INHIBITION EFFECT OF TMP ON $CH_4/O_2/AR$ AND $H_2/O_2/AR$ FLAMES

Oleg Korobeinichev, Tatyana Bolshova, Vladimir Shvartsberg,
Anatoly Chernov, and Vladimir Mokrushin
Institute of Chemical Kinetics and Combustion
Siberian Branch, Russian Academy of Sciences
Novosibirsk 630090 RUSSIA

INTRODUCTION

The interest in studying the destruction chemistry of organophosphorus compounds (OPC) in flames is stimulated by two reasons. The first one is connected with the disposal of toxic and hazardous chemical wastes, including chemical warfare agent (CWA) disposal by incineration. The second one is associated with some OPC ability to affect the combustion process. Phosphine additive in H_2/air flame was found [1,2,3] to catalyze H and OH recombination, thus favoring faster heat release. VUV laser-ionization mass-spectrometry has been employed by Cool and Werner [4] to study a low-pressure hydrogen/oxygen flame doped with dimethylmethylphosphonate (DMMP), which represents a sarin simulant.

Previous papers of this laboratory [5-10] presented the results of studying the structure of premixed $H_2/O_2/Ar$ flame stabilized on a flat-flame burner at 47 torr and doped with trimetylphosphate (TMP) and DMMP by molecular beam mass spectrometry (MBMS) with soft ionization and computer modeling. Mass spectra of the samples taken from flames doped with TMP and the intensity profiles of peaks 2(H_2), 18 (H_2O), 32 (O_2), 40 (Ar), 47 (PO), 63 (PO?), 64 (HOPO), 80($HOPO_2$), 96 (methylphosphite), 110 (dimethylphosphite), 112 (methylphosphate), 126 (dimethylphosphate), and 140 (trimetylphosphate) amu have been measured **as** a function of the distance from the burner surface to the sampling probe [6,8]. The effect of the promotion of $H_2/O_2/Ar$ flame with TMP additive has been observed. Similar results have been obtained for the flame doped with DMMP [5]. Possible detailed chemical mechanisms of the destruction of DMMP and TMP have been presented [8-10]. Based on these mechanisms the modeling of the structure of flames doped with DMMP and TMP has been carried out. The results of modeling and the experiment are in rather good agreement [8,9]. One of the most important conclusions is as follows: the first step of OPC destruction is not OPC unimolecular decomposition, but reaction of CH_3O and CH_3 groups in the OPCs by OH radicals and H atoms. It is noteworthy that this model of OPC destruction partially differs from the one suggested in Reference 4 for DMMP destruction in H_2/O_2 flame.

In connection with the problem of flames inhibition, Hastie and Bonnell [11] studied Bunsen methane-air and hydrogen-air flames doped with TMP. They observed an inhibiting effect on methane-air Bunsen flame and flame extinction. Also, they first suggested a mechanism of inhibiting H_2/O_2 flame doped with TMP, which included the reactions of phosphorous oxides with H, OH, and **O.** Preliminary results of the flame structure study of lean methane-air flame stabilized on a flat burner at 76 torr doped with TMP (0,11%) have been obtained [12] using MBMS. **A** noticeable widening of the burning zone has been observed in the presence of TMP.

Recently, the interest in using OPCs as inhibitors has greatly increased. An opposed-jet burner apparatus was used to study the effectiveness of DMMP [13-14] as an inhibitor of non-premixed methane-air and propane-air flames. It has been demonstrated that phosphorus compounds have efficiencies many times higher than CF_3Br (Halon 1301). Because OPCs have been demonstrated to be more effective fire suppressants than CF_3Br (Halon 1301). and due to the need for replacing the currently used Halon 1301 [15-16], further investigation of the mechanism of OPC effects on flames is of great interest. Several papers devoted to the investigation of the mechanism of the inhibiting effect of OPC on flames were recently published [17-19]. In the present paper, the authors report the results of studying the structure of CH_4/O_2 flames (doped with TMP) by MBMS and the results of the numerical investigation of $CH_4/O_2/Ar$ and $H_2/O_2/Ar$ flame propagation using the CHEMKIN code as *a* function of TMP loading. The last one is based on the TMP destruction mechanism.

EXPERIMENTAL

A premixed lean $CH_4/O_2/Ar$ (mole fractions: 0.078/0.222/0.7) flame with and without TMP additives, stabilized at 76 torr on a Botha-Spalding flat burner 40 mm in diameter was studied. The total volumetric flow rate of the unburned gas mixture was 51.3 cm^3/sec (NTP). The burner was moved along its axis to perform sampling using a fixed probe at various distances from the burner. Quartz probes were used for sampling. The inner angles of the probes were 40–44 deg, an orifice diameter of 0.17–0.21 mm, and an outer diameter of the probe tip was 0.27–0.31 mm.

A probe disturbs flames. producing **a** shift of equal concentration lines in the sampling area relative to unperturbed flame. A "sonic" probe (in the case of molecular beam sampling) produces stronger perturbation than a microprobe. All concentration profiles presented in this paper are corrected for the shift. The sampling shift was estimated using the results of the investigations presented in References 20 and 21 and using the formulas suggested in Reference 21. According to the formulas suggested for the probe with an orifice of 0.17 mm. the sampling shift was 0.7 mm. and for an orifice of 0.21 mm, the sampling shift was 1.1 mm. The sampling shift was also determined by matching the experimental and calculated profiles for CH_4, O_2, H_2O major species in a flame without additives, and using codes PREMIX [22] and CHEMKIN-2 [23] and the mechanism suggested in Reference *13*. Both methods gave the same result (±0.1 mm). TMP (0.37 vol.%) was supplied with a syringe pump (stability ±0.5 %) via an evaporator into the gas mixture. TMP vapor pressure at T=65 °C comprised 1 torr.

The molecular beam sampling system was equipped with *a* quadruple mass spectrometer used to identify species and measure their concentrations in flame. A mass spectrometric setup with a molecular beam sampling system was described previously in References 5–7. An MS 7302 quadruple mass spectrometer was equipped with a modernized ion source with a small spread of electron energies, which correspond to the thermal scattering of electron energy only. The ionization energy of electrons was controlled by a digital-to-analog converter with a stability of 0.005 V. In practice, for example. the ionization potential of argon and oxygen are measured with an accuracy of ±0.2 eV. This ion source permitted operation at low ionization energies close to the ionization potentials of atoms, radicals, and molecules.

Platinum-platinum + 10 % rhodium thermocouples welded from two wires (0.05 mm in diameter) were used to measure temperature profiles. The total length of the thermocouple was about 25 mm. The thermocouple was welded to a wire 0.2 mm in diameter made of the same material. A more detailed description of the thermocouple unit design was offered in Reference 8.

The prepared thermocouple was covered with Ceramabond 569 [24] to prevent catalytic processes. Coating thickness did not exceed 0.05 mm. When carrying out flame temperature measurements with thermocouples, the radiant heat losses of the thermocouple had to be taken into account. For this purpose, a method of compensation [25] was used. The thermocouple was placed in a combustion chamber 15 mm below the probe tip. so the represented temperature data are related to an unperturbed flame. As it was shown in Reference 26, the final temperature decreased by 50 K in comparison with an unperturbed flame when the thermocouple was placed 0.5 mm below the probe (orifice 0.2 mm).

STRUCTURE OF $CH_4/O_2/AR$ FLAME DOPED WITH TMP: EXPERIMENTAL RESULTS AND MODELING

Figures 1 and 2 present temperature and CH_4, H_2O, O_2, CO, and CO_2 concentration profiles in the flames with and without 0.37 % TMP additive. Hereinafter the filled symbols stand for the doped flame. **As** it can be seen from Figures 1 and 2, temperature and concentration profiles of the components in the flame with and without an additive are displaced one from another. So the widening of the burning zone in the presence of TMP takes place because of the preflame zone growth, as supported by visual observation. As it can be seen from Figure 2, the addition of TMP to flame results not only in preflame zone widening, but in the rise of burning-out extent as well. which is evident by the 20% increase in CO_2 concentration in the combustion products. The total widening of the main stable components burning zone **is** about 1 mm. The observed phenomenon can be characterized as an TMP inhibiting effect on the process of methane-oxygen combustion. Analysis of the concentration profiles obtained gives insight into some regularities of the processes taking place in the flame and into the inhibition mechanism. Figure ***3*** shows the concentration profiles of TMP and final phosphorus-containing TMP destruction products: PO, PO_2, HOPO. and $HOPO_2$. These flame components concentration profiles were found when using these species calibration coefficients obtained earlier from the material balance conditions for hydrogen-oxygen flames [7].

One can see from Figure **3** that PO concentration is very low as well as in hydrogen flames. The concentrations of other phosphorus species in post-flame zone are ranged as follows: HOP02 > PO_2 > HOPO > PO. It should he noted that the PO, PO_2, HOPO, $HOPO_2$, and TMP total concentration in the combustion products zone is nearly equal to the TMP initial concentration. This indicates that these species calibration coefficients by argon were found to be correct and accurate.

Modeling was carried out using PREMIX [22] and CHEMKIN-2 [23] computer codes, which provide component concentrations in stabilized flame as well as flame propagation velocity. The mechanism of methane oxidation used in these calculations includes 59 reactions and 20 species and is incorporated in CHEMKIN-2 kinetic database [3]. The modeling of the stabilized flame was performed using specified temperature profiles obtained from the experiment. The results of experiments (symbols) and modeling (lines) of $CH_4/O_2/Ar$ flame structure shown in Figure 4 for the concentration profiles of CH_4, O_2, and H_2O are in good agreement. A kinetic model for methane flame doped with TMP incorporating 93 stages (34 of which represent the reactions involving phosphorus-containing species) was elaborated. The kinetic model is based on the mechanisms of TMP destruction in H_2/O_2 tlames [IO] elaborated earlier and based on the experimental results on the flame structure, and updated by several reactions of phosphorus-

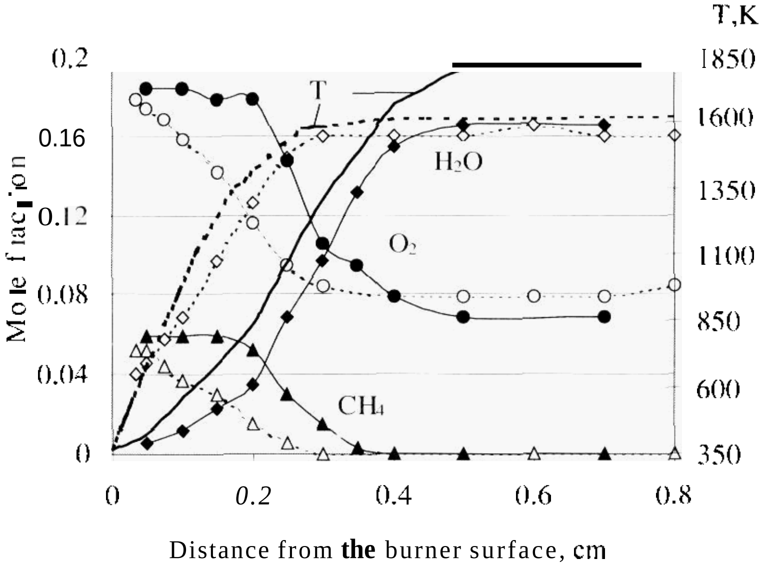

Figure 1. Temperature and some species concentration profiles in $CH_4/O_2/Ar$ flame: with TMP, solid line; without TMP, dotted line.

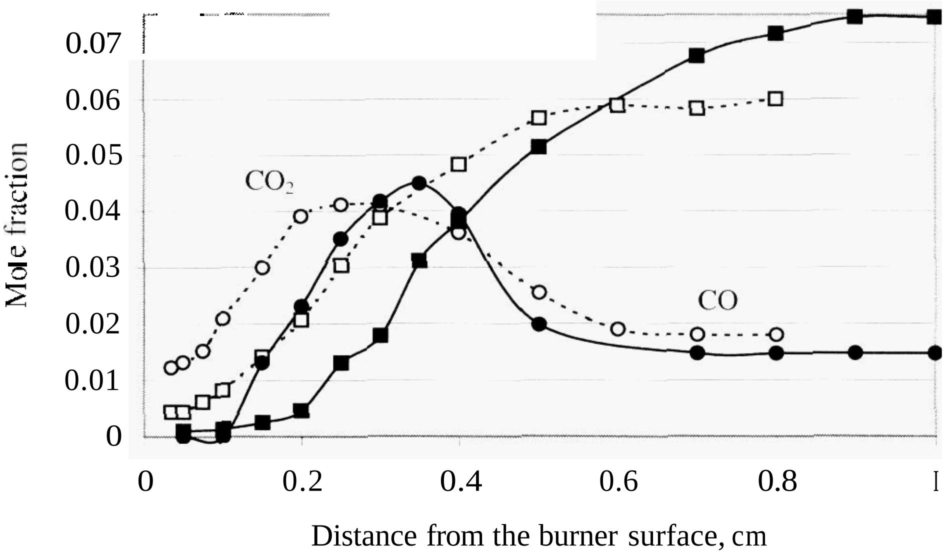

Figure 2. Concentration profiles CO and CO_2 in $CH_4/O_2/Ar$ flame with and without TMP additive.

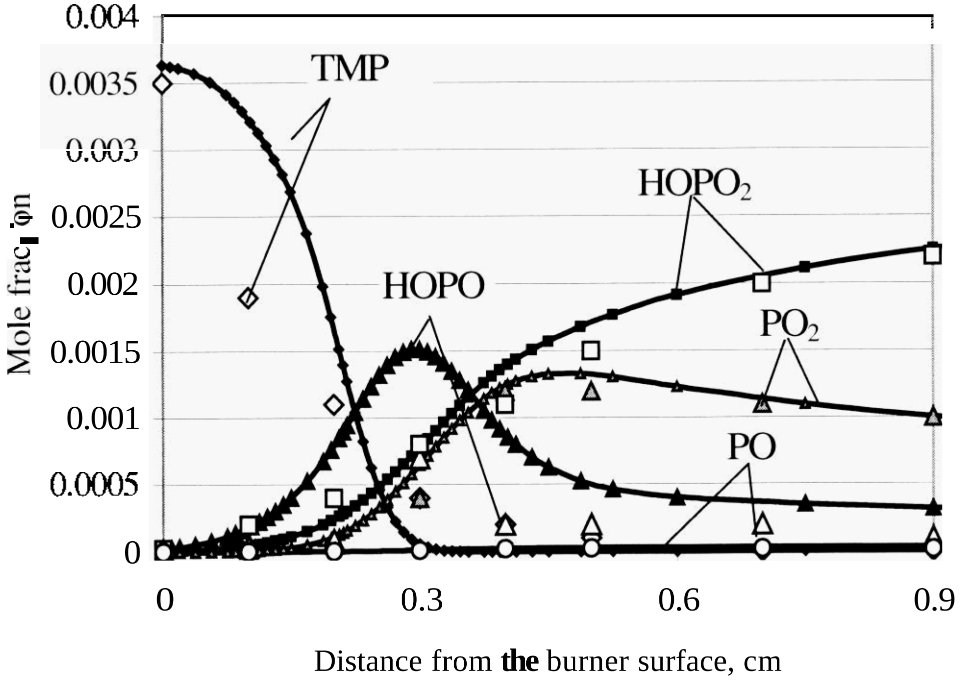

Figure 3. Concentration profiles of final phosphorus-containing products of TMP destruction in $CH_4/O_2/Ar$ flame.

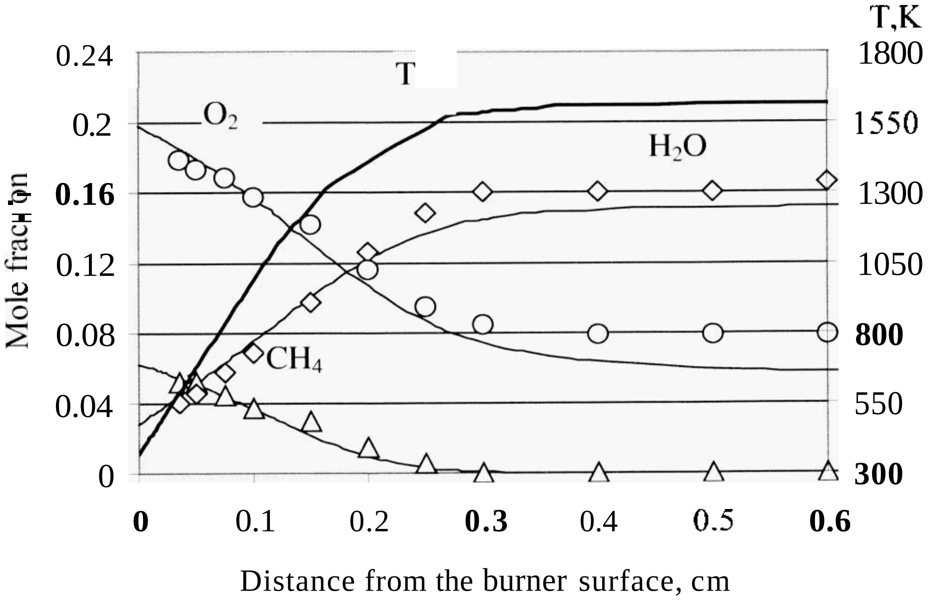

Figure 4. Temperature and some species concentration profiles in $CH_4/O_2/Ar$ flame without additive: lines, modeling; symbol, experiment.

containing species with CH_3, CH_3O, and CO, which are characteristic of methane flames. A distinctive feature of the suggested mechanism unlike the one suggested and accepted by other researchers [4,18] consists in an OPC (DMMP, TMP) destruction pathway through bimolecular reactions with H and OH, but not through a unimolecular decomposition.

Sensitivity analysis shows that the main reactions responsible for the inhibition cffcct are the reactions of promotion (in the case of $H_2/O_2/Ar$ flames doped with TMP) or inhibition (in the case of $CH_4/O_2/Ar$ flame under consideration) cycles with the participation of PO_2, HOPO. $HOPO_2$, and H. O, and OH. These reactions and their rate constants are presented in Table 1. Column I includes the valucs of rate constants developcd to describe the structure of $H_2/O_2/Ar$ flame doped with TMP and DMMP. It is characteristic of mechanism 1. The modified mechanism 2 differs from mechanism 1 by the other value of preexponential factors only represented in columns 2. The comparison of the results of calculation and the experimcnt on flame structure (first of all. on concentration profiles of PO_2, HOPO, and $HOPO_2$) shows that mechanism 1 requires a slight modification to describe the experimental datu on $CH_4/O_2/Ar/TMP$ flame structure satisfactorily. The results of flame structure calculation using mechanism 2 in comparison with the experimental results are shown in Figures 3 and 5. It is necessary to note that the preexponential factors of the two reactions differ just two times in mechanisms I and 2.

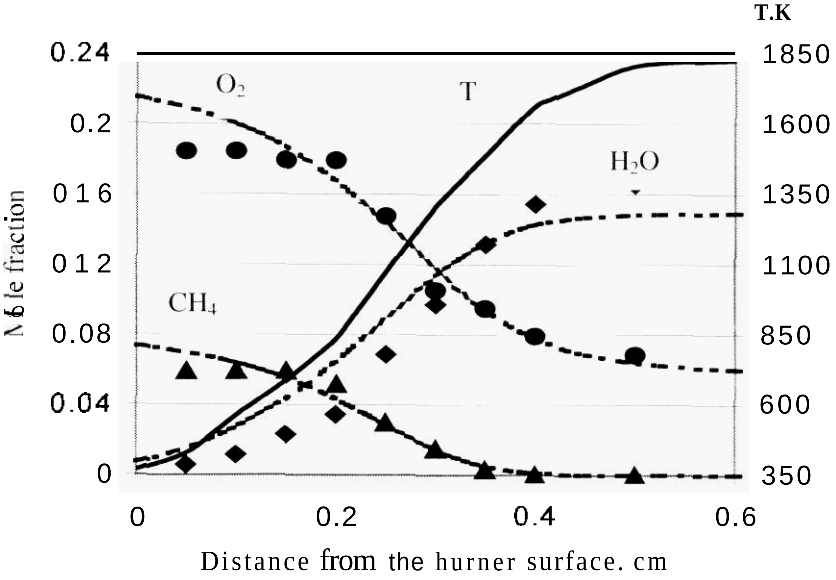

Figure 5. Temperature and some species concentration profiles in $CH_4/O_2/Ar$ flame with additive: lines, modeling, symbol, experiment.

EFFECT OF TMP ON H_2/O_2/AR AND CH_4/O_2/AR FLAMES PROPAGATION VELOCITY: MODELING

The inhibition of the combustion process in its classical sense, first of all, consists of the decrease of flame propagation velocity when a small amount of an inhibitor is added to the flame, which is why it is important to understand whether the observed expansion of the prcflame zone of the stabilized flame is accompanied by the changes in the velocity of the freely propagating

TABLE 1. THE MAIN REACTIONS RESPONSIBLE FOR INHIBITION EFFECTS AND THEIR RATE CONSTANTS. (K = A T^N EXP(-E/RT)).

Reaction	1			2
	A($cm^3 mol^{-1} sec^{-1}$) or, ($cm^6 mol^{-2} sec^{-1}$)	N	E (cal mol^{-1})	A($cm^3 mol^{-1} sec^{-1}$) or, ($cm^6 mol^{-2} sec^{-1}$)
$OH+PO_2+M=HOPO_2+M$	$1.6 \cdot 10^{25}$	-2.28	285.0	$0.8 \cdot 10^{25}$
$H+HOPO_2=H_2O+PO_2$	$6.32 \cdot 10^{11}$	0	11930.0	$6.32 \cdot 10^{11}$
$H+PO_2+M=HOPO+M$	$9.73 \cdot 10^{24}$	-2.04	645.0	$9.73 \cdot 10^{24}$
$OH+HOPO=H_2O+PO_2$	$3.16 \cdot 10^{11}$	0	0	$3.16.10^{11}$
$H+HOPO=H_2+PO_2$	$7.9 \cdot 10^{11}$	0	43.0	$7.9 \cdot 10^{11}$
$O+HOPO=OH+PO_2$	$1.58 \cdot 10^{12}$	0	0.0	$3.16 \cdot 10^{12}$
$O+HOPO+M=HOPO_2+M$	$1.3 \cdot 10^{24}$	-2.11	995.0	$1.3 \cdot 10^{24}$
$O+HOPO_2=O_2+HOPO$	$6.32 \cdot 10^{11}$	0	8236.0	$6.32 \cdot 10^{11}$

flame in the same combustible mixture and at the same pressure and initial temperature. To carry out the modeling of flame doped with TMP, mechanism 1 was first used. Figure 6 represents the dependency of the velocity of freely propagating $CH_4/O_2/Ar$ (0.078/0.222/0.7) flame on TMP initial concentration (pressure is 76 torr, initial temperature is 370 K). Calculations show that the velocity falls linearly with the rise of the introduced additive concentration. Thus, the results obtained demonstrate that the TMP additive inhibits CH_4/O_2 flame, and also preflame zone expansion results for stabilized flame are in agreement with the fall of the velocity of flame propagation. The calculation of flame velocity for the $CH_4/O_2/Ar$ mixture (0.078/0.222/0.7) at 1 atm has been also carried out. The sensitivity analysis demonstrates that the main reactions responsible for the inhibition effect of the velocity of flame propagation at 1 atm are nearly the same as those responsible for the expansion of a flame zone stabilized on a flat burner at low pressure. The results of the calculation of the flame velocity dependency on TMP concentration for mechanism 1 are presented in Figure 7. The application of mechanism 1 leads to similar effectiveness of TMP relative to CF_3Br (Figure 7) [26], in decreasing velocity of flame propagation. Unfortunately there are no measurements on velocity of flame propagation in CH_4/air mixture as a function of OPC loading. We can make conclusions and recommendations on the direction for further investigation. To find a reliable mechanism for OPC - TMP. DMMP inhibition mechanism (that is. the rate constants for the reactions involving H, OH, O, CH_3, PO_2, HOPO, $HOPO_2$, and PO), one should study the structure of $CH_4/O_2/Ar$ flame of different stoichiometric compositions with OPC additives at 1 atm and measurements velocity of flame propagation as a function of OPC loading. These data provide a basis for developing a generalized mechanism of OPC inhibition. Its use in the calculations of flame structure and velocity of flame propagation will allow researchers to check and correct the suggested mechanism in a wide range of experimental conditions, including the data on the extinction concentrations.

Earlier it was demonstrated that the TMP additive promotes a stabilized $H_2/O_2/Ar$ (0.26/0.13/0.61) flame [8], which is revealed in the decrease in the flame zone and rise in complete burnout. Using the complete mechanism 1 for H_2/O_2 flame doped with TMP [10], we have calculated the velocity of a freely propagating flame in stoichiometric hydrogen-oxygen mixture at different TMP initial concentrations (pressure is 47 torr, initial temperature is 370 K). Figure 8 presents

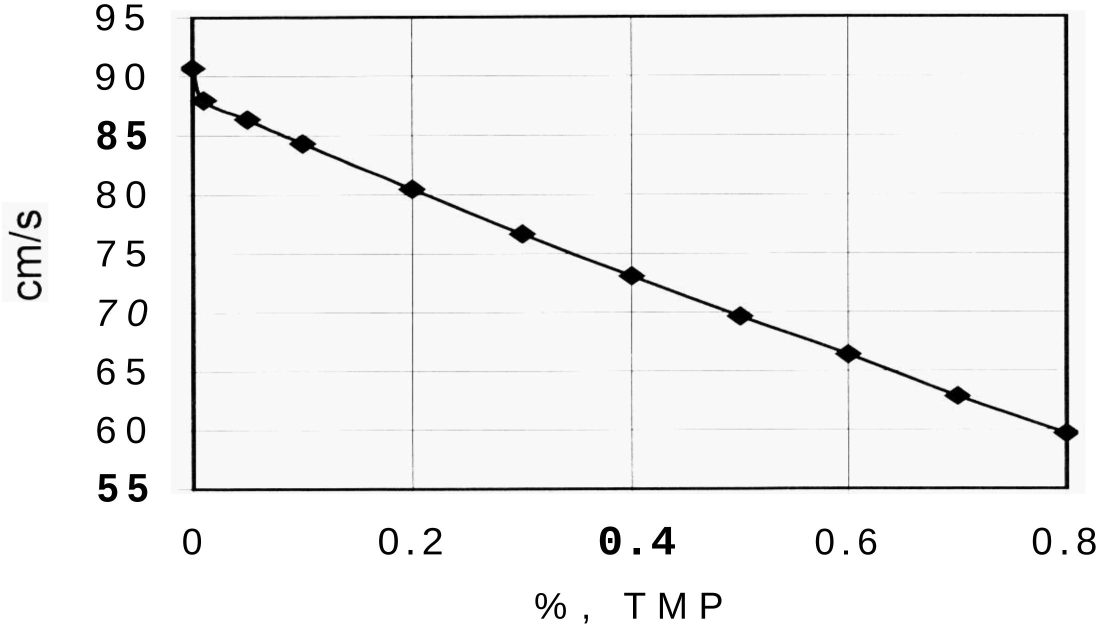

Figure 6. Calculated flame velocity dependence on TMP concentration in the $CH_4/O_2/Ar$ (0.078/0.222/0.7) mixture (P=76 torr, T_0 = 368K).

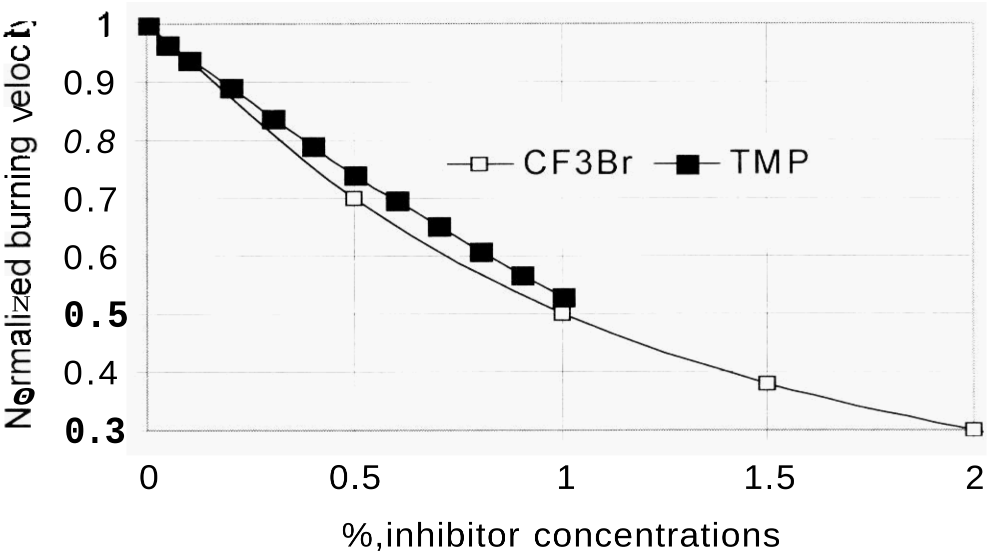

Figure 7. The velocity of flame propagation dependence on TMP concentration in $CH_4/O_2/Ar$ (0.078/0.222/0.7) mixture. p=1 atm, T_0=368 K (■- mechanism 1, □ - data from Reference 26).

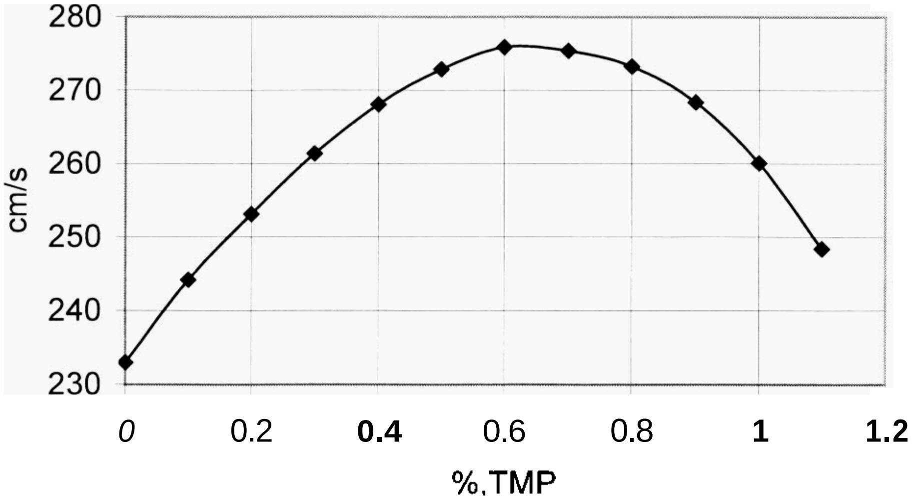

Figure 8. Calculated flame velocity dependence on TMP concentration in the $H_2/O_2/Ar$ (0.26/0.13/0.61) mixture (P=47 torr, T_o=368 K).

the results of these calculations. As can be seen from the data presented in Figure 8, the flame velocity is observed to rise to TMP concentration of 0.6%. and fall afterwards.

It is noteworthy that OPC additives provide a different effect not only on the velocity of the propagation of $H_2/O_2/Ar$ and $CH_4/O_2/Ar$ flames, but also on flame temperature. In the case of the $H_2/O_2/Ar$ flame, the introduction of OPC additive results in a temperature rise of 600-800 "C, while the introduction of OPC in $CH_4/O_2/Ar$ flame results in a slight reduce of the calculated temperature in a freely propagating flame. The measured slight temperature rise (by - 100 "C) of the $CH_4/O_2/Ar$ flame stabilized on a flat burner (when introducing OPC) is associated with a slight decrease in heat loss in a burner in this inhibited flame. The promoting effect and its dependency on the OPC additive concentration in $H_2/O_2/Ar$ flame can be explained by the competition between heat release and chains termination processes, which are affected by a catalytic cycle of reactions (Table 1). At low OPC concentrations (less than 0.6%) the process of **H** and OH catalytic recombination with heat release results in total heat release in the flame zone and its propagation velocity rise. Further rise of additive concentration increases the role of chains termination in the total heat release rate, which results in the decrease of inhibiting effect. It is interesting that the sensitivity analysis has shown the same reactions (Table 1) to be responsible for both the promotion effect and its decrease.

ACKNOWLEDGMENT

This work was supported by the US Army Research Office under Grant DAAG55-97-1-0407, the Russian Foundation for Fundamental Researches under Grant DAA N97-03-32473 and NATO Linkage Grant DISRM 951059. We also would like to thank E. Fisher for helpful discussions.

REFERENCES

1. Twarowski, A. J.. "The Influence of Phosphorus Oxides and Acids on Rate of H+OH Recombination," *Comhustion and Flume.* v. 94. pp. 91-107, 1993.
2. Twarowski, A. J., "Reduction of a Phosphorus Oxide and Acid Reaction Set," *Combustion and Flume,* v. 102, pp. 55-63. 1995.
3. Twarowski. A. J., "The Temperature Dependence of H+OH Recombination in Phosphorus Oxide Containing Combustion Gases," *Combustion and Flame,* v. 105, pp. 407-4 13, 1996.
4. Werner, J. H., and Cool, T. A., "A Kinetic Modcl for Decomposition of DMMP in a Hydrogen/Oxygen Flame," *Combustion and Flume.* v. 1 17, pp. 78, 1999.
5. Korobeinichev O. P., Ilyin S. B., Mokrushin V. V., Shmakov A. G., "Destruction Chemistry of Dimethyl Methylphosphonate in $H_2/O_2/Ar$ Flame Studicd by Molecular Ream Mass Spectrometry," Combustion Science and Technology, v. 116-117, pp. 5 1-67, 1996.
6. Korobeinichev. O. P.. Shvartsberg, V. M., Chernov, A. A., and Mokrushin, V. V., "Hydrogen-Oxygen Flame Doped with Trimethyl Phosphate. Its Structure and TMP Destruction Chemistry," *Twenty-sixth Symposium (International) on Comhustion,* The Combustion Institute, Pittsburgh, PA, p. 1035, 1996.
7. Korobeinichev. O. P., Ilyin. S. B., Shvartsbcrg, V. M., and Chernov, A. A., "The Destruction Chemistry of Organophosphorus Compounds in Flames – I: Quantitative Determination of Phosphorus-Containing Species in Hydrogen-Oxygen Flames," *Comhustion and Flume,* (1999). accepted for publication.
8. Korobeinichev, O. P.. Shvartsberg, V. M., and Chernov, A. A. "The Destruction Chemistry of Organophosphorus Compounds in Flames – II: Structure of Hydrogen-Oxygen Flamc Doped with Trimethyl Phosphate," *Combustion and Flumc,* (1999), accepted for publication
9. Korobeinichev, O. P., Ilyin. S. B, and Mokrushin, V. V., "The Destruction Chemistry of Organophosphorus Compounds in Flames – III: DMMP Destruction Mechanism and Species Concentration Profiles in $H_2/O_2/Ar$ Flame Doped DMMP – Experiment and Modeling," *Comhustion and Flumr* (1999), submitted for publication.
10. Korobeinichev. O. P., Bolshova, T. A., Shvartsberg, V. M., Chernov, A. A., and Mokrushin, V. V., "The Destruction Chemistry of Organophosphorus Compounds in Flames – IV: Kinetic Mechanism and Modeling of TMP Destruction in Hydrogen-Oxygen Flames," *Combustion and Flame* (1999), submitted for publication.
11. Hastie, J. W.. Bonnell, D. W., "Molecular Chemistry of Inhibited Combustion Systems." National Bureau of Standards Report No. NBSIR, 80-2169, 1980.
12. Korobeinichev, O. P., Chernov. A. A, Shvartsberg, V. M., Ilyin, S. B. and Mokrushin. V. V. "Chemistry of Destroying Chemical Warfare Agents in Flame," Final Progress Report. EARO Contract N68 I7194C9056, May 1995 – August 1996.
13. MacDonald , M. A., Juyawera, T. M.. Fisher, E. M., Gouldin, F. C., "Inhibition of Non-Prcmixed Flames by Phosphorus-Containing Compounds," *Combustion urid Flume.* v. 116, pp. 166-176, 1999.
14. Skagg, R. R.. Daniel. E. G., Miziolek. A. W.. McNessby, K. L., "Spectroscopic Studies of Inhibited Oposed Flow Propane/Air Flames," presented for JANAF Meeting, 1998
15. Kaizeman, J. A., Tapscott. R. E. *Advanced Streaming Agent Development. Vol. 3. Phosphorus Compounds,* NMERI, UNM, Albuquerque, NM, 1996.
16. Babushok, V., Tsang. W., "Chemical and Physical Processes in Combustion." Fall Technical Meeting of the Eastern States Section of the Combustion Institute, pp. 70-82, 1997.

17. Nogueira, M. F. M. and Fisher, E. M., "The Effect of Dimethyl Methylphosphonate on a Premixed $CH_4/O_2/Ar$ Flame," presented for the Joint US sections meeting, The Combustion Institute, Washington, DC, March 1999.
18. Babushok, V. Tsang, W., "Influence of Phosphorus-Containing Additives on Methane Flame," presented for the Joint US sections meeting, The Combustion Instite, Washington, DC, March 1999.
19. Hebgen, P., Homann, K. H., "Phosphorus Compounds as Flame Inhibitors- Analysis of Ionic Intermediates," *Twenty-Seventh Symposium (International) on Combustion,* The Cornbustion Institute, Pittsburgh, PA, 1998.
20. Dubinin, V. V., Kolesnikov, B. Ya., Ksandopulo, G. I., "Correction of Probe Sampling in Flames," *Explosion and Shock Waves,* v. 13, pp. 785, 1977.
21. Korobeinichev, **O.** P., Tereshchenko, A. G., Emel'yanov, I. D., Rudnitskii, A. L., Fedorov, S. Yu., Kuibida, L. V., Lotov, V. V., "Substantiation of the Probe Mass-Spectrometric Method for Studying the Structure of Flames with Narrow Combustion Zones," *Cornbustion, Explosion and Shock Waves,* v. 21. No. 5, pp. 524-530, 1985.
22. Kee, R. J., Grcar, J. F., Smooke, M. D., and Miller, J. A., "PREMIX." Sandia National Laboratories Report 1990. N SAND85-8240.
23. Kee, R. J., Rupley, F. M., Miller, J. A., *HEMKIN-II: A Fortran Chemical Kinetics Package for the Analysis of Gas Phase Chemical Kinetics.* Sandia National Laboratories Report. 1989. No. SAND89-8009B.
24. Burton, K. A., Ladouceur, H. D., Fleming, J. W., "An Improved Noncatalytic Coating for Thermocouples," *Combustion Scence. and Technology.* v. 81, **pp.** 141-145, 1992.
25. Hayhurst, A. N., Kittelson, D. B.. "Heat and Mass Transfer Consideration in Use of Electrically Heated Thermocouples of Iridium and Iridium/Rhodium Alloy in Atmospheric flame," *Combustion and Flame,* v. 28, pp. 301-317, 1977.
26. Babushok, V., Noto, T., Burgess D. R., Hamins. A., Tsang, W., "The Influence of Halogenated Fire Suppressants on the Combustion of C_1-C_2 Hydrocarbons," *Proceedings,* Halon Options Technical Working Conference, Albuquerque, NM, pp. 271-282, 1996.