

# Inhibition of Nonpremixed Flames by Phosphorus-Containing Compounds

M. A. MACDONALD, T. M. JAYAWEERA, E. M. FISHER,\* and F. C. GOULDIN

Sibley School of Mechanical and Aerospace Engineering, Cornell University, Ithaca, New York 14853, USA

Phosphorus-containing compounds (PCCs) are proposed as viable alternatives to current, ozone-destroying, flame-inhibiting agents. An opposed-jet burner apparatus was used to study the effectiveness of two low-vapor-pressure PCCs, dimethyl methylphosphonate (DMMP) and trimethyl phosphate (TMP), in extinguishing a nonpremixed methane-air flame. The global extinction strain rate was determined as a function of dopant loadings. Tests were also conducted using nitrogen as an inert additive for reference. Results demonstrate that these phosphorus-containing compounds are significant inhibitors of nonpremixed methane-air flames when introduced into the oxidizer stream, 40 times more effective than nitrogen on a molar basis. A novel technique for measuring the extinction strain rate while maintaining a constant dopant level in one gas stream was developed. © 1998 by The Combustion Institute

## INTRODUCTION

The manufacture of widely used fire-extinguishing agents  $\text{CF}_3\text{Br}$  (Halon 1301) and  $\text{CBrClF}_2$  (Halon 1211) has recently been banned in the United States because of these compounds' deleterious effect on the ozone layer. Consequently, there is great interest in finding highly effective, ozone-friendly alternative agents [1]. At first, much effort was directed toward investigating ozone-friendly alternatives among halogenated compounds with physical properties similar to those of  $\text{CF}_3\text{Br}$  and  $\text{CBrClF}_2$ . However, the relatively poor flame-suppression performance of these alternatives [2] has led to interest in other families of chemicals, despite less favorable physical or toxicological properties in many cases. These other families of candidates include: metal compounds such as iron pentacarbonyl, powders such as sodium bicarbonate, and phosphorus-containing compounds (PCCs). In this paper we report on an experimental investigation of the gas-phase flame-suppression effectiveness of two PCCs. This is, to our knowledge, the first study in which PCCs' effects on the extinction of a counterflow flame have been determined. We also report a novel method of approaching extinction that is convenient for evaluating the effectiveness of low-vapor-pressure additives.

PCCs are used in several practical applications in fire fighting, but there is some ambiguity

as to whether their effectiveness in these applications can be attributed to gas-phase reactions involving phosphorus. The use of various PCCs as fire retardant additives to plastics [3, 4] has increased dramatically [5] in recent years, with the 1998 estimated U.S. market for organophosphorus fire retardants at 80 million pounds per year [6]. In this application, the relative importance of gas-phase chemistry and solid-phase effects such as char promotion has been debated, with recent work suggesting comparable importance for the two mechanisms [4, 7–10]. The PCC monoammonium phosphate has been used for many years as a dry chemical fire-extinguishing agent [11], and has also been found to be very effective in preventing dust explosions [12, 13]. Since it is applied as a powder, it is possible that physical properties may contribute substantially to its effectiveness. Finally, phosphorus is often applied in combination with halogens, making it difficult to assess the contribution of the phosphorus. For example, a mixture of trialkyl phosphates and  $\text{CF}_3\text{Br}$  for fire-fighting applications has been patented [14]. Phosphorus and halogens often appear in the same molecule as well: a recent evaluation of phosphorus compounds as halon replacements focused on fluorinated phosphazenes and phosphines, showing good flame suppression properties for these compounds in cup burner and streaming tests [15, 16].

Well-characterized laboratory-scale investigations of the gas-phase flame inhibition properties of PCCs are sparse, and in some cases

\*Corresponding author.

ambiguous or contradictory. Korobeinichev et al. investigated the flame structure of low-pressure, premixed stoichiometric  $H_2/O_2/Ar$  flames with the nonhalogenated PCC additives trimethyl phosphate (TMP) [17] and dimethyl methylphosphonate (DMMP) [18]. They compared molecular oxygen profiles in flames with and without the PCC additive, interpreting more rapid oxygen consumption as flame promotion and less rapid oxygen consumption as flame inhibition. Both DMMP and TMP acted as inhibitors in the low-temperature zone near the burner surface and as promoters in the higher-temperature region downstream. In contrast, Fenimore and Jones [19] found that TMP addition produced no change in the oxygen consumption rate in a low-pressure, rich,  $H_2/O_2/Ar$  flame. However, in an atmospheric-pressure flame with higher argon levels, they observed a reduction in the oxygen consumption rate with increasing TMP loading. A more comprehensive study was conducted by Hastie and Bonnell [20] with TMP, triphenylphosphine oxide, and  $POCl_3$  additives in premixed and nonpremixed atmospheric-pressure propane, methane, and hydrogen flames. PCC effects were evaluated from measurements of H radical concentrations and burning velocities. Inhibition was observed for rich and lean flames with temperatures up to 2350 K. At higher temperatures, well above those typically of concern in fire suppression applications [21], flame promotion was observed. Lask and Wagner reported inhibition of premixed hexane/air flames by air-side addition of several halogenated PCCs and one nonhalogenated PCC, TMP, on the basis of their observations of laminar flame speeds [22].

It is thought that phosphorus-containing radicals, such as HOPO and  $HOPO_2$  (formed from PCCs during combustion [17, 18]) catalyze the recombination of the important combustion radicals, H and OH, slowing the overall reaction rate and thus inhibiting the flame [20]. Several mechanisms for catalytic cycles resulting in  $H + OH \rightarrow H_2O$  and  $H + H \rightarrow H_2$ , have been suggested [20, 23–26]. Since it is the phosphorus-containing radicals that participate in the recombination mechanism and not the parent PCC, it has been hypothesized that the form of the parent compound is relatively unimportant

[27]. Partial validation of the radical recombination hypothesis is provided by flow reactor experiments showing that the addition of  $PH_3$  (phosphine) to  $H_2-O_2$  combustion product gases increases  $H + OH$  recombination rates following laser photolysis [26]. Flame experiments have also shown that the presence of PCCs affects radical levels. The addition of small quantities of  $POCl_3$ , a halogenated PCC, produced lower OH levels in nonpremixed methane and ethene flames than did other halogenated compounds not containing phosphorus [28]. The addition of TMP lowered H levels in premixed low-pressure  $H_2/O_2/N_2$  flames under rich conditions with high levels of nitrogen dilution, and raised H levels under stoichiometric, less dilute conditions [20]. This result agrees qualitatively with temperature dependence of inhibition observed by Hastie and Bonnell, described above [20].

A significant obstacle to the use of PCCs as a flame-inhibiting agent is that many of these compounds, including the two investigated herein, have low vapor pressures (<1 torr) at ambient temperature [29]. Some PCCs also have a significant heating value due to alkyl and alkoxy groups attached to the phosphorus atom, and some, especially halogenated PCCs, are highly toxic [15]. However, if supporting evidence is found for the hypothesis that the only important contribution of the PCC to flame inhibition is the central phosphorus atom, then further studies of flame inhibition by PCCs can investigate alternative forms of the parent compounds that might be less toxic and more amenable to delivery to the flame. It is important to note that not all PCCs exhibit high toxicity. PCCs range in their toxicity from nontoxic, essential food constituents and FDA-approved additives, to some of the most toxic compounds (chemical warfare agents) known [30].

In this study, a nonpremixed methane-air flame was used to study the inhibiting effects of two PCCs: dimethyl methylphosphonate (DMMP) [CAS #756-79-6,  $P(=O)(CH_3)(OCH_3)_2$ ], and trimethyl phosphate (TMP) [CAS #512-56-1,  $P(=O)(OCH_3)_3$ ]. Experiments were performed using an opposed-jet burner apparatus. This configuration has been used extensively to evaluate the performance of flame inhibitors using

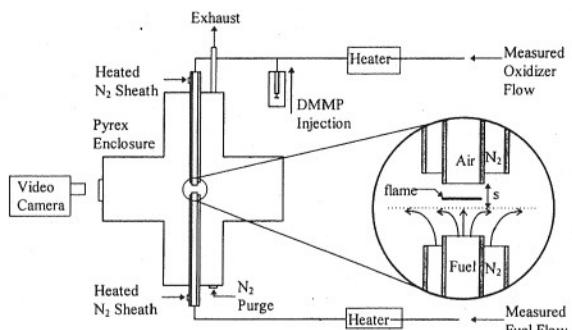


Fig. 1. Schematic of opposed-jet burner.

experimental, numerical, and analytical techniques, (e.g. [2, 31–33]). The counterflow configuration is useful for studying flame-suppressing agents because the flame is thermally isolated and quasi-one-dimensional along the centerline [34, 35]. The flame strength can be characterized by the strain rate at extinction [36, 37].

The usual method of performing extinction measurements is to slowly increase both reactant flowrates until the flame abruptly extinguishes [38]. This approach poses practical difficulties in establishing and maintaining constant inhibitor loadings for low-vapor-pressure flame-inhibiting compounds. An alternative, novel method for performing extinction measurements is presented herein which provides a convenient method for achieving constant inhibitor loadings.

## EXPERIMENTAL

### Apparatus and Materials

Experiments were conducted with an opposed-jet burner, shown schematically in Fig. 1. Mass-flow controllers, supplied by MKS Industries, were used to measure reactant flow rates. Most of the extinction measurements were conducted using premixed oxygen and nitrogen ( $21 \pm 0.2\%$  oxygen mole fraction) or Ultra Zero Grade air ( $21 \pm 2\%$  oxygen mole fraction, total hydrocarbon content  $<0.1$  ppm) as the oxidizer and methane (99% pure) as the fuel. All gases were supplied by MG Industries. For the extinction measurements with flame and stagnation plane coincident, oxygen (99.994% pure) was mixed

with nitrogen (99.998% pure) in measured proportions to form the oxidizer stream, and the methane fuel was diluted with nitrogen (99.998% pure). The burner was aligned vertically with the lower tube used as the fuel source and the upper tube as the oxidizer source. Results of a few experiments conducted with the reverse orientation to study the effect of buoyancy showed no significant change in extinction strain rate. 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 sheath tube exits are offset by approximately 1 cm, upstream of the reactant tube exits, to minimize the impact of the sheath flow on the development of the reactant flows. A flat flame is produced when the oxidant and fuel stream velocities are such that the flame is situated in the central 6 mm of the space between the burner nozzles. When the flame is close to either nozzle, it exhibits curvature toward that nozzle; curvature is pronounced when the flame is within 0.2 mm of the oxidizer nozzle or within 1.9 mm of the fuel nozzle. The entire burner is isolated in a glass enclosure for control of exhaust gases. This enclosure is purged with nitrogen and maintained slightly below atmospheric pressure.

The enclosure has a glass window on one end, approximately 25 cm from the centerline of the flow. A video camera, located a few centimeters from this window, was used to measure flame position. Measurements of flame position were made from magnified images from the camera, displayed on a television screen. Flame position was measured relative to the oxidizer nozzle exit plane using the separation gap between the nozzles for reference.

The chemically active flame inhibitors used during this investigation, DMMP and TMP, supplied by Aldrich Chemical Company (each 97% pure), are liquids at room temperature with low vapor pressures (less than 1 torr at ambient temperature). In order to maintain sufficient concentrations of the PCC in the vapor phase, the reactant lines were heated to approximately 100°C with electrical heating tapes. Wall temperatures on the outside surface

of the heated lines were measured with adhesive thermocouples. The temperatures of the reactant streams 10 cm upstream from the exit of the nozzles were maintained at  $100 \pm 1^\circ\text{C}$  via active control of the sheath flow temperature. These gas temperatures were measured by sheathed thermocouples in direct contact with the gas flow. The liquid PCC dopant was added to the reactant streams via a syringe pump that provided a constant volume flow. The gas flow at the injection site was preheated to approximately  $130^\circ\text{C}$  for a rapid vaporization of the incoming liquid dopant. The liquid density, syringe size, and motor speed fixed the mass flow rates of the dopants. Previous pyrolysis experiments with DMMP and TMP [39, 40] have shown that thermal decomposition is negligible below 1000 K; thus the preheating of the reactant streams should have no effect on their chemical composition.

### Determination of Extinction Strain Rates

The effectiveness of additives as flame inhibitors is determined by measuring the dependence of extinction strain rate on additive loading. The inverse of the strain rate is one of several related measures of the characteristic diffusion time of the flame [41]. In many experiments, the value of the strain rate is evaluated experimentally as the velocity gradient on the oxidant side of the flame, measured using laser-Doppler velocimetry [31]. As our primary interest is to determine the relative reduction of extinction strain rate due to the additive, we chose to approximate the strain rate at extinction using the following expression involving global flame parameters [42]:

$$a_q = \frac{2V_O}{L} \left( 1 + \frac{V_F \sqrt{\rho_F}}{V_O \sqrt{\rho_O}} \right), \quad (1)$$

In Eq. 1,  $L$  refers to the separation distance between the nozzles,  $V$  is the average stream velocity at extinction,  $\rho$  is the stream density, and the subscripts  $O$  and  $F$  refer to oxygen and fuel respectively. This expression, derived by Seshadri and Williams [42], will be referred to as the global strain rate. It is equal to the velocity gradient on the oxidant side of the stagnation plane under certain restrictive con-

ditions: reactions, diffusion, and viscous effects must be confined to a narrow region around the stagnation plane, and plug flow boundary conditions must be imposed at the nozzles. Even under conditions where these restrictions do not apply, the global strain rate expression is useful. Recent measurements [43] performed in an open-tube burner with geometry very similar to our own have found a nearly proportional relationship between the  $a_q$  of Eq. 1 and the maximum local velocity gradient on the oxidant side of the flame, as measured by laser-Doppler velocimetry. The same proportionality was found to hold for methane-air and propane-air flames, with and without flame-inhibiting additives in the air stream. Thus it appears that Eq. 1 may be used to determine relative changes in extinction strain rates obtained on the same apparatus. In particular, the ratio of doped to undoped global strain rate computed using Eq. 1 should be equal to the ratio of doped to undoped local oxidant-side velocity gradients. The validity of this approach is borne out by the good agreement between our normalized results and those of other researchers for inert additives, as described in the Results and Discussion section.

In determining extinction conditions for use in calculating  $a_q$ , we made use of a novel method of approaching extinction, motivated by a need to minimize transient effects of dopant loading. Commonly, extinction studies with opposed-jet burners adjust the strain rate by varying both the oxidizer and fuel streams simultaneously so that the flame position remains constant [31], or so that a momentum balance between the two streams is maintained [38]. This requires varying the mass flow rates of both reactant streams, and results in changing concentrations of the inhibiting agent when the agent is delivered via a constant-mass-flowrate syringe pump. The resulting transients in the adsorption/desorption of the agent on walls make it difficult to predict the concentration of agent at the exit plane of the doped reactant stream at extinction.

The novel method presented here is an alternative technique to circumvent the difficulties associated with dopant loading transients. During our experiments, the concentration of dopant in the relevant reactant stream (fuel or

oxidizer) was fixed by maintaining constant flowrates of all the constituents of the doped reactant stream. After waiting a sufficient time for equilibrium conditions to be established, we approached extinction by varying only the flowrate of the undoped stream. One consequence of using this method is that the position of both stagnation plane and flame vary during the extinction experiment. As described in the following section, this was found to have only a minor influence on the measured extinction strain except when the flame or stagnation plane was very close to one of the nozzles.

## RESULTS AND DISCUSSION

### Validation of Method of Approaching Extinction

We took an empirical approach to validating our novel method of approaching extinction. Experiments were performed over a large range of flow rates of the methane and air streams, achieving extinction with the flame in a variety of positions. To our knowledge, this is the first experimental extinction study in which flame position is varied systematically over a broad range. Figure 2 shows the resulting global extinction strain rates ( $a_q$ ) as a function of the observed flame position. In this figure, flame positions inside either nozzle are plotted at the appropriate nozzle location (0 or 9.5 mm from oxidizer nozzle). Extinction strain varies systematically with flame position, but the variation is small over a large central portion of the region between the burner nozzles. The global extinction strain rate varies less than  $\pm 2\%$  from a mean value of  $359 \text{ s}^{-1}$  for flame positions between 0 and 7 mm from the oxidizer nozzle. This region of nearly constant global extinction strain rates will be referred to as the *acceptable* region. For experiments in which extinction occurs with the flame outside the acceptable region, large deviations in  $a_q$  are observed. Also shown in Fig. 2 are sets of data from two series of experiments conducted with a 300 ppm doping of DMMP and 50,000 ppm doping of  $N_2$ , both added to the oxidizer stream. The limited number of data points in the DMMP series is a

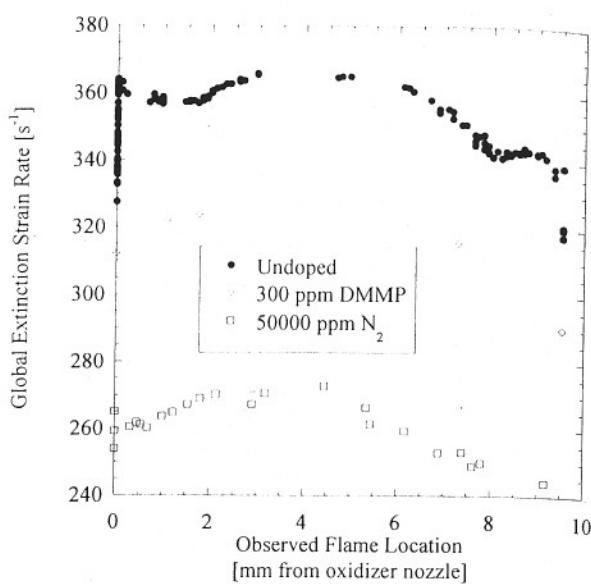


Fig. 2. Variation of global extinction strain,  $a_q$ , with observed flame position at extinction. Results shown are for undoped nonpremixed methane-air flames, with air-side loadings of 300 ppm DMMP and with 50,000 ppm  $N_2$ .  $Z_{st} = 0.054$ .

result of the coarsely quantized mass flow rates of dopant available from the syringe pump. Because of the inhibitory effect of the DMMP or  $N_2$  additive, these data sets have markedly lower mean global extinction strain rates than the data for undoped methane vs. air flames. However, both data sets show very similar systematic trends with flame position, and both have only small variations in extinction strain over the central acceptable region between 0 and 7 mm.

The existence of the same acceptable region for a range of flame extinction strain rates establishes the validity of our method for approaching extinction. Provided that the flame position at extinction lies within this region, the results should be consistent to within 2% of those obtained using more conventional methods that maintain a nearly constant flame position. Caution should be exercised in using this method to measure small changes in strain rate because of the systematic variation of  $a_q$  within the acceptable region.

The nearly constant extinction strain rates over the central region are consistent with previous computational findings. Nishioka et al. compared two methods of approaching extinction: increasing air and fuel stream velocities

while keeping them equal to each other, and increasing air stream velocity while holding fuel stream velocity constant [44]. The resulting calculated global extinction strain rates for  $H_2/N_2$  vs air flames differed by less than 1%. Our larger ( $\pm 2\%$ ) experimentally observed variation of extinction strain rates with flame position can tentatively be attributed to effects not modeled in the flame calculations of Nishioka et al., notably the effects of the flame on velocity boundary conditions and heat losses to the burner nozzles. Of these, effects on the flow field appear to be more important. Laminar convective heat transfer losses are estimated to amount to only a few percent of the chemical enthalpy released during combustion, even if the flame is inside the nozzle.

The asymmetrical dependence of extinction strain rate on flame position appears to be due to the displacement of the flame to the oxidant side of the stagnation plane, which is conveniently characterized using the stoichiometric mixture fraction,  $Z_{st}$ . The stoichiometric mixture fraction,  $Z_{st}$ , is the fraction of the material present at the stoichiometric contour that originated in the fuel stream.  $Z_{st}$  can be evaluated from reactant compositions in the nozzles and the stoichiometry of the overall combustion reaction, using Eq. 2:

$$Z_{st} = Y_{O,-\infty} / \left( \left( \frac{MW_O v_O}{MW_F v_F} \right) Y_{F,+ \infty} + Y_{O,-\infty} \right), \quad (2)$$

where  $Y$  is mass fraction,  $MW$  is molecular weight,  $v$  is the stoichiometric coefficient for complete combustion, the subscripts  $O$  and  $F$  refer to oxygen and fuel respectively, and the subscripts  $\pm \infty$  refer to conditions at the fuel and oxidizer nozzles. The undiluted methane-air flame used for the first series of experiments in Fig. 2 has  $Z_{st} = 0.054$ . Other researchers have found that, near extinction, this corresponds to a displacement of the flame of approximately 1 mm to the oxidizer side of the stagnation plane [34, 35].

The importance of this displacement was investigated by performing a series of measurements in which flame and stagnation plane were coincident. By varying the dilution of the fuel and oxidizer streams it is possible to move the

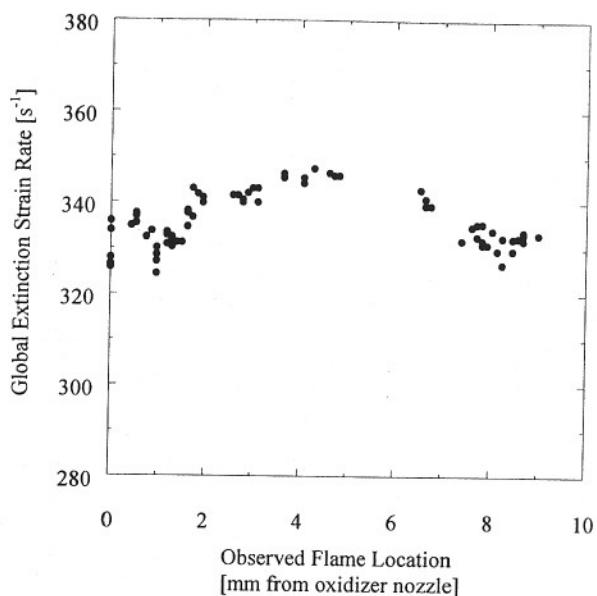


Fig. 3. Variation of global extinction strain,  $a_g$ , with observed flame position at extinction. Results shown are for nonpremixed methane/nitrogen–oxygen/nitrogen flames, with  $Z_{st} = 0.50$ .

location of the stoichiometric contour (the presumed flame location), relative to the stagnation plane. If the reactants have equal diffusivities, setting  $Z_{st} = 0.50$  places the flame at the stagnation plane. Since the value of  $Z_{st}$  depends on two independent variables,  $Y_F$  and  $Y_O$ , fixing  $Z_{st}$  leaves one degree of freedom on reactant concentrations. Unique conditions for the  $Z_{st} = 0.50$  tests were established by choosing the mass fraction of oxygen to give approximately the same undoped global extinction strain rate as was obtained for the undiluted methane–air flame. Results from these conditions,  $Z_{st} = 0.50$  with  $Y_O = 0.387$  and  $Y_F = 0.097$ , are shown in Fig. 3. During these experiments, in which the oxidizer stream was mixed from separate oxygen and nitrogen source bottles, it was found that the global extinction strain rate was very sensitive to the concentration of oxygen, consistent with experimental results from Puri and Seshadri for diluted methane–air flames [38]. This sensitivity contributed to the greater scatter in the  $Z_{st} = 0.50$  tests than in the  $Z_{st} = 0.054$  tests, which were conducted with a premixed oxidizer source. Nonetheless, the global extinction strain rate varies less than 3% of the mean value of  $336 \text{ s}^{-1}$  for flame locations between 0 and 9 mm from the oxidizer nozzle.

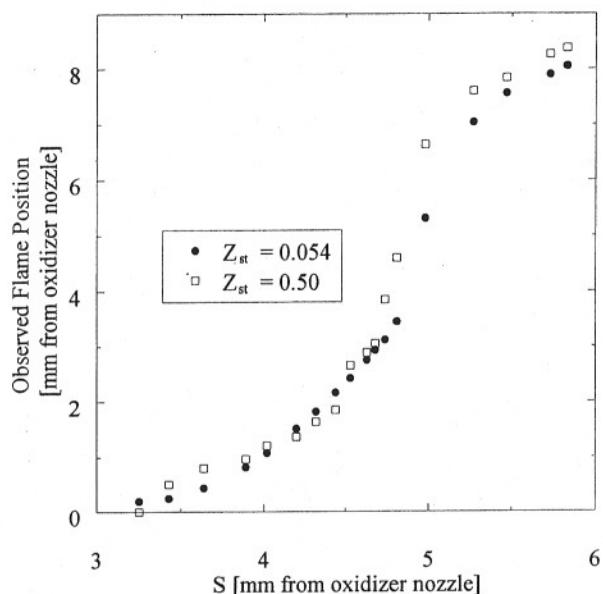


Fig. 4. Observed flame positions as a function of predicted distance to the stagnation plane,  $S$  (based on plug flow model [42]). Results shown are for nonpremixed flames of methane-air ( $Z_{st} = 0.054$ ), and methane/nitrogen-oxygen/nitrogen flames, ( $Z_{st} = 0.50$ ), near extinction.

Within experimental scatter, results with  $Z_{st} = 0.5$  are symmetrical about the center of the region between the two burners, as would be expected for a flame coinciding with the stagnation plane.

Although the acceptable region of Fig. 2 is defined in terms of the observed flame position, in practice it is not necessary to determine by experimental observation the flame location at extinction for all measurements. Rather, a parameter  $S$  is introduced which can be calculated from the reactant stream properties at the nozzles.  $S$  approximates the distance from the oxidizer nozzle to the stagnation plane and is given by the expression in Eq. 3, again derived by Seshadri and Williams for plug flow boundary conditions [42]:

$$S = L \left/ \left( 1 + \frac{V_F \sqrt{\rho_F}}{V_O \sqrt{\rho_O}} \right) \right. \quad (3)$$

Figure 4 shows a plot of observed flame location for both  $Z_{st} = 0.50$  and  $Z_{st} = 0.054$  against the parameter  $S$ . It is interesting to note that the observed flame location does not vary linearly with the predicted location of the stagnation plane, but instead follows a sigmoidal curve, being much more sensitive to flow variations

when it is near the middle of the separation gap. The data presented in Fig. 4 shows flame positions for only high strain cases ( $275\text{--}360\text{ s}^{-1}$ ). It was found that, in general, the steepness of the sigmoidal curve increased with increasing strain rates. For purposes of conducting experiments with the new method, it suffices to observe that the flame location, for each condition, is a well-correlated one-to-one function of this parameter  $S$ . Therefore, one can map the experimentally determined acceptable region in terms of  $S$ , and direct observation of flame position becomes unnecessary. For  $Z_{st} = 0.0544$ , this region is  $3.50\text{ mm} < S < 5.25\text{ mm}$ . All extinction results reported below were for flames inside this acceptable region.

### Extinction Results

Initial tests were conducted with undoped 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 was  $296\text{ s}^{-1}$ . When the reactant streams were preheated to  $100^\circ\text{C}$ , the measured value for  $a_g$  increased to  $360\text{ s}^{-1}$ . Variations in  $a_g$  up to  $80\text{ s}^{-1}$  were observed with different bottles of high purity compressed air, and are attributed to slightly different batch mass fractions of oxygen. However, extinction measurements on undoped flames using the same oxidizer source are consistent to within  $\pm 5\text{ s}^{-1}$ . All results for doped flames presented herein are normalized to undoped experiments under identical conditions, i.e., using the same oxidizer source.

The unheated global extinction strain value we measured is comparable to the value found by Puri and Seshadri [38] of  $280\text{ s}^{-1}$  and to the value of  $255\text{ s}^{-1}$ , computed from flow rates at extinction reported by Papas et al. [31] using Eq. 1. All three numbers fall within the range of variation attributed to differences in composition of high purity air batches. This agreement is surprisingly good in light of the significantly different boundary conditions and aspect ratio of the burner used relative to that of Puri and Seshadri. Agreement with literature values of local extinction strain rate is not as good; measurements and calculations

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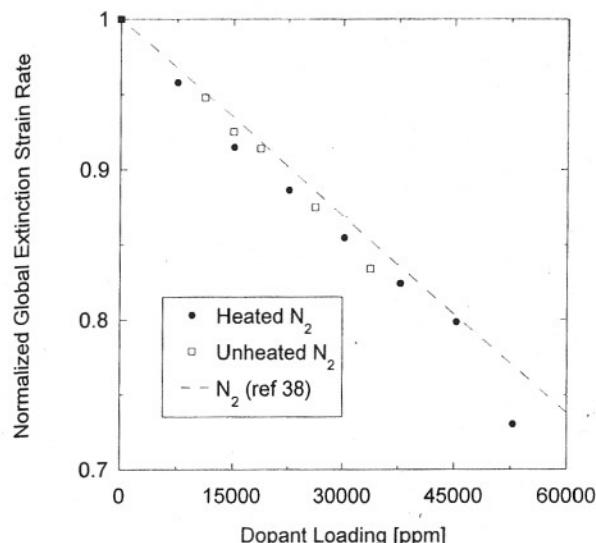


Fig. 5. Inhibition of nonpremixed methane-air flames, based on reduction in the global extinction strain rate, by oxidizer-side addition of nitrogen with and without preheated reactants. Also shown are reported literature values for nonpremixed methane-air flames diluted with nitrogen.

range from 340 to 400 s<sup>-1</sup> [31, 35, 45] and from 354 to 544 s<sup>-1</sup> [35], respectively. We attribute the discrepancy of our measurements with these values to our use of the global strain expression under conditions where it is not strictly valid, as discussed in the Experimental section. Comparable differences between global and local strain rates are observed by other researchers [31].

Further validation experiments were conducted with nitrogen as a chemically inert flame-inhibiting additive. Normalized extinction strain rates for nitrogen addition to the air side of a methane-air flame are shown in Fig. 5. Each data point represents the average of at least three measurements, and is normalized by the extinction strain rate for a pure methane-air flame. Extinction strain rate drops linearly with increasing loading of this additive. Results are the same regardless of whether or not the reactants are preheated to 100°C, consistent with the findings of Trees et al. [46]. The nitrogen dilution data can be compared to room-temperature data of Puri and Seshadri [38], also shown in Fig. 5. Agreement is good, with least-mean-square slopes agreeing within 7%. However, it should be noted that the diluted flame experiments of Puri and Seshadri were conducted at a fixed value of  $Z_{st}$  =

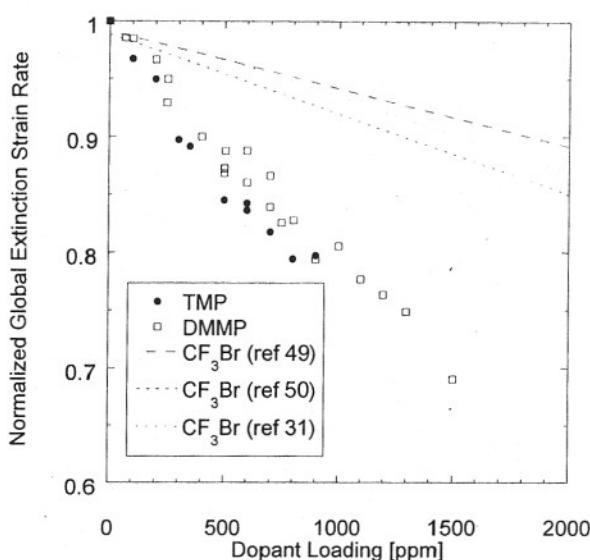


Fig. 6. Inhibition of nonpremixed methane-air flames, based on reduction in the global extinction strain rate, by oxidizer-side addition of the phosphorus-containing compounds TMP and DMMP. Also shown are reported literature values for inhibition by CF<sub>3</sub>Br.

0.0544. This requires some nitrogen addition to the fuel-side flow in contrast to our experiments in which nitrogen was added only to the oxidizer stream. Previous experiments by the authors [47] indicate that correcting for the effect of this fuel-side addition would lower our measured extinction strain rates by about 3%, resulting in an overall discrepancy of 10% with the Puri and Seshadri data.

Figure 6 shows our results for PCC addition to the air stream of methane-air flames. Again, points represent averages of at least three measurements, and are normalized by the undoped extinction strain. For DMMP addition, the global extinction strain rate is observed to decrease linearly with additive mole fraction. Experiments indicate that at a mole fraction of 1500 ppm,  $a_g$  is reduced by 35% of the undoped value. Detectable inhibition (~3% reduction in  $a_g$ ) is found at loadings as low as 100 ppm. For mole fractions below 100 ppm, preheating of reactants was not necessary to prevent condensation of DMMP. This allowed for ambient-temperature testing of low DMMP loadings which demonstrated inhibition effectiveness similar to that found in the preheated experiments. Figure 6 also shows the results from TMP-doped flames. TMP is seen to exhibit similar inhibitory properties to

DMMP over the common range of loadings. This is consistent with the hypothesis [27] that it is phosphorus radicals formed in the flame that are important and not the parent compound. Consistent flame inhibition was observed, with no sign of the flame promotion noted by others [18, 20]. A possible explanation is that the relatively low peak temperatures typical of highly strained methane-air flames [48] are below the 2350 K transition between inhibition and promotion observed by Hastie and Bonnell [20].

Also shown in Fig. 6 are literature flame inhibition data for  $\text{CF}_3\text{Br}$ , the current agent in many fire-suppression systems [31, 49, 50]. The flame inhibition properties of DMMP and TMP are two to four times better, on a molar or mass basis, than those reported in the literature for  $\text{CF}_3\text{Br}$ . Comparisons of these PCCs with  $\text{Fe}(\text{CO})_5$ , one of the most effective flame inhibitors known, show that  $\text{Fe}(\text{CO})_5$  is a stronger inhibitor at low loadings: inhibition at 200 ppm [51] is comparable to the PCC's effectiveness at 1500 ppm. However, the effect of  $\text{Fe}(\text{CO})_5$  as an inhibitor plateaus for mole fractions between 200 and 500 ppm, the highest gas-phase concentration achievable with ambient temperature reactants [51]. The PCCs' inhibition performance can also be compared to the  $\text{N}_2$  data presented in Fig. 5: DMMP and TMP are approximately 40 times more effective than  $\text{N}_2$  on a molar basis ( $\sim 10$  times as effective on a per mass basis). It is important to note that the range of extinction strain rates achieved in these PCC experiments represents only the upper portion of the range of local strain rates encountered in a realistic, turbulent fire [52]. Extending the experimental range to much lower strains would require a different method of introducing the PCC.

We performed an experiment to determine whether the hydrocarbon content of the PCCs contributes significantly to the inhibition effectiveness. In certain chemical systems, such as carbon monoxide-air combustion, trace amounts of hydrocarbons have been observed to inhibit combustion [53, 54]. It is thought that the inhibition occurs because the hydrocarbon acts as a radical sink. Hastie et al. [20, 25] attribute 8% of TMP's inhibition effectiveness in hydrogen flames to this effect. In

order to determine whether radical scavenging by the methyl groups, found in the PCCs under investigation, may be responsible in part for the PCCs' inhibition observed here, tests were conducted with isoctane as the dopant. Isooctane has a similar structure to the PCCs but lacks the central phosphorus atom. It is expected that any contribution from methyl groups to flame inhibition by the PCCs would be observed during the isoctane tests. However, these tests showed a 4% increase in the global extinction strain at a loading of 400 ppm, indicating that the effect of the hydrocarbon was to promote the flame, not to inhibit it. This result provides further support for the hypothesis that the phosphorus atom is crucial to the flame inhibition effects of the PCCs studied here.

## SUMMARY

The present study used an opposed-jet burner configuration to investigate the effectiveness of two PCCs—DMMP and TMP—as flame inhibitors. The global extinction strain rate, used as a measure of flame strength, was estimated in terms of the flow rates of fuel and oxidizer. A novel method for performing extinction measurements was developed to maintain constant PCC loadings in the oxidizer stream with syringe pump PCC delivery. This method causes the locations of the flame and stagnation plane relative to the nozzles to change during an extinction measurement. It has been found that the global extinction strain rate is approximately invariant (within  $\pm 2\%$ ) over a broad range of flame locations for methane-air nonpremixed flames. This technique for performing extinction measurements is shown to give consistent and repeatable results.

Global extinction strain rates were measured for flames doped with PCC loadings from 0–1500 ppm. As a flame inhibitor on a molar basis, PCCs were found to be 40 times more effective than nitrogen and two to four times more effective than the literature values for  $\text{CF}_3\text{Br}$ . The high level of effectiveness of the PCCs (35% reduction in global extinction strain rate at 1500 ppm) encourages the investigation of other phosphorus-containing

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compounds as alternatives to halogenated flame inhibitors.

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