

Influence of Hydrocarbon Moiety of DMMP on Flame Propagation in Lean Mixtures*

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Full-length article

Shortened running title: Effect of Hydrocarbon Moiety of DMMP on Flame

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Abstract

Phosphorus-containing compounds (PCCs) have been found to be significantly more effective than CF₃Br for reducing burning velocity when added to stoichiometric hydrocarbon-air flames. However, when added to lean flames, DMMP (dimethylmethylphosphonate) is predicted to increase the burning velocity. The addition of DMMP to lean mixtures apparently increases the equivalence ratio (fuel/oxidizer) and the combustion temperature, as a result of hydrocarbon content of DMMP molecule. Premixed flames studies with added DMMP, OP(OH)₃, and CF₃Br are used to understand the different behavior with varying equivalence ratio and agent loading. Decrease of the equivalence ratio leads to the decrease of inhibition effectiveness of PCCs relative to bromine-containing compounds. For very lean mixtures CF₃Br becomes more effective inhibitor than PCCs. Calculations of laminar burning velocities for pure DMMP/air mixtures predict the maximum burning velocity of 10.5 cm/s at 4.04 % of DMMP in air and at an initial temperature of 400 K. Adiabatic combustion temperature is 2155 K at these conditions.

Keywords: DMMP, PCCs, CF₃Br, flame inhibition, fire suppressants

1. Introduction

Phosphorus-containing compounds (PCCs) are highly effective flame inhibitors and they are used as fire suppressant compounds as well as fire retardants which are added to polymers to reduce their flammability. PCCs have been considered as possible replacement compounds for Halon 1301 (CF₃Br) [1-3]. DMMP (dimethylmethylphosphonate, OP(CH₃)(OCH₃)₂) is used as a flame retardant for polyurethane foam, polyurethane resin, epoxy resin and other plastic materials, and it was also considered as an effective fire retardant additive to lithium electrolyte batteries [4]. Because of its effectiveness, low toxicity, and convenient vapor pressure, DMMP is often used as a model compound for studies of the inhibition effectiveness and kinetic mechanism of PCCs. Detailed kinetic models for hydrocarbon-air flame inhibition by DMMP have been developed [5-8] and the inhibition mechanism has been investigated and validated through experiments and numerical modeling [5-11].

The DMMP molecule has a rather large hydrocarbon component. Thus, the fuel moiety of DMMP might decrease its inhibition effectiveness for lean mixtures, as has been observed for other inhibitors with significant hydrocarbon components [12, 13]. Also, it is possible that DMMP itself, in mixtures with air, is flammable and has measurable burning velocity. While some of the most effective flame inhibitors (e.g., iron pentacarbonyl [14], methylcyclopentadienyl manganese tricarbonyl [15]) are flammable, they are usually added at trace concentrations, at which their hydrocarbon component does not significantly affect the inhibition process. Since rather high concentrations of DMMP are required to extinguish co-flow diffusion flames, it is of value to examine the performance of DMMP at those high concentrations, explore the importance of fuel contributions of the hydrocarbon component of DMMP at those conditions, and compare these features with those of other inhibitors which do not have the same fuel component, or do not contain phosphorus (e.g., $\text{OP}(\text{OH})_3$ and CF_3Br).

The approach in the present work is to study the inhibition features of DMMP in lean and very lean methane/air mixtures close to the flammability limits, where the contribution of the hydrocarbon part of the DMMP molecule to the flame propagation is most important. To this end we analyze the effect of DMMP on the laminar burning velocity in lean and stoichiometric methane/air mixtures as a function of fire suppressant agent concentration and initial flame equivalence ratio. For comparison, we also analyze the influence of $\text{OP}(\text{OH})_3$ (phosphoric acid, H_3PO_4) and CF_3Br . The former is a product/intermediate species of phosphorus containing compounds in flames, and the latter is a typical flame inhibitor often used as a benchmark compound. Finally, we analyze the combustion properties of mixtures of pure DMMP in air.

2. Kinetic model and calculation procedure

Modeling studies were conducted for methane-air flames inhibited by DMMP, H_3PO_4 and CF_3Br . The hydrocarbon mechanism employed is GRI-mech 3.0 [16], and that for the reactions of the DMMP in hydrocarbon flames is from Jayaweera et al. [5]. Three additional reactions were added to the phosphorus part of mechanism: $\text{PO} + \text{HCO} = \text{HPO} + \text{CO} - 222 \text{ kJ/mol}$, $\text{PO}_2 + \text{HCO} = \text{HOPO} + \text{CO} - 255 \text{ kJ/mol}$ and $\text{PO}_3 + \text{HCO} = \text{HOPO}_2 + \text{CO} - 406 \text{ kJ/mol}$. Rate constants were assumed to be the same as the overall rate constant for reaction $\text{NO}_2 + \text{HCO} = \text{products}$ [17]. Calculations demonstrate that the effect of these reactions is small: varying these rate constants by more than an order of magnitude changes ~~in~~ the burning velocities by less than 1 % (in contrast to bromine or iodine systems, in which the reaction $\text{Br} + \text{HCO} = \text{CO} + \text{HBr}$ has a noticeable effect on burning velocity). The variation of the rate constants by more than an order of magnitude demonstrates the lack of sensitivity of the results to these rate constants. For the flame inhibition by $\text{C}_3\text{H}_2\text{F}_3\text{Br}$, the relevant reactions of bromine- and fluorine-species from a $\text{C}_3\text{H}_2\text{F}_3\text{Br}$ flame-inhibition model was employed [12]. The Chemkin set of programs of Sandia Laboratory was used for combustion equilibrium calculations and for modeling laminar premix flames.

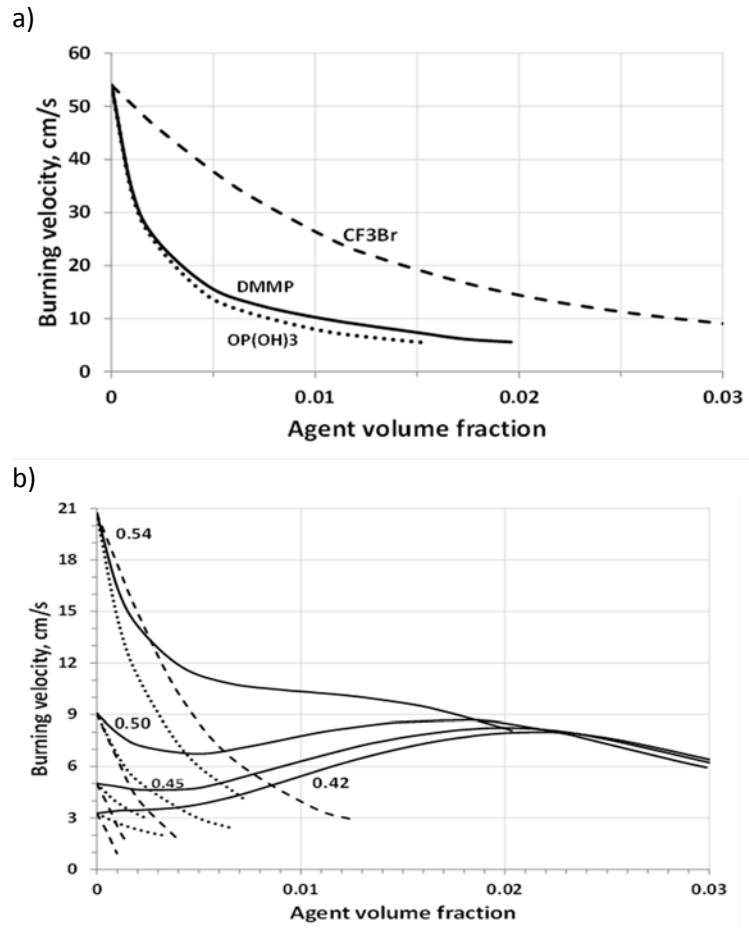
The kinetic models for flame inhibition by DMMP (and other PCCs) have been validated in other work [5-7, 9]. In the present work, we made additional comparisons of the predicted burning velocity with experimental data for TMP [18] and H_3PO_4 [19], and found a reasonable agreement.

3. Results and discussion

For each of the additives, DMMP, CF_3Br and $\text{OP}(\text{OH})_3$, burning velocity calculations were performed for a range of equivalence ratios ϕ , and for initial temperature 373 K. Figure 1 shows the calculated burning velocity of methane/air flames at the indicated initial

stoichiometry, as a function of the agent volume fraction X_a in the mixture. The top frame shows stoichiometric flames, and the bottom frame shows; lean flames. Note that the equivalence ratio refers to that of the methane-air mixture prior to addition of the flame inhibitor. Two general features of the results in Figure 1 are discussed below: 1) the apparent promotion effect of DMMP when added to lean flames; and 2) the switching in the ranking of effectiveness between CF_3Br and $\text{OP}(\text{OH})_3$ with stoichiometry.

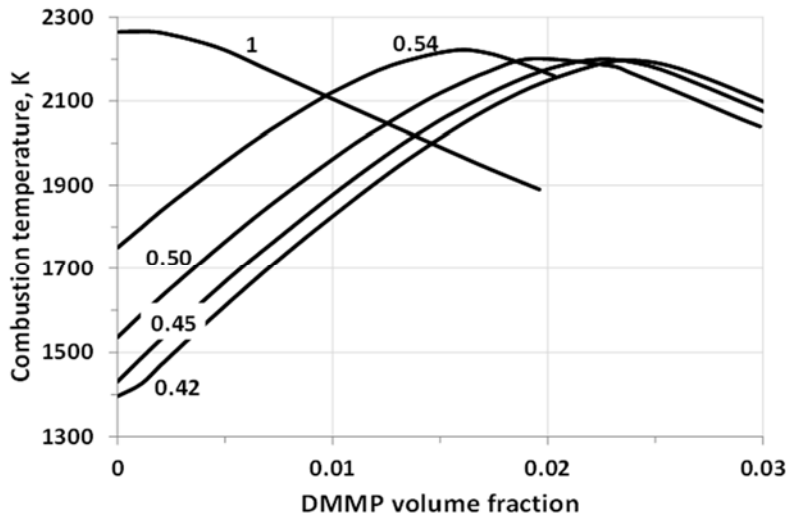
Figure 1. Dependence of laminar burning velocity on inhibitor volume fraction at different equivalence ratios: a.) stoichiometric CH_4/air mixture; b.) lean mixtures (initial temperature 373 K; solid line: DMMP; dotted line: $\text{OP}(\text{OH})_3$; dashed line: CF_3Br)



As indicated in Figure 1, for stoichiometric mixtures (upper frame) with agents added at volume fractions less than about 0.002 volume fraction, both DMMP and $\text{OP}(\text{OH})_3$ are about six

times more effective than CF_3Br . However, the phosphorus compounds experience the reduction in marginal effectiveness with increased volume fraction more severely than does CF_3Br . Moreover, for the initially lean mixtures (lower frame), the effectiveness of DMMP decreases severely with decrease in ϕ , and for lean enough conditions, adding DMMP can actually increase rather than decrease the burning velocity. This result has been observed for other flame inhibitors that also have a hydrocarbon component (for example, $\text{C}_3\text{H}_2\text{F}_3\text{Br}$ [12], $\text{C}_6\text{F}_{12}\text{O}$ [20], and C_2HF_5 [12]), and has been attributed to the effect of the increase in flame temperature caused by agent-supplied fuel species addition. For example, Figure 2 shows the adiabatic flame temperature T_{ad} of methane/air mixtures of different initial equivalence ratios, as a function of the DMMP volume fractions. As indicated, DMMP addition increases T_{ad} by up to 800 K, to values nearly the same as the stoichiometric methane-air system itself, whereas $\text{OP}(\text{OH})_3$ or CF_3Br addition to lean mixtures does not increase T_{ad} .

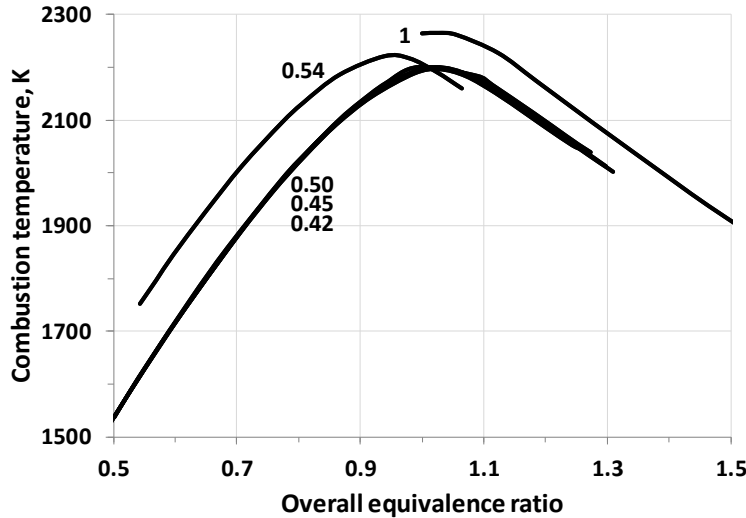
Figure 2. Dependence of the adiabatic combustion temperature on the DMMP concentration at different equivalence ratios (CH_4/air mixture, initial temperature 373 K).



To demonstrate additionally the fuel effect, we can re-plot Figure 2 using the “overall” equivalence ratio as the X-axis instead, taking into account the fuel properties of DMMP. It was assumed that the main combustion products of DMMP are HOPO_2 (or $\text{OP}(\text{OH})_3$), CO_2 and H_2O .

Figure 3 contains the same data as Figure 2 using the overall equivalence ratio as abscissa. It shows that the mixture of methane and DMMP demonstrates the maximum adiabatic temperature close to the overall equivalence ratio 1. Differences in the maximum temperatures and some shifts from the overall equivalence ratio 1 are the result of different heats of combustion of methane and DMMP, and due to the simplified set of assumed combustion products for DMMP. It is of interest that for mixtures with hydrocarbon equivalence ratios below 0.5 the dependencies of combustion temperatures on the overall equivalence ratio are close (Fig. 3).

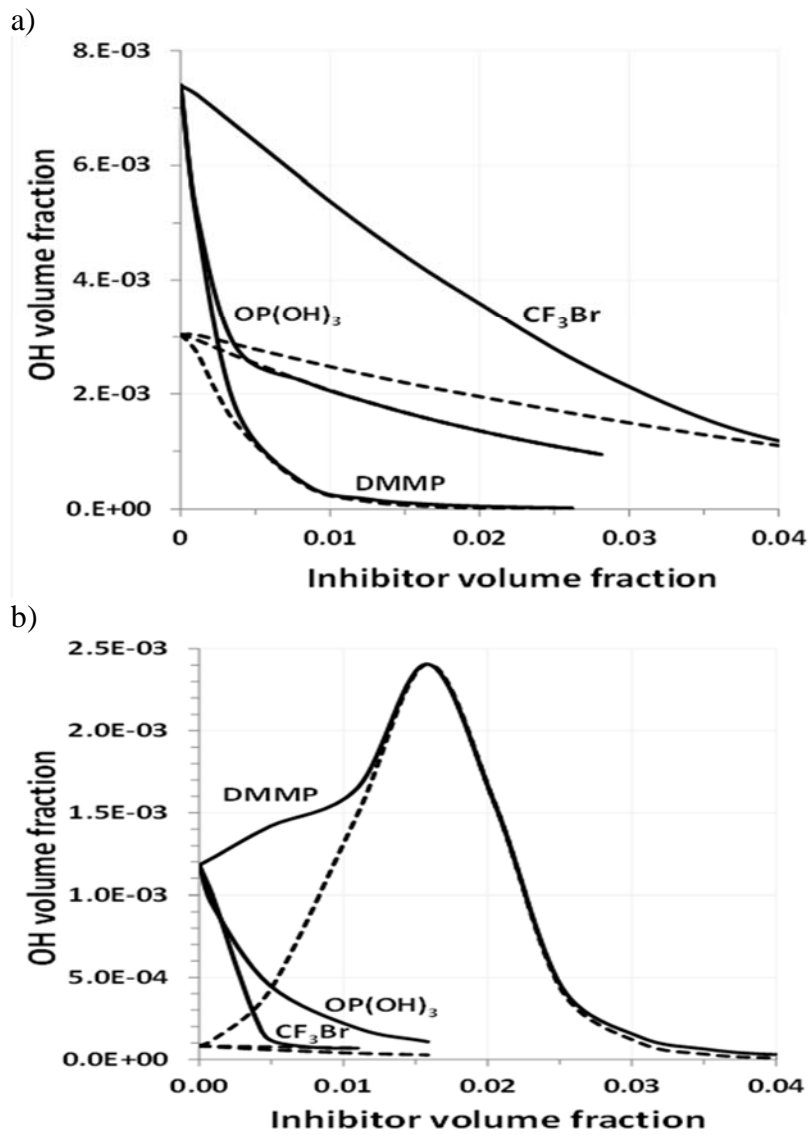
Figure 3. Dependence of the adiabatic combustion temperature on the “overall” equivalence ratio for CH₄-air mixtures of different “hydrocarbon” equivalence ratios (CH₄-DMMP-air mixtures, initial temperature 373 K).



The effect of added DMMP on the radical pool reveals the reasons for the loss of effectiveness with its addition to lean flames. For example, Figure 4 shows the peak and equilibrium volume fraction of OH radical in a premixed flame as a function of X_a , with added DMMP, OP(OH)₃, or CF₃Br (top frame is for flames with $\phi=1.0$ and bottom, $\phi=0.55$). For the stoichiometric flames, the radicals (H, OH, O) are driven to their equilibrium values for values of X_a between 0.005 and 0.01 for either DMMP or OP(OH)₃, whereas for CF₃Br, $X_a=0.04$ is

necessary. That is, the catalytic radical recombination cycle for the phosphorus compounds is about 6 times as effective for the phosphorus compound as for the brominated compound.

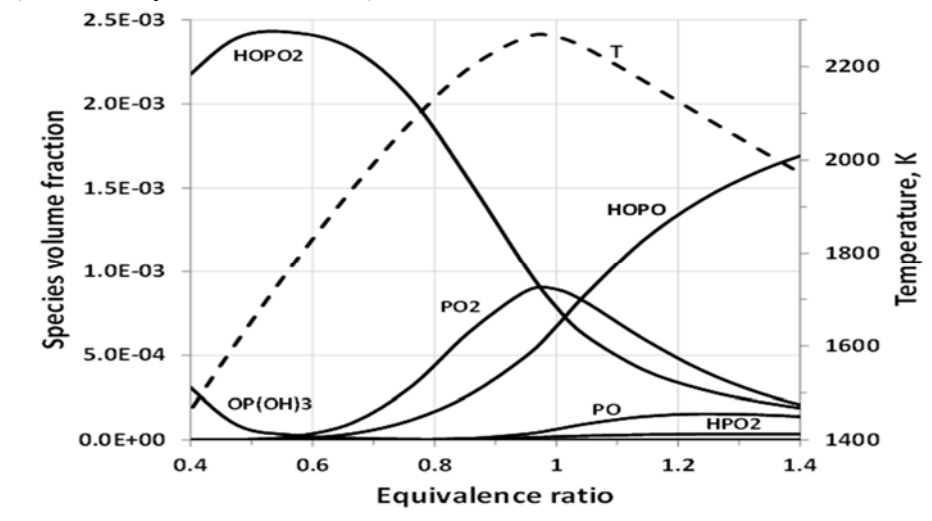
Figure 4. Maximum (solid lines) and equilibrium (dashed lines) OH volume fraction in a premixed methane-air flame with added DMMP, $\text{OP}(\text{OH})_3$, or CF_3Br : a.) stoichiometric flame; b.) lean flame (equivalence ratio: 0.55).



The behavior for the lean flames, however, is different. While the peak and equilibrium concentrations of the radicals is much lower for these lean flames with $X_{\text{O}}=0$, addition of DMMP dramatically increases the equilibrium concentrations of H, O, and OH (due to the temperature increase with DMMP addition to lean flames), and even increases the peak value of radical

concentrations. The catalytic cycles still drive the radical concentrations to their equilibrium values, but the equilibrium concentrations have increased so much that the net effect is higher radical concentrations for OH with DMMP addition than without (Fig. 4). Also, for the lean flames, about twice as much DMMP is needed to drive the peak values to the equilibrium values than was required for the stoichiometric flames. With $\text{OP}(\text{OH})_3$ addition, the quantity of agent required to drive the radicals to equilibrium is about the same as with DMMP; however, the equilibrium radical volume fractions are not increased with agent addition, so the peak values are much lower than with DMMP addition. For CF_3Br addition to lean mixtures, there is no increase in the equilibrium values (they decrease slightly primarily due to lower T_{ad} with CF_3Br addition), and the radical concentrations are driven to equilibrium at a much lower value of X_{a-f} due to the higher efficiency of the Br catalytic cycle at the lower temperature of the lean flames [21].

Figure 5. Equilibrium concentrations vs. equivalence ratio of a phosphorus-containing species in the combustion products of methane/air flame with DMMP added at a volume fraction of 0.25 % (initial temperature — 373 K).



As described above, $\text{OP}(\text{OH})_3$ is more effective than CF_3Br at higher values of ϕ , and less effective at lower ϕ . Since addition of either agent has little effect on T_{ad} , the switch in relative effectiveness is related to the reaction mechanism. The increased effectiveness of the bromine

cycle may be part of the reason. In addition, the phosphorus cycle becomes less effective for leaner flames, as described previously [5, 9]. For example, Figure 5 shows the equilibrium concentrations of phosphorus species in a methane-air mixture as a function of equivalence ratio. As indicated, [HOPO] decreases and [HOPO₂] increases for leaner flames. The result of this is illustrated in Figure 6, which shows the catalytic radical recombination cycles of the phosphorus species. In that figure, the relative contribution of PO₂ \rightleftharpoons HOPO₂ cycle is increased as compared to the HOPO \rightleftharpoons PO₂, for the lean flames compared to stoichiometric. The cycle PO₂ \rightleftharpoons HOPO₂ accounts for about 37 % of the catalytic radical consumption for the lean flames, but only 11 % in the stoichiometric flames. As it was indicated in [5], the interplay of HOPO and HOPO₂ cycles can also be interpreted as interplay of phosphorus chemistries of different degree of oxidation, which reflects, to some extent, different reactivity of phosphorus containing species. HOPO cycle involves phosphorus species of valence of 3, and cycle, HOPO₂ \rightleftharpoons PO₂, involves HOPO₂ species of valence of 5. The decrease of temperature and equivalence ratio increases the relative contribution of the HOPO₂ cycle and increases relative contribution of phosphorus chemistry of oxidized state of 5.

Figure 6. The major reaction pathways of phosphorus-containing species in main reaction zone of a methane/air flame (inhibition cycles HOPO₂ \rightleftharpoons PO₂ \rightleftharpoons HOPO; level of reaction presentation —15 %; initial DMMP volume fraction was of about 0.2 %). Arrows connect the reactants and products of a reaction; the species next to the arrow is the reaction partner, and the number adjacent is the fraction (in %) of the overall consumption rate of the first reactant in that reaction. Diagram is based on the integrated rates through the flame reaction zone.

a) Stoichiometric mixture

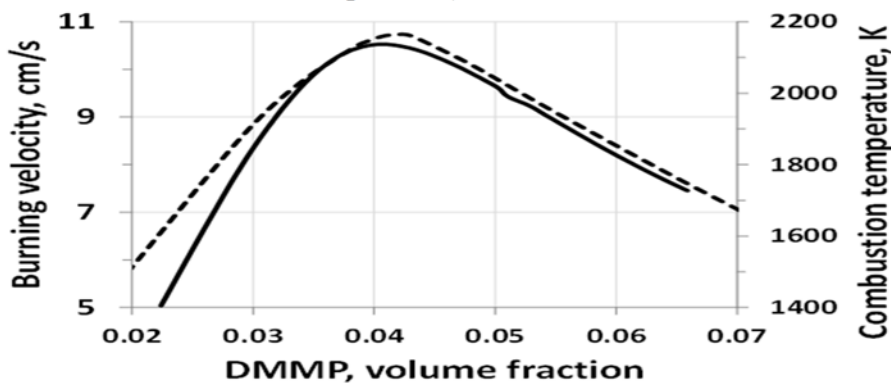


b) Equivalence ratio – 0.45



Because of the high hydrocarbon content of DMMP it is of interest to estimate burning velocities of pure mixtures of DMMP with air. Figure 7 shows the dependence of burning velocity and adiabatic combustion temperature on the DMMP concentration for a DMMP/air mixture initially at 400 K and 101 kPa. The maximum burning velocity (10.5 cm/s) occurs at a DMMP volume fraction of approximately 4.04 %, at which $T_{ad} = 2155$ K. The maximum adiabatic temperature (2165 K) occurs at DMMP volume fraction of 4.11 %. It is of interest that these concentrations of DMMP are close to stoichiometry of propane/air mixtures (4.03 %, of C_3H_8). Adiabatic flame temperature of propane is 2253 K at stoichiometric conditions. If we assume that the main P-containing product is the phosphoric acid $OP(OH)_3$ (or $HOPO_2$), stoichiometric concentration of DMMP in air is close to the stoichiometric propane concentration.

Figure 7. Dependence of burning velocity and adiabatic combustion temperature of DMMP/air mixture on the DMMP concentration (initial temperature: 400 K; solid line: burning velocity; dashed line: combustion temperature)



4. Conclusions

When added at volume fractions of less than 0.002, DMMP or $\text{OP}(\text{OH})_3$ are about six times as effective as CF_3Br for reducing the burning velocity of stoichiometric methane-air flames; however, at volume fractions closer to those required for extinguishing co-flow diffusion flames (several percent), the performance of DMMP is close to that of CF_3Br . Moreover, for lean flames, addition of DMMP increases rather than decreases the burning velocity (and increases the combustion temperature). The reason was found to be the fuel effect of the hydrocarbon moiety of the DMMP molecule. For either stoichiometric or lean flames, the phosphorus radical recombination cycles drive the chain-carrying radicals towards their equilibrium values. However, for DMMP addition to the lean flames, the equilibrium radical concentration of H and OH is increased, so that there is little benefit from radical recombination. This behavior was not observed for CF_3Br or $\text{OP}(\text{OH})_3$, which reduced the burning velocity of lean flames.

The phosphorus compound $\text{OP}(\text{OH})_3$ is more effective than CF_3Br in stoichiometric flames, but less effective for lean flames. The reasons are possibly the increased effectiveness of the bromine cycle at lower temperature, and the decreased effectiveness of the phosphorus cycles at lean conditions. Flame equilibrium and laminar burning velocity calculations confirm the relative decrease in the contribution of the inhibition cycle $\text{HOPO} \rightleftharpoons \text{PO}_2$ with the decrease of the equivalence ratio (and combustion temperature) in comparison with inhibition cycle $\text{HOPO}_2 \rightleftharpoons \text{PO}_2$.

The calculations of burning velocity over a range of DMMP concentrations (pure DMMP/air mixtures, 400 K initial temperature) predict a peak value of 10.5 cm/s at $X_{\text{DMMP}}=0.0404$ volume fraction, which is slightly leaner than that for peak T_{ad} (2165 K, at $X_{\text{DMMP}} = 0.0411$). For studying flame inhibition by phosphorus compounds, consideration should be

given to the fuel effect of the hydrocarbon component of the inhibitor molecule. This can be done by examining the effect of the agent in both stoichiometric and very lean flames.

Acknowledgements. The work was supported under the Cooperative Agreement by the National Institute of Standards and Technology with FXT Consulting, LLC.

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Figure captions:

Figure 1. Laminar burning velocity dependence as a function of inhibitor volume fraction at different equivalence ratios (a – stoichiometric CH₄/air mixture; b- lean mixtures; initial temperature – 373 K; solid line – DMMP; dotted line – OP(OH)₃; dashed line – CF₃Br)

Figure 2. Dependence of the adiabatic combustion temperature on the DMMP concentration at different equivalence ratios (CH₄/air mixture, initial temperature 373 K).

Figure 3. Dependence of the adiabatic combustion temperature on the “overall” equivalence ratio for CH₄-air mixtures of different “hydrocarbon” equivalence ratios (CH₄-DMMP-air mixtures, initial temperature 373 K).

Figure 4. Maximum (solid lines) and equilibrium (dashed lines) OH volume fraction in a premixed methane-air flame with added DMMP, OP(OH)₃, or CF₃Br (a – stoichiometric flame; b – lean flame, equivalence ratio – 0.55).

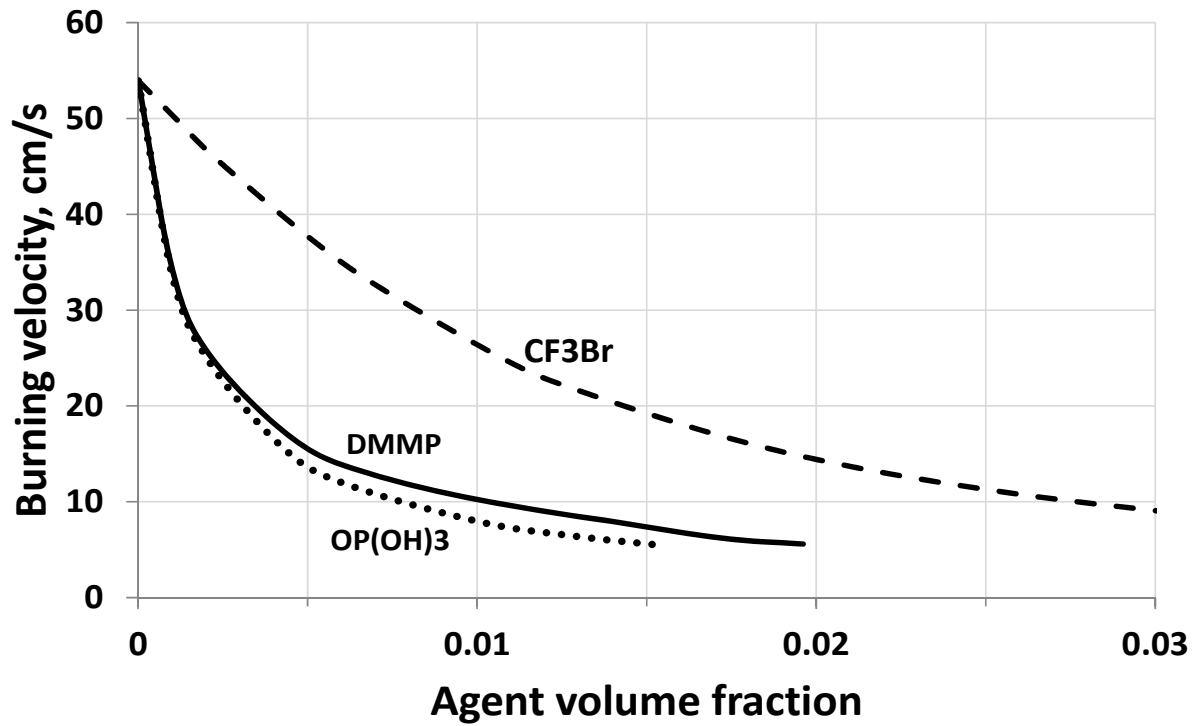
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a)



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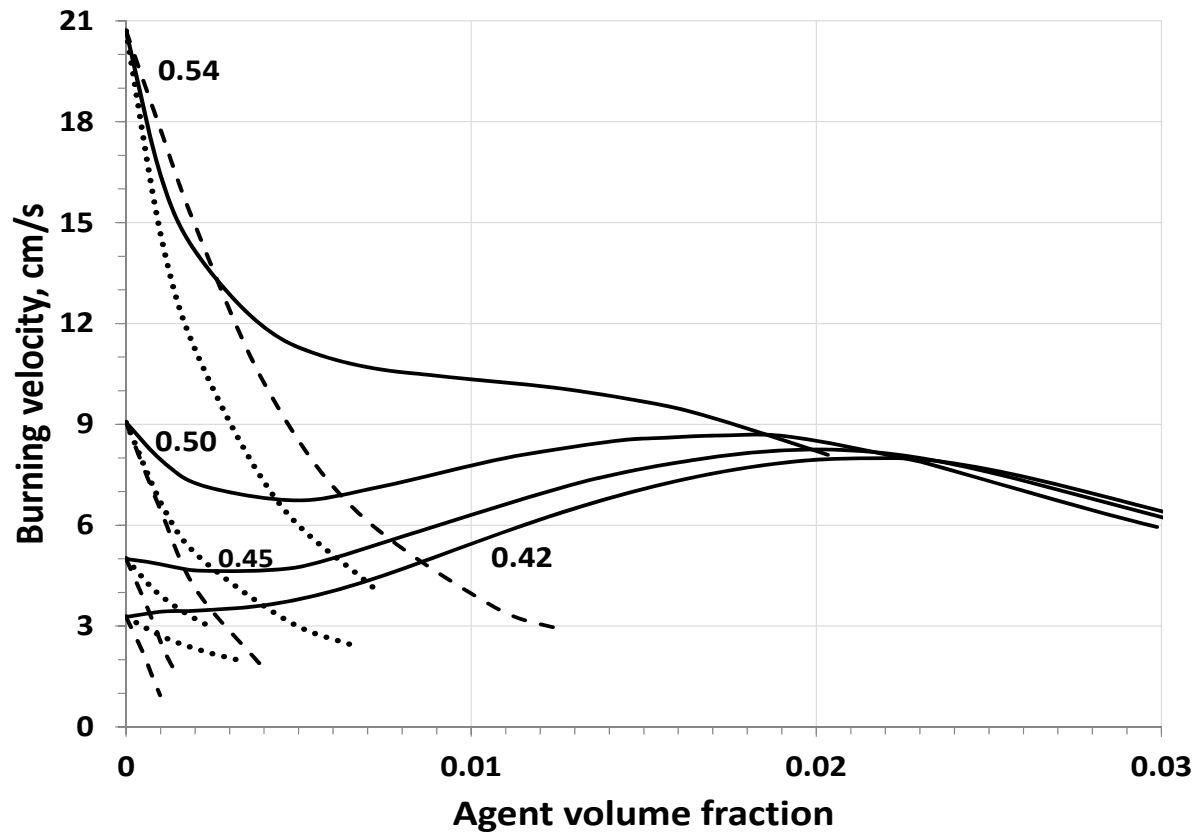


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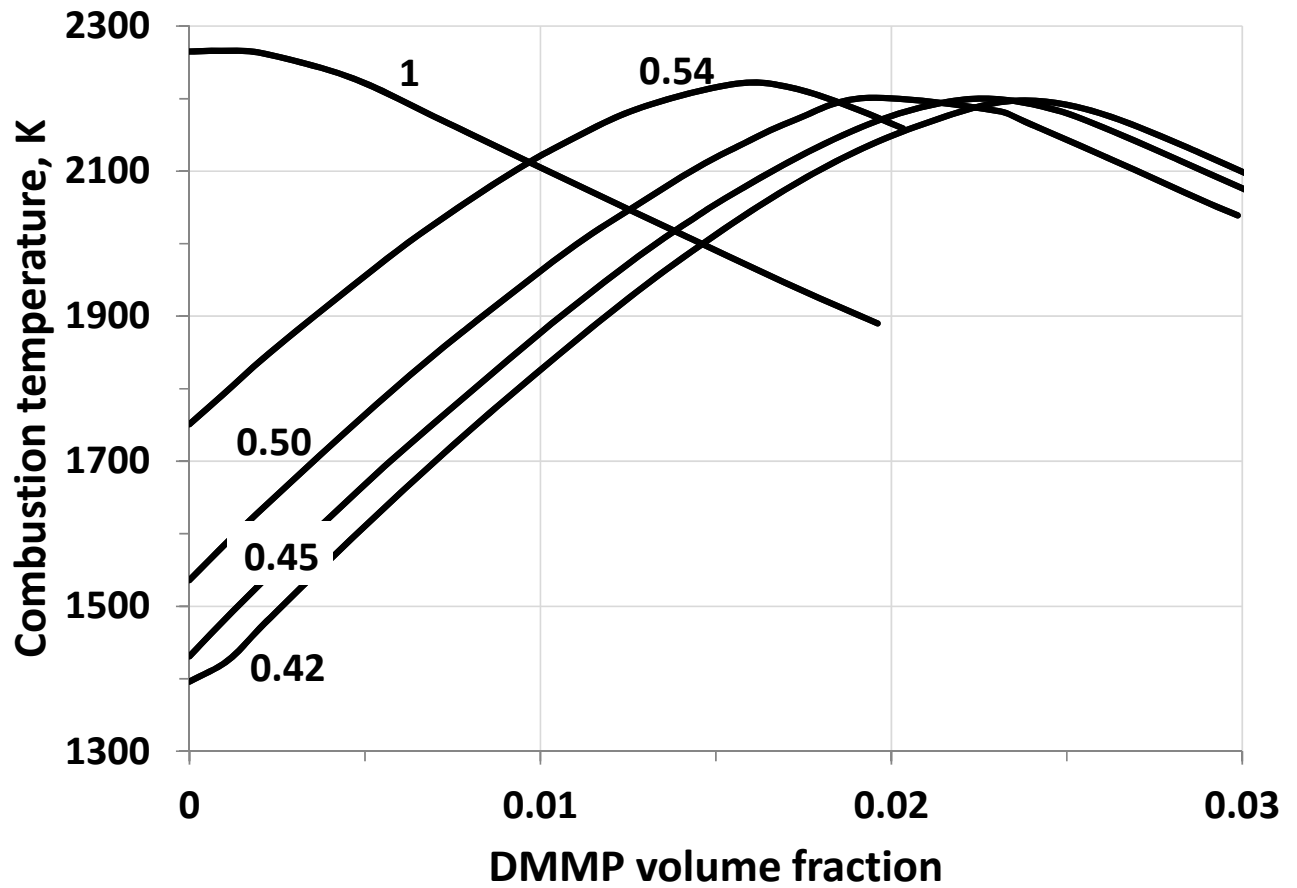


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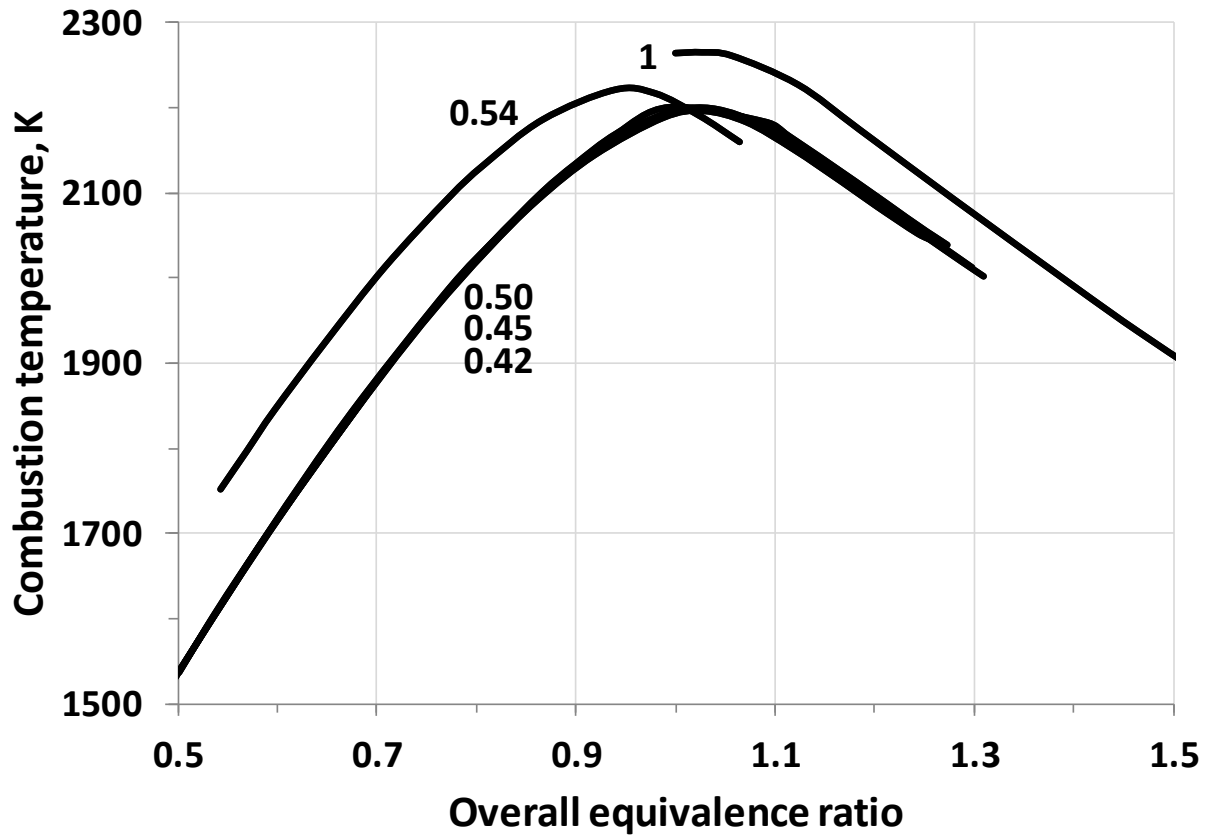
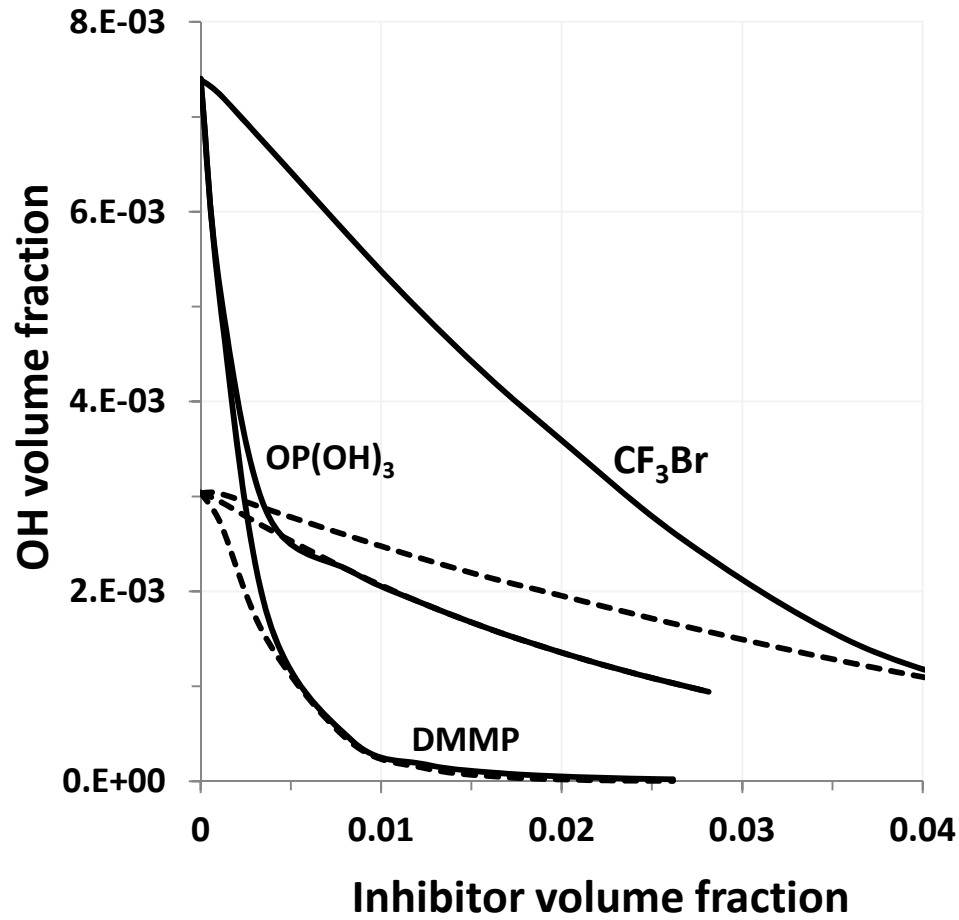


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a)



b)

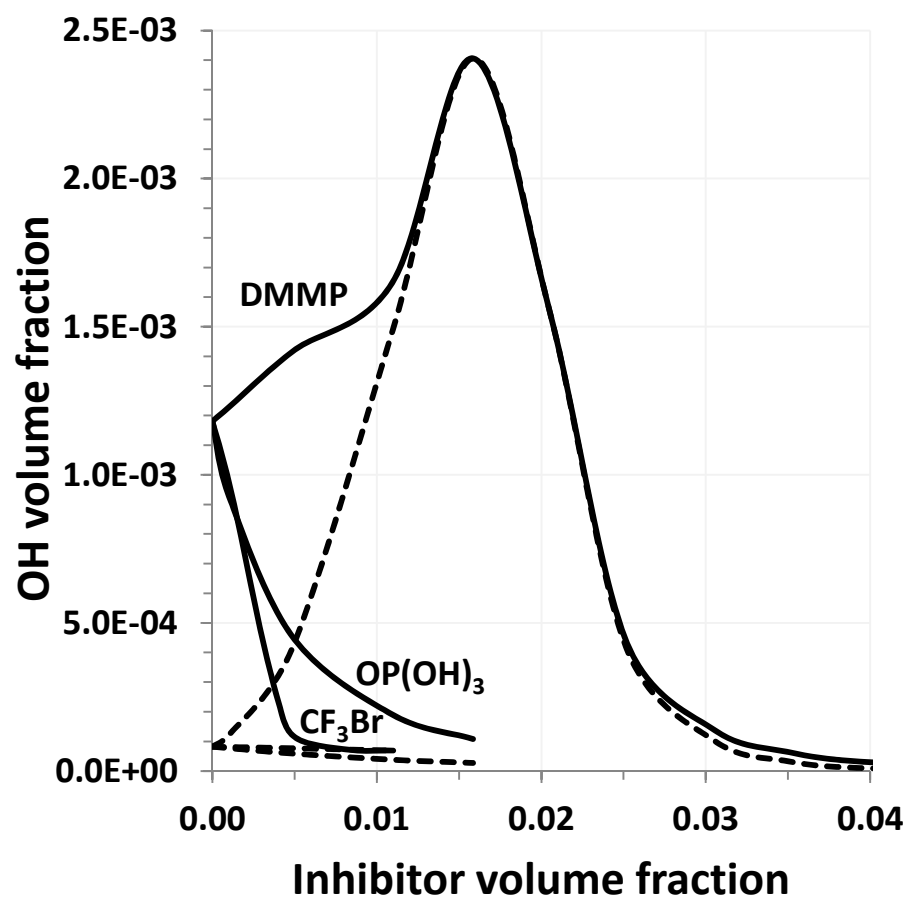


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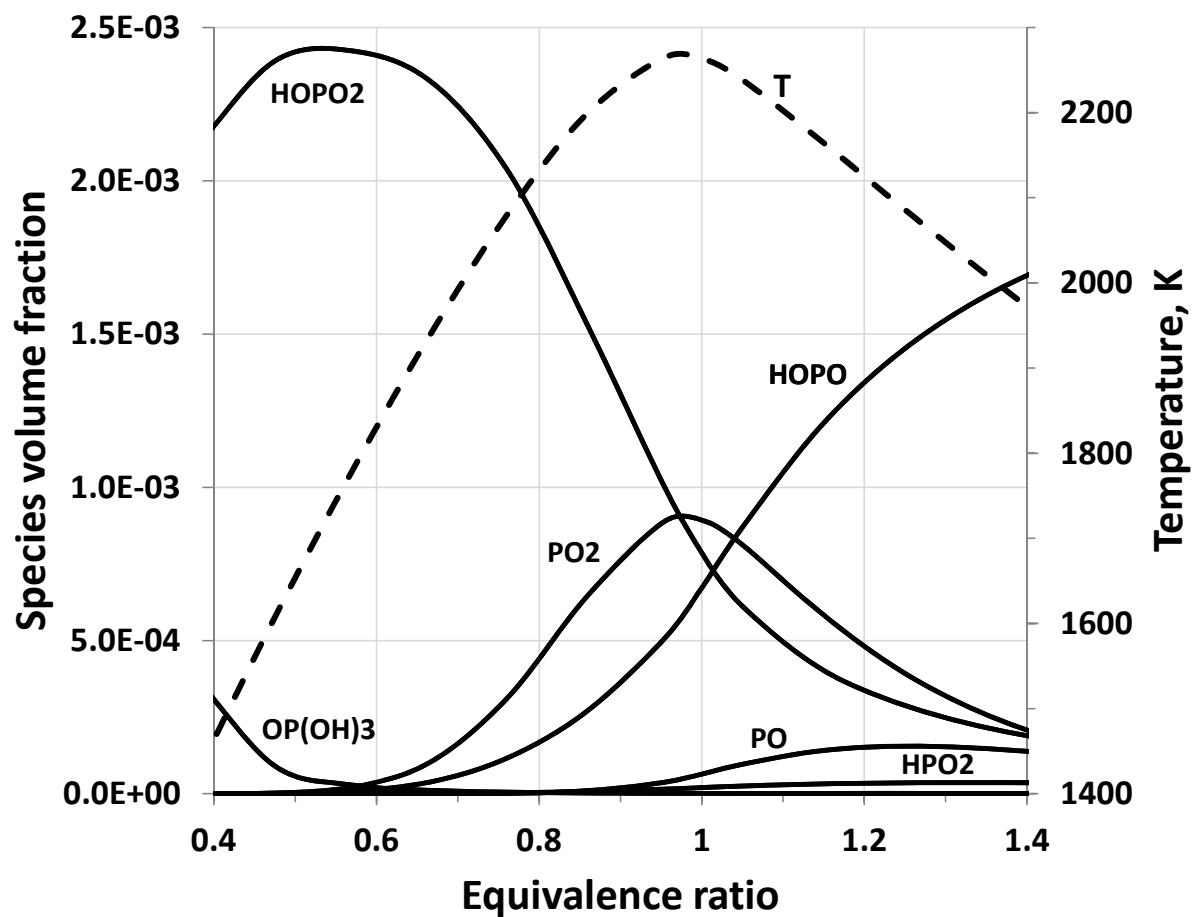
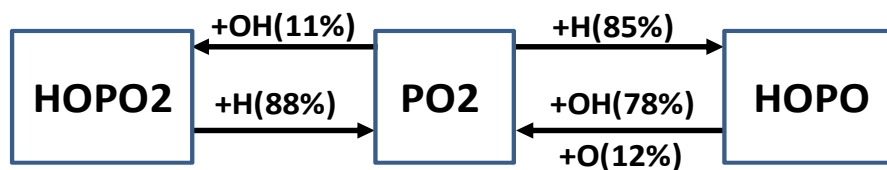


Figure 6. The major reaction pathways of phosphorus-containing species in main reaction zone of a methane/air flame (inhibition cycles $\text{HOPO}_2 \rightleftharpoons \text{PO}_2 \rightleftharpoons \text{HOPO}$; level of reaction presentation – 15 %; initial DMMP volume fraction was of about 0.2 %). Arrows connect the reactants and products of a reaction; the species next to the arrow is the reaction partner, and the number adjacent is the fraction (in %) of the overall consumption rate of the first reactant in that reaction. Diagram is based on the integrated rates through the flame reaction zone.

a) Stoichiometric mixture



b) Equivalence ratio – 0.45

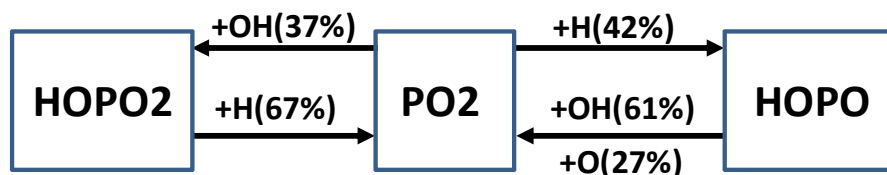


Figure 7. Dependence of burning velocity and adiabatic combustion temperature of DMMP/air mixture on the DMMP concentration (initial temperature – 400 K; solid line- burning velocity; dashed line – combustion temperature)

