STUDY OF EFFECT OF ORGANOPHOSPHORUS FIRE SUPPRESSANTS ON PREMIXED C_3H_8/Air AND DIFFUSIVE COUNTERFLOW CH_4/Air FLAMES

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ABSTRACT

Effect of number of novel organophosphorus compounds (OPC) on burning velocity of a stoichiometric C_3H_8/Air mixture was studied using a Mache-Hebra nozzle burner and the total area method and modeling using PREMIX code. Besides, OPC effect on diffusive counterflow CH_4/Air flame was studied. Burning velocity and global extinction strain rate dependence was studied in the wide range of OPC loading. Fire suppression effectiveness of following OPC was studied: $(CH_3O)_3PO$ (TMP), $(CF_3CH_2O)_3PO$, $(CF_3CH_2O)2(CH_3)PO$, $[(CH_3)_2N]PO$, $(CH_3CH_2O)_3PO$, $(CH_3CH_2O)_2(CH_3)PO$, $(C_3F_7)_3PO$. The tested OPC were ranked on their fire suppression effectiveness. TMP loading dependence of the burning rate of a stoichiometric C_3H_8/Air mixture was calculated using the kinetic model elaborated earlier by the authors and 2 published models. 3 kinetic mechanisms describing the influence of OPC on combustion were demonstrated to provide satisfactory agreement between experimental and calculated results.

INTRODUCTION

Interest in combustion chemistry of organophosphorus compounds (OPC) derives from the need to replace halons as fire suppressants. Environmentally benign, effective organophosphorus fire suppressants are urgently needed to replace ozone-depleting halon compounds such as CF_3Br and CF_2ClBr [1]. Although halon production has been banned for several years under the terms of the Montreal Protocol and its amendments, adequate replacements have not yet been found, especially for mobile applications. Many investigations of the replacement of Halon 1301 have been carried out since 1997 in the frame of the Next-Generation Fire Suppression Technology Program (NGP) [2]. Results have been obtained for flame suppression chemistry (burning velocity - measurement and calculations), screening of candidate fire suppressants using cup-burner technique and the transient-agent, recalculating-pool-fire (TARPF) [3]. OPC's have recently attracted considerable interest (e.g. [4-13]). High effectiveness in flame suppression and inhibition has been demonstrated in laboratory and pilot-scale experiments with several OPC, but problems remain. Physical properties, especially vapor pressure, of most candidates OPC flame suppressants are incompatible with current suppressant delivery systems. Only one OPC, $CH_3PO(OCH_3)_2$ (DMMP), has been studied in detail [7]. Although it possesses exceptional fire suppression efficiency, its high boiling point (181^0C) makes it unsuitable for total-flooding applications. The high boiling point of OPC means that more time is required to evaporate OPC droplets, resulting in their lower efficiency of inhibition, relative to halons, but use of OPC aerosols with smaller drops (1÷10 micron) may help to overcome this drawback. The development of new OPC fire suppressants is hindered by uncertainties in the mechanisms by which OPC's inhibit/suppress flames.

A need of application of various techniques and various flames for study fire suppression effectiveness of OPC is connected with appreciable difference of the effectiveness of fire suppressants in different flames and conditions. Fisher et al [14] by using counter-flow technique studied the dependence of extinction strain rate in CH_4/air flames as a function of loading of such phosphorous compounds as $(HO)_3PO$, $(HO)_3P$, $(OH)_2P(O)H$, $(OH)_2P(O)CH_3$, DMMP and TMP. These phosphorous compounds were applied both as a vapor (DMMP, TMP) and as a droplet and showed similar fire suppression effectiveness per mole of phosphorous loading (for each phase). The TMP was more effective than DMMP. It was shown that water solution of these phosphorous compounds is more effective, than neat compounds. Linteris et al [15] showed, that fire suppression effectiveness of iron-containing compounds is different for premixed and for counter-flow flames. The loss of effectiveness in premixed flames was explained by the formation of particles of iron-containing compounds.

Detailed combustion chemistry mechanisms for OPC have been proposed [16-21]. The investigations of Westbrook et al [16,17] were devoted to the development of mechanisms of OPC destruction in flow reactor and in flames. Kinetic model of DMMP and TMP destruction in a flame includes 202 reactions involving 41 phosphorus-containing species (PCS). Babushok and Tsang [18, 19] proposed a kinetic model for DMMP destruction in CH_4/air atmospheric flame comprising 24 stages with participation of OPC from the model of Werner and Cool [22], 79 reactions from Twarowski mechanism. This model was applied for calculation of burning velocities of stoichiometric CH_4/air flame at atmospheric pressure.

The goal of the present research consists in evaluation of fire suppression effectiveness of number of OPC including novel volatile ones, which contain atoms of fluorine and nitrogen. The tests were performed for both premixed and non-premixed flames by measuring burning velocity and extinction strain rate correspondingly. Another objective of this research is to validate OPC inhibition mechanism through experimental study and modeling of burning velocity of CH_4/air and C_3H_8/air mixtures doped with TMP at atmospheric pressure.

EXPERIMENTAL

Study of OPC fire suppressants effect on burning velocity of flames was performed using Mache-Hebra nozzle burner described elsewhere [23] and the total area method. Burning velocity was calculated as u=W/S, where W - volumetric flow rate of the combustible mixture, S - area of the flame cone. Accuracy of measurement of burning velocity was about 4%. Experimental technique was described earlier [21]. The size of the flame cone was measured by luminous zone. The effectiveness of an inhibitor action have been characterized by ratio of burning velocity of combustible mixture doped with of OPC to that without additive.

OPC were added to a combustible mixture flow using saturator with liquid OPC in controlled temperature bath of 10-85°C with accuracy $\pm 0.5^0C$. The saturator is filled with glass capillaries to increase of a surface. The feed lines were maintained at 95°C to prevent condensation of OPC.

Study the effect of number of OPC on burning velocity of stoichiometric CH_4/air and C_3H_8/air flames was carried out at atmospheric pressure. The fluorine- and nitrogen-containing volatile (in comparison with regular phosphates and phosphonates) compounds are of advanced interest. The studied OPC and their volatility are presented in Table 1. The most volatile among tested OPC is $(C_3F_7)_3PO$.

Table 1. Organophosphorus compounds, which were tested as flame inhibitors and fire suppressants.

Compound	Boiling point [^{0}C] at pressure [Torr]	Temperature* [^{0}C]	Purity, %
$(CH_3O)_3PO$, TMP	180/760	45	98.6
$(C_2H_5O)_3PO$, TEP	215/760	71	99.3
$(CF_3CH_2O)_3PO$	73/8	60	98.8
$[(CH_3)_2N]_3PO$	123/19	80	98.0
$(C_2H_5O)_2P(O)CH_3$	194/760	58	98.5
$(CF_3CH_2O)_2P(O)CH_3$	193/760	48	99.1
$(C_3F_7)_3PO$	144 / 760	21	-

* Temperature of the saturator that provide concentration of OPC 0.2% by volume.

OPC loading dependence of extinction strain rate of atmospheric CH_4/air opposed jet flames was measured. The opposed-jet burner was designed in accordance with recommendations of [13]. The inner diameter of nozzles was 6.8 mm, the distance between nozzles was 6.8 mm. The argon flow was used as a sheath. The maximum of flow rate was 50 cm^3/s for both fuel and oxidizer flows. The burner was aligned upright. Flow rates of the components are presented in Table 2.

Table 2.Volumetric flow rate (NTP cm^3/s) of the components of combustible mixture.

FUEL		OXIDIZER	
CH_4	N_2	O_2	N_2
10	40	20	30

The strain rate was calculated according to equation [24]:

$$a = \frac{2V_{ox}}{L}\left(1 + \frac{V_{fuel}}{V_{ox}}\sqrt{\frac{\rho_{fuel}}{\rho_{ox}}}\right)$$

where V is the stream velocity and ρ is the stream density; L is the separation distance between nozzles. The typical value of strain rate for flames varied from 100 to 800 s^{-1} [13,15,25] and depends on a fuel/oxidizer ratio and burner design. In our experiment the value of extinction strain rate without loading OPC was 750 s^{-1}. The extinction strain rates were measured by increasing the flow rates of fuel and oxidizer until flame is quenched.

RESULTS

INHIBITION EFFECT OF OPC ON BURNING VELOCITY

The dependencies of inhibition effectiveness of OPC tabulated above and CF_3Br for premixed propane flame are presented in Fig. 1. The data shown in Fig. 1 demonstrates that all tested OPC have approximately the same flame inhibition effectiveness. F and N atoms introduced into molecules of OPC do not have strong influence on properties of OPC as flame inhibitors.

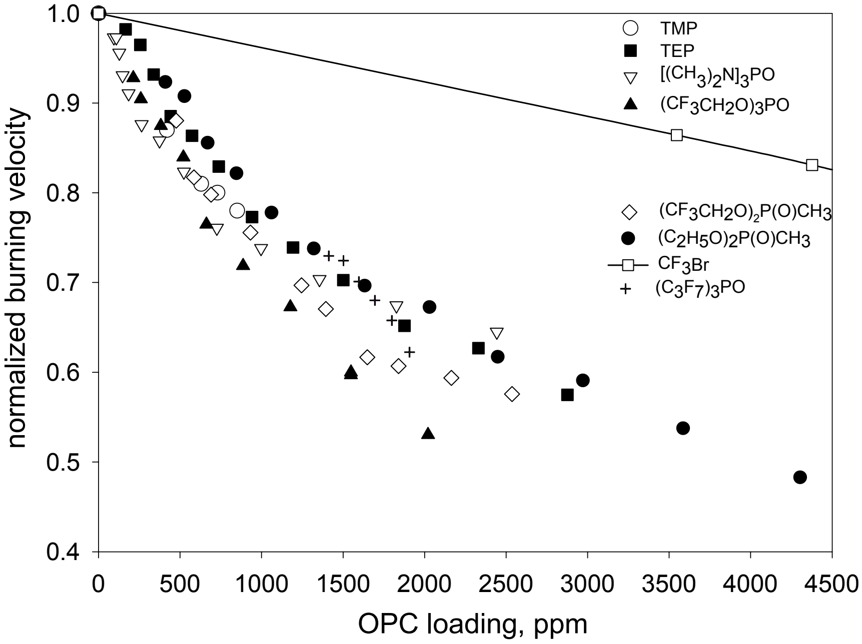

Fig.1 . Normalized burning velocity of stoichiometric premixed C_3H_8/Air flame as a function inhibitor loading.

Comparing OPC loading dependence of burning velocity of a stoichiometric premixed CH_4/air and C_3H_8/air flames (Fig. 2) one can see that for inhibition effectiveness of TMP, $(C_2H_5O)_2P(O)CH_3$, (CF_3CH_2O) does not differ drastically for methane and propane flames. Nevertheless, the inhibition effect of TMP and $(C_2H_5O)_2P(O)CH_3$ on CH_4/air premixed flame is slightly stronger, while inhibition effectiveness of $(CF_3CH_2O)_3PO$ in CH_4/air and C_3H_8/air flames is the same.

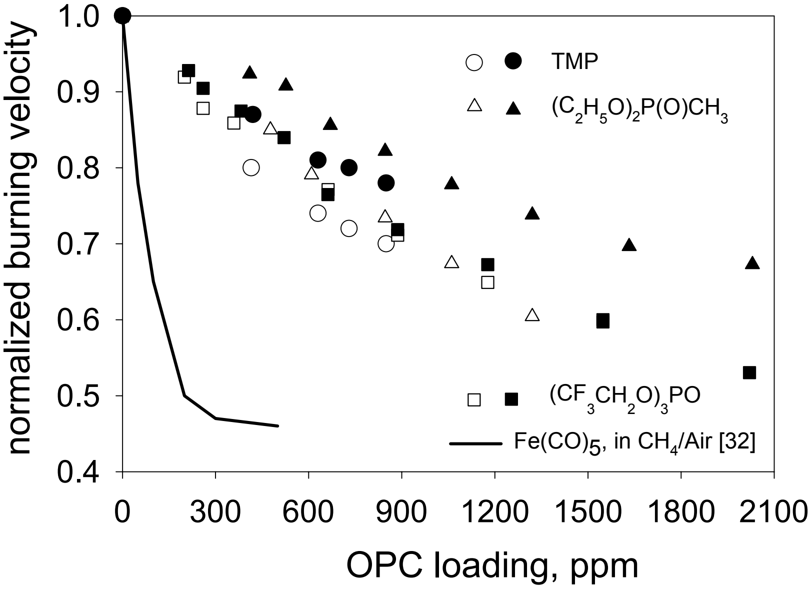

Fig. 2. OPC loading dependence of burning velocity of premixed CH_4/air (open) and C_3H_8/air (filled) flames.

EXTINCTION STRAIN RATE IN A NON-PREMIXED CH_4/AIR FLAME

The OPC and CF_3Br loading dependencies of normalized extinction strain rate for counter-flow CH_4/Air flame are shown in Fig. 3. The most effective fire suppressants were $(CF_3CH_2O)_3PO$ and TMP. The phosphonates were less active than phosphates. All tested OPC showed large fire suppression effect in comparison with CF_3Br in both the premixed C_3H_8/Air and counter-flow CH_4/Air flames. All OPC tested were ranked in order of decreasing of their fire suppression effectiveness and presented below. The rows obtained slightly differ for both types of flames. For premixed C_3H_8/Air flame order of OPC in suppression effectiveness is following:

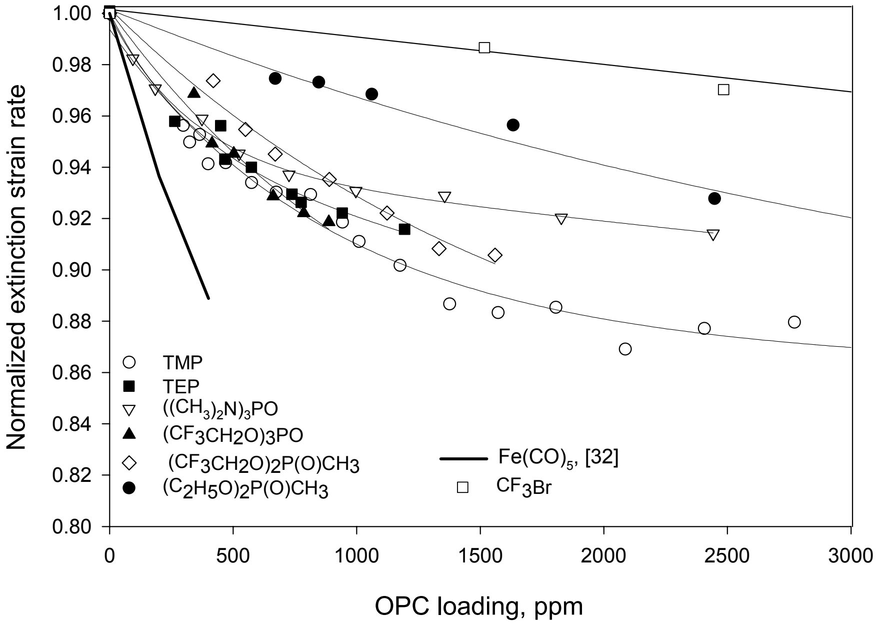

Fig.3. Normalized extinction strain rate of the flame as a function of OPC loading.

$(CF_3CH_2O)_3PO$, $(CF_3CH_2O)_2P(O)CH_3$>$[(CH_3)_2N]_3PO$, TMP, TEP>$(C_3F_7)_3PO$, $(C_2H_5O)_2P(O)CH_3$>>CF_3Br

For counter-flow CH_4/Air flame the order is next:

TMP, $(CF_3CH_2O)_3PO$, TEP>$(CF_3CH_2O)_2P(O)CH_3$>$[(CH_3)_2N]_3PO$> $(C_2H_5O)_2P(O)CH_3$>> CF_3Br

EFFECT OF TMP ON BURNING VELOCITY. EXPERIMENT AND MODELING

TMP loading dependencies of burning velocity of a stoichiometric CH_4/air mixtures doped with TMP measured experimentally and calculated using our kinetic model and 4 different mechanisms of methane oxidation [26-30] are presented in Fig. 4. Figure 5 demonstrates TMP loading dependencies of burning velocity of a stoichiometric CH_4/air flame measured experimentally and calculated using GRI 3.0 [28] mechanism and 3 published kinetic models [16-21] for action of phosphorus-containing species on combustion. The rate constants for most important elementary reactions responsible for inhibition effect are presented in Table 3.

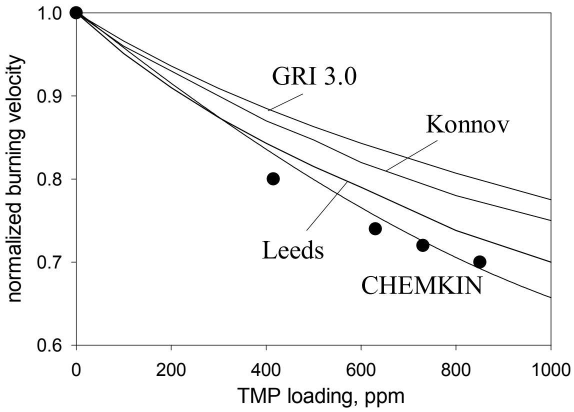

Fig. 4. TMP loading dependence of burning velocity of stoichiometric CH_4/air mixtures doped with TMP measured experimentally (symbols) and calculated by modeling (lines) using our TMP destruction model and 4 various models of CH_4 oxidation.

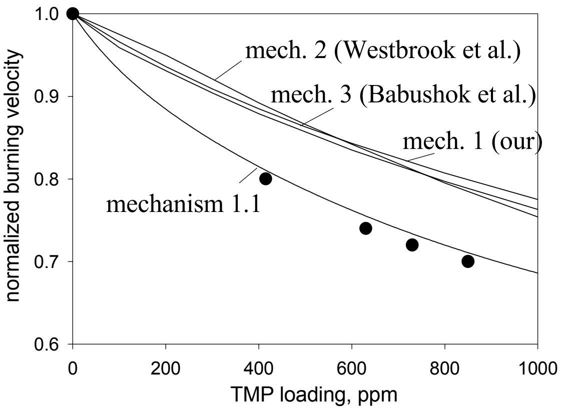

Fig. 5. TMP loading dependence of burning velocity of a stoichiometric CH_4/air mixtures with TMP. Symbols - experiment; lines - modeling performed using GRI 3.0 mechanism and mechanisms 1,2, 3 and mechanism with modified rate constant $H+PO_2+M=HOPO+M$, $A=4.0\times10^{25}$ (mechanism 1.1).

Table 3. The rate constants (expressed as $k = A T^n \exp(-E/RT)$) of elementary reactions responsible for inhibition effect and ξ-coefficients of sensitivity for burning velocity (in %) of the lean (φ=0.8) and rich (φ=1.2) C_3H_8/Air flames.

N	Reaction	A^*	n	E^*	$\xi=(u_0-u_{k/5}/u)\times100\%$	
					φ=0.8	φ=1.2
1.	$H+PO_2+M=HOPO+M$	9.73×10^{24}	-2.04	645.0	-12.7	-12.2
2.	$O+HOPO=PO_2+OH$	1.58×10^{13}	0.00	0.0	-4.7	-4.2
3.	$OH+PO_2+M=HOPO_2+M$	1.6×10^{24}	-2.28	285.0	3.0	0.8
4.	$OH+HOPO=H_2O+PO_2$	3.16×10^{12}	0.00	0.0	-1.6	-4.9
5.	$H+HOPO_2=H_2O+PO_2$	6.32×10^{12}	0.00	11930.0	-1.2	-3.2
6.	$O+HOPO_2=O_2+HOPO$	6.32×10^{12}	0.00	8236.0	-1.1	2.0

where u_0 - burning velocity at recommended rate constant; $u_{k/5}$ - burning velocity at rate constant reduced in 5 times.

*- units are mole, cm^3, s, cal/mole

As one can see all 3 models involving phosphorus substances give very close results. Analyzing Figs. 4 and 5 one can conclude that a disagreement of modeling results with experimental data can be explained possibly by drawbacks of both the phosphorus-involving models and hydrocarbon combustion mechanisms. Nevertheless, a disagreement with experiment can be decreased by increasing the pre-exponential factor of reaction $H+PO_2+M=HOPO+M$ in 4 times. The modeling results obtained using mechanism 1 with modified rate constant (defined as mechanism 1.1) are presented in Fig. 5.

Calculation of burning velocity of the stoichiometric mixture of propane and air as a function of TMP loading was also performed using 3 kinetic model [16-21]. The results of calculation together with experimental data are plotted in Fig. 6. The results obtained demonstrate that all 3 kinetic models provide good agreement with experimental data. Sensitivity analysis for burning

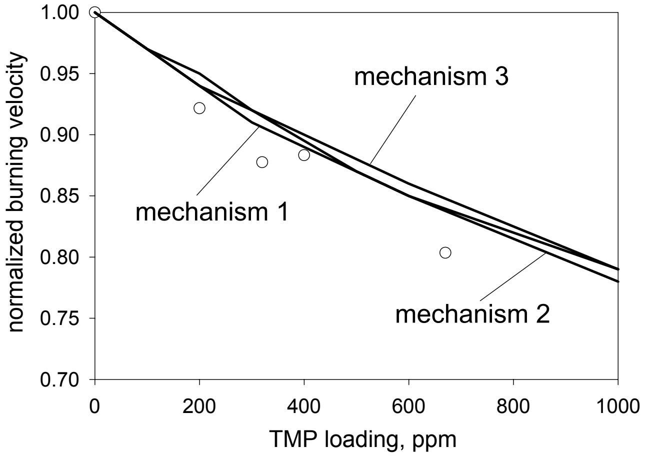

Fig 6. Burning velocity of the stoichiometric C_3H_8/air flame as a function of TMP loading. Symbols - experiment; lines - modeling results obtained using three different mechanisms for C_3H_8/air flame.

velocity [31] of the lean and rich premixed C_3H_8/air flames (φ=0.8 and 1.2) was applied. Rate constants of the most important reactions and sensitivity coefficients ξ are presented in Table 3. Here is $\xi=[(u_0-u_{k/5})/u_0]\times100$ %, where u_0 - burning velocity at used rate constant; $u_{k/5}$ - burning velocity at rate constant of corresponding reaction reduced in 5 times. A good agreement of modeling results obtained using all 3 models and experimental data is explained by close values of the rate constants of the most important reactions 1 and 2 (Table 3). Temperature dependence of the rate constants of these reactions is the same in all models. Pre-exponential factors A differ not more than in 3 times. A value of A in mechanism 1 lies between those of mechanisms 2 and 3. Reaction 2 is the second one in importance for control burning velocity of the lean premixed C_3H_8/air flame. Rate constant of this reaction does not depend on temperature. Its value accepted in mechanism 1 differs in 1.5-2 times only from those in mechanisms 2 and 3.

CONCLUSION

The presented paper has studied the fire suppression properties of number of known and novel OPC. Data obtained confirm that organophosphorus compounds are more effective fire suppressants than CF_3Br for both premixed C_3H_8/Air and none-premixed CH_4/Air atmospheric flames. The strongest fire suppression effect on the both types of flames showed TMP, $(CF_3CH_2O)_3PO$, $(CF_3CH_2O)_2P(O)CH_3$. The N-containing OPC do not have strong fire suppression effect in comparison with other. The phosphonates are less active fire suppressants than phosphates. The inhibition effect of TMP and $(C_2H_5O)_2P(O)CH_3$ on premixed CH_4/air flame is stronger than that on C_3H_8/air flame. OPC inhibition mechanism have been validated by comparing of experimental and modeling data for burning velocity of stoichiometric CH4/air and C3H8/air mixtures doped with TMP. The results of calculation of burning velocity of a stoichiometric mixture of propane and air as a function of TMP loading showed satisfactory agreement with experimental results. The sensitivity analyses of rate constants on burning velocity was applied to specify the most important stages responsible for inhibition: $H+PO_2+M=HOPO+M$ and $O+HOPO=PO_2+OH$. The influence of rate constant of the first reaction on the burning velocity is much higher than that of the other reactions. The value of this rate constant differs in 1.5-2 times in available mechanisms. It explains a good agreement between results of calculation using different models. The results of calculation showed that the importance of reaction depends on equivalence ratio.

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