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VARIATION OF CHEMICALLY ACTIVE AND INERT FLAME-SUPPRESSION EFFECTIVENESS WITH STOICHIOMETRIC MIXTURE FRACTION

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The need to find alternative fire suppressants has motivated experiments to determine the mode of action of possible candidates. An opposed-jet burner was used to characterize the effectiveness of one possible alternative, dimethyl methylphosphonate (DMMP). Similar tests were done with an inert compound, argon, for comparison. Flame strength was characterized by the extinction strain rate. Experiments included both oxidizer-side and fuel-side doping of methane-nitrogen versus oxygen–nitrogen flames of various compositions. The stoichiometric mixture fraction (Z_{st}) is varied systematically while holding the undoped extinction strain-rate constant, by changing the amount of diluent in the reactant flows. This moves the flame location with respect to the stagnation plane, affecting the fraction of a particular reactant stream that reaches the flame. Measured effectiveness of fuel-side and oxidant-side doping versus Z_{st} reflects this change in quantity of dopant reaching the flame. To account for this dependence on quantity, effectiveness was normalized by the amount of dopant calculated to reach the maximum temperature contour of the flame. Argon's normalized effectiveness was found to be independent of Z_{st}, of adiabatic flame temperature, and of whether the oxidizer stream or the fuel stream is doped. DMMP's normalized effectiveness, however, was observed to be significantly greater when introduced in the oxidizer, rather than fuel, stream. It also exhibits a marked dependence on adiabatic flame temperature, with lower values at higher temperatures.

Introduction

Restrictions on the production of the fire suppressant CF_3Br have spurred interest in finding effective ozone-friendly replacements for it. Extinction measurements in opposed-jet diffusion flames [1–6] and laminar and turbulent coflow flames [7,8] have been used to test the effectiveness of CF_3Br and candidate replacements and to shed light on their mechanisms of action. Oxidant-side doping of pure fuel versus pure air flames is the most relevant configuration for fire-fighting applications. Fuel-side doping is also of practical interest for compounds that are used as flame retardants in plastics [9]. Several studies [1,2,7] of both fuel-side and oxidant-side doping of various fuel-inert versus oxygen-inert flames have found dramatic changes in additive effectiveness with these changing conditions.

A key factor affecting suppression is the amount of the additive reaching the non-premixed flame [1,2,6–8]. When hydrocarbons are burned in air, the stoichiometric contour, where the flame is assumed to be, is situated on the oxidant side of the stagnation plane. Fuel-side additives must diffuse across the stagnation plane to reach the flame, while air-side additives are convected through the flame. The result is that fuel-side additive mole fractions at the flame are substantially reduced from their fuel-stream values, while oxidizer-side additive mole fractions are only slightly reduced from their oxidizer-stream values. The extent of this additive loading reduction at the flame location varies with the stoichiometric mixture fraction (Z_{st}), defined as the mass fraction of material originating from the fuel stream at the location where the concentrations of reactants are in stoichiometric proportions. For hydrocarbon-air flames, Z_{st} is typically <0.1. Considerably different values of Z_{st} can be achieved by varying the compositions of the fuel and oxidant streams, either via dilution or enrichment. For $Z_{st} > 0.5$, the flame is on the fuel side of the stagnation plane, and additive loading reduction at the flame is more severe for oxidant-side additives than for fuel-side additives.

In several experimental studies of flame extinction by CF_3Br, the effect of additive loading reduction at the flame location has been quantified, assuming unity Lewis number. Results have been mixed. For methane-air opposed-jet diffusion flames, Trees et al. [1] found that CF_3Br was roughly twice as effective as an air-side additive than as a fuel-side additive, when the quantity of additive at the stoichiometric contour is compared for equal extinction strain rates. Work by Masri [7], on the other hand, found that oxidizer-side and fuel-side addition of

CF_3Br had very similar effectiveness in extinguishing turbulent natural gas and air piloted jet flames, when corrected for additive concentrations at the flame location. Niioka et al. [2] report comparable effectiveness for fuel-side and oxidizer-side addition in extinguishing various ethene–nitrogen versus oxygen–nitrogen opposed-jet diffusion flames, including one with $Z_{st} > 0.5$. Close examination of the Niioka data shows that the fuel-side addition is generally less effective than oxidizer-side addition.

In this study, we systematically investigate the oxidizer-side and fuel-side effectiveness of two additives in extinguishing methane–nitrogen versus oxygen–nitrogen opposed-jet diffusion flames. One additive, dimethyl methylphosphonate (DMMP), is chemically active; the other, argon, is inert. Suppressant effectiveness is defined as the change in extinction strain rate when the additive is introduced, normalized by the undoped extinction strain rate, a_{q0}. Previous studies [1,4,10] indicate that for low loadings of many suppressant agents, the effectiveness, using this definition, varies linearly with dopant loading. By varying the dilution level of the fuel and oxidizer streams, we investigated how the effectiveness of the two additives changes as a function of the adiabatic flame temperature, T_{ad}, and Z_{st}. In the process, we also explore the interdependencies of T_{ad} and Z_{st}, along with the a_{q0}; parameters that characterize the flame.

Dimethyl methylphosphonate (DMMP) has previously been shown to be a highly effective flame suppressant in non-premixed methane-air flames [4]. Its effectiveness is linear with loading in the air stream over the range 0–1000 ppm, with more than a 25% reduction in the extinction strain rate at the highest loading. This effectiveness is between two and four times that of CF_3Br [3,10,11]. Phosphorus-containing compounds, such as DMMP, are among the families of chemicals under consideration as replacements for CF_3Br in fire-fighting applications [4,12].

Experimental

Experiments were conducted with an opposed-jet burner. Methane (99% pure) diluted with nitrogen (99.998% pure) was used as the fuel and a mixture of oxygen (99.994% pure) and nitrogen as the oxidizer. Variable dilution with nitrogen of both reactants allows for non-premixed flames to be stabilized on either the oxidizer or the fuel side of the stagnation plane. The burner was aligned vertically with the lower tube used as the fuel source and the upper tube as the oxidizer source. The burner was constructed from straight, open glass tubes 30 cm long with an ID of 0.98 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 entire burner is isolated in a glass enclosure with nitrogen purge. Reactant flow rates were measured with calibrated mass-flow controllers that have a manufacturer's stated repeatability of ±0.2% of full scale.

The chemically active flame suppressant used during this investigation, DMMP (97% pure), is a liquid at room temperature with a low vapor pressure. 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. DMMP, which does not pyrolize below 910 K [13], is not expected to decompose before it enters the flame zone. The temperature of the reactant streams 10 cm upstream from the exit of the nozzles was maintained at 100 ± 1 °C via active control of the sheath flow temperature. For all tests of chemically suppressed flames, a constant loading of 500 ppm of DMMP was added, via a commercially available syringe pump, to one of the reactant streams. Argon additive testing was conducted with a loading of 25,000 ppm. The disparity between DMMP and argon concentrations is required because of the strong suppression effect of DMMP.

For each set of measured extinction conditions, a global extinction strain rate was calculated from reactant stream flow rates and nozzle geometry and is denoted a_q. We use equation 1 [14] to evaluate a_q:

$$a_q = \frac{2V_O}{L}\left[1 + \frac{V_F}{V_O}\left(\frac{\rho_F}{\rho_O}\right)^{1/2}\right] \qquad (1)$$

L refers to the separation distance between the nozzles, V is the stream velocity, and ρ is the stream density, with the subscripts O and F referring to oxygen and fuel, respectively. Equation 1 assumes plug-flow boundary conditions at the nozzle exit planes.

For a fixed L, extinction is approached by increasing the reactant velocities until the critical strain rate is achieved. In most studies [3,15], the velocities of the fuel and oxidizer streams are increased proportionally such that the flame or stagnation plane position is maintained near the center of the burner. Because in our study DMMP is injected with a constant mass flow syringe pump, changing the doped reactant flow rate would change the dopant concentration, leading to transients in adsorption or desorption of DMMP from the walls of the tubing downstream of the injection site. Because the timescale of these transients is fairly long (on the order of tens of minutes), accurate determination of the effectiveness of DMMP using the traditional method of approaching extinction is impractical. To circumvent this difficulty, a novel method of performing extinction measurements was developed and is described in detail elsewhere [4]. With this method, only the undoped reactant flow rate is altered, resulting in movement of the flame and stagnation plane. For the variety of flame conditions relevant to this study, this method yields global extinction strain rates that agree to within ±2% with the value found using the traditional method, provided that the location of the flame and stagnation plane at extinction is within a specified range. The deviation of up to 2% varies systematically with flame position but is difficult to correct for. The consequences of this effect are discussed in more detail later.

One of the difficulties in conducting experiments such as these, with oxidizer streams formed by mixing oxygen and nitrogen flows, is the extreme sensitivity of the extinction strain to the mass fraction of oxygen in the oxidizer stream [15]. This effect requires very precise metering of reactant flow rates in order to achieve repeatable results. Even with mass-flow controllers, an appreciable variability (±3%) in the global extinction strain has been observed at identical flow-rate settings. We have found a similar sensitivity to dilution of the fuel stream. Consequently, measurements comparing doped and undoped flames were conducted by first evaluating the undoped extinction strain and then adding the dopant to one reactant stream without altering the composition of either stream. This technique minimizes the impact of the sensitivity to stream composition.

Experiments were performed for stoichiometric mixture fractions, Z_{st}, ranging from 0.055 to 0.7. Z_{st} can be evaluated from reactant compositions in the nozzles and the stoichiometry of the overall combustion reaction, using Eq. 2:

$$Z_{st} = \frac{Y_{O,-\infty}}{\left(\left(\frac{MW_O \nu_O}{MW_F \nu_F}\right) Y_{F,+\infty} + Y_{O,-\infty}\right)} \qquad (2)$$

In this equation, Y is mass fraction, MW is molecular weight, ν is the stoichiometric coefficient for complete combustion, and the subscripts $\pm\infty$ refer to conditions at the fuel and oxidizer nozzles. Changing Z_{st} by varying the dilution of the oxidizer and fuel streams moves the location of the stoichiometric contour, and thus the flame, relative to the stagnation plane. Adiabatic flame temperatures for the various values of Z_{st} and overall dilution of the flames considered herein were evaluated for the undoped case using the STANJAN code [16].

To accurately estimate the quantity of dopant at the flame surface, numerical calculations using the OPPDIF code [17] were made with plug-flow velocity boundary conditions, multicomponent diffusion but no thermal diffusion, and detailed chemistry (excluding phosphorus compounds), using the GRI mechanism [18] with nitrogen chemistry omitted. The mole fraction of dopant is evaluated at the maximum temperature in the reaction zone, taken to represent the flame location. The estimated diffusivity of DMMP is based on the interaction potentials of similar molecular weight compounds. The numerical calculations are required because this diffusivity is significantly different from the rest of the reactant stream components, making the effect of preferential diffusion important [1].

In these calculations, the chemically reactive compound DMMP is treated as inert because complete chemical kinetic and transport data are not available for it or its combustion products. This treatment should give a reasonable estimate of the quantity of phosphorus present in all chemical forms: In the approximation of equal diffusivities for all phosphorus species, at a given position the DMMP mole fraction obtained in calculations treating it as inert is equal to the sum of the mole fractions of all phosphorus species present. Furthermore, in studies of other phosphorus-containing compounds [19,20], it has been proposed that it is the phosphorus-containing radicals formed in the flame that are responsible for flame suppression. This implies that the form of the phosphorus compound entering the flame is relatively unimportant [21]. Therefore, modeling DMMP as an inert compound for the numerical simulations is a reasonable approximation for estimating relevant dopant loadings.

Results and Discussion

Two types of measurements were performed. The first test varied Z_{st} from 0.055 to 0.7. At each Z_{st}, a_{q0} was matched to 350 ± 10 s^{-1}, by trial-and-error variation of the dilution of both reactants. This process entails changing the overall dilution, a parameter that is independent of Z_{st}. Due to the high sensitivity of a_{q0} to reactant composition, it is expected that this narrow range in allowed a_{q0} results in an even narrower range of allowed reactant compositions at a given Z_{st}. Experimentally determining those allowed compositions accurately becomes difficult, however, at high Z_{st}, where the low methane flow rates result in a higher percentage uncertainty in their values.

As Z_{st} is increased with fixed a_{q0}, T_{ad} declines steadily, as seen in Fig. 1. Calculations by Grudno et al. [22] for a fixed T_{ad}, are qualitatively consistent with this result, finding that a_{q0} increased monotonically as Z_{st} was increased from 0.055 to 0.4. This variation in a_{q0} and T_{ad} with Z_{st} is attributed to the changing relationship between the strain rate and the appropriate timescale for diffusion of reactants. While the strain rate is always considered to be a good measure of that timescale, the relationship between the two depends on Z_{st} [22–25]. Error bars in Fig. 1 represent standard deviations of the measurements. The large error at high Z_{st} represents the methane flow-rate uncertainty previously described.

The second type of test varied only the adiabatic flame temperature at a fixed Z_{st}. This was accomplished in two ways: changing the overall dilution of

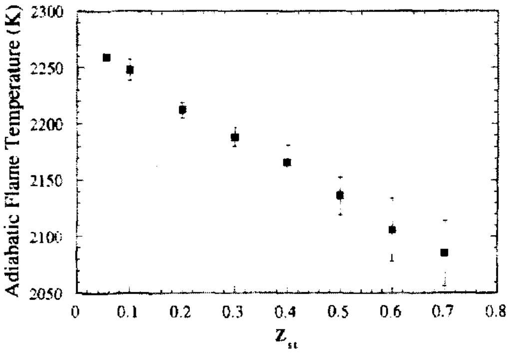

FIG. 1. Adiabatic flame temperature versus stoichiometric mixture fraction for a methane–nitrogen versus oxygen–nitrogen flame with the extinction strain rate held constant at 350 ± 10 s^{-1}. Error bars represent standard deviation of data.

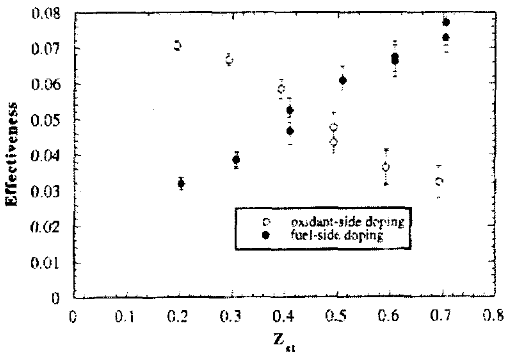

FIG. 2. Flame-suppression effectiveness of 25,000 ppm argon as an oxidant-side or fuel-side additive versus stoichiometric mixture fraction. Effectiveness is defined as $[(a_{q0} - a_q)/a_{q0}]$. Flames are methane–nitrogen versus oxygen–nitrogen; a_{q0} = 350 ± 10 s^{-1}. Error bars represent standard deviation of data.

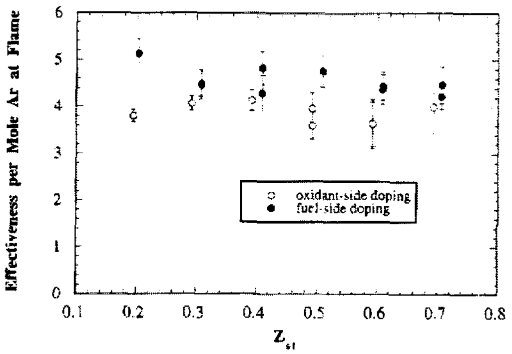

FIG. 3. Normalized flame-suppression effectiveness of argon-doped flames versus stoichiometric mixture fraction at fixed a_{q0}. Effectiveness is normalized by the quantity of argon at the maximum temperature contour in flame, as predicted by a numerical simulation. Error bars represent standard deviation of data and uncertainty in calculated loading.

the flame at a fixed Z_{st} and manipulating the temperature of the reactant streams. These experiments were intended to isolate the temperature dependence of the suppression from other effects.

Inert Tests

Argon was introduced as an inert suppressant for both tests previously described. In these measurements, we expected the inert dopant's effectiveness to depend solely on the quantity of dopant present at the flame. Previous experiments have demonstrated that, for a range of loadings greater than that considered in the current study, the effectiveness of the inert suppressant nitrogen increases linearly with dopant loading, at fixed Z_{st} [4,15,22]. Because flame temperature is reduced by the addition of dopant, this implies temperature invariance of suppression effectiveness over that loading range. Results from the first series of tests in which Z_{st} varied from 0.2 to 0.7 are shown in Fig. 2. The effectiveness of the argon, with both the oxidizer- and fuel-side addition, is illustrated. Each data point represents the average of four extinction measurements. The error bars on the figures represent the standard deviation of the observed values, which in this case is larger than the systematic error due to the method of approaching extinction. As expected, effectiveness with oxidant-side doping decreases as the flame moves toward the fuel side (increasing Z_{st}). The converse is true with fuel-side doping. Argon has a diffusivity similar to that of the reactants; thus, the quantity present at the stoichiometric contour, which determines its effectiveness, will vary linearly with Z_{st}.

Figure 3 depicts the argon results, normalized by the numerically predicted quantity of argon present at the maximum temperature contour. The uncertainty in the calculated mole fraction of dopant at the flame should be dominated by the uncertainty in the experimental flow rate of the dopant: ±10% as determined by the manufacturer's stated repeatability of the mass-flow controller. However, the smooth trends in the data indicate a significantly better repeatability. The normalization process reveals the anticipated behavior for the effectiveness of argon. The effectiveness curves show no trend with Z_{st}, indicating that the concomitant changes in T_{ad} and flame structure, collectively, have no significant influence on the argon effectiveness. Other tests, subsequently described, further demonstrate that the argon effectiveness is independent of T_{ad}. In addition, Fig. 3 shows no significant difference, in view of the experimental uncertainty, between the effectiveness of argon with oxidizer- or fuel-side addition.

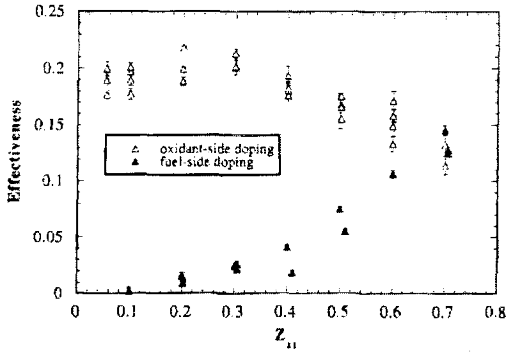

FIG. 4. Flame-suppression effectiveness of 500 ppm DMMP as an oxidant-side or fuel-side additive versus stoichiometric mixture fraction. Effectiveness is defined as $[(a_{q0} - a_q)/a_{q0}]$. Flames are methane–nitrogen versus oxygen–nitrogen; $a_{q0} = 350 \pm 10\ \mathrm{s}^{-1}$. Error bars represent standard deviation of data.

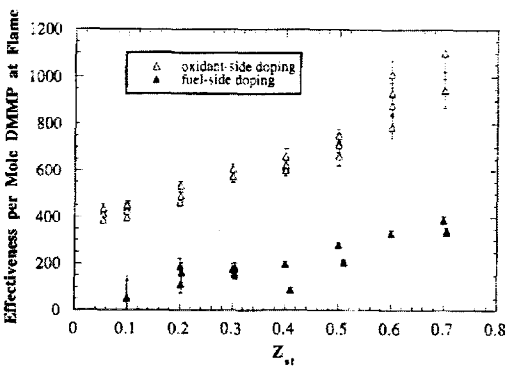

FIG. 5. Normalized flame-suppression effectiveness of DMMP-doped flames versus stoichiometric mixture fraction at fixed a_{q0}. Effectiveness is normalized by the quantity of nonreacting DMMP at the maximum temperature contour in flame, as predicted by a numerical simulation. Error bars represent standard deviation of data and uncertainty in calculated loading.

To further clarify the influence of temperature on this system, a series of tests were performed for a fixed $Z_{st} = 0.055$. T_{ad} was manipulated by varying the reactant stream temperature from 22 to 112 (±1) °C. This resulted in a range of T_{ad} from 2237 to 2283 K. There was a significant influence on the overall flame strength, as seen in the variation of a_{q0} from 254 to 375 s^{-1}. However, the effectiveness for argon at different temperatures varied less than 4% and showed no trend with T_{ad}. These results confirmed that argon's effectiveness displays no temperature dependence.

Chemically Active Dopant

Having shown that our experimental and normalization techniques produce the expected result of no temperature or Z_{st} dependence for an inert suppressant, we next considered the chemically active agent, DMMP. Figure 4 shows the results from extinction measurements performed with DMMP for Z_{st} between 0.055 and 0.7. The observed effectiveness variation with Z_{st} is somewhat more complicated than for the inert tests, although it still follows the same general trend. Each data point in Fig. 4 represents the average of eight extinction measurements, with error bars representing the standard deviation of the measured values. Differences between individual data points at a given Z_{st} show that tests repeated at identical conditions yielded slightly different results. This variation is attributed largely to the repeatability of the dopant injection system. The dopant effectiveness may also be influenced by small changes in flame temperature resulting from lack of repeatability of the reactant stream compositions. The resulting overall experimental scatter that we observed was significantly higher than the inert tests. The systematic uncertainty due to the method of approaching extinction becomes significant for the oxidizer-side addition tests due to the high observed effectiveness. We estimate an overprediction between 3% and 15% of DMMP effectiveness for this range of conditions due to this systematic uncertainty. The effect is small for the fuel-side addition data.

The normalized effectiveness results for DMMP (seen in Fig. 5) have some interesting features. First, it is notable that the DMMP effectiveness per unit mole fraction is roughly 100 times that of argon, indicating strong chemical suppression by DMMP.

Second, the curves for oxidizer- and fuel-side addition are offset significantly with respect to one another. This increased oxidizer-side effectiveness has also been observed for the chemically active agent CF_3Br [1]. The oxidizer-side curve in Fig. 5 displays an effectiveness roughly twice that of the fuel-side curve. The slight systematic overprediction of the oxidizer-side addition effectiveness, described earlier, would reduce the magnitude of this disparity but would not reconcile the difference in these curves. It is possible that because the chemically active suppressant works by interfering with the radical chemistry rather than as a heat sink within the flame, the maximum flame temperature contour may not be the most relevant location for evaluating the mole fraction of dopant. Rather, the appropriate normalization depends on the quantities present in the regions of the flame where the most important radical chemistry occurs. Because key radical reaction rates peak on the oxidizer side of the flame, a more appropriate normalization might involve mole fractions at some location to the oxidizer side of the maximum temperature contour. We examined an alternative normalization using mole fractions at the

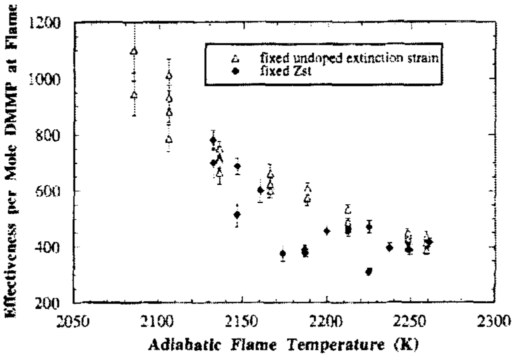

FIG. 6. Normalized effectiveness of DMMP-doped flames as a function of adiabatic flame temperature. △ represents changing Z_{st} from 0.1 to 0.7, fixed $a_{q0} = 350 \pm 10$ s^{-1}, and ◆ represents a fixed $Z_{st} = 0.5$, changing a_{q0} from 294 to 572 s^{-1} by varying mass fraction of oxygen. Error bars represent standard deviation of data for each set of data runs.

point of the maximum reaction rate for the chain-branching reaction $O_2 + H \rightarrow OH + O$. Because the concentration gradients of oxidizer- and fuel-side dopants have opposite directions, this shift in location toward the oxidizer side brings the two curves in Fig. 5 closer together. However, even considering systematic error, oxidant-side doping remains more effective.

The disparity between oxidizer- and fuel-side addition may also be associated with the types and quantities of radicals and products that are formed from the parent molecule as it approaches the flame from different directions and their relevance to the suppression action [7]. If we assume that the important suppression action takes place on the oxidizer side of the flame, then additives to the fuel stream must travel through the flame to reach this point. This may have a significant effect on what phosphorus-containing species are present in the region of important radical chemistry for different modes of addition, that is, oxidizer- or fuel-side doping.

A third feature of Fig. 5 is that for both the oxidizer- and fuel-side tests, the normalized effectiveness increases with Z_{st}. The existence of this slope implies that the suppressant effectiveness varies with either temperature or structure of the flame or both. Studies in a variety of premixed flames have indicated that at high temperatures (above 2350 K) [20,27], DMMP can become a flame promoter. Thus, presumably, the suppression effectiveness of DMMP should decrease with increasing flame temperature. Figure 5 is consistent with this expectation, showing decreasing suppressant effectiveness with increasing adiabatic flame temperature (lower Z_{st} values). However, it is possible that changes in flame structure, which occur at different Z_{st} values, may be influencing suppressant effectiveness as well.

Further tests were conducted to clarify this temperature dependence. Due to condensation of the dopant below 80 °C, we were unable to use control of the reactant temperatures to vary T_{ad} over a significant range. Instead, the overall dilution of the flame, at a fixed value of $Z_{st} = 0.5$, was used to vary T_{ad}. In this experiment, the mass fraction of oxygen in the oxidizer stream ranged from 0.39 to 0.44, resulting in a T_{ad} ranging from 2132 to 2261 K and an a_{q0} range of 294–572 s^{-1}. Unfortunately, the variation in reactant stream compositions increased the susceptibility of the results to the sensitivity to random uncertainties in relative flow rates, producing considerable scatter. The results from this experiment are shown in Fig. 6, along with the data for oxidizer-side addition at fixed a_{q0}, but varying Z_{st} values; all plotted against T_{ad}. Although the large experimental scatter makes it difficult to draw quantitative conclusions, a clear trend of decreasing effectiveness with increasing T_{ad} is observed, comparable to that seen in the constant a_{q0} data. However, these results do not conclusively eliminate the possibility of flame structure and the detailed chemistry of dopant action influencing dopant effectiveness.

Conclusions

Experimental results indicate that the flame-suppression properties of an inert compound, argon, added to methane–nitrogen versus oxygen–nitrogen non-premixed flames can be characterized solely by the quantity of suppressant present at the flame surface. There was no significant observed dependence on adiabatic flame temperature or mode of delivery, that is, oxidizer- or fuel-side doping. There was also no dependence on the value of the stoichiometric mixture fraction, excepting that related to its influence on the quantity of dopant reaching the flame surface.

Determination of effectiveness for the chemically active flame-suppressant compound DMMP is more complex. Even when normalized by the quantity at the flame, the suppressant is significantly more effective when added to the oxidizer-side, rather than fuel-side, of the flame. This disparity in effectiveness is consistent with other researchers' observations for the chemically active flame-suppressant CF_3Br. Experiments also indicate that the effectiveness of DMMP has a strong temperature dependence, with lower effectiveness at higher adiabatic flame temperatures.

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COMMENTS

Yuko Saso, National Research Institute of Fire and Disaster, Japan. I am interested in the strong temperature dependence of DMMP effectiveness. Our recent work suggests that the temperature dependence of CF_3Br effectiveness is caused by the inhibitor regeneration cycles, which are enhanced at lower temperatures.

Recognizing that DMMP oxidation kinetics is not well known, if you compare the magnitude of temperature dependence of DMMP with that of CF_3Br, rough estimation of contribution of catalytic inhibition cycle with DMMP would be possible.

Is the magnitude of the temperature dependence of DMMP larger than that of CF_3Br?

Author's Reply. The temperature dependence of CF_3Br's effectiveness has been investigated experimentally in cup burner extinction tests [1] and in laminar flame-speed experiments [2]. Effectiveness is evaluated in terms of suppressant concentration at extinction for the cup burner tests and as the fractional change in laminar flame speed for the premixed flame experiments. In both cases, effectiveness was found to have a significant dependence on temperature, dropping by 15–35% with a rise of 100 K in adiabatic flame temperature. Although these results are comparable to our observations for DMMP, based on fractional reduction in extinction strain rate, caution must be used when making comparisons across three different measures of effectiveness. There is also a serious difficulty in consistently evaluating the temperature range over which the change in effectiveness is observed. In the case of the cup burner and premixed flames, the adiabatic flame temperature is more representative of the actual flame temperature than in our highly strained flames. We look forward to seeing your results, which may shed light on the relationship between catalytic recombination mechanisms and the temperature dependence of suppressant effectiveness.

REFERENCES

1. Lott, J. L., Christian, S. D., Sliepcevich, C. M., and Tucker, E. E., *Fire Technol.* 32:260–271 (1996).
2. Fristrom, R. M. and Van Tiggelen, P., in *Seventeenth Symposium (International) on Combustion,* The Combustion Institute, Pittsburgh, 1978, pp. 773–785.

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Sandra Olson, NASA Lewis Research Center, USA. How does DMMP toxicity compare to Halon 1301, which was fairly benign in its unreacted state?

Author's Reply. CF_3Br is almost completely inert under ambient conditions. In contrast, DMMP is classed as an irritant to the eyes, skin, and respiratory system. There is also evidence from animal studies that DMMP may be carcinogenic and have reproductive effects [1,2]. Our recent unpublished work indicates that several organic phosphates and phosphonates perform very similarly to DMMP as flame suppressants. This finding supports the hypothesis that it is the phosphorus content of a molecule, not its structure, that is of primary importance in determining fire-suppression effectiveness. This suggests the possibility of identifying a less toxic phosphorus-containing compound with flame-suppression effectiveness comparable to that of DMMP.

REFERENCES

1. Bennett, S. R., Bane, J. M., Benford, P. J., and Pyatt, R. L., "Environmental Hazards of Chemical Agent Simulants," Chemical Research and Development Center, Aberdeen Proving Ground, Technical CRDC-TR-84055, 1984.
2. Material Safety Data Sheet—Dimethyl Methylphosphonate, MDL Information Systems, Inc., Nashville, TN, 1998.

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Dave Zerkle, Los Alamos National Laboratory, USA. The flame inhibitor is a benign chemical. Where does the phosphorus end up after the flame? Comment on the toxicity of these compounds.

Author's Reply. Thermochemical equilibrium calculations indicate that the preferred product of phosphorus combustion is P_2O_5, or P_2O_3 for rich flames [1]. We have measured combustion products from DMMP-doped slightly subatmospheric premixed flames using extractive sampling followed by chemical derivatization and GC/MS analysis [2]. These measurements showed significant quantities of orthophosphoric acid [$P(O)(OH)_3$] and methylphosphonic acid [$P(CH_3)(O)(OH)_2$]; P_2O_5 and P_2O_3 are not likely to be detectable with this technique. All these phosphorus oxides and acids have significantly higher toxicities and corrosivities than the parent compound. Available health and safety information [3] indicates that health risks for these compounds are comparable to the products of combustion of CF_3Br (i.e., HBr and HF).

REFERENCES

1. Fisher, E. M., "Equilibrium Composition Calculations for Combustion of Organophosphorus Compounds," 1995 Fall Technical Meeting of the Eastern States Section of the Combustion Institute, Worcester, MA, 1995.
2. Rapp, D. C., Nogueira, M. F. M., Fisher, E. M., and Gouldin, F. C., *Environ. Eng. Sci.* 14:133–140 (1997).
3. Sax, N. I. and Lewis, R. J., *Dangerous Properties of Industrial Materials,* 7th ed., Van Nostrand Reinhold, New York, 1989.