Inhibition effect of OPC in hydrogen- and hydrocarbon-air flames

I.V. Rybitskaya[1,2], A.G.Shmakov[1], O.P.Korobeinichev[1,2],
[1]Institute of Chemical Kinetics & Combustion SB RAS, Novosibirsk, Russia
[2]Novosibirsk State University, Novosibirsk, Russia

Organophosphorus compounds (OPC) are known to be effective fire suppressants and are perspective candidates for replacement of halons forbidden for production by Montreal Protocol now because of their destroying influence on atmospheric ozone. At the same time OPC can serve as simulant of chemical warfare agents, such as sarin, soman, and also other toxic substances (pesticide, etc.) for improvement of their incineration technology. Despite of large quantity of theoretical and experimental works, many questions about inhibition mechanisms of flames doped with OPC still remain. One of the main goals is to develop a mechanism that is able to predict the characteristics of OPC-doped flames (chemical and thermal structure, burning velocity) in a wide range of equivalence ratio.

This study presents the results of theoretical investigation and modeling of burning velocity of premixed CH_4-Air and C_3H_8-Air flames in the range of equivalence ratio ϕ= 0.6-1.6 at atmospheric pressure without and with addition of 600 ppm of trimethylphosphate (TMP). The modeling of burning velocity of H_2-Air flame in range $0.7<\varphi<4.5$ without and with addition of 1000 ppm of TMP was also carried out.

The burning velocity of flame was measured by heat flux method [1, 2] that allow to stabilize flame on flat burner in near adiabatic conditions. The brass plate of burner 24 mm in diameter and 3 mm thick had orifices 0.5 mm in diameter located on distance 0.7 mm from each other. The temperature of burner plate and combustible mixture was supported by a thermostats at 60 ^oC and 35 ^oC respectively. TMP was introduced into a combustible mixtures using a saturator in the temperature-controlled bath.

PREMIX and CHEMKIN-II codes were used for simulation of burning velocity of flames. The mechanism for TMP destruction in a flame developed by Westbrook and mechanisms for hydrogen and hydrocarbons oxidation developed by Curran [3] were used for modeling. Also the mechanism GRI 3.0 [4] was used for CH_4/Air flame.

Comparison of burning velocity of CH_4- and C_3H_8-Air flames without additive determined in experiments and available from literature (obtained by the same heat flux method [5]) showed a good agreement. Comparison of experimental and modeling data both in flame without additive and in that doped with TMP showed a satisfactory agreement for C_3H_8-Air flame and some discrepancy for CH_4-Air flame. The modeling using mechanism GRI 3.0 for CH_4-Air flame provides the best agreement with experimental data for flame with $\phi\approx1$ whereas in lean and rich flames the best agreement provided mechanism [3].

The inhibition efficiency of C_3H_8-Air doped with TMP was determined as $F=(Uo-U)/Uo$, where Uo, U- burning velocity without and with additive respectively is shown in Fig. 1 A.

The modeling predicts an increasing of inhibition efficiency at φ up to 1.3 and its further decreasing in more rich flames. The experimental data have the similar tendencies of abrupt decreasing of the efficiency in rich flames, while in lean and near-stoichiometric flames the divergence with the data of modeling is observed: the experimental dependence of F from φ is weekly expressed. The observed discrepancies between experimental and modeling data are probably connected with imperfection both phosphorus and hydrocarbons combustion mechanisms.

The modeling of burning velocity of H_2/Air flame (at P=1 atm, T_0=298 K) without and doped with 1000 ppm of TMP showed opposite dependencies of inhibition efficiency (Fig.1 B). The inhibition efficiency of TMP in this flame have minimum at φ=1.4 and increased in lean and rich flames.

Figure 2 A and B shows the sensitivity coefficients of burning velocity to change of rate constants of the most important reactions for inhibition in C_3H_8-Air and H_2-Air flames respectively. The sensitivity coefficients were determined from expression $\xi=(U-U_{5A})/U\times100\%$, where U is the burning velocity at a specified rate constant by mechanism [3], U_{5A} is the burning velocity at rate constant increased by a factor of 5.

The difference in dependence of inhibition efficiency of TMP versus φ in C_3H_8-Air and H_2-Air flames connected with changing of reaction importance order, responsible for inhibition in these flames. The reaction 4.$HOPO+OH=PO_2+H_2O$ is most important at inhibition of rich C_3H_8-Air flame as the

dependence of the sensitivity coefficients of this reaction (Fig. 2 A) correlates with dependence of inhibition efficiency of TMP (Fig. 1 A). In rich H_2-Air flame at $\varphi>2.5$ the most important becomes reaction is 6.HOPO+H=H_2+PO_2 that in combination with other reactions causes growth of inhibition efficiency.

Thus in the present work the influence of the TMP additive on burning velocity of atmospheric C_3H_8-Air, CH_4-Air and H_2-Air in flames is investigated. It is shown that in hydrocarbons flames doped with TMP the character of dependence of inhibition efficiency versus equivalence ratio has a specific maximum, while in H_2-Air flame the dependence opposed. The explanation of observable effect is connected with change of the contribution of the most important reactions responsible for inhibition is offered.

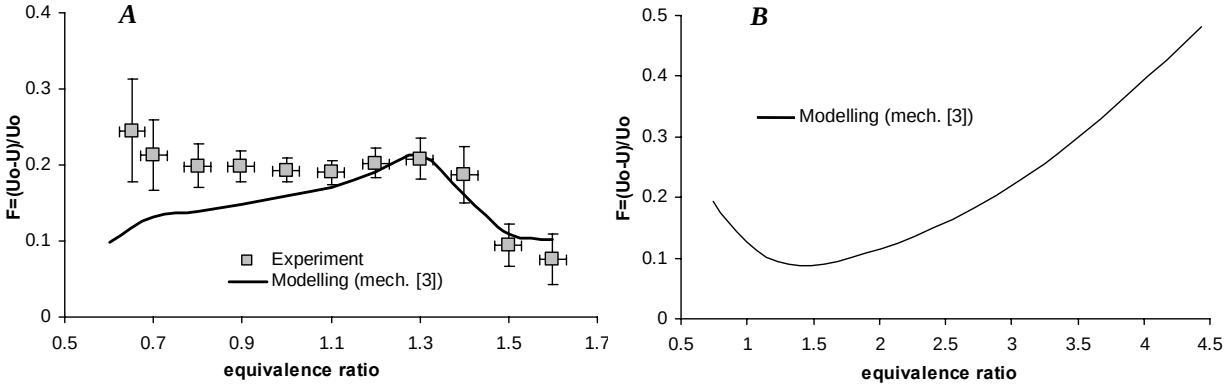

Figure 1. *Inhibition efficiencies of C_3H_8-Air (A) and H_2-Air (B) flames doped with TMP*

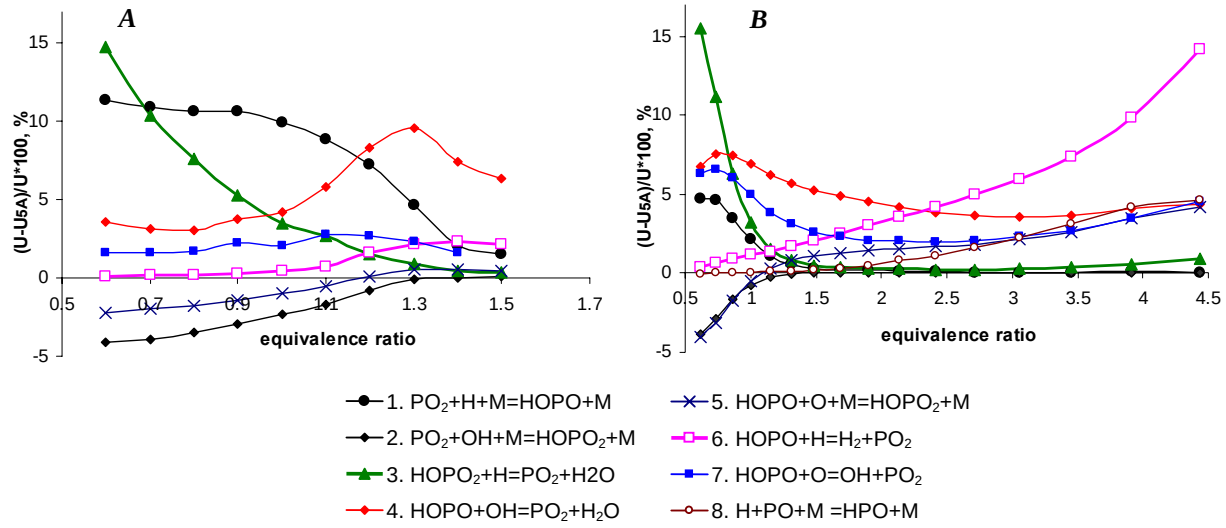

Figure 2. *Sensitivity coefficients of burning velocity to change of rate constants of reactions in C_3H_8-Air (A) and H_2-Air (B) flames.*

This work was supported by INTAS under grant 03-51-4724, Russian Science Support Foundation and Siberian Branch of Russian Academy of Sciences under grant for Young Scientists № 76.

References

1. De Goey, L.P.H., Van Maaren, A., Quax, R.M.. Stabilization of adiabatic premixed laminar flames on a flat flame burner // Combust. Sci. Technol. 1993. V. 92. P. 1-3.

2. Van Maaren, A., Thung, D.S., de Goey, L.P.H.. Measurement of flme temperature and adiabatic burning velocity of methane/air mixtures // Combust. Sci. and Tech. 1994. V. 96. P. 327-344.

3. Jayaweera, T.M., Melius, C.F., Pitz, W.J., Westbrook C.K.; Korobeinichev, O.P., Shvartsberg, V.M.,. Shmakov, A.G, Rybitskaya, I.V.; Curran, H. Flame inhibition by phosphorus-containing compounds over a range of equivalence ratios // Combustion and Flame. 2005. V. 140. P. 103-115.

4. G. P. Smith, D.M. Golden, M. Frenklach, N.W. Moriarty, B. Eiteneer, M. Goldenberg, C.T. Bowman, R.K. Hanson, S. Song, C. William, J. Gardiner, V.V. Lissianski, Z. Qin, GRI Mech 3.0. 1999. Available from: http://www.me.berkeley.edu/gri_mech/.

5. Bosschaart, K.J., de Goey, L.P.H., Burgers, J.M. The laminar burning velocity of flames propagation in mixtures of hydrocarbons and air measured with the heat flux method // Combustion and Flame. 2004. V. 136. N. 3 . P. 261-269.