INFLUENCE OF PHOSPHORUS-CONTAINING ADDITIVES ON METHANE FLAME

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Comparison of relative inhibitor efficiencies in terms of the reduction in burning velocities or extinction strain rates [1-4] demonstrates that phosphorus containing compounds may have efficiencies 3-8 times higher than CF_3Br (Halon 1301). Phosphorus additives are used as retardants in fire-resistant polymers and fire suppressants (e.g., dihydrogen ammonium phosphate). Due to the need for replacing currently used Halon 1301, studies of the fire suppression efficiency of phosphorus compounds and the mechanism for its action are of interest.

In this work we report on results of numerical studies on the inhibition of methane flames by phosphorus-containing additives (DMMP, TEP). The dependencies of burning velocity on inhibitor concentration and additive decomposition rate have been analyzed and the influence of flame temperature on inhibition efficiency is considered.

Experimental Data on the Influence of Phosphorus Compounds on Flame Propagation. There are considerable experimental results on the influence of the addition of phosphorus compounds on burning velocity, suppression concentrations of compounds (cup burner tests), influence of additives on an extinction strain rate for opposed diffusion flames and the results of streaming laboratory tests. The phosphorus compounds studied include $POCl_3$, $PSCl_3$, $PSBr_3$, PCl_3, PBr_3, TMP, DMMP, triphenylphosphine, monoammonium phosphate, diammonium phosphate, $P_3N_3F_6$, $P_3N_3ClF_5$, $P_3N_3Cl_2F_4$, $P_3N_3(OCH_3)_6$ and fluroalkoxyphosphazenes.

Experimental data can be divided on the basis of inhibitor loading. At the lowest loadings comparisons can be made on the basis of burning velocity reductions. This can be considered the maximum chemical effect of the suppressants. With increasing additive concentrations, the contributions of heat capacity and dilution increase. At the same time, the chemical influence of the additive decreases (saturation effect, [5]) due to the lowering of chain carrier concentration down to equilibrium level.

Analysis of scattered data on the burning velocity of inhibited hydrocarbon flames (methane, hexane, n-heptane, hydrogen) using a procedure described earlier[3] shows that it is possible to separate studied compounds according inhibitor efficiency into two groups: 1) $PSBr_3$, PBr_3, $PSCl_3$, PCl_3, $POCl_3$ which have inhibition efficiencies higher than CF3Br 6-7 times more, and 2) $OPCH_3(OCH_3)_2$ (DMMP), $(CH_3)_3PO_4$ (TMP) and $(C_2H_5O)_3PO$ (TEP) which have a coefficient of efficiency relative to CF_3Br of 3-4. The scattered data on suppression concentrations of phosphorus compounds are however not in agreement with these results. It is possible to expect that extinction concentrations are in the range 0.5-5% by volume.

Calculational procedure and kinetic model. The modeling results described were derived from the CHEMKIN suite of programs. Compiled kinetic model is based on the data suggested for the analysis of the influence of PH_3 products on the recombination of hydrogen atoms in products of hydrogen flame [6], and kinetic models [7,8] used for describing destruction of DMMP and TMP in low pressure hydrogen flames. Reactions of simple P-containing species with radicals and some intermediate species of methane system to reflect methane combustion have been included. It has been assumed that P-species are non-reactive to the stable hydrocarbon species. There exist some indications on low reactivity of phosphorus-containing species. Some reactions have been added to the scheme to complete the reaction pathways for the consumption of some of the species. The model has been adjusted to take into account recent data for P-species.

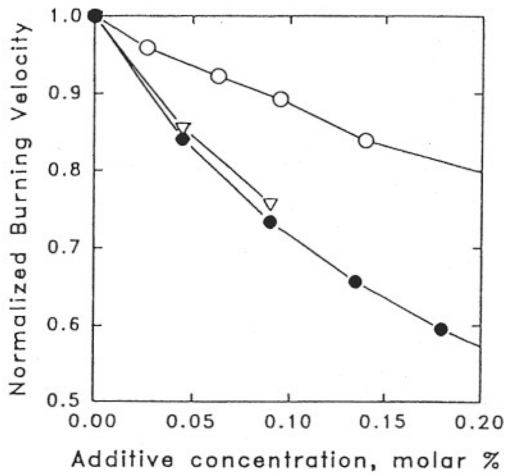

Fig.1 Burning velocity dependence on inhibitor concentration (stoichiometric air/methane flame, 1 atm). Open circles - DMMP additive, rate constants of [6]; closed circles - DMMP, modified model; triangles - TEP additive.

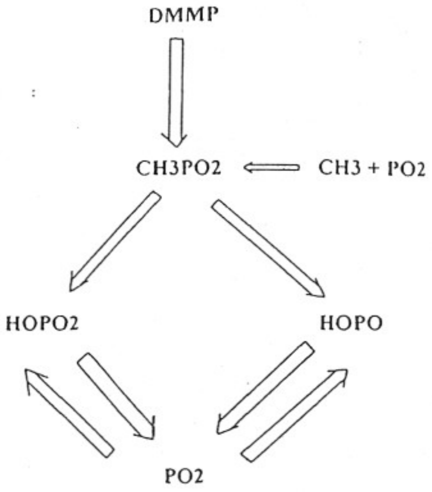

Fig.2 The abbreviated inhibition cycle of DMMP influence.

Thermochemical data are mostly from [9,10,11,6]. For the modeling of the TEP influence the overall decomposition kinetics has been used [12].

Additive influence on burning velocity. Inhibition mechanism. Fig. 1 contains calculated burning velocities as a function of the concentration of DMMP and TEP. These results show that application of original rate constants in the model of Twarowski[6] leads to efficiencies of DMMP relative to CF_3Br that are about a factor of 1.5 larger. Following the decomposition of DMMP in the flame zone the main P-containing species are PO_2, HOPO and $HOPO_2$. Sensitivity and reaction pathway analysis show two main inhibition cycles with PO_2 (Fig.2) leading to decreases in concentrations of radicals:

1) $H + PO_2 + M = HOPO + M$
$OH + HOPO = H_2O + PO_2$
$H + HOPO = H_2 + PO_2$
$O + HOPO = PO_2 + OH$

2) $OH + PO_2 + M = HOPO_2 + M$
$H + HOPO_2 = H_2O + PO_2$

Analysis of the influence of rates of different reactions shows that reasonable adjustment of the rate constants of addition reactions $H + PO_2 + M = HOPO + M$ and $OH + PO_2 + M = HOPO_2 + M$ leads to approximate agreement with experimental data on the efficiency of DMMP and TEP relative to CF_3Br.

Influence of decomposition rate on inhibition efficiency. It is known that phosphorus compounds have a wide range of thermal stability. Overall activation energies of decomposition are in the range, 15 - 90 kcal/mol. The influence of the decomposition rate has been studied using global kinetics for decomposition to PO_2 or to HOPO through varying the activation energy of decomposition. Fig.3 demonstrates that, for an assumed kinetic model and using experimental initial conditions, activation energies less than 60 kcal/mol show no effect on the burning velocity. Further increase in the activation energy leads to decrease of inhibitor efficiency. At approximately 90-100 kcal/mole the influence of additive disappears. For values in the 20-30 kcal/mol range the inhibitor decomposes in the low temperature region of the flame zone or before 1000 K is achieved. For 80 kcal/mol, the degree of decomposition at the position of maximum H-atom concentration constitutes 60-70%.

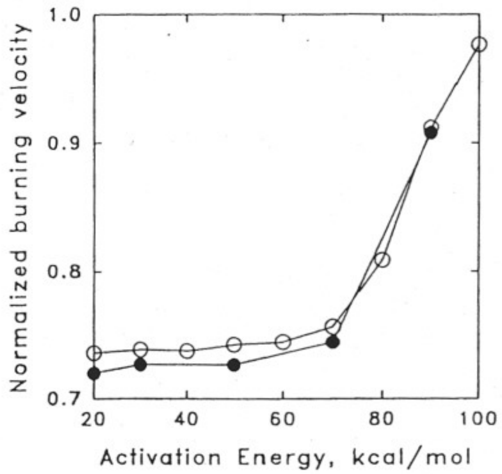

Fig.3 Dependence of burning velocity on the decomposition rate. Closed circles - HOPO product; open circles - PO_2 product (stoichiometric air/methane flame, 1 atm, DMMP 0.09%).

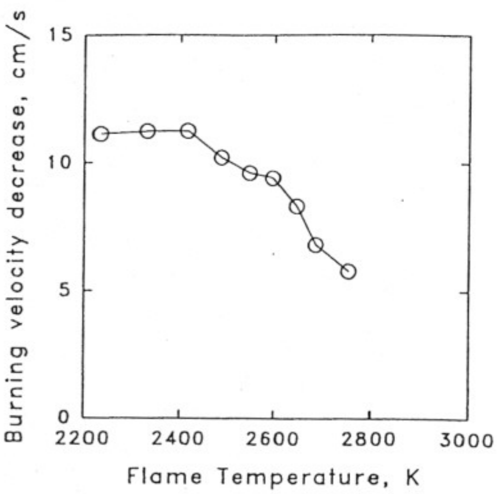

Fig.4 Dependence of decrease of burning velocity on flame temperature. Stoichiometric methane/air flame, 0.09% DMMP.

Influence of flame temperature. In earlier works [13,14,15] the possible promotion effect of phosphorus compounds has been discussed. According to Hastie and Bonnell [13], the increase of flame temperature may lead to decrease of inhibitor efficiency. The estimated crossover flame temperature point is near 2350 K. Numerical calculations do not show any promotion effect of DMMP in the temperature range 2100-2900K. Fig.4 contains the dependence of burning velocity decrease on flame temperature. For these calculations, the decrease of nitrogen content in mixture 2yO2+xN2+yCH4+0.09%DMMP is used to provide the increase in the flame temperature. It can be seen that flame temperatures higher than 2500 K are required before inhibitor influence is lessened. In fact, the crossover point, where promotion becomes dominating, was not observed until 3000K. The decrease of the inhibitor effect is mostly due to the relative increase of rates of formation of species in the radical pool in comparison with recombination rates of P-species with chain carriers.

Saturation of inhibition effect. Calculations have been carried out across the entire range of additive loadings or until the level of suppression. These are all based on a gas phase model without taking into account the condensation processes. The modeling results show "strong" saturation effect with the increase of the inhibitor concentration, e.g., decrease of burning velocity down to 10cm/s requires loading less than 0.9 %; an additional 1.4 % of DMMP is needed to decrease burning velocity from 10 cm/s down to the extinction level. Such strong saturation effect leads to a substantial increase in extinction concentration (2.3%) and to a decrease of inhibitor efficiency relative to CF_3Br.

Additionally, Table 1 contains extinction concentrations for iron pentacarbonyl (gas phase model) and for a perfect inhibitor [16], showing the possible minimum level of inhibitor concentration required for flame extinction. The analysis of saturation effect strongly supports the use of composite inhibitors [5].

Table 1.

DMMP	CF_3Br	$Fe(CO)_5$ *	Perfect inhibitor **
2.3	3.5	0.3 - 0.5	0.05

* Calculated values depend on assumed rate constants.

** Rate constants of an inhibition cycle are 5.E13 cm3/(mol s).

Summary. A first cut kinetic model for inhibition by phosphorus compounds on methane flames has been developed. The main contribution to inhibition effect is due to reactions with simple P-containing species: PO_2, HOPO, $HOPO_2$. The important reactions of the inhibition cycle appear to involve reactions of species HOPO<=>PO_2<=>$HOPO_2$ and their scavenging reactions with the chain carriers. To obtain the agreement with experimental data on relative inhibition efficiency in comparison with CF_3Br, the increase of the rates of PO_2 radical recombination reactions in 5-10 times is required. For studied initial conditions (stoichiometric methane mixture) the decomposition processes of phosphorus compounds do not show influence until the level of overall activation energy reaches 60 kcal/mol. The calculations do not demonstrate the possible promotion effect of DMMP on methane flame for the flame temperature range 2200-2900K. Calculations for additive level of flame suppression concentrations demonstrate the strong saturation effect.

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