# The phenomenon of promotion and inhibition of a hydrogen-oxygen flame by the additives of organophosphorus compounds at low pressure. The detailed kinetic analysis.

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## Abstract

The work is devoted to the detailed kinetic analysis of the unusual influence of the additives of organophosphorus compounds (OPC) on speed of stoichiometric hydrogen-oxygen flame diluted by argon at low pressure (47.5 torr)promotion at low concentration OPC (0.2-0.4 % mole fraction) and inhibition at 0.6-0.8 %. Such effect was not observed in other conditions - at pressure 1 atm, and also in others flames (methane-oxygen) at anyone pressures. The analysis of sensitivity of flame speed to rate constants of the basic reactions in the mechanism of hydrogen oxidation (not containing phosphorus) at different concentration TMP has shown that only rate constant of a chain branching reaction OH+H<sub>2</sub>=H<sub>2</sub>O+H have an influence on flame speed. The analysis of sensitivity of a rate constants of reactions containing phosphorus species has shown the strongest dependence of a flame speed from reactions which are reactions of catalytic recombination of H, OH and O. These reactions increase flame speed at concentrations of the additive TMP less than 0.6 % but inhibit flame at concentrations of the additive more than 0.6 %. The originality of the phenomenon consist in that the reactions of catalytic recombinations are reactions of chain terminations. It would seem they always to reduce reaction rate and a flame speed. However, as a result of these reactions the rate of heat release increases at low pressures. And it results in increase of flame temperature (up to temperature at thermodynamic equilibrium) and as a consequence increase of a chain branching and growth of a flame speed. Reactions of non-catalytic recombinations are trimolecular ones and their rate at low pressures is very slow. As result maximal flame temperature is much less than that at thermodynamic equilibrium.

#### Introduction

The structure the hydrogen-oxygen flames, just as the mechanism of oxidation of hydrogen by oxygen, is considered well investigated. As it is noted in [1], The system H<sub>2</sub>/O<sub>2</sub> is most complex of all systems investigated in details. The plenty of works devoted to measurement and calculation of speed of the hydrogenoxygen flames at various initial compositions of combustible mixes is published [1-3]. The most part of works is devoted to research of chemical structure hydrogen-oxygen flames at low pressure [4-6]. The influence of the additives on hydrogen-oxygen flames was studied with the purpose of study of the mechanism of flame inhibition. The authors of Ref.[8] studied influence of the additives trimethyl phosphate (TMP) on speed and structure of methane-oxygen and hydrogen oxygen flames of a various type and composition by a molecular beam mass spectrometry (MBMS), thermocouple and optical methods at 1 atm. Twarowski determined that the addition of phosphine catalyses the recombination of hydroxyl and hydrogen atoms in the hydrogen-air flame [9]. He proposed the mechanism of catalytic reactions of the recombination of atoms H and O and radical OH with participation oxides of phosphorus and phosphoric acids PO, PO<sub>2</sub>, HOPO и HOPO<sub>2</sub> as catalysts. Rate constants of these reactions also were evaluated.

Later in [11] was shown, that the rate constants accepted in the Twarowski mechanism incorrectly predict concentration of PO, PO<sub>2</sub>, HOPO  $\mu$  HOPO<sub>2</sub> in a hydrogen-oxygen flame with the additive TMP and dimethyl methyl phosphonate (DMMP).

For the experiment matching a rate constant of reactions which are included in this mechanism, were refined [11]. The structure of a stoichiometric H<sub>2</sub>/O<sub>2</sub>/Ar flame with the additives TMP, DMMP at low pressure has been studied [11-13] with MBMS for the better understanding of kinetic and chemistry of combustion processes, determination of the chemical mechanism of influence of the additive TMP and DMMP on a flame. Basing on the experimental data [11,13] and Melius's thermochemical calculations [14], the destruction mechanism of TMP and DMMP with the modified rate constants of reactions which are included in the Twarowski mechanism was suggested. This mechanism satisfactorily describes experimental data on flame structure. Thermochemistry of reactions for many new OPC was investigated using BAC-MP4 method and applied for destruction of sarin [15] and inhibition of propane flame [16].

A theoretical investigation of the effects of  $PO_2$ on the H + OH radical recombination reaction was reported in Ref. [17]. The focus of the study was the computation of rate coefficients by *ab initio* quantum

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chemical and RRKM methods for the reactions of catalytic recombination. The computed rate constants are consistent with the available experimental data and the results of modeling [12].

The unusual influence of the additives of organophosphorus compounds (OPC) on speed of stoichiometric hydrogen-oxygen flame diluted by argon at low pressure (47.5 torr) was determined by a modeling in [12] – promotion at low concentration OPC (0.2-0.4 % mole fraction) and inhibition at 0.6-0.8 %. Such effect was not observed in other conditions - at pressure 1 atm, and also in others flames (methane-oxygen) at anyone pressures. This work is devoted to the detailed kinetic analysis of this phenomenon.

#### Kinetic model and modeling procedure

Numerical simulation was performed by using the one-dimensional flame code PREMIX [18] and CHEMKIN-II [19]. Sensitivity analysis for the flame speed in premixed H<sub>2</sub>-O<sub>2</sub> flames was carried out using the procedure by Warnatz [7]. The focus of the study was the speed of premixed hydrogen-oxygen flame H<sub>2</sub>/O<sub>2</sub>/Ar (26/13/61) with TMP and without TMP at pressure p=47.5 torr, T<sub>0</sub>=370K. Concentration of the additive TMP varied from 0.05 % to 1 % mole fraction. The additive was introduced instead of argon. The speed of stoichiometric premixed hydrogen-oxygen flame H<sub>2</sub>/O<sub>2</sub>/Ar is found to be in agreement with the literature [7].

The reaction mechanism for the hydrogenoxygen flame with the additive TMP includes 35 components and 92 reactions [11]. The mechanism is formed by four groups of reactions. 23 reactions represent the mechanism of oxidation of hydrogen. Mechanism includes 34 elementary stages describing the oxidation of methane, added in the oxidation mechanism of TMP. 15 reactions are those of the Twarowski mechanism for which we changed the rate constants. 20 reactions are stages of destruction of TMP and organophosphorus intermediate products of its destruction in a flame. The comparison of modeling results of structure of flame without the additive with experimental data obtained using MBMS has shown, that the accepted mechanism with good accuracy profile of concentration both stable components of a flame, and atoms and radicals [10]. The good agreement of results of experiment and modeling was received also for a flame with the TMP concentration of 0.2 vol. % [10].

## **Results and discussion**

Hydrogen-oxygen flames at low pressure are characterized by an establishment of partial equilibrium on three fast reactions

$$OH+H_2=H_2O+H$$
(1)

$$H+O_2=OH+O$$
 (2)

$$O+H_2=OH+H$$
 (3)

in postflame zone, which determines concentration of H, O and OH. The only mechanism for achievement of final equilibrium should be a way of reactions of recombinations of atoms and radicals similar H+H+M  $\rightarrow$  H<sub>2</sub>+M;

H+OH+M → H<sub>2</sub>O+M etc., where M - any molecule. The TMP additives promote H<sub>2</sub>/O<sub>2</sub> premix stoichiometric flame stabilized on the flat burner at subatmospheric pressures. The promotion effect consists in increase of final combustion temperature and completeness of combustion at TMP addition. In [10] was determined that introduction 0.2 % mole fraction of TMP in premix stoichiometric H<sub>2</sub>/O<sub>2</sub>/Ar flame stabilized on the flat burner at pressure 47.5 torr result in increase of final temperature on 300K. The increase of temperature of a flame is not connected with introduction of the TMP additive with additional fuel in a combustible mixture. Results of calculations show,



Fig.1. Final calculated temperature in premixed free propagating  $H_2/O_2/Ar$  (26/13/61) flame as a function of TMP loading at p=47.5 torr,  $T_0$ =370K. Light circles are adiabatic flame temperatures.

that thermodynamic equilibrium temperature of stoichiometric flame at the small additives (~ 0.1 % mole fraction) increases insignificantly (~ 3K). The calculations of structure of free propagating a hydrogen-oxygen flame have shown, that (Fig. 1) with introduction of the TMP additive (less than 0.6 % mole fraction) final temperature grows. Calculated final temperature for a hydrogen-oxygen flame without



Fig. 2 Sensitivity analysis for the laminar speed of  $H_2/O_2/Ar$  flames.



Fig. 3. Reaction rates of  $H+O_2=OH+O$  in a premixed  $H_2/O_2/Ar$  flames with TMP and without TMP.

additive on distance 20.0 cm from a flame zone is 1720K, that on ~700K is lower than adiabatic temperature. Calculated adiabatic temperature of a  $H_2/O_2/Ar$  (26/13/61) mixture is 2408K (at pressure p=47.5 torr). The growth of final temperature at addition TMP in  $H_2/O_2/Ar$  a flame is connected with catalysis of reactions of recombination of H, OH and O by phosphorus containing species. As a result of it the system faster and closer comes to thermodynamic equilibrium. At concentration TMP ~0.5 % mole fraction calculated final temperature of a flame reaches thermodynamic equilibrium temperature. The analysis of sensitivity of flame speed U to rate constants of the



Fig. 4. Comparison between reaction rates of  $H+O_2=OH+O$  and temperature profiles for premixed  $H_2/O_2/Ar$  flames with TMP (blue lines) and without TMP (black lines). Concentration of TMP is 0.4 %.

basic reactions in the mechanism of hydrogen oxidation (not containing phosphorus) at different concentration TMP shows the only rate constant of a chain branching reaction  $OH+H_2=H_2O+H$  (1) have an influence on flame speed. With increase of the additive concentration this influence raises (Fig. 2). The rate of reaction of a branching  $H+O_2=OH+H$  was determined as a difference of direct and back reaction rates. Thus the maximum rate of this reaction grows and moves in area of high temperatures with growth of concentration of the additive (Fig. 3). The introduction of the additive TMP in a hydrogen-oxygen flame results in spatial narrowing of area of reaction (Fig. 4).



Fig. 5. Mole fraction of H in a premixed  $H_2/O_2/Ar$  flames with TMP and without TMP, calculated using a full mechanism (lines and symbol) and using assumption of the partial equilibrium (lines).

Mole fraction of H as a function of local temperature in a hydrogen-oxygen stoichiometric flame without and with the additive 0.4 % TMP are presented in Fig. 5. Results of calculation with using full mechanism are shown by symbols, those using the assumption of partial equilibrium - by solid lines. The assumption of partial equilibrium is provided only at high temperatures. For a flame without additive it is temperature above 1240K, for a flame with the additive 0.4 % TM $\Phi$  this temperature is higher - 1560K.

The growth of rate of a chain branching reaction is not connected with growth of concentration of atoms H. Fig. 6 shows, that the concentration H falls with increase of concentration of the additive. It is possible to explain increase of reaction rate by increase of the



Fig. 6. Mole fractions of the radicals H in premixed  $H_2/O_2/Ar$  flames with TMP and without TMP.



Fig.7. Influence of varied rate constant of elementary reactions on calculated value  $\xi = 100\% \times (U-U(k/5)/U)$ , where U- speed of H<sub>2</sub>/O<sub>2</sub>/Ar flames doped with TMP of different concentration, U(k/5) – flame speed for the rate constants decreased in 5 times.

exponential factor of a rate constant connected with increase of temperature of a flame. Activation energy of this reaction equals 14.79 kkal/mol. The analysis of sensitivity of a rate constants of reactions containing phosphorus species has shown the strongest dependence of a flame speed (Fig. 7) from reactions

$$H+PO_2+M = > HOPO+M$$
(4)

$$H+HOPO = > H_2 + PO_2 \tag{5}$$

$$O+HOPO = > OH+PO_2 \tag{6}$$

These reactions play the important role in a case of promotion flame at concentration of the additive TMP less than 0.6 %. In this case additive raises flame speed. At concentration of the additive more than 0.6 % its



Fig.8. Comparison of the laminar flame speed found with different reaction mechanisms. Rate constants of the reactions  $H+PO_2+M=HOPO+M$  and  $H+HOPO=H_2+PO_2$  are the double (light circles).

introduction lowers flame speed. Thus, the reactions (4) and (5) are most effective. The modeling with rate constants of reactions (4) and (5), increased in 2 time, shows (Fig. 8) that the maximum of flame speed is displaced in area of smaller concentration of the additive, and inhibiting effectiveness of TMP begins to appear at its smaller concentration.

The calculations of rate of reaction (4) on a zone depending on concentration of the additive TMP have shown, that with increase of concentration of the additive the reaction rate grows and maximum rate is displaced in area of higher temperatures (Fig. 9).

Thus, with growth of concentration of the additive the rate of a chain branching (Fig. 2, 3) grows. The concentration H decreases, but the concentration OH increases. At the same time at concentration of the additive 0.1 - 0.5 % reaction of catalytic recombination of atoms and radicals (4), (5), (6), resulting in growth of a flame temperature (Fig.1) and speed (Fig. 7), plays a major role. The temperature reaches the maximal value at 0.5 % TMP. At the further increase of the additive ocncentration of more than 0.5 % temperature of a flame not only does not grow, but even decreases. As the rate of catalytic recombination results in increase of rate of chain termination (reactions (4) and (5)), the total rate of oxidation of hydrogen falls.

The originality of the phenomenon consists in that the reactions of catalytic recombinations are reactions of chain terminations. It would seem they always to reduce reaction rate and a flame speed. However, as a result of these reactions the rate of heat release increases at low pressures. And it results in increase of flame temperature (up to temperature at thermodynamic equilibrium) and as a consequence increases of a chain branching and growth of a flame speed. Reactions of non-catalytic recombinations are trimolecular ones and their rate at low pressures is very slow. As results maximal flame temperature much less than thermodynamic one.



Fig.9 Reaction rates of H+PO2+M->HOPO+M in a premixed  $H_2/O_2/Ar$  flames with TMP and without TMP.

In [20] is shown, that the similar effects of inhibition were observed in rich premixed laminar  $H_2/O_2/Ar$  flat flames doped with SO<sub>2</sub> at 100-150 torr. The reactions of catalytic recombination are similar in these two systems. However, the efficiency of inhibition by the additives OPC is higher, than that by additives SO<sub>2</sub>, since the rate constants of reactions such as  $H+PO_2+M \rightarrow HOPO+M$  are much higher than that of similar reaction such as  $H+SO_2+M \rightarrow HOSO+M$ .

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