

EXPERIMENTAL AND NUMERICAL SIMULATIONS OF THE GAS-PHASE EFFECTIVENESS OF PHOSPHORUS COMPOUNDS¹

Nicolas Bouvet, Gregory Linteris, Valeri Babushok
National Institute of Standards and Technology, U.S.A.

Fumiaki Takahashi
Case Western Reserve University, U.S.A.

Viswanath Katta
Innovative Scientific Solutions, U.S.A.

Roland Krämer
BASF SE, Advanced Materials and Systems Research, Germany

ABSTRACT

The effectiveness of phosphorus-containing compounds as gas-phase combustion inhibitors varies widely with flame type. To understand this behavior, experiments are performed with dimethyl methylphosphonate (DMMP) added to the oxidizer stream of methane-air co-flow diffusion flames (cup-burner configuration). At low volume fraction, phosphorus (via DMMP addition) is shown to be about four times as effective as bromine (via Br₂ addition) at reducing the amount of CO₂ required for extinguishment; however, above about 3000 µL/L to 6000 µL/L, the marginal effectiveness of DMMP is approximately zero. In contrast, the diminished effectiveness does not occur for Br₂ addition. To explore the relevant chemical kinetics in a simpler configuration, premixed burning velocity simulations with detailed kinetics are performed for DMMP addition to methane-air flames. Analyses of the numerical results are performed to understand the variation in the inhibition mechanism with temperature, agent loading, and stoichiometry, to interpret the loss of effectiveness for DMMP in the present experiments.

INTRODUCTION

Phosphorus compounds are widely used as a fire retardants in polymers, where they can act in the condensed phase, promoting char formation (which blocks heat flow back to the polymer) or in the gas phase, where phosphorous-containing decomposition products interfere with the normal gas-phase combustion reactions. The present paper focuses on the gas-phase action of phosphorus.

The effects of phosphorus compounds in flames have been studied. Early experiments in premixed flames measured the reduction in laminar burning velocity with added phosphorus compounds^{1, 2}, and found some to be about five times as effective as Br₂. Oxygen index tests in diffusion flames over polymers showed effectiveness and suggested gas-phase action by phosphorus compounds^{3, 4}. Molecular-beam mass sampling in premixed flames^{5, 6} outlined the basic catalytic radical recombination mechanism of phosphorus species in the gas phase, and later work investigated the reaction mechanism in more detail^{7, 8}, leading eventually to detailed kinetic mechanisms for phosphorus compounds in flames⁹⁻¹⁵. Concurrent experimental work with premixed^{12, 16-19}, counterflow diffusion²⁰⁻²² and co-flow diffusion flames¹⁷ helped to further refine the mechanisms and provide insight into the flame inhibition by phosphorus compounds.

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While phosphorus compounds are generally very effective, their efficiency varies widely with flame type. For example, in a premixed flame, DMMP was found to be about 141 times as effective (on a molar basis) as CO₂ at reducing the burning velocity^{21, 23}; in a counterflow diffusion flame^{24, 25}, about 30 times as effective in reducing the extinction strain rate; but in a cup-burner flame, only about 3 times as effective as CO₂ in causing extinguishment²⁶. Apparently, the flame structure is affecting the gas-phase action of the phosphorus compounds in these laboratory flames; however, no work has been done to determine the reason for this large variation in effectiveness. Similarly, the effectiveness of phosphorus compounds as fire retardants, believed to act in the gas phase, has been found to vary widely with polymer type²⁷, and the reasons for this variation are unknown. The present work was undertaken to provide insight into these phenomena.

One possible reason for the variation in effectiveness with flame type is the loss of active species to condensed-phase particles. This was found to be the case for organometallic fire retardants added to the air stream (in a variety of flames). Some metal species, in the gas-phase, are up to 100 times more effective than Br in premixed flames²⁸, somewhat less effective in counterflow diffusion flames²⁸, and essentially ineffective in cup-burner flames²⁹. Rayleigh scattering measurements in the flames³⁰⁻³² and numerical modeling³³⁻³⁵ revealed that particles of metal oxides species were likely to condense, limiting the gas-phase concentration of the active species, and hence the additive effectiveness. For phosphorous compounds, particle formation has been observed¹⁷, and may be limiting the effectiveness. Hence, the present work investigates particle formation in methane-air co-flow diffusion flames (which demonstrated the poor effectiveness) with added DMMP in the air stream.

APPROACH

The flame configuration selected is a co-flow methane-air diffusion flame in the so-called cup-burner configuration. This burner is a widely-used standard test for fire suppressant effectiveness³⁶, and there is a large empirical database of the minimum extinguishing concentration (MEC) of inhibitors added to the air stream (for example ref.³⁷). In the present experiments, the agent is added to the air stream, and the volume fraction of CO₂ required for flame extinguishment is determined. This approach, adopted in the past^{17, 29}, is similar to the widely-used limiting oxygen index (LOI) test for polymer flammability³⁸, which determines (for a polymer sample) the volume fraction of O₂ (or equivalently, N₂) in the oxidizer required for flame extinguishment (as compared to added CO₂ in the present approach). This method has the advantage (over more typical MEC measurements) of quantifying an extinguishing condition even for an agent which might not extinguish the flame on its own. Also, addition of CO₂ eliminates soot formation (in these otherwise slightly sooting methane-air flames), the presence of which would complicate both the particle formation and their measurement (in the otherwise weakly-scattering gases). Finally, addition of CO₂ suppresses flame flickering, simplifying the scattering measurements. Note that another difference between the present approach and the LOI is that in the latter, the chemical inhibitor is always added to the fuel (typically a solid); whereas, in the present work, the agent is added to the air stream. Near extinction, the reaction kernel (which is responsible for maintaining flame attachment) is lifted, allowing good mixing of the fuel and air stream³⁹, so that agent addition to either stream should, qualitatively, have the same effect. Nonetheless, the air stream was selected for the present work for two reasons: 1.) air-side addition allows a higher mass of agent to reach the reaction kernel (the upper limit is controlled by the vapor pressure of the DMMP in the stream and the stoichiometric ratio of fuel and air in the premixed reaction kernel), and 2.) transport of the agent to the reaction kernel is better characterized (by the agent volume fraction) with agent addition to the air stream (because the flow streamlines tend to convect the air stream directly into the reaction kernel, whereas the fuel stream tends to have to diffuse into these streamlines).

The phosphorus compound selected for study is dimethyl methylphosphonate (DMMP, C₃H₉O₃P, CH₃PO(OCH₃)₂), a phosphorus-based fire retardant, and well-studied flame inhibitor. The potential for condensation in the flame is assessed via thermodynamic equilibrium calculations for the inlet gases at stoichiometric conditions, for a range of temperatures occurring in flames. Calculations are performed for all possible intermediate and final flame species (condensed phase and gaseous) for which data are available. To detect the presence of particles, an optical system (described below) is used to measure

the Rayleigh scattering signal from the inlet and product gases in the flame region, with and without DMMP addition. Finally, premixed flame simulations are used to examine the flame chemistry at the measured extinguishing conditions (the relevance of these premixed flame simulations to the present co-flow diffusion flames is explained below).

EXPERIMENT

Burner Assembly

The burner assembly (Figure 1) is similar to that described ref.²⁹. A cylindrical glass cup (28 mm exit diameter) is centered in a glass chimney (95 mm I.D., 142 mm height), and each has glass beads (3 mm and 6 mm diameter, respectively) to create a flat velocity profile in the fuel and co-flowing oxidizer streams. The fuel cup exit plane (provided with two 15.8 mesh/cm SS screens) is located 1 mm above the chimney edge and about 80 mm above the bead level in the oxidizer stream. A second chimney (150 mm I.D., 450 mm height), with a shroud flow of air, shields the flame from ambient disturbances and minimizes recirculation of the product gases. The burner assembly is attached to a three-axis translation stage (minimum step size of 1.6 μm) which positions the flame in the stationary optical path. Bellows on the input, output, and scattering optical paths allow translation of the burner while isolating the clean burner gases from ambient air, and eliminating windows (and their reflections). A small (2 L/min to 5 L/min) flow of air through the optics on the bellows shields them from product gases and particles.

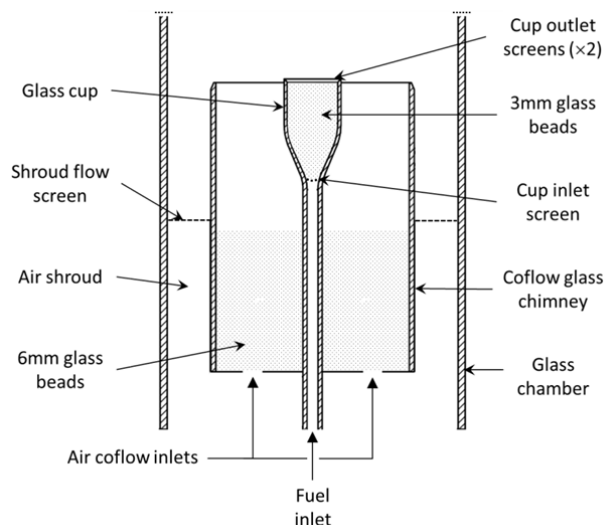


Figure 1 – Simplified view of the burner apparatus.

Gas & liquid agent delivery

The reactant gases are methane (Matheson UHP, 99.97%), carbon dioxide (MG Industries), and house compressed air (filtered and dried), which is additionally cleaned by passing it through a 0.01 μm filter, a carbon filter, and a desiccant bed to remove small aerosols, organic vapors, and water vapor. Mass flow controllers (Sierra Instruments Inc., 860C), calibrated with dry piston flow meters (Bios DC-Lite and Mesa Labs Definer 220), regulate the gas flows with an uncertainty of 2 % of the indicated flow. The gases flow through copper coils in a controlled temperature silicone oil bath (Neslab EX-251HT, $\pm 0.1^\circ\text{C}$ accuracy), followed by heated downstream delivery lines, whose temperatures are thermostatically controlled and monitored (to avoid DMMP condensation). The burner body and glass beads are also thermostatically heated and monitored. The DMMP (Sigma Aldrich, purity $\geq 97.0\%$) can be added to either the oxidizer or fuel streams using (depending on the quantity required) either a two-stage saturator maintained in a hot water bath (Cole Parmer 1095-00) or a syringe/evaporator assembly. The two-stage bath is identical to that used in previous work⁴⁰, and the vapor pressure data for DMMP is from ref.⁴¹. The syringe/evaporator assembly consists of two computer-controlled stepper-motor driven syringe pumps connected to evaporator (a stainless steel tube (23.6 mm I.D., 305 mm length) packed with 3 mm glass beads). The carrier gas (i.e., the oxidizer

stream or some fraction of it) enters one end of the evaporator tube, and the DMMP is injected through a 3.2 mm O.D. stainless steel tube, about 50 mm downstream from the carrier gas inlet. The evaporator is heated and insulated, and a controller maintains the temperature at a specified value (measured on the evaporator wall, near the point of liquid injection). Two precision glass/Teflon syringes (Hamilton Gas-tight, 10 cc) meter the DMMP into the evaporator. Manual valves and tubing allow one syringe pump to inject DMMP, while the other refills (from a reservoir). The selected syringe size provides a well determined, small flow rate, and smooth operation with sufficient run time before pump reversal (during which data are not collected).

Optical System

The Rayleigh scattering system (Figure 2) is based on those in refs.^{40, 42}, with some modifications. The light source is an Ar-Ion laser (LEXEL 95-4 series, 4.0 W all-lines) with a vertically polarized, 500 mW beam at 488 nm. An optical chopper (Stanford Research 540) modulates the signal at 1.5 kHz, and a polarization-maintaining fiber (Newport F-SPA, 3.6 μ m core diameter) carries the beam into a chemical fume hood, which contains the experiment. Microscope objectives (20X) couple the beam into and out of the fiber (with an overall coupling efficiency of about 20%). A lens (achromatic doublet, $f = 250$ mm, Newport PAC067) focuses the beam in the test region, after which it passes into a high-efficiency beam trap (reflectivity $< 10^{-4}$). For a reference signal, a beam splitter (optical wedge) directs a portion ($\approx 4\%$) of the incident beam through a neutral density filter (OD 0.5), an opal diffusing glass and a double-concave lens ($f = -25$ mm) to an integrating sphere, fitted with a laser line filter (1.9 nm bandwidth) and photodiode (Melles Griot 13 DSI 009). The output signal is amplified and filtered (RC low-pass, $f_c = 13.3$ Hz).

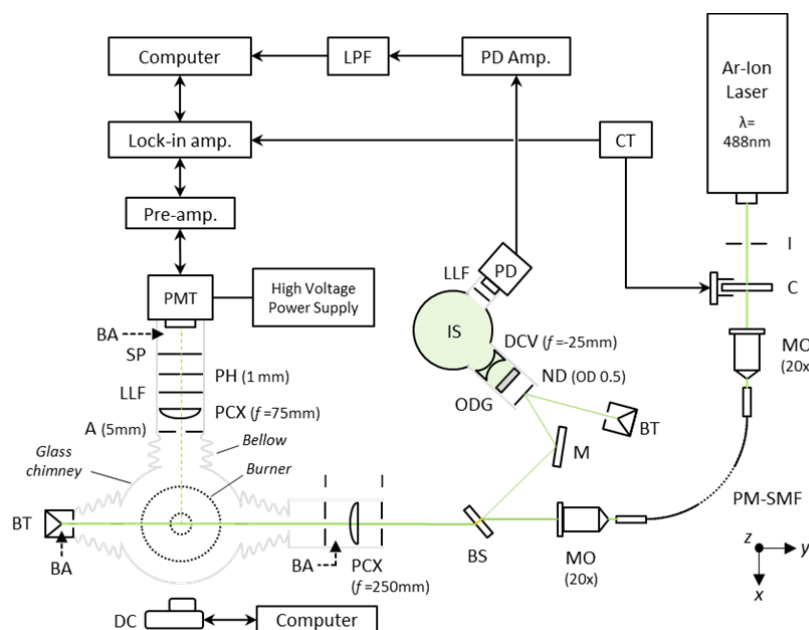


Figure 2 – Rayleigh scattering experimental layout. Nomenclature – A: aperture; BA: bleed air; BS: beam sampler; BT: beam trap; C: chopper; CT: chopper controller; DC: digital camera; DCV: double concave lens; I: iris; IS: integrating sphere; LLF: laser line filter; LPF: low pass filter; M: mirror; MO: microscope objective; ND: neutral density filter; ODG: opal diffusing glass; PCX: plano-convex lens; PD: photodiode; PH: pinhole; PM-SMF: polarization-maintaining single mode fiber; PMT: photomultiplier; SP: sheet polarizer.

The detection system for the light scattered perpendicular to the laser beam consists of a photomultiplier tube (PMT- Hamamatsu 1P28, powered at -0.95 kV), preceded by a 5 mm circular aperture, a plano-convex lens ($f = 75$ mm), a laser line filter (1.9 nm bandwidth), a 1 mm pinhole and a sheet polarizer. The circular aperture is located 13.5 cm away from the laser focus point, providing a

10^{-3} sr collection angle. The PMT output is pre-amplified (Stanford Research 552) before entering a lock-in amplifier (Stanford Research 530), with the reference signal from the chopper controller. A data acquisition board (Strawberry Tree DynaRes Ultra8) in a computer collects the analog voltage output from the signal lockin and the reference photodiode. The performance of the system was verified by measuring the Rayleigh scattering signal from gases of known scattering cross section⁴³⁻⁴⁵, as shown in Figure 3.

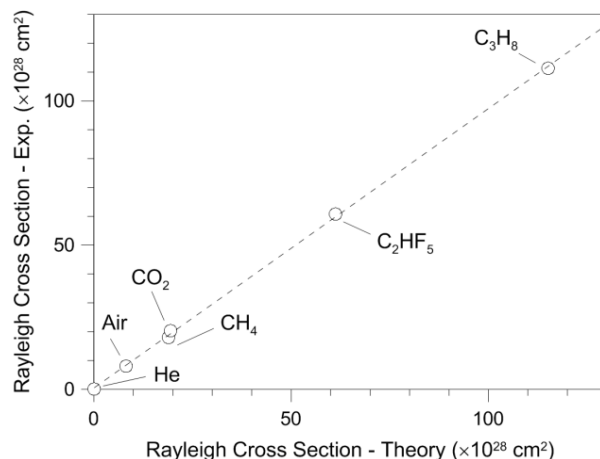


Figure 3 - Experimentally measured Rayleigh cross-sections versus literature values for air, CH₄, CO₂ and C₃H₈⁴³; C₂HF₅⁴⁴ and He⁴⁵.

During experiments, the burner/chimney assembly is set at a defined height (z-axis) and data are acquired by translating the assembly in increments of 0.7 mm $\pm$ 0.0016 mm along the y –axis with respect to the stationary laser path. At each horizontal position, 150 samples at 200 Hz. are collected for the scattering and reference signals, averaged, and the scattering signal is normalized by the reference signal. Flame shapes and colors are also documented by taking photographs with a DSLR camera (Kodak professional DCS 620) equipped with a Nikkor lens (AF 28/2.8D).

An uncertainty analysis was performed, consisting of calculation of individual uncertainty components and their root mean square summation. All uncertainties are reported as *expanded uncertainties*: $X \pm ku_c$, from a combined standard uncertainty (estimated standard deviation) u_c , and a coverage factor $k = 2$ (95 % confidence level). Likewise, when reported, the relative uncertainty is ku_c / X . The expanded relative uncertainties for the experimentally determined quantities in this study are: CO₂ volume fraction, 4 %, and DMMP volume fraction, 2 %.

NUMERICAL APPROACH

Numerical simulations of 1D adiabatic freely propagating laminar flames are carried out using the commercial code Chemkin⁴⁶, together with the kinetic mechanism proposed by Jayaweera et al.¹². This mechanism (682 reactions and 121 species) describes hydrocarbon combustion inhibition by organo-phosphorous compounds. The mechanism has been validated against experimental data for a variety of phosphorus additives. In the premixed flame simulations, final solutions had 250-300 grid points (GRAD and CURV $\leq$ 0.1), and were found to be independent of further grid refinement. Thermal diffusion and multicomponent transport were not included. For the thermodynamic equilibrium calculations, the Sandia EQUIL code⁴⁷ was used, with the thermodynamic databases from Goos et al.⁴⁸, Gurvich et al.⁴⁹, McBride et al.⁵⁰, and Jayaweera et al.¹².

RESULTS AND DISCUSSION

The run conditions for the experiments are shown in Table 1. The methane flow was always 0.0140 mole/min, and the oxidizer co-flow varied from 0.82 mole/min to 2.25 mole/min (but was always within the plateau regime, in which the extinction condition is insensitive to the co-flow

velocity⁵¹). Extinction tests were performed for burner and gas temperatures of 70 °C, 100 °C, and 130 °C, with DMMP volume fractions in the oxidizer stream of 0 % to 1.3 %.

Table 1 – Run conditions for extinction and scattering experiments.

Measurement	Burner Temp	Gas Flows (mole/min)					
		Methane	Oxidizer(co-flow)	Shroud (2 nd co-flow)	DMMP	Air	CO ₂
Extinction	70 °C	0.0140	0.819	1.18	Variable	“	“
Extinction	100	”	1.84	1.98	“	“	“
Extinction	130	”	2.25	2.42	“	“	“
Scattering	70	”	1.84	2.58	0	1.62	0.221
Scattering	70	”	1.84	2.67	0.00190	1.68	0.155

Typical images of the flames are shown in Figure 4 for the neat methane-air cup-burner flame, a flame with 8.4 % CO₂ in the oxidizer, and a flame with 8.4 % CO₂ and 1035 μL/L of DMMP in the oxidizer. The bright orange color is likely to be resonant emission from HPO (at 500 nm to 600 nm)^{52, 53}. The flame was steady for all conditions in Table 1, with minimal flame flicker. Particles were observed visually in the product gases far downstream of the flame, and their presence increased greatly as the DMMP volume fraction increased. The air flow rate in the outer co-flow (the shroud flow) was selected to avoid recirculation of the particles in the product gases to the flame base. Deposition of particles on the chimney and burner surfaces did not occur; however, after long run times, a clear film of solid material formed on the chimney walls and cup-burner screen, likely polyphosphoric acid⁵⁴. While it would have been desirable to obtain the minimum extinguishing concentration of DMMP alone in the oxidizer stream (estimated by Tapscott et al.²⁶ to be around 5 %), this proved to be impractical; at X_{DMMP} above about 1.3 %, the formation of particles downstream of the flame and subsequent coating of surfaces was too strong to obtain reliable data.



Figure 4 - Flame images: (a) CH₄ - air, (b) CH₄ - (air + CO₂), (c) CH₄ - (air + CO₂ + DMMP).

For a given burner temperature, the blowoff conditions are determined by adding the desired amount of catalytic agent (starting at 0) to the co-flowing oxidizer (which is held at a constant total flow), and then adding CO₂ (in increments of < 1 % of the CO₂ flow) until blowoff is observed. The amount of DMMP was increased, and the process repeated, to generate the curves shown in Figure 5. As illustrated, the amount of CO₂ required for extinguishment drops rapidly for DMMP volume fractions below about 1000 μL/L, and then the marginal effectiveness of the DMMP diminishes, so that above about 7000 μL/L of DMMP, the additional DMMP is essentially ineffective. The behavior is essentially the same at the three temperatures, although the DMMP volume fraction for diminished

effectiveness increases slightly at higher temperatures. The behavior is in marked contrast to Br_2 ⁵⁵ (Figure 6), for which the marginal effectiveness, although it decreases, does not go to zero, and the flame can be extinguished by Br_2 itself.

While the saturation in the effectiveness of DMMP may be due to the fuel effect of the agent (as alluded to in ref.¹⁷), it starts to occur at a loading of only about 1000 $\mu\text{L/L}$ to 2000 $\mu\text{L/L}$. At this low concentration, the contribution of DMMP combustion to the heat release is still less than 5 % of the total, so it is not expected to have a major effect on flame extinguishment.

The behavior for DMMP is very similar to that observed for metallic compounds added to cup-burner flames²⁹, which were many more times as effective as Br_2 at low loading, but also had greatly diminished marginal effectiveness at higher loadings. The loss of effectiveness for the metals was believed to be due to particle formation (which acts as a sink for the active gas-phase intermediate species that catalytically recombine radicals³⁵). Since particles are observed visually in the present DMMP-inhibited cup-burner flames, and were reported to be present in other work¹⁷, their potential to sequester active species is discussed below.

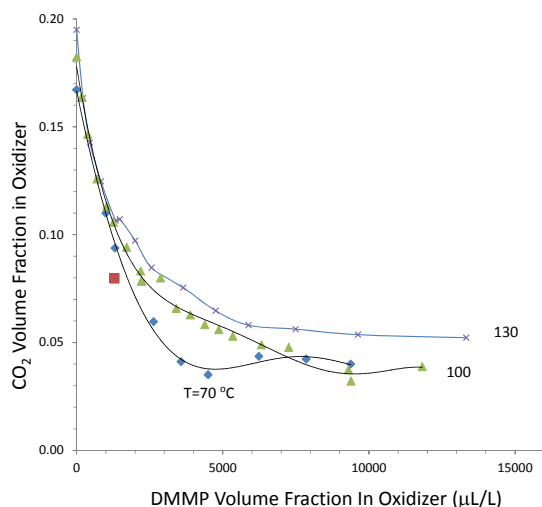


Figure 5 – Extinction volume fraction of CO_2 vs. DMMP volume fraction in the oxidizer (methane fuel, air oxidizer, reactant initial temperature of 70 °C, 100 °C, and 130 °C). (note: red square is the condition for scattering measurements described below).

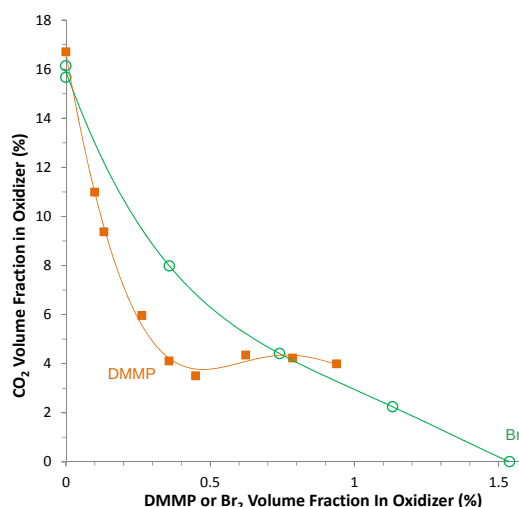


Figure 6 – Extinction volume fraction of CO_2 vs. DMMP or Br_2 ²⁹ volume fraction in the oxidizer (methane fuel, air oxidizer, burner temperature 21°C for Br_2 , 70°C for DMMP).

As a first step in understanding the role of particles in the flame inhibition by DMMP, the equilibrium concentrations of intermediate species (gas, liquid, and solid) were calculated for a premixed system corresponding to a stoichiometric methane-air mixtures with DMMP added at a volume fraction of 2%. As Figure 7 shows, for $T < 700$ K, most of the phosphorus is present as liquid phosphoric acid ($\text{OP}(\text{OH})_3$ (L)); for $700 \text{ K} < T < 1200$ K, gaseous phosphoric acid dominates; and for $1200 \text{ K} < T < 2100$ K, HOPO dominates. For $700 \text{ K} < T < 1200$ K, liquid phosphorus has a peak mole fraction of about 1700 $\mu\text{L/L}$, and is a possible condensed-phase species.

To quantify the presence of particles in the cup-burner flames, Rayleigh scattering measurements were performed with added DMMP. To establish a baseline, measurements were first performed on flames with no added DMMP (but 12 % CO_2 in the oxidizer stream). Figure 8 shows the scattering signal (normalized by the scattering signal from air at 70°C) as a function of radial position from the burner centerline. Referring to the coordinate system shown in the lower right of Figure 2, the radial distance from the burner center line refers to measurements along the y coordinate, with the x position of the measurement at the burner center. The different curves in Figure 8 refer to measurements taken at

different heights above the burner surface (z direction). As the figure shows, the scattering signal decreases between $15 \text{ mm} > |y| > 10 \text{ mm}$ as the density of the gases are reduced in the flame zone. In the flame core ($|y| < 10 \text{ mm}$), the scattering signal is reduced (although methane has a larger cross section) because of the higher temperature (as compared to that of the co-flowing air at larger radii).

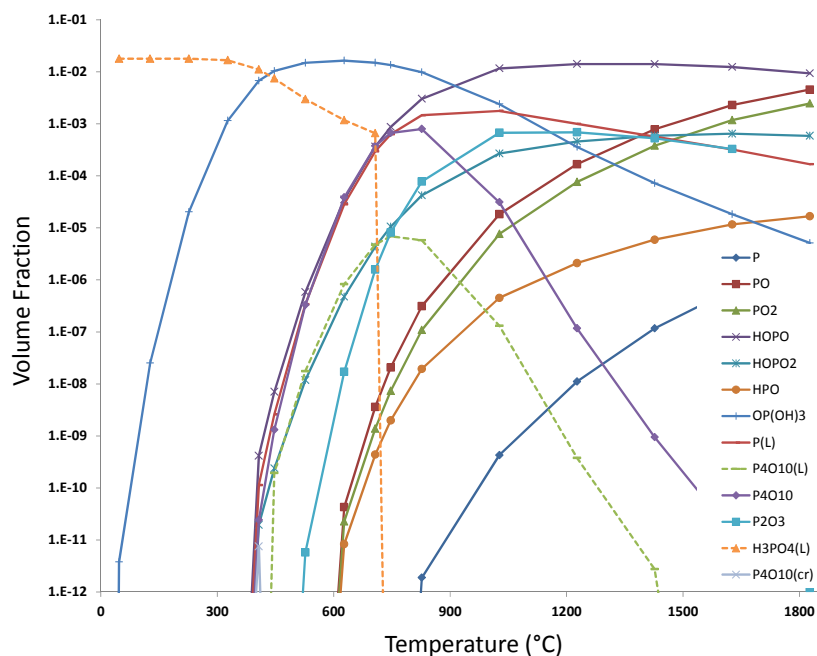


Figure 7 – Equilibrium phosphorus-containing species volume fractions in a stoichiometric methane-air flame with 2% added DMMP.

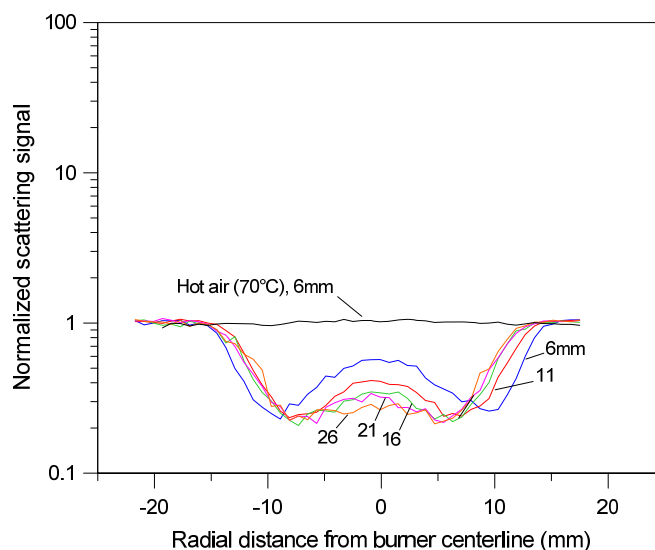


Figure 8 - Radial profiles of Rayleigh scattering signal (normalized by the scattering from the air only), at different heights above the burner, in a methane-air cup-burner flame ($T = 70^\circ\text{C}$, CO_2 volume fraction in air = 12 %). Top curve is normalized scattering signal from hot air (no flame).

Figure 9 shows the results of scattering measurements in the cup-burner flame with added DMMP and CO_2 . For these tests, the burner and inlet gases were maintained at 70°C , and the oxidizer stream had $1035 \mu\text{L/L}$ DMMP and 8.4 % CO_2 (volume fraction); these conditions are shown by the square

symbol in Figure 5, and are listed in Table 1. Each curve in Figure 9 shows the radial variation in the scattering signal (normalized to that of air at the burner temperature) for measurements at the indicated height above the burner outlet (the burner radial dimensions are indicated at the base of the figure). As shown, the scattering signal increases as the height from the burner surface increases, with noticeable increase even 6 mm above the burner. At the highest height (36 mm), the scattering signal is about 60 times that of the 70°C air, clearly indicating the presence of particles. An important question is where the particles are forming relative to the flame location. Using a visible image of the flame for these conditions, the flame location is shown (dashed lines) together with the scattering signal in Figure 10. As indicated, the particle location is from 2 mm to 5 mm outside the visible flame location, which is relatively far from the flame reaction zone, reducing the likelihood that particle formation is the reason for the lowered marginal effectiveness of DMMP at higher loading.

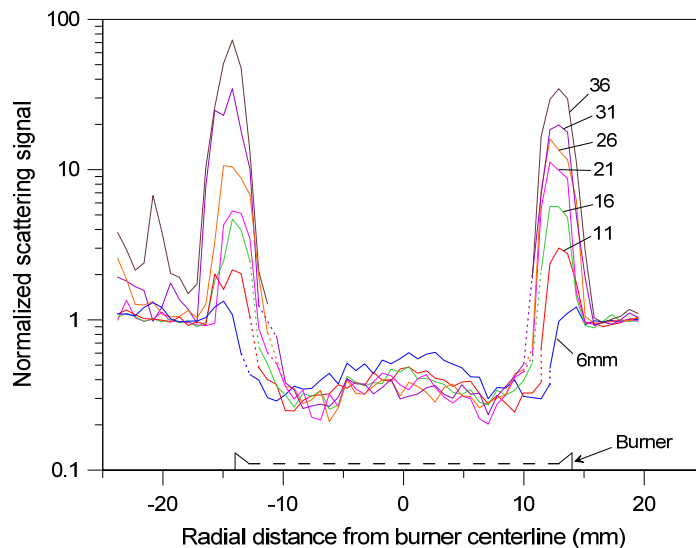


Figure 9 - Radial profiles of Rayleigh scattering signals in the CH_4 -oxidizer (91.6% air / 8.4% CO_2 / 1034 ppm DMMP) cup-burner flame at different flame heights above the burner (burner and gases at $T = 70^\circ\text{C}$). Dotted lines separates data intervals acquired using different lock-in amplifier sensitivities.

Given the lack of phosphorus intermediates likely to condense at flame temperatures (based on the equilibrium calculations), and given that the measured particles are well outside the flame region, it seems unlikely that their presence is affecting the flame chemistry (i.e., by sequestering active gas-phase phosphorus intermediates into less active solid particles (as was the case for iron flame inhibition³⁵). To further investigate the present flames, we turn to premixed flame simulations.

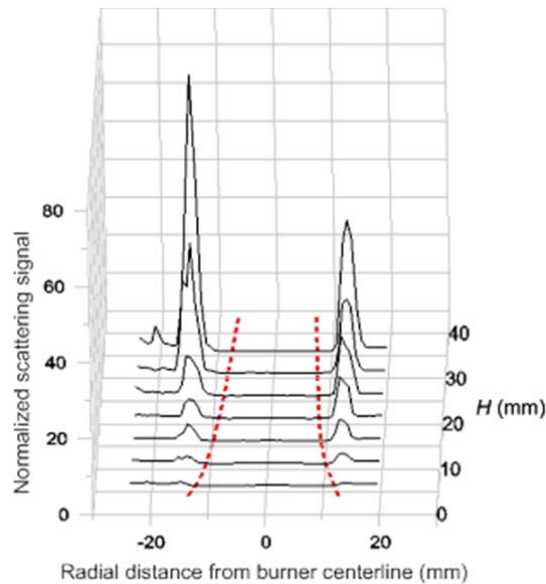


Figure 10 - Radial profiles of Rayleigh scattering (conditions of Figure 9). Dotted line denotes the main reaction zone of the flame (from a separate visible image).

As shown by Takahashi and co-workers⁵⁵⁻⁵⁷, the blow-off extinguishment of the cup burner flames is controlled by the properties of the reaction kernel, a peak-temperature, premixed region at the flame base, where the local flow velocity matches the premixed burning velocity of the mixture at that point. Cup-burner flames are not extinguished uniformly due to thermal or chemical inhibition; rather, the flame is stabilized at the base, and added inhibitor tends to disrupt the stabilization and cause the flame to lift off, blow-off, and then extinguish. Because the flames of the cup-burner near extinguishment are lifted from the burner rim, they typically have good mixing at the reaction kernel, so that flame propagation velocity of the mixture is approximated reasonably well by the premixed burning velocity of a mixture of the fuel and oxidizer at the stoichiometry of peak reactivity (i.e., peak burning velocity). Hence, for a given concentration of additives (CO_2 and DMMP) in the oxidizer stream, the volume fractions of all reactants in the reaction kernel can be estimated by finding the ratio of fuel (methane) and oxidizer (air, CO_2 , and DMMP) that gives peak burning velocity. To understand the unexpected saturation in the effectiveness of DMMP in the cup burner, we investigate the conditions at the extinguishment boundary (i.e., the locus of points given by one of the curves of $[\text{CO}_2]$ and [DDMP] in Figure 5). Proceeding, for example for the case with the burner at 100°C , we define the oxidizer mixture according to the volume fractions of CO_2 and DMMP at the points along the 100°C extinguishment curve of Figure 5. At a given point (i.e., for the given DMMP and CO_2 loading), we establish the fuel/oxidizer ratio as that which provides the peak temperature. A premixed flame simulation is performed for this condition, from which the properties of the flame are extracted. This procedure is repeated for selected points (i.e., those for which experimental data were obtained) along the extinction boundary defined in Figure 5. The logic is that this is what is happening to the reaction kernel⁵⁶: it finds its location based on the peak reactivity of the given mixture, which typically occurs at the location of peak temperature.

Figure 11 shows the results of these calculations. The three frames, left, middle and right, give the results for a burner temperature of 70°C , 100°C , and 130°C . Within each frame, data are given for the H, O, and OH radical volume fractions, peak (dotted lines) and equilibrium (solid lines). Below these are the peak temperature T and burning velocity S_L , and at the bottom, the curve representing the extinction boundary from the cup-burner experiments at that burner temperature (i.e., data from Figure 5, repeated). The results can be interpreted as follows. At a given burner temperature, as the CO_2 in the oxidizer decreases, the temperature increases, and when $[\text{CO}_2]$ is nearly constant (i.e., after the knee in the bottom curve), the temperature is nearly constant. The increased flame temperature (from

decreasing CO₂ addition) affects the radical concentrations. As the top three curves show, the *equilibrium* (solid lines) volume fraction of H, O, and OH all increase, as T increases, up to the DMMP loading at which the temperature is constant, above which the equilibrium radical concentrations are also roughly constant. In the absence of a catalytic agent, one would expect the peak radical volume fractions to also increase with temperature; however, in this calculation, DMMP is added also, and it reduces peak radical concentrations (via the catalytic radical recombination cycle by phosphorus intermediates). Thus, at low DMMP volume fractions, the catalytic effects dominate over any increase which might have occurred due to higher temperature (from reduced CO₂). The interesting finding is that as DMMP is added, the peak radical levels come down and the equilibrium levels increase, such that at the DMMP loading where the marginal effectiveness goes to zero (about 4000 $\mu\text{L/L}$ to 8000 $\mu\text{L/L}$, depending upon the burner temperature), the radicals in the flame are at equilibrium. That is, additional DMMP has little effect on the flame since the radicals are already at equilibrium; the gas-phase catalytic cycle of the phosphorus compounds has driven the radicals to equilibrium, after which they do little else.

As indicated in

Figure 11, the burning velocity at blow-off is mildly decreasing as X_{DMMP} increases. This is not unexpected, since the reaction kernel is free to find any spot where it can match the flow velocity to the burning velocity³⁹. Since DMMP, especially at higher loadings, acts as an important fuel-like species, it tends to move the reaction kernel to larger radii, where the flow velocity will be lower (since buoyancy-induced flow is strongest nearest the flame).

CONCLUSIONS

In order to study the gas-phase flame inhibition properties of a commonly added phosphorus-based fire retardant, DMMP was studied in a co-flow diffusion flame (cup-burner) of methane and air. The extinction conditions were determined by finding the volume fraction of CO₂ necessary to extinguish the flame, as a function of the DMMP volume fraction. Experiments were performed at burner temperatures of 70°C, 100°C, and 130°C, and DMMP volume fraction of up to 1.3 %. At low loading, DMMP was very effective at reducing the CO₂ required for extinction (about a factor of two better than Br₂); however, at a volume fraction of about 4000 $\mu\text{L/L}$ to 8000 $\mu\text{L/L}$, the DMMP lost its marginal effectiveness, and further increases in X_{DMMP} resulted in no decreases in X_{CO_2} for extinguishment. In contrast, the agent Br₂ did not show this loss of effectiveness. In order to explore the possibility of particle formation as the cause of the loss of effectiveness (via sequestration of the active phosphorus-containing intermediates as inactive condensed-phase particles), laser scattering measurements in the inhibited flames were performed, and equilibrium calculations were performed. Particles were detected, however they formed outside of the flame zone, and hence are not believed to be influencing the inhibition chemistry. Similarly, the equilibrium calculations did not indicate any phosphorus species likely to condense at the in-flame conditions.

In order to explore the extinction conditions of the present flames in more detail, premixed flames simulations were performed at conditions expected to approximate those of the flame base stabilization region (which is responsible for flame extinguishment of the cup-burner flames). These simulations indicated that at the volume fraction of DMMP for which the marginal effectiveness was greatly reduced in the cup-burner flame, the peak radical volume fractions for H, O, and OH were already reduced to their equilibrium level, so that addition of further DMMP would have no additional catalytic effect.

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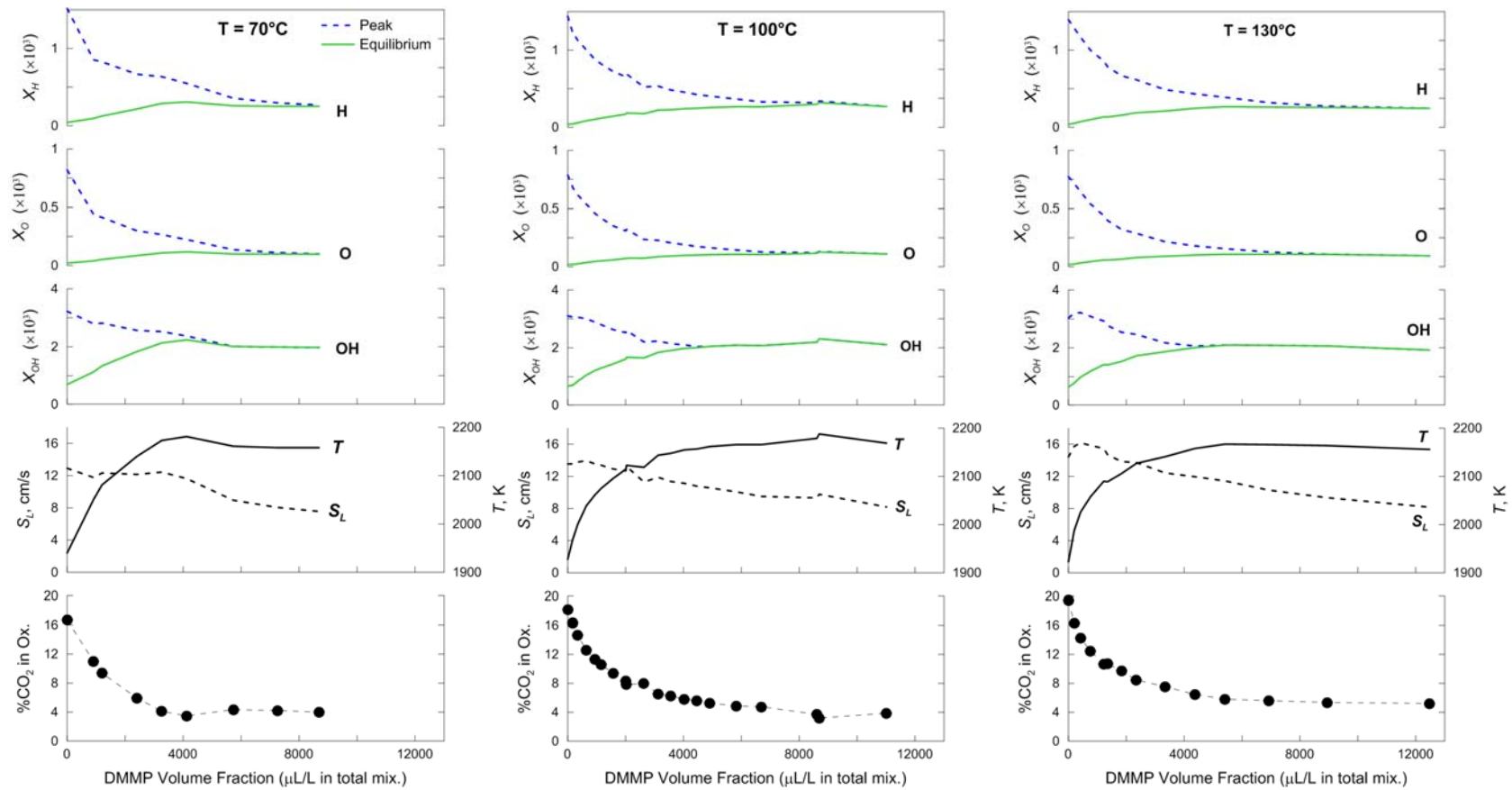


Figure 11 – Premixed flame simulation results at the extinction conditions of Figure 5 for burner temperature of 70 °C (left frame), 100 °C (middle frame), 130 °C (right frame). For each case, the following are shown (as a function of DMMP volume fraction): volume fractions of H, O, and OH, adiabatic flame temperature T_{ads} burning velocity S_L , and CO₂ volume fraction for extinction in the cup-burner (data repeated from Figure 5).

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