A COMPARISON OF THE GAS-PHASE FIRE RETARDANT ACTION OF DMMP AND Br_2 IN CO-FLOW DIFFUSION FLAME EXTINGUISHMENT

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ABSTRACT

Phosphorus-containing compounds are added to polymers as fire retardants and they are believed to act in both the gas and solid phase. In gaseous flame studies, they have been shown to be very effective gas-phase flame inhibitors; however, their performance varies with flame type. In particular, their effectiveness in co-flow diffusion flames is much lower than in other flames. To understand this behavior, co-flow diffusion flame experiments have been performed using dimethyl methylphosphonate (DMMP) added to the fuel stream. CO_2 flame extinguishing tests show that phosphorus (via DMMP addition) is much more effective (~4 times) than bromine (Br_2) at low concentrations. At higher concentrations (above ~5000 $\mu\text{L/L}$), the efficiency ranking is reversed due to saturation of the DMMP inhibition effect, which is not observed in the case of Br_2 addition. The role of particle formation (via condensation of active phosphorus-containing species) in the loss of effectiveness of DMMP is investigated using Rayleigh scattering measurements. In order to understand the behavior of the flame stabilization region that is disrupted during flame extinguishment, premixed burning velocity simulations with detailed kinetics are performed for DMMP or Br_2 addition to the flames.

KEYWORDS

Cup burner flame; Fire retardants; phosphorus; dimethyl methylphosphonate (DMMP); particle formation; Rayleigh scattering, bromine.

INTRODUCTION

Brominated compounds together with antimony oxide are widely used as fire retardants in polymers, and there is motivation in industry to find alternatives. Phosphorus compounds are

leading candidates, and they are believed to work either in the condensed phase by promoting char formation, or in the gas phase, by interfering with the normal combustion reactions. Previous work [1, 2] has studied the behavior of a phosphorus-containing compound (dimethyl methylphosphonate, DMMP, $C_3H_9O_3P$, $CH_3PO(OCH_3)_2$) in the gas phase via extinction experiments in a co-flow diffusion flame, with the DMMP added to the oxidizer co-flow. In that work, the volume fraction of CO_2 required to extinguish the flame was determined, as a function of the amount of DMMP added. This measurement is much like the limiting oxygen index (LOI) test for polymers [3] in which a diffusion flame is formed over a candle-like polymer sample, and the oxygen volume fraction at extinction (or equivalently, the amount of added N_2) is used as a measure of the flammability of the polymer (or as a measure of the effectiveness of an added fire retardant). While adding N_2 or CO_2 clearly changes the temperature and hence the chemical environment of the system, we maintain this approach in the present work for consistency with the large body of previous flame retardant work based on LOI. In addition, CO_2 addition in the present work yields non-sooting flames, which are more amenable to our laser-scattering particle measurements described below. Of course, in future work it would be of interest to explore changes in flame chemistry due to the presence of CO_2 and the reduced temperature.

In the previous work [1], DMMP was found to be very effective at reducing the amount of CO_2 required for extinguishment, about twice as effective as Br_2 at low volume fraction. As the volume fraction of DMMP increased above about 0.6 %, however, the marginal effect of additional DMMP was very small. Although particle formation was observed phenomenologically, and was suspected as being the cause of the loss of effectiveness, particle measurements in the inhibited flames implied that particle formation was not the cause (since for agent addition to the air stream, particle formation occurred far from the main reaction zone of the flame). Rather, simulations of the flame stabilization region (i.e., the reaction kernel) via premixed flame calculations indicated that the phosphorus may have lost its effectiveness because, at DMMP volume fraction around 0.5 %, radicals were driven to their equilibrium levels, so that additional DMMP had no more chemical effect on the flame.

While the results of the tests with DMMP added to the oxidizer stream are instructive, in practice, actual fire retardants are added to the fuel stream. Hence, it is of value to perform the tests with the DMMP added to the fuel stream, which is the topic of the present paper.

BACKGROUND

The gas-phase effects of phosphorus compounds in flames have been studied, primarily in simplified configurations involving gas-phase reactants (often in the context of fire suppressants). For example, using conical flames above cylindrical nozzle burners, Lask and Wagner [4] determined the quantity of inhibitor required to reduce the burning velocity of premixed hexane-air flames by 30 %. For PBr_3 , $PSCl_3$, or $PSBr_3$, a volume fraction of about 0.14 % was required, while for trimethylphosphate (TMP), about 0.25 % was required. Similarly, Miller et al. [5] found PCl_3 and $POCl_3$ to reduce the burning velocity of premixed H_2 /air flames about 2.6 and 4.1

times as effectively as CF_3Br . Fenimore and co-workers used oxygen index tests with fire-retarded polymers [6, 7] and found phosphorus compounds to be effective, and to be acting in the gas phase. Hastie and co-workers [8, 9] performed detailed measurements of premixed flame structure with molecular-beam mass sampling, and outlined the mechanism of radical recombination by phosphorus-containing intermediates in the gas phase. Twarowski developed a more detailed reaction mechanism [10, 11], which formed the basis of comprehensive kinetic modeling work [12-18]. Concurrent experimental work with premixed flames by Korobeinichev and co-workers [15, 19-22], counterflow diffusion flames by Fisher and co-workers [23-25] and co-flow diffusion flames by Shmakov et al. [20] provided additional insights into the detailed inhibition process of phosphorus compounds. The action of gas-phase acting *fire retardants* containing phosphorus is often inferred from the behavior of model phosphorus compounds added to purely gaseous flames. It has been found that the effectiveness of phosphorous compounds in gaseous flames varies widely with flame type [1]. Clearly, the flame configuration has an impact on the gas-phase action of the phosphorus compounds, and work is being conducted to understand the reasons [1, 26, 27].

The loss of active species to condensed-phase particles is a possible reason for the variation in effectiveness with flame type. This is the case for iron-based compounds for which condensation of active Fe-intermediates play a key role in their inhibition characteristics [28-30]. Particle formation has also been noticed in the course of combustion studies with phosphorous compounds [20], and it might affect the inhibition effectiveness. Previous work has measured particle formation in methane-air co-flow diffusion flames with added DMMP in the *air* stream [1] (which demonstrated the poor effectiveness). The goals of the present work are to assess the performance of DMMP when added to the *fuel* stream, and if a loss of effectiveness occurs, measure particle formation to evaluate its influence. For comparison, experiments and analyses are also conducted with Br_2 addition to the fuel stream, Br_2 being a model compound widely used to simulate brominated fire retardants.

APPROACH

The cup burner flame configuration is adopted. This configuration has been widely used in the fire research community to assess the effectiveness of various fire suppressants [31]. In its usual operation, the 38 mm diameter cup is maintained filled to its rim with a liquid fuel (typically heptane), and the fire suppressant is gradually added to the air stream until flame extinguishment is obtained. Minimum extinguishing concentration (MEC) databases have been collected for many inhibitors added to the air stream (see for instance ref. [32]), and the fuel can be varied. With gaseous fuels (as in the present work), the flame is essentially a co-flow diffusion flame, with a low velocity fuel stream that mimics the flow-field above a condensed-phase fuel.

As in refs. [20, 33], the inhibitor and inert (CO_2) are added to the fuel and the air stream, respectively. The CO_2 volume fraction for which flame extinguishment is observed is used as a

metric of inhibiting efficiency. This mode of operation has several advantages compared to the traditional cup burner tests: i/ agents that will not extinguish the flame on their own can be studied, ii/ CO_2 reduces soot formation and suppresses flame flickering which significantly facilitate investigations where detailed information on the flame structure is required (e.g. particle formation).

The phosphorus compound of interest is DMMP, a fire retardant and flame inhibitor widely studied in the past. For comparison purposes, experiments are also performed for bromine (Br_2) addition to the fuel stream. Rayleigh scattering measurements are used to assess whether particle formation occurs in flames doped with DMMP and, if occurring, determine the precise location of formation. Since flame stabilization in the cup burner is controlled by a region of peak heat release near the base (i.e. the reaction kernel) with premixed-like properties³, flame simulations are run for premixed flames with compositions corresponding to the present experiments to provide insight into the relevant flame chemistry at the measured extinguishing concentrations.

EXPERIMENT

Burner Assembly

The burner assembly (Figure 1) used for the Rayleigh scattering and flame extinction measurements is similar to that in ref. [33] and identical to that in ref. [1]. In brief, the glass cup (28 mm exit diameter), is positioned in the center of a glass chimney (95 mm I.D.). Both are fitted with glass beads (3 and 6 mm, respectively) to promote uniform velocity profiles in their exit planes. This assembly is itself located in the center of a secondary chimney (150 mm I.D.) that creates a shroud flow of air designed to minimize both perturbations in the zone of interest and recirculation of combustion products. The burner base and all gas flows are heated to the desired burner temperature (100 °C for the present results). The entire assembly, mounted on an automated three-axis translation stage, can be moved with respect to the stationary laser beam path. Further details regarding the integration of the optical diagnostic in the cup burner apparatus are given in [1].

For the present experiments with Br_2 added to the fuel stream, the fuel jet is identical to that described above. The first chimney is acrylic, 600 mm tall (instead of just slightly taller than the fuel cup), and there is no outer chimney. The burner is not heated, and is at the laboratory ambient temperature $22\text{ °C} \pm 2\text{ °C}$. Note that the normalized burning velocity reduction for methane-air flames with added bromine elements (via CF_3Br addition) is insensitive to the initial temperature for reactants at either 298K or 353K, as shown in ref. [34].

³ A detailed discussion on the relevance of premixed flame calculations to the cup burner flame stabilization problem can be found in ref. [1], p. 10-11.

FIG_1.PPTX

Figure 1 – Cup burner schematic.

Gas delivery systems

The reactant gases used in the present experiments are methane (Matheson UHP, 99.97%), carbon dioxide (MG Industries), and house compressed air. The air is filtered and dried and undergoes additional purification steps to remove small aerosols, organic vapors, and water vapor. Flow rates are set and monitored using thermal mass flow controllers that are calibrated in-house with dry piston flow meters. The gas flow rate uncertainty is estimated to be 2 % of the indicated flow. The DMMP (Sigma Aldrich, purity $\geq 97.0\%$) or Br₂ (Sigma Aldrich, purity $\geq 99.5\%$) is added to the fuel stream using a two-stage saturator maintained in a controlled-temperature water bath. The vapor pressure data for DMMP and Br₂ are taken from ref. [35] and [36] respectively, and the water bath temperature for Br₂ addition is maintained at 14.5 °C $\pm$ 0.7 °C. Variation in the DMMP volume fraction in the fuel stream are achieved by varying the water bath temperature (in the range of 70 to 90 °C), whereas for Br₂, it is achieved via two mass flow controllers: one supplying the saturator, the other bypassing it.

Optical system

The Rayleigh scattering system has been described in detail in previous work [1]. An Ar-Ion laser (500 mW at 488 nm) delivers a collimated, vertically polarized beam, and an optical chopper modulates the beam at 1.5 kHz. A single mode, polarization-maintaining fiber and dedicated coupling optics (overall coupling efficiency $\sim 20\%$) direct the beam to a chemical hood that contains the experiment. An achromatic doublet focuses the beam in the test region, which is

followed by a beam trap. A beam splitter, located after the fiber output optics, directs a portion ($\sim 4\%$) of the incident beam towards a photodiode detector to normalize for variations in the laser power [1].

The light scattered perpendicular to the incident beam passes into a circular aperture, a converging lens, a laser line filter, a 1 mm pinhole, a sheet polarizer and finally, a photomultiplier tube (PMT- Hamamatsu 1P28). A lock-in amplifier (Stanford Research 530) collects the pre-amplified (Stanford Research 552) signal from the PMT as well as the reference signal from the optical chopper. A personal computer and data acquisition board (NI USB-6281) record the analog signals from the lock-in & photodiode output. The system was tested and calibrated via Rayleigh scattering measurements of the cross sections of known gases as described in ref. [1].

Data acquisition is performed at a defined height above the fuel cup while translating the assembly laterally across the burner in small increments ($0.7\text{ mm} \pm 0.0016\text{ mm}$). At each location, scattering and reference signals are collected for $\sim 0.3\text{ s}$ at 1 kHz , divided and averaged to yield a normalized scattering value. Visual images of the flames are also recorded with a digital camera equipped with a Nikkor objective.

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: CO_2 volume fraction, 4 %, DMMP volume fraction 5.0 % (max.), and Br_2 volume fraction, 6.5 % (max).

NUMERICAL APPROACH

As described below, the Sandia PREMIX flame code [37] is used to simulate 1D, adiabatic, freely-propagating laminar flames for methane-air mixtures with added Br_2 (calculations for DMMP-inhibited flames were described previously in ref. [1] and use the kinetic mechanism proposed in [15]). For the kinetic mechanism, the Br-species reactions are taken from the recently-developed 2-BTP kinetic mechanism [38], and added to the methane-air mechanism from GRI-MECH 3.0 [39]. Both of these mechanisms have been validated against experimental data. The values of GRAD and CURV used were 0.05 and 0.10, which produced about 223 to 297 active grid points. Further refinement in the grid showed less than 1% change in S_L or the maximum radical volume fraction. The domain was 50 cm in length, and the equilibrium values correspond to the volume fractions at that location. For the thermodynamic equilibrium calculations, the Sandia EQUIL code [40] is used, with the thermodynamic databases from Goos et al. [41], Gurvich et al. [42], McBride et al. [43], and Jayaweera et al. [15].

RESULTS AND DISCUSSION

For the experiments with Br₂ addition to the fuel stream, the flow rates of oxidizer (air plus CO₂) and fuel (methane) were maintained constant, at 41.5 SLPM (standard liters per minute, at 294 K, 1.01 bar), and 0.34 SLPM, respectively. For DMMP addition, the methane and oxidizer flows in the absence of added DMMP are methane: 0.341 SLPM, and oxidizer co-flow: 44.9 SLPM, which correspond to gas flow velocities of 0.923 cm/s and 11.6 cm/s. For CO₂ extinguishing concentration tests and DMMP addition, however, the flow of methane is reduced correspondingly to maintain the total heat release approximately constant. Table 1 lists the flow conditions for the experiments. For the tests with Br₂ addition to the fuel, the run conditions are given for the extinguishment by pure CO₂ in the oxidizer stream (1st line) and for pure Br₂ in the fuel stream (2nd line); conditions for intermediate combinations of CO₂ and Br₂ fall between these. Similarly, for DMMP addition to the fuel stream, the first line gives the extinguishment conditions for pure CO₂ in the oxidizer stream. The second gives the condition for the highest amount of DMMP added to the fuel stream. Note that the experiments were not carried out to flame extinguishment with pure DMMP. Beyond the value indicated line 2, large concentrations of particles were observed in the product gases, and these would lead to experiment fouling. For Br₂ addition, the burner was operated at laboratory conditions (22 °C), and for DMMP addition, 100 °C (because of the low vapor pressure of DMMP). The final line of Table 1 shows the flow rates for the condition under which the scattering measurements were taken for DMMP addition to the fuel stream. The flame was non-flickering for this condition.

Table 1 – Run conditions for cup-burner experiments with Br₂ or DMMP addition to the fuel stream.

TABLE_1.DOCX

Typical images of the cup burner flames with the different additives are shown in Figure 2. In this figure, image b shows that the introduction of CO₂ in the air co-flow suppresses yellow emissions due to soot which is a prerequisite to perform the intended experiments. Upon addition of DMMP (image c), a bright orange color is observed which was previously identified as

resonant emission from HPO (between 500 and 600 nm) [44, 45]. Far downstream of the flame (not shown here), particles could be visually seen in the product gases, and these are believed to be condensed polyphosphoric acid H_3PO_4 (Levchik, personal communication, 2014), which is also supported by equilibrium calculations performed in ref [1] for methane air flames doped with 2% DMMP. Addition of Br_2 (image d) led to the formation of markedly thinner flames, with a bright yellow color.

Figure 2 – Images of CH_4 -air cup burner flames with: (a) no additive (neat flame), (b) 8.4 % CO_2 in the oxidizer, (c) 13 % CO_2 in oxidizer and 2.85 % DMMP in the fuel, (d) 5.8 % CO_2 in oxidizer and 7.5 % Br_2 in the fuel.

As in previous work [1, 33], the inhibitor (DMMP or Br_2) is progressively added to the reactant stream of interest (fuel side in the present case), and CO_2 is incrementally introduced in the oxidizer stream (increments of $< 1\%$ of the CO_2 flow) until blowoff occurs. The inhibitor concentration in the fuel is increased, and the process repeated. For the air stream addition (previously studied), the amount of CO_2 required for flame blowoff was found to drop rapidly for DMMP volume fractions below 0.1 %, and in this range, DMMP was about four times as effective as Br_2 . At volume fractions of DMMP in the fuel above $\sim 0.7\%$, however, DMMP rapidly lost its effectiveness so that further addition had little influence on the CO_2 extinguishing concentration (which remained near 4 %). This behavior is in marked contrast to Br_2 (or CF_3Br [46]), for which the marginal effectiveness, although decreasing at higher inhibitor concentration, does not go to zero and the flame can be extinguished by CF_3Br or Br_2 alone.

Figure 3 shows the equivalent results for DMMP or Br_2 addition to the fuel stream. As indicated in the left frame, at low volume fraction, DMMP is much less effective when added to the fuel stream as compared to the air stream. As with the air-side addition, fuel-side addition leads to saturation in the inhibition effect. Above 1 % volume fraction of DMMP, there is very little marginal effect on the CO_2 concentration for extinguishment and a plateau occurs at $\sim 14.5\%$ CO_2 in the oxidizer stream. In contrast, the right frame of Figure 3 shows that Br_2 does not lose

its effectiveness at higher concentrations, and extinguishes the flame at a fuel-stream volume fraction of 13.6 %.

Figure 3 – Methane-air cup burner extinction volume fraction of CO₂ in oxidizer stream vs. agent volume fraction in the fuel stream (left frame: DMMP addition, burner temperature 100 °C; right frame: Br₂ addition, burner temperature 22 °C).

Much of the reason for the required higher concentrations in the fuel stream is due to the stoichiometric conditions for methane and air. As described previously [48], for lifted flames near blow-off, the transport of the oxidizer gases to the reaction kernel is dominated by convection. To first order, the local concentration of an agent expected at the reaction kernel will be controlled by the stoichiometric air requirement. Thus, the fuel stream volume fractions of the agents (DMMP and Br₂) can be converted to an equivalent air stream volume fraction by dividing the fuel stream value by the stoichiometric ratio of air-to-fuel in the flame. The conversion factor equals 9.5 for a methane–air flame, and ranges from 9.5 to 9.9 and 7.9 to 9.1 for the DMMP-methane-air and Br₂-methane-air flames respectively. Accordingly, data in Figure 3 are re-plotted in Figure 4 in terms of the *equivalent* air-stream volume fraction of the agent. Also shown are the actual air-stream volume fraction of agent from refs. [1, 33] (i.e., the actual and equivalent air stream volume fractions are the same for air-stream addition). As indicated, DMMP behaves differently when added to the air or fuel streams, while for Br₂, air-or fuel-stream addition are comparable, with air-side addition somewhat more effective. To explore these differences, particle measurements in the flame are described below.

Figure 4 – Extinction volume fraction of CO₂ in oxidizer stream vs. volume fraction of DMMP (left frame) or Br₂ (right frame) in the oxidizer stream (*equivalent* value when added to the fuel stream, *actual* value when added to the air stream).

Since DMMP itself is flammable, a loss of effectiveness with its addition to the air stream might be related to the heat release from DMMP reaction itself (as alluded to in ref. [20]). Moreover, as discussed previously [23, 47], the oxygen demand of the agent can cause a consequent movement of the reaction kernel in the flow field to a region of different strain, affecting the extinction volume fraction. However, the effectiveness change is occurring at fairly low DMMP concentration (<0.2 % in oxidizer) and in this range, the heat release from the DMMP combustion is less than 5% of the total heat release, in turn suggesting that this “fuel effect” is negligible. Of course, when added to the fuel stream, this effect is not relevant, yet the loss of effectiveness of DMMP is even more apparent for fuel-stream addition.

The behavior for DMMP discussed above is reminiscent of that observed for metallic compounds [33], for which diminished marginal effectiveness occurred for iron, manganese, and tin compounds at higher loadings. This loss of effectiveness has been investigated for FeCO₅ addition [30], for which particle formation was responsible for this saturation effect. Condensation of iron-containing intermediates (e.g. FeO) to particles deprives the system of the active gas-phase iron species that are part of the radical scavenging catalytic cycle, thereby limiting the inhibition process. Since particles are observed in the present experiments with added DMMP, were reported in earlier work [1, 20], and previous equilibrium calculations showed the possibility of condensation of some phosphorous species (H₃PO₄ (L), P₄O₁₀ (L) and P (L)) [1], their formation is described below.

To assess the importance of particle formation in cup-burner flames with DMMP added to the fuel stream, Rayleigh scattering measurements were first performed in a neat methane-(air+CO₂) flame (Figure 5, left frame) and then in an inhibited methane-(air + CO₂) flame with 2.85% DMMP in the fuel stream (see Figure 5, right frame). Figure 5 shows the scattering signal as a function of the radial distance from the burner centerline, with each curve representing one distance above the burner (5 mm, 15 mm, and 25 mm). The scattering signal is normalized by the laser power, and then by the scattering at large radii (i.e., from the scattering from the clean co-flow gases of the oxidizer stream). Rayleigh scattering signals for the undoped case (left frame) display the expected variations: moving from large radii to smaller, the signal decreases near the high-temperature reaction zone of the flame (15 mm > |y| > 8 mm) where gas density decreases, and then increases in the central region |y| < 8 mm), where the temperature is lower (at low heights) and cross section is larger (from the methane as compared to air/CO₂ mixtures). Results obtained for DMMP addition in the fuel stream (right frame) are not significantly different from those for the neat flames (left frame). The scattering signal decrease mentioned previously at 15 mm > |y| > 8 mm is less evident here, due perhaps to a broadening of the reaction zone, and the higher scattering cross section of DMMP as compared to methane. The spurious three sharp peaks for z = 25 mm and one peak for z = 15 mm are believed to be due to recirculation of particles formed downstream of the flame.

Figure 5 – Radial profiles of normalized Rayleigh scattering signal at different heights above the burner (T = 100 °C). Left frame: neat methane-air cup-burner flame (baseline), right frame: with added DMMP (same conditions as in Table 1). Numbers indicate the height above the fuel cup exit plane at which data was acquired.

The results shown in Figure 5 (right frame) for fuel-side addition are significantly different from those reported in [1] for air side addition. Both datasets are plotted in Figure 6 for comparison. For the air-stream DMMP addition (gray dotted lines), the burner and inlet gases were maintained at 70 °C, and the oxidizer stream had 1035 µL/L DMMP and 8.4 % CO₂ by volume; As indicated, the scattering signal was found to peak at a radial distance from the burner centerline of about 14 mm, and the magnitude of the peak at the highest height (36 mm) was

about 60 times that of the 70 °C air. This clearly confirmed particle formation. Results for DMMP added to the fuel stream (burner at 100 °C, and the fuel stream had 2.85 % DMMP and the oxidizer stream, 13 % CO₂ by volume) are the black continuous lines in Figure 6. It can be seen that there is no coherent increase in scattering signal with DMMP addition. This suggests that, for the fuel side addition case, particles observed during the experiment are formed only further downstream of the flame, hence these are not likely to play an active role in the flame inhibition chemistry. A similar conclusion was reached for the air side case by considering signal peak locations with respect to the actual flame reaction zone position (shown by the gray dots in Figure 6): particle locations were found to be about 2 to 5 mm away from the reaction zone. Given the results shown in Figure 4 and Figure 6 it seems legitimate to rule out the role of particle formation as a reason for the lowered marginal effectiveness of DMMP at higher loadings.

Figure 6 – Radial profiles of scattered light; black continuous lines: DMMP fuel side addition ($T_b = 100$ °C, 2.85 % DMMP in fuel stream, 13 % CO₂ by volume in oxidizer stream), gray dotted lines: DMMP air side addition, data from [1] ($T_b = 70$ °C, 1035 μ L/L DMMP and 8.4 % CO₂ by volume in air stream). Gray dots indicate the flame location (outer luminous zone) for the air side addition (ref. [1]).

To better understand the differences in the flame extinction behaviors shown in Figure 4 for DMMP and Br₂, premixed flame simulations were performed. As discussed in previous work [46, 48, 49], cup burner flame stability is related to the properties of the reaction kernel (region of peak heat release) formed at the flame base. For lifted flames (especially near extinguishment), the structure of this kernel is similar to that of a premixed flame propagating against the incoming flow. To examine how the flame chemistry in the reaction kernel near extinguishment changes as a function of DMMP loading, the locus of points along the extinguishment curve in Figure 4 (oxidizer side addition) provide the initial mixing conditions for the premixed flame simulations. The air-side reactant concentrations are used since transport to the reaction kernel is dominated by convection for the air stream, so that the quantity of inhibitor is more easily quantified for air-side addition than for fuel-side [48]. Additional details regarding the procedure are given in ref. [1].

Figure 7 shows the results of these calculations. For comparison, the left frames give the results for DMMP addition ($T_{burner} = 100$ °C – results previously reported and discussed in [1]), while the right frames give the results for Br₂ addition ($T_{burner} = 21$ °C). Each set of results give the peak (dotted lines) and equilibrium (solid lines) volume fractions of H, O, and OH radicals in the flame; the burning velocity S_L and temperature T ; and the extinction boundary (bottom graphs; data repeated from Figure 4). As shown and discussed previously [1], a key finding for DMMP was that at the DMMP volume fraction for which the marginal burning velocity reduction becomes small (4000 µL/L), the catalytic radical recombination cycles have driven radical concentrations to their equilibrium values, so that additional flame inhibition by the catalytic cycles is not possible, explaining the saturation effect in the flame inhibition by DMMP. That is, additional DMMP has little effect in the flame because radicals have already been driven to their equilibrium levels. It is of interest to determine if Br₂ addition has the same effect on radicals.

The results for Br₂ addition (Figure 7, right frames) are significantly different. As either DMMP or Br₂ is added, the amount of CO₂ required decreases, increasing the peak flame temperature. With DMMP addition, however, the decrease in required CO₂ for extinguishment and consequent increase in temperature is faster at low loadings (due to the stronger catalytic cycle of phosphorus compounds) as compared to the case of Br₂ addition. Consequently, the equilibrium levels of radicals (which rise with temperature) rise somewhat more slowly with Br₂ addition than with DMMP addition. More important is the difference in peak radical volume fractions. Despite the more rapid increase in temperature with DMMP addition, the peak radical volume fractions decrease much faster with DMMP than Br₂, due to the stronger catalytic cycle of the phosphorus compounds. Most important, Br₂ addition alone can extinguish the flames, and at volume fraction of Br₂ which extinguishes the flame without added CO₂ ($X_{Br_2} = 0.0154$), the marginal effect of Br₂ is still good. Interestingly at this condition, the peak radical volume fractions (top three frames on the right half of Figure 7, dotted lines) are still not lowered to the

equilibrium volume fractions (solid lines) as they were with DMMP when it lost its marginal effectiveness.

Figure 7 – Premixed flame simulation results at the extinction conditions of Figure 4 for DMMP addition to the air stream, with burner temperature at 100 °C (left frame – from ref. [1]), or Br₂ addition to air stream, at 21 °C (right frame). For each case, the following are shown (as a function of inhibitor volume fraction): volume fractions of H, O, and OH (dotted line: peak, continuous line: equilibrium), adiabatic flame temperature T_{ad} , burning velocity S_L , and the required CO₂ volume fraction in oxidizer stream for extinction in the cup-burner (X_{CO_2} data repeated from Figure 4).

While the above results which treat the reaction kernel as a premixed flame are interesting and informative, they are only approximations. The actual reaction kernel represents a region of peak reaction that has a range of stoichiometry over a narrow spatial region [48], and is strongly influenced by flow field. Note here that large additions of DMMP (a fuel-like species) and Br₂ (strong oxidizer) in the fuel stream will respectively move the reaction kernel to larger/smaller radii. This can be seen in the flame images shown in Figure 2. Flame blowoff is expected to be strongly dependent on the flame kernel location and its surrounding flow field. These complex effects cannot be captured and understood on the basis of 1D simulations. Direct numerical simulation of the flames with full chemistry would be very helpful for understanding the reasons for the limiting effectiveness of phosphorus additives. These would be especially helpful since

similar calculations for a cylindrical configuration like the UL94 test [50, 51] (as widely used standard test for fire retardant effectiveness) are possible as a logical extension of the present results for co-flow diffusion flames, and would shed light on the mechanisms acting in flame extinguishment of the UL-94 tests.

CONCLUSIONS

In order to study the gas-phase flame inhibition properties of commonly added phosphorus-based fire retardants, DMMP was added to the fuel stream of a co-flow diffusion flame (cup-burner) of methane and air. As in other work in the literature, the metric for gas-phase effectiveness was the volume fraction of CO_2 in the oxidizer stream necessary to extinguish the flame. Experiments were performed for DMMP volume fraction in the fuel stream of up to 3.6 %. At low loading (volume fractions less than 1 %), DMMP was effective at reducing the CO_2 required for extinction (about a factor of two better than Br_2); however, above this concentration, the marginal effectiveness of DMMP was greatly reduced. Comparisons of fuel-side addition with previous results for air-side addition showed that the lower marginal effectiveness was much more pronounced for fuel-side addition than air-side.

Since particles have been observed in flames inhibited by phosphorus, and particle formation has been associated with loss of gas-phase active flame inhibiting species, laser scattering measurements were made in the present flames to explore the role of particle formation in the loss of effectiveness of DMMP. While previous works performed for air-side addition found particle formation to occur in the cup burner flames (albeit outside the flame reaction zone), no evidence of particles (formed in the vicinity of the flame) has been found for fuel side addition of DMMP. Thus particle formation is not expected to be the cause of the loss of effectiveness in the cup burner flames inhibited with DMMP, for either air-side or fuel-side DMMP addition.

For comparison, experiments were also conducted for Br_2 addition to the fuel stream, since brominated species are very commonly used in fire retardant formulations. Added Br_2 in the fuel did not show a loss of effectiveness (as has been found previously for Br_2 addition to the oxidizer stream), and the extinction curves for the fuel and oxidizer side addition of Br_2 were found to be comparable.

The present flames are extinguished via destabilization of the flame base. Since the peak reaction zone (the reaction kernel) is in some ways similar to a premixed flame of near-stoichiometric mixtures of the reactants, premixed flame modeling studies of the mixtures (at the extinction conditions) were used to understand the relevant flame chemistry near extinguishment. Previous studies showed that for the phosphorus-inhibited flames, very small volume fractions of DMMP (about 0.5 %) reduce the chain-carrying radical super-equilibrium to equilibrium levels, and this DMMP concentration matches that above which there is the lowered marginal effectiveness. Hence, the lowered marginal effectiveness may be due to very effective radical recombination by the phosphorus catalytic cycles.

In contrast, premixed flames calculations for the extinguishing conditions of the flames with added Br₂ showed that at the extinguishing volume fraction of Br₂, the marginal effectiveness of Br₂ was not drastically reduced and the radicals were not yet driven to the equilibrium conditions, yet the flame extinguished none-the-less. Hence, further research is necessary to unravel the much lower lowered effectiveness of added DMMP in the fuel stream as compared to the air stream (not observed with Br₂), and the reasons why Br₂ is so effective, despite significant radical super-equilibrium even at the extinguishment condition with pure Br₂. It is expected that detailed numerical modeling of the flame structure of the inhibited flames will be useful. The present results are relevant to fire retardant applications since the mechanism of flame extinguishment for co-flow diffusion flames is very similar to that of standard test methods, which resemble diffusion flames attached to cylinders.

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Table 1 – Run conditions for cup-burner experiments with Br₂ or DMMP addition to the fuel stream.

Measurement	Burner Temp. (°C)	Gas Flows (L/min @ 294 K, 1.01 bar)					
		Methane	Oxidizer (co-flow)	Shroud (2 nd co-flow)	Br ₂	Air	CO ₂
Extinction	21	0.341	41.4	-	0	34.9	6.50
Extinction	21	0.332	41.6	-	0.0523	41.6	0
					DMMP	Air	CO ₂
Extinction	100	0.341	44.9	48.5	0	36.5	8.53
Extinction	100	0.303	44.9	48.5	0.01100	38.4	6.50
Scattering	100	0.341	44.9	53.9	0.00999	39.1	5.83

Fig 1

Fig 2

Fig 3 left

fig 3 right

fig 4 left

Fig 4 right

Fig 5 left

Fig 5 right

Fig 6

Fig 7 left

Fig 7 right