INHIBITION EFFECT OF ORGANOPHOSPHORUS COMPOUNDS ON STRUCTURE OF ATMOSPHERIC PREMIXED $C_3H_8/O_2/Ar$ AND $CH_4/O_2/Ar$ FLAMES

Oleg P. Korobeinichev, Tatyana A. Bolshova,
Vladimir M. Shvartsberg, Andrey G. Shmakov
Institute of Chemical Kinetics & Combustion,
Novosibirsk, 630090 Russia
Phone: +7-3832-332852; Fax: +7-3832-342350
E-mail: korobein@ns.kinetics.nsc.ru

INTRODUCTION

Interest in combustion chemistry of organophosphorus compounds (OPC) derives from the need to incinerate pesticides and chemical warfare agents, their use as fire suppressants, and potential catalytic applications in aircraft turbines [1-11]. After signing Montreal Protocol forbidding production of Halon 1301 and search of candidates for its replacement OPC attracted attention as fire suppressants and the need of study of mechanism of action of OPC on combustion has emerged. In connection with this problem the mechanism of action of OPC additives on low pressure and atmospheric hydrocarbon flames was studied. Structure of methane premixed laminar flat flames was studied using molecular beam mass spectrometry (MBMS) and computer modeling [12-15]. Methane opposed-jet flames were studied using laser-induced fluorescence and computer modeling [16]. Effectiveness of number of OPC as fire suppressants was determined using cup-burner technique [17]. The investigations [14,15] revealed the drawbacks of early proposed mechanism of OPC action and all efforts were exerted for its refinement. The investigations of Westbrook and coworkers [18,19] were devoted to the development of mechanisms of OPC destruction in flow reactor and in flames. Comparison of calculated data obtained with experimental results on structure of low pressure $H_2/O_2/Ar$ flame doped with DMMP and TMP demonstrated satisfactory agreement not only for stable flame species but also for labile PCS such as PO, PO_2, HOPO and $HOPO_2$ [18]. Babushok and Tsang [20,21] proposed a kinetic model for DMMP destruction in CH_4/air atmospheric flame. This model was applied for calculation of burning velocities of stoichiometric CH_4/air flame at atmospheric pressure. One of prospective candidate fire suppressants is $Fe(CO)_5$ that have shown to be up to orders of magnitude more effective than CF_3Br. for premixed and diffusive non-premixed flame at very low concentration below 100 ppm. A dramatic loss of effectiveness of this compound at loading above 100 ppm was observed for premixed flames. These phenomena are explained by condensation of iron-containing intermediates followed by subsequent formation of particles [22]. Unlike iron-containing compounds OPC are devoid of these faults. A considerable interest to the fluorinated and partly fluorinated OPC as candidate fire suppressant appeared after number of such compounds were tested for their extinguishing properties using modified ionization detector [23]. In spite of higher molecular weight in comparison with ordinary OPC fluorinated compounds are more volatile and, therefore, are suitable for practical use. Mather and Tapscott have selected nine tropodegradable fluorinated and hydrofluorinated the most prospective OPC by volatility [24]. A study of inhibition effect of number of OPC including fluorinated substances on premixed (burning velocity vs. OPC loading) and diffusive non-premixed (extinction strain rate vs. OPC loading) CH_4/air and C_3H_8/air flames demonstrated higher fire suppression effectiveness of some fluorinated compounds in comparison with regular OPC [25].A wide application of OPC as fire suppressants is restrained also by unknown toxicity of majority of OPC as well as their combustion products. Practically, the only OPC, which was screened for its toxicity is DMMP, which is widely used as flame retardant in halogenated polyester resigns and rigid polyurethane foams. The study [26] revealed its mutagenic and carcinogenic activity at long-term exposure. The data obtained demonstrate an urgent need for search and screening novel organophosphorus candidate fire suppressant.

In spite of significant progress in study of combustion chemistry of OPC there is a deficit of quantitative experimental data on flame structure, which are needed for more detailed comprehension of inhibition chemistry and further refinement of a mechanism of action of OPC on combustion. Besides, the above-mentioned models were applied to simulate only a several experimental data on flame structure and burning velocity. This study presents further investigation of combustion chemistry of OPC extended for atmospheric propane-oxygen flames. The goal of present research is on the one hand to improve our understanding of OPC combustion chemistry and the inhibition mechanism by OPC through experimental study and modeling of structure of atmospheric $C_3H_8/O_2/Ar$ flames doped with TMP and on the other hand to summarize the modeling and experimental data for $CH_4/O_2/Ar$ and $C_3H_8/O_2/Ar$ flames.

EXPERIMENTAL. METHODICAL PROBLEMS.

To investigate the effect of TMP additive on a flame structure two $C_3H_8/O_2/Ar$ flames of composition 0.025/0.136/0.839 ($\varphi \approx 0.9$) and 0.029/0.121/0.85 ($\varphi \approx 1.2$) were chosen. Both flames were stabilized on a flat Botha-Spolding type burner 16 mm in diameter at atmospheric pressure and temperature 370-400 K. Combustible mixture was prepared with a help of mass flow controllers (MKS Instruments Inc., model 1299S). Total volumetric flow rate was 1.5 slpm. TMP was added to a combustible mixture flow using saturator with liquid TMP in controlled temperature bath. Temperature profiles of the flames were measured by Pt-Pt+10%Rh thermocouples welded from wire 0.02 mm in diameter. Thermocouples were covered by a thin layer of SiO_2 to prevent catalytic recombination of radicals on their surface. Total diameter of the thermocouple was 0.03 mm. The length of the thermocouple shoulders was about 3 mm. At such ratio of shoulder to diameter the heat losses into the cold contacts are negligible. The construction of the thermocouple unit was describes elsewhere [2]. The temperature profiles of the flames were measured by a thermocouple placed at the distance 0.3±0.03 mm from the probe's tip and far from it. MBMS setup with soft ionization by electron impact described earlier [8] was used to measure concentration profiles of stable and labile flame species. Synchronous demodulation was applied to measure flame species in low concentration

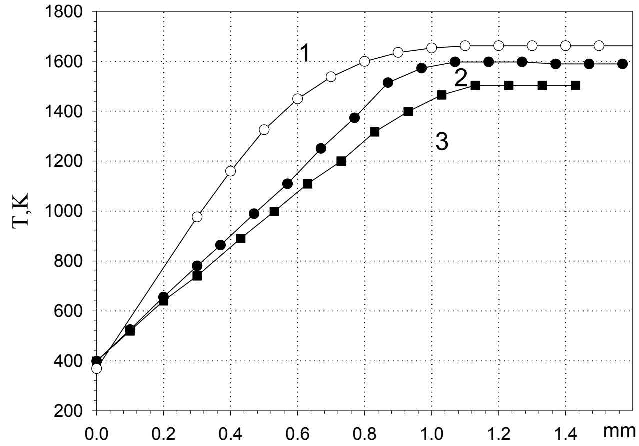

Fig.1. Temperature profiles in lean $CH_4/O_2/Ar$ (0.06/0.15/0.79) flame at 1 bar. Curve 1-without probe($\delta=\infty$), curve 2-δ=0.3mm, curve 3-δ=0.13mm.

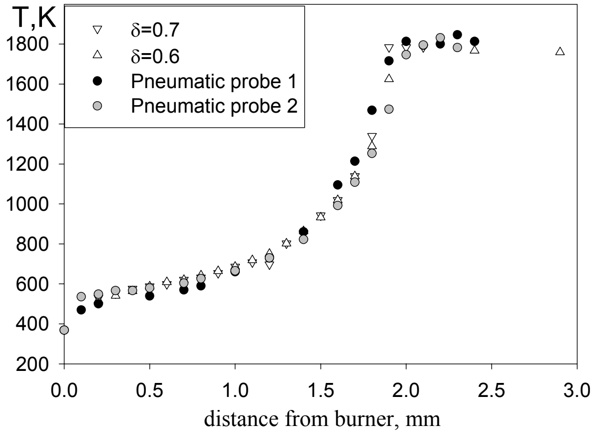

Fig. 2. Temperature profiles in the lean $CH_4/O_2/Ar$ (0.06/0.15/0.79) flame doped with 1200 ppm of TMP measured by a thermocouple placed at distances $\delta=0.6$ and 0.7 mm from the probes and by pneumatic probes.

up to 10 ppm with a mean square error not more than 50 %. Concentration of stable flame species was measured with standard deviation not more than 10 %. Quartz cones with inner angle 40 deg., wall thickness 0.05 mm and orifice diameter 0.05-0.09 mm were used as the probes. As a probe disturbs a flame producing a shift of lines of equal concentration in comparison with unperturbed flame the sampling shift was taken into account [27].

There are two methodical problems in study of flame structure by MBMS at atmospheric pressure. During experimental study it has been found out that the time of exploitation of quartz probes is much shorter in atmospheric flames than in low-pressure flames. It occurs because of the phosphorus compounds form a solid film of pyrophosphoric acids (especially near the tip of the probe) which alloys with heated quartz to form easily melted phosphate glass. This is a first problem. Second one is connected with the appreciable perturbations of the flames caused by a sonic probe. They are stronger at atmospheric pressure than in low one. Fig. 1 demonstrates a perturbation of the flat atmospheric methane lean flame without additive by a sonic probe. Comparing the temperature profiles obtained with a help of thermocouple placed at various distances from the tip of the probe one can see that the probe decreases final flame temperature for about 50 K and increases the width of a combustion zone. The modeling of structure of a flame should be carried out with use specified, measured temperature profile. The best account of perturbations of species concentration profiles measured by a sonic probe and temperature profile, and also best agreement between calculated and measured species concentration profiles will be in that case, when the temperature profile is measured with the help of a pneumatic probe [28] or with the help of the thermocouple located near to tip of the probe on certain distance from it. The experiments demonstrated optimal distance to be $\delta=0.3\pm0.03$ mm for above lean methane flame and probe used. But for another probe and flame the temperature profile obtained using the method of pneumatic probe satisfactorily coincided with that measured by a thermocouple placed at the distance of 0.6-0.7 mm from the probe's tip (Fig 2). Besides it is

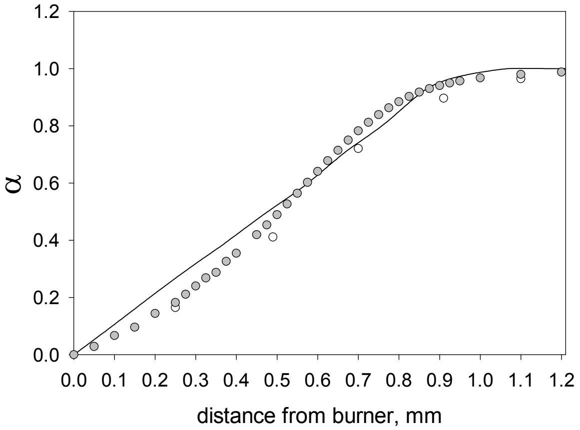

Fig. 3. Normalized profiles of temperature $\alpha_T=(T-T_0)/(T_f-T_0)$ and concentration of O_2 $\alpha_C=(C-C_0)/(C_f-C_0)$ in a near stoichiometric $CH_4/O_2/Ar$ flame without additive of TMP. Line - temperature; filled symbols - results of modeling; open symbols - results of experiment.

necessary to note that modeling data justified the similarity of profiles of temperature and species concentrations in flame. Accordingly to the data of modeling of structure of $C_3H_8/O_2/Ar$ flame stabilized on the flat burner (without specification of temperature profile), concentration profile of H_2O is similar to temperature profile (Fig.3). Thus, regularity of the choice of the "proper" temperature profile should be checked out also by the similarity of the measured temperature and species concentration profile (for example O_2 concentration profile).

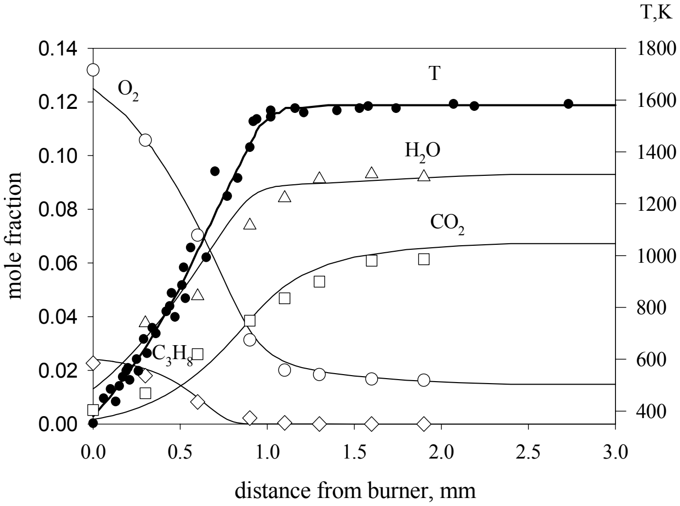

Fig. 4 Profiles of temperature (experiment) and concentration of stable species in the lean $C_3H_8/O_2/Ar$ flame without additive. Symbols - experiment, lines - modeling.

MODELING

PREMIX and CHEMKIN-II codes [29,30] were used for simulation of concentration profiles. For numerical study of atmospheric $CH_4/O_2/Ar$ flames the mechanisms for methane combustion CHEMKIN (18 species, 58 stages) [31] and GRI 3.0 (53 species, 325 stags) [32] mechanisms were used. For simulation of the structure of $C_3H_8/O_2/Ar$ flames at atmospheric pressure Konnov's detailed reaction model [33] for combustion of small hydrocarbons was used. Elaborated earlier mechanism involving phosphorus containing species (PCS) [10,12,14] have been used at modeling. Simulation of flat flame structure was performed using specified experimentally measured profiles of temperature.

RESULTS

Figure 4 shows the profile of temperature and concentration of stable species C_3H_8, O_2, H_2O and CO_2 in the lean $C_3H_8/O_2/Ar$ flame without additive. Fig. 5 presents the temperature and concentration profiles for the lean flame doped with 1200 ppm of TMP. Figures 6 and 7 present the corresponding data for the rich $C_3H_8/O_2/Ar$ flame without additive and doped with 1200 ppm of TMP. Inhibition effect of the additive results in an appreciable removal of the flame front away from the burner accompanied with a decrease of heat losses in to the burner as it was earlier demonstrated for $CH_4/O_2/Ar$ flames [15]. Maximal temperature of perturbed undoped flames ranges 1500-1600K whereas the temperature of the doped flames ranges 1700-1800 K. The temperature rise is connected with a decrease of the heat losses into the burner and increase of completeness of combustion in the doped flames rather than with an

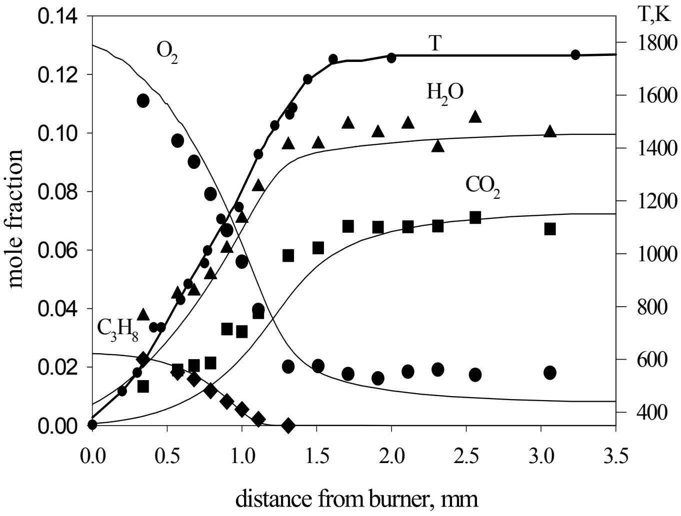

Fig. 5. Profiles of temperature (experiment) and concentration of stable species in the lean $C_3H_8/O_2/Ar$ flame doped with 1200 ppm of TMP. Symbols - experiment, lines - modeling.

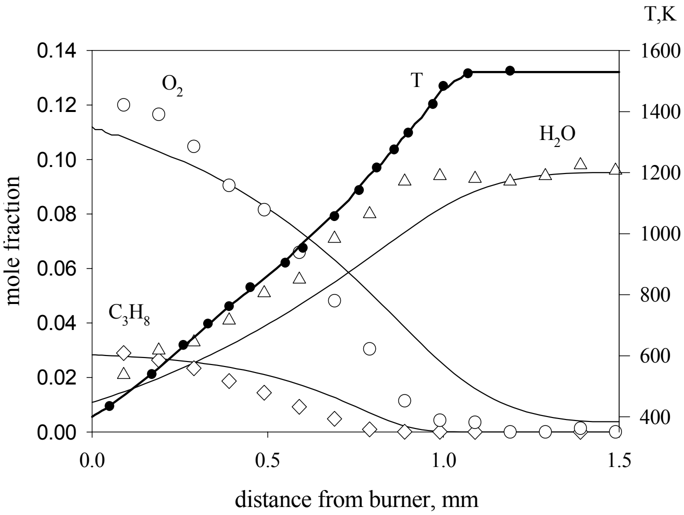

Fig. 6 Profiles of temperature (experiment) and concentration of stable species in the rich $C_3H_8/O_2/Ar$ flame without additive. Symbols - experiment, lines - modeling.

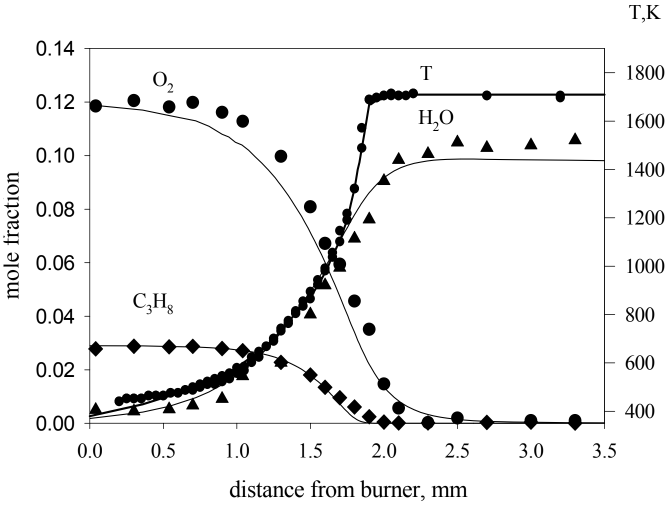

Fig 7. Profiles of temperature (experiment) and concentration of stable species in the rich $C_3H_8/O_2/Ar$ flame doped with 1200 ppm of TMP. Symbols - experiment, lines - modeling.

effect of OPC on thermophysical properties of the flame. The concentration profiles of final phosphorus-containing products of TMP destruction in the lean and rich flames - PO, PO_2, HOPO, $HOPO_2$ and $OP(OH)_3$ are shown in Fig. 8 and 9. Comparing the data obtained for both $C_3H_8/O_2/Ar$ flames doped with TMP (Figs. 8 and 9) one can observe appreciable differences between composition of PCS in the lean and rich flames. Fig. 10 presents the profiles of concentration of TMP and PCS in the lean $CH_4/O_2/Ar$ (0.06/0.15/0.79) flame doped with 2200 ppm of TMP. In the both lean flames the major final product of TMP destruction is $HOPO_2$, which comprises more than 80 % of phosphorus, unlike the rich $C_3H_8/O_2/Ar$ flame where HOPO, PO_2 and $OP(OH)_3$ were discovered in higher concentrations. Although the compositions of PCS in the lean methane and propane flames are very close (considering the difference in TMP loading) the compositions of these species in the rich methane and propane flames are quite different. Thus, in methane flame the main species comprising about 80 % of phosphorus is HOPO while in the rich propane flame none of the products prevail over the rest species. At the same time a difference in the final temperature in all flames is negligible and can not be a reason of the distinction.

COMPARISON WITH MODELING

The simulated concentration profiles of stable flame species (Figures 4-7) demonstrated a satisfactory agreement with experimental data. It verifies reliability of the experimental data, validity of kinetic model of propane oxidation and correctness of used specified experimental temperature for flame structure calculation. The concentration profiles of PCS in all flames were simulated using 3 different mechanisms for flame inhibition by OPC: our model (defined as mechanism 1), model elaborated by Westbrook and coworkers [18,19] (mechanism 2), and the mechanism proposed by Babushok and Tsang [20,21] (mechanism 3). The most important reactions responsible for ihibition effect (decrease of burning velocity [25]) and their rate constants in our model, model of Westbrook and coworkers, model of Babushok-Tsang are presented in Table 1.

TABLE 1. THE MOST IMPORTANT REACTIONS RESPONSIBLE FOR INHIBITION EFFECT AND THEIR RATE CONSTANTS IN OUR MODEL, MODEL OF WESTBROOK AND COWORKERS, MODEL OF BABUSHOK-TSANG (EXPRESSED AS $k = A\ T^n * \exp(-E/RT)$)

#	Reaction	our model			Westbrook et al.			Babushok-Tsang		
		A	n	E	A	n	E	A	n	E
1	$OH+PO_2+M=HOPO_2+M$	1.6×10^{24}	-2.3	285	3.2×10^{25}	-2.3	285	1.6×10^{24}	-2.3	285
2	$H+HOPO_2=H_2O+PO_2$	6.32×10^{12}	0.0	11930	-	-	-	3.16×10^{13}	0.0	8000
3	$H+PO_2+M=HOPO+M$	9.73×10^{24}	-2.0	645	1.46×10^{25}	-2.0	645	5.0×10^{24}	-2.0	645
4	$OH+HOPO=H_2O+PO_2$	3.16×10^{12}	0.0	0	1.2×10^{6}	2.0	-1500	3.16×10^{12}	0.0	0
5	$H+HOPO=H_2+PO_2$	7.9×10^{11}	0.0	43	6.8×10^{13}	0.0	8100	3.16×10^{13}	0.0	8000
6	$O+HOPO=OH+PO_2$	1.58×10^{13}	0.0	0	1.0×10^{13}	0.0	0	3.16×10^{13}	0.0	0
7	$O+HOPO+M=HOPO_2+M$	1.3×10^{23}	-2.1	995	1.2×10^{27}	-3.0	2040	4.8×10^{31}	-4.3	4400
8	$O+HOPO_2=O_2+HOPO$	6.32×10^{12}	0.0	8236	5.0×10^{12}	0.0	15000	1.0×10^{13}	0.0	10000

Units are mol, cm^3 , s, K and $cal\times mol^{-1}$

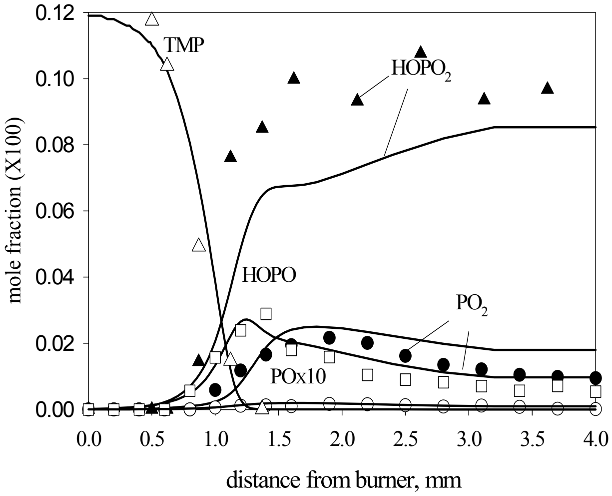

Fig. 8. Concentration profiles of TMP and of final phosphorus-containing products of its destruction PO, PO_2, HOPO, $HOPO_2$ in the lean $C_3H_8/O_2/Ar$ flame doped with 1200 ppm of TMP. Symbols - experiment, lines - modeling.

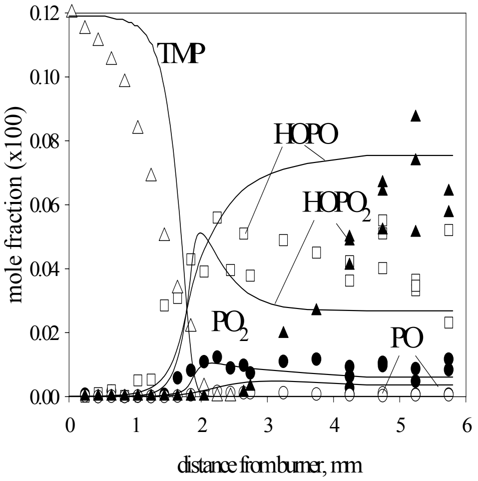

Fig. 9. Concentration profiles of TMP and of final phosphorus-containing products of its destruction PO, PO_2, HOPO, $HOPO_2$ in the rich $C_3H_8/O_2/Ar$ flame doped with 1200 ppm of TMP. Symbols - experiment, lines - modeling.

Figures 8-10 demonstrate the simulated profiles calculated using only our mechanism. Final concentrations of PCS in the propane flames obtained with the help of mechanism 1, 2 and 3 are presented in Tables 2 and 3. They present measured final concentrations of PCS and equilibrium concentrations of these products at the final flame temperatures. The same results for $CH_4/O_2/Ar$ flames were published elsewhere [15]. To evaluate an agreement of the simulated and measured species concentrations properly the errors of determination of calibration coefficients of the species should be taken into consideration [8]. Final concentrations of some species in the lean $CH_4/O_2/Ar$ flame (Table 2) differ from those published earlier [15]. The experimental and modeling data published in [15] were obtained for the distance of 3 mm above the burner whereas the present results are referred to the distance of 5 mm from the burner. Fig. 10 demonstrates that the area at 4.5-5.5 mm above the burner rather than 3-that at 3.5 mm can be considered s the post-flame zone for concentration profiles of PCS.

TABLE 2. FRACTION OF NUMBER OF MOLES OF A PHOSPHORUS-CONTAINING COMPOUND IN TOTAL NUMBER OF MOLES OF PCS (IN %) IN POST-FLAME ZONE OF THE LEAN DOPED $C_3H_8/O_2/Ar$ FLAME CALCULATED USING 3 DIFFERENT MECHANISMS, EQUILIBRIUM STATE AND MEASURED EXPERIMENTALLY

Species	Mole fractions			Equilibrium concentrations at 1760K	Experimental results
	1	2	3		
PO	0.0	0.0	0.0	0.0	0.1±0.1
PO_2	15.5	1.2	29.6	3.0	9±6
HOPO	8.3	2.5	8.6	1.9	5.2±1.6
$HOPO_2$	73.0	96.0	59.4	91.3	80±20
$PO(OH)_3$	3.2	0.3	2.4	3.8	-

TABLE 3 FRACTION OF NUMBER OF MOLES OF A PHOSPHORUS-CONTAINING COMPOUND IN TOTAL NUMBER OF MOLES OF PCS (IN %) IN POST-FLAME ZONE OF THE RICH DOPED $C_3H_8/O_2/Ar$ FLAME CALCULATED USING 3 DIFFERENT MECHANISMS, EQUILIBRIUM STATE AND MEASURED EXPERIMENTALLY

	Mole fractions			Equilibrium concentrations	Experiment
Species	1	2	3	at 1700 K	al results
PO	4.3	0.0	0.2	0.8	0.55±0.55
PO_2	6.6	4.9	14.1	4.8	6.8±4.6
HOPO	63.9	61.6	75.5	85.2	31.5±9.5
$HOPO_2$	23.8	32.7	9.6	8.7	49±15
$PO(OH)_3$	1.4	0.1	0.6	0.5	10±5

All three models provide an agreement between experiment and modeling for the lean flames. The concentration of PO_2can be recognized to be the only exception as only mechanism 1 provides an agreement. Though the mechanisms 1, 2 and 3 differ significantly from one another in number of species involved, number of stages and kinetic rate constants none of the models provide an agreement between modeling and experiment neither for the rich propane flame nor for the methane one. Results of thermodynamic calculation of the concentrations of PCS at the corresponding flame temperatures was performed for both $C_3H_8/O_2/Ar$ flames using thermochemical data accepted in mechanism 1. It is noteworthy that thermochemical constants of mechanism 2 as well as our model are based on calculations of C. Melius [4]. The authors of mechanism 3 have developed own thermochemistry for this model. Comparison of these data with results of experiment and calculation using PREMIX code demonstrated a distinction between them. It indicates that thermodynamic equilibrium in these conditions is not achieved. Only concentrations of some of these PCS are close. Calculation of the equilibrium compositions involving all species from mechanism 2 gave the same results. Thermodynamic calculations using mechanism 3 showed that at the temperature range 1200 K and higher $P(OH)_3$ was the only PCS. But modeling did not confirm formation of this compound in post-flame zone.

DISCUSSION AND CONCLUSION

As phosphorus-containing products of OPC destruction in a flame are known to be responsible for inhibition effect an appreciable efforts were made to measure and simulate their concentration profiles. Two other published models for OPC destruction in a flame were validated by

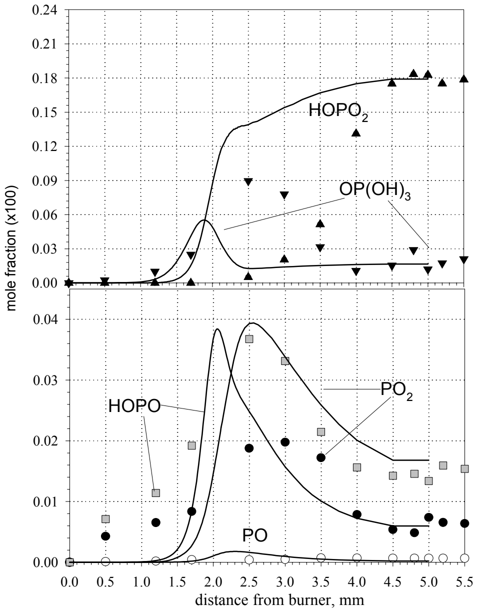

Fig.10. Profiles of concentration of phosphorus-containing products of its destruction in the lean $CH_4/O_2/Ar$ flame doped with 2200 ppm of TMP; symbols - experiment, lines-modeling.

comparing simulated and experimental profile of concentration of these products. There are several conclusions, which can be done. None of the tested models can predict concentration profiles of PO, PO_2, HOPO, $HOPO_2$ and $OP(OH)_3$ in the rich flames. It can be connected with insufficient understanding of combustion chemistry of rich flames as well as combustion chemistry of OPC. As an illustration several examples can be cited. Possibility of presence of the species, which are the products of addition of hydrocarbon radicals to phosphorus oxides in rich flames, was reported in paper [34]. A variety of PCS of complex structure was found in combustion products of rich $C_2H_2/O_2/Ar$ flames doped with TMP and tri(dimethylamino)phosphine. Results reported in [35] indicate that combustion chemistry of OPC is not well understood. Thus, the experimental data obtained demonstrated that an additive of DMMP to the lean and rich methane-oxygen atmospheric flame results in rise of concentration of CH_3OH in 10 times. But results of modeling using mechanisms 2 and 3 failed to describe this fact. The models for oxidation of hydrocarbons, especially those involving C_2-C_4 species may contain rate constants, which are determined insufficiently accurate. The influence of a model for methane oxidation on final concentration of phosphorus-containing species in the lean and rich $CH_4/O_2/Ar$ flame doped with 2200 ppm of TMP can be demonstrated by the following data shown in Tables 4 and 5.

TABLE 4. FINAL CONCENTRATIONS OF PHOSPHORUS-CONTAINING SPECIES IN THE LEAN $CH_4/O_2/Ar$ FLAME DOPED WITH 2200 PPM OF TMP CALCULATED USING OUR INHIBITION MECHANISM AND 3 DIFFERENT MECHANISMS OF CH_4 OXIDATION.

Species	Experimental results	Simulated final concentrations		
		CHEMKIN	Konnov	GRI 3.0
PO	0.3±0.3	0	0	0
PO_2	3±2	11.7	8.7	7.7
HOPO	6.8±2	4.4	3.1	2.7
$HOPO_2$	79±21	76.8	81.5	82.0
H_3PO_4	9±4.5	7.1	7.6	7.6

TABLE 5. FINAL CONCENTRATIONS OF PHOSPHORUS-CONTAINING SPECIES IN RICH $CH_4/O_2/Ar$ FLAME DOPED WITH 2200 PPM OF TMP CALCULATED USING OUR INHIBITION MECHANISM AND 3 DIFFERENT MECHANISMS OF CH_4 OXIDATION.

Species	Experimental data	Simulated final concentrations		
		CHEMKIN	Konnov	GRI 3.0
PO	5.7±5.7	4.2	2.6	2.9
PO_2	6.6±4.4	8.1	7.9	7.8
HOPO	78.2±16.6	60.7	50.7	53.3

$HOPO_2$	9.4±2.8	26.1	37.3	34.6
H_3PO_4	0	1.0	1.5	1.3

Although the concentrations simulated using different methane oxidation mechanisms differ not more than in 1.5-2 this fact is of interest. The modeling results can be explained by different concentrations of active species predicted by different mechanisms of methane combustion as phosphorus-containing components of a flame react actively with free atoms and radicals. As the concentration of active species in the studied flames is higher than summary concentrations of phosphorus species a small change in their concentration can result in appreciable change of concentrations of phosphorus-containing products. Tables 6 and 7 presented below give an example of the effect of the model applied for simulation of the flame structure on concentration of active species.

TABLE 6. MAXIMAL CONCENTRATION OF ACTIVE SPECIES IN THE RICH $CH_4/O_2/Ar$ FLAME DOPED WITH 2200 ppm OF TMP CALCULATED USING (1) GRI 3.0 FOR METHANE OXIDATION AND MECHANISMS 1, 2 AND 3 FOR TMP DESTRUCTION (SECTION 1); (2) USING MECHANISM 1 FOR TMP DESTRUCTION AND 3 VARIOUS MECHANISM FOR METHANE OXIDATION SECTION2).

Species	Section 1			Section 2		
	mechanism1	Mechanism2	mechanism3	CHEMKIN	Konnov	GRI 3.0
H	1.03×10^{-3}	5.72×10^{-4}	7.37×10^{-4}	1.61×10^{-3}	9.75×10^{-4}	1.03×10^{-3}
OH	3.87×10^{-4}	2.37×10^{-4}	3.13×10^{-4}	4.64×10^{-4}	3.94×10^{-4}	3.87×10^{-4}
O	5.45×10^{-5}	4.78×10^{-5}	4.70×10^{-5}	8.34×10^{-5}	4.32×10^{-5}	5.45×10^{-5}

TABLE 7. MAXIMAL CONCENTRATIONS OF THE ACTIVE SPECIES IN THE RICH C3H8/O2/Ar FLAME DOPED WITH 1200 ppm OF TMP CALCULATED USING KONNOV'S MECHANISM FOR PROPANE OXIDATION AND MECHANISMS 1, 2 AND 3 FOR TMP DESTRUCTION.

species	mechanism1	mechanism2	mechanism3
H	1.44×10^{-3}	9.08×10^{-4}	1.06×10^{-3}
OH	5.09×10^{-4}	3.93×10^{-4}	4.41×10^{-4}
O	1.01×10^{-4}	8.54×10^{-5}	8.89×10^{-5}

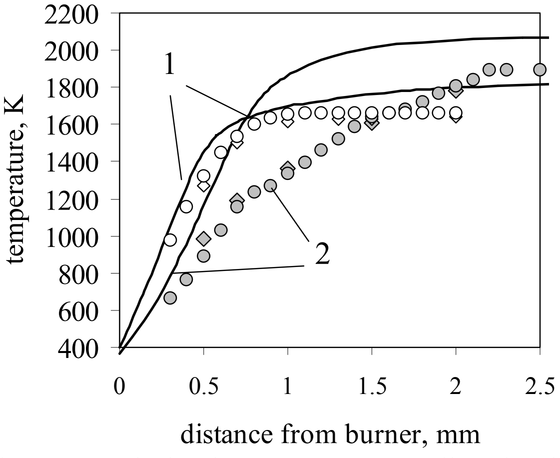

Fig. 11 Calculated temperature profiles in lean $CH_4/O_2/Ar$ flame at 1 atm without additive (1, open circle) and with 2200 TMP (2, black circle). Experiment – points, modeling- solid lines.

Thus, it is difficult to expect an agreement between simulated and measured concentration of phosphorus-containing species better than ±50 % for several flames simultaneously. In spite of necessity of further modification of the models describing inhibition action of OPC on a flame, the problems with a kinetic mechanism of hydrocarbon oxidation should be taken into consideration. The direction of further research to refine the models for inhibition of combustion should be specially discussed. The updating a model with new stages involving phosphorus-containing compounds seems to be a good idea. But the example of published models demonstrated that an introduction of new stages describing the interaction of phosphorus oxides with carbon-containing species was not quite

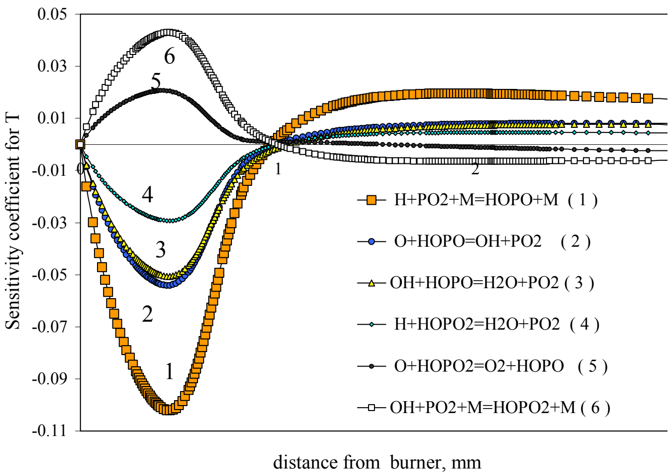

Fig. 12 Results of sensitivity analysis for temperature in lean $CH_4/O_2/Ar$ flame doped 2200 TMP.

helpful. The introduction of additional stages should be well founded and directed to solution of definite problems and based on sensitivity analysis. Another way of refinement consists in calculation of rate constants of reactions. Although this way is very difficult and consumes a lot of time it seems to be on of prospective.

It is noteworthy that all 3 above mentioned models involving phosphorus containing reactions provide a good agreement for burning velocity of atmospheric stoichiometric propane-air flame doped with TMP [25]. It is connected with a close value of the rate constant of the key reaction #3 (Table 1), which controls burning velocity, in all 3 mechanisms. To check out and improve OPC inhibition mechanism we compared results of flame structure modeling (which have been conducted without using specified temperature profile) with similar results of experiment in which flame was not disturbed. These data are flame temperature profiles measured with help of thermocouple located far from the tip of the probe. Results of such comparison are presented in Fig. 11. At modeling rate constant only of reaction # 3 in mechanism 1 (mechanism 1.1 according to [25]) was modified (the pre-exponential factor has been increased in 4 times). This mechanism gave best agreement between experiment and modeling on burning velocity of CH_4/air doped TMP. Results of sensitivity analysis of phosphorus-involving reactions on temperature profile are presented in Fig. 12. They show that reaction #3 is most important one in inhibition in low temperature flame zone and in promotion in high temperature zone of flame. The data presented in this paper give possibility to increase a number of parameters for matching modeling and experimental results. The further research in this direction will allow to refine the existing models and obtain a more reliable mechanism.

ACKNOWLEDGEMENT

This work was supported by US Army Research Office under grant DAAD 19-00-1-0136 Modification No. P00001.

REFERENCES

1. Korobeinichev, O.P., Chernov, A.A., Shvartsberg, V.M., "Mass-spectrometric Investigations of a Stoichiometric $H_2/O_2/Ar$ Flame Doped with Trimethylphosphate and Tributhylphosphate ", *Preprint Pap. Am. Chem. Soc., Division of Fuel Chemistry* 39: 193 (1994).
2. Korobeinichev O.P., Ilyin S.B., Mokrushin V.V., Shmakov A.G., "Destruction chemistry of dimethyl methylphosphonate in $H_2/O_2/Ar$ flame studied by molecular beam mass spectrometry ", *Combust. Science and Technology* 116-117: 51 (1996).
3. Werner, J.H., and Cool, T.A., "A Kinetic Model for the Decomposition of DMMP in a Hydrogen/Oxygen Flame ", *Combust. Flame* 117: 78 (1999).

4. Melius, C., http://herzberg.ca.sandia.gov/carl_melius.html/
5. Twarowski, A..J., "The Influence of Phosphorus Oxides and Acids oπ Rate of H+OH Recombination ', *Combust. Flame* 94: 91 (1993).
6. Twarowski, A.J., "Reduction of a Phosphorus Oxide and Acid Reaction Set "*Combust. Flame* 102: 55 (1995).
7. Twarowski, A.J., "The Temperature Dependence of H+OH Recombination in Phosphorus Oxide Containing Combustion Gases", *Combust. Flame* 105: 407 (1996).
8. Korobeinichev, O.P., Ilyin, S.B., Shvartsberg, V.M., and Chernov, A.A., "The Destruction Chemistry of Organophosphorus Compounds in Flames - I: Quantitative Determination of Final Phosphorus-containing Species in Hydrogen-Oxygen Flames ", *Combust. Flame* 118: 718 (1999).
9. Korobeinichev, O.P., Shvartsberg, V.M., and Chernov, A.A., " The Destruction Chemistry of Organophosphorus Compounds in Flames - II: Structure of a Hydrogen-Oxygen Flame Doped with Trimethyl Phosphate ", *Combust. Flame* 118: 727 (1999).
10. Korobeinichev, O.P., Ilyin, S.B, Bolshova, T.A., Shvartsberg, V.M., Chernov, A.A., *"* The Destruction Chemistry of Organophosphorus Compounds in Flames - III: The Destruction of DMMP and TMP in a Flame of Hydrogen and Oxygen*", Combust. Flame* 121: 593 (2000).
11. Korobeinichev, O.P., Chernov, A.A., Bolshova, T.A. "Destruction of Organophosphorus Compounds in Flames IV: Destruction of DIMP in a Flame of H_2 + O_2 + Ar", *Combust. Flame* 123: 412 (2000).
12. Korobeinichev, O.P., Bolshova, T.A., Shvartsberg, V.M., Chernov, A.A. "Inhibition and Promotion of Combustion by Organophosphorus Compounds Added to Flames of CH_4 or H_2 in O_2 and Ar", *Combust. Flame* 125: 744 (2001).
13. Korobeinichev, O.P., Bolshova, T.A., Shvartsberg, V.M., Chernov, A.A., and Mokrushin, V.V., "Inhibition Effect of TMP on $CH_4/O_2/Ar$ and $H_2/O_2/Ar$ Flames ", *Proceedings of Halon Option Technical Working Conference*, Albuquerque, NM, 1999, p.488.
14. Korobeinichev, O.P., Mamaev, A.L., Sokolov, V.V., Bolshova, T.A., and Shvartsberg V.M., " Inhibition of Methane Atmospheric Flame by Organophosphorus Compounds ", *Proceedings of Halon Options Technical Working Conference*, Albuquerque, NM, 2000, p.164.
15. Korobeinichev, O.P., Mamaev, A.L., Sokolov, V.V., Bolshova, T.A., Shvartsberg, V.M., " Experimental Study and Modeling of the Effect of Phosphorous-Containing Compounds on Premixed Atmospheric Methane-Oxygen Flame Structure and Propagation Velocity ", *Proceedings of Halon Option Technical Working Conference*, Albuquerque, NM, 2001, p.173.
16. MacDonald, M.A., Gouldin, F.C., Fisher, E.M. "Temperature Dependence of Phosphorus-Based Flame Inhibition", *Combust. Flame* 124:668 (2001).
17. Kaizeman, J.A., Tapscott, R.E., "*Advanced Streaming Agent Development. Vol. 3. Phosphorus Compounds*", NMERI, Report No. NMERI 96/5/32540, 1996.
18. Glaude P.A., Curran H.J., Pitz W.J. and Westbrook C.K., "Kinetic Study of the Combustion of Organophosphorus Compounds", *Proceedings Twenty-Eighth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 2001, p.1749.
19. http://www-cms.llnl.gov/combustion/combustion_home.html.
20. Wainner, R.T., McNessby, K.L., Daniel, R.G., Miziolek, A.W., Babushok, V.I., *Proceedings of Halon Option Technical Working Conference*, Albuquerque, 2000, p.141.
21. Babushok, V., Tsang, W., *Proceedings of the Third International Conference on Fire Research and Engineering*, Society of Fire Protection Engineers, Bethesda, 1999, p.257.

22. Rumminger, M.D., Linteris, G.T., "The Role of Particles in the Inhibition of Counter-Flow Diffusion Flames by Iron Pentacarbonyl", *Combust. Flame* 128:145 (2002).
23. Riches, J., Knutsen, L., Morrey, E., and Grant, K.A., "A Flame Ionisation Detector As a Screening Toll for Halon Alternatives", Proceedings, Halon Option Technical Working Conference, Albuquerque, NM, pp. 115-125, 2000.
24. Mather, J.D., and Tapscott, R.E., "Project Reviews: Tropodegradable Bromocarbon Extinguishants - II and Fluoroalkyl Phosphorus Compounds", proceedings, Halon Options Technical Working Conference, Albuquerque, NM, pp. 197-203, 2001.
25. Shmakov, A.G., Korobeinichev, O.P., Bolshova, T.A., Knyazkov, D.A., Zakharov, L.S., Kudryavtsev, I.Yu., "Study of Effect of Organophosphorus Fire Suppressants on Premixed C_3h_8/Air and Diffusive Counterflow CH_4/Air Flames". Proceedings, Halon Option Technical Working Conference, Albuquerque, NM, 2002, pp. ??
26. Nyden, M.R., Yang, J.C., and Mather, J.D., "Screening of Candidate Fire Suppressant", Proceeding of Halon Option Technical Working Conference, Albuquerque, NM, 2000, p. 104-114.
27. Korobeinichev, O.P., Tereshenko, A.G., Emel'yanov, I.D., Fedorov, S.Y., Kuibida, L.V., and Lotov V.V., "Use of a mass-spectrometric probe in structural studies of flames with narrow combustion zones ", *Combust. Explos. Shock Waves* 21: 524 (1985).
28. Fristrom, R.M., *Flame Structure and Processes*, Oxford University Press: New York, 1995, p.124.
29. Kee, R.J., Grcar, J.F., Smooke, M.D., and Miller J.A., "PREMIX", Sandia National Laboratories Report No. SAND85-8240.
30. Kee, R.J., Rupley, F.M., Miller, J.A., "CHEMKIN-II: A Fortran Chemical Kinetics Package for the Analysis of Gas Phase Chemical Kinetics," Sandia National Laboratories SAND89-8009B.
31. http://www.cstl.nist.gov/div836/ckmech
32. Smith, G. P., Golden, D. M., Frenklach, M., Moriarty, N. W., Eiteneer, B., Goldenberg, M., Bowman, C. T., Hanson, R. K., Song, S., Gardiner, W. C. Jr., Lissianski, V. V. and Qin, Z. GRI Mech 3.0 (1999) http://www.me.berkeley.edu/gri_mech/
33. KONNOV, A.A. Detailed reaction mechanism for small hydrocarbons combustion. Release 0.5 http://homepages.vub.ac.be/~akonnov/, 2000.
34. Hebgen, P., Homan, K.H., "Phosphorus Compounds as Flame Inhibitors - Analysis of Ionic Intermediates," *Proceedings Twenty-Seventh Symposium (International) on Combustion*, Pittsburgh, 1998*, Book of Abstracts,* p.497.
35. Nogueira, M.F.M., Fisher, E.M. "Effect of Dimethyl Methylphosphonate on Premixed CH_4/O_2/Ar Flame," *Proceedings of the Joint US section meeting*, The Combustion Institute, Washington, DC, March 1999.