Research paper

The determination of the third body efficiencies for the $H+O_2+M=HO_2+M$ reaction (M=Ar, H_2O)

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Abstract

The detailed chemical reaction model for H_2/O_2 combustion proposed by Koshi was estimated in a high pressure state. In this paper, two rate coefficients of the terminating reactions are discussed. The numerical ignition delay time in $H_2/O_2/Ar$ mixture were compared with the experiments measured by Petersen et al. and the rate coefficient of the reaction $H+O_2+Ar \rightarrow HO_2+Ar$ was decided as $k=2.96\times10^{19}T^{-1.40}$. The numerical laminar flame velocity in $H_2/O_2/H_2O$ mixture at various pressures is compared with the experimental data measured by Kusharin et al. The rate coefficient of the reaction $H+O_2+H_2O \rightarrow HO_2+H_2O$ is determined as $k=1.62\times10^{23}T^{-2.29}$.

Keywords : Detailed chemical reaction model, High pressure, H_2/O_2combustion

1. Introduction

High pressure is required in a combustion chamber of a liquid rocket engine in order to obtain higher thrust performance. For example, in the combustion chamber of H-IIA rocket's first stage engine, the pressure is over 10 MPa and the hydrogen and oxygen in the chamber are in a supercritical state. A detailed chemical reaction model is necessary to simulate H_2/O_2 combustion under such a high pressure because the chamber temperature calculated using one step chemical reaction model is much higher than the experimental data and the adiabatic flame temperature. However, the pressure dependence of the rate coefficients in the detailed chemical reaction models is still unclear. Therefore, it is necessary to pick up and modify the dominant reactions under high pressure states by comparing with the experimental data.

Recently, Petersen and Hanson model[1], Williams model[2], Li et al. model[3], and Koshi model[4] were proposed

as the detailed chemical reaction models including pressure dependence. Petersen and Hanson model and Koshi model were constructed for simulations of supersonic combustions and detonations. Their models include the pressure dependence in H_2O_2 decomposition and recombination reaction ; $OH+OH+M \rightarrow H_2O_2+M$. The availability of Petersen and Hanson model is confirmed by Tsuboi et al.[5] [6]Williams model and Li et al. model also include the pressure dependence in terminating reaction ; $H+O_2+M \rightarrow HO_2+M$ in addition to H_2O_2decomposition and recombination reaction.

In this paper, the detailed reaction model proposed by Koshi was evaluated for ignition delay time and laminar flame velocity using CHEMKIN 4.1.1. At first, the ignition delay time was calculated and compared with experimental data measured by Petersen et al.[7] One of the most important reactions was selected by the sensitivity analysis. Then, the rate coefficient of the reaction was modified and compared with other data. Secondly, the laminar flame velocity was calculated and compared with the experimental data measured by Kusharin et al.[8] One of the most important reactions was selected by the sensitivity analysis and its rate coefficient was modified by comparing with other data.

2. Calculation Method and Condition

2.1 Ignition Delay Time

The calculation conditions are ideal gas, constant volume, and closed homogeneous system. The ignition delay time τ is defined as the time when the maximum slope of temperature is obtained.

2.2 Sensitivity Analysis

The sensitivity analysis shows influence of each elementary reaction on whole reaction. The sensitivity analysis for temperature $S_i(\tau)=\frac{\partial \ln T}{\partial \ln A_i}$ can be calculated by CHEMKIN 4.1.1. The values for ignition delay time are required to calculate $S_i(\tau)$, therefore, the equation has to be modified. The values of sensitivity analysis for ignition delay time τ are calculated by the following equation ; $S_i(\tau)=\frac{\partial \ln \tau}{\partial \ln A_i}=\frac{T}{\tau}\frac{\partial \tau}{\partial T}S_i(T)$,where T is temperature, A_i is frequency factors of the rate coefficient, and subscript i means the ith elementary reaction, respectively. After calculating $S_i(\tau)$, each value is normalized by the maximum value.

2.3 Laminar Flame Velocity

The one−dimensional laminar flame is assumed as a freely propagating flame under constant pressure and adiabatic condition. The calculation was carried out using CHEMKIN 4.1.1.

3. Results and Discussion

3.1 The Modification of the Rate Coefficient of the Reaction $H+O_2+Ar \rightarrow HO_2+Ar$

3.1.1 Ignition Delay Time

The compositions of the initial gas mixtures are 2% H_2, 1% O_2, and 97% Ar and the initial pressures are 1~64 atm. The present results and the experimental data measured by Petersen et al.[1] are shown in Fig. 1. The numerical results on the high temperature region at each pressure agree well with the experimental data, however, both data on the low temperature region at each pressure do not coincide. Therefore, the sensitivity analysis is necessary to estimate the dependence of the elementary reaction on the ignition delay time at the low temperature region.

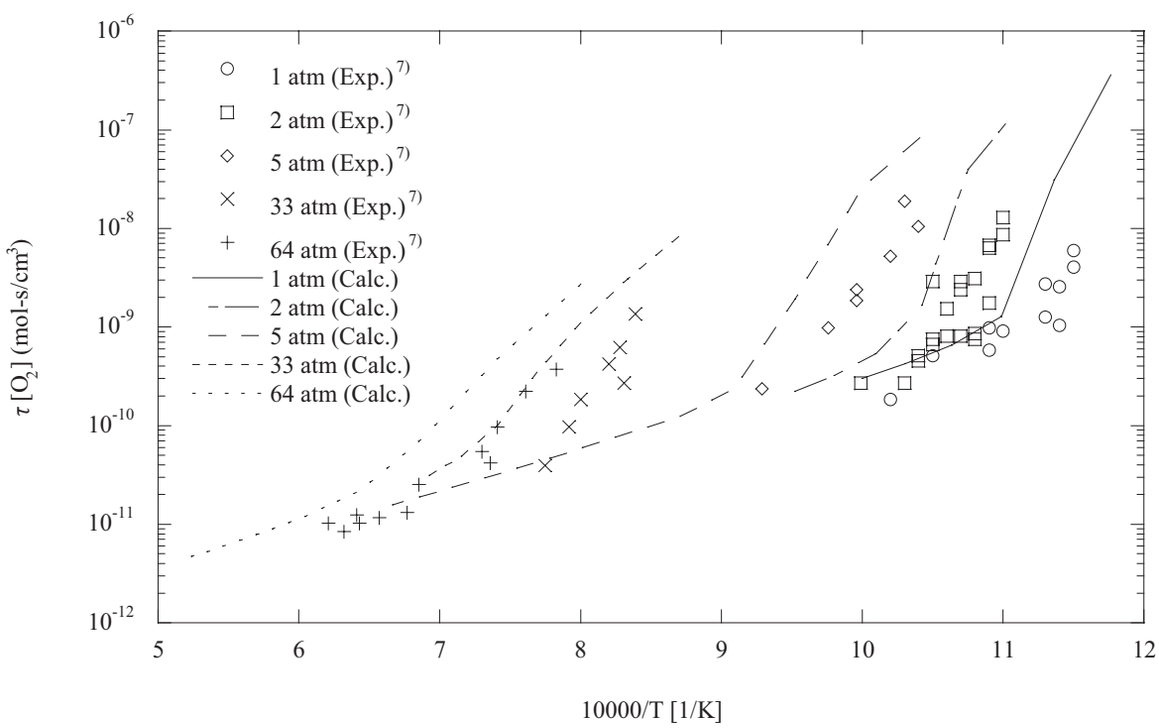

Fig. 1 The comparison of ignition delay time between numerical results and experimental data for temperature range from 850 to 1950 K, and pressure range from1to 64 atm.

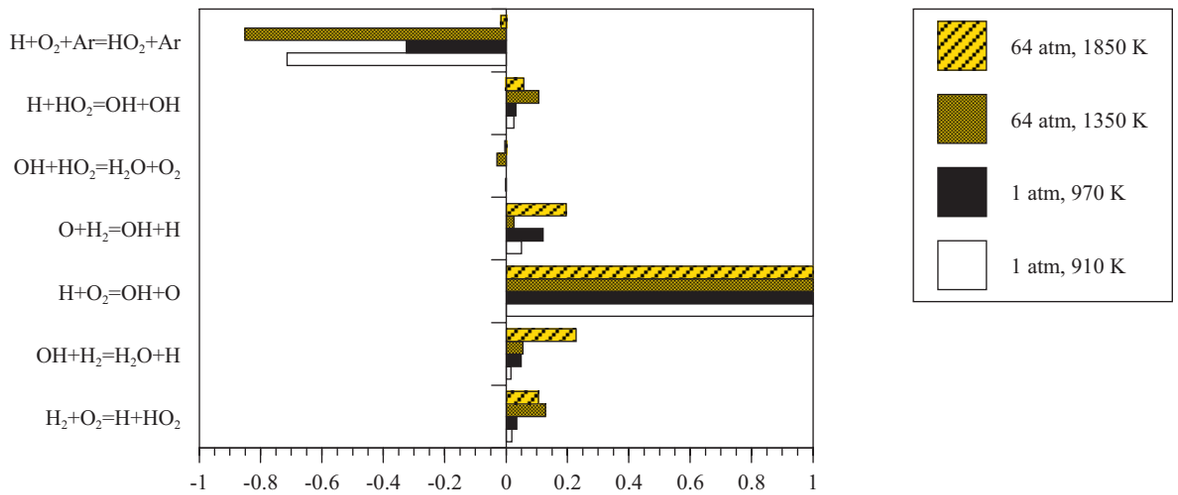

Fig. 2 The sensitivity analysis of ignition delay time at1and 64 atm under low and high temperature region.

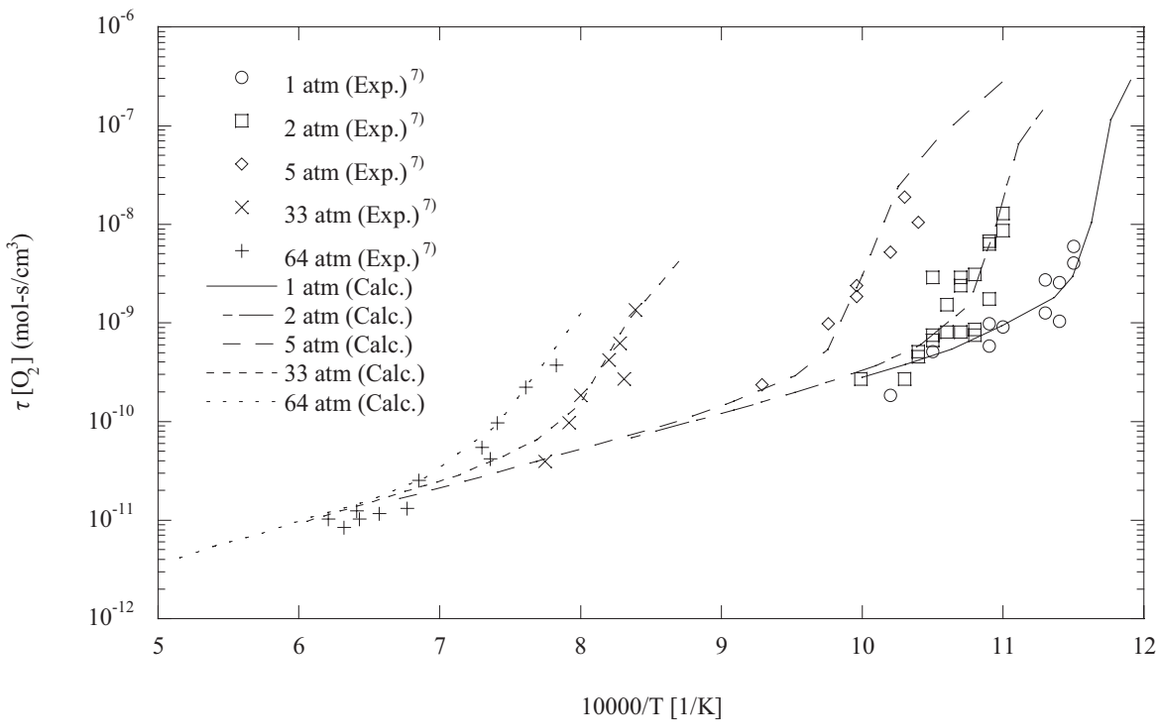

Fig. 3 The ignition delay time of numerical results and experimental data for the modified rate coefficient of $H+O_2+Ar \rightarrow HO_2+Ar$.

3.1.2 Sensitivity Analysis

The sensitivity analysis of ignition delay time is calculated at1and 64 atm under low and high temperature region. Figure 2 shows that the terminating reaction of $H+O_2+Ar \rightarrow HO_2+Ar$ is dominant effect on the ignition delay time near the low temperature region. Because of the rate coefficient of this reaction is inaccurate, the numerical results do not agree with the experimental data on the low temperature region. Therefore, the rate coefficient of the reaction $H+O_2+Ar \rightarrow HO_2+Ar$ is modified.

3.1.3 The Modification of the Rate Coefficient of $H+O_2+Ar \rightarrow HO_2+Ar$

The rate coefficient of $H+O_2+Ar \rightarrow HO_2+Ar$ in Koshi model is $k=5.40\times10^{16}T^{-0.41}$. The rate coefficient is assumed as $k=AT\exp(-E/RT)$. At first, the frequency factor A is changed at each pressure to fit the numerical results to the experimental data. Then, k is decided by the least square method based on the second explosion limit temperature. As a result, the rate coefficient of $H+O_2+Ar \rightarrow HO_2+Ar$ is $k=2.96\times10^{19}T^{-1.40}$. The comparison between the experimental data and the results calculated using the modified Koshi model are plotted in Fig. 3. The numerical results agree well with the experimental data.

3.1.4 The Comparison of the Present Rate Coefficient with Others

The rate coefficient of terminating reaction $H+O_2+Ar \rightarrow HO_2+Ar$ has large effect on the ignition delay time near the low temperature region. The rate coefficient of this reaction is also obtained by various experiments. The rate coefficient against inverse T is plotted in Fig. 4. The results calculated by original Koshi model and modified Koshi model, those by Michael et al.[10], and those by Baulch et

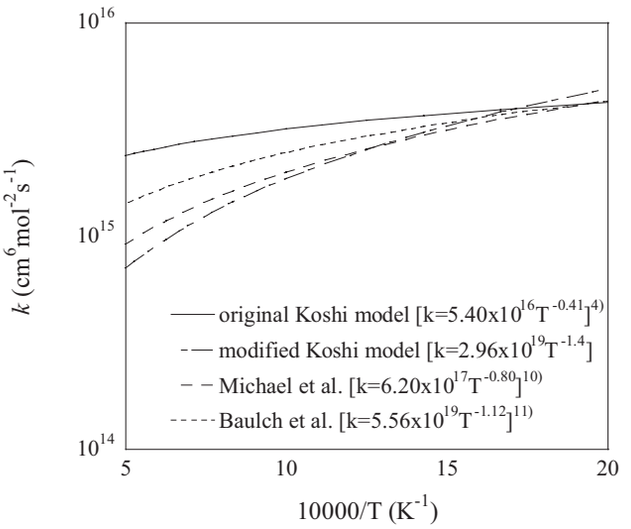

Fig. 4 The rate coefficient against 10000/T plots for H+O_2+Ar→HO_2+Ar at each rate coefficients.

al.[11] are shown in this figure. The modified Koshi model agrees well with others.

3.2 The Modification of the Rate Coefficient of the Reaction H+O_2+H_2O→HO_2+H_2O

3.2.1 Laminar Flame Velocity

The composition of initial gas mixtures are 23.33% H_2, 11.67% O_2, and 65% H_2O. The calculations were carried out at the temperature of 473 K and the pressure between 0.1 MPa and 5 MPa using modified Koshi model as shown in Sec. 2. The comparison between the present results and the experimental data measured by Kusharin et al. are shown in Fig. 6. The numerical results do not agree with the experimental data. Therefore, the sensitivity analysis of laminar flame velocity is carried out and the dominant reaction is determined to modify its rate coefficient.

3.2.2 Sensitivity Analysis

The results of sensitivity analysis at each pressure show that the terminating reaction of H+O_2+H_2O→HO_2+H_2O is dominant at1MPa. Because the rate coefficient of this reaction is inaccurate, the numerical results do not agree with the experimental data around1MPa. Therefore, the rate coefficient of H+O_2+H_2O→HO_2+H_2O is modified.

3.2.3 The Modification of the Rate Coefficient of H+O_2+H_2O→HO_2+H_2O

The rate coefficient of H+O_2+H_2O→HO_2+H_2O in original Koshi model is $k=2.50\times10^{17}T^{-0.40}$. At first the frequency factor is changed to fit the calculated results to the experimental data around1MPa. Then, k is decided by the least square method based on the second explosion limit temperature. Therefore, the modified rate coefficient is determined as $k=1.62\times10^{23}T^{-2.29}$. The experimental data and numerical results calculated using the modified Koshi model are plotted in Fig. 6. The numerical results agree with the experimental data over1MPa, however, they do not coincide under1MPa. This reason is that other elementary reactions would have large effects on the laminar flame velocity under1MPa. So far, the calculations of laminar flame velocity agree well with the experimental data under the region where the reaction H+O_2+H_2O→HO_2+H_2O is the dominant reaction.

4. Conclusion

In order to modify more reliable rate coefficient of H+O_2

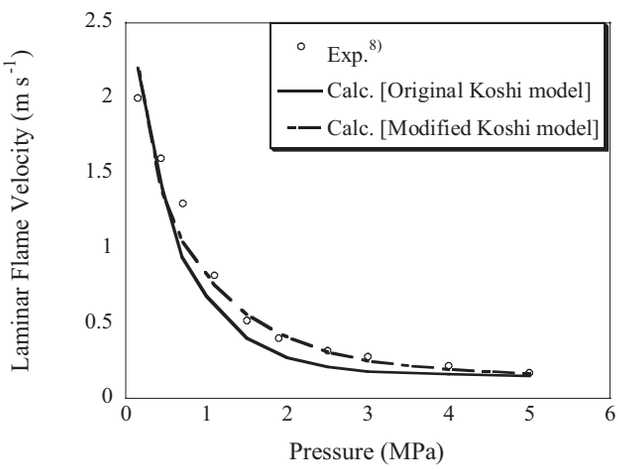

Fig. 6 The laminar flame velocity against pressure of the experimental data and numerical results.

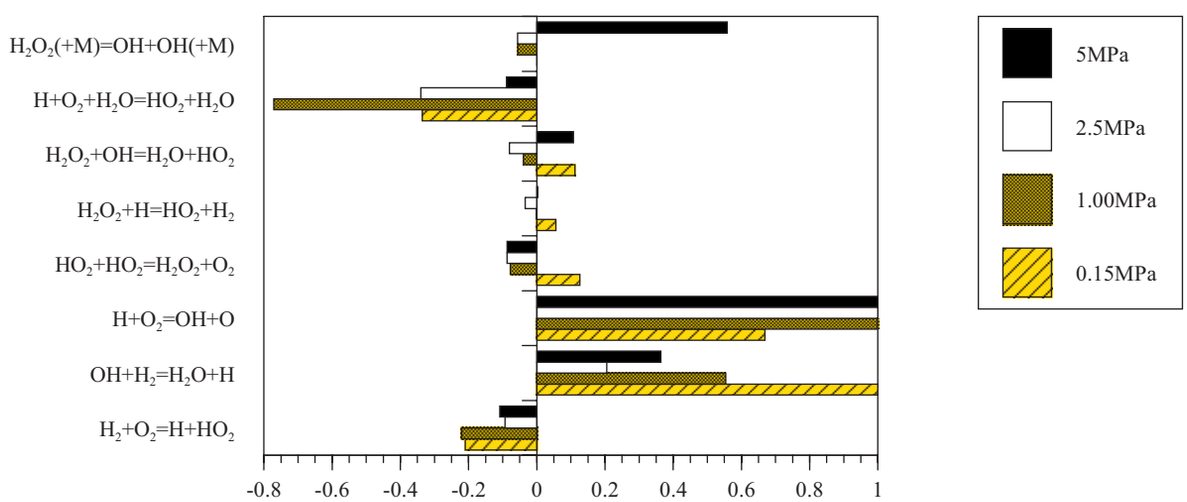

Fig. 5 The sensitivity analysis of laminar flame velocity from 0.15 to5MPa at 473 K.

+M=HO_2+M reaction, the calculations of ignition delay time and laminar flame velocity are carried out using CHEMKIN 4.1.1. The rate coefficients of the terminating reaction H+O_2+Ar→HO_2+Ar and H+O_2+H_2O→HO_2+H_2O are decided as $k=2.96\times10^{19}T^{-1.40}$ and $k=1.62\times10^{23}T^{-2.29}$, respectively. For the rate coefficient of H+O_2+Ar→HO_2+Ar, the numerical results of the ignition delay time agree well with the experimental data. By using new rate coefficient of H+O_2+H_2O→HO_2+H_2O, the numerical results of the laminar flame velocity agree well with the experimental data under the region where the reaction H+O_2+H_2O→HO_2+H_2O is the dominant reaction.

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素反応H+O_2＋M=HO_2＋M (M=Ar, H_2O)の速度定数の決定

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素反応H+O_2＋M＝HO_2＋Mの速度定数を決定するために，この素反応が支配的となる第二爆発限界近傍において，商用計算コードであるCHEMKIN4.1.1を用いて着火遅れ時間・層流燃焼速度を計算し，実験値との比較を行った。結果として，M＝Arの場合には$k=2.96\times10^{19}T^{-1.40}$，M＝$H_2O$の場合には$k=1.62\times10^{23}T^{-2.29}$が得られた。ここで得られた速度定数を用いて計算した結果，計算値は実験値と良い一致を示すことを確認した。したがって，得られた結果を素反応H+O_2＋M＝HO_2＋M (M＝Ar, H_2O)の速度係数として決定した。