INHIBITION OF METHANE ATMOSPHERIC FLAMES BY ORGANOPHOSPHORUS COMPOUNDS

Oleg Korobeinichev, Alexey Mamaev, Vladimir Sokolov, Tatyana Bolshova, and Vladimir Shvartsberg,
Institute of Chemical Kinetics and Combustion, Siberian Branch, Russian Academy of Sciences

Leonid Zakharov and Igor' Kudravtsev
Institute of Organo-Element Compounds of the Russian Academy of Sciences

ABSTRACT

This work was stimulated by the need of replacement of currently used Halon 1301 as fire suppressant. The goal **of** the research was to improve our understanding of the mechanism of the influence **of** organophosphorus compounds (OPC) **on** combustion processes. To validate known kinetic models explaining the inhibition effect of OPCs on methane-oxygen flames the structure of lean atmospheric $CH_4/O_2/Ar$ (6/15/79 %) flame stabilized on flat burner with trimethylphosphate (TMP) additive was investigated. Molecular beam mass spectrometry together with microprobe sampling has been applied. Comparison of the experimental data with modeling results demonstrated that the kinetic mechanism suggested earlier provided good agreement between calculated and experimental data. In addition, the propagation velocity of stoichiometric atmospheric CH_4-air flames, doped with the number of fluorinated OPCs, TMP and DMMP was studied experimentally and by modeling.

INTRODUCTION

It is well known that organophosphorus compounds (OPC) exert an inhibiting influence on flames. Hastie and Bonnell [1] found that trimethylphosphate (TMP) inhibited flames stabilized on a Bunsen burner. The authors studied the influence of TMP on methane-oxygen and hydrogen-oxygen flames of various types and composition by means of molecular beam mass spectrometry. Using visual observation of the height of the flame cone, the authors established that TMP additive resulted in a decrease of the velocity of free propagation of methane-oxygen flame, and they have been the first to propose a simplified mechanism involving organophosphorus compounds for inhibition of methane-oxygen flames. In Twarowski's works it was established that the addition of phosphine to hydrogen-air flame catalyzed recombination of H and OH radicals [2-4]. Twarowski hypothesized that phosphorus oxides and phosphoric acids—PO, PO_2, HOPO and $HOPO_2$—were the compounds that catalyzed the recombination of radicals. The author proposed a mechanism of catalytic recombination with participation of mentioned compounds.

Recently, the interest in using OPCs as inhibitors has greatly increased. In the works carried out at the our laboratory, the influence of TMP and dimethylmethylphosphonate (DMMP) addition on the structure of premixed $H_2/O_2/Ar$ flame stabilized on a flat flame burner at a pressure of 47 Torr was studied with the purpose of establishing the chemical mechanism of OPCs destruction in flames and of effects of TMP and DMMP doping on the flame [5-9]. Concentration profiles of practically all stable and labile compounds of flames doped with TMP and DMMP (CH_4, O_2, H_2O, CO_2, CO, H, OH, O), including concentration profiles of intermediate and final TMP and DMMP decomposition products (PO, PO_2, HOPO, $HOPO_2$, $PO(OH)_3$) were measured. On the basis of these data, and using the rate constants proposed in the works of Werner and Cool [10] and Twarowski [2-4], a mechanism of DMMP and TMP destruction was proposed. The results of simulation based on this mechanism are in satisfactory accord with experimental data. This mechanism has been confirmed also for methane-oxygen flame doped with TMP at a pressure of 76 Torr [11].

An opposed-jet burner apparatus was used to study the effectiveness of DMMP [12,131 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). Several investigations of the mechanism of the inhibiting effect of OPC on flames were recently published [14,15]. Because OPCs have been demonstrated to be more effective fire suppressants than Halon 1301, and due to the need for replacing the currently used Halon I301, further investigation of the mechanism of the inhibiting effect of OPC on flames is of great interest.

Babushok and Tsang [16] offered an OPCs destruction mechanism based on the work of Twarowski, Werner, and Cool. Babushok compared his calculations with the data on the dependence of flame propagation velocity on CF_3Br concentration, since no experimental data on OPC-doped CH_4-air flame propagation velocity are available in literature. There are some works dedicated to the comparison of inhibitory efficiency of various novel OPCs and CF_3Br. Riches et al. [17] used a modified chromatographic flame ionization detector with hydrogen-methane-air flame doped with TMP, DMMP, and other OPCs with fluorocarbon groups to study extinguishing properties of novel OPCs. The extinguishing concentrations of OPCs and gradients of curves in detector signal-additive concentration coordinates were measured. By means of comparing these characteristics for various OPCs and for Halon 1301, one can conclude that TMP is the most efficient extinguishing agent. The same authors [18] measured heat absorbed by the burner as a function of additive concentrations. TMP, DMMP, triethylphosphate, and three fluorinated OPCs were studied, and it was found that the extinguishing concentrations were approximately equal for these compounds.

hi the present paper, the authors report the results of studying the structure of CH_4/O_2 flames doped with TMP at 1 atm. by MBMS, microprobe technique and modeling. Also, the influence of various OPCs addition on the propagation velocity of stoichiometric methane-air flame at the atmospheric pressure was studied experimentally and by modeling.

EXPERIMENTAL

The structure of the $CH_4/O_2/Ar$ (6/15/79 %) flame stabilized on a flat-flame Botha-Spalding burner at an atmospheric pressure was studied. The burner temperature was maintained at 65 °C by using a thermostat. The volumetric velocity of unburned mixture was 25 cm^3/s under normal conditions. The burner was made of a brass disk with a diameter of 16 mm having 150 orifices with a diameter of0.7 mm. The combustible mixture was prepared by mixing of the tlows 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.

For the temperature profiles measurement, a Pt-Pt/Rh 10% thermocouple welded from wires 0.02 mm in diameter was used. The thermocouple junction did not exceed 0.03 mm in diameter. Flame species concentration measurements were performed on a experimental setup including a quadrupole mass-spectrometer MS-7302 with a molecular beam sampling and soft ionization by electron impact [5-8]. 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 completely preventing) ion fragmentation. **A** quartz sonic probe had the following parameters: orifice diam. 0.08 mm, wall thickness near the orifice 0.08 mm, inner angle near the orifice 40 deg.

To measure the concentration profiles of stable species in the flame, a quartz microprobe with the orifice diameter of 0.04 mm was used. The wall thickness near the probe orifice was 0.04 mm. The inner angle of the probe cone was 30 deg. The outer angle exceeded the inner one, but insignificantly. When using the microprobe, sampling was made into the ion source of the mass-spectrometer. The accuracy of species concentration measurement in the flame depended on the signal magnitude and on the background signal level. The error of stable species concentration values did not exceed relative 10%; in the case of phosphorus-containing intermediate products, it was relative 30%.

As it is known [19, 20], introduction of the probe into the flame results in distortion of equal concentration lines. Therefore, sampling is made at a certain distance from the orifice downstream of the gas flow. For this reason, the concentration profiles measured turn out to be shifted downstream with respect to the unperturbed flame by a certain distance (so-called shift). This shift was calculated according to Korobeinichev et al. [20] and amounted to 0.44 mm for the microprobe. To take into account the thermal perturbations introduced into the flame by the probe, the temperature profiles were measured by means of a thermocouple placed at the distance of 0.1 mm from the orifice of the probe. It turned out that microprobe did not introduce any considerable changes into the flame temperature profiles, whereas the sonic probe brought a shift of temperature profiles of about 0.5 mm and a decrease in the final temperature by 200 °C. That is why, while simulating flame structure, studied with the help of a sonic probe, a fixed temperature profile measured by a thermocouple fixed close to the tip of the probe was used.

Measurement of the influence of OPC additives on the flame propagation velocity was carried out on a Mache-Hebra burner, identical to that used by Linteris and Truett [21]. The burner consists of 27-cm long quartz tube with an area contraction ratio of 4.7 (over a 3-cm length) and a final nozzle diameter of 1 cm. The nozzle contour is designed to obtain the straight-sided visible image of a flame cone. The burning velocity was measured using visible cone digitized image obtained by CCD. In these experiments, a stoichiometric CH_4/Air 9.5/90.5% flame was used, and the unburned mixture volumetric flow rate was 44 cm^3/sec under normal conditions. The combustible mixture was prepared as described above. To eliminate OPCs condensation, the feeding line and burner were maintained at 65 °C using a thermostat. The following substances were tested: TMP, DMMP, and two fluorinated OPCs-tri-(2,2,2-fluoroethyl)phosphate and di-(2,2,2-fluoroethyl) methylphosphonate.

MODELING

Simulation of concentration profiles was camed out using PREMIX and CHEMKIN-II codes [22-23], which allow calculation of flame structure and propagation velocity. The methane oxidation mechanism, the same as Skaggs et al. [12], was used. It includes 59 reactions and 20 species from the CHEMKIN-II database. The kinetic model for methane flame with TMP additive consists of 95 stages, 38 of them being reactions, involving phosphorus-containing species. This model was proposed earlier by us [5-9] on the basis of experimental measurements of the structure of $H_2/O_2/Ar$ flame at 47 Torr doped with TMP and confirmed recently for the $CH_4/O_2/Ar$ flame at 76 Torr [11]. The main reactions responsible for the inhibiting effect of TMP additive are listed in Table 1. The first column represents rate constants suggested earlier [9, 11]; these constants were used in this work. The second column shows rate constants, corresponding to the maximal inhibitory effect (see Discussion below).

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

REACTION	1			2
	A($cm^3 mole^{-1} sec^{-1}$) or ($cm^6 mole^{-2} sec^{-1}$)	N	E (cal $mole^{-1}$)	A($cm^3 mole^{-1} sec^{-1}$) or ($cm^6 mole^{-2} sec^{-1}$)
$OH+PO_2+M=HOPO_2+M$	1.6E+25	-2.28	285.0	1.6E+24
$H+HOPO_2=H_2O+PO_2$	6.32E+11	***0.00***	11930.0	6.32E+12
$H+PO_2+M=HOPO+M$	9.73E+24	-2.04	645.0	9.73E+25
$OH+HOPO=H_2O+PO_2$	3.16E+11	***0.00***	***0.0***	3.16E+12
$H+HOPO=H_2+PO_2$	7.9E+11	***0.00***	43.0	7.9E+12
$O+HOPO=OH+PO_2$	1.58E+12	***0.00***	***0.0***	1.58E+13
$O+HOPO+M=HOPO_2+M$	1.3E+24	-2.11	YY5.0	1.3E+23
$O+HOPO_2=O_2+HOPO$	6.32E+11	***0.00***	8236.0	6.32E+12

RESULTS AND DISCUSSION

Figure 1 shows the experimental temperature profiles for the flame with the TMP additive (350 ppm) and flame without additive. **As** one can see, TMP addition results in widening of the reaction zone width for the main species—H_2O, O_2, CH_4 (i.e., addition of the TMP results in flame inhibition). Also, TMP addition slightly increases final temperature. **As** observed, the flame attained an orange color. and the distance from the burner surface and the luminescent boundary (dark zone) increased.

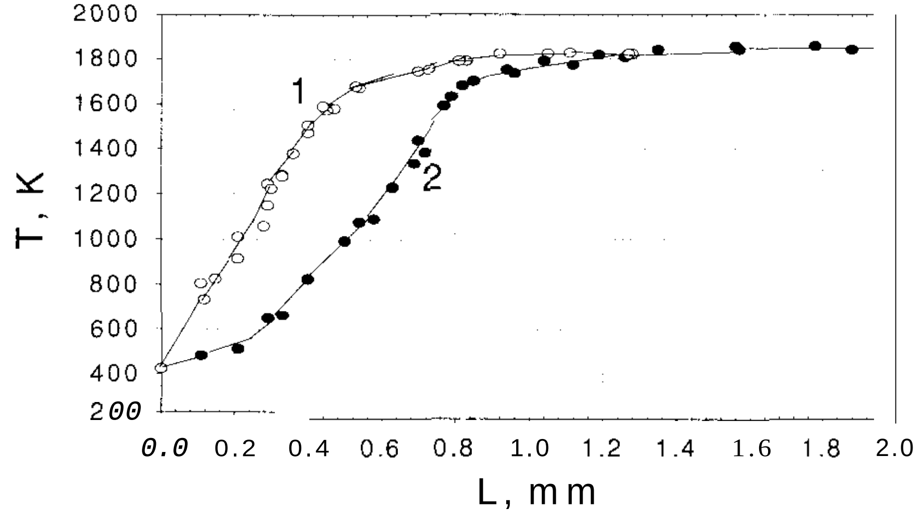

Figure 1. Temperature profiles for uninhibited flame $CH_4/O_2/Ar$ (1) and flame with TMP additive 350 ppm (2).

Figure 2 depicts the effect of the TMP addition on the main species concentration profiles obtained by microprobe-CH_4, O_2, H_2O; it also shows species concentration profiles, obtained by modeling. A satisfactory agreement between experimental results and modeling can be clearly seen.

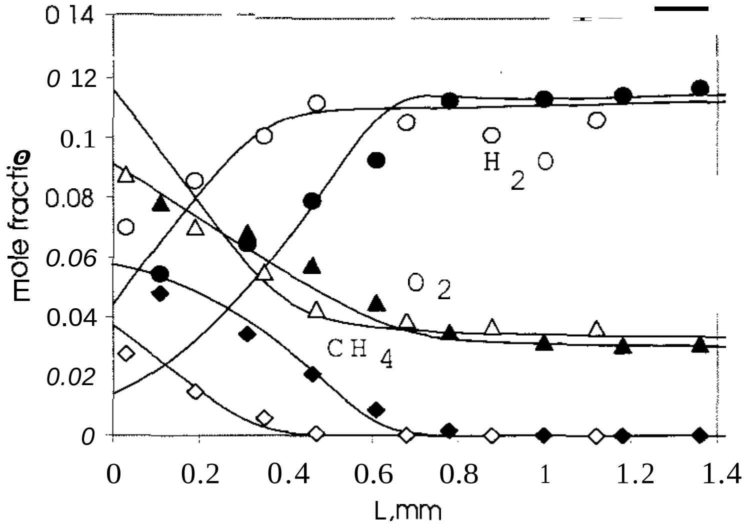

Figure 2. Comparison of the concentration profiles for undoped and doped $CH_4/O_2/Ar$ flame obtained with microprobe. Solid lines: modeling; symbols: experiment. Black symbols: TMP doped flame; open symbols: flame without additive.

Concentration profiles for the stable flame species (CH_4, O_2, H_2O, CO, CO_2) withdrawn by the sonic probe are in good agreement with concentration profiles derived by modeling. This fact justifies the correctness of the sonic probe application for the concentration measurements of the stable species in atmospheric methane-oxygen flame. The final concentrations of the phosphorus-containing decomposition products of TMP in flame were obtained using molecular beam sampling. These data and the modeling results are shown in Table 2.

TABLE 2. MOLE FRACTIONS OF PHOSPHORUS CONTAINING SPECIES IN $CH_4/O_2/AR$ FLAME WITH TMP ADDITIVE 350 ppm AT THE DISTANCE 3 mm FROM THE BURNER SURFACE.

Species	PO	PO_2	HOPO	$HOPO_2$
Experiment	9.3	14.3	3.9	72.6
Modeling by mechanism [11] (Col. 1,Table 1)	0.04	1.3	4.6	94.1
Modeling by mechanism [24]	0.07	11.3	2.4	86.3

Experimental data and the modeling **by** mechanism for PO, PO_2, HOPO, and HOP02 species are in satisfactory agreement. The mechanism [11] describes PO_2 data worse than that reported by Babushok.* In Figure 6 equilibrium concentrations of PO, PO_2, HOPO, and HOP02 in the

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* Babushok, V., personal communication, March 2000.

$CH_4/O_2/Ar/TMP$ flame (350 ppm by volume) as a function of temperature are presented. Comparing the equilibrium data in Figure 3 and experimentally measured concentrations of the above species (Table 2), one can see that both sets of concentrations coincide within the error of determination of calibration coefficients for PO, PO_2, HOPO, and $HOPO_2$ described earlier [7]. It is noteworthy that the final temperature of the flame at the distance of 0.1 mm from the probe's orifice is 1600 K. Therefore, we can conclude that unlike low pressure flames doped with DMMP [9] in atmospheric flames concentrations of PO. OP_2, HOPO and $HOPO_2$ are nearly equal to equilibrium. The OPC decomposition mechanism previously proposed [11]* allows prediction and characterization of the TMP inhibiting intluence on the atmospheric methane-oxygen flame structure.

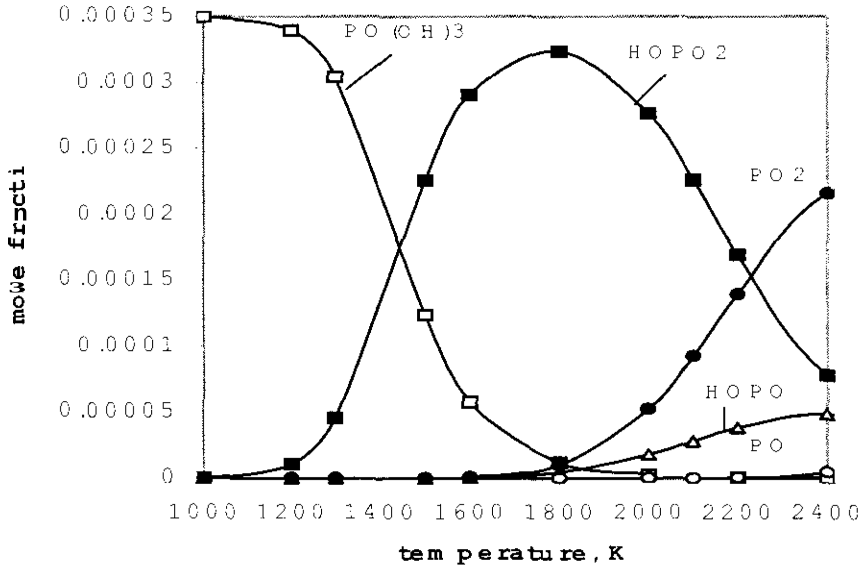

Figure 3. Equilibrium concentrations of PO, PO_2, HOPO, $HOPO_2$, and $PO(OH)_3$ for TMP doped $CH_4/O_2/Ar$ flame as a function of temperature.

Figure 4 denotes the CH_4-air propagation velocity dependence on the OPC additives concentration. Solid line "A" at the top of the picture corresponds to the calculation by the mechanism [11] used in this work for the modeling of the CH_4-oxygen flame structure. The second from the top solid line "B" corresponds to the modeling with mechanism.* The next solid line "C" corresponds to the mechanism providing maximal inhibitory effect (Column 2, Table I). Solid line "5" corresponds to the experimental dependence of flame propagation velocity on the concentration of CF_3Br [24].

As one can see from Figure 4, all of the OPCs tested exert influences on the flame that are equal within the error limits. The addition of fluorine to the OPCs does not intluence significantly the inhibiting properties of these compounds, which demonstrates that inhibiting properties of OPCs are associated with phosphorus atom exclusively. These data are in good agreement with those calculated when choosing the mechanism corresponding to the maximal inhihitory effect.

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* Babushok, V., personal communication, March 2000.

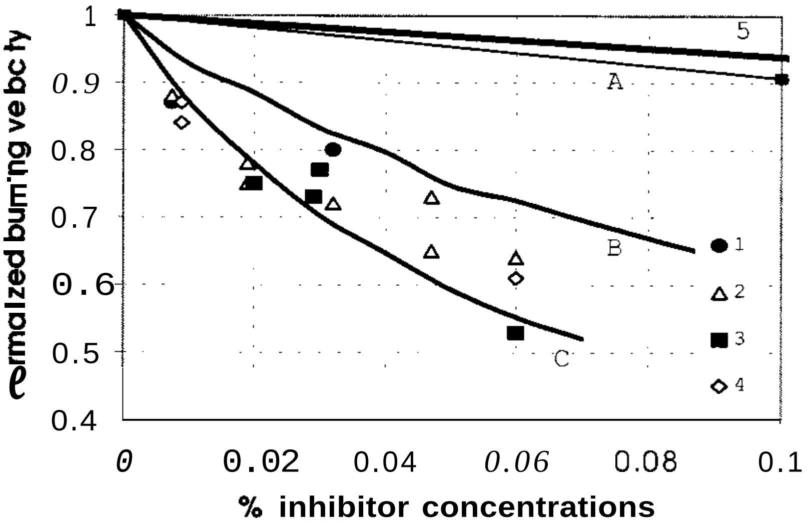

Figure 4. Dependence of the methane-air 9.5/90.5 flame propagation velocity on the additive concentration: 1 - tri-(2,2,2-fluoroethyl)phosphate; 2 - di-(2,2,2-fluoroethyl) methylphosphonate; 3 - TMP; 4 - DMMP; 5 - CF_3Br (Halon 1301).

Analysis of data obtained shows that there is no general inhibiting mechanism for satisfactorily describing both flame structure and flame velocity propagation. To find such a mechanism is the task of future research.

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