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## Confirmation of paper submission

Berlin, 28. April 2014

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methylphosphate  
**Program:** Laminar flames  
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## Skeletal Mechanism for Flames Inhibition by Trimethylphosphate

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### Abstract

On the basis of a multi-step kinetic mechanism for flames inhibition by organophosphorus compounds including more than 200 reactions, a reduced skeletal mechanism for flames inhibition by trimethylphosphate was developed. The mechanism consists of 22 irreversible elementary reactions, involving 9 phosphorus-containing species.

### Introduction

At present, methods of computational fluid dynamics are being intensively developed makes it possible to study 3D dynamics of fire propagation and suppression, including the case when the inhibitors and fire suppressants are used. The models used in these simulations involve fluid dynamics and also consider phase and chemical transformations of the substances.

The chemical processes are usually described by detailed mechanisms that can include thousands of elementary reactions involving hundreds of chemical species. Up to date, many skeletal and reduced mechanisms for combustion of some fuels have been elaborated.

Against the background of multiple skeletal and reduced mechanisms for combustion of hydrogen and many hydrocarbons, only few reduced mechanisms for flame inhibition have been proposed. 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) [1-6], speed and limits of flame propagation, a detailed mechanism for flame inhibition by phosphorus-containing species (PCSs) has been proposed [7]. Later [4] this mechanism was modified for predicting speed and structure of atmospheric-pressure hydrogen flames doped with TMP.

In this connection, the works [8, 9] should be mentioned. Basing on mechanism [7] the authors developed two different skeletal mechanisms for atmospheric-pressure propane/air inhibition by dimethyl methylphosphonate (DMMP). The first skeletal mechanism [8] includes 268 elementary reactions involving 57 species and the second one [9] includes 356 steps involving 65 species. Both mechanisms were validated by comparing the speed of DMMP-doped propane flames ( $\phi=0.8-1.3$ ) calculated using mechanism [12] and the skeletal mechanisms. Besides, authors [8, 9] compared simulated concentration profiles of radicals.

In spite of a good predictive ability of the developed mechanism, following limitations should be pointed out. Authors [8, 9] have not listed the reactions comprising the mechanisms; therefore, PCCs-involving reactions and their number remain unknown. Also the authors do not compare modeling results with experimental data that could provide more validations of the developed mechanisms.

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



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by trimethylphosphate (TMP). As a starting mechanism, we took the previously developed detailed mechanism for flame inhibition by OPCs [8, 12]. Primarily we expect the developed mechanism to be able to predict the speed of hydrogen and methane flames with appropriate accuracy.

## Approach

For numerical modeling PREMIX code from CHEMKIN package was used. The element pathways were calculated using FluxViewer software.

## Results and Discussion

### *Development of the Mechanism*

The mechanism for flames inhibition by OPCs [2, 7] was taken as a starting mechanism for developing the skeletal mechanism. The mechanism [3, 7] 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 [7] 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 are unstudied. In the first turn, it comes under reactions involving  $P_2O_3$ ,  $P_2O_4$ ,  $P_2O_5$  and organophosphorus intermediates. Besides, the starting mechanism contains some identical reactions with different rate constants. It is noteworthy that the authors [3] focused their attention on improvement of the kinetic parameters of reactions of the so-called small PCCs, i.e. phosphorus oxides and acids with one phosphorus atom in their molecules. It is explained by the prevailing viewpoint that these reactions are responsible for removal of active species from the flame. It follows from the above that the starting mechanism contains a high potential its reduction.

Earlier [10] eight crucial reactions responsible for the inhibition of hydrocarbon flames were identified. When studying the peculiarities of inhibition of TMP-doped  $H_2/O_2/N_2$  flames at atmospheric pressure [4, 5], ten PCCs-involving crucial reactions, which have the strong effect the flames speed, were revealed using the sensitivity analysis. The specific feature of inhibition of atmospheric-pressure hydrogen flames by TMP was shown to be the participation of TMP and some organophosphorus intermediated in recombination of radicals. Four reactions involving small PCCs also contribute to removal of the active flame species but these reactions play a less important role as compared with those involving OPCs, especially in the less diluted flames. In hydrocarbon flames, OPCs-involving reactions do not make any noticeable contribution to inhibition of hydrocarbon flames if they do not limit formation of small PCCs.

The calculated rates of production of TMP have demonstrated that its consumption mainly proceeds via its interaction with H atom while its formation occurs via recombination of  $PO(OCH_3)_2(OCH_2)$  with H atom. The sum of the net rates of these two reactions approximately coincides with the total rate of production of TMP. Our investigations have demonstrated these 2 reactions to play key role inhibition of hydrogen flames at 1 bar. The consumption of  $PO(OCH_3)_2(OCH_2)$  was shown mainly to proceed via its thermal destruction, yielding  $PO(OCH_3)_2$  and formaldehyde  $CH_2O$ . Taking into account the high sensitivity of the hydrogen flames speed to these reactions  $TMP$   $PO(OCH_3)_2(OCH_2)$   $PO(OCH_3)_2$ , we included them in the skeletal

mechanism (steps 1-3, Table 2). Further transformation of organophosphorus intermediates in PO<sub>2</sub> is described by 4 reactions (steps 4-7, Table 2). Selection of exactly these reactions was made based on P-element fluxes from species to species (Fig. 1) and by calculating net reaction rates of phosphorus-involving reactions versus the flames zone. In the starting mechanism reactions 1-7 were considered as irreversible but calculation of the rates of direct and reverse reactions (using Mechmode software [11]) has demonstrated the reverse reactions to be neglected.

We have included 10 reactions involving small PCCs into the skeletal mechanism. The calculations demonstrated that steps 8, 9, 12, 15, and 20 can be considered as irreversible reactions but for the remaining ones both direct and reverse reactions should be considered. For these reactions, the rate constants of reverse reactions were calculated using the Mechmode software [11]. Direct and reverse reactions are given in Table 2 as separate reactions equations: 10 and 11, 13 and 14, 16 and 17, 18 and 19, 21 and 22.

Table 2. The developed skeletal mechanism for flames inhibition.

#	Reaction	A*	n	E*
1	PO(OCH <sub>3</sub> ) <sub>3</sub> +H=>PO(OCH <sub>3</sub> ) <sub>2</sub> (OCH <sub>2</sub> )+H <sub>2</sub>	2.20×10 <sup>9</sup>	1.5	7140.0
2	PO(OCH <sub>3</sub> ) <sub>2</sub> (OCH <sub>2</sub> )+H=>PO(OCH <sub>3</sub> ) <sub>3</sub>	1.50×10 <sup>14</sup>	0.0	0.0
3	PO(OCH <sub>3</sub> ) <sub>2</sub> (OCH <sub>2</sub> )=>PO(OCH <sub>3</sub> ) <sub>2</sub> +CH <sub>2</sub> O	2.00×10 <sup>12</sup>	0.0	38950.0
4	PO(OCH <sub>3</sub> ) <sub>2</sub> =>CH <sub>3</sub> OPO <sub>2</sub> +CH <sub>3</sub>	4.00×10 <sup>13</sup>	0.0	36000.0
5	CH <sub>3</sub> OPO <sub>2</sub> +H=>CH <sub>2</sub> OPO <sub>2</sub> +H <sub>2</sub>	7.2010× <sup>8</sup>	1.5	4860.0
6	CH <sub>3</sub> OPO <sub>2</sub> +OH=>CH <sub>2</sub> OPO <sub>2</sub> +H <sub>2</sub> O	3.60×10 <sup>6</sup>	2.0	-1000.0
7	CH <sub>2</sub> OPO <sub>2</sub> =>CH <sub>2</sub> O+PO <sub>2</sub>	2.00×10 <sup>13</sup>	0.0	21000.0
8	PO <sub>2</sub> +OH+M=>HOPO <sub>2</sub> +M	1.60×10 <sup>24</sup>	-2.3	285.0
9	HOPO+O+M=>HOPO <sub>2</sub> +M	1.20×10 <sup>27</sup>	-3.0	2040.0
10	HOPO <sub>2</sub> +H=>PO <sub>2</sub> +H <sub>2</sub> O	5.16×10 <sup>19</sup>	-1.8	10726.0
11	PO <sub>2</sub> +H <sub>2</sub> O=>HOPO <sub>2</sub> +H	3.56×10 <sup>10</sup>	0.4	18567.8
12	PO <sub>2</sub> +H+M=>HOPO+M	5.36×10 <sup>24</sup>	-2.0	645.0
13	HOPO+H=>H <sub>2</sub> +PO <sub>2</sub>	1.00×10 <sup>13</sup>	0.0	11000.0
14	H <sub>2</sub> +PO <sub>2</sub> =>HOPO+H	7.18×10 <sup>8</sup>	1.2	21409.1
15	HOPO+O=>OH+PO <sub>2</sub>	1.00×10 <sup>13</sup>	0.0	0.0
16	HOPO+OH=>PO <sub>2</sub> +H <sub>2</sub> O	1.80×10 <sup>6</sup>	2.0	-1500.0
17	PO <sub>2</sub> +H <sub>2</sub> O=>HOPO+OH	1.14×10 <sup>4</sup>	2.8	24538.7
18	PO+OH=>H+PO <sub>2</sub>	1.00×10 <sup>13</sup>	0.0	0.0
19	H+PO <sub>2</sub> =>PO+OH	2.09×10 <sup>17</sup>	-0.9	19691.7
20	PO+O <sub>2</sub> =>PO <sub>2</sub> +O	1.00×10 <sup>12</sup>	0.0	0.0
21	HOPO+H=>H <sub>2</sub> O+PO	3.00×10 <sup>12</sup>	0.0	8300.0
22	H <sub>2</sub> O+PO=>HOPO+H	9.10×10 <sup>5</sup>	1.7	14647.0

\* – Units are mole-cm-s and cal/mole

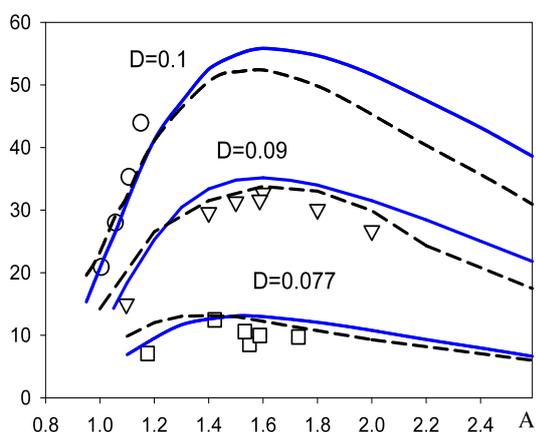
### Validation of the Mechanism

Validation of the developed mechanism was performed by comparing the measured and calculated speed of H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> and CH<sub>4</sub>/air flames doped with TMP. The flames simulation was performed using the starting [7] and skeletal mechanism (Table 2). Mechanism [7], 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 [7].

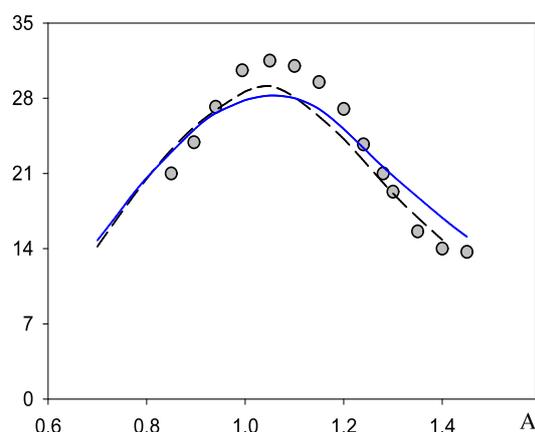
Figure 1 shows the speed of H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> flames doped with 400 ppm TMP at a pressure 1 bar versus the equivalence ratio. The inhibition effectiveness of

H<sub>2</sub>/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 [4] for flames with  $D=0.1$  and  $0.09$ .

Figure 2 shows the speed of atmospheric-pressure CH<sub>4</sub>/air flames doped with 600 ppm TMP versus the equivalence ratio. Both mechanisms predict close values of the flames speed, which differ only for the richest flames. Experimentally measured speed of CH<sub>4</sub>/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. Prediction of chemical structure of a flame especially of concentration profiles of labile species is a stringent test for a reaction mechanism.



The speed of atmospheric-pressure H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub>/TMP (400 ppm) flames with various dilution ratios ( $D$ ) versus the equivalence ratio ( $\phi$ ); symbols – experiment, dashed line – modeling using mechanism [12], solid line – modeling using the skeletal mechanism.



The speed of atmospheric-pressure CH<sub>4</sub>/air/TMP (600 ppm) flame versus the equivalence ratio ( $\phi$ ); symbols – experiment, dashed line – modeling using mechanism [12], solid line – modeling using the skeletal mechanism.

## Conclusions

By reducing the starting multi-step mechanism [12], 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. Attempts of further reduction of the skeletal mechanism (Table 2) without modifying the rate constants recommended in the starting mechanism resulted in noticeable disagreement of the flames speed and structure.

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