SIMULATIONS OF GAS-PHASE INTERACTIONS OF PHOSPHORUS FLAME RETARDANTS WITH DIFFUSION FLAME STRUCTURE

<u>Fumiaki Takahashi</u>¹, Viswanath R. Katta², Gregory T. Linteris³ & Valeri I. Babushok³ ¹Case Western Reserve University, USA; ²Innovative Scientific Solutions, Inc., USA; ³National Institute of Standards and Technology, USA

ABSTRACT

The interaction of the gas-phase mechanisms of phosphorus flame retardants with the co-flow diffusion flame structure has been investigated computationally to complement the experimental research at NIST. Time-dependent axisymmetric computation was performed for cup-burner flames of methane with full gas-phase chemistry and transport to reveal the flame structure and inhibition processes. For the simulation of the effects of dimethyl methylphosphonate (DMMP) on the flames, a detailed chemical-kinetics model (77 species and 886 reactions) was constructed by combining the methane-oxygen combustion and phosphorus inhibition chemistry. A simple model for radiation from CH₄, CO, CO₂, H₂O, and soot based on the optically thin-media assumption was incorporated into the energy equation. The calculated minimum extinguishing concentrations for a combination of DMMP added to the oxidizer or fuel flow and CO_2 added to the oxidizer were in reasonable agreement with the measured values. There were striking differences in the effectiveness of DMMP, depending on where the retardant was introduced: the oxidizer or fuel. DMMP in the fuel stream (in comparison to the oxidizer) was practically ineffective in gas-phase inhibition of co-flow diffusion flames because of (1) a small stoichiometric mixture fraction (0.055 for methane), (2) the flame location on the oxidizer side of the dividing streamline, and (3) low concentrations of active phosphorus intermediate species $(HOPO_2, HOPO, PO_2)$ in the flame stabilizing region.

INTRODUCTION

Fire retardants (FRs) are used in polymers, textiles, and coatings to increase their ignition time and reduce their heat release rates when burning. The FRs are often classified as acting either in the condensed-phase or in the gas phase ¹⁻³. Gas-phase active FRs have the advantage of working for a variety of polymers, and are very widely used. The most common gas-phase active FR formulations are those containing bromine compounds, with antimony trioxide usually added as a synergist. Due to environmental and health concerns, however, there is impending movement, on the part of polymer companies and fire retardant manufactures, away from the bromine-based fire retardants. To maintain fire safety, alternatives to these compounds must be developed so that elimination of these fire retardants would not increase the contribution of polymers to fires. The chemical systems of highest interest to industry, and the subject of the most intense recent investigations, are those containing phosphorus ^{4,5}.

A model for the gas-phase kinetics of phosphorus compounds has been developed ⁶⁻¹¹ over the years. The basic gas-phase inhibition mechanism is believed to be dominated by two main radical recombination cycles:

$H + PO_2 + M \rightarrow HOPO + M$	[1]
$OH + HOPO \rightarrow H_2O + PO_2$	[2]
$H + HOPO \rightarrow H_2 + PO_2$	[3]

 $O + HOPO \rightarrow OH + PO_2$ [4]

Net:
$$H + H \rightarrow H_2$$
 [5]

$$H + O \rightarrow OH$$

$$H + OH \rightarrow H_2O$$
[6]
[7]

and

$$\begin{array}{l} OH + PO_2 + M \rightarrow HOPO_2 + M \\ H + HOPO_2 \rightarrow H_2O + PO_2 \end{array}$$

$$[8]$$

$$[9]$$

Net:
$$H + OH \rightarrow H_2O$$
 [10]

This mechanism has been used ¹²⁻¹⁶ to model the inhibition of premixed and counterflow diffusion flames with reasonable results. Nonetheless, no researchers have modeled or extensively studied co-flow diffusion flames, for which poor performance has been observed ¹⁷.

The effectiveness of compounds in gaseous flame inhibition is quite complex, depending upon the additive type as well as flame properties. Different inhibitors can be more or less effective depending upon the flame type. Dimethyl methylphosphonate (DMMP) is about 141 times as effective as CO_2 in a premixed flame ¹⁷, 30 times as effective in a counter-flow diffusion flame ¹⁸ but only 3 times as effective in a cup-burner flame ¹⁹ (i.e., the phosphorus essentially has no chemical effect in cup-burner flames). For phosphorus, this large variation in effectiveness with flame type has not been explained. Since phosphorous is and will be used as a gas-phase active FR, it would be of great value to understand the conditions for which it is expected to work.

The effects of DMMP in methane-air co-flow diffusion flames, in the cup-burner configuration, have recently been investigated experimentally²⁰ at the National Institute of Standards and Technology (NIST). The inhibitor effectiveness was measured as the minimum extinguishing concentrations (MECs) of CO_2 (added to the oxidizer) as a function of the DMMP loading (added to the oxidizer or fuel stream), in a similar manner as reported²¹ in the literature for n-heptane flames. The particle formation in the flame with added DMMP was studied using the laser scattering technique. In addition, premixed flame simulations were used to examine the flame chemistry at the measured extinguishing conditions²⁰.

By using comprehensive numerical simulations, the authors ^{22,23} have studied the flame structure and inhibition (or combustion enhancement) processes in the cup-burner flames. The properties of the flame itself profoundly affect the effectiveness of the chemical additive, and are themselves changed by the additive, which further changes the additive effectiveness. The overall goal of the present work is to understand how the properties of flames interact with the gas-phase inhibition in support of the experimental research at NIST. The knowledge of detailed flame structure (temperature, species concentration, flow field, etc.) that affects fire retardant effectiveness will help to understand the reasons for the variation of effectiveness for phosphorus with flame type when added as a gas-phase active fire retardant and to shed light on how fire retardants which act in the gas phase actually retard ignition or reduce heat release. Ultimately, this work aims to aid in the development and application of new compounds that are likely to be used in flame-retarded high-volume thermoplastics to replace the widely used brominated retardants (and their antimony synergist).

COMPUTATIONAL METHODS

A time-dependent, axisymmetric numerical code (UNICORN)^{24,25} is used for the simulation of diffusion flames stabilized on the cup burner. The code solves the axial and radial (z and r) full

Navier-Stokes momentum equations, continuity equation, and enthalpy- and species-conservation equations on a staggered-grid system. A clustered mesh system is employed to trace the gradients in flow variables near the flame surface. The thermo-physical properties such as enthalpy, viscosity, thermal conductivity, and binary molecular diffusion of all of the species are calculated from the polynomial curve fits developed for the temperature range 300 K to 5000 K. Mixture viscosity and thermal conductivity are then estimated using the Wilke and Kee expressions, respectively. Molecular diffusion is assumed to be of the binary-diffusion type, and the diffusion velocity of a species is calculated using Fick's law and the effective-diffusion coefficient of that species in the mixture. A simple radiation model based on the optically thin-media assumption is incorporated into the energy equation. Radiation from CH_4 , CO, CO_2 , H_2O and soot is considered in the present study.

A comprehensive reaction mechanism (77 species and 886 elementary reactions) is assembled and integrated into the UNICORN code for the simulation of methane flames with DMMP added to either the fuel or air stream. A chemical-kinetics model is compiled from a detailed reaction mechanism of GRI-V3.0²⁶ for methane-oxygen combustion and a phosphorus mechanism ²⁷ (41 additional species and 448 reactions).

The finite-difference forms of the momentum equations are obtained using an implicit QUICKEST scheme²², and those of the species and energy equations are obtained using a hybrid scheme of upwind and central differencing. At every time-step, the pressure field is accurately calculated by solving all the pressure Poisson equations simultaneously and using the LU (Lower and Upper diagonal) matrix-decomposition technique.

Unsteady axisymmetric calculations for the cup-burner flames are made on a physical domain of 120 mm by 47.5 mm using a 301×151 non-uniform grid system that yields 0.2 mm by 0.15 mm minimum grid spacing in the z and r directions, respectively, in the flame zone. The computational domain is bounded by the axis of symmetry and a chimney wall boundary in the radial direction and by the inflow and outflow boundaries in the axial direction. The outflow boundary in z direction is located sufficiently far from the burner exit (~9 fuel-cup radii) such that propagation of boundary-induced disturbances into the region of interest is minimal. Flat velocity profiles are imposed at the fuel and air inflow boundaries, while an extrapolation procedure with weighted zero- and first-order terms is used to estimate the flow variables at the outflow boundary. The cup burner outer diameter is 28 mm and the chimney inner diameter is 95 mm. The burner wall (1-mm long and 1-mm thick tube) temperature is set at 600 K, and the wall surface is under the no-slip velocity condition. The mean gas velocities and temperature are set at 1.24 cm/s and 15.5 cm/s, respectively, for the fuel (methane) and oxidizer streams and 374 K. The low fuel velocity represents low momentum conditions typical of condensed material fires. The air velocity is in the middle of the so-called "plateau region"²², where the extinguishing agent concentration is independent of the oxidizer velocity.

Validation of the UNICORN code has been performed for a variety of flame systems, fuels, and inhibitors with the kinetic model used. The predicted global strain rates at extinction of methane-air opposing-jet flames at the reactant temperature of 100 °C are 380 s⁻¹ without the inhibitor, which is close to the measured value $(360 \text{ s}^{-1})^{17}$, and those with DMMP added to the flames with different stretch rates are within a range of 10 % of the experiments.

RESULTS AND DISCUSSION

Minimum Extinguishing Concentrations (MECs)

First, stable flames with DMMP were calculated by increasing incrementally (starting at 0) the loading of DMMP in the oxidizer or fuel stream. Then, the flame extinguishing conditions were determined by increasing the CO₂ volume fraction (X_{CO2}) in the oxidizer (starting at 0; in increments of < 1 % of X_{CO2} as the limit approached) until the flame blew off. The process was repeated at different DMMP loadings. Figure 1 shows the calculated and measured²⁰ inhibitor effectiveness expressed as the MECs of CO₂ added to the oxidizer as a function of the DMMP loading: (a) added



Figure 1. Minimum extinguishing concentrations of agents in methane cup-burner flames: (a) both CO_2 and DMMP added to the oxidizer and (b) CO_2 added to the oxidizer and DMMP to the fuel stream.

to the oxidizer or (b) fuel stream. The calculated MEC without DMMP was $X_{CO2} = 0.1985$, which was in reasonable agreement (≈ 7 %) with the measurement (0.185 at 100 °C) ²⁰. With an addition of DMMP to the oxidizer (Fig. 1a) at very low volume fractions ($X_{DMMP-O} < 0.003$), both measured and calculated MECs of CO₂ decreased rapidly as a result of efficient chemical inhibition. The calculated MEC of CO₂ became significantly larger than the measured value, probably because of particle formation just outside the actual flames with DMMP ²⁰. Since the calculation did not take into account particle formation, the actual flame temperature could be much lower than the calculation due to the radiative heat loss from the high-temperature particles, thus requiring much lower X_{CO2} at

extinguishment. As the DMMP volume fraction was increased further, the rate of decrease (slope) of the MEC curves decreased, particularly for the experiment, and thus the two curves crossed at $X_{\text{DMMP-O}} = 0.012$.

In the experiment²⁰, the marginal effectiveness of the DMMP diminished, and for $X_{\text{DMMP-O}} > 0.07$, the additional DMMP was essentially ineffective. The behavior for DMMP was very similar to that observed for metallic compounds added to cup-burner flames²⁸. The loss of effectiveness for the metals was believed to be due to particle formation (which acted as a sink for the active gas-phase intermediate species that catalytically recombined radicals²⁹). Premixed flame structure calculations²⁰ implied that DMMP addition reduced the concentrations of the chain-carrier radicals (H, O, and OH) to the equilibrium levels so that additional DMMP had little effect on the flame.

The inhibitor effectiveness of DMMP was reduced markedly when added to the fuel stream (Fig. 1b). As the DMMP volume fraction was increased to $X_{\text{DMMP-F}} = 0.04$, the calculated MEC of CO₂ decreased gradually from $X_{\text{CO2}} = 0.1985$ to 0.175 (only ≈ 12 % reduction). In the experiment, the MEC of CO₂ decreased from 0.185 to ≈ 0.15 (at $X_{\text{DMMP-F}} = 0$ to 0.01) and remained nearly constant (i.e., ineffective) for $X_{\text{DMMP-F}} > 0.01$. The calculated MEC of CO₂ for $X_{\text{DMMP-F}} > 0.01$ was ≈ 20 % larger than the measured value, presumably due to the afore-mentioned radiative cooling by particles.

Interaction of DMMP in Oxidizer with Flame Structure

The numerical simulations reported previously^{30,31} show that the flame-base region supported a trailing flame and controlled the flame attachment, detachment, and oscillation processes. Small variations in the agent volume fraction in the coflowing oxidizing stream resulted in profound changes near the extinguishment limit. The calculated inner structure of the flame base region provided detailed physical and chemical insights into the flame stabilizing mechanism and inhibition processes.

Figure 2 shows the calculated structure of an agent-free methane flame in air (Fig. 2a) and a near-limit flame in air with CO₂ at $X_{CO2} = 0.1965$ (Fig. 2b). The variables include the velocity vectors (ν), isotherms (*T*), and heat-release rate (\dot{q}). The base of the agent-free flame (Fig. 2a) was anchored at the burner rim at the height from the burner rim, $z_k = 0.8$ mm. The velocity vectors showed the longitudinal acceleration in the hot zone due to buoyancy. As a result of the continuity of the fluid, surrounding air was entrained into the lower part of the flame. The entrainment flow inclined inwardly as a result of the overall stream-tube (streamline spacing) shrinkage due to the significantly low velocity of the fuel compared to that of the oxidizer as well as the flow acceleration downstream. The heat-release rate contours showed a peak reactivity spot (i.e., the reaction kernel³⁰) at the flame base, where the chain-carrier radicals (H, O, and OH), as well as heat, diffused back against the oxygen-rich incoming buoyancy-induced flow, thus promoting chain-branching (H + O₂ \rightarrow OH + O) and subsequent vigorous reactions to form the reaction kernel. For the near-limit flame (Fig. 1b), the flame base detached and lifted above the burner rim ($z_k = 4.6$ mm) in the nearly horizontal entrainment flow. The maximum temperature in the trailing flame decreased to ≈ 1700 K, which was found ²² to be the critical temperature at which the blow-off extinguishment occurred for chemically passive fire-extinguishing agents (CO₂, N₂, He, Ar).

Figure 3 shows the calculated structure of a methane flame in air with DMMP at $X_{\text{DMMP-O}} = 0.012$ (Fig. 3a) and a near-limit flame in air with DMMP at $X_{\text{DMMP-O}} = 0.012$ and CO₂ at $X_{\text{CO2}} = 0.034$ (Fig. 3b). As DMMP was added (Fig. 3a), the maximum flame temperature increased, compared to the neat flame (Fig. 2a), and the broadened reaction kernel moved up from the burner rim (at $z_k = 3.2 \text{ mm}$), although it was still thermally interacting with the burner rim. The heat-release rate contour showed a weak branch on the oxidizer side extending downstream from the reaction kernel. This feature was similar to the two-zone flame structure for halon replacement fire-extinguishing agents with fuel components, as found previously²³. As CO₂ was added in addition to DMMP (Fig. 3b), the flame lifted ($z_k = 5.0 \text{ mm}$) and disconnected thermally from the burner rim. As a result of



Figure 2. Calculated structure of methane cup-burner flames in air: (a) no agent, (b) CO₂ added to the oxidizer at $X_{CO2} = 0.1965$.

mixing of the fuel and oxidizer streams, the reaction kernel broadened further laterally, and the twozone flame structure became more evident.

Figure 4 shows the maximum temperature in the trailing diffusion flame and the peak heat-release rate at the reaction kernel in the flame with pure DMMP or pure CO₂ in the oxidizer. As CO₂ was added to the oxidizer, the maximum temperature decreased linearly to $T_{\text{max}} \approx 1700$ K when the flame blew off at $X_{\text{CO2}} = 0.1985$. By contrast, as DMMP was added to the oxidizer even at an order-of-magnitude lower volume fraction, T_{max} increased due to combustion enhancement by additional heat release, and the flame was still stable at $X_{\text{DMMP-O}} = 0.013$. Nonetheless, as DMMP or CO₂ was added to the oxidizer, the reaction kernel weakened (lower heat-release rate).



Figure 3. Calculated structure of methane cup-burner flames with agents: (a) DMMP added to the oxidizer at $X_{\text{DMMP-O}} = 0.012$, (b) DMMP and CO₂ added to the oxidizer at $X_{\text{DMMP-O}} = 0.012$ and $X_{\text{CO2}} = 0.034$, respectively.

Figure 5 shows the radial variations of calculated temperature and the heat-release rate crossing the reaction kernel at $z_k = 5.0$ mm and the trailing flame at z = 8.0 mm ($z_k + 3$ mm) in the near-limit flame with DMMP at $X_{DMMP-O} = 0.012$ and CO₂ at $X_{CO2} = 0.034$ (see Fig. 3b). At $z_k = 5.0$ mm, the heat-release rate peak resided slightly on the oxidizer side of the temperature peak, as the reaction kernel broadened laterally as a result of fuel-air mixing in the region between the flame base and the burner rim. At z = 8.0 mm, the flame was characterized by "two-zone" structure ²³ (inner and outer) as was evident from two heat-release rate peaks. The inner zone (8.8 mm < r < 10.5 mm) was formed by the hydrocarbon-O₂ combustion with the heat-release rate peak residing on the temperature peak.



Figure 4. Calculated maximum temperature and reaction-kernel heat-release rate in methane cupburner flames with DMMP or CO_2 added to the oxidizer.



Figure 5. Calculated radial variations of the temperature and heat-release rate at z = 5 mm and 8 mm in a methane cup-burner flame with DMMP and CO₂ added to the oxidizer at $X_{\text{DMMP-O}} = 0.012$ and $X_{\text{CO2}} = 0.034$, respectively.

The outer zone (10.5 mm < r < 12 mm) was formed by exothermic reactions of the retardant itself.

Figure 6 shows the radial variations of the volume fractions (X_i) of phosphorus-containing species and the chain-carrier radicals (H, O, and OH) crossing the reaction kernel with DMMP added at X_{DMMP-O}



Figure 6. Calculated radial variations of the volume fractions at z = 5 mm in a methane cupburner flame with DMMP and CO₂ added to the oxidizer at $X_{\text{DMMP-O}} = 0.012$ and $X_{\text{CO2}} = 0.034$, respectively.

= 0.012 and CO₂ at X_{CO2} = 0.034 at z_k = 5.0 mm. DMMP in the oxidizer stream reacted with O₂ and the radicals, fragmented, and diminished in the region surrounding the reaction kernel.

As a result, the concentration peaks of species such as $PO(OH)_3$, CH_3PO_2 , $P(OH)_3$ were formed in this peripheral region. Relatively high concentrations (X_i in the order of 10⁻³) of active phosphorus intermediates (HOPO₂, HOPO, PO₂) presented in the high-temperature central region, where the peaks of the chain-carrier radicals (H, O, and OH) were formed. Consequently, the afore-mentioned phosphorus inhibition reactions of radical recombination cycles are taking place vigorously at the reaction kernel.

Interaction of DMMP in Fuel with Flame Structure

Figure 7 shows the calculated structure of a methane flame in air with DMMP added to the fuel stream at $X_{DMMP-F} = 0.04$ (Fig. 7a) and a near-limit flame in air with DMMP at $X_{DMMP-F} = 0.04$ and CO₂ added to the oxidizer at $X_{CO2} = 0.172$ (Fig. 7b). As DMMP was added to the fuel stream (Fig 7a), no obvious changes are evident in the overall flame structure (i.e., the location, velocity, temperature, and heat-release rate) compared to the neat flame (Fig. 2a). As CO₂ was added to the oxidizer in addition to DMMP in the fuel (Fig. 7b), the flame lifted ($z_k = 4.6$ mm) and disconnected thermally from the burner rim. As a result of mixing of the fuel and oxidizer streams, the reaction kernel broadened laterally as was the flame with CO₂ added to the oxidizer (Fig. 2b).

Figure 8 shows the maximum temperature in the trailing diffusion flame and the peak heat-release rate at the reaction kernel in the flame with DMMP added to the fuel stream. As DMMP was added to the fuel stream up to $X_{\text{DMMP-F}} = 0.04$, the maximum temperature and the reaction-kernel heat-release rate remained nearly constant at $T_{\text{max}} \approx 2000$ K and $\dot{q}_k \approx 120$ W/cm³, respectively, and the flame was stable. Therefore, DMMP added to the fuel stream was ineffective in this range, and the flame blew off solely by the cooling effect of CO₂ added to the oxidizer.



Figure 7. Calculated structure of methane cup-burner flames with agents: (a) DMMP added to the fuel stream at $X_{\text{DMMP-F}} = 0.04$, (b) DMMP added to the fuel stream at $X_{\text{DMMP-F}} = 0.04$ and CO₂ added to the oxidizer at $X_{\text{CO2}} = 0.172$.

Figure 9 shows the radial variations of calculated temperature and the heat-release rate crossing the reaction kernel at $z_k = 4.6$ mm and the trailing flame at z = 7.6 mm ($z_k + 3$ mm) in the near-limit flame with DMMP added to the fuel stream at $X_{DMMP-F} = 0.04$ and CO₂ added to the oxidizer at $X_{CO2} = 0.172$ (see Fig. 7b). At $z_k = 4.6$ mm, the heat-release rate shows double peaks as the reaction kernel broadened laterally and curved up toward the oxidizer side as a result of fuel-air mixing in the region above the burner rim. The temperature was generally lower (due to the higher CO₂ volume fraction) than the DMMP-in-oxidizer case (Fig. 5), but the reaction-kernel heat-release rate was twice larger. At z = 7.6 mm, although the heat-release rate showed a small outer hump due to the broadened reaction kernel upstream, it did not develop to the two-zone structure downstream as was the case for



Figure 8. Calculated maximum temperature and reaction-kernel heat-release rate in methane cupburner flames with DMMP added to the fuel stream.



Figure 9. Calculated radial variations of the temperature and heat-release rate at z = 4.6 mm and 7.6 mm in a methane cup-burner flame with DMMP added to the fuel stream at $X_{\text{DMMP-F}} = 0.04$ and CO₂ added to the oxidizer at $X_{\text{CO2}} = 0.172$.

DMMP added to the oxidizer (see Fig. 5).

Figure 10 shows the radial variations of the volume fractions (X_i) of phosphorus-containing species and the chain-carrier radicals (H, O, and OH) crossing the reaction kernel at $z_k = 4.6$ mm. Since DMMP needed to diffuse through the oxidizer stream to reach the reaction kernel, its concentration



Figure 10. Calculated radial variations of the volume fractions at z = 4.6 mm and 7.6 mm in a methane cup-burner flame with DMMP added to the fuel stream at $X_{\text{DMMP-F}} = 0.04$ and CO₂ added to the oxidizer at $X_{\text{CO2}} = 0.172$.

was orders-of-magnitude lower, particularly on the oxidizer side, compared to the DMMP-in-theoxidizer case. As a result, the concentrations (X_i in the order of 10⁻⁴ or less) of active phosphorus intermediates (HOPO₂, HOPO, PO₂) were one or two-orders-of-magnitude lower--even less than those of the chain-carrier radicals (H, O, and OH), which remained at high levels ($X_i \approx 10^{-3}$).

A diffusion flame zone is generally formed where a stoichiometric ratio of the fuel and oxygen is obtained. The stoichiometric mixture fraction, determined by the element mass fractions of carbon, hydrogen, and oxygen ³², for a methane-air flame is 0.055. Therefore, the flame zone is formed where the fuel-stream fluid was reduced by the mixing to the mass fraction of 0.055, whereas the oxidizer fluid is reduce only to 0.945. This fact implies that a chemical additive to the fuel stream is ≈ 17 times less effective, on a mass basis, compared to that to the oxidizer. In addition to this intrinsic nature of hydrocarbon-air flames, the small stoichiometric mixture fraction dictates that the flame zone is formed on the oxidizer side of the dividing streamline between the fuel and oxidizer streams. As a result, the oxidizer stream (including the additive) flows into the flame zone, and thus the convective fluxes of the oxygen and additive (in addition to the diffusive fluxes) to the flame zone are significant. By contrast, the fuel and the additive must diffuse into the oxidizer stream to reach the flame zone as described above. Consequently, the active phosphorus intermediates concentrations are low and, in turn, the inhibiting radical-recombination cycles are weak, thus resulting in ineffectiveness of DMMP in the fuel stream.

CONCLUSIONS

The physical and chemical effects of the phosphorus flame retardant (DMMP), acting in the gas phase, on the structure and inhibition of methane-air co-flow diffusion flames, in the cup-burner configuration, were studied computationally. The minimum extinguishing concentrations for a combination of DMMP and CO_2 were predicted in reasonable agreement with the measured values, but particle formation in the actual flames probably resulted in complications due to the radiative heat loss. The effectiveness of DMMP added to the oxidizer was outstanding. Although DMMP in the oxidizer increased the maximum flame temperature in the trailing diffusion flame, it weakened the

flame attachment point (reaction kernel) at the flame base, thereby inducing the detachment, lifting, and blowout extinguishment. The two-zone flame structure was predicted with the DMMP addition to the oxidizer due to the reactions of the retardant itself. DMMP in the fuel stream was practically ineffective in gas-phase inhibition of co-flow diffusion flames primarily because of three potential reasons: (1) a small stoichiometric mixture fraction (0.055 for methane), which required more retardant to affect the flame, (2) the flame location on the oxidizer side of the dividing streamline, which required the retardant diffusion (instead of convection) to the flame, and (3) low concentrations of active phosphorus intermediate species (HOPO₂, HOPO, PO₂) in the flame stabilizing region, so that the catalytic reactions to recombine the chain-carrier radicals (H, O, and OH) were relatively slow.

ACKNOWLEDGMENTS

This work was supported under the Cooperative Agreement by the National Institute of Standards and Technology with FXT Consulting, LLC.

REFERENCES

¹ Fenimore, C.P, and Jones, G.W., Modes of inhibiting polymer flammability, *Combustion and Flame* 10 (1966) 295-301.

²Linteris, G.T., Gas-phase mechanisms of fire retardants, NIST IR 6889, National Institute of Standards and Technology, Gaithersburg, MD, 2002.

³ Levchik, S.V., Introduction to flame retardancy and polymer flammability, In: Flame Retardant Polymer Nanocomposites (A.B. Morgan and C.A. Wilkie, eds.), John Wiley & Sons, Inc., 2007, pp.1-29.

⁴ Schartel, B., Phosphorus-based flame retardancy mechanisms-old hat or a starting point for future development?, *Materials* 3 (2010) 4710-4745.

⁵ Levchik, S.V. and Weil, E.D., A review of recent progress in phosphorus-based flame retardants, *Journal of Fire Science* 24 (2006) 345-364.

⁶ Hastie J.W., and Bonnell D.W., Molecular Chemistry of Inhibited combustion Systems, National Bureau of standards. NBSIR 80-2169, Gaithersburg, MD: National Bureau of Standards, 1980.

⁷ Twarowski, A., The influence of phosphorus oxides and acids on the rate of H+OH recombination, *Combustion and Flame* 94 (1993) 91-107.

⁸ Werner, J.H., and Cool, T.A., Kinetic Model for the Decomposition of Dmmp in a hydrogen/Oxygen Flame, *Combustion and Flame* 117 (1999) 78-98.

⁹ Babushok, V.I., and .Tsang, W, Influence of phosphorus-containing fire suppressants on flame propagation, In: Society of Fire Protection Engineers, Boston, MA, 1999.

¹⁰ Wainner, R.T., McNesby, K.L., Daniel, R.G., Miziolek, A.W., and Babushok, V.I., Experimental and mechanistic investigation of opposed-flow propane/air flames by phosphoruscontaining compounds, Proceedings of the Halon Options Technical Working Conference (HOTWC 2000), Albuquerque, NM, May 2-4, 2000, pp 141-153.

¹¹ Glaude, P.A., Curran, H.J., Pitz, W.J. Westbrook, C.K., Kinetic study of the combustion of orgnophophorus compounds, *Proceedings of the Combustion Institute* 28 (2000) 1749-1756.

¹² McDonald, M.A., Gouldin, F.C., and Fisher, E.M., Temperature dependence of phosphorus-based flame inhibition, *Combustion and Flame* 124 (2001)668-683.

¹³ Korobeinichev, O.P., Bolshova, T.A., Shvartsberg, V.M., and Chernov, A.A., Inhibition and promotion of combustion by organophosphorus compounds added to flames of CH_4 or H_2 in O_2 and Ar, *Combustion and Flame* 125 (2001) 744-751.

¹⁴ Korobeinichev, O.P., Rybitskaya, I.V., Shmakov, A.G., Chernov, A.A., Bolshova, T.A., and Shvartsberg, V.M., Inhibition of atmospheric-pressure $H_2/O_2/N_2$ flames by trimethylphosphate over range of equivalence ratio, *Proceedings of the Combustion Institute* 32 (2009) 2591-2597.

¹⁵ Korobeinichev, O.P., Rybitskaya, I.V., Shmakov, A.G., Chernov, A.A., Bolshova, T.A., and Shvartsberg, V.M., Mechanism of inhibition of hydrogen/oxygen flames of various compositions by trimethyl phosphate, *Kinetics and Catalysis* 51 (2010) 154-161.

¹⁶ Bolshova, T.A., and Korobeinichev, O.P., Promotion and inhibition of a hydrogen-oxygen flame by the addition of trimethyl phosphate, *Combustion Explosion and Shock Waves* 42 (2006) 493-502.

¹⁷ McDonald, M.A., Jayaweera, T.M., Fisher, E.M., and Gouldin, F.C., Inhibition of nonpremixed flames by phosphorus-containing compounds, *Combustion and Flame* 116 (1999) 166-176.

¹⁸ Korobeinichev, O., Mamaev, A., Sokolov, V., Bolshova, T., Shvartsberg, V., Zakharov, L., and Kudravtsev, I., Inhibition of methane atmospheric flames by organophosphorus compounds, Halon Options Technical Working Conference, Albuquerque, NM, May 2-4, 2000, pp. 164-172.

¹⁹ Tapscott, R.E., Mather, J.D., Heinonen, E.W., Lifke, J.L., and Moore, T.A., Identification and Proof Testing of New Total Flooding Agents: Combustion Suppression Chemistry and Cup-Burner Testing, NMERI 97/6/33010, Albuquerque, NM: New Mexico Engineering Research Institute, 1998.

²⁰ Bouvet, N., Linteris, G.T., Babushok, V.I., Takahashi, F., Katta, V.R., and Krämer, R.H., Experimental and numerical simulations of the gas-phase effectiveness of phosphorus compounds, Fire and Materials 2015, Interscience Communications Ltd, London, UK.

²¹ Shmakov, A.G., Korobeinichev, O.P., Shvartsberg, V.M., Knyazkov, D.A., Bolshova, T.A., and Rybitskaya, I.V., Inhibition of premixed and nonpremixed flames with phosphorus-containing compounds, *Proceedings of the Combustion Institute* 30 (2005) 2345-2352.

²² Takahashi, F., Linteris, G., and Katta, V.R., Extinguishment mechanisms of coflow diffusion flames in a cup-burner apparatus, *Proceedings of the Combustion Institute* 31 (2007) 2721-2729.

²³ Takahashi, F., Katta, V.R., Linteris, G.T., and V.I. Babushok, V.I., Combustion Inhibition and Enhancement of Cup-Burner Flames by CF₃Br, C₂HF₅, C₂HF₃Cl₂, and C₃H₂F₃Br, *Proceedings of the Combustion Institute* 35 (2014).

²⁴ Katta, V.R., Goss, L.P., and Roquemore, W.M., Numerical investigations of transitional H2/N2 jet diffusion flames, *AIAA Journal* 32 (1994) 84.

²⁵ Roquemore, W.M., and Katta, V.R., Role of Flow Visualization in the Development of UNICORN. *Journal of Visualization* 2, 3/4 (2000) 257-272.

²⁶ Frenklach, M., Wang, H., Goldenberg, M., Smith, G.P., Golden, D.M., Bowman, C.T., Hanson, R.K., Gardiner, W.C., Lissianski, V., GRI-Mech—An optimized detailed chemical reaction mechanism for methane combustion, Report No. GRI-95/0058, Gas Research Institute, Chicago, IL, 1995.

²⁷ Korobeinichev, O.P., Shvartsberg, V.M., Shmakov, A.G., Bolshova, T.A., Jayaweera, T.M., Melius, C.F., Pitz, W.J. and Westbrook, C.K., Flame inhibition by phosphorus-containing compounds in lean and rich propane flames, *Proceedings of the Combustion Institute* 30 (2004) 2350-2357.

²⁸ Linteris, G.T., Katta, V.R., Takahashi, F., Experimental and Numerical Evaluation of Metallic Compounds for Suppressing Cup-Burner Flames, *Combustion and Flame* 138 (2004) 78-96.

²⁹ Linteris, G.T., Rumminger, M.D., Babushok, V.I., Catalytic Inhibition of Laminar Flames by Transition Metal Compounds, *Progress in Energy and Combustion Science* 34 (2008) 288-329.

³⁰ Takahashi, F., and Katta, V.R., A reaction kernel hypothesis for the stability limit of methane jet diffusion flames, *Proceedings of the Combustion Institute* 28 (2000) 2071-2078.

³¹ Takahashi, F., Linteris, G., and Katta, V. R., Vortex-coupled oscillations of edge diffusion flames in coflowing air with dilution, *Proceedings of the Combustion Institute* 31 (2007) 1575-1582.

³² Bilger, R.W., The structure of turbulent nonpremixed flames, *Proceedings of the Combustion Institute* 22 (1988) 475-488.