Inhibition of Non-Premixed Flames by Dimethyl Methylphosphonate

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Phosphorus-containing compounds are suggested as a viable alternative to current, ozone-destroying, fire-suppressing agents. An opposed-jet burner apparatus was used to study the effectiveness of one such compound, dimethyl methylphosphonate (DMMP). A global extinction strain rate was found for a range of DMMP loadings, using nitrogen as an inert additive for reference. A novel technique for measuring the extinction strain rate while maintaining a constant dopant level in one gas stream is discussed. Results demonstrate that when DMMP is introduced with the oxidizer, it is a significant inhibitor of non-premixed methane-air flames, approximately 40 times more effective than nitrogen on a molar basis. It was found that the extinction strain rate decreased linearly with the mole fraction of DMMP for loadings up to 1500ppm.

Introduction

In accordance with the Montreal Protocol, the US government has recently banned the manufacture of CF_3Br, a prevalent fire-suppressing agent, due to its deleterious effect on the ozone layer. Consequently, there is tremendous interest in chemically active fire-suppressant alternatives, including phosphorus-containing compounds (PCCs). It is thought [1,2] that phosphorus-containing radicals, such as HOPO and $HOPO_2$ (formed from PCCs during combustion) catalytically recombine the important combustion radicals, H and OH, slowing the overall reaction rate and thus inhibiting the flame. Several mechanisms for the catalytic cycle resulting in $H + OH \rightarrow H_2O$ and $H + H \rightarrow H_2$, have been suggested [1,2]. Experiments have shown increased recombination rates of OH with the addition of PCCs [1].

A non-premixed methane-air flame has been used to study the inhibiting effects of one PCC, dimethyl methylphosphonate (DMMP), $[P(=O)(CH_3)(OCH_3)_2]$. Experiments were performed in an opposed-jet burner apparatus. The counter-flow configuration is useful for studying flame-suppressing agents because the flame is thermally isolated and two dimensional [3-5]. The flame strength can be characterized by the local strain rate at extinction, which is well defined in this geometry and equal to the axial velocity gradient, measured just upstream of the flame along the center line. Results from asymptotic analysis of non-premixed flames in this geometry [6] relate this extinction strain rate to an overall reaction rate in terms of parameters such as temperature and species concentration at the fuel and oxidizer inlets, and heat of reaction. Thus, for low additive loadings, decreases in extinction strain rate can be interpreted as chemical inhibition, i.e. as the lowering of the overall reaction rate by the additive[7-9].

During an extinction measurement, reactant flow rates are slowly increased until the flame abruptly extinguishes. For flame-suppressant compounds that are liquids at room temperature, such as DMMP, there are practical difficulties in establishing and maintaining constant loadings of the inhibitor as the flow rates are adjusted. A novel technique for performing extinction measurements is presented herein which provides a practical method for achieving constant inhibitor loadings.

Reported here are results of an initial study of DMMP as a flame suppressant. Addition of DMMP to both the oxidizer and the fuel side are considered. Inert dopant tests using nitrogen as an additive were conducted for reference. Comparisons are also made to work by other researchers studying halogenated compounds and iron pentacarbonyl $[Fe(CO)_5]$ as flame suppressants in the same geometry [10].

Experimental

Experiments were conducted on an opposed-jet burner, shown schematically in fig 1. Methane was used as the fuel and air as the oxidizer. These conditions allow for non-premixed flames to be stabilized on the oxidizer side of the stagnation plane. The burner was constructed from glass tubes 30 cm long with an ID of 0.95 cm, and a separation distance of 0.95 cm between opposing nozzles. Annular sheath flows of nitrogen are provided through 2.22 cm ID glass tubes. The sheath tube exits were offset by approximately 1 cm, upstream of the reactant tube exit, to minimize the impact of the sheath flow on the development of the reactant flows. The entire burner is

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Proceedings of the 1997 Technical Meeting of the Central States Section of the Combustion Institute

isolated in a glass enclosure for control of exhaust gases. This enclosure is purged with nitrogen and maintained slightly below atmospheric pressure.

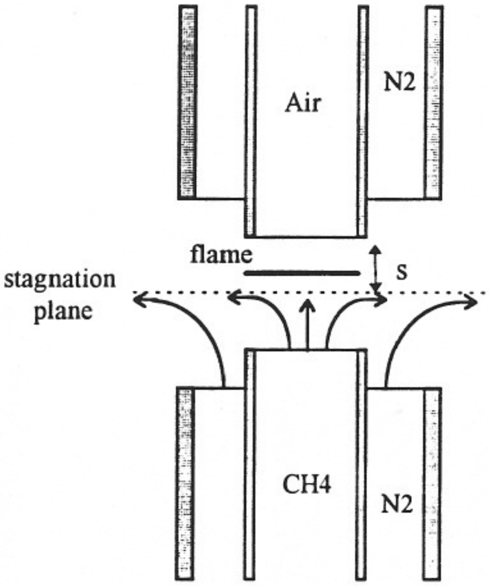

Figure 1. Schematic diagram of opposed-jet burner apparatus.

The flame suppressant under investigation in this work, DMMP, is a liquid at room temperature with a low vapor pressure (less than one torr at ambient temperature). In order to maintain sufficient concentrations of DMMP in the vapor phase, the reactant lines were heated to approximately 100°C with electrical heating tapes. The temperature of the reactant streams 10 cm upstream from the exit of the nozzles was maintained at 100±1°C via active heating control of the sheath flow. This method of reactant temperature control was found to give short settling times and stability of the reactant temperatures during testing.

There are two common methods for determining the extinction strain rate in flame measurements: direct measurement of the local strain rate using techniques such as Laser Doppler Velocimetry (LDV), or estimation of the strain from global parameters. For our experiments, the extinction strain rate was estimated using the latter method and will be referred to as the global strain rate, a_q. Williams [11] proposes the following relation for evaluating the global strain rate:

$$a_q = \frac{2V_{ox}}{L}\left(1+\frac{V_{fuel}\sqrt{\rho_{fuel}}}{V_{ox}\sqrt{\rho_{ox}}}\right) \qquad (1)$$

This equation is derived assuming a uniform velocity profile across the exit planes of the nozzles. In equation 1, L refers to the separation distance between the nozzles. V is the stream velocity and ρ is the stream density. Equation 1 evaluates the strain rate at the stagnation plane for a nonreactive flow. This global strain rate is used as an approximation to the local strain just upstream of the flame surface for flames near extinction.

All testing of DMMP was performed using the lower tube as the fuel source and the upper tube as the oxidizer source. A few experiments were conducted with the reverse orientation to study the effect of buoyancy. No change in global extinction strain rate was observed.

Methodology

One of the few practical methods of delivering small, metered quantities of liquid dopants, such as DMMP, to the reactant stream is via a syringe pump which provides a constant mass flow of the compound. Previous extinction studies using opposed-jet burners have adjusted the strain rate by varying both the oxidizer and fuel streams simultaneously so that the flame position remains constant [8], or so that a momentum balance between the two streams is maintained [9]. These methods of approaching extinction would result in variable concentrations of the inhibiting agent, due to the changing mass flow of the reactant stream and the resulting transients in the adsorption/desorption of the agent on walls. During our experiments, the concentration of DMMP in the reactant stream was fixed by maintaining a constant reactant flow for sufficient time for the system to reach equilibrium. Then extinction conditions were approached by varying the undoped stream flow rate while maintaining a constant flow on the doped side. One of the consequences of using this novel technique for approaching extinction is that the flame position varies during the extinction experiment. An investigation was conducted to determine the effect of flame position on the global extinction strain rate.

Figure 2 shows results from experiments performed with methane and air which demonstrate that a_q varied less than ±2% over a range of flame positions, referred to as the acceptable region. The distance from the exit plane of the oxidizer nozzle to the stagnation plane, S, was chosen as the independent variable instead of the actual flame location because it can be estimated with the following expression from a momentum balance between the reactant streams [11],

$$S = L \Bigg/ \left(1+\frac{V_{fuel}\sqrt{\rho_{fuel}}}{V_{ox}\sqrt{\rho_{ox}}}\right) \qquad (2)$$

For a fixed local strain rate field, the flame will lie at a

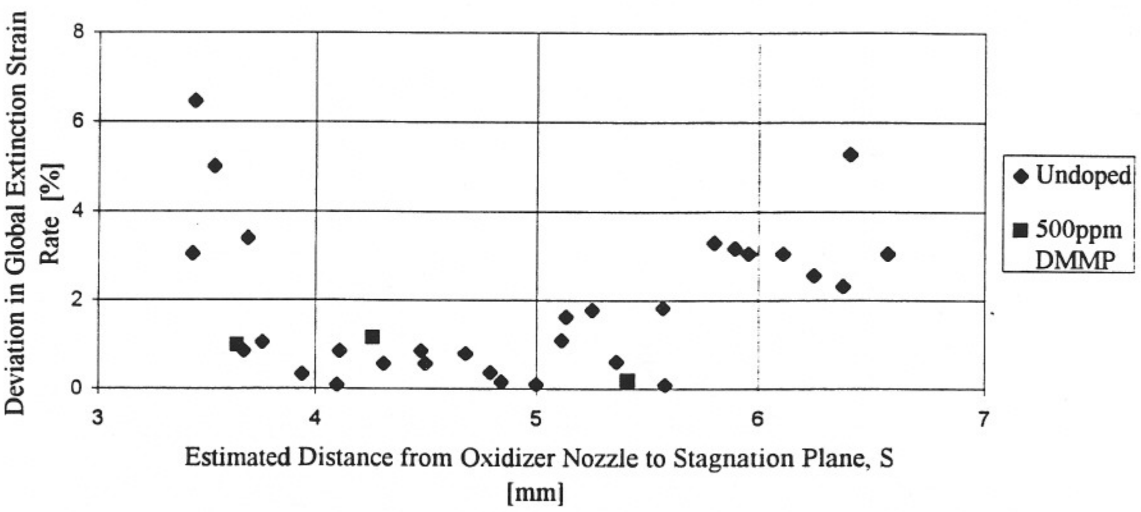

Figure 2. Percent deviation of global extinction strain rate from its mean value in acceptable region. The acceptable region, where deviations are less than 2%, falls where S is between approximately 3.75 and 5.75 mm.

fixed location relative to the stagnation plane; this distance is controlled by the local strain rates (i.e. the velocity field), the diffusivities of the reactants and their concentrations at the inlets.

For experiments in which extinction occurs with the stagnation plane location, as estimated using equation 2, outside the acceptable region, large deviations in a_q occur. We attribute these deviations to influences of the nozzles on the flmae and mixing layer. For experiments in which extinction occurs in the acceptable region, the magnitude of a_q is consistent to within 2% of the result that would be obtained maintaining a fixed flame position while approaching extinction. A limited number of experiments with DMMP-doped flames confirmed that the region in which a_q was invariant with S was the same as that for the undoped case. The existence of this acceptable region establishes the validity of our method for approaching extinction with a constant oxidizer flux and dopant concentration, provided the value of S at extinction falls within that region.

Results and Discussion

Initial tests were conducted with reactant streams at ambient temperature to compare results from our experimental apparatus with those of other researchers. For undiluted methane burning in air, our measured global extinction strain rate is 296 s^{-1}. This value is comparable to the value found by Puri and Seshadri [9] of 280 s^{-1}, and both of these values are lower than the local strain rates directly measured by other authors using LDV, which vary from 340 to 400 s^{-1} [4,8,12]. A similar discrepancy is seen in global and local extinction strain rates obtained in a single experiment. Papas et al. [12] report LDV measurements of a local extinction strain rate of 400 ± 25 s^{-1}. Using equation 1 with their reported flow data and geometry, we compute a significantly lower global extinction strain rate of 255 s^{-1}. There is also an observed variation in the literature of ±30 s^{-1} for extinction strains measured on different experimental apparatus, which is attributed to variations in specific burner geometry[9]. Numerical predictions of local extinction strain rates give a similar range of values (354 to 544 s^{-1}) depending on the choice of constants used to evaluate the elementary reaction rates [5].

When the reactant streams were preheated to 100°C, the measured value for a_q increased to 431 s^{-1}. There was some scatter, ±15 s^{-1}, in this value over the course of this investigation which is attributed in part to variations in the purity of methane in different cylinders used as fuel sources. Therefore, results presented in this section have been normalized to a reference, methane-air extinction measurement for the appropriate bottle of fuel.

Figure 3 shows our results for methane-air flames doped with DMMP, with the DMMP addition to the oxidizer stream. Each data point in figure 3 represents the average of at least three measurements. The global extinction strain rate is observed to decrease linearly with DMMP mole fraction. Experiments indicate that at a mole fraction of 1500ppm, a_q is reduced by 35% of the undoped value. Detectable inhibition (~3% reduction in a_q) is found at loadings as low as 100ppm. For mole fractions below 100ppm, preheating of reactants was not necessary to prevent condensation of DMMP. This allowed for ambient- temperature testing of low DMMP

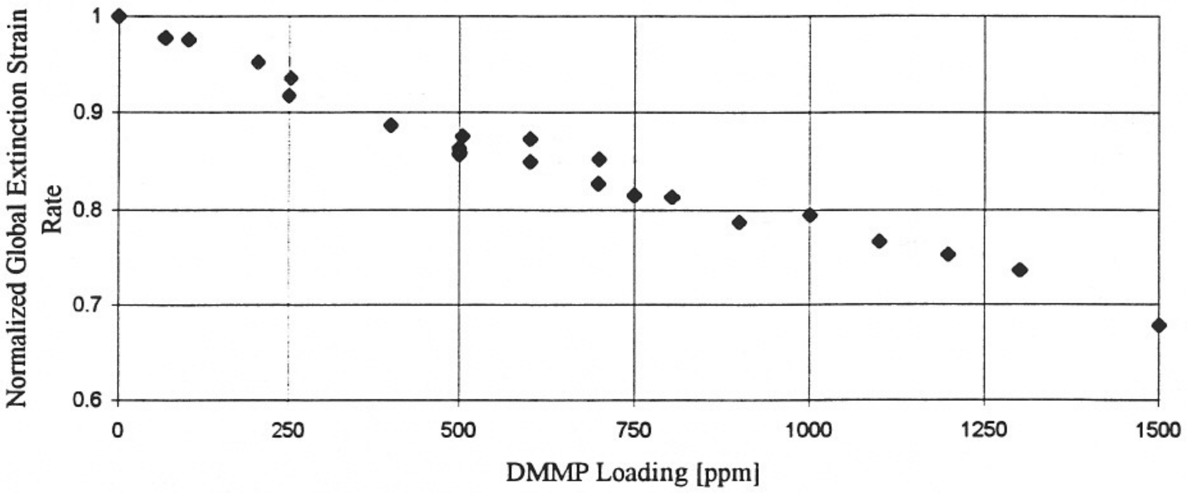

Figure 3. Global extinction strain rate for methane-air non-premixed flames doped with DMMP on oxidizer side. Data normalized to undoped strain of 431 s^{-1}.

loadings which demonstrated suppression effectiveness that was similar to the preheated experiments. The results from figure 3 show inhibition by DMMP that is roughly four times stronger than that reported in the literature for CF_3Br, the current agent in many suppression systems [13]. On a molar basis, DMMP is ~26 times more effective than literature values for CF_4 [12]. Although Fe $(CO)_5$ is a stronger inhibitor at lower loadings, its effect as a suppressant plateaus, in the range of observed loadings, for mole fractions over 500ppm. giving DMMP a similar effectiveness at 1500ppm [10]. For further comparison, tests were conducted using nitrogen as an inert suppressant, both with and without preheating the reactants. Results from these tests, shown in figure 4, indicate that preheating of the reactants has no influence on the effectiveness of nitrogen as a suppressant. The reduction in normalized global strain rate for nitrogen- doped flames agrees to within 2% with

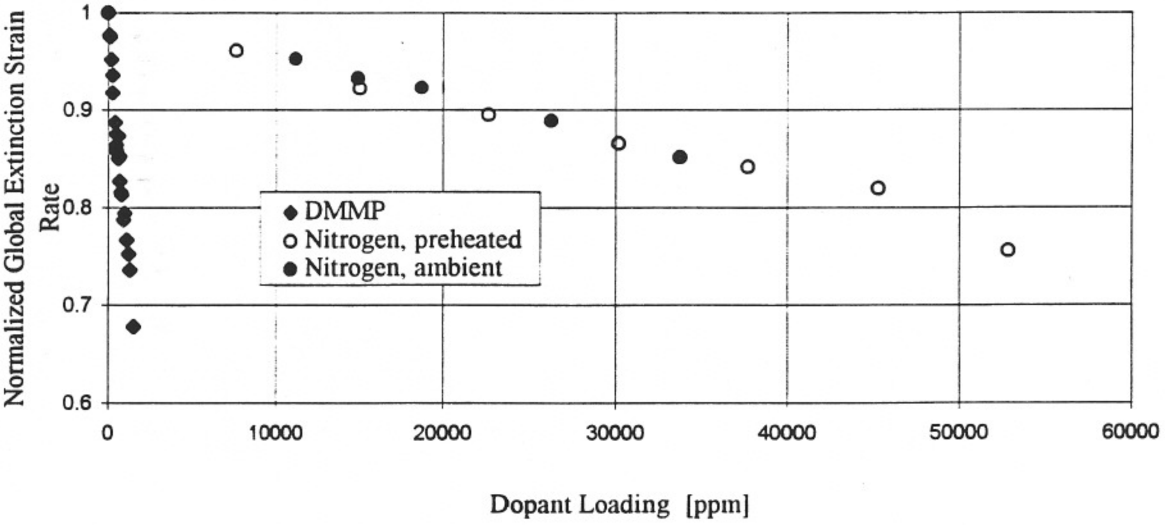

Figure 4. Global extinction strain rates of inhibited methane-air, non-premixed flames doped on oxidizer side. Data normalized to undoped strain of 431 s^{-1} for DMMP, 409 s^{-1} for nitrogen with reactants preheated to 100°C and 296 s^{-1} for nitrogen with ambient temperature reactants.

the results of Puri and Seshadri [9]. Furthermore, these results demonstrate that DMMP is approximately 40 times more effective on a per mole basis than nitrogen (9 times as effective on a per mass basis).

Tests conducted with DMMP addition to the fuel side showed a negligible (within experimental scatter) effect over the range of fuel side loadings achievable with our current experimental apparatus (0-900ppm). This is an expected result with the flame positioned on the oxidizer side of the stagnation plane. In this position the bulk of the DMMP added to the oxidizer stream passes through the flame front, while DMMP added to the fuel side must diffuse, with the fuel, through the product region to reach the flame. Since the concentration of methane at the flame is roughly 10% of its value in the fuel jet, it is likely that for DMMP, which is a larger and heavier molecule and probably has a lower diffusivity, even less than 10% of its initial concentration will reach the flame.

One of the major obstacles to the use of DMMP as a fire-suppressing agent is the compound's low vapor pressure at ambient temperature (<1 torr). The maximum loading achievable at ambient temperature is just under 100ppm. DMMP also has a significant heating value due to the one methyl and two methoxy groups attached to phosphorus atom. Further studies in flame suppression by PCCs will investigate alternative forms of the parent compound that might be more amenable for delivery to the flame.

Conclusions

The present study used an opposed-jet burner configuration to investigate the effectiveness of dimethyl methylphosphonate (DMMP) as a flame suppressant. A new method for performing extinction measurements was developed to maintain constant DMMP loadings in the oxidizer stream using a syringe pump. This new method is shown to give consistent and repeatable results. The global extinction strain rates are estimated in terms of the flow rates of fuel and oxidizer. It has been found that the global extinction strain rate is approximately invariant (within ±2%) over a range of stagnation plane locations for methane-air non-premixed flames.

Global extinction strain rates were measured for flames doped with DMMP loadings from 0 - 1500 ppm. As a flame suppressant on a molar basis, DMMP was found to be 40 times more effective than nitrogen and approximately four times more effective than the literature values for CF_3Br. The high level of effectiveness of DMMP (35% reduction in global extinction strain rate at 1500ppm) encourages the investigation of other phosphorus-containing compounds as alternatives to halogenated fire suppressants. Further research is also suggested to elucidate the consistent differences found in the literature between global strain rate estimates and true local strain rates measured by in-situ techniques.

Acknowledgments

This research is part of the Department of Defense's Next Generation Fire Suppression Technology Program, funded by the DoD Strategic Environmental Research and Development Program under DARPA contract MDA972-97-M-0013. Additional support was provided by the Army Research Office, under contract number DAAL03-92-G-0113. The authors wish to thank J. Fleming and B. Williams at Naval Research Laboratory for useful discussions.

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