

**NASA  
Technical  
Paper  
2129**

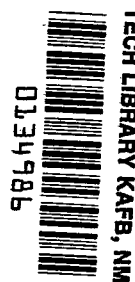
February 1983

NASA  
TP  
2129  
c.1

# A Chemical Kinetic Mechanism for the Ignition of Silane/Hydrogen Mixtures

Casimir J. Jachimowski  
and Allen G. McLain

LOAN COPY: RETURN TO  
AFWL TECHNICAL LIBRARY  
KIRTLAND AFB, N M.



**NASA**

**NASA  
Technical  
Paper  
2129**

1983

TECH LIBRARY KAFB, NM



0134986

# A Chemical Kinetic Mechanism for the Ignition of Silane/Hydrogen Mixtures

Casimir J. Jachimowski  
and Allen G. McLain  
*Langley Research Center  
Hampton, Virginia*

**NASA**

National Aeronautics  
and Space Administration

Scientific and Technical  
Information Branch

## SUMMARY

A chemical kinetic reaction mechanism for the combustion of silane/hydrogen was assembled through the analogy of silane to methane. The mechanism was refined by comparing the observed kinetic behavior as determined in shock tube studies with that predicted by the mechanism. Good agreement between the experimental and the calculated results was achieved by the adjustment of the rate coefficient for the reaction  $\text{SiH}_3 + \text{O}_2 \rightarrow \text{SiH}_2\text{O} + \text{OH}$ . The reaction mechanism was used to theoretically investigate the ignition characteristics of silane/hydrogen mixtures. The results revealed that over the entire range of temperature examined (800 K to 1200 K), substantial reduction in ignition delay time is obtained when silane is added to hydrogen.

## INTRODUCTION

Much attention is being paid to the use of silane ( $\text{SiH}_4$ ) as an ignition aid for hydrogen-fueled supersonic combustion ramjet engines. Experiments in the Langley Hypersonic Propulsion Test Cells and at contractor facilities have positively demonstrated that the addition of silane to the hydrogen fuel enhances combustion and helps sustain stable combustion (Beach et al. 1980). In addition, recent shock tube studies (McLain et al. 1983) have shown that adding silane to hydrogen-oxygen-nitrogen mixtures decreases the ignition delay time substantially. To take full advantage of the effect of silane, a better understanding of the chemical reaction process by which silane participates in the combustion process is needed. A chemical kinetic mechanism which describes the essential features of the silane/hydrogen combustion process would be a useful tool not only for assessing the sensitization capabilities at other conditions but also for the analysis and interpretation of combustor results.

Beach et al. (1980) assembled a preliminary chemical kinetic mechanism for silane oxidation obtained by direct analogy with the methane oxidation reaction mechanism. The mechanism was tested by comparing the calculated consumption of silane with experimental results from a low temperature (500 K to 700 K) isothermal flow reactor. Rate coefficients for five reactions were adjusted to obtain agreement between theoretical and experimental results. Since a large number of rate coefficient adjustments and some unusually large values for some of the rate coefficients were required to obtain agreement, it is thought that heterogeneous processes as well as gas phase homogeneous processes were occurring in the flow reactor. In this report, a detailed chemical mechanism for the oxidation of silane/hydrogen mixtures is presented and discussed. Rate coefficients in this mechanism are refined by comparing calculated ignition delay times with the experimental data reported by McLain et al. (1983).

## SILANE/HYDROGEN REACTION MECHANISM

Since very little kinetic and mechanistic information is available on the high temperature silane oxidation process, the basic features were taken from the methane oxidation mechanism. This reaction has been studied for many years, and the essential reaction paths, intermediates, and products are well known. The silane molecule has a structure similar to that of the methane molecule, and the silane oxidation

products (SiO, SiO<sub>2</sub>) are similar to the methane oxidation products (CO, CO<sub>2</sub>). Therefore, it seems reasonable to assume that similar reactions and reaction intermediates would occur. Because silicon bonding and carbon bonding are not identical, it is recognized that reactivity and the nature of the intermediate species may be different from the methane scheme. It was not the intent, however, to assemble an extensive list of reactions such as those recently developed for methane (Westbrook 1979; Olson and Gardiner 1978). Instead, the objective was to develop a silane mechanism which contained enough detail to describe the essential features of the oxidation process. The mechanisms used to describe the combustion of silane and hydrogen are shown in tables I and II. Rate coefficients for the hydrogen mechanism were selected from the literature. Whenever possible, the same was done for silane. However, since very little kinetic information on silane is available, most rate coefficients were estimated.

TABLE I.- SILANE REACTION MECHANISM

Reaction	Rate coefficient *
SiH <sub>4</sub> → SiH <sub>2</sub> + H <sub>2</sub>	6.0 × 10 <sup>13</sup> exp(-54960/RT)
SiH <sub>4</sub> + O <sub>2</sub> → SiH <sub>3</sub> + HO <sub>2</sub>	2.0 × 10 <sup>11</sup> exp(-44000/RT)
SiH <sub>4</sub> + HO <sub>2</sub> → SiH <sub>3</sub> + H <sub>2</sub> O <sub>2</sub>	3.0 × 10 <sup>12</sup> exp(-5600/RT)
H + SiH <sub>4</sub> → H <sub>2</sub> + SiH <sub>3</sub>	1.5 × 10 <sup>13</sup> exp(-2500/RT)
O + SiH <sub>4</sub> → OH + SiH <sub>3</sub>	4.2 × 10 <sup>12</sup> exp(-1600/RT)
OH + SiH <sub>4</sub> → H <sub>2</sub> O + SiH <sub>3</sub>	8.4 × 10 <sup>12</sup> exp(-100/RT)
H + SiH <sub>3</sub> → SiH <sub>2</sub> + H <sub>2</sub>	1.5 × 10 <sup>13</sup> exp(-2500/RT)
O + SiH <sub>3</sub> → SiH <sub>2</sub> O + H	1.3 × 10 <sup>14</sup> exp(-2000/RT)
OH + SiH <sub>3</sub> → SiH <sub>2</sub> O + H <sub>2</sub>	5.0 × 10 <sup>12</sup>
SiH <sub>3</sub> + O <sub>2</sub> → SiH <sub>2</sub> O + OH	†8.6 × 10 <sup>14</sup> exp(-11400/RT)
SiH <sub>2</sub> + O <sub>2</sub> → HSiO + OH	1.0 × 10 <sup>14</sup> exp(-3700/RT)
H + SiH <sub>2</sub> O → H <sub>2</sub> + HSiO	3.3 × 10 <sup>14</sup> exp(-10500/RT)
O + SiH <sub>2</sub> O → OH + HSiO	1.8 × 10 <sup>13</sup> exp(-3080/RT)
OH + SiH <sub>2</sub> O → H <sub>2</sub> O + HSiO	7.5 × 10 <sup>12</sup> exp(-170/RT)
H + HSiO → H <sub>2</sub> + SiO	2.0 × 10 <sup>14</sup>
O + HSiO → OH + SiO	1.0 × 10 <sup>14</sup>
OH + HSiO → H <sub>2</sub> O + SiO	1.0 × 10 <sup>14</sup>
HSiO + ‡M → H + SiO + M	5.0 × 10 <sup>14</sup> exp(-29000/RT)
HSiO + O <sub>2</sub> → SiO + HO <sub>2</sub>	3.0 × 10 <sup>12</sup>
SiH <sub>2</sub> O + HO <sub>2</sub> → HSiO + H <sub>2</sub> O <sub>2</sub>	1.0 × 10 <sup>12</sup> exp(-8000/RT)
SiO + O + M → SiO <sub>2</sub> + M	2.5 × 10 <sup>15</sup> exp(-4370/RT)
SiO + OH → SiO <sub>2</sub> + H	4.0 × 10 <sup>12</sup> exp(-5700/RT)
SiO + O <sub>2</sub> → SiO <sub>2</sub> + O	1.0 × 10 <sup>13</sup> exp(-6500/RT)

\*The rate coefficient is defined by  $k = A \exp(-E/RT)$  where A is in s<sup>-1</sup> for unimolecular reactions, cm<sup>3</sup>/mole-s for bimolecular reactions, and cm<sup>6</sup>/mole<sup>2</sup>-s for termolecular reactions. The activation energy E is in cal/mole, R = 1.987 cal/mole-K, and T is temperature in K.

†Determined in this study.

‡M is a third-body molecule.

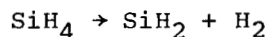
TABLE II.- HYDROGEN REACTION MECHANISM

Reaction	Rate coefficient*	Reference
$H_2 + O_2 \rightarrow OH + OH$	$1.7 \times 10^{13} \exp(-48100/RT)$	Jachimowski and Houghton 1971
$H + O_2 \rightarrow OH + O$	$1.2 \times 10^{17} T^{-0.91} \exp(-16600/RT)$	Schott 1973
$O + H_2 \rightarrow OH + H$	$2.1 \times 10^{14} \exp(-13750/RT)$	Schott 1973
$OH + H_2 \rightarrow H_2O + H$	$3.2 \times 10^7 T^{1.8} \exp(-3030/RT)$	Gardiner et al. 1974
$OH + OH \rightarrow H_2O + O$	$5.5 \times 10^{13} \exp(-7000/RT)$	Gardiner et al. 1973
$H + OH + {}^\dagger M \rightarrow H_2O + M$		
M = $H_2O$	$1.4 \times 10^{23} T^{-2.0}$	Baulch et al. 1972
M = All other	$2.2 \times 10^{22} T^{-2.0}$	Baulch et al. 1972
$H + H + M \rightarrow H_2 + M$		
M = $H_2$	$2.6 \times 10^{12} T^{-1.0}$	Baulch et al. 1972
M = $H_2O$	$3.9 \times 10^{12} T^{-1.0}$	Baulch et al. 1972
M = All other	$6.5 \times 10^{17} T^{-1.0}$	Baulch et al. 1972
$H + O_2 + M \rightarrow HO_2 + M$		
M = $H_2$	$7.0 \times 10^{18} T^{-1.0}$	Slack 1977
M = $H_2O$	$4.4 \times 10^{19} T^{-1.0}$	Slack 1977
M = All other	$3.2 \times 10^{18} T^{-1.0}$	Slack 1977
$OH + HO_2 \rightarrow H_2O + O_2$	$5.0 \times 10^{13} \exp(-1000/RT)$	Lloyd 1974
$H + HO_2 \rightarrow H_2 + O_2$	$2.5 \times 10^{13} \exp(-700/RT)$	Lloyd 1974
$H + HO_2 \rightarrow OH + OH$	$2.0 \times 10^{14} \exp(-1900/RT)$	Lloyd 1974
$O + HO_2 \rightarrow OH + O_2$	$5.0 \times 10^{13} \exp(-1000/RT)$	Lloyd 1974
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$2.0 \times 10^{12}$	Slack 1977
$HO_2 + H_2 \rightarrow H_2O_2 + H$	$3.0 \times 10^{11} \exp(-18700/RT)$	Slack 1977
$OH + H_2O_2 \rightarrow HO_2 + H_2O$	$1.0 \times 10^{13} \exp(-1800/RT)$	Baulch et al. 1972
$M + H_2O_2 \rightarrow OH + OH + M$	$1.2 \times 10^{17} \exp(-45500/RT)$	Baulch et al. 1972

\*The rate coefficient is defined by  $k = AT^n \exp(-E/RT)$ . The rate coefficient units are  $s^{-1}$  for unimolecular reactions,  $cm^3/mole-s$  for bimolecular reactions, and  $cm^6/mole^2-s$  for termolecular reactions. The activation energy  $E$  is in cal/mole,  $R = 1.987$  cal/mole-K,  $T$  is temperature in K, and  $n$  is a temperature exponent.

${}^\dagger M$  is a third-body molecule.

When gaseous mixtures of reactants are suddenly heated by a shock wave, ignition is preceded by a period during which the concentration of free radicals grows very rapidly. The initial phase of this ignition period is often characterized by decomposition of the fuel molecules. Whereas the high temperature decomposition of methane occurs primarily through the rupture of a C-H bond to form a methyl radical ( $\text{CH}_3$ ) and a hydrogen atom, the initial reaction in the decomposition of silane is the molecular elimination of hydrogen



Newman et al. (1979) investigated the homogeneous gas phase decomposition of silane using the single-pulse shock tube technique. They found decomposition rates which were in good agreement with the high pressure unimolecular rate coefficient,  $k_{\infty} = 3 \times 10^{15} \exp(-59600/RT)$ ,  $\text{s}^{-1}$ . In table I, the decomposition rate coefficient is given for the temperatures and pressures of the silane/hydrogen shock tube studies reported by McLain et al. (1983). This rate coefficient was obtained from  $k_{\infty}$  and the results of the RRKM unimolecular reaction theory calculations given by Newman et al. (1979).

Also included in the silane mechanism as an initiation step is the hydrogen abstraction reaction



The rate coefficient for this reaction was estimated by setting the activation energy equal to the heat of reaction  $\Delta H$  at 298 K and using the preexponential factor reported for the analogous  $\text{CH}_4$  reaction (Tsuboi 1976). The rate coefficient for the reaction



was estimated by using the relation  $E = \Delta H + E(\text{reverse})$  to calculate the activation energy; the preexponential factor was set equal to the preexponential reported for the analogous  $\text{CH}_4$  reaction (Westbrook 1979). In the above relation,  $\Delta H$  is the heat of reaction at 298 K and  $E(\text{reverse})$  is the activation energy for the reverse (exothermic) reaction. The latter was calculated using Hirschfelder's rule (Wayne 1969);  $E(\text{reverse}) = 0.055 D_{\text{O-H}}$ , where  $D_{\text{O-H}}$  is the OH bond energy in the  $\text{H}_2\text{O}_2$  molecule. The rate coefficients for the primary chain propagating and branching reactions in the silane mechanism

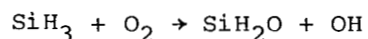
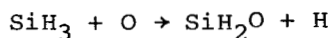


were obtained from the studies reported by Atkinson and Pitts (1978) and Arthur and Bell (1978) for temperatures between 297 K and 438 K. The rate coefficient for the reaction

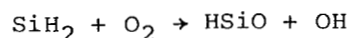


was set equal to the rate coefficient for the  $\text{H} + \text{SiH}_4$  reaction. Olson and Gardiner (1978) made the analogous assumption when developing a detailed methane mechanism.

The rate coefficients for the  $\text{SiH}_3$ -consuming reactions

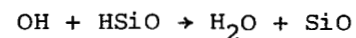
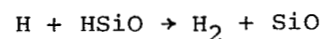
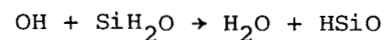
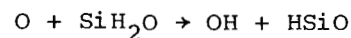
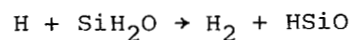


were set to the rate coefficients for the analogous  $\text{CH}_3$  reactions as reported by Peeters and Mahnen (1973a), Peeters and Vinckier (1974), and Jachimowski (1974), respectively. The rate coefficient for the  $\text{SiH}_2$ -consuming reaction

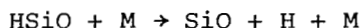


was set equal to the rate coefficient for the analogous  $\text{CH}_2$  reaction as reported by Peeters and Mahnen (1973b).

The rate coefficients for the reactions

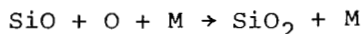
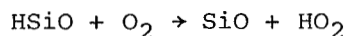


were set equal to the rate coefficients for the analogous  $\text{CH}_2\text{O}/\text{HCO}$  reactions as reported by Dean et al. (1980) in their study of the oxidation of  $\text{CH}_2\text{O}$  behind shock waves. The rate coefficient for the decomposition reaction

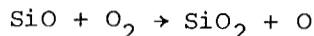
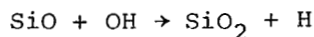


was estimated by setting the activation energy equal to the heat of reaction  $\Delta H$  at 298 K and the preexponential factor for the analogous HCO reaction (Jachimowski 1977).

The rate coefficients for the reactions



were set equal to the rate coefficients for the analogous carbon reactions by using the expressions recommended by Olson and Gardiner (1978), Jensen and Jones (1978), and Lloyd (1974), respectively. The rate coefficients for the  $\text{SiO}_2$ -forming reactions



were estimated using Hirschfelder's rule to calculate the activation energies. The preexponential factors were set equal to the preexponential factors for the analogous CO reactions as reported in Gardiner et al. (1973) and Jensen and Jones (1978). It should be noted that SiO is not a stable species like CO, and that its reactivity is likely to be different.

The hydrogen reaction mechanism listed in table II was taken from Slack (1977). This mechanism successfully reproduced experimental ignition time data from shock tube studies of hydrogen-oxygen mixtures over the temperature range 980 K to 1176 K.

#### MECHANISM EVALUATION AND REFINEMENT

As previously noted, the experimental shock tube results reported by McLain et al. (1983) were used to evaluate and refine the silane mechanism. McLain et al. (1983) reported ignition delay times for two silane/hydrogen mixtures, 2 percent  $\text{SiH}_4$ , 8 percent  $\text{H}_2$ , 4 percent  $\text{O}_2$ , and 86 percent  $\text{N}_2$  (Overall equivalence ratio = 2),



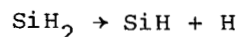
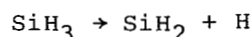
and 1.68 percent  $\text{SiH}_4$ , 6.72 percent  $\text{H}_2$ , 6.74 percent  $\text{O}_2$ , and 84.86 percent  $\text{N}_2$  (Overall equivalence ratio = 1), at 1.25 atm and 1.35 atm, respectively, for the temperature range 800 K to 1050 K. Numerical simulation of the shock tube experiments was carried out using the chemical kinetic computer program described by McLain and Rao (1976). The program was operated in a constant volume mode to simulate the conditions behind a reflected shock wave. The ignition delay time is defined as it is in the shock tube experiments; that is, it is defined to be the elapsed time between the heating of the gas mixture by the reflected shock wave and the sudden pressure increase due to combustion. The rate coefficients for the reverse reactions were calculated within the program by using the forward rate coefficient and the appropriate thermochemical data.

Thermochemical data for the hydrogen, oxygen, and nitrogen species were taken from the JANAF tables (1971) and were used in the analytical form described by Wakelyn and McLain (1975). Thermochemical data for the species  $\text{SiH}_4$ ,  $\text{SiH}$ ,  $\text{SiO}$ , and  $\text{SiO}_2$  were obtained from the tables prepared by McBride et al. (1963). The thermochemical data for the other silicon-containing species which appear in the silane mechanism were not available and had to be estimated.

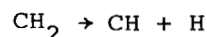
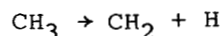
The thermochemical data for the radicals  $\text{SiH}_3$  and  $\text{SiH}_2$  were obtained by assuming that their heat capacities at constant pressure were equal to the heat capacities for the analogous carbon-containing species,  $\text{CH}_3$  and  $\text{CH}_2$  (Bahn 1973). The enthalpies of formation at 298 K were determined using the bond dissociation energies,  $D_{\text{H}_3\text{Si-H}}$  and  $D_{\text{H}_2\text{Si-H}}$ , reported by Doncaster and Walsh (1981). The standard entropies at 298 K ( $S^\circ$ ) were determined using the relation

$$S^\circ(\text{SiH}_x) = S^\circ(\text{SiH}_{x-1}) + S^\circ(\text{H}) - \Delta S^\circ$$

where  $\Delta S^\circ$  is the entropy change for the chemical change  $\text{CH}_x \rightarrow \text{CH}_{x-1} + \text{H}$ . In other words, the entropy changes for the reactions



were assumed to be equal to the entropy changes for the analogous carbon reactions



Thermochemical data for  $\text{SiH}_2\text{O}$  and  $\text{HSiO}$  were obtained by assuming that the heat capacities are the same as for the analogous carbon-containing species  $\text{CH}_2\text{O}$  and  $\text{HCO}$ . The enthalpies of formation at 298 K,  $\Delta H_f^\circ$ , were estimated using the relations

$$\Delta H_f^\circ(\text{SiH}_2\text{O}) = \Delta H_f^\circ(\text{HSiO}) + \Delta H_f^\circ(\text{H}) - D_{\text{H-HSiO}}$$

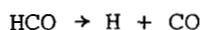
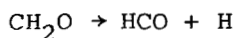
$$\Delta H_f^\circ(\text{HSiO}) = \Delta H_f^\circ(\text{SiO}) + \Delta H_f^\circ(\text{H}) - D_{\text{H-SiO}}$$

where the bond dissociation energies  $D_{\text{H-HSiO}}$  and  $D_{\text{H-SiO}}$  were set equal to  $D_{\text{H-HCO}}$  and  $D_{\text{H-CO}}$ , respectively. The standard entropies at 298 K were estimated using the relations

$$S^\circ(\text{SiH}_2\text{O}) = S^\circ(\text{HSiO}) + S^\circ(\text{H}) - \Delta S'$$

$$S^\circ(\text{HSiO}) = S^\circ(\text{SiO}) + S^\circ(\text{H}) - \Delta S''$$

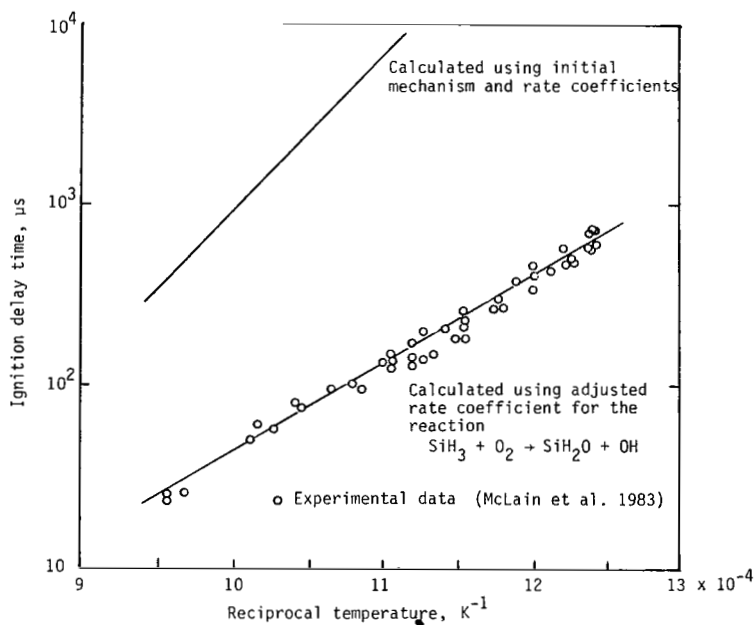
where  $\Delta S'$  and  $\Delta S''$  are the standard entropy changes for the reactions



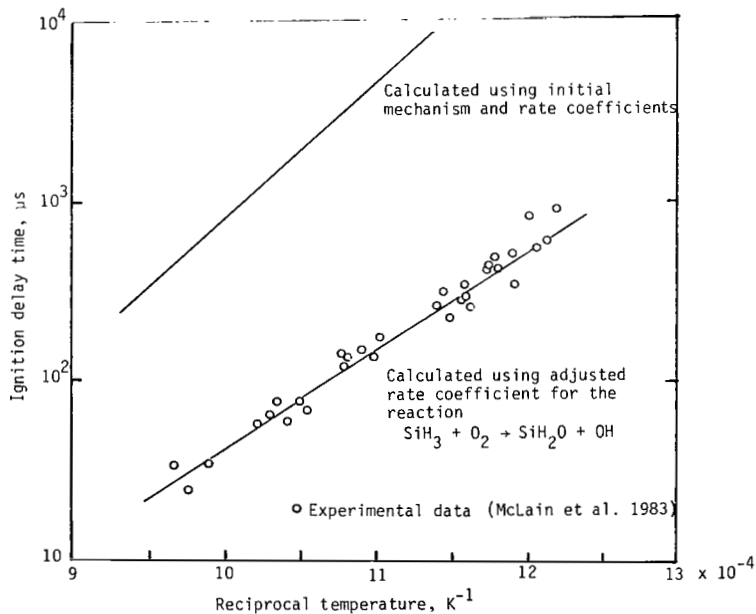
All the estimated thermochemical data were put into the polynomial format required by the chemical kinetic computer program.

The results of the computer simulations of the shock tube experiments for the two silane/hydrogen mixtures are plotted in figures 1(a) and 1(b), together with the corresponding experimental results. The results which were calculated with the estimated rate coefficients show ignition delay times much longer than the observed times. As a first step toward refining the model, a sensitivity study was carried out to determine which reactions had the largest influence on the calculated ignition times. The sensitivity study was performed by individually varying the rate coefficients for all the reactions in the silane mechanism so that they had values between 0.1 and 10.0 times the values listed in table I.

The results of the sensitivity study were virtually identical to similar sensitivity studies carried out with the methane oxidation mechanism (Jachimowski 1974; Bowman 1975). This could have been expected since the silane reaction mechanism was patterned after the methane oxidation scheme, and many of the rate coefficients are



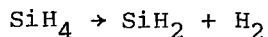
(a) 2 percent  $\text{SiH}_4$ , 8 percent  $\text{H}_2$ , 4 percent  $\text{O}_2$ , and 86 percent  $\text{N}_2$  mixture; Pressure = 1.25 atm.



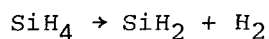
(b) 1.68 percent  $\text{SiH}_4$ , 6.72 percent  $\text{H}_2$ , 6.74 percent  $\text{O}_2$ , 84.86 percent  $\text{N}_2$  mixture; Pressure = 1.35 atm.

Figure 1.- Comparison between calculated and measured ignition delay times.

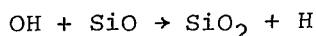
similar. Varying the rates of the following reactions had the largest influence on the calculated ignition delay times.



The results of the sensitivity study did not indicate how much each of these rate coefficients should be modified to bring calculated results into agreement with observed ignition delay times. Good agreement could be obtained by simultaneously increasing the rate coefficients for all three reactions or by adjusting the rate coefficient for any one of the three reactions. However, some of the adjustments did not yield reasonable rate coefficient expressions. For example, the adjustment required to the rate of the decomposition reaction



resulted in a rate coefficient several times the high pressure (upper limit) expression reported by Newman et al. (1979). Similarly, the adjustment required to the rate of the reaction



resulted in a preexponential factor greater than  $5 \times 10^{15}$ , which is an unreasonably large value for a bimolecular reaction. Consequently, it was decided that it would be more prudent to modify the rate coefficient for the reaction



which had the largest influence on the calculated ignition delay times. The rate coefficient which gave the best agreement between the calculated and experimental results was  $k = 8.6 \times 10^{14} \exp(-11400/RT)$ ,  $\text{cm}^3/\text{mole-s}$ . The calculated results for the two mixtures using the modified rate coefficient are plotted in figures 1(a) and 1(b). The agreement between the calculated and observed ignition delay times is very good.

Because of the scarcity of chemical kinetic data at high temperatures, it cannot be claimed that the mechanism presented here is unique. It is possible that other reactions that were not included in the mechanism may be important. Still, the mechanism does accurately reproduce experimental results for silane/hydrogen oxidation in a shock tube with only a minimal amount of reaction rate modification; this suggests that the proposed mechanism and assigned rate coefficients are reasonably correct.

Nonetheless, experimental verification of the individual reactions and rate coefficients is still required.

### IGNITION CHARACTERISTICS OF SILANE/HYDROGEN MIXTURES

To acquire a better understanding of the effect of silane on the ignition characteristics of hydrogen-air mixtures, a series of calculations were made for a range of silane/hydrogen mixtures, from pure hydrogen to pure silane. For each mixture, ignition delay period calculations were performed at several initial temperatures over the range 800 K to 1200 K for a constant pressure of 1 atm. The ignition delay time was defined as the time to achieve ignition as signified by the sudden increase in temperature. This definition gave ignition delay times which are essentially the same as those defined to be the time required to reach a temperature equal to the initial temperature plus 5 percent of the total temperature rise from the initial state to the final state (Beach et al. 1980). The overall fuel-air equivalence ratios ( $\phi$ ) considered were 1.0 and 0.5. The silane/hydrogen mechanism with the modified rate coefficient was used.

The results of these calculations are given in figures 2(a) and 2(b). The sensitization effect of silane is shown to be somewhat greater in stoichiometric

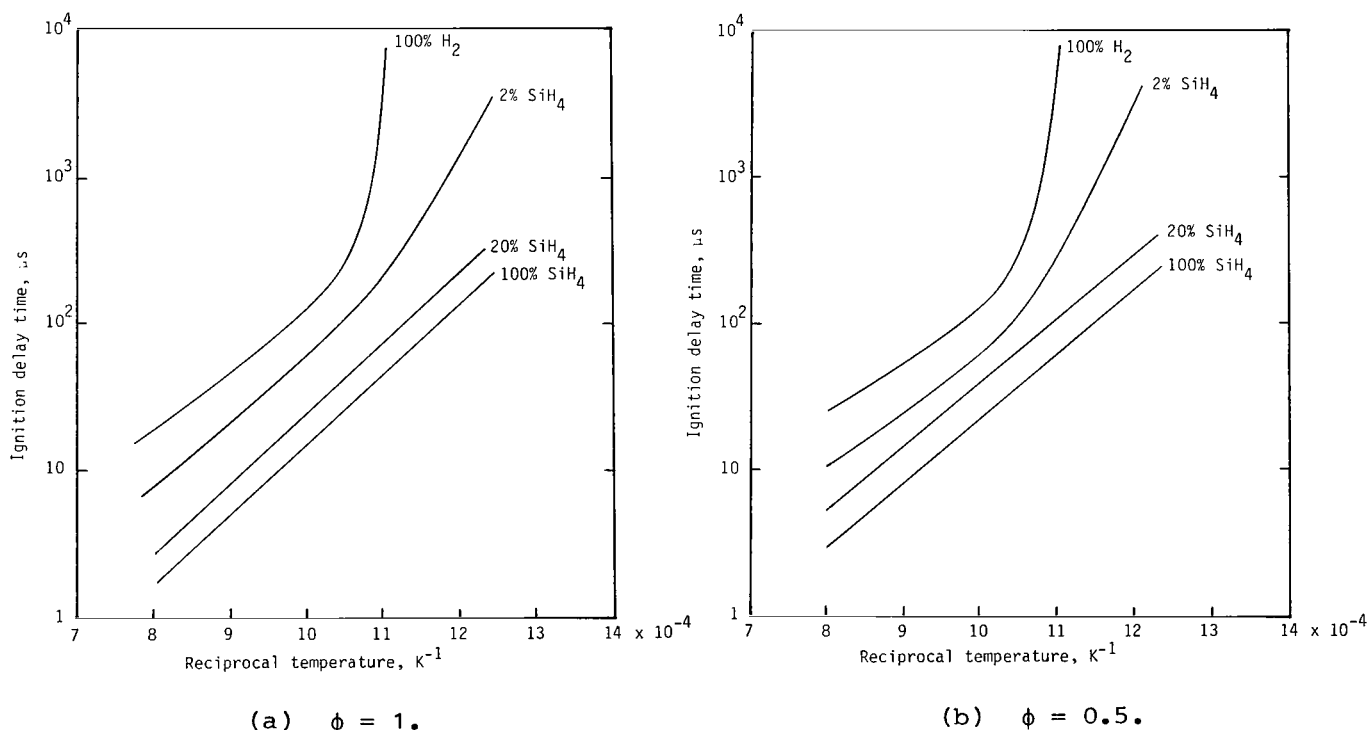


Figure 2.- Ignition delay time as a function of temperature for various silane/hydrogen mixtures at 1 atm.

mixtures than in the fuel-lean mixture. It is also evident from these figures that the ignition delay time decreases rapidly from the pure hydrogen value as the amount of silane is increased. Similar results were reported by Beach et al. (1980). However, whereas the Beach mechanism predicts that the same ignition delay times will be obtained for temperatures above 900 K and for all percentages of added silane, the

present mechanism predicts that over the entire range of temperature examined, the ignition delay time decreases as the quantity of silane increases.

The results in figures 2(a) and 2(b) indicate that the rate of decrease of the ignition delay time at a given temperature becomes smaller as the mixture becomes richer in silane. An additional illustration of this trend appears in figures 3(a) and 3(b), which show ignition delay time at a given initial temperature as a function

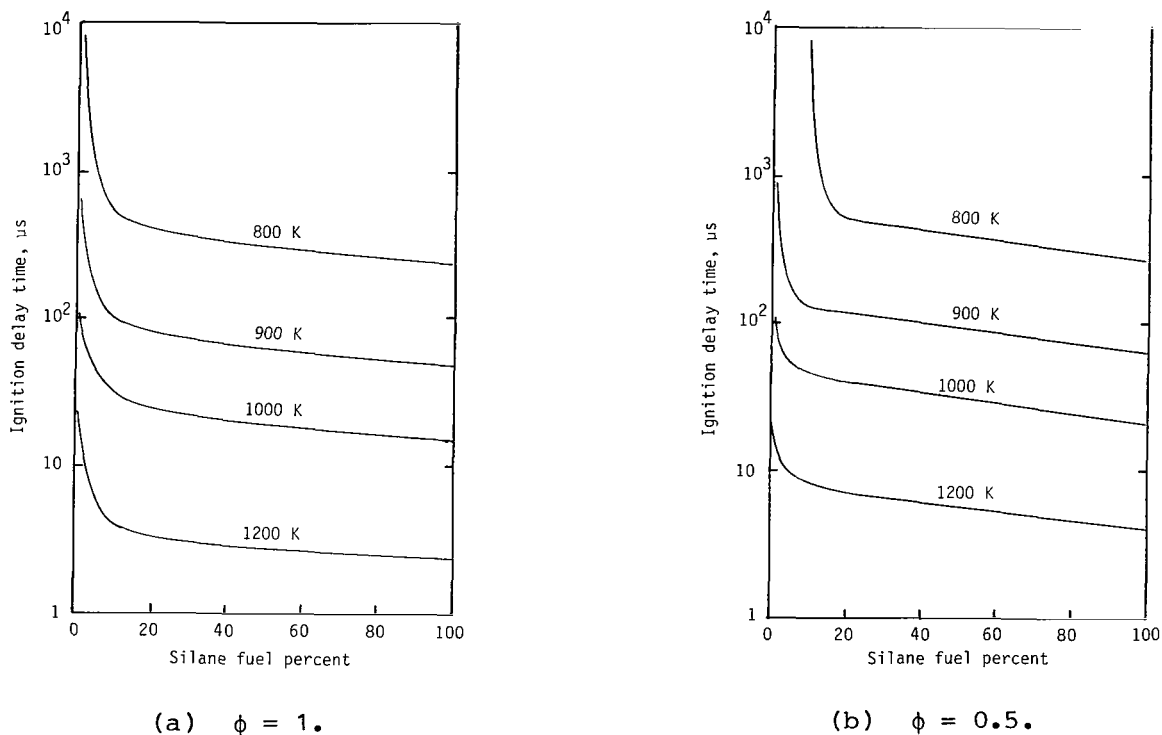
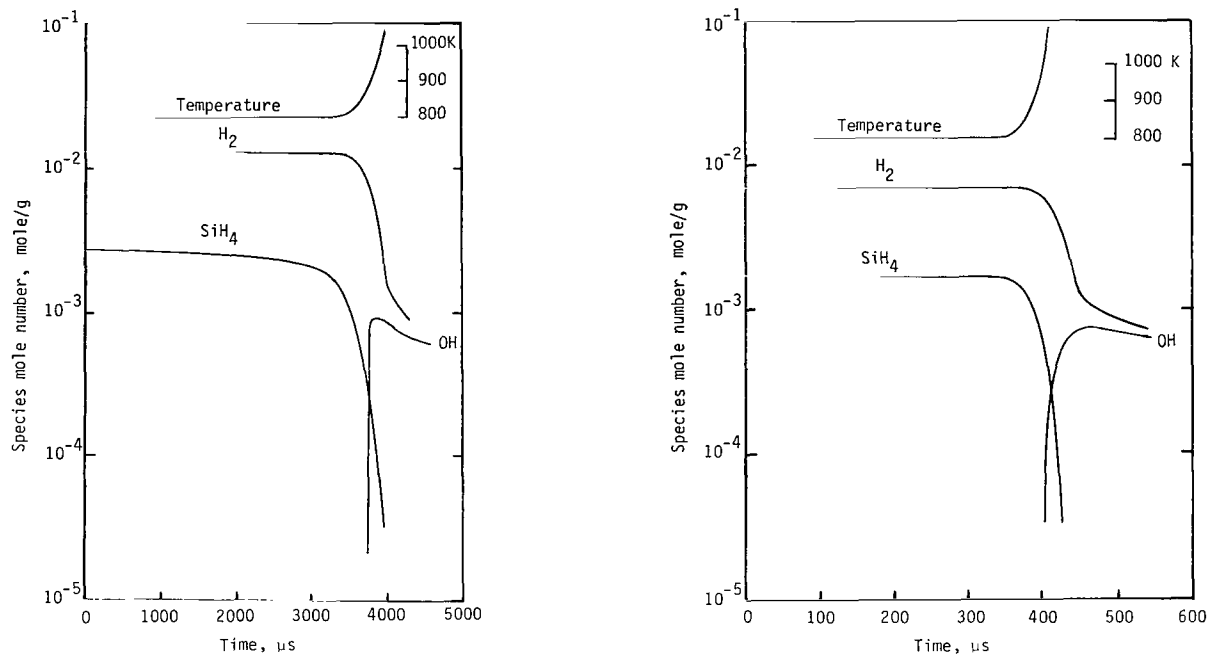


Figure 3.- Ignition delay time as a function of fuel mixture at various temperatures and a pressure of 1 atm.

of silane/hydrogen fuel fraction. The increased curvature of these lines as the mixture approaches pure hydrogen points out the rapid sensitization of ignition provided by adding a small amount of silane to hydrogen. Similar sensitization behavior has been predicted for methane ignition in the presence of ethane (Westbrook 1979).

Examination of the time history of various reactants and products during the ignition period provides some further insight into the ignition characteristics of silane/hydrogen mixtures. A calculated time history of silane, molecular hydrogen, and hydroxyl radical concentrations and mixture temperature for the stoichiometric 2 percent silane/98 percent hydrogen mixtures at constant pressure and initially at 800 K is shown in figure 4(a). It is evident from this figure that the silane is consumed before any significant amounts of hydrogen begin to react. The ignition of the hydrogen is then enhanced (aided) by the large amounts of free radicals H, O, and OH which are rapidly generated during the ignition of the silane. As the silane content is increased, a thermal effect (temperature increase) also contributes to the enhanced oxidation of the hydrogen. This effect becomes important for silane amounts greater than 10 percent. This combined free radical and thermal effect is evident in

the time histories shown in figure 4(b) for a stoichiometric 20 percent silane/80 percent hydrogen mixture initially at 800 K. After most of the silane has been



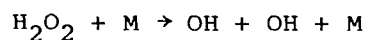
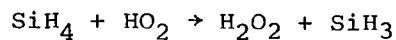
(a) 2 percent  $\text{SiH}_4$ /98 percent  $\text{H}_2$ .

(b) 20 percent  $\text{SiH}_4$ /80 percent  $\text{H}_2$ .

Figure 4.- History of  $\text{SiH}_4$ ,  $\text{H}_2$ , and OH concentrations and mixture temperature during the ignition of stoichiometric  $\text{SiH}_4/\text{H}_2$  mixtures at 1 atm and initially at 800 K.

consumed and prior to any significant oxidation of the hydrogen, the temperature has increased almost 200 K. This increase in temperature and the presence of free radicals both contribute to the increased rate of hydrogen oxidation. At initial temperatures greater than 1000 K, the oxidation of silane and hydrogen is very rapid and takes place almost simultaneously.

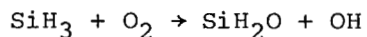
In addition to the enhancement of the ignition process through the generation of free radicals, silane also aids ignition to some extent by scavenging the  $\text{HO}_2$  radical through the reaction sequence



However, at temperatures above 800 K, free radical generation and the thermal effect are the dominant enhancement mechanisms. At temperatures below 800 K, the scavenging may become more important.

## CONCLUDING REMARKS

A chemical kinetic reaction mechanism for the combustion of silane/hydrogen has been assembled through analogy with methane and refined by comparing the observed kinetic behavior as determined in shock tube studies with that predicted by the mechanism. It was determined that reasonably good agreement between the experimental and the calculated results could be achieved by the adjustment of the rate coefficient for the reaction



Calculations made with the refined reaction mechanism indicate that addition of small amounts of silane to hydrogen-air mixtures effectively sensitizes the mixture to ignition. This sensitization occurs because the silane additive rapidly oxidizes and provides free radicals (H, O, OH) in large amounts which subsequently accelerate the ignition of the hydrogen. As the amount of silane is increased, the rate of sensitization decreases. For silane amounts greater than 10 percent, a thermal effect (temperature increase due to the combustion of silane) also contributes to the sensitization effect.

The credibility of the results given here depends to a very large extent on the reasonableness of the silane/hydrogen mechanism. The basic assumption of a silane mechanism analogous to the methane mechanism seems reasonable. However, the accuracy of the many assigned rate coefficients cannot be assessed. It is recommended that additional kinetic studies be carried out to evaluate and improve the high temperature silane oxidation mechanism. More direct evidence is needed to show that the proposed mechanism describes the actual process. The research program should include the identification of intermediate species using spectroscopic techniques, matching of the shape of measured concentration-time profiles with those predicted, and quantitative matching of concentration-time curves with predictions. Species of particular interest would include  $\text{SiH}_3$ ,  $\text{SiH}_2$ ,  $\text{SiH}$ , and  $\text{H}$ .

Langley Research Center  
National Aeronautics and Space Administration  
Hampton, VA 23665  
January 10, 1983



## REFERENCES

- Arthur, N. L.; and Bell, T. N. 1978. An Evaluation of the Kinetic Data for Hydrogen Abstraction From Silanes in the Gas Phase. *Rev. Chem. Intermed.*, vol. 2, no. 1, pp. 37-74.
- Atkinson, R.; and Pitts, J. N., Jr. 1978. Absolute Rate Constants for the Reactions of O(3p) Atoms and OH Radicals With SiH<sub>4</sub> Over the Temperature Range of 297-438°K. *Int. J. Chem. Kinet.*, vol. 10, no. 11, pp. 1151-1160.
- Bahn, Gilbert S. 1973. Approximate Thermochemical Tables for Some C-H and C-H-O Species. NASA CR-2178.
- Baulch, D. L.; Drysdale, D. D.; Horne, D. G.; and Lloyd, A. C. 1972. Evaluated Kinetic Data for High Temperature Reactions. Volume 1 - Homogeneous Gas Phase Reactions of the H<sub>2</sub>-O<sub>2</sub> System. CRC Press.
- Beach, H. L., Jr.; Mackley, E. A.; Rogers, R. C.; and Chinitz, W. 1980. Use of Silane in Scramjet Research. 17th JANNAF Combustion Meeting, Volume I, Debra Sue Eggleston, ed., CPIA Publ. 329 (Contract N00024-78-C-5384), Appl. Phys. Lab., Johns Hopkins Univ., pp. 639-659.
- Bowman, Craig T. 1975. Non-Equilibrium Radical Concentrations in Shock-Initiated Methane Oxidation. Fifteenth Symposium (International) on Combustion, Combustion Inst., pp. 869-882.
- Dean, Anthony M.; Johnson, Ron L.; and Steiner, Don C. 1980. Shock-Tube Studies of Formaldehyde Oxidation. *Combust. & Flame*, vol. 37, no. 1, pp. 41-62.
- Doncaster, Alan M.; and Walsh, Robin 1981. Kinetics of the Gas-Phase Reaction Between Iodine and Monosilane and the Bond Dissociation Energy D (H<sub>3</sub>Si - H). *Int. J. Chem. Kinet.*, vol. 13, no. 5, pp. 503-514.
- Gardiner, W. C., Jr.; Mallard, W. G.; McFarland, M.; Morinaga, K.; Owen, J. H.; Rawlins, W. T.; Takeyama, T.; and Walker, B. F. 1973. Elementary Reaction Rates From Post-Induction-Period Profiles in Shock-Initiated Combustion. Fourteenth Symposium (International) on Combustion, Combustion Inst., pp. 61-75.
- Gardiner, W. C., Jr.; Mallard, W. G.; and Owen, J. H. 1974. Rate Constant of OH + H<sub>2</sub> = H<sub>2</sub>O + H From 1350 to 1600K. *J. Chem. Phys.*, vol. 60, no. 6, pp. 2290-2295.
- Jachimowski, Casimir J. 1974. Kinetics of Oxygen Atom Formation During the Oxidation of Methane Behind Shock Waves. *Combust. & Flame*, vol. 23, no. 2, pp. 233-248.
- Jachimowski, Casimir J. 1977. An Experimental and Analytical Study of Acetylene and Ethylene Oxidation Behind Shock Waves. *Combust. & Flame*, vol. 29, no. 1, May 1977, pp. 55-66. Errata in *Combust. & Flame*, vol. 30, no. 2, p. 102.
- Jachimowski, Casimir J.; and Houghton, William M. 1971. Shock-Tube Study of the Initiation Process in the Hydrogen-Oxygen Reaction. *Combust. & Flame*, vol. 17, no. 1, pp. 25-30.
- JANAF Thermochemical Tables 1971. Second ed. NSRDS-NBS 37, U.S. Dep. Commer.

- Jensen, D. E.; and Jones, G. A. 1978. Reaction Rate Coefficients for Flame Calculations. *Combust. & Flame*, vol. 32, no. 1, pp. 1-34.
- Lloyd, A. C. 1974. Evaluated and Estimated Kinetic Data for Phase Reactions of the Hydroperoxyl Radical. *Int. J. Chem. Kinet.*, vol. 6, no. 2, pp. 169-228.
- McBride, Bonnie J.; Heimerl, Sheldon; Ehlers, Janet G.; and Gordon, Sanford 1963. Thermodynamic Properties to 6000° K for 210 Substances Involving the First 18 Elements. NASA SP-3001.
- McLain, Allen G.; Jachimowski, Casimir J.; and Rogers, R. Clayton 1983. Ignition of  $\text{SiH}_4\text{-H}_2\text{-O}_2\text{-N}_2$  Behind Reflected Shock Waves. NASA TP-2114.
- McLain, Allen G.; and Rao, C. S. R. 1976. A Hybrid Computer Program for Rapidly Solving Flowing or Static Chemical Kinetic Problems Involving Many Chemical Species. NASA TM X-3403.
- Newman, C. G.; O'Neal, H. E.; Ring, M. A.; Leska, F.; and Shipley, N. 1979. Kinetics and Mechanism of the Silane Decomposition. *Int. J. Chem. Kinet.*, vol. 11, no. 11, pp. 1167-1182.
- Olson, D. B.; and Gardiner, W. C., Jr. 1978. Combustion of Methane in Fuel-Rich Mixtures. *Combust. & Flame*, vol. 32, no. 2, pp. 151-161.
- Peeters, Jozef; and Mahnen, Gilbert 1973a. Reaction Mechanisms and Rate Constants of Elementary Steps in Methane-Oxygen Flames. Fourteenth Symposium (International) on Combustion, *Combustion Inst.*, pp. 133-146.
- Peeters, Jozef; and Mahnen, Gilbert 1973b. Structure of Ethylene-Oxygen Flames. Reaction Mechanism and Rate Constants of Elementary Reactions. Combustion Institute European Symposium 1973, F. J. Weinberg, ed., Academic Press, Inc., pp. 53-58.
- Peeters, Jozef; and Vinckier, Christiaan 1974. Production of Chemi-Ions and Formation of CH and  $\text{CH}_2$  Radicals in Methane-Oxygen and Ethylene-Oxygen Flames. Fifteenth Symposium (International) on Combustion, *Combustion Inst.*, pp. 969-977.
- Schott, Garry L. 1973. Further Studies of Exponential Branching Rates in Reflected-Shock Heated, Nonstoichiometric  $\text{H}_2\text{-CO-O}_2$  Systems. *Combust. & Flame*, vol. 21, no. 3, pp. 357-370.
- Slack, M. W. 1977. Rate Coefficient for  $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$  Evaluated from Shock Tube Measurements of Induction Times. *Combust. & Flame*, vol. 28, no. 3, pp. 241-249.
- Tsuboi, Takao 1976. Mechanism for the Homogeneous Thermal Oxidation of Methane in the Gasphase. *Japan. J. Appl. Phys.*, vol. 15, no. 1, pp. 159-168.
- Wakelyn, N. T.; and McLain, Allen G. 1975. Polynomial Coefficients of Thermochemical Data for the C-H-O-N System. NASA TM X-72657.

Wayne, R. P. 1969. The Theory of the Kinetics of Elementary Gas Phase Reactions. Comprehensive Chemical Kinetics, Volume 2 - The Theory of Kinetics, C. H. Bamford and C. F. H. Tipper, eds., Elsevier Pub. Co., pp. 189-301.

Westbrook, Charles K. 1979. An Analytical Study of the Shock Tube Ignition of Mixtures of Methane and Ethane. Combust. Sci. & Technol., vol. 20, no. 1 & 2, pp. 5-17.

1. Report No. NASA TP-2129		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle A CHEMICAL KINETIC MECHANISM FOR THE IGNITION OF SILANE/HYDROGEN MIXTURES				5. Report Date February 1983	
7. Author(s) Casimir J. Jachimowski and Allen G. McLain				6. Performing Organization Code 505-32-73-01	
9. Performing Organization Name and Address NASA Langley Research Center Hampton, VA 23665				8. Performing Organization Report No. L-15542	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546				10. Work Unit No.	
15. Supplementary Notes				11. Contract or Grant No.	
16. Abstract  A chemical kinetic reaction mechanism for the oxidation of silane/hydrogen mixtures is presented and discussed. Shock-tube ignition delay time data were used to evaluate and refine the mechanism. Good agreement between experimental results and the results predicted by the mechanism was obtained by adjusting the rate coefficient for the reaction $\text{SiH}_3 + \text{O}_2 \rightarrow \text{SiH}_2\text{O} + \text{OH}$ . The reaction mechanism was used to theoretically investigate the ignition characteristics of silane/hydrogen mixtures. The results revealed that over the entire range of temperature examined (800 K to 1200 K), substantial reduction in ignition delay times is obtained when silane is added to hydrogen.				13. Type of Report and Period Covered Technical Paper	
17. Key Words (Suggested by Author(s)) Silane combustion Ignition time Chemical kinetics				14. Sponsoring Agency Code	
18. Distribution Statement Unclassified - Unlimited				Subject Category 25	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 18	
				22. Price A02	

National Aeronautics and  
Space Administration

THIRD-CLASS BULK RATE

Postage and Fees Paid  
National Aeronautics and  
Space Administration  
NASA-451



Washington, D.C.  
20546

Official Business

Penalty for Private Use \$300

4 1 11,0, 830304 50090305  
DEPT OF THE AIR FORCE  
AF WEAPONS LABORATORY  
ATTN: TECHNICAL LIBRARY (SUL)  
KIRTLAND AFB NM 87117

**NASA**

POSTMASTER: If Undeliverable (Section 158  
Postal Manual) Do Not Return