Twenty-Seventh Symposium (International) on Combustion/The Combustion Institute, 1998/pp. 2431–2439

NUMERICAL STUDY OF LOW- AND HIGH-TEMPERATURE SILANE COMBUSTION

V. I. BABUSHOK, W. TSANG, D. R. BURGESS JR. AND M. R. ZACHARIAH
National Institute of Standards and Technology
Gaithersburg, MD 20899, USA

Self-ignition and flame propagation properties of silane combustion systems have been studied through computer simulations using a database of kinetic and thermodynamic information that is consistent with current understanding of the elementary processes. These new inputs include the mechanism for chain branching through the SiH_3 radical, rate constants for the reactions of HO_2 with silane and its breakdown products, and the reaction of SiO with oxygen. Over the entire temperature range, the simulations show two distinct mechanisms. At low temperatures, the kinetics of SiH_3 is controlling, whereas at high temperatures, SiH_2 chemistry is of key importance. The results demonstrate that the upper explosion limit and ignition at room temperature and 1 bar can be described by the same set of reactions. With the new database, many of the experimental observations can be reproduced, and predictions are made regarding dependencies on process parameters. These include the critical conditions for chain ignition, the dependence of the critical pressure on the ratio of silane and oxygen concentration, and the temperature dependence of the critical ratio of silane to oxygen concentration. A scenario for low-temperature ignition is presented. At high temperatures, the importance of condensation processes for accurate prediction of flame velocities is clear. For very lean flames, the maximum reaction rate occurs at the lower temperature region of the flame zone.

Introduction

Silane is widely used in the semiconductor industry. The pyrophoric nature of SiH_4-air mixtures raises safety problems and, from a combustion point of view, interesting technical issues. In this paper, we report on the results of computer simulations that bear on important combustion processes including self-ignition and reactions proceeding at low temperatures and flame propagation in premixed mixtures. Although there are still considerable uncertainties in the elementary steps in silane oxidation, the increased understanding of the fundamental chemistry of silane oxidation does permit more reasonable estimates. Particular attention was paid to the effect of mixture composition, pressure, and temperature on the combustion characteristics of silane.

Background

Silane combustion and oxidation have been studied since the 1930s [1,2]. The combustion phenomena covered included self-ignition [3–5], laminar premixed flame propagation [6], counter diffusion flame [7], and ignition delay behind shock waves [8]. Experimental data on explosion limits demonstrate considerable scatter [4]. There is essentially no information on the temporal characteristics of the process. Ignition delays behind shock waves for the temperature range 850–1050 K [8] are not compatible with very short ignition delays at low temperatures. Kalkanov and Shavard [9] give an estimate of 1 ms at room temperature and 1 bar. It is clear that the phenomenology of silane combustion is different than that for hydrocarbon combustion [10,11]. Some of the unusual behavior include the following:

1. Silane mixtures are characterized by very low self-ignition temperatures [10–12]. Autoignition can occur at room or even lower temperatures.
2. The lower and upper limits of chain ignition are observed experimentally at low pressures. Most data indicate the chain-branching nature of ignition at room temperature and 1 bar. There are no data on the existence of the third explosion limit.
3. The reaction product SiO_2 (as well as SiO, Si) is a solid at flame temperatures. Its formation implies important contributions to the reaction enthalpy.
4. Flammability and self-ignition limits are very wide [10–12]. Ignition in air occurs at very low silane concentrations; for example, a mixture of 1% silane in nitrogen ignites when it is exposed to the air.
5. The properties of self-sustaining flames of silane with air are ill-defined. It was found that at the lean flammability limit, silane flame can have a maximum temperature as low as 700 K [6].

Previous simulation studies of silane combustion are summarized in Table 1. In this type of chemical kinetic simulation, where much of the data are

TABLE 1
Previous simulation studies on the combustion of the SiH_4–O_2 system

Combustion Mode	Calculated Parameter	Comparison with experiment	Kinetic Model	Ref.
Self-ignition	upper limit (treated as a thermal limit)	[4]	70 reactions	13
	upper limit (same procedure as in Ref. [13])	[4]	103 reactions 35 species	14
CSTR combustion	blowout limit		modified Ref. [16] 45 reactions	15
Ignition behind shock waves	ignition delay	[8]	analogy to CH_4 oxidation 39 reactions 15 species	16
	ignition delay reaction time (global model)	[8] [4]	70 reactions	13
	ignition delay	[8]	103 reactions 35 species	14
Premixed laminar flame	burning velocity flame temperature product distribution	own data	based on Ref. [16] 39 reactions 16 species	6
	burning velocity flame structure		based on Ref. [16] 45 reactions 15 species	17
Counter flow diffusion flame	flame structure		based on Ref. [16] 45 reactions 15 species	18

estimated, one could always fit a particular experimental result. The true test is the quality of the fits over the widest range of existing experimental conditions. Jachimowski and McLain [16] developed a kinetic model based on analogies with methane oxidation. It was used to predict the temperature dependence of the ignition delay. Later, this model was used by Chinitz for modeling silane combustion in a continuous stirred tank reactor (CSTR) [15], and by Tokuhashi et al. [6] and Fukutani et al. [17] for the calculation of burning velocities of a silane laminar flame. Britten et al. [13], using the results of Hartman et al. [4], developed a kinetic model to explain the observed pressure and temperature dependencies of the ignition delay, the product distribution from silane oxidation, and, with some further assumptions, predicted an upper explosion limit. The calculations [13,14] did not obtain the "pure" chain explosion limit. Instead, it was estimated by comparison of the ignition delay and characteristic time for heat loss. Thus, the nature of the upper explosion limit is uncertain.

Kinetic Model and Calculational Procedure

The kinetic model [19] of silane combustion used in this work is based on previously suggested mechanisms for silane oxidation and pyrolysis [13,16,20–23]. It is adjusted to take into account recent experimental and theoretical studies for Si-containing species [24–32]. Some additional reactions have been added to the kinetic scheme to complete the reaction pathways for the consumption of some of the species. The chemical kinetic model consists of 220 elementary reactions with 39 species, and it is posted on the NIST web site [19].

The calculations are based on the CHEMKIN suite of programs. For simulation of silane oxidation at low temperatures, it was necessary to use the "absolute accuracy parameter" of the code ATOL $< 10^{-25}$. Such low values of the ATOL parameter are due to the very low concentration level of the species of importance in silane oxidation at low temperatures.

Important Reactions

Mechanism for the Reaction $SiH_3 + O_2$

The most important mechanistic problem impinging on low-temperature ignition of silane is the source of chain branching. Radicals can readily attack silane to form SiH_3. The subsequent reaction must involve interaction with O_2. Recently, *ab initio* calculations of the

$$SiH_3 + O_2 \rightarrow SiH_3O_2 \rightarrow SiH_3O + O$$

reaction [24–26], a long-discussed candidate for chain branching, demonstrate that stabilization of the SiH_3O_2 radical does not occur and that the decomposition channel is too endothermic (46–70 kJ/mol) to be important as the chain-branching step for low-temperature ignition. From experiments and simulations, it is estimated that the upper limit of the activation energy for the chain-branching step is about 21 kJ/mol.

The overall rate constant for the $SiH_3 + O_2$ reaction is well established near room temperature [27]. According to Quandt et al. [33], the rate expression is $1.25 \times 10^{12} \exp(+463/T)$ cm^3 mol^{-1} s^{-1} in the temperature range 230–490 K. This is in agreement with the measurement of 7.6×10^{12} cm^3 mol^{-1} s^{-1} (300 K) as determined by Koshi et al. [29]. There have been several experimental measurements of branching ratios for this reaction [25,29,30]. At room temperature,the data suggest the following branching ratios:

H atom production	0.65	[30]
OH radical production	0.25	[29,30]
SiO production	0.3–0.7	[14,25]

Consideration of possible products from reaction sequences starting from $SiH_3 + O_2$ show that reasonable reaction enthalpies are possible for the following processes that lead to chain branching:

$$\begin{aligned} SiH_3 + O_2 &\rightarrow Si(O)OH + H + H && -82 \text{ kJ/mol} \\ &\rightarrow Si(OH)_2 + H && -477 \text{ kJ/mol} \\ &\rightarrow HSiOH + OH && -247 \text{ kJ/mol} \\ &\rightarrow SiO + H_2 + OH && -259 \text{ kJ/mol} \\ &\rightarrow SiO + H_2O + H && -318 \text{ kJ/mol} \\ &\rightarrow H_2SiOH + O && -56.9 \text{ kJ/mol} \end{aligned}$$

Recent work [26] has shown that the first process is in fact responsible for chain branching at low temperatures. The reaction sequence includes the formation of the vibrationally excited adduct $SiH_3O_2^*$ whose main channel for decomposition involves formation of cyclic c-$OSiH_2O$ [25]. The isomerization of c-$OSiH_2O$ to yield HSi(O)OH is followed by decomposition to Si(O)OH + H leading to chain branching:

$$SiH_3 + O_2 \Rightarrow SiH_3O_2^* \Rightarrow c-OSiH_2O + H$$

$$\Rightarrow HSi(O)OH + H \Rightarrow Si(O)OH + 2H$$

HSi(O)OH may also isomerize to $Si(OH)_2$ followed by decomposition to H + Si(O)OH. Ab initio calculations show that there are no thermodynamic or kinetic barriers to this process [26]. The calculations carried out here are based on the values given earlier.

Ab initio calculations [24,25] demonstrate the possibility of the formation of biradicals $Si(OH)_2$ and HSiOH simultaneously with the formation of H, OH, and SiO. Subsequent reactions of these species may lead to chain propagation and ultimately branching. The consequences should be similar to the mechanism used here. Kondo et al. [26] were not able to find a reaction pathway linking the initial reactants to the products $SiH_2OH + O$, a chain-branching step that leads to the formation of O atoms.

Role of SiO

SiO is an important species in the flame chemistry of silane. It can be formed in the sequence of reactions suggested by Murakami et al. [25]:

$$SiH_3 + O_2 \Rightarrow SiO + H + H_2O \quad -321 \text{ kJ/mol}$$

and if the assigned large rate constants for the reaction $SiO + O_2 = SiO_2 + O$ are correct, it may also lead to chain branching [14,32]. Surprisingly, there have been no direct measurements on the rate constants for this reaction. The high value of rate constant for this reaction [16] and those for HO_2 interaction with SiH_4 and SiH_2O (discussed later) leads to additional channels for generation of chains and prevents chain termination, which is required to obtain an upper explosion limit. The reaction expression used in this work ($5 \times 10^{12} \exp(-15{,}000/T)$ cm^3 mol^{-1} s^{-1}) removes SiO as an important factor in the lower temperature range. It is more compatible with the thermochemistry than the older expression with a low activation energy.

Role of H Atoms and HO_2 Reactions

The production of H atoms means that it must be consumed by O_2 via the reaction

$$H + O_2 + M = HO_2 + M$$

The ratio between the rate constants for the chain propagation and termination of the HO_2 radical will then define the upper explosion limit. For this purpose, the following reactions are of interest:

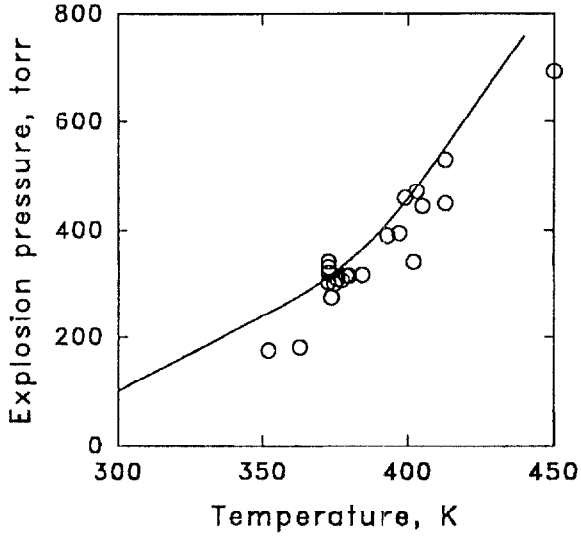

FIG. 1. Critical pressures in silane–oxygen explosions (SiH_4/O_2 = 30/70) Line: results of calculations; symbols: experimental data [4].

$$HO_2 + SiH_4 = SiH_3 + H_2O_2 + 23.4 \text{ kJ/mol}$$

$$10^{13} \exp(-7000/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$HO_2 + SiH_2O = SiHO + H_2O_2 - 21.4 \text{ kJ/mol}$$

$$1.5\times 10^{12} \exp(-6000/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$HO_2 + SiH_2O = HSi(O)OH + OH - 349.8 \text{ kJ/mol}$$

$$10^{11} \exp(-4000/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$HO_2 + HO_2 = H_2O_2 + O_2$$

$$HO_2 + H = OH + OH$$

where the thermochemistries are from the literature [4,13,20–32]. Because measurements for reactions of HO_2 and silicon compounds do not exist, estimates have been made for modeling purposes. The simulation results show that the high values of rate constants of HO_2 radical with SiH_4 and SiH_2O used in kinetic models [16,13] lead to chain propagation through the HO_2 radical and are responsible for the lack of chain termination in many cases. Assignment of higher activation energies for these reactions lead to increasing HO_2 consumption through the disproportionation reaction

$$HO_2 + HO_2 = H_2O_2 + O_2$$

and hence chain termination with H_2O_2 formation.

For the branching scheme with the SiO formation channel, a large quantity of H atoms reacts with SiO to form HSiO. With increasing temperature, the reaction direction changes and decomposition dominates.

Contribution from SiH_2

The contribution of the SiH_2 radical to the oxidation process is small at low temperatures. Increasing temperatures leads to contributions from the reaction

$$SiH_4 + M = SiH_2 + H_2 + M + 241.4 \text{ kJ/mol}$$

to silane consumption and thus the greater importance of SiH_2 reactions. SiH_2 is the key radical in high-temperature silane oxidation. Possible channels for reaction with oxygen are

$$SiH_2 + O_2 = SiHO + OH - 199 \text{ kJ/mol [16]}$$

$$SiH_2 + O_2 = SiO_2 + H + H - 148 \text{ kJ/mol}$$

$$SiH_2 + O_2 = SiO + H_2O - 611 \text{ kJ/mol [14]}$$

These reactions are competitive with processes that consume SiH_2:

$$SiH_2 + SiH_4 = H_3Si_2H + H_2$$

$$SiH_2 + SiH_2 = Si_2H_4$$

An additional channel for SiH_4 decomposition is through the reaction

$$H_3Si_2H + SiH_4 = Si_2H_6 + SiH_2$$

Results and Discussion

Modeling of Upper Explosion Limit. Chain Ignition at 1 bar

Chain ignition limits under both isothermal and nonisothermal conditions have been determined. Figure 1 contains the results of calculations of the upper limit for a 30–70 silane–oxygen mixture. Also included are the experimental data [4]. The discrepancies can be reasonably accounted for by taking into account termination reactions of chain carriers on the surface or through a reasonable adjustment of rate constants. The upper explosion limit of silane is a chain explosion limit determined by competition of the chain-branching reaction $SiH_3 + O_2$ and termolecular reaction $H + O_2 + M = HO_2 + M$.

For any given pressure and temperature, there exists a critical ratio of SiH_4 to O_2 above which chain ignition is observed. This ratio reflects the ratio of rates of the reactions $SiH_4 + H = SiH_3 + H2$ and $H + O_2 + M = HO_2 + M$ and determines the fraction of H atom concentration consumed in the chain propagation step. The importance of this ratio for the determination of critical conditions has been discussed by Kondo et al. [3]. The numerical calculations show that the critical ratio is 3.7 for 1 atm and 300 K (silane/air). Experimental data give a critical ratio 9.5 at T = 292–296 K with nitrogen-diluted

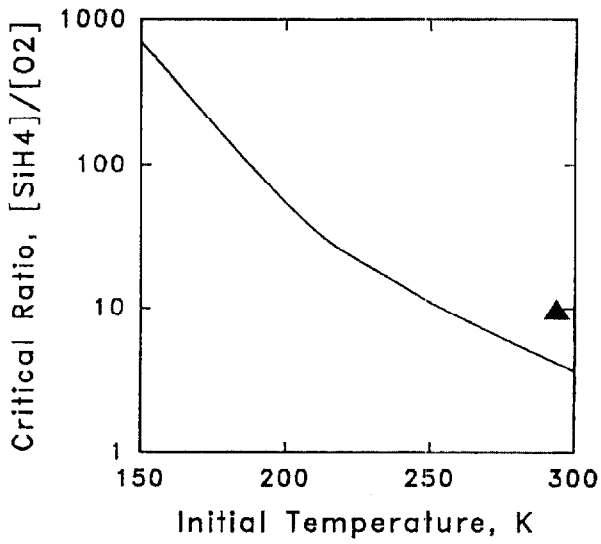

FIG. 2. Temperature dependence of the critical ratio $[SiH_4]/[O_2]$. 1 bar, silane-air mixture. Line: results of calculations; triangle: experimental results [3].

mixtures [3]. Reasonable adjustment of rate constants can improve agreement with experiments.

The numerical simulations show a strong dependence of the ignition delay on silane content. For example, the ignition delay is decreased by a factor of 100 with an increase of silane concentration from 15% to 50% (1 bar, 400 K). It should be remembered that a stoichiometric silane–oxygen mixture is 9.5% silane by volume. The strong dependence of the ignition delay is consistent with the literature [11] on the difficulties in preparing stable silane–oxygen mixtures without ignition and contrasts with the stability of prepared mixtures at certain concentrations. Ignition is the result of the very short ignition delay for mixtures with $(SiH_4/O_2) > (SiH_4/O_2)_{cr}$. The estimates of Kalkanov and Shavard [9], of 1 ms have been mentioned. Based on the experimental results for silane ignition in a counterflow diffusion flame apparatus [7], we estimate an upper limit for ignition delay is 30–50 ms. During mixing, chain ignition in "an optimum composition layer" of gas with a lifetime higher than the ignition delay will lead to ignition of the whole volume of reactants. The possibility of such an explosion event has been suggested earlier in Ref. [9]. In practice, slow mixing and fast stopping of mixing jets usually leads to an explosion [11].

Figure 2 contains the dependence of a critical ratio on temperature at 1 bar in the 150–300 K temperature range. Decreasing the temperature leads to an increase in the critical ratio; for example, at 200 K, the critical ratio is approximately 55. Under such conditions, the adiabatic temperature increases are small (ca. 100–200 K at a temperature of 200 K). Nevertheless, at low temperatures, an explosion of the whole volume is possible for an optimum combination of concentration gradient, ignition delay gradient, and "heating time." With coherent combination of gradients, it is possible to observe gradient chain ignition of a mixture with the transfer of ignition from one layer to another. Experimentally, self-ignition of silane has been observed at temperatures as low as −142 °C for a mixture of the composition 10% SiH_4/7% O_2/N_2 [12].

The mechanism of silane ignition at low temperatures is, to some degree, analogous to the SWACER (shock-wave amplification of coherent energy release) mechanism of detonation formation by free radical initiation [34,35]. The weak chain explosion of one layer would not cause a significant reaction in the next layer if it had not been preconditioned for ignition. When gradients have the proper shape, the localized chain ignition of the layer with optimum mixture composition generates a temperature and radical concentration wave that propagates to the neighboring layer and decreases the ignition delay in that layer. This will trigger ignition of the whole volume.

Critical Conditions of Chain Explosion

It is possible to deduce an analytical form for the critical condition necessary for chain explosion using an abbreviated kinetic scheme. The simplified mechanism is

$$SiH_4 + O_2 \Rightarrow SiH_3 + HO_2 + 183 \text{ kJ/mol},$$

$$7.6 \times 10^{13} \exp(-22{,}160/T) \text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (0)$$

$$SiH_3 + O_2 \Rightarrow H + H + Si(O)OH - 82 \text{ kJ/mol} \quad (1)$$

$$\Rightarrow SiH_2O + OH - 252 \text{ kJ/mol} \quad (2)$$

$$\Rightarrow HSi(O)OH + H - 453 \text{ kJ/mol} \quad (3)$$

$$H + O_2 + M \Rightarrow HO_2 + M \quad (4)$$

$$SiH_4 + O \Rightarrow SiH_3 + OH - 38 \text{ kJ/mol},$$

$$2 \times 10^{13} \exp(-1390/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (5)$$

$$SiH_4 + H \Rightarrow SiH_3 + H_2 - 46.9 \text{ kJ/mol},$$

$$1.5 \times 10^{13} \exp(-1259/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (6)$$

$$SiH_4 + OH \Rightarrow H_2O + SiH_3, -108.8 \text{ kJ/mol},$$

$$8.7 \times 10^{12} \exp(-250/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (7)$$

Assuming quasi-stationary concentrations for H, OH, and O, one obtains

$$d[SiH_3]/dt = W_0 + SiH_3 \times \varphi$$

where W_0 is the rate of the initiation reaction and φ is a branching factor

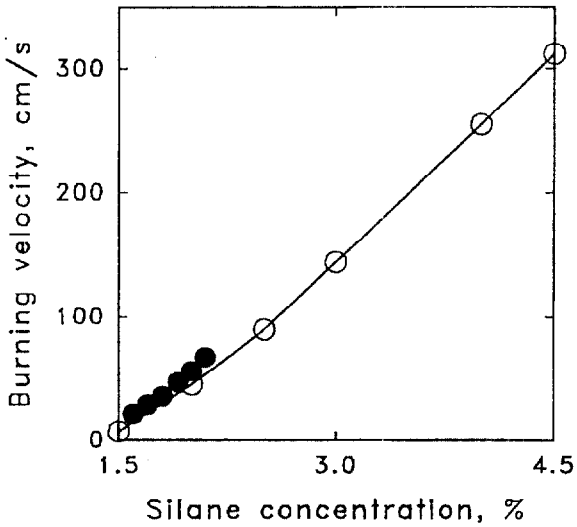

FIG. 3. Burning velocity dependence on silane concentration, 300 K, 1 bar, 21% O_2 + SiH_4 + N_2. Simulation results: line and open circles; experimental data: closed circles [6].

$$\varphi = O_2[k_1k_6SiH_4 - (k_1 + k_3)k_4O_2M]/$$

$$[k_4O_2M + k_6SiH_4]$$

The critical condition of a chain explosion is attained when the branching factor is equal to zero. This leads to the following relation for the critical pressure of the upper explosion limit as a function of temperature and SiH_4 and O_2 concentrations:

$$M = \{k_1k_6/[k_4(k_1 + k_3)]\}\ (SiH_4/O_2)$$

In earlier work [3], the following relation has been suggested for the ignition limit:

$$M = (k_6/k_4)\ (SiH_4/O_2)$$

on the basis of a comparison of the rates of reactions 6 and 4. This relationship, however, does not demonstrate the dependence of the critical pressure on the rate constant for the chain-branching reaction. Both formulas do show that critical pressure depends on the ratio of silane and oxygen concentrations. Treatment of experimental results of Ref. [4] leads to the conclusion that the ratio k_3/k_1 is approximately 5.6. A comparison of calculations using the derived critical conditions and the numerical simulations show differences in the prediction of critical pressure and the ratio (SiH_4/O_2) of factors from 1.5 to 3. This difference is probably due to the neglect of some nonlinear processes that are not included in the simplified model, for example, the well-known stage for quadratic branching $H + HO_2 = 2OH$.

Flame Propagation in $SiH_4/O_2/N_2$ Mixtures

It is interesting to compare silane flame characteristics with those for hydrocarbons. Experimental data [6] show that lean silane–oxygen mixtures can sustain flame propagation in a wide range of concentrations. The burning velocity of very lean mixtures (containing 1.6–2% SiH_4) is relatively high at 20–40 cm/s. Another interesting feature, mentioned earlier, is the very low flame temperature of 700 K at the lean flammability limit [6]. This contrasts with 1600 K for the comparable situation with hydrocarbons.

Figure 3 contains the calculated dependence of burning velocity of an adiabatic premixed flame on silane concentration. Comparison with experimental data [6] shows reasonable agreement. At low SiH_4 concentrations (1–3%), the calculations show that the maximum reaction rate occurs early in the flame or in a preheating zone where the temperature is approximately 700 K. The maximum flame temperature of a 2.5% silane mixture is approximately 1350 K. In contrast, for hydrocarbon flames, the maximum reaction rate is observed in the vicinity of the maximum flame temperature. This is indicative of the differences in the reaction mechanisms for hydrocarbon and silane combustion.

Numerical experiments show that heat release from condensation processes is a very important driving force in silane combustion. If silicon containing compounds are maintained in the gas phase and with HSi(O)OH as the main product, calculated flame velocities are very low (for 2.5% SiH_4 in air, the burning velocity is less than 1 cm/s). With 50–70% of silicon compounds remaining in the gas phase, the burning velocity is in the 5–10-cm/s range. These results demonstrate the necessity of including very fast condensation processes, leading to completion of condensation in the reaction zone of the flame, in the kinetics database. Thus, in previous models [6,13], instantaneous formation of SiO_2 in the solid phase has been assumed. The chemistry that brings about rapid formation of condensed products requires the formation of SiO directly (or at a very early stage) in the reaction of SiH_3 + O2 [25,32]. In these calculations, the SiO branching ratio is set to be 30% and is based on earlier work [14]. However, a serious problem is the relatively slow conversion of SiO to SiO_2 needed for the description of the lower temperature phenomena. At higher temperatures, condensation is proceeding directly through SiO. This is in accord with the results [28] that show fast condensation proceeding through SiO polymerization with gas kinetic rate constants. In addition, our calculations include formation of appreciable amounts of SiH_2O and HSi(O)OH, and these can also polymerize [28]. All these reactions proceed with large heat release and therefore fulfill the requirements for matching experimental data. Another possibility of increasing SiO_2 formation rate is through the reaction $Si(O)OH + O_2 \rightarrow SiO_2 + HO_2$.

In the range of low silane concentrations, the

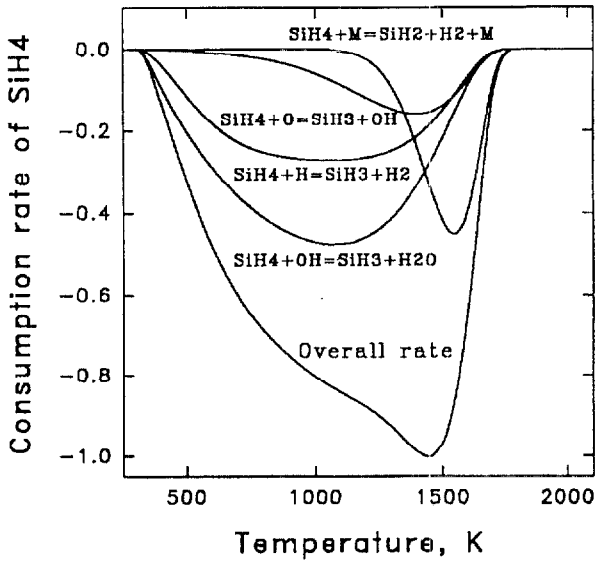

FIG. 4. The relative contributions of different reactions to the consumption rate of silane in flame. 1 atm, 300 K, 0.21 O_2 + 0.045 SiH_4 + 0.745 N_2. The maximum flame temperature is 2090 K.

flame structure is indicative of two reaction zones. The first corresponds to SiH_4 consumption and the second to that of the hydrogen formed in the first zone. It is suggested that the two-reaction zone corresponds to nonstationary propagation due to fast oxidation of silane and a relatively slow consumption of hydrogen on the timescale of SiH_4 consumption. Some stationary solutions have been obtained for rough grids and in a relatively small space domain. Attempts to increase the numerical accuracy and the domain of calculations leads to difficulties in obtaining stationary solutions. The argument that the derived solutions reflect a true two-zone reaction process is as follows. The calculated burning velocities are in rough agreement with experimental data [6]. Formation of hydrogen as a product is observed for small concentrations of SiH_4 (<2.5%) and an excess of oxygen [6]. Naturally, hydrogen will react with oxygen under adiabatic conditions.

Reaction pathway analysis verifies the importance of contributions of SiH_3 radical kinetics at small concentrations of silane. The reaction mechanism in the flame zone accounts for self-ignition kinetics. Increasing silane content leads to an increase of the flame temperature. In the range of 3–6% silane concentration, transition to SiH_2 radical kinetics occurs. Figure 4 contains simulation results on the contributions of various reactions responsible for silane consumption as a function of temperature. It demonstrates the wide range of temperatures in the reaction zone. The contribution of the decomposition reaction to silane consumption increases with the temperature in the flame zone leading to corresponding increases in the contribution of SiH_2 to silane oxidation. The increase in flame temperature for silane concentrations greater than 3% shifts the maximum reaction rate to higher temperatures. The maximum reaction rate is attained at 1600 K for a 6% SiH_4 mixture. For these initial conditions, the maximum rate of reaction for $OH + SiH_4 = SiH_3 + H_2O$ is attained at 1200 K and for $SiH_4 = SiH_2 + H_2$ at 1650 K, where the rate is now twice that of the former. This is another indication of the transition from SiH_3 to SiH_2 kinetics. Thus, the large burning velocities and the existence of flame propagation at low adiabatic temperatures is a consequence of the high reaction rate due to self-ignition kinetics.

The conclusion that silane oxidation in a flame proceeds by two different reaction pathways depending on the temperature is similar to that deduced by Fukutani et al. [17] from simulations using the model of Jachimowski and McLain [16]. This model [16], however, is not consistent with the new kinetics that we have introduced. Although it leads to reasonable values of the burning velocity of silane flames [6], this model cannot be applied to low-temperature phenomena.

Summary

1. A model has been designed to capture the upper explosion limit of silane under isothermal and nonisothermal conditions. The determining factor is the balance of rates of a chain-branching reaction ($SiH_3 + O_2$) and the termination process ($H + O_2 + M = HO_2 + M$).
2. The critical conditions for chain ignition have been deduced. The critical pressure is proportional to the ratio of silane to oxygen concentration. The reactivity of the SiH_4–O_2 mixture increases monotonically with hydride content.
3. Increase of the SiH_4/O_2 ratio at room temperature and 1-bar pressure leads to a chain ignition of silane mixtures. The temperature dependence of the critical ratio of silane and oxygen concentrations has been calculated to be in the temperature range 150–300 K and 1 bar. The results of the present work demonstrate that the upper explosion limit and ignition at room temperature and 1 bar are described by the same mechanism.
4. Simulation studies show two distinct reaction mechanisms, one occurring at high temperatures and the other at low temperatures. At high temperatures, reactions of the SiH_2 radical dominate, and at low temperatures, the kinetics of SiH_3 is controlling.
5. The high values of burning velocity at low flame temperatures for very lean silane mixtures are explained in terms of the reaction proceeding by

a self-ignition kinetic mechanism. Simulations show the importance of processes leading to condensation for accurate burning velocity predictions.

6. The maximum reaction rate is considerably shifted to low temperatures for the flame zone. For lean mixtures, calculations show a two-stage reaction process. The first stage corresponds to silane consumption and the second to hydrogen oxidation.

Acknowledgments

We wish to thank Prof. L. Krasnoperov for the discussions concerning the mechanism for silane oxidation and Prof. M. Koshi for providing Ref. [14] prior to publication.

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COMMENTS

A. Tezaki, University of Tokyo, Japan. The self-ignition nature of silane at room temperature remains a mystery after the talk. The absence of O atoms as products of $SiH_3 + O_2$ makes the establishment of chain branching mechanism difficult, as the authors mentioned. Production of SiO is another striking feature of this reaction. However, it is unlikely that SiO is a chain carrier. Low concentrations of SiO are very stable in O_2 as we found in unpublished experiments. This is consistent with the author's previous calculation.

Author's Reply. Recent work (Ref. [26] in the paper) has shown that the process responsible for chain branching is the reaction sequence starting from $SiH_3 + O_2$ to form two hydrogen atoms and is used in the present work. The analysis of possible products from the reaction $SiH_3 + O_2$ demonstrate that we have a restricted number of reaction sequences with reasonable reaction enthalpies (see text) leading to chain branching. Three important issues are considered in this paper: (1) the source of chain branching; (2) the absence of a chain explosion limit in simulations with chain branching step for wide range of initial conditions due to the high rate constants for some of the chain propagation reactions used in previous kinetic models; and (3) the nature of "unpredictable" ignition behavior of silane. In our opinion, the present work leads to understanding of the mechanism of low-temperature ignition and unpredictable ignition behavior of silane. Of course, there remain many uncertainties in the reaction mechanism, and we did not obtain an exact quantitative agreement of the modeling results with all the existing experimental data.

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S. S. Kumaran, Cabot Corp, USA.

1. What is the release rate fraction due to condensation?
2. How much of the condensation plays the role of heat source or catalyze heterogeneous processes?

Author's Reply. For stoichiometric mixture, heat release due to condensation constitutes more than 30% of overall reaction heat (solid product SiO_2). The value of heat release due to condensation depends on a product distribution and equivalence ratio. Condensation has no influence on the initial reaction stage and on the critical ignition conditions (upper explosion limit). At the same time, simulations show the importance of processes leading to condensation for burning velocity calculations. The heat of condensation increases the burning velocity due to thermal feedback. Heterogeneous reactions have not been considered in the present work.