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Flame Inhibition by Trimethylphosphate: Skeletal Mechanism and Modeling

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Abstract

On the basis of a multi-step kinetic mechanism for flame inhibition by organophosphorus compounds including more than 200 reactions, a reduced skeletal mechanism for flames inhibition by trimethylphosphate (TMP) was developed. The mechanism consists of 22 irreversible elementary reactions, involving 9 phosphorus-containing species. The developed mechanism was validated by comparing the modeling results with measured and simulated (using the starting initial mechanism) speed and chemical structure of H_2/O_2 and CH_4/O_2 flames doped with TMP. The mechanism was shown to satisfactorily predict the speed of $H_2/O_2/N_2$ flames with various dilution ratios and CH_4/air flames doped with TMP. Besides, the skeletal mechanism satisfactorily predicts the spatial variation of H and OH radicals and final phosphorus-containing products of the inhibitor combustion. The mechanism is implemented in a fluid dynamics code intended for simulation of subsonic laminar and turbulent flames.

Introduction

Organophosphorous compounds have recently received much attention as a basis for prospective fire extinguishing agents. They possess high flame suppression efficiency, both in the gaseous state and when delivered in the form of aerosols. In the context of CFD modeling, detailed kinetic models including large numbers of species and reactions are often of limited use because of very high computational overheads, especially for realistic (diesel, aviation) fuels. Therefore, global and reduced kinetic schemes are of particular interest because they have lower computational requirements. Such mechanisms have been developed for different fuels, including, for example, hydrogen [1], methane [2], syngas [3]. In contrast to hydrocarbon fuels, only few reduced mechanisms for flame inhibition have been proposed so far. Based on the results of comprehensive studies, including the structure of premixed and diffusive flames of hydrogen, methane and propane doped with organophosphorus compounds (OPCs, speed and limits of flame propagation) [4], a detailed mechanism for flame inhibition by phosphorus-containing species (PCSs) has been proposed [5].

The goal of the present research was to work out a skeletal mechanism with a minimum number of stages for inhibition of hydrogen and methane flames by trimethylphosphate (TMP). As a starting mechanism, we took the previously developed detailed mechanism for flame inhibition by OPCs [4, 5]. Primarily we expect the developed mechanism to be able to predict the speed of hydrogen and methane flames with appropriate accuracy. The mechanism is implemented in CFD program which enables calculation of laminar and turbulent flames.

Development of the Mechanism

The mechanism for flames inhibition by OPCs [4, 5] was taken as a starting mechanism for developing the skeletal mechanism. The mechanism [4, 5] was developed by collecting the maximum number of elementary reactions involving PCCs. Besides PCCs-involving reactions this mechanism includes submechanisms for combustion of hydrogen, methane and propane. Overall, the mechanism consists of 682 steps for 121 species, 44 of which contain P-atoms. The general reaction scheme of PCCs-involving reactions [5] contained submechanisms for TMP and dimethyl methylphosphonate (213 reactions). Since the overall number of steps is high, the influence of most of them on the speed, structure and other characteristics of flames have not been studied so far, especially for reactions involving P_2O_3, P_2O_4, P_2O_5 and organophosphorus intermediates.

The skeletal mechanism was developed by the analysis of the crucial reactions having the most significant effect on the speed of hydrogen and methane flames. Also, the mechanism is supposed to preserve the main pathways of transformation of TMP to final PCCs. The developed skeletal mechanism for flame inhibition is presented in Table 1.

Validation of the Mechanism

Validation of the developed mechanism was performed by comparing the measured and calculated speed of $H_2/O_2/N_2$ and CH_4/air flames doped with TMP. The flames simulation was performed using the starting [5] and skeletal mechanism (Table 1). Mechanism [5], except the phosphorus-involving reactions, contains a submechanism for oxidation of propane, methane and hydrogen. For the flames simulation using the skeletal mechanism was completed with submechanism for fuel oxidation from [5].

Figure 1 shows the speed of $H_2/O_2/N_2$ flames doped with 400 ppm TMP at a pressure 1 bar versus the equivalence ratio (symbols are experiments, dashed line is the detailed mechanism, solid line is skeletal mechanism). The inhibition effectiveness of H_2/air flames by TMP is too low, therefore, the flames with the dilution ratio $D=[O_2]/([O_2]+[N_2])=0.1$, 0.09 and 0.077 were chosen for the mechanism validation. Both mechanisms provide a good agreement with the experimental data [6] for flames with D=0.1 and 0.09. The speed of the most diluted flame (D=0.077) is predicted less accurately (discrepancy up to 35%), due to low flame speed (10 cm/s and less) and lower accuracy of measurements. Some disagreements between modeling results are observed for rich flames with D=0.1 and 0.09 and for lean flame with D=0.077.

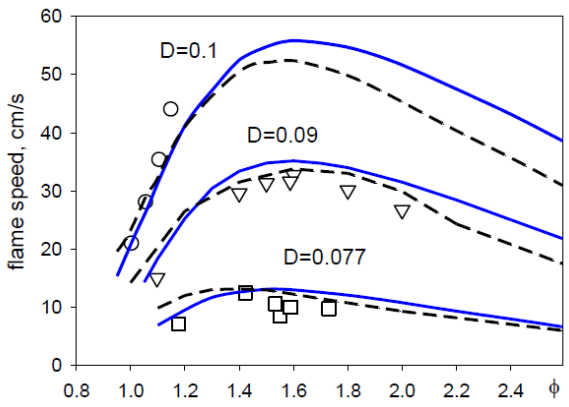

Fig. 1

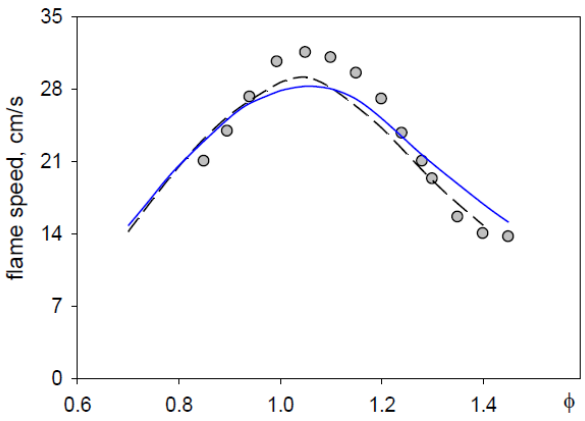

Fig. 2

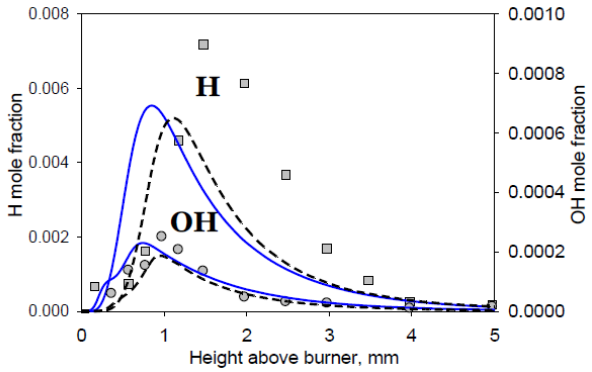

Fig. 3

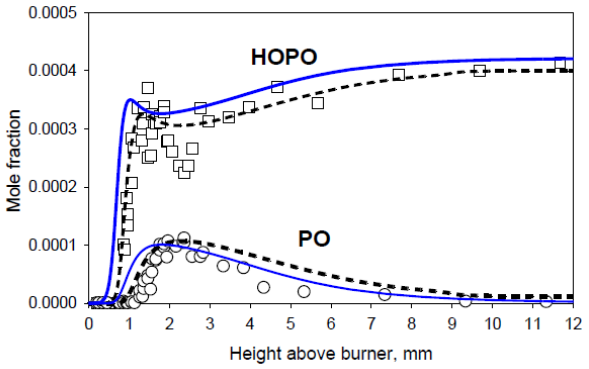

Fig. 4

Figure 2 shows the speed of atmospheric-pressure CH_4/air flames doped with 600 ppm TMP versus the equivalence ratio (symbols are experiments, dashed line is the detailed mechanism, solid line is skeletal mechanism). Both mechanisms predict close values of the flames speed, which differ only for the richest flames. Experimentally measured speed of CH_4/air/TMP flames [7] are well predicted by both mechanisms (discrepancy does not exceed 15%). So, the skeletal mechanism satisfactorily predicts the speed of TMP-doped hydrogen and methane flames at atmospheric pressure.

Figure 3 shows spatial variations of concentration of H and OH radicals in atmospheric pressure $H_2/O_2/N_2$ flame with ϕ=1.6, D=0.09 doped with 400 ppm TMP. Concentrations were measured using molecular-beam mass spectrometry in near adiabatic flame stabilized on a flat burner using the heat flux method [6]. The simulated profiles using both mechanisms are in satisfactory agreement, and the measured OH concentration profile is well predicted by both mechanisms. As to H atom concentration, in experiment its maximum is noticeably higher than that predicted by modeling. However, as the error in measuring active species using is about 50%, the agreement can be considered satisfactory. Figure 4 shows the spatial variation of final products of TMP combustion PO and HOPO in $H_2/O_2/N_2$ flame with ϕ=1.6, D=0.09 doped with 400 ppm TMP at 1 bar. The results of experiment and modeling are in perfect agreement, considering very low concentration of PCCs.

Implementation of the Mechanism

The skeletal mechanism developed was implemented in a CFD program intended for calculation of laminar and turbulent flames and their extinguishment by organophosphorous compounds. The program is an extended version of CFD code which was applied earlier for simulation of flame and fire extinguishment [8] using a single global reaction with empirical factor accounting for the effect of extinguishing agent.

Conclusions

By reducing the starting multi-step mechanism [5], we have elaborated a skeletal mechanism for flames inhibition by TMP, consisting of 22 irreversible elementary reactions. The developed mechanism satisfactorily predicts the speed and structure of TMP-doped hydrogen and methane flames at atmospheric pressure. It follows from satisfactory agreement between modeling using both mechanisms and experiment that most of the key reactions are included in the skeletal mechanism and all these reactions satisfactorily predict the inhibition process by TMP. Further reduction of the skeletal mechanism (Table 1) without modifying the rate constants recommended in the starting mechanism [5] resulted in noticeable disagreement of the flames speed and structure.

Table 1. Skeletal mechanism for flame inhibition by TMP (*units are mole-cm-s and cal/mole*)

#	Reaction	A	n	E
1	$PO(OCH_3)_3+H=>PO(OCH_3)_2(OCH_2)+H_2$	2.20×10^{9}	1.5	7140.0
2	$PO(OCH_3)_2(OCH_2)+H=>PO(OCH_3)_3$	1.50×10^{14}	0.0	0.0
3	$PO(OCH_3)_2(OCH_2)=>PO(OCH_3)_2+CH_2O$	2.00×10^{12}	0.0	38950.0
4	$PO(OCH_3)_2=>CH_3OPO_2+CH_3$	4.00×10^{13}	0.0	36000.0
5	$CH_3OPO_2+H=>CH_2OPO_2+H_2$	7.20×10^{8}	1.5	4860.0
6	$CH_3OPO_2+OH=>CH_2OPO_2+H_2O$	3.60×10^{6}	2.0	-1000.0
7	$CH_2OPO_2=>CH_2O+PO_2$	2.00×10^{13}	0.0	21000.0
8	$PO_2+OH+M=>HOPO_2+M$	1.60×10^{24}	-2.3	285.0
9	$HOPO+O+M=>HOPO_2+M$	1.20×10^{27}	-3.0	2040.0
10	$HOPO_2+H=>PO_2+H_2O$	5.16×10^{19}	-1.8	10726.0
11	$PO_2+H_2O=>HOPO_2+H$	3.56×10^{10}	0.4	18567.8
12	$PO_2+H+M=>HOPO+M$	5.36×10^{24}	-2.0	645.0
13	$HOPO+H=>H2+PO_2$	1.00×10^{13}	0.0	11000.0
14	$H_2+PO_2=>HOPO+H$	7.18×10^{8}	1.2	21409.1
15	$HOPO+O=>OH+PO_2$	1.00×10^{13}	0.0	0.0
16	$HOPO+OH=>PO_2+H_2O$	1.80×10^{6}	2.0	-1500.0
17	$PO_2+H_2O=>HOPO+OH$	1.14×10^{4}	2.8	24538.7
18	$PO+OH=>H+PO_2$	1.00×10^{13}	0.0	0.0
19	$H+PO_2=>PO+OH$	2.09×10^{17}	-0.9	19691.7
20	$PO+O2=>PO_2+O$	1.00×10^{12}	0.0	0.0
21	$HOPO+H=>H_2O+PO$	3.00×10^{12}	0.0	8300.0
22	$H_2O+PO=>HOPO+H$	9.10×10^{5}	1.7	14647.0

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