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Influence of hydrocarbon moiety of DMMP on flame propagation in lean mixtures☆

V.I. Babushok[a,*], G.T. Linteris[a], V.R. Katta[b], F. Takahashi[c]

[a] National Institute of Standards and Technology, Gaithersburg, MD, United States
[b] Innovative Scientific Solutions, Inc., Dayton, OH, United States
[c] Case Western Reserve University, Cleveland, OH, United States

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ABSTRACT

Phosphorus-containing compounds (PCCs) have been found to be significantly more effective than CF_3Br for reducing burning velocity when added to stoichiometric hydrocarbon-air flames. However, when added to lean flames, DMMP (dimethylmethylphosphonate) is predicted to increase the burning velocity. The addition of DMMP to lean mixtures apparently increases the equivalence ratio (fuel/oxidizer) and the combustion temperature, as a result of hydrocarbon content of DMMP molecule. Premixed flames studies with added DMMP, $OP(OH)_3$, and CF_3Br are used to understand the different behavior with varying equivalence ratio and agent loading. Decrease of the equivalence ratio leads to the decrease of inhibition effectiveness of PCCs relative to bromine-containing compounds. For very lean mixtures CF_3Br becomes more effective inhibitor than PCCs. Calculations of laminar burning velocities for pure DMMP/air mixtures predict the maximum burning velocity of 10.5 cm/s at 4.04% of DMMP in air and at an initial temperature of 400 K. Adiabatic combustion temperature is 2155 K at these conditions.

1. Introduction

Phosphorus-containing compounds (PCCs) are highly effective flame inhibitors and they are used as fire suppressant compounds as well as fire retardants which are added to polymers to reduce their flammability. PCCs have been considered as possible replacement compounds for Halon 1301 (CF_3Br) [1–3]. DMMP (dimethylmethylphosphonate, $OP(CH_3)(OCH_3)_2$) is used as a flame retardant for polyurethane foam, polyurethane resin, epoxy resin and other plastic materials, and it was also considered as an effective fire retardant additive to lithium electrolyte batteries [4]. Because of its effectiveness, low toxicity, and convenient vapor pressure, DMMP is often used as a model compound for studies of the inhibition effectiveness and kinetic mechanism of PCCs. Detailed kinetic models for hydrocarbon–air flame inhibition by DMMP have been developed [5–8] and the inhibition mechanism has been investigated and validated through experiments and numerical modeling [5–11].

The DMMP molecule has a rather large hydrocarbon component. Thus, the fuel moiety of DMMP might decrease its inhibition effectiveness for lean mixtures, as has been observed for other inhibitors with significant hydrocarbon components [12,13]. Also, it is possible that DMMP itself, in mixtures with air, is flammable and has measurable burning velocity. While some of the most effective flame inhibitors (e.g., iron pentacarbonyl [14], methylcyclopentadienyl manganese tricarbonyl [15]) are flammable, they are usually added at trace concentrations, at which their hydrocarbon component does not significantly affect the inhibition process. Since rather high concentrations of DMMP are required to extinguish coflow diffusion flames, it is of value to examine the performance of DMMP at those high concentrations, explore the importance of fuel contributions of the hydrocarbon component of DMMP at those conditions, and compare these features with those of other inhibitors which do not have the same fuel component, or do not contain phosphorus (e.g., $OP(OH)_3$ and CF_3Br).

The approach in the present work is to study the inhibition features of DMMP in lean and very lean methane/air mixtures close to the flammability limits, where the contribution of the hydrocarbon part of the DMMP molecule to the flame propagation is most important. To this end we analyze the effect of DMMP on the laminar burning velocity in lean and stoichiometric methane/air mixtures as a function of fire suppressant agent concentration and initial flame equivalence ratio. For comparison, we also analyze the

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* Corresponding author.
E-mail address: vbabushok@nist.gov, vbabushok@hotmail.com (V.I. Babushok).

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influence of $OP(OH)_3$ (phosphoric acid, H_3PO_4) and CF_3Br. The former is a product/intermediate species of phosphorus containing compounds in flames, and the latter is a typical flame inhibitor often used as a benchmark compound. Finally, we analyze the combustion properties of mixtures of pure DMMP in air.

2. Kinetic model and calculation procedure

Modeling studies were conducted for methane-air flames inhibited by DMMP, H_3PO_4 and CF_3Br. The hydrocarbon mechanism employed is GRI-mech 3.0 [16], and that for the reactions of the DMMP in hydrocarbon flames is from Jayaweera et al. [5]. Three additional reactions were added to the phosphorus part of mechanism: PO+HCO=HPO+CO −222 kJ/mol, PO_2+HCO=HOPO+CO −255 kJ/mol and PO_3+HCO=$HOPO_2$+CO −406 kJl/mol. Rate constants were assumed to be the same as the overall rate constant for reaction NO_2+HCO=products [17]. Calculations demonstrate that the effect of these reactions is small: changes in burning velocities were less than 1% (in contrast to bromine or iodine systems, in which the reaction Br+HCO=CO+HBr has a noticeable effect on burning velocity). The variation of the rate constants by more than an order of magnitude demonstrates the lack of sensitivity of the results to these rate constants. For the flame inhibition by CF_3Br, the relevant reactions of bromine-and fluorine-species from a $C_3H_2F_3Br$ flame-inhibition model was employed [12]. The Chemkin set of programs of Sandia Laboratory was used for combustion equilibrium calculations and for modeling laminar premix flames.

The kinetic models for flame inhibition by DMMP (and other PCCs) have been validated in other work [5–7,9]. In the present work, we made additional comparisons of the predicted burning velocity with experimental data for TMP [18] and H_3PO_4 [19], and found a reasonable agreement.

3. Results and discussion

For each of the additives, DMMP, CF_3Br and $OP(OH)_3$, burning velocity calculations were performed for a range or equivalence ratios ϕ, and for initial temperature 373 K. Figure 1 shows the calculated burning velocity of methane/air flames at the indicated initial stoichiometry, as a function of the agent volume fraction X_a in the mixture. The top frame shows stoichiometric flames, and the bottom frame, lean flames. Note that the equivalence ratio refers to that of the methane-air mixture prior to addition of the flame inhibitor. Two general features of the results in Fig. 1 are discussed below: (1) the apparent promotion effect of DMMP when added to lean flames; and (2) the switching in the ranking of effectiveness between CF_3Br and $OP(OH)_3$ with stoichiometry.

As indicated in Fig. 1, for stoichiometric mixtures (upper frame) with agents added at volume fractions less than about 0.002 volume fraction, both DMMP and $OP(OH)_3$ are about six times more effective than CF_3Br. However, the phosphorus compounds experience the reduction in marginal effectiveness with increased volume fraction more severely than does CF_3Br. Moreover, for the initially lean mixtures (lower frame), the effectiveness of DMMP decreases severely with decrease in ϕ, and for lean enough conditions, adding DMMP can actually increase rather than decrease the burning velocity. This result has been observed for other flame inhibitors that also have a hydrocarbon component (for example, $C_3H_2F_3Br$ [12], $C_6F_{12}O$ [20], and C_2HF_5 [12], and has been attributed to the effect of the increase in flame temperature caused by agent-supplied fuel species addition. For example, Fig. 2 shows the adiabatic flame temperature T_{ad} of methane/air mixtures of different initial equivalence ratios, as a function of the DMMP volume fractions. As indicated, DMMP addition increases T_{ad} by up to 800 K, to values nearly the same as the stoichiometric methane-air

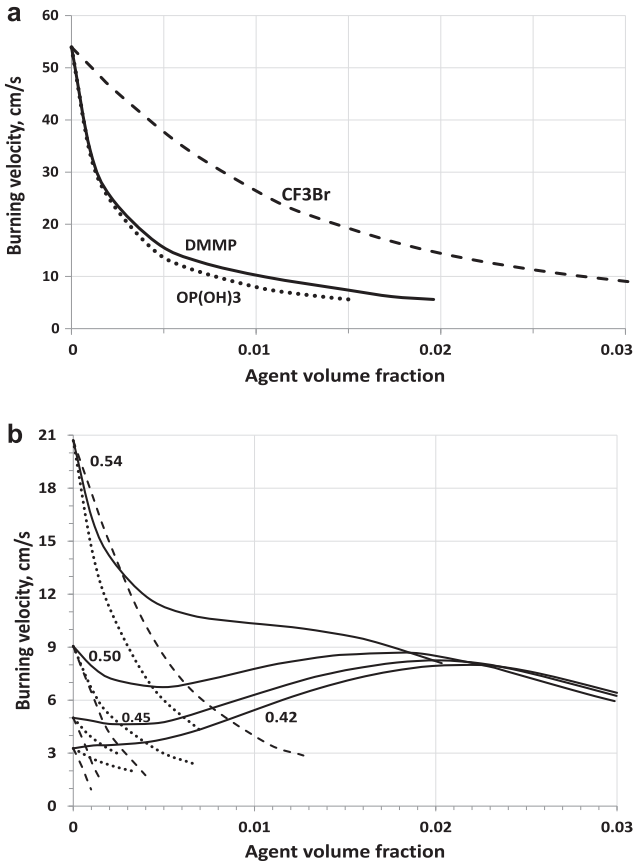

Fig. 1. Laminar burning velocity dependence as a function of inhibitor volume fraction at different equivalence ratios (a – stoichiometric CH_4/air mixture; b- lean mixtures; initial temperature – 373 K; solid line – DMMP; dotted line – $OP(OH)_3$; dashed line – CF_3Br).

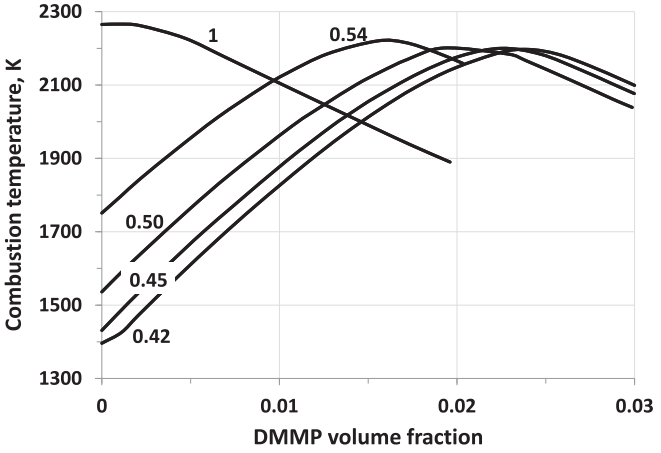

Fig. 2. Dependence of the adiabatic combustion temperature on the DMMP concentration at different equivalence ratios (CH_4/air mixture, initial temperature 373 K).

system itself, whereas $OP(OH)_3$ or CF_3Br addition to lean mixtures does not increase T_{ad}.

To demonstrate additionally the fuel effect, we can re-plot Fig. 2 using the "overall" equivalence ratio as the X-axis instead DMMP concentration taking into account the fuel properties of DMMP. It was assumed that the main combustion products of DMMP are $HOPO_2$ (or $OP(OH)_3$), CO_2 and H_2O. Figure 3 contains the same data as Fig. 2 using the overall equivalence ratio as abscissa. It shows that the mixture of methane and DMMP demonstrates the maximum adiabatic temperature close to the overall