

EXPERIMENTAL STUDY AND MODELING OF INHIBITION EFFECT OF DIMETHYL METHYLPHOSPHONATE ON BURNING VELOCITY OF STOICHIOMETRIC PROPANE/AIR MIXTURES AT ATMOSPHERIC PRESSURE

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ABSTRACT

The work is dedicated to study of inhibition mechanism of premixed atmospheric propane-air flame doped with dimethyl methylphosphonate (DMMP). Burning velocity was measured using Mache-Hebra nozzle burner and the of total area method from the flame image. The introduction of DMMP into the flame was performed by a nebulizer providing the particle size of about 5 microns. The simulation of the burning velocity of the flame was carried out with the help of PREMIX and CHEMKIN codes using 2 detailed kinetic mechanisms proposed by the authors and by Westbrook et al. DMMP loading dependence of burning velocity was similar to those of trimethylphosphate. Modeling and experimental results obtained using both mechanisms were compared and discussed. Sensitivity analysis revealed that the stage $H+PO_2+M=HOPO+M$ plays the key role in the flame inhibition. The data obtained made it possible to understand and explain the mechanism of flame inhibition by organophosphorus compounds.

Keywords: burning velocity, inhibition, organophosphorus compounds, detailed kinetic mechanism.

INTRODUCTION

An interest to organophosphorus compounds (OPC) was caused by their unique properties. These compounds can serve as simulants for adjustment of the technology of incineration of chemical warfare agents (sarin, soman) and other toxic compounds (pesticides and others). OPC are of interest as catalysts for aircraft turbines [1] and fire suppressants [2,3]. OPC are especially prospective for substitution of halons, which are used for fire extinguishing. Production of halons was forbidden by Montreal Protocol because of destroying action on ozone layer of the atmosphere. That is why the investigation of OPC combustion chemistry is of great interest. Moreover, the study of chemical structure of flames and burning velocity presents one of the main sources of information on detailed kinetics (kinetic mechanism) of combustion process.

The first studies of $H_2/O_2/Ar$ flame doped with DMMP and stabilized on a flat burner at 50 Torr were performed using molecular beam mass spectrometry with soft ionization by electron impact [4] and photoionization by VUV [5]. The first kinetic model for DMMP destruction was proposed by Werner and Cool [5] and was based on experimental data on low pressure $H_2/O_2/Ar$ flame structure, and kinetic and thermochemical data of Melius for DMMP destruction [6]. To describe the interaction of final phosphorus-containing species with H and OH the

mechanism of Twarowski was applied [1,7,8]. The authors of the works [9,10] carried out a versatile investigation of $H_2/O_2/Ar$ flame doped with TMP (DMMP) and stabilized on a flat burner at 50 Torr [9,11-13] and developed a kinetic model, which satisfactory predicted flame structure including concentration profiles of labile species and radicals H, O, OH, PO, PO_2 , HOPO, $HOPO_2$, $OP(OH)_3$ in the flame at 50 Torr. Because OPC are effective fire suppressants and prospective candidates for halon replacement, the study of the mechanism of their action on flames was needed. In this connection the mechanism of action of OPC on hydrocarbon flames at low and atmospheric pressure have been studied. Using molecular beam mass spectrometry and numerical modeling the structure of premixed $CH_4/O_2/Ar$ flame was studied [3,9,14,15]. The interrelation between promotion effect of TMP at low pressure (50 Torr) $H_2/O_2/Ar$ flame and its inhibition effect at atmospheric $CH_4/O_2/Ar$ flame have been demonstrated. It was indicated that in both cases the reaction of catalytic recombination of H and OH is responsible for these effects. Depending on conditions the reaction can result in opposite effect (promotion or inhibition). Modeling results on thermal and chemical structure of the premixed $CH_4/O_2/Ar$ flame doped with TMP and stabilized on a flat burner at a pressure 80 Torr demonstrated a satisfactory agreement with experimental data. A kinetic model elaborated earlier [9,11,12] for TMP (DMMP) destruction in $H_2/O_2/Ar$ flame have been used. The structure of atmospheric $CH_4/O_2/Ar$ flat flame was studied [3,15]. Basing on comparison of results of experiment and modeling of flame structure and sensitivity analysis the rate constants of 6 the most important stages responsible for flame inhibition were modified [3]. The refined mechanism provided a satisfactory agreement between simulated and measured flame structure and burning velocity of the CH_4/Air mixtures doped with OPC.

Investigations of Glaude et al. [16,17] were dedicated to development of the mechanism for destruction of OPC in a flow reactor and a flame. The kinetic model includes 202 stages involving 41 phosphorus-containing species. The authors [16,17] suggested rate constants for a number of stages differing from those evaluated by Twarowski. The comparison of simulated structure of $H_2/O_2/Ar$ low pressure flame doped with OPC obtained using both models with experimental results revealed a good agreement not only on stable species but on labile active phosphorus-containing compounds like PO, PO_2 , HOPO and $HOPO_2$ [16]. Babushok and Tsang [18,19] proposed a kinetic model for DMMP destruction in atmospheric CH_4/air flame. This model included 24 stages involving OPC from Werner-Cool mechanism [5], 79 reactions

from Twarowski mechanism (including reactions of phosphine oxidation, which involve PH_3 , PH_2 , PH species, and reactions of interaction of CH_3 and CH_3O with phosphorus oxides. This model was applied to calculate burning velocity of stoichiometric mixture CH_4/Air doped with DMMP at atmospheric pressure.

In spite of significant progress in understanding OPC combustion chemistry, a deficit of quantitative experimental data on flame structure and burning velocity, which is necessary for refining of a inhibition mechanism, is observed. Besides, above-mentioned models were applied for simulation of small number of flames studied experimentally. That is why, the experimental data are of great interest. The goal of present research is to improve our understanding of combustion chemistry of OPC and inhibition mechanism by means of modeling and experimental measurement of burning velocity of atmospheric CH_4/air flame doped with DMMP.

EXPERIMENTAL

Burning velocity was measured using Mache-Hebra nozzle burner and total area method from the flame image as described elsewhere [20]. The burner is glass tube 2 cm in diameter and 27 cm long converging up to diameter of 1 cm on the length 3 cm. The ratio of the sectional areas for this burner is 4.7. This burner makes it possible to obtain a cone-shaped flame. The burning velocity of a flame was calculated using the formula $V=W/S$, where W is volumetric flow rate of the combustible mixture, S is the square of the flame cone, which was determined from flame image obtained by video camera. The combustible mixture of dry air and propane containing 4% of butane was prepared using mass flow controllers (MKS Instruments Inc., model 1299S). Volumetric flow rate of the combustible mixture was 3.3 slpm. The temperature of the burner was maintained at 95°C with the help of thermostat. OPC was introduced into the flow using a nebulizer, which was installed in the lower part of the burner. Figure 1 presents a scheme of the experimental setup.

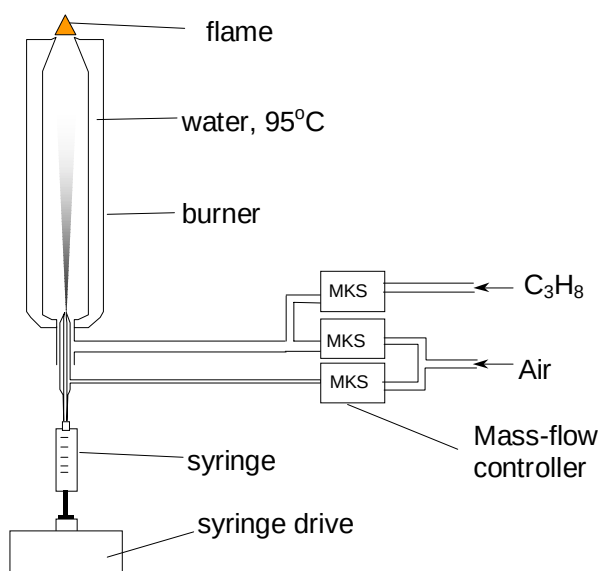


Fig. 1. Experimental setup.

The construction of the nebulizer is shown in Fig. 2. Inner diameter of the nebulizer is 0.1 mm, the thickness of the walls of the central capillary is 0.04 mm, and the width of the annular gap

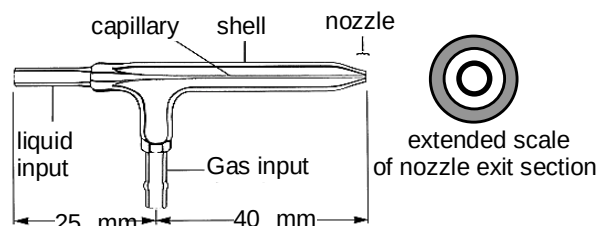


Fig. 2. Construction of nebulizer.

is 0.05 mm. Working pressure of the nebulizer was 5 atm. At these conditions the size of the particles was about 5 microns that was determined for 50% solution of glycerin in water. OPC feeding in to the nebulizer was performed by a syringe pump that made it possible to vary the flow rate of the liquid in the wide range.

RESULTS AND DISCUSSION

Burning velocity. Experiment and Modeling.

Dependence of burning velocity of a stoichiometric mixture $\text{C}_3\text{H}_8/\text{air}$ on DMMP loading is presented in Fig. 3. Measured burning velocities were normalized on that of undoped flame. Dependencies of burning velocity carried out in a range of additive concentration up to 3000 ppm. Further increase of loading resulted in a liftoff of a flame. For $\text{TM}\Phi$ liftoff of a flame occurred at 1500 ppm. To compare inhibition effectiveness of currently used CF_3Br (halon 1301) and TMP - prospective candidate for its replacement dependence of burning velocity of a stoichiometric mixture $\text{C}_3\text{H}_8/\text{air}$ on CF_3Br loading was measured. Experimental results are plotted in Fig. 3. The data obtained demonstrate that OPC are much more effective fire suppressants than CF_3Br .

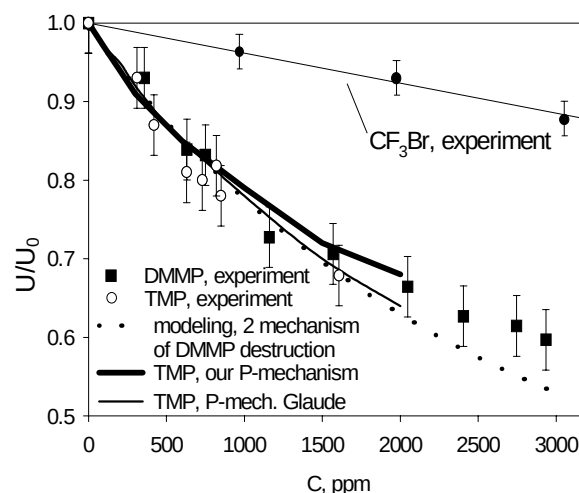


Fig. 3. Normalized burning velocity of stoichiometric premixed $\text{C}_3\text{H}_8/\text{Air}$ flame as a function inhibitor loading.

Calculation of burning velocity was performed with help of codes PREMIX and CHEMKIN-II. Two different models have been used for modeling: (1) the first one proposed by Westbrook et al. [21], which includes mechanism of DMMP destruction, shown in Fig. 4 and Table 1, (2) the second one is "our mechanism" [9]. The latter one includes a model for DMMP destruction elaborated in [9] for $\text{H}_2/\text{O}_2/\text{Ar}$ flame (Fig.

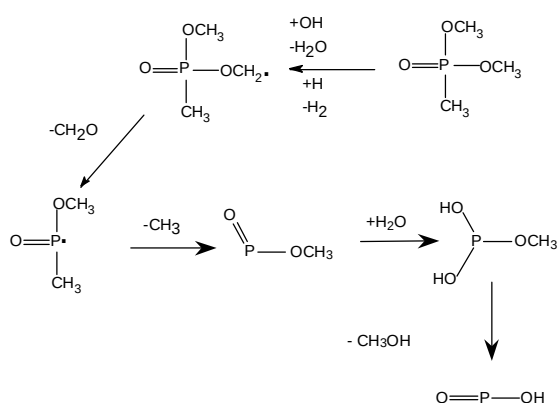


Fig. 4. Mechanism for the destruction of DMMP [21].

5, Table 2) and also mechanism for propane oxidation developed by Konnov [22]. The mechanism of Westbrook et al. [16,17] for transformation of phosphorus containing species is the same for both models.

Modeling results obtained using both models were quite close and provided a good agreement with experimental results (Fig. 3). Figure 3 also presents the experimental data for the same C_2H_8 /air flame doped with TMP.

Table 1. The main Rate constant for DMMP destruction ($k=AT^n\exp(-E/RT)$) [21]

#	Reactions	A	n	E
1	DMMP+OH=POME[OME][OCH ₃]+H ₂ O	7.20×10 ⁶	2.00	750
2	DMMP+H=POME[OME][OCH ₃]+H ₂	1.44×10 ⁹	1.50	7140
3	POME[OME][OCH ₃]=POME[OME]+CH ₃ O	2.00×10 ¹³	0.00	38950
4	POME[OME]=CH ₃ OPO+CH ₃	1.00×10 ¹⁴	0.00	32100
5	CH ₃ OPO+H ₂ O=PO[H][OH][OME]	1.00×10 ¹²	0.0	2000
6	PO[H][OH][OME]=HOPO+CH ₃ OH	7.00×10 ¹³	0.0	45000

*- units are mole, cm³, s, cal/mole

Table 2. The rate constants for DMMP intermediates (k=ATⁿexp(-E/RT)) [9]

#	Reactions	A	n	E
1.	$\text{DMMP} + \text{OH} = \text{PO}(\text{OCH}_3)(\text{OH})\text{CH}_3 + \text{CH}_3\text{O}$	1.00×10^{13}	0	4000
2.	$\text{DMMP} + \text{H} = \text{PO}(\text{OCH}_3)(\text{OH})\text{CH}_3 + \text{CH}_3$	1.00×10^{12}	0	4000
3.	$\text{DMMP} + \text{OH} = \text{PO}(\text{OCH}_3)_2(\text{OH}) + \text{CH}_3$	3.00×10^{12}	0	4000
4.	$\text{DMMP} + \text{OH} = \text{PO}(\text{OCH}_3)(\text{OCH}_2)\text{CH}_3 + \text{H}_2\text{O}$	1.00×10^{11}	0	4000
5.	$\text{DMMP} + \text{H} = \text{PO}(\text{OCH}_3)(\text{OCH}_2)\text{CH}_3 + \text{H}_2$	1.00×10^{11}	0	4000
6.	$\text{PO}(\text{OCH}_3)_2(\text{OH}) = \text{PO}_2\text{OCH}_3 + \text{CH}_3\text{OH}$	1.70×10^{12}	0	39001
7.	$\text{PO}(\text{OCH}_3)(\text{OCH}_2)\text{CH}_3 = \text{PO}(\text{OCH}_3)\text{CH}_3 + \text{CH}_2\text{O}$	3.70×10^{14}	0	38950
8.	$\text{PO}(\text{OCH}_3)(\text{OCH}_2)\text{CH}_3 + \text{H} = \text{PO}(\text{OCH}_3)\text{CH}_3\text{H} + \text{CH}_2\text{O}$	1.00×10^{14}	0	0
9.	$\text{PO}(\text{OCH}_3)(\text{OH})\text{CH}_3 + \text{OH} = \text{PO}(\text{OH})_2\text{CH}_3 + \text{CH}_3\text{O}$	1.00×10^{13}	0	4000
10.	$\text{PO}(\text{OCH}_3)(\text{OH})\text{CH}_3 + \text{H} = \text{PO}(\text{OH})_2\text{CH}_3 + \text{CH}_3$	1.00×10^{12}	0	4000
11.	$\text{PO}(\text{OCH}_3)(\text{OH})\text{CH}_3 = \text{PO}_2\text{OCH}_3 + \text{CH}_4$	1.00×10^{12}	0	39001
12.	$\text{PO}(\text{OCH}_3)(\text{OH})\text{CH}_3 = \text{CH}_3\text{PO}_2 + \text{CH}_3\text{OH}$	1.70×10^{12}	0	39001
13.	$\text{PO}(\text{OH})_2\text{CH}_3 + \text{OH} = \text{PO}(\text{OH})_3 + \text{CH}_3$	1.00×10^{13}	0	4000
14.	$\text{PO}(\text{OH})_3 + \text{H} = \text{PO}(\text{OH})_2 + \text{H}_2\text{O}$	1.00×10^{12}	0	7998
15.	$\text{PO}(\text{OH})_3 = \text{HOPO}_2 + \text{H}_2\text{O}$	1.00×10^{12}	0	50000
16.	$\text{PO}(\text{OH})_2 + \text{OH} = \text{HOPO}_2 + \text{H}_2\text{O}$	1.00×10^{13}	0	0
17.	$\text{PO}(\text{OH})_2 + \text{H} = \text{HOPO}_2 + \text{H}_2\text{O}$	1.00×10^{12}	0	0
18.	$\text{PO}(\text{OH})_2 = \text{PO}_2 + \text{H}_2\text{O}$	1.00×10^{12}	0	29951
19.	$\text{PO}_2\text{OCH}_3 + \text{OH} = \text{HOPO}_2 + \text{CH}_3\text{O}$	3.00×10^{12}	0	3993
20.	$\text{PO}_2\text{OCH}_3 + \text{H} = \text{HOPO}_2 + \text{CH}_3\text{O}$	1.00×10^{12}	0	3993
21.	$\text{PO}(\text{OCH}_3)\text{CH}_3\text{H} + \text{OH} = \text{PO}(\text{OCH}_3)\text{CH}_3 + \text{H}_2\text{O}$	3.00×10^{13}	0	0
22.	$\text{PO}(\text{OCH}_3)\text{CH}_3\text{H} + \text{H} = \text{PO}(\text{OCH}_3)\text{CH}_3 + \text{H}_2$	1.00×10^{14}	0	3993
23.	$\text{PO}(\text{OCH}_3)\text{CH}_3 = \text{CH}_3\text{PO}_2 + \text{CH}_3$	1.00×10^{14}	0	17970
24.	$\text{CH}_3\text{PO}_2 + \text{OH} = \text{HOPO}_2 + \text{CH}_3$	3.00×10^{14}	0	7987
25.	$\text{CH}_3\text{PO}_2 + \text{H} = \text{PO}(\text{OH})\text{CH}_3$	1.00×10^{12}	0	16.72
26.	$\text{PO}(\text{OH})\text{CH}_3 = \text{HOPO}_2 + \text{CH}_3$	1.00×10^{11}	0	19967

*- units are mole, cm³, s, cal/mole

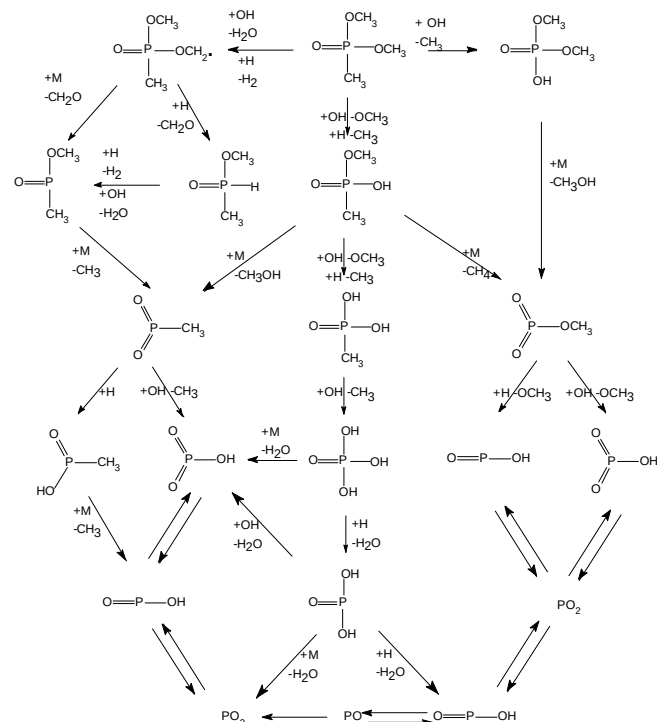


Fig. 5. Mechanism for the destruction of DMMP in a $H_2/O_2/Ar$ flame [9].

Comparison of the experimental and modeling results on dependence of burning velocity vs. TMP and DMMP loading revealed that TMP and DMMP have practically the same inhibition effectiveness. This fact indicates that inhibition effect of OPC is mainly determined by presence of atom of phosphorus in a molecule and practically does not depend on the molecular structure and the first stages of OPC destruction in a flame. It is reasonable to propose that other OPC have approximately the same inhibition effectiveness. Sensitivity analysis [23] made it possible to determine the most important stages responsible for inhibition of C_3H_8 /air flame, which are given in Table 3. The most important reaction was found to be $H+PO_2+M=HOPO+M$, which results in a loss of active species providing a combustion.

Table 3. The rate constants for OPC intermediates expressed as $k = AT^n \exp(-E/RT)$ [17]

#	Reactions	A	n	E
1	$\text{OH} + \text{PO}_2 + \text{M} = \text{HOPO}_2 + \text{M}$	3.2×10^{25}	-2.3	285
2	$\text{H} + \text{PO}_2 + \text{M} = \text{HOPO} + \text{M}$	1.46×10^{25}	-2.0	645
3	$\text{OH} + \text{HOPO} = \text{H}_2\text{O} + \text{PO}_2$	1.2×10^{26}	2.0	-1500
4	$\text{H} + \text{HOPO} = \text{H}_2 + \text{PO}_2$	6.8×10^{13}	0.0	8100
5	$\text{O} + \text{HOPO} = \text{OH} + \text{PO}_2$	1.0×10^{13}	0.0	0
6	$\text{O} + \text{HOPO} + \text{M} = \text{HOPO}_2 + \text{M}$	1.2×10^{27}	-3.0	2040
7	$\text{O} + \text{HOPO}_2 = \text{O}_2 + \text{HOPO}$	5.0×10^{12}	0.0	15000

*- units are mole, cm³, s, cal/mole

CONCLUSION

At this moment an appreciable progress in understanding of combustion and destruction chemistry of OPC. Main pathways of OPC destruction in flames are established and intermediate and final products of their destruction are identified. It is

proved that destruction of OPC in flame proceeds mainly due to their interaction with radicals, but not due to pyrolysis. The mechanism of OPC effect (promotion or inhibition) on a flame has been revealed in general. The effect of number of OPC on the burning velocity of a flame has been compared. Kinetic models, which with a satisfactory accuracy simulate OPC destruction, flame inhibition and burning velocity, of the flames have been elaborated. Nevertheless, preliminary studies demonstrated that the available models fail to simulate concentration profiles of phosphorus species in the rich flames. It may be connected with a wrong or insufficient account of the processes of interaction of phosphorus oxides with carbon-containing flame species. A deficit of experimental data in the first turn on the structure of flames of various composition doped with OPC may be a main factor, which prevents the further progress in this area. This fact impedes validation and refining of the models. Besides, the problem of validity of rate constants of reactions involving phosphorus-containing species is quite urgent. It should be also mentioned that toxicity of OPC has not been practically studied. For successful practical use of OPC as fire suppressants it is necessary to continue the study of the inhibition mechanism and carry out the search of novel volatile OPC that are effective fire suppressants.

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