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Flame inhibition by phosphorus-containing compounds over a range of equivalence ratios

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Abstract

There is much interest in the combustion mechanism of organophosphorus compounds (OPCs) due to their role as potential halon replacements in fire suppression. A continuing investigation of the inhibition activity of organophosphorus compounds under a range of equivalence ratios was performed experimentally and computationally, as measured by the burning velocity. Updates to a previous mechanism were made by the addition and modification of reactions in the mechanism for a more complete description of the inhibition reactions. Reaction pathways for $HOPO_2 + H$ and $HOPO + H$ are analyzed using the BAC-G2 approach. A new reaction pathway for $HOPO_2 + H = PO_2 + H_2O$ has been identified which results in a higher rate constant than that reported in the literature. In this work, the laminar flame speed is measured experimentally and calculated numerically for a premixed propane/air flame at 1 atm, under a range of equivalence ratios, undoped and doped with dimethyl methylphosphonate (DMMP). A detailed investigation of the catalytic cycles involved in the recombination of key flame radicals is made for two equivalence ratios, fuel lean and fuel rich. From this, the importance of different catalytic cycles involved in the lean versus rich case is discussed. The chemical kinetic model indicates that the $HOPO_2 \Leftrightarrow PO_2$ inhibition cycle is more important in the lean flame than the rich. The OPCs are similarly effective across the range, demonstrating the robustness of OPCs as flame suppressants. In addition, it is shown that the phosphorus compounds are most active in the high-temperature region of the flame. This may, in part, explain their high level of inhibition effectiveness.

Keywords: Flame inhibition; Organophosphorus compounds; Laminar flame speed; Detailed chemical kinetic modeling

1. Introduction

For many years, halogenated hydrocarbons, such as CF_3Br, were used as fire suppressants. However, due to their high ozone depletion potential, they are no longer being manufactured in industrialized coun-

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tries, as stipulated in the 1990 Montreal Protocol. The search for effective replacements has led to a family of organophosphorus compounds (OPCs) that have shown considerable promise as flame inhibitors [1–3]. Early work of Twarowski [4–6] demonstrated that phosphine (PH_3) accelerated radical recombination in hydrogen oxidation, and subsequent work by Korobeinichev et al. began to explain how OPCs inhibited hydrogen flames [7] and hydrocarbon flames [8].

Chemically active flame inhibitors alter flame chemistry by catalytic recombination of key flame radicals, especially H and O atoms and OH radicals. H atoms are particularly important in flame propagation, since the principal chain branching reaction in hydrogen and hydrocarbon flames is $H + O_2 \rightarrow OH + O$. Fast elementary reactions interconnect these small radical species, and removal of any of them through recombination reduces concentrations of all of them correspondingly. Therefore, radical recombination leads to fewer H atoms in the reaction zone, which leads to reduced chain branching and a lower burning velocity in a premixed flame. This applies to familiar halogenated suppressants such as HBr and CF_3Br [9,10] and OPCs such as dimethyl methylphosphonate (DMMP) [11].

In his studies on addition of small amounts of phosphine combustion products to water vapor, Twarowski [4–6] found that small P-containing species promote catalytic recombination of radicals:

$$PO_2 + H + M \rightarrow HOPO + M, \tag{1a}$$

$$HOPO + H \rightarrow H_2 + PO_2, \tag{1b}$$

$$PO_2 + OH\ (+M) \rightarrow HOPO_2\ (+M), \tag{2a}$$

$$HOPO_2 + H \rightarrow H_2O + PO_2. \tag{2b}$$

These reaction sequences act as termination reactions, converting highly reactive H and OH radicals to molecular species H_2 or H_2O, the latter being a stable combustion product. In the present work, we will be focusing on these catalytic recombination reactions.

This work extends a previous investigation of phosphorus-doped premixed flames, by the same authors [12]. In the previous work, phosphorus-doped premixed flames were investigated with respect to their species concentrations profiles under a lean and rich condition in a flat flame burner (equivalence ratios of 0.9 and 1.2). In the present work, flame speeds are investigated over a range of equivalence ratios in a Mache–Hebra nozzle burner [13,14]. We also examine the effect of equivalence ratio on the key inhibition cycles.

2. Experimental work

The speed of premixed C_3H_8/air flames was measured using a Mache–Hebra nozzle burner [13,14] at 1 atm and the total area method using an image of the flame. The experimental technique is described in detail elsewhere [8]. To evaluate the influence of a heat loss from the flame to the burner on the measured values, the speed of undoped propane/air flames of various stoichiometries was measured for an unburned gas temperature of 298 K. The obtained result of 41.7 cm/s for a stoichiometric flame is comparable with experimental data measured by different techniques [15–17]. This comparison gives validity to the method used for the measurement of flame burning velocities.

In addition, we measured the flame speed of DMMP-doped propane/air flames at 1 atm and over a range of equivalence ratios. The fuel/air equivalence ratio was varied from 0.8 to 1.3 in 0.1 increments. In this case, to minimize condensation of DMMP on the burner surface, the reactant temperature was increased to 368 K. The loadings tested were 0, 300, and 600 ppm of DMMP. The results from these experiments are shown in Fig. 1. Uncertainty in measured values is included in the figure for the undoped flame. The same percentage error can be applied for the doped flames. The main source of uncertainty in measuring burning velocity is from the measurement of the contour of the flame cone. The flame cone is blurred and the maximum blurring occurs for the fuel-rich case. Additionally, the uncertainty in the dopant loading is ±40 ppm and the relative uncertainty in the equivalence ratio is ±2%.

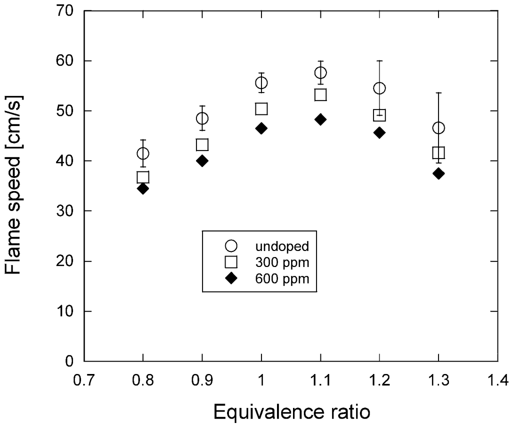

Fig. 1. Experimentally measured flame speed, over a range of equivalence ratios, for propane/air flames with various loadings of DMMP (0, 300, and 600 ppm) and for an unburned reactant temperature of 368 K. Error bars are shown on undoped data, but the same percentage uncertainty can be applied to the doped data, as well.