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Numerical Study of the Ignition of Silane/Hydrogen Mixtures

V. I. Golovitchev*
Chalmers University of Technology, 412 96 Göteborg, Sweden
and
Claudio Bruno†
University of Rome, 00184 Rome, Italy

The use of silane, SiH_4, as an ignition improver for hydrogen/air (H_2/O_2) mixtures, has been evaluated numerically, using a chemical mechanism constructed by analogy with methane low-temperature oxidation kinetics. The mechanism rate parameters are redefined by comparing numerical results with data from shock-tube experiments. The computer results reveal that over entire temperature and pressure ranges examined, substantial reduction in ignition delays has been confirmed when SiH_4 is added to H_2. It is shown that the H_2/O_2 ignition anomaly, known as the extended second explosion limit, is essentially degenerated in the presence of SiH_4.

Introduction

RECENTLY, special attention has been paid to the role of chemical kinetic effects on the performance of supersonic combustion engines using hydrogen (H_2) as the main fuel.[1] The current kinetic data on H_2 combustion in air (O_2) indicate that the second explosion limit can be extended to the region of higher pressures and temperatures typical of future hypersonic engine combustor inlet parameters. Below this limit, the induction delay time increases with pressure. To ensure ignition and stable burning, various combustion enhancement schemes have been proposed. One scheme[2] involving the usage of silane (SiH_4) (because of its hypergolic nature), to initiate or sustain H_2 combustion, has proven its applicability, but requires further study. In addition, SiH_4 is important for ground testing of hypersonic combustor chambers, whenever reservoir enthalpy would result in unacceptable combustion length.

A chemical mechanism of SiH_4 combustion in air was proposed for the first time by Jachimowski and McLain[3] by assuming the analogy of SiH_4 to CH_4, which was used to reproduce the ignition delays of SiH_4–H_2–O_2–N_2 mixtures in shock-tube experiments.[4] Calculations performed using this mechanism showed that small amounts of SiH_4 can sensitize the combustion of H_2 over a wide range of conditions. This study is recognized as a pioneering work. However, silicon bonding and carbon bonding are not identical, making this analogy very approximate. The fact that one of the principal oxidation products, SiO_2, is solid at flame temperatures may become very important as far as heterogeneous effects are concerned. In fact, the heterogeneous recombination of O, OH, and other radicals occurs much more readily on a solid surface than in the gas phase. These recombinations are highly exothermic and may affect induction and combustion times. Since the work of Ref. 3, a comprehensive kinetic mechanism of SiH_4 oxidation has been proposed,[5] and recent findings are summarized in Ref. 6. In the present study, a detailed chemical mechanism for the combustion of SiH_4/H_2 mixtures is constructed, then refined by comparing calculated ignition delays with experimental data reported in Ref. 3, and new findings in the modeling are discussed.

Model Description

The construction of a mechanism of H_2/O_2 combustion promotion by SiH_4 requires a choice of reacting species, specification of their thermodynamic properties, identification of the reaction paths and of the important stages, and selecting or estimating the reaction rate parameters. The mechanism studied in this paper has been developed in essentially this order.

In the case of SiH_4/H_2 combustion, the fundamental chemistry (owing to the SiH_4 excellent ignition performance) is not well understood. There are insufficient thermodynamic data on many reaction intermediates. We have started with a comprehensive mechanism of H_2/O_2 combustion consisting of eight reactive (H_2, O_2, OH, H_2O, H, O, HO_2, and H_2O_2) species participating in 26 reversible reactions, which are listed in Table 1. Nitrogen (N_2) is considered to be an inert gas. Most of these reactions have been studied experimentally, and the mechanism has previously been used for propulsion combustion modeling.[7] The reaction-rate parameters in the form $k_j = a_j T^{\zeta_j} \exp(-E_{aj}/R_0 T)$ are taken from different sources, but mainly from Ref. 8. Reactions 19 and 23 are represented by the sum of two Arrhenius expressions. This mechanism is more elaborate than those proposed by Miller and Bowman,[8] or Balakrishnan and Williams,[9] and it is used in modeling.

The current kinetic data indicate that the second H_2 explosion limit can be extended to a region of higher pressures and temperatures. The existence of this limit has been confirmed by Yetter et al.[10] Below this limit, the induction delay time decreases with pressure. The increase of τ_{ind} with pressure takes place in the region above this boundary. This phenomenon is basically a consequence of a competition between reactions 3 and 6 of the mechanism (see Table 1). The first reaction is an endothermic, chain-branching reaction, whereas the second one is an exothermic, radical-terminating reaction. Their Arrhenius parameters were updated according to newly evaluated kinetic data.[11] For higher pressures, the overall reaction rate increases again via new reactions involving HO_2 and H_2O_2 (reactions 23–26 in Table 1), providing additional radicals in the pool. Our mechanism is close to that described in Ref. 10, and the improved agreement with experimental data is achieved mainly as a result of reactions added to the mechanism and to the updated data for reaction 6. However, we have chosen to use the Arrhenius form of a rate coefficient of the reaction OH + OH → H_2O + O instead of the non-Arrhenius form recommended in Ref. 10. The main goal was to use the most comprehensive mechanism to correctly cover the rather ill-exploded mixtures above the extended second explo-

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*Associate Professor, Department of Thermo and Fluid Dynamics.

†Associate Professor, Department of Mechanical and Aeronautical Engineering. Member AIAA.

Table 1 Reaction submechanism of H_2/O_2 combustion[a]

Reaction	a_f^r	ζ_f^r	E_{af}^r
$H_2 + O_2 \rightleftharpoons OH + OH$	6.7×10^{13}	0.0	47,780
$H_2 + OH \rightleftharpoons H_2O + H$	1.2×10^{99}	1.30	3626
$O + OH \rightleftharpoons O_2 + H$	5.0×10^{14}	−0.5	0
$O + H_2 \rightleftharpoons OH + H$	5.1×10^{44}	2.67	6290
$O + OH + M \rightleftharpoons HO_2 + M$	1.0×10^{16}	0.0	0
$H + O_2 + M_2 \rightleftharpoons HO_2 + M_2$	2.8×10^{19}	−1.25	0
$OH + HO_2 \rightleftharpoons H_2O + O_2$	7.9×10^{13}	0.0	−497
$H + HO_2 \rightleftharpoons OH + OH$	1.7×10^{14}	0.0	874
$O + HO_2 \rightleftharpoons O_2 + OH$	2.4×10^{13}	0.0	1073
$OH + OH \rightleftharpoons O + H_2O$	6.0×10^{88}	1.3	0
$H + H + M_1 \rightleftharpoons H_2 + M_1$	1.0×10^{18}	−1.0	0
$H + H + H_2 \rightleftharpoons H_2 + H_2$	9.2×10^{16}	−0.6	0
$H + H + H_2O \rightleftharpoons H_2 + H_2O$	6.0×10^{19}	−1.25	0
$H + OH + M \rightleftharpoons H_2O + M$	1.6×10^{22}	−2.0	0
$H + O + M \rightleftharpoons OH + M$	6.2×10^{16}	−0.6	0
$O + O + M \rightleftharpoons O_2 + M$	1.9×10^{13}	0.0	−1788
$H + HO_2 \rightleftharpoons H_2 + O_2$	6.3×10^{13}	0.0	1411
$H + HO_2 \rightleftharpoons H_2O + O$	3.1×10^{10}	0.0	3590
$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$	1.3×10^{11}	0.0	−1640
$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$	4.2×10^{14}	0.0	12,000
$H_2O_2 + M \rightleftharpoons OH + OH + M$	1.3×10^{17}	0.0	45,500
$H_2O_2 + H \rightleftharpoons HO_2 + H_2$	1.6×10^{12}	0.0	3800
$H_2O_2 + H \rightleftharpoons H_2O + OH$	1.0×10^{13}	0.0	3590
$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$	1.3×10^{11}	0.0	−1630
$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$	5.8×10^{14}	0.0	9560
$H_2O_2 + O \rightleftharpoons H_2O + O_2$	8.4×10^{11}	0.0	4260
$H_2O_2 + O \rightleftharpoons OH + HO_2$	2.0×10^{13}	0.0	5900
$HO_2 + H_2 \rightleftharpoons H_2O + OH$	6.5×10^{11}	0.0	18,800

[a] Rate coefficients are in cm^3 mol^{-1} s^{-1} units; third bodies, M_i, and chaperon efficiencies are in the same form as in Ref. 8.

sion limit, and to assess changes in ignition when SiH_4 is added to the H_2/O_2 mixture.

The submodel of SiH_4/O_2 chemistry including 11 reacting species (SiH_4, SiH_3, SiH_2, SiH, SiO, SiO_2, HSiO, SiH_2O, SiH_3O, SiH_3O_2, and SiH_4O_2), participating in 39 reactions, is presented in Table 2. The initial stages of SiH_4 combustion are associated with the decomposition of SiH_4 via the molecular elimination of H_2 in the *fall-off* reaction

$$SiH_4 \rightleftharpoons SiH_2 + H_2$$

and the production of silyl, SiH_3, radicals by abstraction of H_2 atoms from SiH_4 in the reactions

$$SiH_4 + O_2 \rightleftharpoons SiH_3 + HO_2$$

$$SiH_4 + X \rightleftharpoons SiH_3 + HX$$

where X represents atomic and radical species.

The silyl then reacts with O_2, producing hot silylperoxy, SiH_3O_2, radicals. This peroxy radical can decompose much faster than CH_3O_2 radicals in low-temperature methane oxidation. This is because the Si–O bond is much stronger than the C–O bond, and energy for the dissociation of other weaker bonds is provided from the *recombination* reaction between SiH_3 and O_2 (Ref. 6, p. 520). The following reaction paths are suggested:

$$SiH_3 + O_2 \rightarrow SiH_3O_2^*$$

$$SiH_3O_2^* + M \rightarrow SiH_3 + O_2 + M$$

$$SiH_3O_2^* \rightarrow SiH_3O + O$$

$$SiH_3O_2^* \rightarrow SiH_2O + OH$$

where * implies vibrational excitation.

This reaction *family* represented by stages 36, 37, and 41, listed in Table 2, basically determines the character of SiH_4 ignition, as it provides enough energy to break other bonds in the system. Recent experimental information concerning the dissociation channels in SiH_4 combustion can be found in Ref. 12. Radicals H and OH, produced in the decomposition processes, lead to chain branching. This is the main distinction from the classical mechanism of Ref. 3, in which the silylperoxy radical was not accounted for, albeit the reaction $SiH_3 + O_2 \rightarrow SiH_2O + OH$ was found to be the leading path in the course of ignition. We have assumed also that H_2 is basically produced in reactions 27, 43, and 50, but not in the hydrolysis reaction proposed in Ref. 5 or in reactions on the surface of solid particles. While the reaction proceeds, the following stage becomes important:

$$SiH_2 + O_2 \rightleftharpoons HSiO + OH$$

and, finally, silicon monoxide (SiO) and dioxide (SiO_2) are produced, completing the combustion process. The effect of the nucleation of SiO_2 has not been taken into account in this study. The other heterogeneous and vibrational excitation effects on kinetics were also neglected, but thermal properties of SiO_2 were taken into account as for a solid compound.

Thermochemical properties of SiH_4 and silicon hydrides SiH_n were taken from the NASA CET93 code database,[13] and properties of the other silicon-containing species taking part in the constructed mechanism were calculated with the help of the PAC91 code[14] using the information from the NIST Chemistry WebBook‡ and from Ref. 6, p. 514. The calculated values appear to be practically identical to the values given to us by C. J. Jachimowski; the properties of a few silicon hydrides can be found also in the Chemkin database.[15] Silylidyne (SiH) radicals do not play an important role in silane ignition.§

To simulate the ignition behind a reflected shock wave, the KINETICS package[16] was used, operating in a constant-density

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‡http://webbook.nist.gov/cgi/cbook.exe.

§An electronic copy of this mechanism along with the NASA-formatted thermodynamic data may be downloaded from the following Web site: http://www.tfd.chalmers.se/valeri/DME+ SiH_4.mech.

Table 2 Reaction submechanism of SiH_4/O_2 combustion[a]

Reaction	a_f^r	ζ_f^r	E_{af}^r
$SiH_4 \rightleftharpoons SiH_2 + H_2$	2.0×10^{13}	0.0	57,200
$SiH_2 + O_2 \rightleftharpoons HSiO + OH$	3.2×10^{14}	0.0	8000
$SiH_2 + H_2O \rightleftharpoons SiH_2O + H_2$	3.0×10^{12}	0.0	11,400
$SiH_4 + O_2 \rightleftharpoons SiH_3 + HO_2$	4.0×10^{13}	0.0	42,800
$SiH_4 + H \rightleftharpoons SiH_3 + H_2$	1.1×10^{13}	0.0	2500
$SiH_4 + O \rightleftharpoons SiH_3 + OH$	4.2×10^{12}	0.0	1600
$SiH_4 + OH \rightleftharpoons SiH_3 + H_2O$	8.4×10^{12}	0.0	100
$SiH_4 + HO_2 \rightleftharpoons SiH_3 + H_2O_2$	2.0×10^{12}	0.0	10,000
$SiH_4 + SiH_3O_2 \rightleftharpoons SiH_3 + SiH_4O_2$	1.1×10^{13}	0.0	18,500
$SiH_3 + O_2 \rightleftharpoons SiH_3O_2$	1.0×10^{15}	0.0	1200
$SiH_3O_2 \rightleftharpoons SiH_2O + OH$	2.0×10^{12}	0.0	4000
$SiH_3O_2 + HO_2 \rightleftharpoons SiH_4O_2 + O_2$	3.0×10^{11}	0.0	0
$SiH_4O_2 + H \rightleftharpoons SiH_3O_2 + H_2$	4.8×10^{13}	0.0	7950
$SiH_4O_2 \rightleftharpoons SiH_3O + OH$	6.5×10^{14}	0.0	48,700
$SiH_3 + O_2 \rightleftharpoons SiH_3O + O$	3.0×10^{12}	0.0	0
$SiH_3O + O_2 \rightleftharpoons SiH_2O + HO_2$	2.0×10^{13}	0.0	0
$SiH_3 + H \rightleftharpoons SiH_2 + H_2$	2.0×10^{13}	0.0	0
$SiH_3 + O \rightleftharpoons SiH_2O + H$	2.0×10^{13}	0.0	0
$SiH_3 + OH \rightleftharpoons SiH_2O + H_2$	6.0×10^{12}	0.0	0
$SiH_3 + HO_2 \rightleftharpoons SiH_2 + H_2O_2$	2.0×10^{13}	0.0	0
$SiH_3 + SiH_3 \rightleftharpoons SiH_2 + SiH_4$	2.0×10^{12}	0.0	0
$SiH_2O + O_2 \rightleftharpoons HSiO + HO_2$	4.0×10^{14}	0.0	35,000
$SiH_2O + M \rightleftharpoons HSiO + H + M$	2.0×10^{15}	0.0	84,500
$SiH_2O + H \rightleftharpoons HSiO + H_2$	5.3×10^{14}	0.0	10,500
$SiH_2O + O \rightleftharpoons HSiO + OH$	1.8×10^{13}	0.0	3080
$SiH_2O + OH \rightleftharpoons HSiO + H_2O$	7.5×10^{12}	0.0	170
$SiH_2O + HO_2 \rightleftharpoons HSiO + H_2O_2$	1.0×10^{13}	0.0	12,000
$HSiO + M \rightleftharpoons H + SiO + M$	5.0×10^{14}	0.0	29,000
$HSiO + O_2 \rightleftharpoons SiO + HO_2$	3.0×10^{12}	0.0	0
$HSiO + H \rightleftharpoons SiO + H_2$	2.0×10^{14}	0.0	0
$HSiO + O \rightleftharpoons SiO + OH$	1.0×10^{14}	0.0	0
$HSiO + OH \rightleftharpoons SiO + H_2O$	1.0×10^{14}	0.0	0
$HSiO + HO_2 \rightleftharpoons SiO + H_2O_2$	1.0×10^{14}	0.0	0
$SiO + OH \rightleftharpoons SiO_2 + H$	4.0×10^{12}	0.0	5700
$SiO + HO_2 \rightleftharpoons SiO_2 + OH$	1.0×10^{12}	0.0	0
$SiO + H_2O_2 \rightleftharpoons SiO_2 + H_2O$	2.0×10^{12}	0.0	0
$SiO + O + M \rightleftharpoons SiO_2 + M$	3.5×10^{15}	0.0	4370
$SiO + O_2 \rightleftharpoons SiO_2 + O$	4.0×10^{13}	0.0	6500
$SiH_2 + O_2 \rightleftharpoons SiH + HO_2$	1.0×10^{13}	0.0	22,800

[a]Rate coefficients are in $cm^3\ mol^{-1}\ s^{-1}$ units, mainly compiled from Refs. 3 and 5.

mode. The sensitivity of the change of temperature to a change in the reaction rate parameters has been used to resolve the leading stages in the combustion mechanism. The ignition delay has been defined as the time at which the temperature gradient picks up (point of inflection of the temperature vs time profile).

Results and Discussion

To test the accuracy of the mechanism assembled, which is the union of reaction sets listed in Tables 1 and 2, we initially calculated the H_2/O_2 ignition delays in the pressure range of interest (1–2 atm), and compared the predictions with available experimental data for stoichiometric H_2/O_2 mixtures[17] (Fig. 1). The agreement is quite good and is better than that obtained using the reaction schemes taken from Refs. 8 and 9. The mechanism proposed in Ref. 8 is, in fact, quite good, but it overpredicts the ignition delay time in the low-temperature region at high pressure. The mechanism[9] predicts ignition delays that are too lengthy in the low-temperature region, under all pressures studied. The crossing of ignition delay curves corresponding to different pressures (1 and 2 atm) emphasizes the anomaly in H_2/O_2 ignition related to the extended second explosion limit discussed earlier.

A peculiar ignition feature of the reactive system is illustrated in Fig. 2, where the ignition delays for a stoichiometric H_2/O_2 mixture are presented as a function of pressure for different initial temperatures. In this figure, one can see the nonmonotonic behavior of ignition delays with pressure forming the short-lived explosion limit. In the range of strong pressure sensitivity, the ignition delay can be increased drastically by a moderate pressure rise and vice versa. This nonmonotone behavior could result in difficulties in engines. Because the combustion control must be achieved over the widest possible range of combustor inlet conditions, the use of SiH_4 as a combustion improver seems advisable to change the ignition character at these conditions.

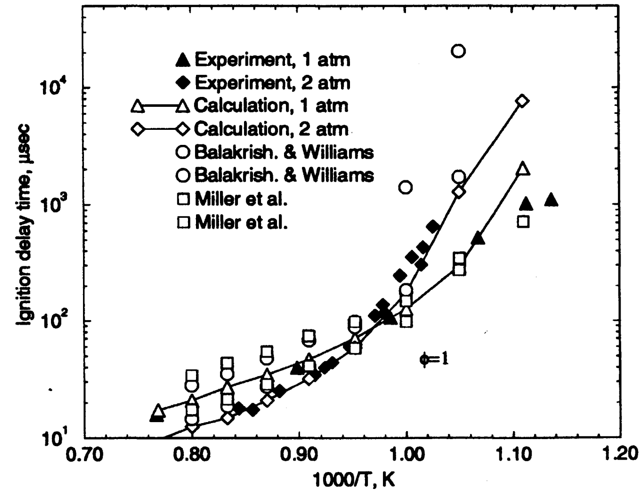

Fig. 1 Comparison of calculated (using different kinetic mechanisms) and measured ignition delays for a stoichiometric H_2/O_2 mixture at extended second explosion limit conditions.

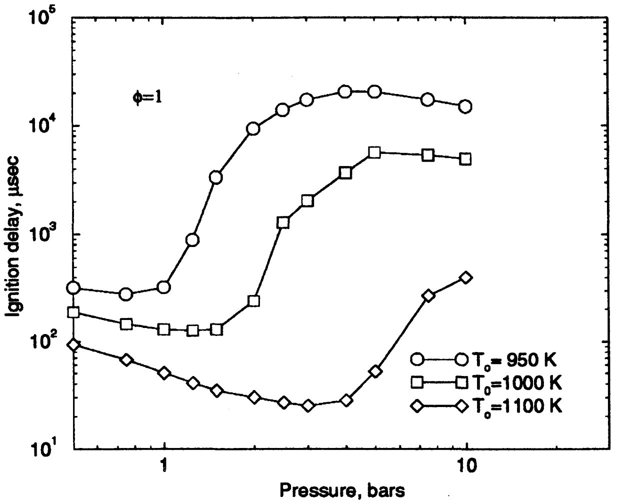

Fig. 2 Ignition delays for a stoichiometric H_2/O_2 mixture as a function of pressure for different initial temperature at the extended second explosion limit conditions.

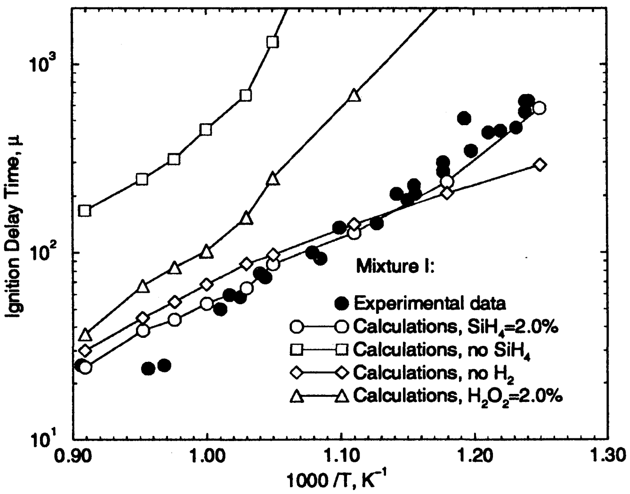

Fig. 3 Comparison of calculated and measured ignition delays for mixture I of Ref. 3. Results for the promotor-free mixture and in the presence of H_2O_2 illustrate the efficiency of SiH_4.

At first, two $SiH_4/H_2/O_2/N_2$ mixtures representing SiH_4/O_2 equivalence ratios of 1.0 (mixture I: SiH_4 = 2.0, H_2 = 8.0, O_2 = 4.0, and N_2 = 86.0 mole percent), and 0.5 (mixture II: SiH_4 = 1.68, H_2 = 6.72, O_2 = 6.74, and N_2 = 84.86), were studied similarly to Ref. 4 at initial temperatures in the range of 800–1050 K and pressures in the range of 1.25–1.35 atm. The definition of the equivalence ratio is based on the overall reaction $SiH_4 + 2O_2 \rightarrow SiO_{2(s)} + 2H_2O_{(g)}$, which is not realistic, as H_2 is recognized to be the main volatile combustion product.[6] Thermodynamic analysis at the equilibrium predicts a composition that includes a considerable amount of H_2 and SiO, together with H_2O and SiO_2, even for a stoichiometric mixture. In practice, however, kinetics will determine the actual composition of combustion products. From the results of calculations and comparisons presented in Figs. 3 and 4, it follows that a reasonably good agreement between the experimental and computer results has been achieved.

The promotion effect of SiH_4 is well pronounced in both stoichiometric and fuel-lean mixtures over the entire range of temperature and pressure studied. Comparing the curves in Fig. 3 for the H_2-free and SiH_4-free mixtures, one can conclude that there is an advanced ignition of SiH_4, i.e., SiH_4 is consumed before any significant amount of H_2 begins to react. The preferential oxidation of SiH_4 affects the ignition of H_2 through the associated heat release and radical production. The thermal effect becomes important for SiH_4 amounts greater than 10%. It is interesting to note that the SiH_4/H_2 mixture at high temperatures triggers combustion even more rapidly than for the H_2-free mixture. This can be attributed to the role of the radical pool formed in the course of H_2 ignition. SiH_4 is a more effective promoter for H_2 ignition than, for example, hydrogen peroxide studied in Ref. 16, particularly at low temperatures (as shown in Fig. 3). As the amount of SiH_4 is increased, its relative efficiency decreases.

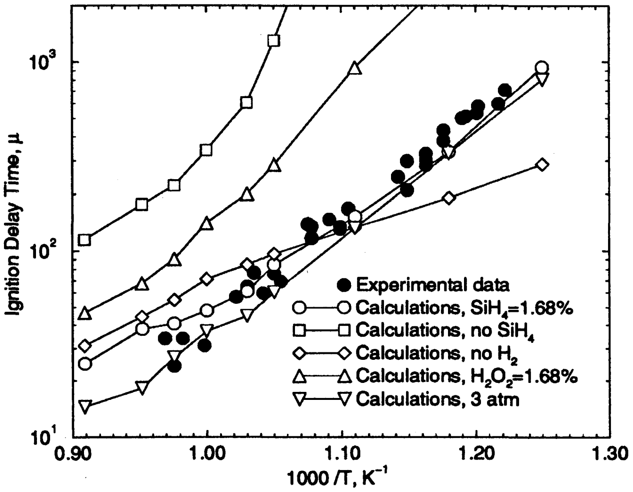

Fig. 4 Comparison of calculated and measured ignition delays for mixture II of Ref. 3. Results for the promotor-free mixture in the presence of H_2O_2 are presented to evaluate the efficiency of SiH_4. Results at 2 atm illustrate that the extended second limit becomes less pronounced in the presence of SiH_4.

The same ignition features occur for lean SiH_4/O_2 mixtures, as can be seen in Fig. 4. The ignition delay curve corresponding to a pressure of 3 atm is also plotted, illustrating the fact that the dependence of ignition delays on pressure becomes nearly monotone in the presence of SiH_4. Good agreement with the measured ignition delays has been achieved using the results of the sensitivity study summarized in Table 3, by adjusting the rate coefficients for the few most sensitive stages of the SiH_4/O_2 submechanism. The H_2/O_2 combustion submechanism parameters have been herewith left unchanged. A similar analysis made in Ref. 3 resulted in singling only the $SiH_3 + O_2 \rightarrow SiH_2O + OH$ stage to be accelerated for the best approximation. The results of our analysis are not so conclusive. In our model, this reaction is replaced by three stages, 36, 37, and 41, where reactions 36 and 41 are listed in Table 3 as being the important ones, with stage 36 increasing the ignition delay, if its forward constant is increased. SiH_4 shows the highest reactivity toward H atoms, and the following stage is found to be the main factor contributing to enhancement of the overall reaction rate:

$$SiH_4 + H \rightleftharpoons SiH_3 + H_2$$

Because the following reaction is among the most important, SiH_4, in addition to ignition enhancement, can scavenge HO_2 radicals, which are responsible for the extended second explosion limit, thus moderating the ignition delay dependence on pressure:

$$SiH_4 + HO_2 \rightleftharpoons SiH_3 + H_2O_2$$

This is well illustrated by Fig. 5, where a more realistic stoichiometric H_2/O_2 mixture with the addition of a small amount (5% volumetric) of SiH_4, demonstrates a nearly monotone dependence of ignition delays on pressure in contrast with the ignition character for promoter-free mixtures.

Table 3 Reaction sensitivities in the presence of SiH_4[a]

Reaction	t = 702 μs	t = 1206 μs
$H + O_2 + M \rightleftharpoons HO_2 + M$	−504	−98.6
$SiH_4 + H \rightleftharpoons SiH_3 + H_2$	410	43.8
$H_2 + OH \rightleftharpoons H_2O + H$	−338	−68.8
$SiH_4 + OH \rightleftharpoons SiH_3 + H_2O$	311	45.4
$SiH_3 + O_2 \rightleftharpoons SiH_3O + O$	205	37.0
$SiH_3 + O_2 \rightleftharpoons SiH_3O_2$	−205	−37.0
$SiH_2O + OH \rightleftharpoons HSiO + H_2O$	154	43.3
$SiH_4 + HO_2 \rightleftharpoons SiH_3 + H_2O_2$	128	22.9
$SiH_4 \rightleftharpoons SiH_2 + H_2$	90.2	19.9
$SiH_2 + O_2 \rightleftharpoons HSiO + OH$	89.4	35.3
$O + OH \rightleftharpoons O_2 + H$	88.0	9.47
$OH + HO_2 \rightleftharpoons H_2O + O_2$	−70.2	−13.9
$H + HO_2 \rightleftharpoons OH + OH$	50.1	6.88
$H_2 + HO_2 \rightleftharpoons OH + H_2O$	21.7	3.84
$SiH_2O + H \rightleftharpoons HSiO + H_2$	15.4	45.7
$H + HO_2 \rightleftharpoons H_2 + O_2$	−13.8	−2.02
$SiO + OH \rightleftharpoons SiO_2 + H$	−0.002	42.5
$SiH_2 + H_2O \rightleftharpoons SiH_2O + H_2$	0.0063	−35.5
$SiO + O_2 \rightleftharpoons SiO_2 + O_2$	12.9	20.8

[a] Absolute temperature-rate sensitivities for mixture I of Ref. 4 (T_0 = 800 K, τ_{ig} = 752 μs), calculated at two instants during the ignition course, the one before ignition, 702 μs, and the second, 1206 μs, after ignition.

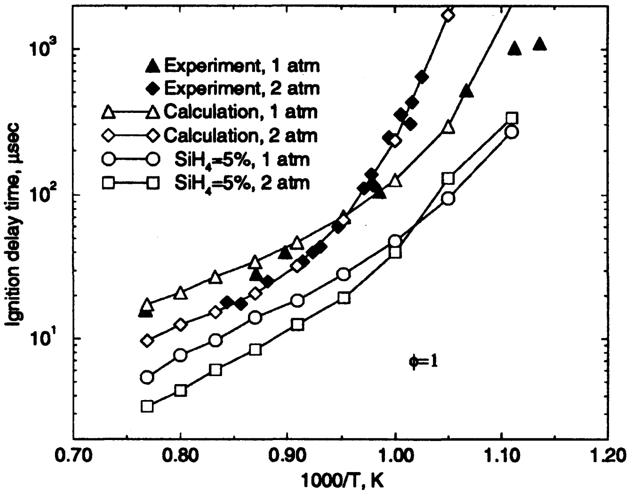

Fig. 5 Moderation of the ignition delay dependence on pressure for the stoichiometric H_2/O_2 mixture (two curves from Fig. 1 are once again reproduced here), by adding a small amount of SiH_4.

Conclusions

A chemical mechanism to evaluate the SiH_4 promotion effect on H_2/O_2 mixtures has been assembled and refined by comparing numerical predictions and shock-tube data on ignition delays. A reasonably good agreement has been achieved by adjustment of rate coefficients of the mechanism leading stages.

The promotion effect of a small amount of SiH_4 is well illustrated for both stoichiometric and fuel-lean mixtures over all initial temperatures and pressures. The effect is mainly attributed to two factors: the high reactivity of SiH_4 toward H atoms, and the formation of SiH_3O_2 radicals that can decompose rapidly even at low temperatures, providing energy for thermal acceleration of the reaction. The preferential oxidation of SiH_4 affects the ignition of H_2 through heat release and radical production. As the amount of SiH_4 is increased, its relative efficiency decreases.

SiH_4, in addition to the ignition enhancement, scavenges HO_2 radicals, moderating the ignition-delay dependence on pressure under initial conditions corresponding to the extended second explosion limit for H_2/O_2 mixtures. Thus, it can prevent some possible difficulties in the functioning of high Mach number combustion systems.

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