mentioned in the last stage of the reaction route from $SiH_3 + O_2$ to H + SiO + H_2O. It should be noted that the barrier height of this reaction is calculated to be only 3.92 kcal/mol and the energy difference −36.20 kcal/mol. Therefore, this reaction can proceed at a significant rate even at room temperature. On the other hand, it is interesting that SiO_2(g) can react with water vapor to give $OSi(OH)_2$ with no barrier at all (reaction 8 in Table 4).

(iii) Other Reactions. As shown in Tables 3 and 4, the energetics of isomerization reactions of SiH_2O have been re-evaluated by using Gaussian-2 theory. The barrier for the isomerization to yield HSiOH is calculated to be 57.20 kcal/mol (reaction 3 in Table 4), while the one to yield H_2 + SiO is 79.52 kcal/mol (reaction 4 in Table 4). On the other hand, the barrier for self-decomposition of HSiOH to give H_2 + SiO is 41.29 kcal/mol (reaction 7 in Table 4).

As the main carrier in the low-temperature oxidation of silane, reactions of hydrogen atoms are very imporatnt, and many of them have already been mentioned above. In addition to these, the activation energies of a few other reactions of hydrogen atoms have been calculated. The activation energy of the H reaction with HSiOOH is zero, and the energy difference between the reactants and products is 29.81 kcal/mol (reaction 12 in Table 4). The activation energy of the reaction with HOSiOH is 13.11 kcal/mol (reaction 22 in Table 4), and that for the reaction with SiO is 9.70 kcal/mol (the reverse of reaction 2 in Table 4).

Conclusion

Ab initio MO calculations have been carried out for a number of elementary reactions relevant to low-temperature silane oxidation by using Gaussian-2 theory. Investigation of the chain-branching process for the spontaneous ignition of silane has revealed a possibility that a series of reactions starting from $SiH_3 + O_2$ to give OSiOH + 2H are responsible for the characteristic phenomenon. In this reaction scheme, the production of *c*-$OSiH_2O$ and its isomerization to yield OSiHOH, followed by self-decomposition to H + OSiOH, is of particular importance.

In silane combustion, there are a number of radical species that can easily react with water vapor which either exists in the air or is produced in the combustion reaction. Energetic calculations have been made for reactions with such molecules as H_2SiO, HSiOOH, and SiO. Also, it should be realized that the hydrogen atom is a predominant chain carrier in the low-temperature silane combustion. Energetics of the hydrogen reactions of major radical species in silane combustion have been calculated.

The data obtained in the present study will be useful for complete understanding of the details of low-temperature silane combustion phenomenon.

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