

Numerical Study on Decoupling the Chemical and Thermal Effects of a Specific Elementary Reaction on the Laminar Flame Speed

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ABSTRACT

In a combustion system, some elementary reactions act in two folds: inhibiting combustion by scavenging active radicals (H, O, and OH) and promoting combustion by releasing lots of heat. Sometimes, it is meaningful to distinguish the size of the inhibition and promotion effects. To decouple the thermal and chemical effects of a concerned elementary reaction, a numerical study was conducted based on self-modified premix codes. The decoupling of the thermal and chemical effects on flame speed and temperature was achieved by using a self-modified function to calculate the generating rate of the targeted species in the considered elementary reaction and then deciding whether or not to include the contribution of target reaction when solving the component equations and the energy equations. This work takes the elementary reaction R812 ($\text{PO}_2 + \text{H} = \text{HOPO}$) in combustion system of dimethyl methylphosphonate (DMMP) in methane/air premixed flame as the research object. Results show that, with 0.1% DMMP addition, contribution of thermal effect to flame temperature is generally greater than that of the chemical effect. However, the contribution of thermal effect to flame speed is consistently smaller than that of the chemical effect. If ignoring the heat release from R812, the flame temperature reduces quickly to below 1700 K which will lead to flame extinguishing. Sensitivity analysis on the laminar flame speed reveals that the inhibition efficiency of chemical effect is greater than the promotion efficiency of thermal effect of R812.

KEYWORDS: Chemical effect; thermal effect; DMMP; flame suppressant.

INTRODUCTION

The production and use of the high efficient fire suppressant, Halon-1301 (CF_3Br), and some other Halogenated chlorofluorocarbons (CFCs) have been expressly prohibited, except for some specific application [1]. The huge demand of high-performance fire suppressants makes the researchers to focus on finding appropriate replacements. Phosphorus-containing compounds (PCCs) are recognized as potential replacements of the CFCs for its good performance in flame inhibition.

Generally, dimethyl methylphosphonate (DMMP) and trimethylphosphate (TMP) are the two common used PCCs in scientific research works because of the high saturated vapor pressure [2]. Hastie et al. [3] proposed the first version of the detailed chemical kinetic mechanism of PCCs in flames. Then, the mechanism was updated by Twarowski et al. [3-4] and Korobeinichev et al. [5-7]. Recently, Babushok et al. [8] updated the mechanism by adding three new elementary reactions. And according to the newly constructed mechanism, they found DMMP was approximately 6 times as efficient as CF_3Br in inhibiting the stoichiometric methane/air premixed flames at low concentrations. They also declared that DMMP worked as fuel in the lean mixtures according to the increase of flame temperature after DMMP addition. Bouvet et al. [9-10] proved that DMMP was

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more effective than Br_2 at low concentrations in extinguishing the co-flow diffusion flames. However, further addition of DMMP brought negligible marginal inhibition effect. Our early work [11] also proved the saturation effect of DMMP in extinguishing the diffusion flames. The peak concentration of OH radical in the flames kept almost the same at a high level with further addition of DMMP when the concentration of DMMP was larger than 0.36%.

According to the previous work [12], when it is used to suppress methane/air premixed Bunsen flames at $\phi = 0.9\text{--}1.2$, DMMP becomes less efficient in reducing the laminar burning velocities on a molar basis at high loadings. Further analysis of the reaction kinetic mechanism reveals that some of the phosphorus-containing elementary reactions scavenge active radicals (H, O, and OH) in the flame, leading to a decrease in the laminar flame speed; on the other hand, these reactions (e.g., R812: $\text{PO}_2 + \text{H} = \text{HOPO}$) release a considerable amount of heat which would accelerate the burning rate. The influences of the chemical and thermal effects of these reactions are opposite to each other in reducing the burning velocity. To illustrate the kinetic mechanism of the saturation effect on the inhibition efficiency of DMMP, it is inevitable to decouple and to compare the two effects to each other. Therefore, the present study is going to achieve this by modifying the Premix codes [13].

NUMERICAL APPROACH

Calculation conditions

Laminar flame speeds and sensitivity coefficients were calculated by the modified premixed codes. The modification methodology is discussed in next section. The mechanism used here was the same as used in [12], which was constructed by three sub-models: USC Mech Version II [14], PCCs sub-model extracted from [15] and the three reactions extracted from [8]. The GRAD and CURV factors were both set to 0.08. Convergence studies on the meshes indicated that such grid parameters gave a proper prediction of the flame speeds because further increasing the grids resulted in less than 1.5% difference in the flame speeds. All the calculations were performed at an initial temperature of 373 K and pressure of 1 atm.

Table 1. Operating conditions for simulations

Equivalence ratio (ϕ)	DMMP addition (X_a)			
	Including coupled effect flame speed	Including chemical effect flame speed	Including thermal effect flame speed	Sensitivity analysis
0.8	0-0.3%	0-0.3%	0-0.3%	N/A
0.9	0-0.3%	0-0.3%	0-0.3%	0-0.3%
1.0	0-0.3%	0-0.3%	0-0.3%	0.15%,0.2%
1.1	0-0.3%	0-0.3%	0-0.3%	N/A
1.2	0-0.3%	0-0.3%	0-0.3%	N/A

Table 1 gives the operating conditions for the numerical studies. Due to the fact that DMMP concentration is much smaller relative to those of methane and air, the DMMP concentration was approximately calculated as:

$$X_a = 100\% \frac{n_{\text{DMMP}}}{n_{\text{CH}_4} + n_{\text{air}}}, \quad (1)$$

where n_i is the moles of component i in the mixture. Sensitivity coefficients [16] with respect to the laminar flame speeds of major influential reactions were calculated as:

$$C_{s_b} = \frac{A_0 (S_1 - S_0)}{S_0 (A_1 - A_0)}, \quad (2)$$

where A is the pre-exponential factor of the Arrhenius rate expression, S is the laminar flame speed and the subscript 0, 1 represent the condition before and after modification of the pre-exponential factor, respectively.

Methodology

According to our previous calculations [12], it is found that reaction R812 is dominated in both thermal and chemical effects among the phosphorus-containing reactions. Therefore, this work focus on the chemical and thermal effects caused by reaction R812.

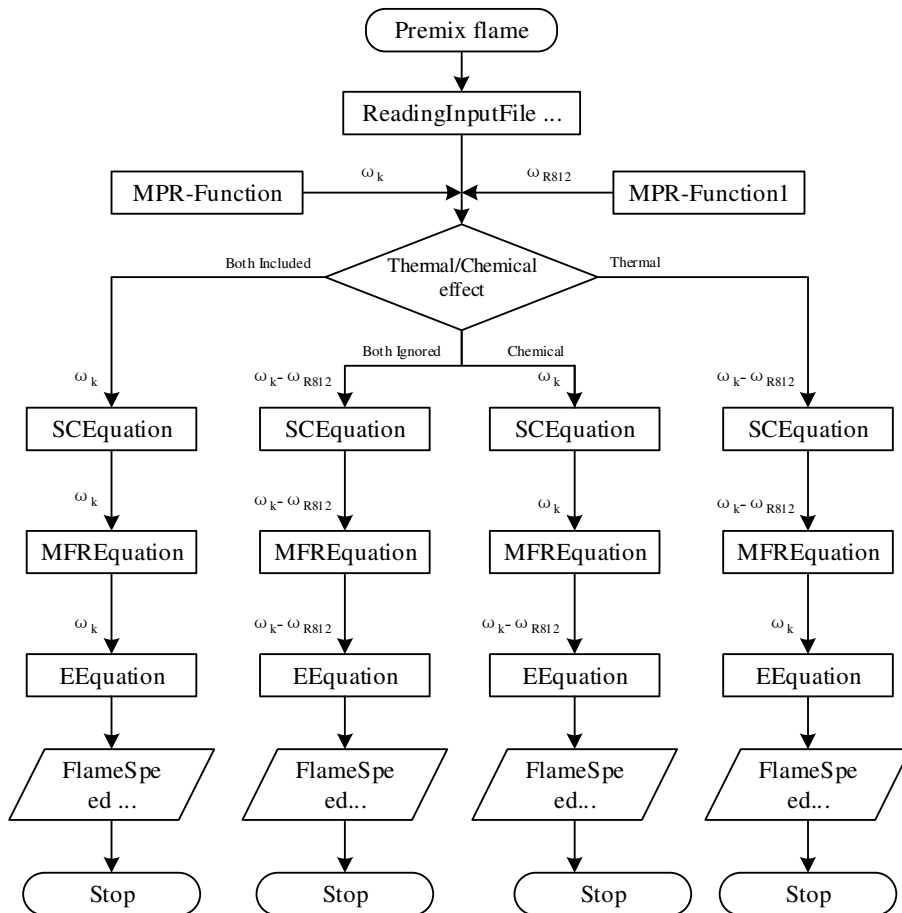


Fig. 1. Schematic flow chart of the premix code.

The premix codes calculate the heat release at some specific mesh point in the 1-D free propagating flame by summing up the products of the enthalpy of formation and the generating rate of the combustion products (including intermediate products). And the temperature is calculated according to the total heat release and the component types and quantities. On each middle point in the calculation domain, the Premix code solves the problem by firstly calculating the total chemical generating rate (ω_k) of each species; Then the code solves the species conservation equation

(SCEquation), the mass flow rate equation (MFREquation), the energy conservation equation (ECEquation), and other following equations one by one until the loop of the middle grid ends. To illustrate the methods of decoupling the thermal and chemical effects more intuitively, the schematic flow chart of the program is provided as shown in Fig. 1.

After reading the input files, allocating the initial mesh points and setting some other initial parameters, the program calls the molar production rates function (MPR-Function) to calculate the ω_k based on the pressure, temperature, and mass fractions. The original Premix code solves the problem using ω_k as shown by the first branch in Fig. 1. To decouple the chemical and thermal effects, we create a function (MPR-Function1) to calculating the chemical generating rates of the species related to R812 (ω_{R812}). The generating rates of the species caused by the other molecular reactions are set to zero in ω_{R812} . Then, according to the choice of considering which effects, we use different chemical generating rates to solve the three equations. When both of the two effects are ignored, $(\omega_k - \omega_{R812})$ is used to solve the three equations as indicated by the second branch in Fig. 1. When considering chemical effect and ignoring thermal effect, we use ω_k to solve the SCEquation and the MFREquation; however, $(\omega_k - \omega_{R812})$ is used to solve the EEquation. By doing so, the contributions of R812 to the species concentrations are taken into account, but the heat release from R812 is ignored. This working model is indicated by the third branch in Fig. 1. When only thermal effect is considered, $(\omega_k - \omega_{R812})$ is used to solve the SCEquation and MFREquation; but ω_k is used to solve the EEquation. In this case, the generating rates of the species by R812 are not take into account, but the heat release of R812 is considered. This working model is indicated by the forth branch in Fig. 1. After solving the three equations, the flowing calculation processes are the same.

RESULTS AND DISCUSSION

Validation of the self-modified codes

To evaluate the credibility of the modified premix codes, Fig. 2 shows the comparison of the calculated laminar flame speeds (including both the thermal and chemical effects) with the measured data extracted from the literature. As shown in Fig. 2a, the model predicts the laminar flame speeds very well for the stoichiometric and rich mixtures. Although the model overestimates the speeds for the lean mixtures, the discrepancy of the speeds is less than 3.5 cm/s. For the lean mixture doped with DMMP (Fig. 2b), the predicted speeds are consistently little bigger than the measurements. But for the stoichiometric premixed flames (Fig. 2c), the model predicted the speeds very well for a wide range of DMMP concentration. For the rich flames (Fig. 2d), the model worked well except for DMMP concentration varying from 0.1% to 0.25%. Despite of the discrepancy in specific conditions, the modified premix codes give a credible predictions of the laminar flame speeds and the changing trends of the inhibited methane/air premixed flames. Since the present study focuses on the mechanism study of decoupling the thermal and chemical effects of a specific elementary reaction, the accuracy of the modified premix codes is enough.

Thermal and chemical effects on flame with different equivalence ratio

Fig. 3 shows the thermal and chemical effect of R812 on the flame temperature and speeds. Owing to the high heat release rate of R812, the coupled effect of thermal and chemical effects on the flame temperature is positive (Dash line is higher than solid line in Fig. 3a). The temperature influenced by chemical effect alone increases unexpectedly first, then it decreases for flame at $\phi = 1.0$ and 1.1, and finally it increases again at $\phi = 1.2$. This can be attributed to the increase of heat release of the lean premixed flame with the increase of equivalence ratio. The second increase of temperature might be attributed to the heat release from R816 ($\text{HOPO} + \text{OH} = \text{PO}_2 + \text{H}_2\text{O}$) [12]. The coupled effect of thermal and chemical effects on the flame speed is negative (Dash line is lower than solid line in Fig. 3b). The flame speed influenced by chemical effect alone keeps decreasing with the increase of

equivalence ratio. The thermal effect influenced flames speed is about 2.5-3 times that of the chemical influenced for the lean flames. But for the stoichiometric and the rich flames, it becomes 6-8 times greater.

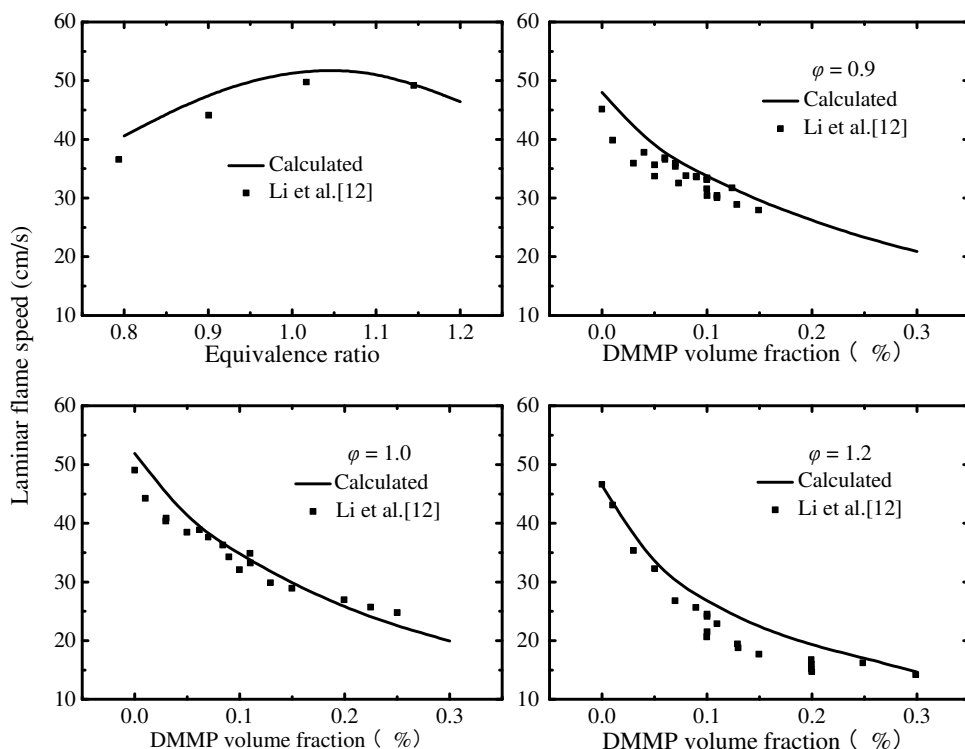


Fig. 2. Comparison of calculated laminar flame speeds with measured data extracted from literature.

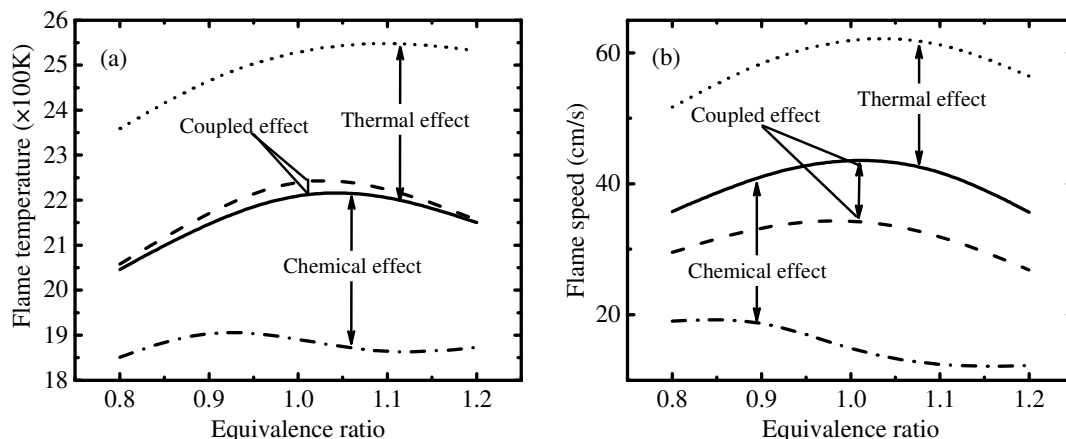


Fig. 3. Comparison of thermal and chemical effects of R812 on the flame temperature and speeds with 0.1% DMMP addition (Solid: both are ignored; Dash: both are included; Dash dot dot: only thermal effect is included; Dash dot: only chemical effect is included).

To more quantitatively discuss the contribution of the thermal and chemical effects, Fig. 4 shows the normalized contribution of each effect on the flames. The contribution on a specific parameter is

measured by the difference between the value influenced flame and that of the unaffected flame. Then the contribution is normalized by the value of the corresponding unaffected flame. The contribution of chemical effect first increases and then decreases with the increase of equivalence ratio. The maximum contribution of chemical effect is 16% (absolute value) at $\phi = 1.1$. As the equivalence ratio increase, the contribution of thermal effect first decreases and then increases with a minimum value of 14% at $\phi = 1.0$. The coupled effect is positive over the studied equivalence ratio and the maximum contribution is 1.6% at $\phi = 1.0$. The trends of thermal and chemical contributions to the flame speed are the same as that to flame speed. The contribution of coupled effect on flame speed increases slowly with the increase of equivalence ratio.

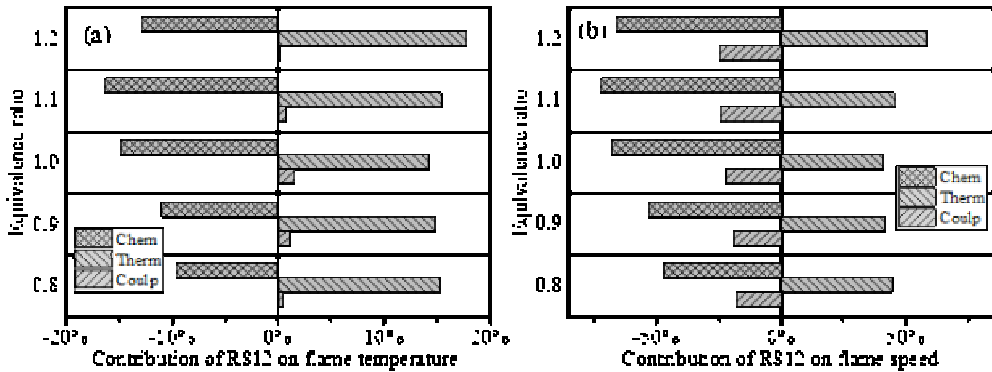


Fig. 4. Relative contribution of thermal, chemical and both effects of R812 to the flame temperature and speed of methane/air premixed flame (Chem: only chemical effect is included; Therm: only thermal effect is included; Coupl: both thermal and chemical effects are included).

Thermal and chemical effects on flame with different DMMP addition

The effects of heat release and H-scavenging of R812 as a function of DMMP concentration are illustrated in Fig. 5. Because of ignoring the heat release from R812, calculations only considering the chemical effect for flames inhibited with more than 0.2% DMMP (0.1% for the rich flame) are dead. So the corresponding data are missing in Fig. 5.

When the chemical effect is included in the calculation, the flame speeds all decrease with the increase of DMMP addition. Conversely, the flame speeds calculated by the model which only considers the thermal effect increase with DMMP addition. The decline rates of the flame speeds calculated by the models which consider the chemical effect are greater than the increasing rate calculated by considering the thermal effect. However, the trend of the flame temperature is just the opposite. By considering the thermal effect, all the temperature increase with DMMP addition. When both the thermal and chemical effects are considered, the temperature increases for the lean flames, but it increases first and then decreases with DMMP addition for the stoichiometric and rich flames. The increasing rate of the flame temperature calculated by the model which considers the thermal effect is greater than the decline rate calculated by considering the chemical effect. An interesting phenomenon is that the increasing rate of temperature declines when the DMMP concentration is greater than 0.1%. This might be attributed to that there was a balance between the heat release rate of the flame and the heat loss rate due to convection.

Sensitivity analysis

To further explain the thermal and chemical effects of R812 on the flame speed, Fig. 6 shows the sensitivity coefficients of R812 of flame speeds for lean flames. Duo to the chemical effect is too strong, the stoichiometric and rich flames with more than 0.15% DMMP addition are extinguished when only considering the chemical effect. Therefore, here only the sensitivity analysis for the lean

flames is provided. When both thermal and chemical effects are included, the negative sensitivity coefficients keep decreasing with DMMP concentration increasing, which indicates the inhibition efficiency of R812 keeps growing. But the decline speed is much slower than that for the model only including the chemical effect. Meanwhile, the decline of the coefficients for chemical effect is bigger than the increase for the thermal effect. Furthermore, the sum of the coefficients for the thermal and chemical effect is much smaller than that for the model including both the two effects, which means the effect of heat release is greater than that of H-scavenging for R812 on the lean premixed methane/air flame speeds.

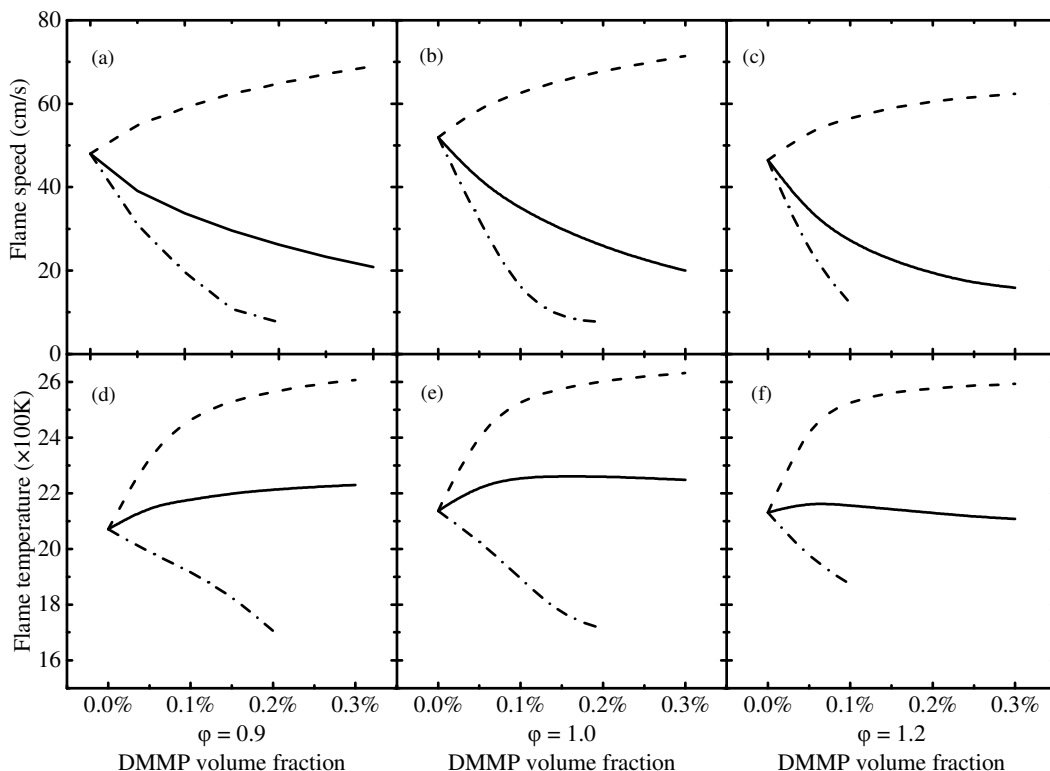


Fig. 5. Decoupling of the effects of R812 on flame speeds and temperature of methane/air premixed flames with different DMMP addition (Solid line: both thermal and chemical effects are included; Dash line: only thermal effect is included; Dash dot line: only chemical effect is included).

CONCLUSION

To decouple the thermal and chemical effects of an elementary reaction, a numerical study was conducted based on self-modified premix codes. The decoupling of the thermal and chemical effects on flame speed and temperature is achieved by saving the generating rates of target species in the considered elementary reaction to an added array and then deciding whether or not to include the contribution of target reaction when solving the component equations and the energy equations. The main conclusions are summarised as follow:

(1) With 0.1% DMMP addition, thermal effect is generally greater than chemical effect on flame temperature; however, the flame speed shows a higher dependency on chemical effect than on thermal effect.

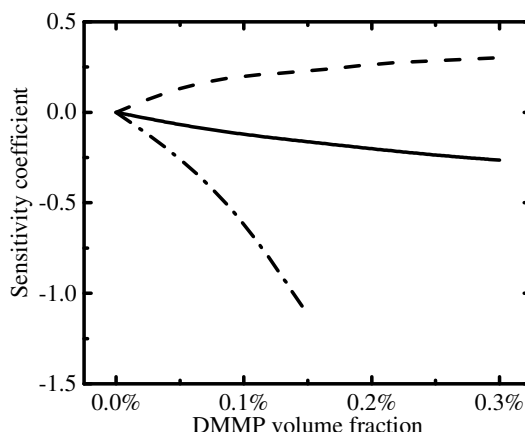


Fig. 6. Sensitivity coefficients of flame speeds for $\phi = 0.9$ flames with different DMMP concentration (Solid line: both thermal and chemical effects are included; Dash line: only thermal effect is included; Dash dot line: only chemical effect is included).

(2) Sensitivity analysis, in consideration of the laminar flame speed, reveals that the inhibition efficiency of chemical effect is greater than the promotion efficiency of thermal effect of R812.

(3) If ignoring the thermal effect of R812, the flame temperature reduces quickly to below 1700 K which cannot sustain a flame.

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REFERENCES

- [1] K.M. Sarma, G.M. Bankobeza, The Montreal Protocol on Substances that Deplete the Ozone Layer, U. Nations (Ed.), Kenya, USA, 2000.
- [2] Fan, C.L., Wang, L.S., Vapor Pressure of Dimethyl Phosphite and Dimethyl Methylphosphonate, J. Chem. Eng. Data 55 (2010) 479-481.
- [3] J.W. Hastie, D.W. Bonnell, Molecular Chemistry of Inhibited Combustion Systems, National Bureau of Standards Information Report, US, 1980.
- [3] A.J. Twarowski, The Influence of Phosphorus Oxides and Acids on the Rate of $H + OH$ Recombination, Combust. Flame 94 (1993) 91-107.
- [4] A.J. Twarowski, Reduction of a Phosphorus Oxide and Acid Reaction Set, Combust. Flame 102 (1995) 41-54.
- [5] O.P. Korobeinichev, S.B. Ilyin, V.M. Shvartsberg, A.A. Chernov, The Destruction Chemistry of Organophosphorus Compounds in Flames—I: Quantitative Determination of Final Phosphorus-containing Species in Hydrogen-oxygen Flames, Combust. Flame 118 (1999) 718-726.
- [6] O.P. Korobeinichev, V.M. Shvartsberg, A.A. Chernov, The Destruction Chemistry of Organophosphorus Compounds in Flames—II: Structure of a Hydrogen-oxygen Flame Doped with Trimethyl Phosphate, Combust. Flame 118 (1999) 727-732.
- [7] O.P. Korobeinichev, S.B. Ilyin, T.A. Bolshova, V.M. Shvartsberg, A.A. Chernov, The Chemistry of the Destruction of Organophosphorus Compounds in Flames—III: The Destruction of DMMP and TMP in a Flame of Hydrogen and Oxygen, Combust. Flame 121 (2000) 593-609.

- [8] V.I. Babushok, G.T. Linteris, V.R. Katta, F. Takahashi, Influence of Hydrocarbon Moiety of DMMP on Flame Propagation in Lean Mixtures, *Combust. Flame* 171 (2016) 168-172.
- [9] N. Bouvet, G. Linteris, V. Babushok, F. Takahashi, V. Katta, R. Krämer, Experimental and Numerical Investigation of the Gas-phase Effectiveness of Phosphorus Compounds, *Fire Mater.* 40 (2016) 683-696.
- [10] N. Bouvet, G.T. Linteris, V.I. Babushok, F. Takahashi, V.R. Katta, R. Krämer, A Comparison of the Gas-phase Fire Retardant Action of DMMP and Br₂ in Co-flow Diffusion Flame Extinguishment, *Combust. Flame* 169 (2016) 340-348.
- [11] W. Li, Y. Jiang, Y. Jin, L. Wang, W. Xu, Experimental Study of the Influence of Dimethyl methylphosphonate on Methane/air Coflow Diffusion Flames Using OH-PLIF, *Fuel* 235 (2019) 39-44.
- [12] W. Li, Y. Jiang, Y. Jin, X.L. Zhu, Investigation of the Influence of DMMP on the Laminar Burning Velocity of Methane/air Premixed Flames, *Fuel* 235 (2019) 1294-1300.
- [13] R.J. Kee, J.F. Grcar, M.D. Smooke, J.A. Miller, E. Meeks, PREMIX: A FORTRAN Program for Modeling Steady Laminar One-Dimensional Premixed Flames, Sandia national laboratories, Livermore CA, 1998.
- [14] H. Wang, X. You, A.V. Joshi, S.G. Davis, A. Laskin, F. Egolfopoulos, C.K. Law, USC Mech Version II. http://ignis.usc.edu/USC_Mech_II.htm.
- [15] T.M. Jayaweera, C.F. Melius, W.J. Pitz, C.K. Westbrook, O.P. Korobeinichev, V.M. Shvartsberg, A.G. Shmakov, I.V. Rybitskaya, H.J. Curran, Flame Inhibition by Phosphorus-containing Compounds over a Range of Equivalence Ratios, *Combust. Flame* 140 (2005) 103-115.
- [16] C. Luo, B.Z. Dlugogorski, E.M. Kennedy, Influence of CF₃I and CBrF₃ on Methanol–Air and Methane–Air Premixed Flames, *Fire Technol.* 44 (2008) 221-237.