EXPERIMENTAL STUDY AND MODELING OF THE EFFECT OF PHOSHORUS-CONTAINING COMPOUNDS ON PREMIXED ATMOSPHERIC METHANE-OXYGEN FLAME STRUCTURE AND PROPAGATION VELOCITY

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INTRODUCTION

Organophosphorus compounds (OPC) are known to be effective fire retardants and fire suppressants and are perspective candidates for replacement of halons forbidden for production by Montreal Protocol. Appreciable progress in the comprehensive study of the flames doped with OPC achieved in recent years [1-24] resulted in the creation of number of kinetic models of OPC destruction in flames and the mechanisms of their action on a combustion process [10,14,15,17,23]. The study of Twarowski [2-4] who discovered that the products of phosphine oxidation catalyze the recombination of H and OH radicals, proposed and refined the kinetic mechanism of this process that preceded the appearance of these models. PO, PO_2, HOPO, $HOPO_2$ and $OP(OH)_3$ were identified in the flame doped with OPC and their concentrations were measured [14].

One of the first published models for OPC destruction in a flame was the model of the destruction of dimethyl methylphosphonate (DMMP) in a H_2/O_2 flame proposed by Werner and Cool [10] and based on the theoretical calculation of Melius [24]. Unfortunately, this model was insufficiently validated by experimental data. Authors of the present papers proposed the models for the destruction of TMP and DMMP in a H_2/O_2 flame slightly different from the model [10]. The simulated structure of subatmospheric H_2/O_2 flames doped with TMP and DMMP was in satisfactory agreement with experimental results. The model was refined later [19, 20] and applied for simulation of structure of CH_4/O_2 flame doped with TMP at a pressure of 0.1 bar and calculation of its burning velocity at P=I bar. The results were compared with experimental data obtained by the authors of the model. Babushok and Tsang [17, 23] proposed a kinetic model, composed of the stages with participation of OPC from the model of Werner and Cool [10], 79 reactions from the Twarowski mechanism (including reactions of phosphine oxidation with participation of PH_2, PH_3, PH), and several stages of interaction of CH_3 and CH_3O with phosphorus oxides. The rate constants of main Twarowski reactions have been modified including their dependencies from the temperature. Unfortunately, there are no published data on simulated structure of a flame doped with OPC using this model that could facilitate validation of the model by comparing the calculated data with experimental results. This model was applied only for calculation of burning velocities of stoichiometric CH_4/air flame at a pressure of 1 **bar.** The investigations of Westbrook and co-workers [15] devoted to the development of mechanisms of destruction and pyrolysis of OPC in flames are of great interest. This study is significant because the results of the calculation of thermo-chemical properties of OPC obtained using BAC-MP4 and PM3 codes are presented and compared with published data. The kinetic model of DMMP and TMP destruction in a flame includes 202 reactions involving 41 phosphorus-containing species. At the same time the model takes into consideration practically **all** intermediates. Rate constants of many reactions are proposed by the authors. Rate constants of the reactions of the Twarowski mechanism have been modified. Comparison of calculated data obtained with a help of this model with experimental results on structure of subatmopheric H_2/O_2 flame doped with DMMP and TMP demonstrated satisfactory agreement not only for stable flame species but also for labile phosphorus-containing species PO, PO_2, HOPO and $HOPO_2$ [5,8]. The mechanism predicts the promoting effect of TMP and DMMP additives on H_2/O_2 flame stabilized on a flat burner at a pressure of 0.062 bar. In the work neither scheme of reactions in a flame nor rate constants are presented. Nevertheless, there is a reference [22] to the kinetic data on the web site.

The perspectives of practical use of OPC as fire suppressants and flame inhibitors set the need to study the processes that occur in the flames doped with OPC at a pressure of 1 bar and elaboration of a kinetic model that can predict the structure and burning velocity of a flame doped with OPC in the range of pressure from low to atmospheric one. In Korobeinichev et al. [20], the investigation of the structure of a CHJO, flame doped with TMP and stabilized on a flat burner at 1 bar began. The goal of the present work is the experimental and theoretical study of the structure of CHJO, flames without additives and doped with TMP at a pressure of 1 bar and calculation of their burning velocities. Modeling of these flame structures and calculation of their burning velocities will make it possible to validate the model proposed earlier and maybe refine it. Another goal of the present study is the search for new, high-vapor-pressure OPC fire suppressants with high suppression efficiency.

EXPERIMENTAL, METHODICAL PROBLEMS

The systematic research of chemical structure of gaseous flames at 1 bar using mass spectrometry (MBMS) was not performed in the past. It may be explained mainly by methodical difficulties in taking into account the appreciable perturbations of the flames caused by a sonic probe. When studying the structure of atmospheric flat flames using MBMS, it has been discovered that measured concentration profiles of main flame species CH_4, O_2, and H_2O, shifted in accordance with the shift of lines of equal concentrations in a flame caused by a probe, are displaced from the temperature profile. It is explained by appreciable heat losses from the flame not only into the burner but into a probe and surrounding space. The flame heat losses into the probe depend on the probe's position relatively the burner and cannot be estimated. To measure temperature profile of the perturbed flame correctly one should use a thermo-couple placed near the probe's tip. This technique was proposed by two groups of authors [25, 26] and was applied for flat flames stabilized at low pressure. We demonstrated earlier that for the probes having a wall thickness of **0.05** mm, the temperature profiles in low pressure flames measured by a thermo-couple near the probe's tip and far off probe practically do not differ from one another [27]. The authors [25,26] recommend placing a thermocouple at the distance of **2-3** diameter of the thermocouple junction from the probe that is **0.2-0.3** mm in the case of the thermocouple 0.1 mm in diameter. At atmospheric pressure, when the effect of a probe on the flame is stronger, the selection of optimal distance between a probe and a thermocouple is made by comparison of concentration profiles of CH,, O_2, and H_2O with profiles of temperature measured by a thermocouple, the junction of which is placed at varied distances (δ) from the probe's tip. It is noteworthy that, in order to correct data, the measured concentration profiles should be moved toward the burner relative to the temperature profile on the value of sampling shift. The goal of the comparison is to achieve the similarity of profiles of concentrations of stable flame species and temperature. The experiments demonstrated optimal distance to be δ=0.3 ± **0.03** mm. It is evident that this recommendation can be applied for certain types of probes and thermocouples.

The structure of $CH_4/O_2/Ar$ **(6/15/79** and **7.5/12.5/80%)** flame stabilized on a flat-flame Botha-Spalding burner at atmospheric pressure was studied. The burner temperature was maintained at **338** K by using a thermostat. The volumetric flow rate of unburned mixture was **25** cm^3/s under normal conditions. Errors of measurement of volumetric flow rate did not exceed 1%. The burner was made of a copper disk with a diameter of 16mm having **150** orifices with a diameter of 0.7 mm. The combustible mixture was prepared by mixing of the flows of three gases. Individual flows were controlled with the aid of "MKS Instruments" flow meters. The TMP was added to the common flow by means of a bubblier. The additive concentration measured by the decrease of TMP mass in the bubblier. Measurements of flame species concentration were performed on a experimental setup including a quadrupole mass spectrometer **MS–7302** with a molecular beam sampling and soft ionization by electron impact [5, 7]. Due to the use of electrons with low energies close to the potential of ionization of molecules, atoms, and radicals, there was a possibility of diminishing (or complete preventing) of ion fragmentation. A quartz sonic probe with the following parameters was used: orifice diameter **0.05** mm, wall thickness near the orifice 0.08 mm, inner angle near the orifice 40 deg.

The temperature of the flames was measured by a Pt - Pt+10% Rh thermocouples welded from wire of 0.02 mm in diameter (junction of 0.03 mm in diameter). The thermocouple had a Π-shape with length of shoulders about 2 mm. At such ratio between diameter and shoulder length, the heat losses in the cold ends of thermocouple are negligibly small.

The study of OPC additives on velocity of freely propagating flame in CH_4/air mixture was performed using Mache- Hebra nozzle burner described elsewhere [28] and the total area method from an image. Burning velocity was estimated 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%. The experimental technique was described earlier [20]. The size of the flame cone was measured by the luminous zone but not with the help of the Schlieren method. This technique introduced an error in absolute values of burning velocity, which is why we present here the ratio (f) of burning velocity of inhibited flame (u_g) to burning velocity of undoped flame (u_0) as a value characterizing the effectiveness of an inhibitor. To ascertain the reliability of the data obtained, the magnitude of (f) was measured in a different way. For that the height of the cone of doped flame was decreased and became equal to the cone of a undoped flame owing to the decrease of volumetric flowrate of the combustible mixture. In this case, the effectiveness of an inhibitor was estimated as $f=W_g/W_0$, where W_g and W_0 are the volumetric flow rate of combustible mixture for inhibited and for uninhibited flames, respectively. Results obtained by both methods demonstrated satisfactory coincidence.

RESULTS

Figures 1 and 2 show concentration profiles for CH_4, O_2, and H_2O and temperature profiles (measured by the thermocouple placed at $\delta=0.3$ mm) in the lean $CH_4/O_2/Ar$ flame without additive and with 2200 ppm of TMP. The additive increases the combustion zone width of the flame for about 1 mm. Here and below all concentration profiles are shifted toward the burner surface for the value of sampling shift [29].

The sampling shift (z) according to [29] depends on the flame temperature as $z = z_0 \sqrt{\dfrac{T_0}{T}}$ where T_0 - is

initial temperature of the combustible mixture, T - is a flame temperature for a certain distance from the burner, z_0 - sampling shift at $T=T_0$ [29]. In the present study, the sampling shift varied from 0.51 to 0.27 mm.

The concentration profiles of CH_4, O_2, and H_2O and temperature profiles (measured by the thermocouple placed at $\delta=0.3$ mm) in the rich $CH_4/O_2/Ar$ flame without additive and with 2200 ppm of TMP are shown in Figures 3 and 4 correspondingly. As it is clear from a comparison of data in these figures, the introduction of the additive into the flame results in increasing of the pre-flame zone with a simultaneous increase in concentration gradients for CH_4, O_2 and H_2O. It is evidently connected with strong inhibition effect resulting in appreciable remove of the flame front away from the burner, which is accompanied by a decrease of heat losses into the burner.

The concentration profiles of final phosphorus-containing products of TMP destruction in the rich flame are shown in Figure 5. The energy of ionizing electrons of 12.8 eV for PO, PO_2, and HOPO, 14.5 eV for $HOPO_2$, and 17.5 eV for $OP(OH)_3$ made it possible to use the calibration coefficients for the species obtained earlier [7]. In the peak at 80 amu measured at energy of ionizing electrons of 14.5 eV, the molecular ion $HOPO_2^+$ and fragmentary ions of TMP and some intermediate products of TMP destruction in flames such as dimethylphosphate, dimethylphosphite and others contribute. As appearance potentials of above-mentioned fragmentary ions of OPC are lower than the ionization potential of $HOPO_2$, it is impossible to escape contribution of fragmentary ions into peak at 80 amu. To obtain Concentration profile of $HOPO_2$, it is necessary to subtract from the intensity of peak at 80 amu the contribution of all OPC, intermediates of TMP destruction in flame. Unfortunately, it is impossible as mass spectra of some of the intermediates (methylphosphate, methylphosphite and others) are unknown because of their instability
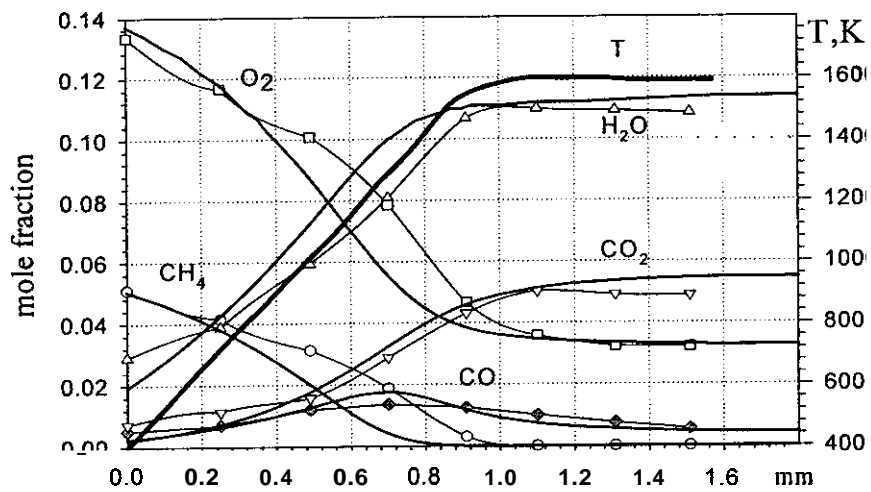
Figure 1. The concentration profiles for **undoped lean** $CH_4/O_2/Ar$ (0.06/0.15/0.79) **flame.**
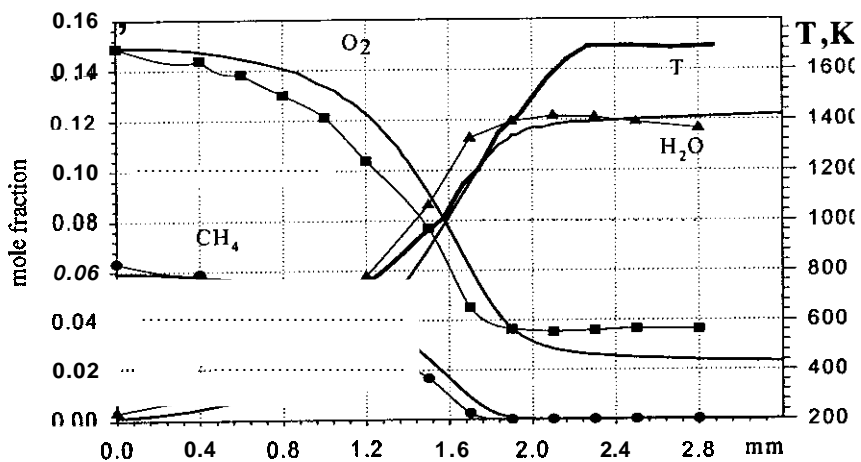**Solid lines – modeling; symbols – experiment.**

Figure 2. The concentration profiles for **doped lean** $CH_4/O_2/Ar$ (0.06/0.15/0.79) **flame**
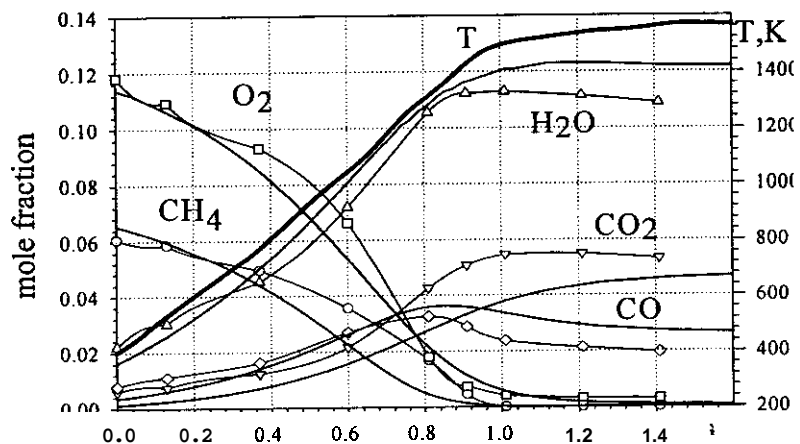**with 2200 ppm of TMP. Solid lines – modeling; symbols – experiment.**

Figure 3. The concentration profiles for **undoped rich** $CH_4/O_2/Ar$ (0.075/0.125/0.80) **flame.**
Solid lines – modeling; symbols – experiment.
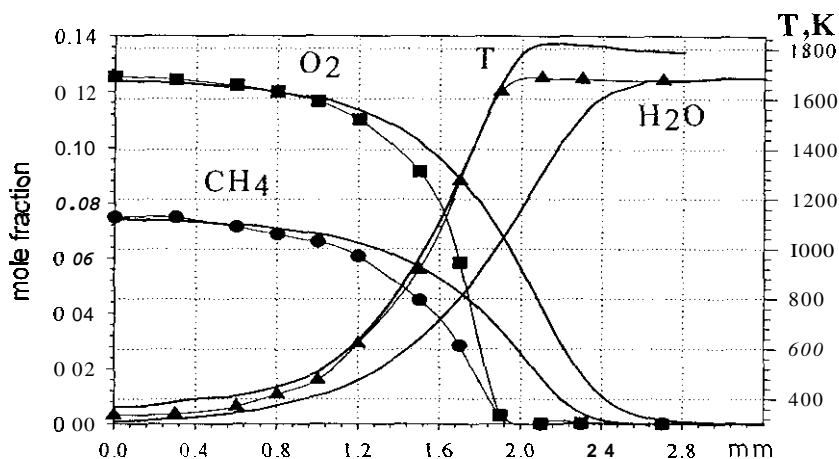
Figure 4. The concentration profiles for doped rich $CH_4/O_2/Ar$ (0.075/0.125/0.80) flame with 2200 ppm of TMP. Solid lines − modeling; symbols − experiment.
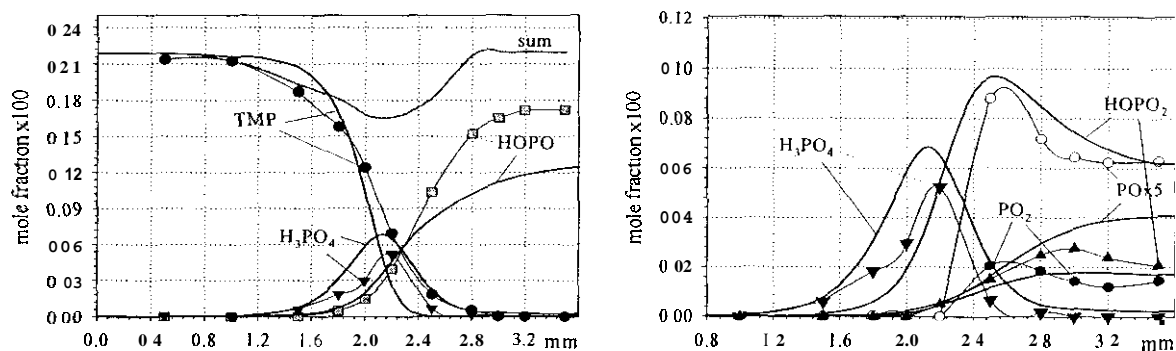
Figure 5. Concentration profiles of final phosphorus containing products of TMP destruction in $CH_4/O_2/Ar$ (0.075/0.125/0.80) and sum of experimentally measured concentration of TMP, H_3PO_4, $HOPO_2$, HOPO, PO_2, PO. Solid lines − modeling; symbols − experiment

and therefore inaccessibility at normal conditions. Taking into account the contributions in peak at 80 amu from TMP and dimethylphosphate (peak at 126 amu), assuming the concentration profile should be smooth and relying on conservation of phosphorus, the profile of concentrations of HOPO, in the rich $CH_4/O_2/Ar$ flame was plotted (Figure 5). Figure 5 represents the final concentration of HOPO, in the flame reliably only at about 3 mm and more from the burner surface where there are no OPCs. The thermodynamic calculation of equilibrium concentrations of these species in the rich flame (Figure 6) demonstrates that concentration of HOPO is maximal, that is in accordance with experimental data. Orthophosphoric acid is an intermediate product of TMP destruction in the rich flame. Thermodynamic calculation of equilibrium concentrations predicts an absence of $OP(OH)_3$ at the temperatures above 1600K (Figure 6). Unlike the lean flame, the main final phosphorus-containing compound in the rich flame is HOPO, which is in accordance with the thermodynamic calculation (Figure 6).

Combustion is well known to be a process controlled by radicals. Therefore, a mechanism of action all inhibitors including OPC on combustion is based on the effect of inhibitor's destruction products in flame on concentration of active flame species. Thus, a study of influence of OPC additives on profiles of temperature, concentration of stable and active (H, O, OH) species in CH_4/O_2 flames and, besides, determination of concentrations of active phosphorus-containing destruction products PO, PO_2, HOPO, $HOPO_2$, and $OP(OH)_3$ is necessary to understand the mechanism of influence of OPC on combustion. If the kinetic model of combustion of a CH_4/O_2 doped with OPC correctly predicts the concentration profiles

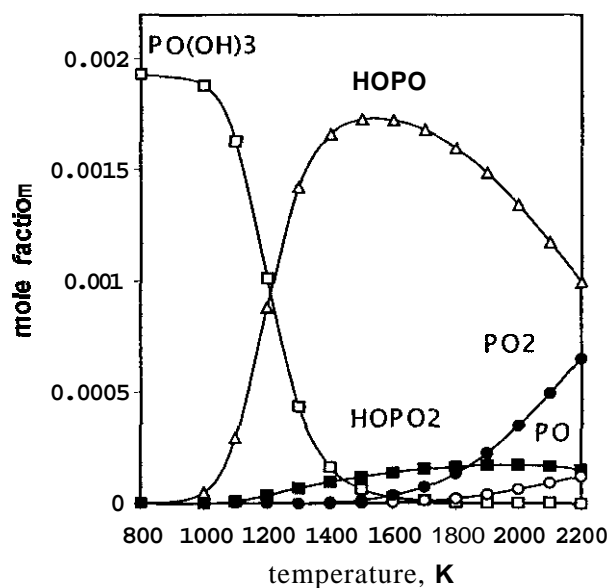Figure 6. Equilibrium concentrations of PO, PO,, HOPO, HOPO, and $PO(OH)_3$ for TMP
doped $CH_4/O_2/Ar$ (0.075/0.125/0.80) flame as a function of temperature.

of free radicals and phosphorus oxides and acids, this model can be recognized to be perfect. Determination of concentration of H, O, and OH in final combustion products of flames is based on the detailed equilibrium of three "fast" reactions and quasi-stationary approximation. This method made it possible to obtain concentration profiles of H and OH in the lean undoped flame and flame doped with 350 ppm of TMP (Figures 7 and 8). Measurement of intensities of peaks at 1 and 17 amu (H and OH, respectively) was carried out at ionization energy of 16.5 eV. Figures 7 and 8 demonstrate that introduction of the inhibitor results in a noticeable decrease in concentrations of both species. When the inhibitor was added, the concentration of H decreased about 40% and that of OH decreased in 2 times. The results obtained demonstrate a strong decrease of concentration of the most active species in CH_4/O_2 flame doped with OPC at 1 bar. It is noteworthy that earlier [8] an increase of OH concentration for 20% in $H_2/O_2/Ar$ flame stabilized at flat burner at low pressure when an additive of TMP was introduced. As to oxygen atom, it is impossible to measure in CH_4/O_2 flame the intensity of peak at 16 amu corresponding only O as its ionization potential (13.618 eV) is higher than ionization potential of CH_4 (12.98 eV) [30]. Figure 9 presents the intensity profiles of peak at 15 amu corresponding to CH, in the lean $CH_4/O_2/Ar$ flame without the additive and in the same flame but doped with 350 ppm of TMP. The measurement of the mass peak intensity was performed at ionization energy of 14.2 eV.

The profiles (Figure 9) show that the addition of TMP effects the concentration of CH, similarly to that of H and OH by decreasing it twice. The data shown above indicate that effectiveness of OPCs as inhibitors consists in strong nonselective influence on concentration of the most active flame species.

The effect of number of OPC on efficiency of inhibition of stoichiometric CH_4/air flame was studied at atmospheric pressure. The fluorine- and nitrogen-containing volatile (in comparison with regular phosphates and phosphonates) are of special interest. The OPC and some of their properties studied are presented in Table 1.
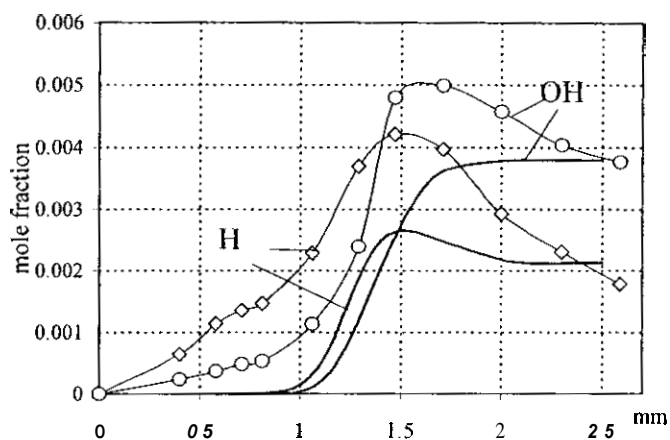
Figure 7. Concentration profiles of H and OH in the lean undoped $CH_4/O_2/Ar$ flame. Solid lines – modeling; symbols – experiment.
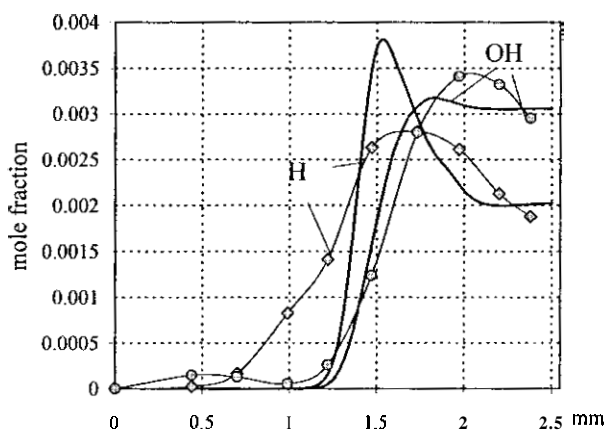

Figure **8.** Concentration profiles of H and OH in the lean $CH_4/O_2/Ar$ flame doped with 350 ppm of TMP. Solid lines – modeling; symbols – experiment.
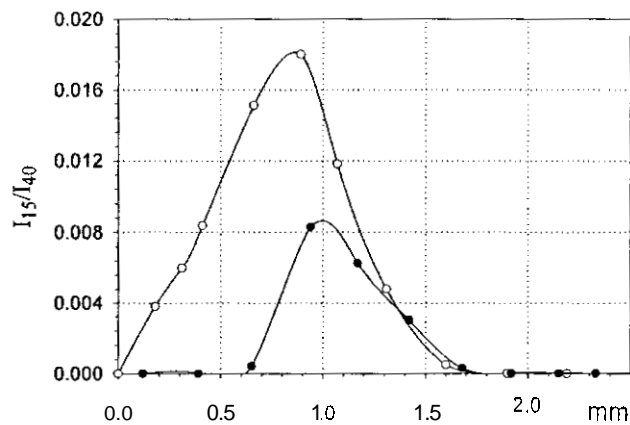

Figure **9.** Profiles of intensities of peak at 15 amu (CH,) in lean $CH_4/O_2/Ar$ (0.06/0.15/0.79) flame without additive (open symbols) and doped with *0.035%* of TMP (filled symbols).

TABLE 1. ORGANOPHOSPHORUS COMPOUNDS TESTED AS FIRE SUPPRESSANTS.

Compound	Boiling Point [°C] at Pressure [Torr]
$(C_2H_5O)_2PO(CH_3)$	194 / 760
$(C_2H_5O)_3P$	57 / 20
$(CF_3CH_2O)_3P$	57	20
$[(CH_3)_2N]_3P$	55 / 17
$[(CH_3)_2N]_3PO$	123 / 19

Dependencies of inhibiting effectiveness for OPC tabulated above are presented in Figure 10. The dependencies of burning velocity of CH_4/air mixture on its equivalence ratio (φ) as well as on TMP loading were measured. The data obtained for the undoped flames are in agreement with reference data [31]. The results of measurements plotted in Figure 11 show that different inhibition effectiveness for rich and lean flames is observed. Thus, for φ=1.30 at the increase of the inhibitor loading from 80 ppm up to 3.50 ppm(more than in 4 times) inhibition effectiveness slightly changes. Whereas for the flame with φ=0.9 the same increase of TMP loading results in decrease of (f) in 1.5 times. Therefore, the inhibition effectiveness for a flame appreciably depends on its equivalence ratio.
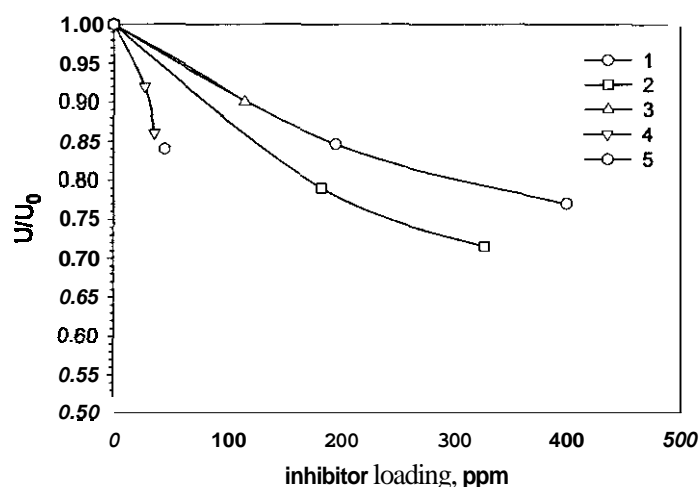

Figure 10. Normalized burning velocity (u/u_0) of stoichiometric CH_4/air flame mixture as a function of loading: 1 - $(C_2H_5O)_3P$, 2 - $(CF_3CH_2O)_3P$, 3 - $[(CH_3)_2N]_3P$, 4 - $[(CH_3)2N]_3PO$, 5 - $(C_2H_5O)_2PO(CH_3)$.

MODELING AND DISCUSSION OF RESULTS

For modeling the flame structure and calculation of velocity of freely propagating flame at a pressure of 1 bar, the kinetic model proposed earlier was first used. This mechanism (Mech. 1) provided good results when simulating the structure of $H_2/O_2/Ar$ and $CH_4/O_2/Ar$ flat flames doped with TMP and DMMP stabilized at low pressure of 0.062-0.1 bar. Mechanism 1 includes 58 elementary stages describing the oxidation of hydrogen and methane, 14 reactions of destruction of TMP and organophosphorus intermediate products of its destruction in a flame, 5 stages with participation of orthophosphoric acid, and 15 reactions, representing the so-called Twarowski mechanism for which we changed the kinetic constants [14, 19].

The comparison of results of simulated flame structure and calculation of burning velocity with experimental data obtained at 1 bar revealed an appreciable drawback of Mechanism 1. First, Mechanism 1 predicted lower inhibition effectiveness as a function of OPC loading in comparison with experimental results. Consequently, for calculation of the burning rates of atmospheric flames doped with OPC, the
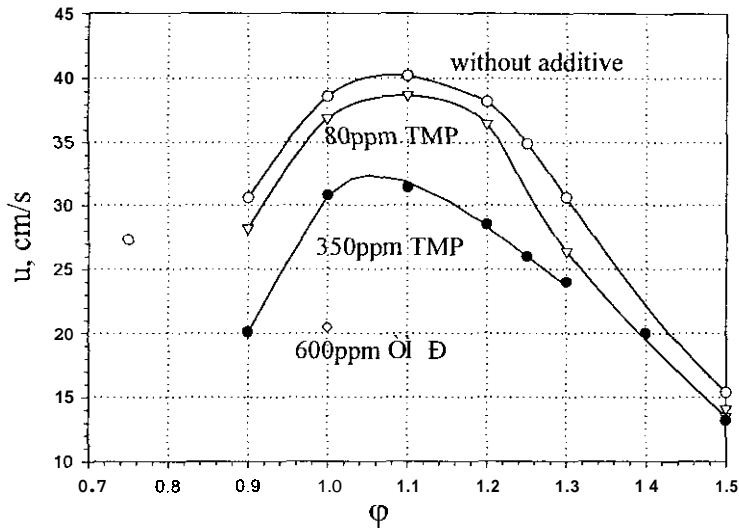
Figure 11. Burning velocity in the CH_4-air flame (T_0= 332 K, p=1 bar).

rate constants of 8 reactions from the Twarowski mechanism that produce the strongest effect on burning velocity have been changed (Table 2, col. 1). At the same time, the modification of the rate constants did not change their dependencies on temperature. These reactions were selected from the Twarowski mechanism (15 reactions) with the help of the following procedure. Velocities of freely propagating inhibited flames were calculated with the consequent reduction of the pre-exponential factor **of** each of 15 reaction rate constants in 5 times (as proposed by Warnatz [31]). To reach maximal inhibition effectiveness, the rate constants of the selected reactions were then changed in 10 times (Table 2, col. 2). The modified mechanism (Mech. 2) gave appropriate results of calculation of burning rates, but failed to predict satisfactory final concentrations of PO, PO_2, HOPO, $HOPO_2$, and $OP(OH)_3$ in the flames stabilized on a flat burner at a pressure **of** 1 bar. To elaborate **a** kinetic model that satisfactorily simulates the flame structure, properly predicts the burning velocities and, besides, **final** concentrations of phosphorus-containing flame species, the sensitivity coefficients of **all** reactions in the Mechanism 2 have been calculated.

TABLE 2. MOST IMPORTANT REACTIONS RESPONSIBLE FOR INHIBITION EFFECT AND THEIR RATE CONSTANTS FOR MECHANISMS 1, 2, AND 3 (EXPRESSED AS $K = A\ T^N * EXP(-E/RT)$).

Reaction	1			2	3
	A	N	E	A	A
$OH+PO_2+M=HOPO_2+M$	1.6×10^{25}	-2.28	285.0	1.6×10^{24}	1.6×10^{24}
$H+HOPO_2=H_2O+PO_2$	6.32×10^{11}	0.00	11930.0	6.32×10^{12}	6.32×10^{12}
$H+PO_2+M=HOPO+M$	9.73×10^{24}	-2.04	645.0	9.73×10^{25}	9.73×10^{24}
$OH+HOPO=H_2O+PO_2$	3.16×10^{11}	0.00	0.0	3.16×10^{12}	3.16×10^{12}
$H+HOPO=H_2+PO_2$	7.9×10^{11}	0.00	43.0	7.9×10^{12}	7.9×10^{11}
$O+HOPO=OH+PO_2$	1.58×10^{12}	0.00	0.0	1.58×10^{13}	1.58×10^{13}
$O+HOPO+M=HOPO_2+M$	1.3×10^{24}	-2.11	995.0	1.3×10^{23}	1.3×10^{23}
$O+HOPO_2=O_2+HOPO$	6.32×10^{11}	0.00	8236.0	6.32×10^{12}	6.32×10^{12}

Note: Units **are** mol, cm^3, **s,** K and cal×mol⁻¹

The sensitivity coefficients selected were those that influenced the concentrations of PO, and HOPO. The calculated concentrations of these flame species were in the strongest disagreement with experimental results. The rate constants of the selected reactions were changed to achieve better agreement between modeling and experimentation. It is noteworthy that only those rate constants were changed which did not result in decrease of inhibition effectiveness. Thus, the rate constants of two reactions in Mechanism 2 were changed and Mechanism 3 was obtained (Table 2, col. 3). Final concentrations PO, PO,, HOPO, HOPO,, and $OP(OH)_3$ in the lean and rich $CH_4/O_2/Ar$ flames were calculated with a help of Mechanisms 1, 2, and 3 (Tables 3 and 4).

TABLE 3. FRACTIONS (%) OF PHOSPHORUS-CONTAINING SPECIES CONCENTRATION IN SUMMARY CONCENTRATION OF PHOSPHORUS IN FINAL COMBUSTION PRODUCTS OF THE LEAN FLAME DOPED WITH 2200 PPM OF TMP.

Species	Modeling Using Various Mechanisms			Experimental Results	
	1	2	3	Range	Average Value
$PO(OH)_3$	7.9	7.1	6.8	2.5t1.5	5.1
HOPO	3.0	11.4	8.3	5.8÷8.8	7.3
HOPO,	88.7	16.7	14.3	51.0÷95	73.0
PO	0.0	0.1	0.0	0.0÷0.6	0.3
PO_2	0.4	4.8	10.6	4.7÷24.3	14.3

TABLE 4. FRACTIONS (%) OF PHOSPHORUS-CONTAINING SPECIES CONCENTRATION IN SUMMARY CONCENTRATION OF PHOSPHORUS IN FINAL COMBUSTION PRODUCTS OF THE RICH FLAME DOPED WITH 2200 PPM OF TMP.

Species	Modeling Using Different Mechanisms			Experimental Results	
	1	2	3	Range	Average Value
$PO(OH)_3$	2.1	2.3	1.1	0.0	0.0
HOPO	34.6	34.1	58.1	62.6÷93.8	18.2
$HOPO_2$	56.2	59.7	28.9	6.6÷12.1	9.4
PO	4.5	1.0	3.8	1.9t9.5	5.7
PO_2	2.6	2.9	8.0	2.2÷11.0	6.6

It should be especially noted that modeling of structure of flame stabilized on the flat burner were performed using specified, experimentally measured profile of temperature, as was mentioned previously. The necessity of this procedure is explained by heat losses from the flame into a probe that cannot be taken into account when modeling. Figures 1 and 2 present simulated (using Mechanism 3) profiles of concentrations of stable species CH,, O_2, and H_2O in the lean $CH_4/O_2/Ar$ flame without additive and doped with 2200 ppm of TMP, respectively. Comparison of calculated and measured data demonstrates satisfactory agreement between modeling and experimentation. It is noteworthy that Mechanism 3 provides better agreement between simulated and experimentally measured concentration profiles of CH,, O_2, and H_2O than Mechanism 2. Figures 3 and 4 present simulated profiles of concentrations of CH_4, O_2, and H_2O in the rich $CH_4/O_2/Ar$ flame without additive and doped with 2200 ppm of TMP, respectively. There is satisfactory agreement between modeling and experimental results.

Figure 5 shows simulated and measured concentration profiles of TMP and phosphorus-containing products of its destruction in the lean $CH_4/O_2/Ar$ flame. To compare the calculated concentration profiles with those obtained in experimentation, the errors of estimation of calibration coefficients for these species [7] are presented in Table 5.

TABLE 5. ERRORS OF ESTIMATION OF CALIBRATION COEFFICIENTS FOR
PO, PO,, HOPO, HOPO, AND OP(OH),.

Species	PO	PO,	HOPO	HOPO,	OP(OH),
Relative error (%)	100	67	13	29	29

The errors of measurement of intensity of the corresponding peaks are sometimes even more than errors tabulated above. Thus, the error of measurement of intensities of peaks at 64 amu (HOPO) is 20%; for peaks at 80 (HOPO,) and **98** amu (OP(OH),), the errors are 30 and 35%, respectively. Figure 5 presents the concentration profiles of PO, PO,, HOPO, HOPO,, and OP(OH), in the rich $CH_4/O_2/Ar$ flame doped with 2200 ppm of TMP. In this case, one can see that a satisfactory agreement is observed not only on the final concentration of the species, but that the refined mechanism predicts properly the concentration profiles of the phosphorus oxides and acids along the combustion zone. The simulated and measured profiles of H and OH radicals in the lean $CH_4/O_2/Ar$ flame without additive and with 350 ppm of TMP are shown in Figures 7 and 8. The data presented in these figures demonstrate that experimental and calculated profiles of concentrations are in satisfactory agreement along the combustion zone. This indicates that modification of Mechanisms 1 and 2 aimed at reaching an agreement between calculated and experimental data on final concentration of phosphorus-containing flame species did not result in discrepancies between calculated and measured concentrations of other active flame species.

The results of calculation of inhibition effectiveness of TMP using Mechanisms 1-3 for stoichiometric CH_4/air flame at 1 bar are presented (Figure 8). The best agreement between the experiment and modeling is observed for Mechanisms 2 and 3. At this moment the refined kinetic model can simultaneously predict the flame structure (concentration profiles of stable components, some active species, and final phosphorus-containing products of OPC destruction in a flame) and burning velocity on TMP loading.

To reveal advantages and disadvantages of the model presented in comparison to the published one [17], a final one has been analyzed. Mechanism [17] includes a kinetic model of Werner and Cool for DMMP destruction in a flame and the Twarowski mechanism. This mechanism is composed of *79* reactions including stages with participation of P, PH, HPO, HPOH, and PO_3, which are not included in our kinetic model. The sensitivity analysis performed by us revealed that these species do not affect concentrations of final products of TMP (DMMP) destruction in a flame and were not included in our mechanism. The kinetic model [17] was also supplied with stages of interaction of CH, with PO,, HOPO, HOPO,, PO,, *HPO,* and of CH_3O with PO, and PO.

To explore the kinetic model [17], the burning velocity of stoichiometric CH_4/air flame doped with various concentration of TMP at 1 bar has been calculated. The rate constants of all 89 reactions involving phosphorus-containing species were varied (using the procedure proposed by Wamatz [31] and described above). Thus the reactions effecting the burning velocity have been determined (Figure 12). The results of this investigation revealed that most important reactions for inhibition of atmospheric CH_4/O_2 flame are $H+PO_2+M=HOPO+M$ and $H+HOPO=H_2O+PO_2$. So, the reduction *of* the rate constant of reaction $H+PO_2+M=HOPO+M$ in 5 times for the flame doped with 0.3% of TMP increases the burning velocity from 23.0 to 31.9 cmls. Effect of reactions involving radicals CH, and CH_3O on burning velocity have not been found. Thus, the mechanism [17] does not include additional important stages affecting the inhibition process as compared with our mechanism. The rate constants of reactions responsible for the inhibition effect and those that the authors [17] recommend for their model are absolutely different from those we recommend. Analysis of Table 6 and also Figure 13 demonstrates that Mechanism **3** provides some better agreement with experimental data than the mechanism [17].
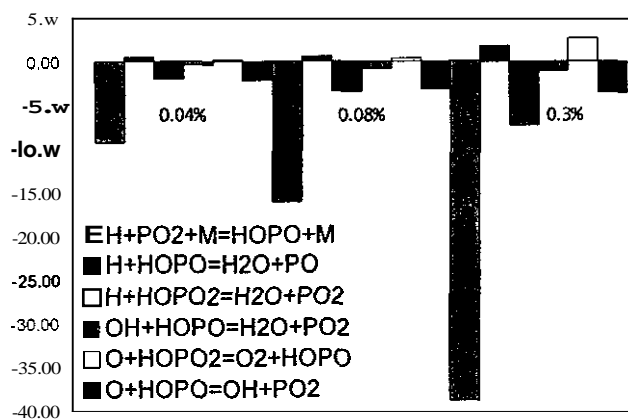
Figure 12. Influence of varied rate constants of elementary reactions on calculated value $\xi=100\%\times(u-u(k/5))/u$ for mechanism [17], where u- burning velocity in stoichiometric CH_4/air mixture doped with TMP of different concentrations at 1 bar, $u(k/5)$ – burning velocity for the rate constants decreased in 5 times.
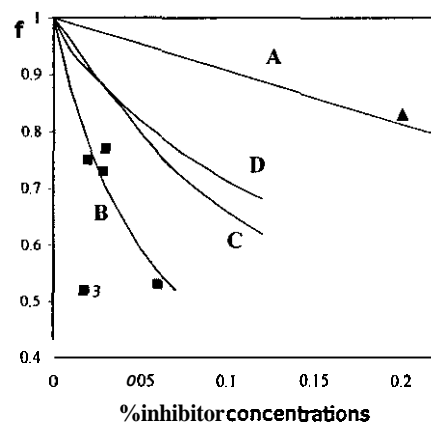
Figure 13. Dependence f on the additive concentration for the methane – air 9.5/90.5 flame: ■– TMP; ▲- CF_3Br (Halon 1301) [32]; Solid lines – modeling, A - using Mechanism 1, B - Mechanism 2, C - Mechanism 3, D - mechanism [17].

TABLE 6. COMPARISON OF CALCULATED CONCENTRATIONS OF FINAL PHOSPHORUS-CONTAINING PRODUCTS OF TMP DESTRUCTION IN THE LEAN AND RICH FLAMES USING DIFFERENT KINETIC MODELS WITH EXPERIMENTAL DATA.

Species	Mechanism		Experimental Results	
	3	[17]	Range	Average Value
Lean Flame				
$PO(OH)_3$	6.8	4.3	2.5÷7.5	5.1
HOPO	8.3	7.7	5.8÷8.8	7.3
HOPO2	74.3	47.5	51.0–95	73.0
PO	0.0	0.4	0.0–0.6	0.3
PO_2	10.6	37.1	4.7a24.3	14.3
Rich Flame				
$PO(OH)_3$	1.1	0.3	0.0	0.0
HOPO	58.1	60.3	62.6÷93.8	78.2
HOPO2	28.9	8.3	6.6÷12.1	9.4
PO	3.8	5.7	0.0÷11.4	5.7
PO_2	8.0	25.3	2.2-11 1.0	6.6

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