Inhibition by Phosphorus-Containing Compounds In H_2, CH_4 and C_3H_8 Flames

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Abstract

A study of the mechanism of combustion on molecular level is the foreground task of the combustion science. The measurement of flame structure in its turn is the main source of information on kinetics and mechanism of combustion. The combination of experimental methods of study of flame structure and laminar flame speed as well as numerical modeling enable to solve the problem quite effectively. In the present work such methodology was applied to study the inhibition mechanism of hydrogen and hydrocarbon flames by organophosphorus compounds (OPC). Chemical inhibition of laminar hydrogen, methane and propane flames by organophosphorus compounds has been studied experimentally and with a computational flame model. Both fuel-lean and fuel-rich methane and propane flames were studied to examine the role of equivalence ratio in flame inhibition. The experiments examined a wide variety of organophosphorus compounds. We report on the experimental species flame profiles for trimethylphosphate and dimethyl methylphosphonate and compare them with the species flame profile results from modeling. The chemical inhibition is due to reactions involving the small P-bearing species $HOPO_2$, PO_2 and HOPO that are produced by the organophosphorus compounds (OPCs). The mechanism of flame inhibition by the OPCs additives, and also way of the its further refinement are discussed.

1. Introduction

Combustion interest in thermochemistry and reaction mechanisms of organophosphorus compounds derives from their roles in incineration of pesticides, as chemical warfare agents, in fire suppression [1-4], and potential catalytic applications in aircraft turbines [5,6].

Hastie and Bonnell [7] were the first to find out that the additive of trimethylphosphate (TMP) to CH_4/O_2 flame decreases its burning velocity. They also proposed a simplified kinetic mechanism for CH_4/O_2 flames inhibition involving phosphorus-containing species. Later Twarowski [5,6] demonstrated that combustion products of phosphine (phosphorus oxyacids) increase the rate of recombination of H and OH that can be applied for increasing the combustion completeness in the combustion chamber of ramjet.

In USA the incineration of CWA was recognized to be basic technology. A program of study mechanism of destruction and combustion of OPC – stimulants of CWA (nerve and mustard gas) in flames was elaborated in the USA. In its implementation the scientists from Cornell University, NIST, Sandia Laboratory and Institute of Chemical Kinetics and Combustion (Novosibirsk) took part. Dimethyl methylphosphonate and TMP were chosen as CWA simulants and the study of chemical structure of $H_2/O_2/Ar$ flame doped with OPC at low pressure by molecular beam mass spectrometry (MBMS) and numerical modeling was used as an approach for investigation the mechanism for OPC destruction in flames. The results on the structure of flames doped with OPC obtained in frames of the above program and using MBMS with soft ionization by electron impact [8] and vacuum ultraviolet were published [9]. The first model for DMMP destruction in low-pressure H_2/O_2 flame was developed by Werner and Cool [9] on the base of these results, thermochemical computations of Melius and Twarowski mechanism [5, 6, 10, 11], which describes interaction of phosphorus oxyacids with atoms and radicals. Twarowski proposed his mechanism on the base of elementary

reactions of recombination H and OH catalyzed by phosphorus oxyacids and roughly evaluated the rate constants. The drawback of the model [9] consists in bad quantitative qualitative description of the experimental data on the flame structure. Some more papers were published devoted to studies of destruction of TMP, DMMP and diisopropyl methylphosphonate in flame at subatmospheric pressure [12-16]. On the base of measurements of chemical and thermal structure of flames doped with OPC the alternative models for destruction of TMP and DMMP were developed [12]. These mechanisms differed from [9] by values of rate constants of some key stages, which were determined by matching the measured and simulated flame structure. It is necessary to mention the studies [17-19] on pyrolysis of DMMP and other aspects of OPC combustion chemistry [20,21].

In the course of research of OPC destruction chemistry in flames it was found out that OPC promote the hydrogen combustion at low pressure, i.e. to increase final temperature and flame speed. At the same time at atmospheric pressure OPC inhibit combustion of hydrogen [4, 22].

After signing the Montreal Protocol, which banned production of substances depleting the ozone layer (including a number of halons - effective fire suppressants), an exigency in search for novel effective and ecologically safety inhibitors and fire suppressants arose. OPC as well as other phosphorus-containing compounds are perspective candidates for replacement in the first turn of widely used halon 1301 CF_3Br. To evaluate the perspectives of OPC application as inhibitors and fire suppressants it was necessary to study in details the mechanism of their action. This necessity stimulated the continuation of the study.

The main attention of the researchers was concentrated at interaction of phosphorus oxyacids with active flame species as it had been shown that destruction of parent OPC does not effect on inhibition. So further refinement of the models did not concern intermediate compounds.

As rate constants in Twarowski mechanism had been estimated with significant errors authors [12] modified their values for obtaining an agreement between measured and simulated profiles of concentration of PO, PO_2, HOPO and $HOPO_2$ in H_2/O_2 flame at 50 Torr. At LLNL an alternative mechanism, which also predicts well the structure of the same flames including concentrations of labile phosphorus-containing combustion products, was developed. Besides Babushok and Tsang [23, 24] proposed a model for inhibition of atmospheric CH_4/air flame by DMMP. But this model satisfactorily predicted a decrease of the flame speed versus the dopant loading have not been applied for description of experimental data on flame structure. At all their distinctions the models have the same basement but their ability of predicting the structure of various flames in wide range of pressures as well as their speed should be tested. Later the model [25, 26] was refined by using new thermochemical data. It was also updated with stages involving fluorine-containing OPC. Westbrook at al. [27] comparing the action of CF_3Br and OPC came to conclusion that OPC have the maximal inhibition activity at high temperature whereas CF_3Br - at low flame temperature. The latest works with participation of these authors [28, 29] are dedicated to further development of the model for flame inhibition by OPC by improvement of thermochemical data for phosphorus species [30]. Calculation of potential energy surfaces for known stages of the model revealed additional reaction paths with lower activation energy.

The goal of present paper is to summarize briefly the status of the study of mechanism for inhibition of hydrogen and hydrocarbon flames by OPC, and to present some new data, which can stimulate the further research.

2. Experimental

2.1 Structure of Premixed Flames

Premixed laminar flames were stabilized on a flat Botha-Spolding flat-flame burner 16 mm in diameter for atmospheric pressure and 40 mm for 47 Torr and slightly elevated unburned gas temperatures of about 380K. TMP (1200 ppm) was added to the combustible mixtures using a saturator with liquid TMP in a controlled temperature bath or by syringe pump.

The automatized molecular beam mass spectrometric complex, which was used for measuring chemical structure of flames, includes a quadrupole mass spectrometer to be used for analysis of the flame gases and measurement of the concentrations of different species in the flame. The molecular-beam sampling system shown in Figure 1 has been partially described earlier [8]. For the current experiments, the geometry of the sampling system was: probe-skimmer distance was 20mm, probe-collimator distance - 320 mm, probe-ion source distance - 390 mm. Stage 1 was pumped by an oil diffusion pump 1110 1/s., which provided a working pressure of 5.10^{-4} Torr when a 0.2 mm orifice was used to sample from the flame at 80 Torr. Stages 2 and 3 were pumped by a turbomolecular pump 500 1/s, which maintained pressures of the order 10^{-5} Torr (stage 2) and 7.10^{-8} Torr (stage 3) during the experiments. The signal of the photodiode was used in measurements of the modulated component of the molecular beam under ion-counting conditions by a CAMAC apparatus and computer. The modulation frequency was 33-49 Hz. The duration of the measurement was not more than 12 sec. The MS 7302 quadrupole mass-spectrometer had an improved ion source with a small spread of electron energies (±0.25 eV), which corresponds to the thermal scattering of electron energy (approximately 2 kT, where T is the cathode temperature). This permitted operation at low ionization energies close to the ionization potentials of the atoms, radicals and molecules.

Two types of electronic multipliers were used. The power supply that drives the chopper motor is controlled by a computer. A timer defines the frequency of rotation. The

photodiode signal is a base signal for a phasor. The phasor chooses the start of the time interval that is the time gate for a pulse counter operating. The signal from the electronic multiplier is passed through a pulse amplifier and then enters the pulse counter. Pulse duration in the signal is not more than 25ns. A generator produces the base frequency of 1 MHz for the timers.

Chemical species profiles were measured by MBMS, using soft ionization by electron impact reported previously [8, 14]. Synchronous demodulation was applied to measure flame species in low concentration up to 10 ppm with a mean square error not more than 50%, and stable species with standard deviations not more than 10%.

Quartz cones with inner angles of 40°, wall thickness of 0.05 mm and orifice diameter 0.05 – 0.09 mm were used as probes. A typical quartz probe, which was used in experiment and its bracing to the water-cooled steel flange are schematically shown in Fig. 2. It was found that in atmospheric flames, the lifetime of the quartz probe is limited by the formation of a solid film of pyrophosphoric acids, especially near the probe tip, which alloys with heated quartz to form easily melted phosphate glass. It can be explained by a higher temperature of the probe in atmospheric flames due to better conductivity of combustion products at atmospheric pressure than at subatmospheric one. Disturbance of the flames by the probe has been taken into account [31].

Temperature profiles in the flames were measured by Pt-Pt+10%Rh thermocouples welded from wire 0.02 mm in diameter, covered by a thin layer of SiO_2 to prevent catalytic recombination of radicals on their surfaces. The resulting thermocouple junction has a diameter of 0.03 mm and a shoulder length of about 3 mm, providing negligible heat losses to the cold contacts. Further details of the thermocouple design for subatmospheric flames can be found elsewhere [8].

2.2 Burning Velocity

In a separate set of experiments, the laminar burning velocity of premixed air flames was measured using heat flux method. The method consists in stabilizing the premixed flame on a flat burner under adiabatic conditions by measuring the heat flux from the center to edge of the burner's plate. If the flame is stabilized under sub-adiabatic conditions, the gas velocity is lower than the adiabatic flame burning velocity and the sum of the heat loss and heat gain is higher than zero. Then the center of the burner plate is hotter than the heating jacket. If the unburned gas velocity is higher than the adiabatic burning velocity (super-adiabatic conditions), the net heat flux is lower than zero and the center of the burner plate is cooler than the heating jacket. By changing the flow rate of the gas mixture, an appropriate value of the gas velocity can be found to nullify the net heat flux. In this case the radial temperature distribution in the burner plate is uniform and equal to the temperature of the heating jacket. Experimentally the series of thermocouples attached to the burner plate allow measuring the temperature distribution in it. The flow rate at which the net heat flux is zero is shown to be the adiabatic flame burning velocity [32]. In Ref. [33] authors report that the total relative error of the burning velocity measurements is below 1 % in fastest flames, increasing up to 3 % in slowly burning flames. The overall error of the measurements employing the Heat Flux method is therefore estimated to be better than ± 0.8 cm/s (double standard deviation with 95 % confidence level). Nevertheless we observed appreciably higher error especially for slow flames doped with TMP (see Fig. 8). Measured burning velocity of stochiometric propane/air mixture using Mahe-Hebra nozzle burner at atmospheric pressure and T_0=300K in present work is 42 cm/sec, that is comparable with experimental data measured by different technique 39 cm/sec [34] and 39.5 cm/sec [35].

3. Modeling

In this work, PREMIX, in the CHEMKIN suite of programs [36], was used to calculate the structure and laminar burning velocity. The stabilized and freely propagating premixed flames, with and without OPC, were studied. The structure of the flames was simulated using specified profile of temperature measured experimentally. The equivalence ratio was varied from ϕ =0.6-1.5 and the TMP loadings tested were 0 and 600 ppm, to match the experimental work. In all calculations, the energy equation was solved, and mixture-averaged diffusion was used. Windward differencing was used and the grid was refined down to a value of GRAD=0.1 CURV<0.2. These values of GRAD and CURV supplied a sufficient refinement of the grid such that the flame speed was independent of number of grid points (~200-250).

A recently refined high temperature hydrocarbon oxidation mechanism [27] was used for the hydrocarbon species, with updated thermodynamics parameters. At T=300 K, P=1 atm and ϕ=1, this mechanism computes a laminar burning velocity of 41.1 cm/sec, in good agreement with our own experimental value above and other experimental studies.

4. Results and discussion

4.1 Inhibition and Promotion Effects in H_2/O_2 Flames

TMP and DMMP additives promote combustion in a $H_2/O_2/Ar$ flame stabilized on a flat burner [12, 14, 15]. Promotion effect consists in an increase of final flame temperature and combustion completeness when TMP or DMMP is added. In the case of a stoichiometric flame of $H_2/O_2/Ar$ at 47 Torr, the addition of 0.5% by volume of an OPC induces a temperature rise of up to ≈600 K (see Fig.3). So, the final temperature becomes close to the equilibrium one. The final temperature rise of a flame doped with an OPC may not be caused by the introduction of additional fuel into the combustible mixture. The results of calculations demonstrated that the thermodynamic equilibrium temperature of the flame increases 40 K by adding 0.37 vol. % of

TMP. It was demonstrated that such appreciable temperature rise also can not be explained by a decrease of heat losses from the flame into the burner when inhibitor is added as it occurs with CH_4/air flame doped with CF_3Br. The increase of the temperature of H_2/O_2/Ar flame doped with TMP is connected with the catalysis of H and OH recombination reaction by phosphorus-containing species. As the result the system approaches thermodynamic equilibrium. Modeling data and experimental results of flame structure study are in a satisfactory agreement. Using the full mechanism for a H_2/O_2 flame doped with TMP [12], we have calculated the burning velocity versus TMP loading at a pressure of 47 Torr and 1 atm. The temperature of unburned gases of 370 K was in both cases. Figure 4 indicates that an increase of the flame speed is observed up to 0.6 vol. % of TMP loading and a decrease afterwards. The curve representing the speed in a stoichiometric H_2/O_2/Ar flame at 1 atm versus TMP loading demonstrates no promotion by TMP. In fact the burning velocity decreases with the loading of TMP. So OPC promote a hydrogen-oxygen flame at 47 Torr and low OPC loading, but inhibit it at TMP loading more than 0.65 % by volume. At atmospheric pressure OPC inhibit H_2/O_2 flames at any loading.

Combustion is known to be a complex process which speed according the Zeldovich thermal theory depends on the one hand on the maximal flame temperature and on the other hand on concentration of the reagents in the flame zone. OPC addition to a hydrogen flame provides an additional path for water formation with large heat release that results in a temperature rise.

Such reaction can be reaction of H-atom recombination:

$$HOPO_2+H+M=PO_2+H_2O+M \qquad (1)$$

Thus the heat release rate except temperature depends also on concentration of H atom. An increase of OPC loading results in temperature rise and therefore in increase of flame speed. However when maximal (equilibrium) flame temperature is already reached further increase of OPC loading results in a decrease of H atom concentration, reaction rate

and flame speed due to termination of radical chains. At atmospheric pressure the role of reaction (1) is not so important as the rate of trimolecular reaction $H+OH+M=H_2O+M$ increases and temperature becomes close to equilibrium one even in an undoped flame. In this case main reaction is branching one

$$H+O_2 \rightarrow OH+O \qquad (2)$$

That is why an increase of OPC loading in atmospheric flame results in increase of termination rate of the chains and flame speed. That is supported by calculation results presented in Fig.4.

4.2 Inhibition of Hydrocarbon Flames

The structure of the lean (ϕ=0.9) and rich (ϕ=1.2) propane flames, with 1200 ppm TMP in the unburned gases was measured and simulated. The new kinetic model, with updated thermochemistry, was used to calculate the structures of flames. The computed results for the major reactant and product species and the spatial extent of each flame were in excellent agreement with the experimentally observed values for all of the flames. The experimental values of the P-bearing species for the lean and rich inhibited flames are shown together with computed species mole fractions in Figures 5 and 6. Overall agreement between experimental and computed values is very good for all of the species in the lean flame. However, there are significant disparities between the model results and experimental data in the rich flame. To ensure that all possible P-bearing species were included, we included the P_2O_3, P_2O_4 and P_2O_5 species within the model. We found that their concentrations were insignificant (several orders of magnitude smaller than the PO, PO_2 and PO_3 species), in both the lean and rich flames. Thus the diphosphorus species cannot account for the discrepancies in the rich flame at low dopant concentrations and flame pressures. Further studies, both of the experimental profile measurements and of the computational reaction mechanism, must be carried out to determine the cause of the discrepancy.

4.3. Effect of OPC concentration on Speed of Premixed stoichiometric atmospheric C_3H_8/air Flame

To further understand the nature of the P-bearing species with respect to the inhibition mechanism, we also considered other OPCs. A recent study [37] showed that many different organophosphate compounds are approximately equal in inhibition effectiveness for hydrocarbon flames. This is illustrated in Figure 7, which shows the relative reductions in burning velocity from addition of other inhibitors to a stoichiometric propane/air mixture. Burning velocity reductions produced by other OPC additives (Table 1), many of them including F atoms in addition to P atoms were very similar to the purely OPC results shown here. These results are compared to the reduction in burning velocity produced by addition of CF_3Br, which is clearly much less effective than any of the OPC additives.

These results demonstrate clearly that the flame inhibition kinetics for all additives depend on the reactions and thermochemistry of HOPO, $HOPO_2$, PO_2 and other small species, and not on the details of the molecular structure of the initial organophosphorus compound. The core inhibition mechanism for all of these compounds in Fig.7 is the same set of catalytic recombination cycles of reactions, and the only major distinction between different organophosphate inhibitors appears to depend on how rapidly these catalytic cycles are established in a given flame. The different inhibitors in Fig. 7 have different hydrocarbon contents, and this will have a minor influence on their inhibition efficiencies because their different C/H/O compositions can affect the equilibrium between HOPO and $HOPO_2$, and additional components such as F atoms will also have minor influences on inhibition efficiencies. Experimentally we have not observed any noticeable increase of inhibition effectiveness of phosphorus compounds due to presence of fluorine in their molecules. For example, for pairs of compounds $(C_2H_5O)_3P$ - $(CF_3CH_2O)_3P$, $(C_2H_5O)_2P(O)H$ - $(CF_3CH_2O)_2P(O)H$ data are exactly the same and for $(C_2H_5O)_3PO$ - $(CF_3CH_2O)_3PO$ the

effectiveness of the fluorinated compound is for 3% higher in the premixed flame. However, as shown in Fig.7 the primary inhibition mechanisms for all of these organophosphorus compounds are exactly the same.

4.4. Inhibition of Premixed Flames over a Range of Equivalence Ratios

Earlier [28, 29] we studied experimentally and by modeling the influence of DMMP additive on speed of C_3H_8/air flames over the range of equivalence ratio φ=0.8-1.3. Modeling predicted that inhibition effectiveness (expressed as relative decrease of the flame speed when the inhibitor is added $E_f=(Su_0-Su)/Su_0$) increases along with excess of fuel at $\varphi>1$. The experimental results obtained with Mache-Hebra nozzle burner and total area flame cone method [28, 29] did not reveal such dependence.

In the present paper we carried out analogies study of methane-air flames in wider range of equivalence ratio in order to verify the dependence obtained earlier. Results of measurements using heat flux method and calculations of burning velocity in mixtures without additive and in those doped by 600 ppm of TMP are shown in Fig. 8. The data in Fig. 8 demonstrate a satisfactory agreement between experimental and modeling results for the undoped flames in practically all range of ϕ except 1 point in the lean region and 2 points in the rich one. There are quite noticeable disagreements between modeling and experiment for the doped flames. There are noticeable disagreements between experiment and modeling for the doped flames. It is noteworthy that systematic errors of measurement of flame speed are quite significant on the margins of the ϕ range especially for the doped flames.

The effectiveness of inhibition $E_f=(Su_0-Su)/Su_0$ estimated from experimental and modeling data are shown in Fig. 9. The modeling predicts a smoothed growth of E_f *about in 2 times) from $\phi\approx0.6$ to 1.2 and its decrease up to 1.6. The experimental results demonstrate quite reliably that such appreciable growth of E_f doesn't take place with $\phi>1.2$. The same conclusion can be made from experimental data on propane/air flames. At the same time

experimental data demonstrate a decrease of E_f at $\phi>1.2$ that was not observed in propane flames.

In Ref. [28, 29] a detailed and conclusive explanation of the fact why the kinetic model predicts a rise of inhibition effectiveness in propane flames along with increase of ϕ is presented. But the growth of E_f is not supported experimentally for methane flames. It is of interest that in spite of disagreements in absolute value of E_f determined from experiment and modeling the measurement results justify the decrease of E_f in flames with $\phi>1.2$.

The decrease of E_f in the rich flames with $\phi<1.2$ is of great interest. Evidently it occurs because of a decrease of rate of catalytic recombination of H and OH radicals. Possible explanation consists in suggestion that in very rich flames final products of OPC destruction are not only PO, PO_2, HOPO and $HOPO_2$ but also carbon-containing species. Such compounds are known to form in the incinerators sometimes. The species of $H_xC_yO_zP_t$ type possibly are not able to catalyze recombination of the radicals and therefore decrease the effectiveness of inhibition.

5. Analysis of mechanism

Calculation of Potential Energy Surfaces for Reactions

The goal of the study is a search of new reaction pathways for known stages with minimal activation energy by proposing intermediates (adducts) of various structure. The adducts are isomers and their transformation is intramolecular rearrangement (1,2-shift of proton). This approach in fact is a new method of refining of kinetic model for OPC combustion, which was earlier applied by Mackie [38].

The reaction character for a lean flame was analyzed. The pathway of reaction of $HOPO_2$ with H was calculated by Mackie via adduct [38]:

$HOPO_2+H \rightarrow PO(OH)_2 \rightarrow PO_2+H_2O$

Another pathway was proposed and calculated at LLNL [29]:

$HOPO_2$+H–>HPO(OH)O–>1,2 shift–> $PO(OH)_2$–>PO_2+H_2O

The introduction of the additional intermediate (first step) made it possible to decrease the activation energy for 1.5 kcal/mol that at 1500 K increases the reaction rate in 10 times. The cycle closure proceeds through reaction PO_2+OH=$HOPO_2$.

For a rich flame the multichannel reaction with H atom was proposed by analogy. The structure of the adducts are similar to those for HOPO2 reaction:

HOPO+H–>PO_2+H_2 (low rate)

HOPO+H–>PH(OH)O–>$P(OH)_2$–>PO+H_2O

HOPO+H–>$P(OH)_2$–>PO+H_2O

The reaction presented does not only demonstrate the key role PO_2 in the mechanism but studies parallel pathways of the reaction to find the pathway with minimal activation energy.

Rate-of-Production of PO_2

Analysis of consumption and production pathways of PO_2, which was shown to be a key species in the inhibition mechanism, is of interest. The main reaction of PO_2 production

Í ÎÐ Î + Î Í–>Ð $Î_2$+ $Í_2$ Î

The main reaction of PO_2 consumption

PO_2+H+M–>HOPO+M

One may propose Í ÎÐ Î + Í–>Ð $Î_2$+ $Í_2$ to be the most effective. However it is not so because of high activation energy - 11 kcal/mol. The same reason makes H+OH recombination much more effective than that of H atoms. Reaction of $HOPO_2$+H–>PO_2+H_2O gives small contribution in rate of PO_2 production because of high-energy barrier.

Sensitivity H

Sensitivity coefficient of rate constant of PO_2+OH+M–>$HOPO_2$+M by H atom concentration has a positive value. Moreover this stage produces the maximal contribution

into H formation [29]. This effect is explained by conversion of phosphorus in the less active form ($HOPO_2$) as the cycle with $HOPO_2$ is less effective than that with HOPO.

The most effective cycle of H and OH recombination in both rich and lean flames is $PO_2 \Leftrightarrow HOPO$. The cycle $PO2 \Leftrightarrow HOPO_2$ is also quite important for inhibition but nevertheless it is for 30% less effective. A higher concentration of HOPO in a rich flame explains the higher inhibition effectiveness by OPC in comparison with a lean flame. The main pathways interconversions of phosphorus-containing oxyacids that cause H and OH recombination are shown in Fig. 10. The Figure demonstrates that PO_2 is a common key flame species.

6. Conclusion

In the present paper we have summarized the status of studies of chemistry and mechanism for inhibition of hydrogen and hydrocarbon flames of various composition by OPC additives. In particular the main measurement and modeling data on the structure of lean and rich $C_3H_8/O_2/Ar$ flames doped with TMP, speed of a stoichiometric C_3H_8/air flame versus loading of various OPC were presented. The new model for flame inhibition by phosphorus-containing compounds was analyzed.

In the paper we have also presented new results on measurement and modeling of burning velocity versus TMP loading in rich and lean CH_4/air mixtures. Two regions of different dependence of the inhibition effectiveness on equivalence ratio were discovered. In the range of ϕ 0.6 – 1.2 the model predicts a smoothed increase of the inhibition effectiveness. At the same time experimental measurements demonstrated that the inhibition effectiveness does not change or changes insignificantly in the same range. At ϕ>1.2 both experiment and modeling indicate an appreciable decrease of the inhibition effectiveness of methane flames. However in propane flames the decrease of the inhibition effectiveness was observed neither in experiment nor in modeling. The results presented in our paper indicate that the existing model should be refined to improve description of inhibition of rich flames.

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TABLE 1.

PCCs investigated and their boiling point

#	PCC	Boiling point [^{0}C] at pressure [Torr]
1	$(CH_3O)_3PO$, TMP	180/760
2	$(C_2H_5O)_3PO$	215/760
3	$(CF_3CH_2O)_3PO$	187/760
4	$(HCF_2CF_2CH_2O)_3PO$	90/0,5
5	$(C_3F_7CH_2O)_3PO$	97/2,5
6	$(CH_3O)_2$ P(O)CH_3, DMMP	181/760
7	$(C_2H_5O)_2P(O)CH_3$	194/760
8	$(CF_3CH_2O)_2P(O)CH_3$	193/760
9	$(C_3F_7CH_2O)_2P(O)$Ñ Í$_3$	92/9
10	$(C_3F_7)_3PO$	144/760
11	$(CH_3O)_3P$	111/760
12	$(C_2H_5O)_2P(O)H$	204/760
13	$(CF_3CH_2O)_2P(O)H$	194/760
14	$(C_2H_5O)_3P$	158/760
15	$(CF_3CH_2O)_3P$	131/760
16	$(HCF_2CF_2CH_2O)_3P$	95/3
17	$(CF_3CH_2O)_2P(O)CF_3$	147/760
18	$(CF_3CH_2O)_2PO(OCH(CF_3)_2)$	83/10
19	$POCl_3$	105/760
20	H_3PO_4 60% water solution	-
21	$(HCF_2CF_2CH_2O)_2P(O)CH_3$	115/6

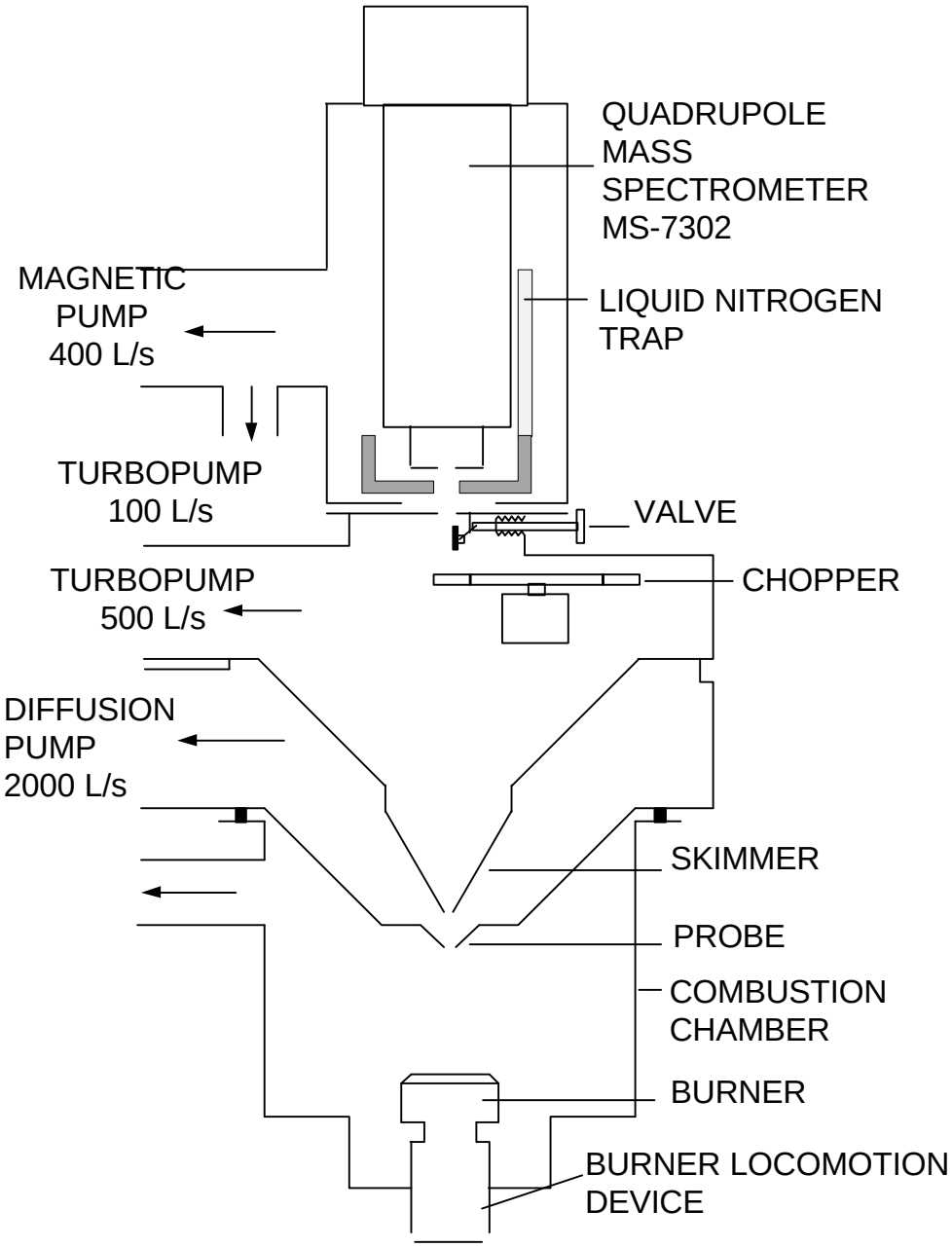

Fig. 1. A scheme of molecular beam mass spectrometric setup.

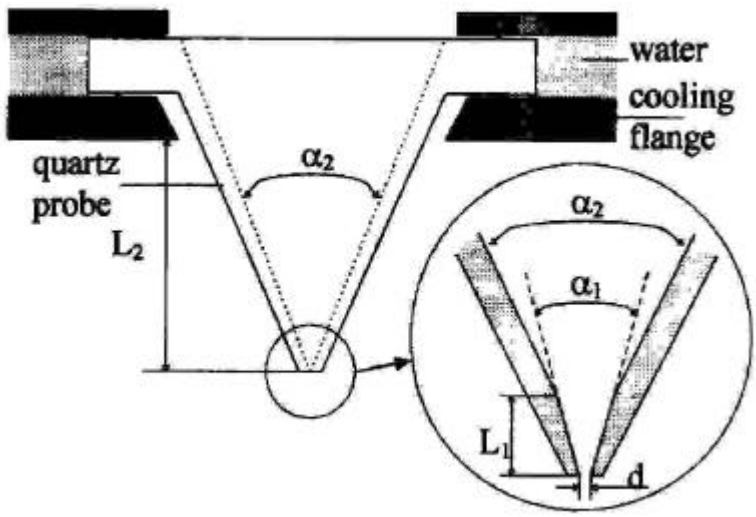

Fig. 2. Scheme of probe.

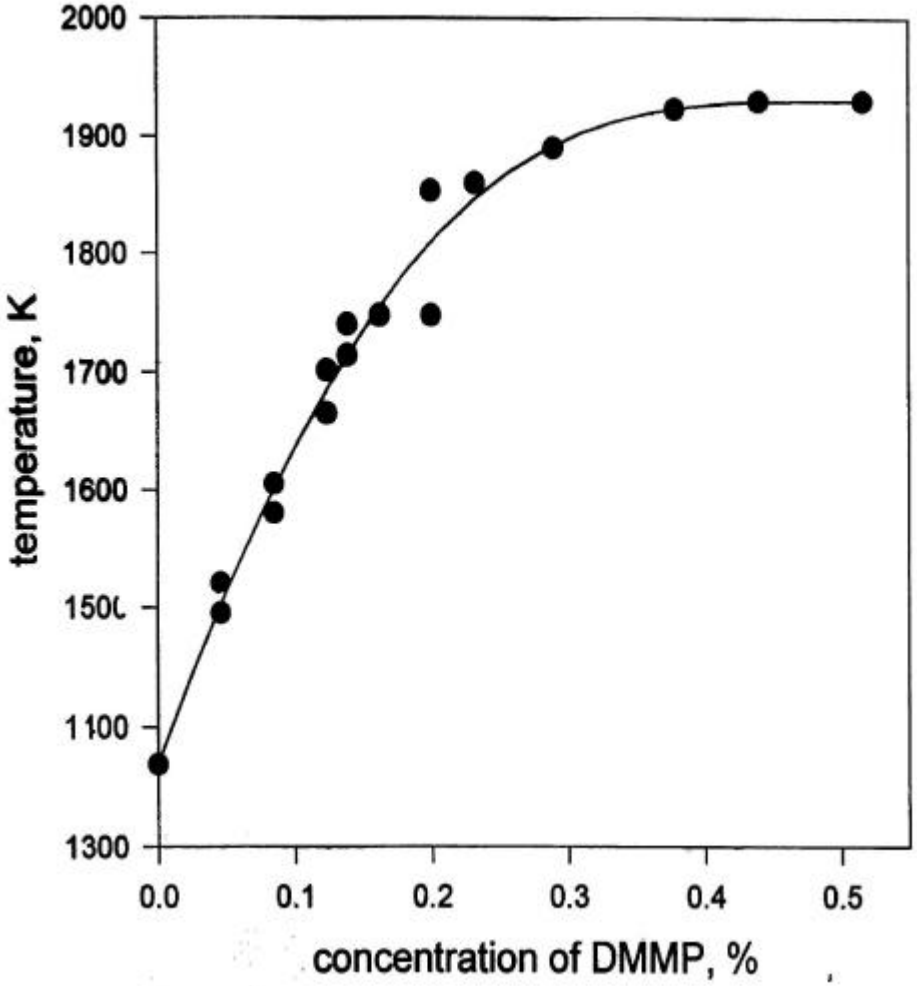

Fig. 3. Final temperature of H2/O2/Ar flame stabilized at 50 Torr versus DMMP loading (experiment).

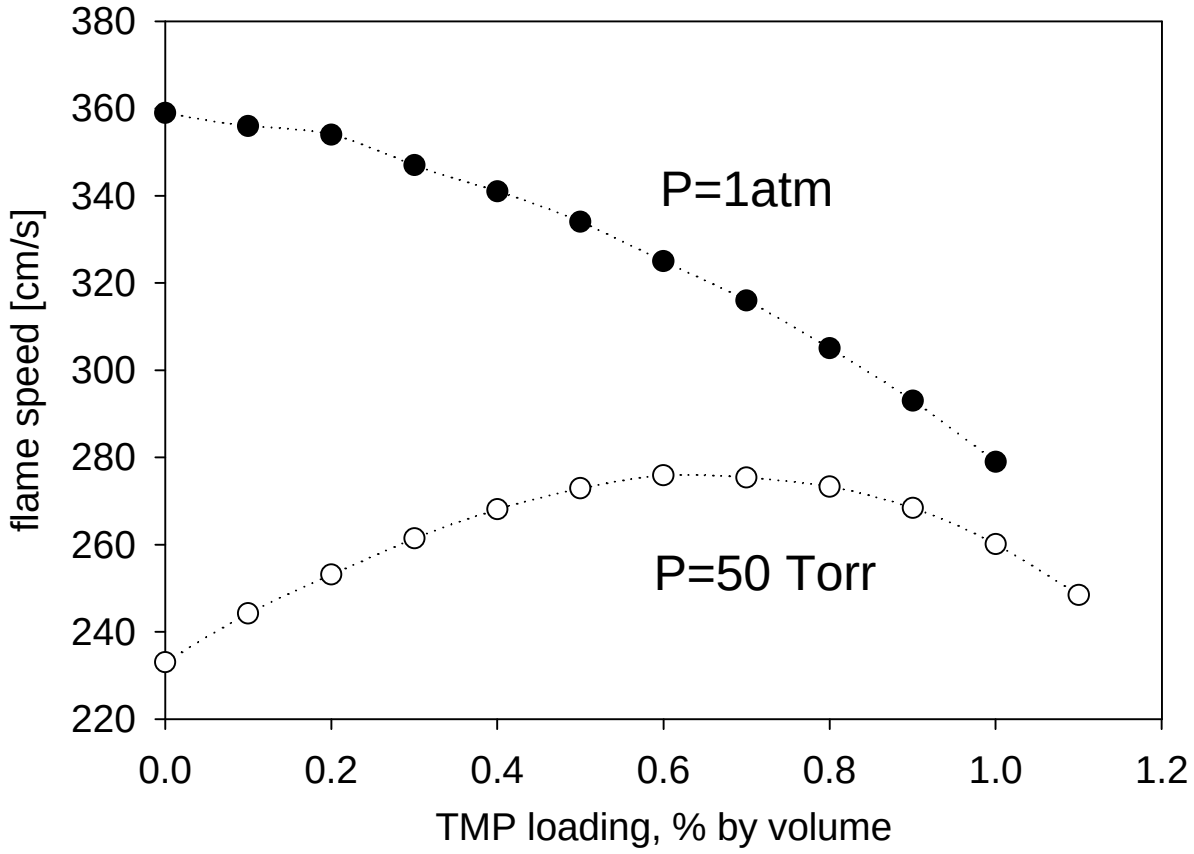

Fig 4. TMP loading dependence of velocity of $H_2/O_2/Ar$ flame.

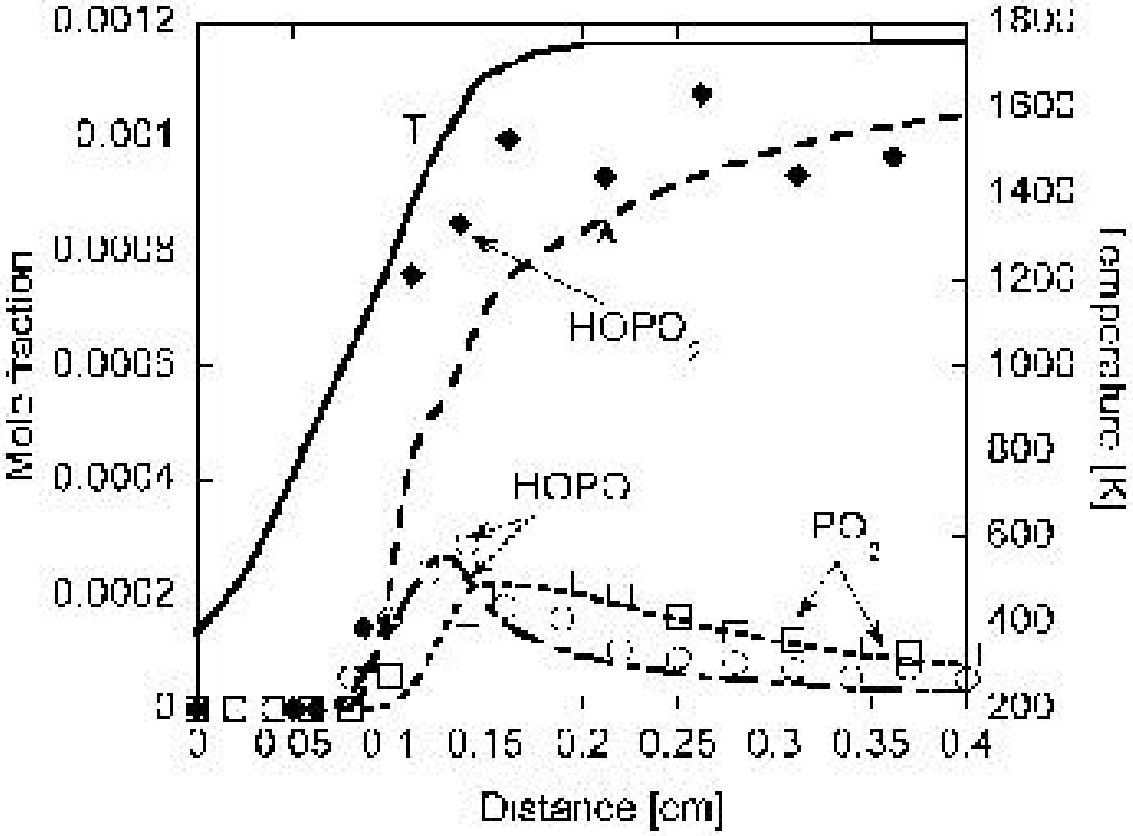

Fig. 5. Spatial variations of temperature and major P-bearing species in the lean flame doped with 1200 ppm of TMP. Symbols show experimental data, curves are computed results.

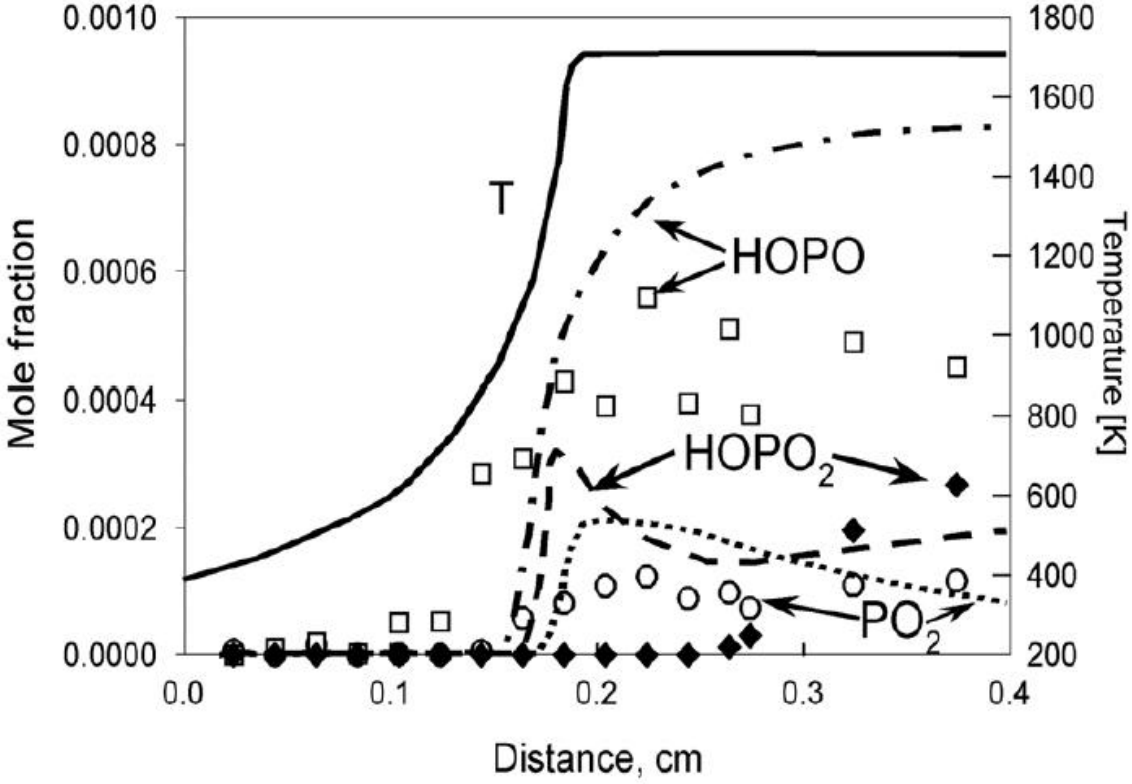

Fig. 6. Spatial variations of temperature and major P-bearing species in the rich flame doped with 1200 ppm of TMP. Symbols show experimental data, curves are computed results.

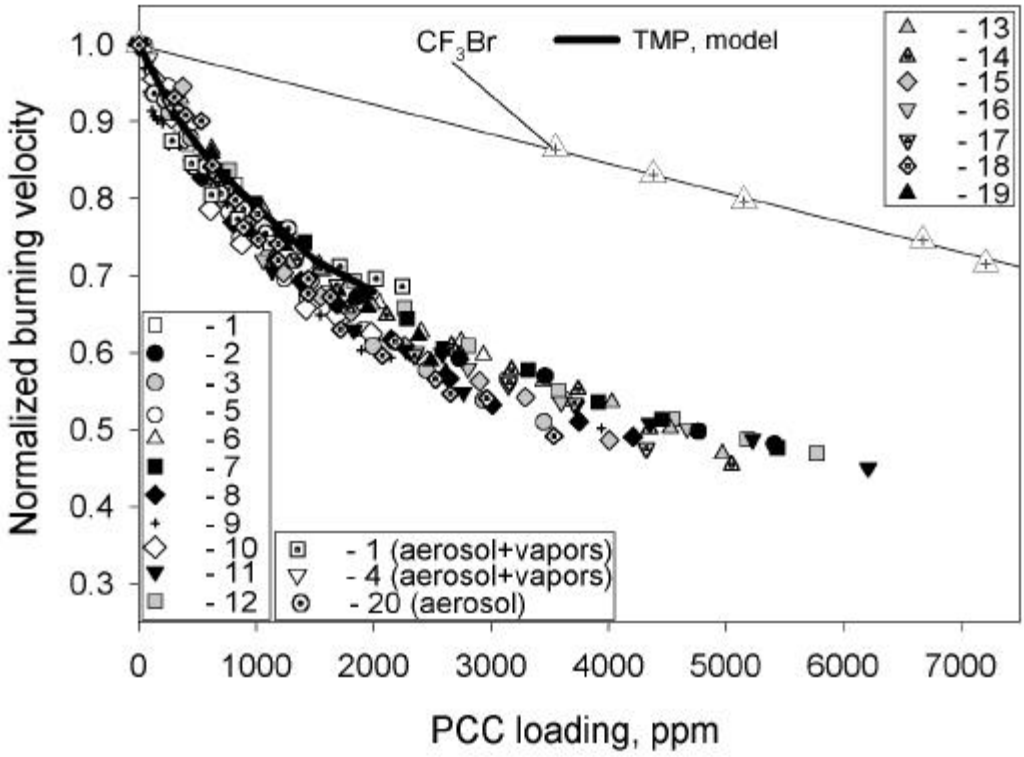

Fig. 7. Normalized burning velocity of stoichiometric premixed C_3H_8/Air flame as a function of PCCs loading.

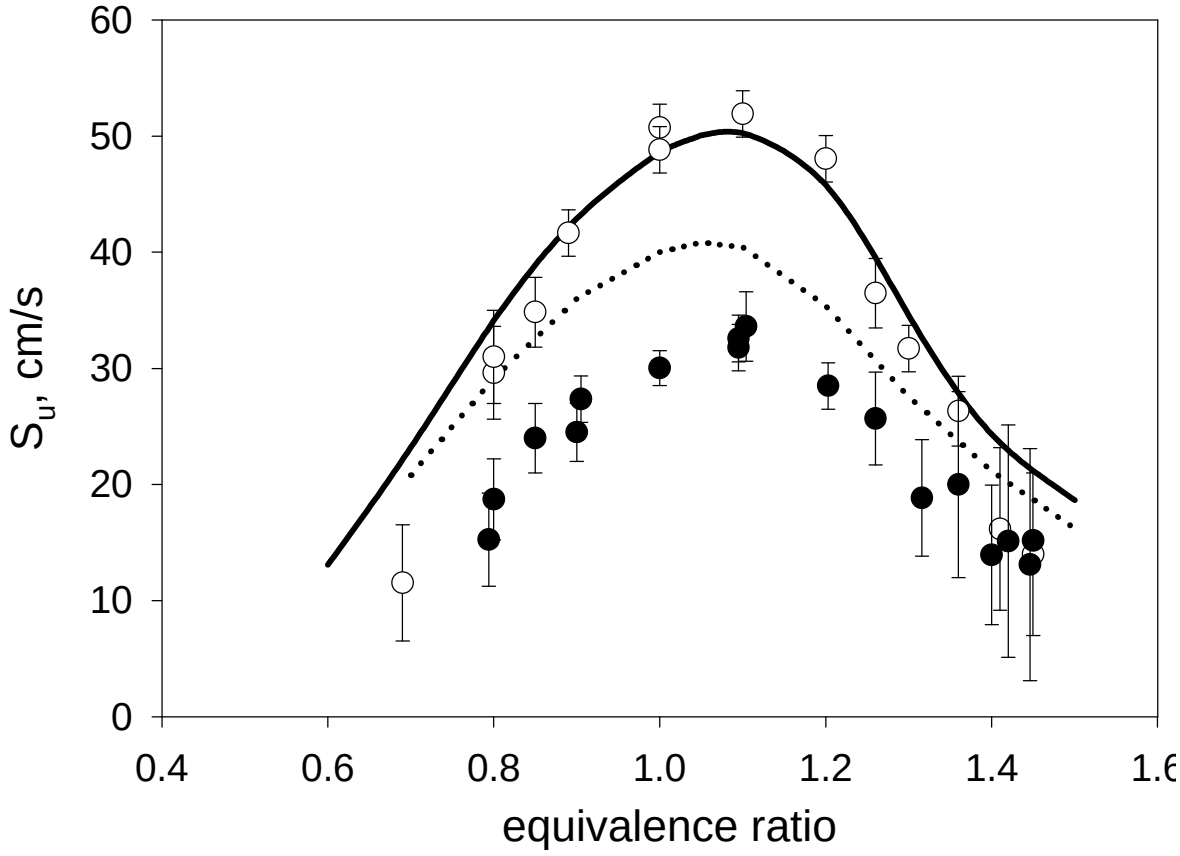

Fig. 8. Speed of CH_4/air flames without additives and doped with 600 ppm of TMP over various equivalence ratios. Symbols - experiment (open - undoped, filled - doped), lines - modeling (solid - undoped, dotted - doped).

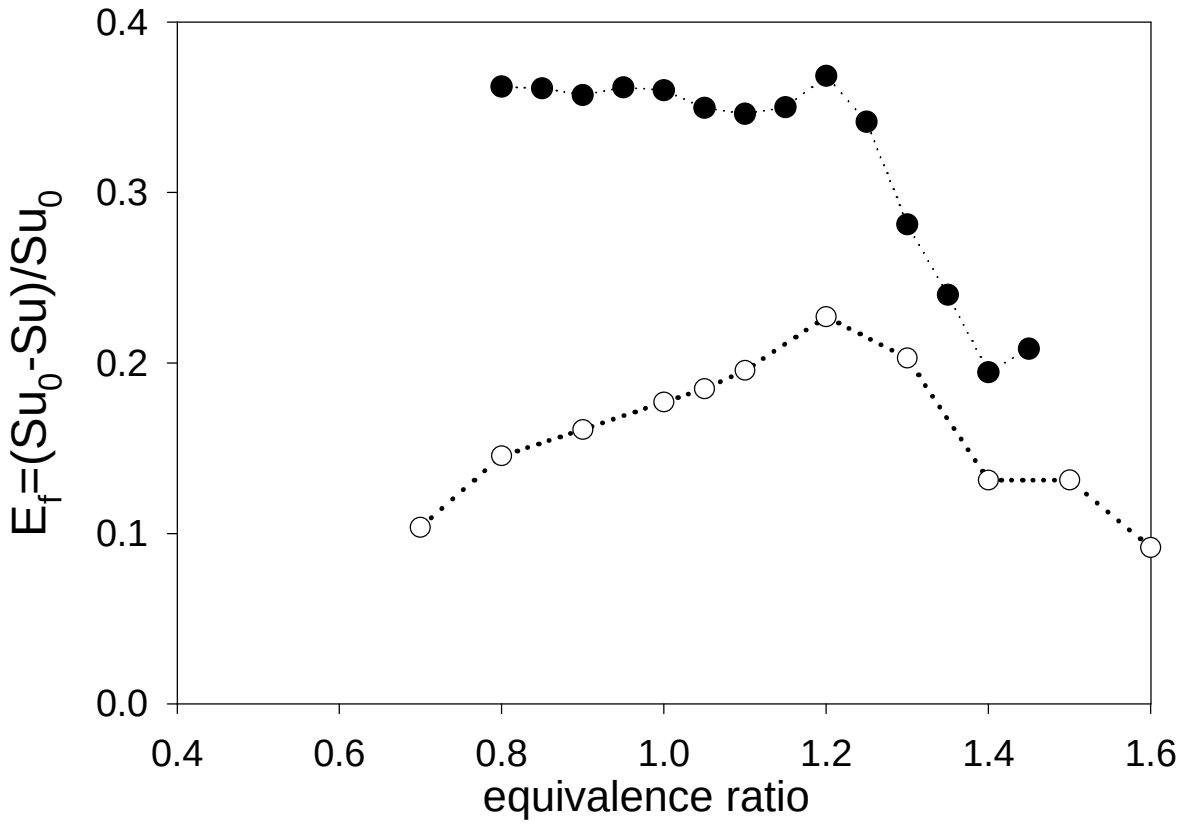

Fig. 9. Effectiveness of inhibition expressed as $E_f=(Su_0-Su)/Su_0$ estimated from experimental data (filled symbols) and from modeling results (open symbols).

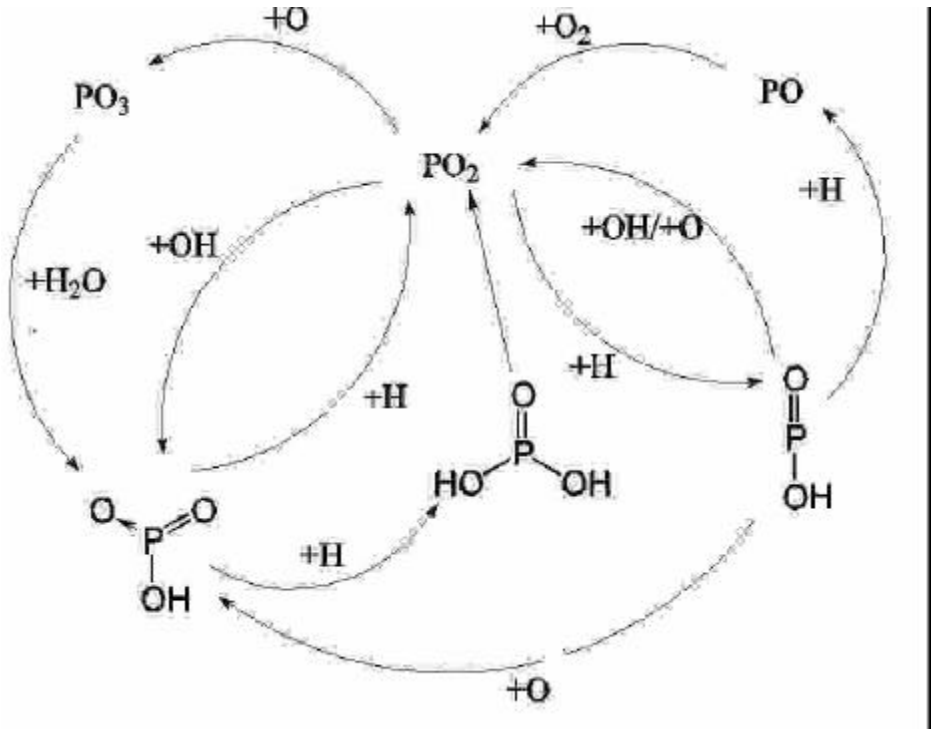

Fig. 10. The main pathways interconversions of phosphorus-containing oxyacids