Inhibition of Hydrogen-Air Detonations Using Organophosphorus Compounds

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1 Introduction

Hydrogen has received widespread interest as a clean and efficient energy carrier, mainly due to its potential to reduce greenhouse gas emissions and mitigate climate change. However, the inherent physicochemical properties of hydrogen lead to substantial safety concerns, requiring thorough investigation into mitigating hazards such as unintended explosions and detonations. The safety challenges are primarily attributed to its high flammability, wide flammability range (4-75% by volume in air), and minimal ignition energy [1,2]. Additionally, its low molecular weight facilitates rapid diffusion, which, while advantageous for combustion efficiency, significantly increases the risks of leaks. Unlike deflagration, which involves subsonic combustion, detonation involves shock-induced chemical reactions, resulting in rapid energy release in a very short timescale. Thus, to harness the full potential of hydrogen fuel, it is necessary to address the safety challenges and develop strategies for explosion and detonation mitigation.

Detonation inhibition can be achieved by physical, geometric, and chemical methods. However, chemical inhibition remains one of the most effective strategies, involving the use of chemically active compounds that interact with the combustion chemistry to suppress detonation. Halogenated compounds have historically been at the forefront of chemical inhibition research [3-5]. Bromotrifluoromethane (CF_3Br) emerged as a highly effective inhibitor due to its ability to inhibit the chain branching reactions during combustion. However, the production and use of CF_3Br were phased out due to the Montreal Protocol, owing to its high ozone-depleting properties. The search for alternatives led to the investigation of different halogenated and non-halogenated inhibitors, amongst which trifluoroiodomethane (CF_3I) demonstrated effective detonation suppression [5-7]. Despite its efficacy, the toxicity and associated health risks limit its usability, particularly in occupied environments. These limitations necessitated the search for environmentally friendly and less hazardous alternatives [8].

Organophosphorus compounds (OPCs) have recently gained attention as promising candidates for chemical inhibition. Several studies have explored the effects of OPCs on flame structure, propagation, and suppression, providing valuable insights into their mechanisms and effectiveness [9-12]. Unlike halogenated inhibitors, organophosphorus compounds are characterized by lower environmental impact and reduced toxicity, making them suitable for a broader range of applications [8]. Compounds such as trimethyl phosphate (TMP) and dimethyl methyl phosphonate (DMMP) exhibit significant inhibition potential due to their ability to interfere with chain branching kinetics. Wang et al. investigated the

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impact of trimethyl phosphate (TMP) on methane-oxygen flames. The study highlighted that TMP significantly alters the flame structure and reduces propagation velocity, demonstrating its potential as a flame suppressant [9]. Korobeinichev et al. explored the dual role of OPCs in CH_4/O_2 and H_2/O_2 flames. It was observed that compounds like TMP and DMMP could either inhibit or promote combustion depending on their concentration and the combustion environment [10]. These studies collectively demonstrate the potential of organophosphorus compounds in flame inhibition. However, their dual role necessitates careful consideration. Despite significant research on the effects of TMP and DMMP in flame inhibition, there is a notable gap in the literature regarding their application to detonation environments. The existing studies primarily focus on flame propagation and suppression, leaving the mechanisms and effectiveness of OPCs in detonation environments largely unexplored. The current work aims to address this gap by conducting an evaluation of TMP and DMMP as detonation inhibitors using one-dimensional ZND computations that incorporate detailed chemistry. The current work aims to lay a foundation for future investigations into detonation inhibition using TMP and DMMP.

2 Methodology

One-dimensional ZND computations were carried out using the Caltech Shock and Detonation Toolbox [13]. The relevant chemical kinetic and thermodynamic parameters were evaluated using Cantera integrated with MATLAB. The induction zone length (Δ_i) of a ZND detonation structure is defined as the post-shock distance to the thermicity peak ($\dot{\sigma}_{\max}$) where the maximum temperature gradient also occurs [$\max(dT/dx)$]. The ZND model has been successfully used to evaluate the effect of detailed chemical kinetics on the detonation structure and the critical detonation parameters [14].

The chemical kinetics for hydrogen combustion were modeled using the FFCM2 model, which is used for simulating high-temperature combustion [15]. The model has been validated against experimental data from both constant pressure and constant volume combustion tests, making it a reliable tool for simulating detonation initiation and propagation in hydrogen-based mixtures [15]. The chemical kinetics model for TMP and DMMP was adopted from the work of Jayaweera et al. [11]. Their model accurately describes the combustion and decomposition behavior of TMP and DMMP under high-temperature conditions. The model has been validated against experimental data for TMP and DMMP combustion in both lean and stoichiometric mixtures [11]. The complete chemical kinetics model (FFCM2 + Jayaweera et al.) consists of 140 species and 1279 reactions.

The ZND model simplifies the inherently multidimensional nature of detonation. Practical detonations exhibit complex cellular structures due to interactions between the leading shock, transverse waves, and Mach stems. The detonation cell width reflects the detonation sensitivity of a mixture under given conditions. The induction length of a ZND detonation structure can be directly correlated with the cell width of multi-dimensional detonations. Larger induction lengths generally correspond to wider detonation cells, indicating reduced detonation sensitivity. In the present work, the inhibition effect of TMP and DMMP is evaluated using induction length as the primary parameter. The induction length provides a direct measure of the effectiveness of inhibitors in the chemical reaction zone.

3 Results and Discussions

3.1 Effect of TMP, DMMP, and CF_3I inhibitors on hydrogen-air detonations

The effect of TMP and DMMP on hydrogen-air detonations was examined using ZND computations. The initial pressure and temperature for all the computations were 100 kPa and 298 K. The detonation velocity was observed to decrease with the addition of TMP and DMMP; however, a slight increase can be observed at lower concentrations (up to 3000 ppmv). The detonation velocity is primarily a function of the energy content of the reactant mixture. Thus, the increase in the velocity is due to the additional energy content provided by the fuel components of TMP and DMMP (refer to Fig. 1a). Both compounds contain significant organic elements that contribute to the overall energy content of the reactant mixture. However, as the concentration of TMP and DMMP increases beyond 3000 ppm, the detonation velocity decreases with increasing inhibitor concentration.

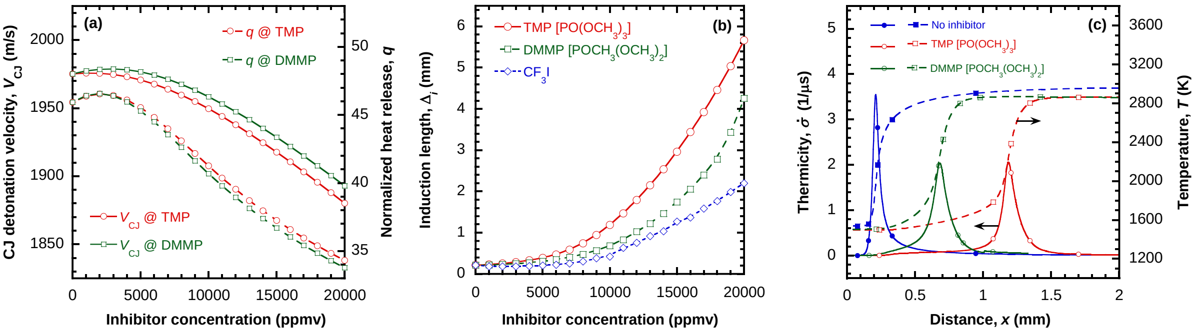

Figure 1: Effect of varying inhibitor concentration on (a) the CJ detonation velocity and normalized heat release of H_2-air-TMP/DMMP detonations and (b) the induction length of H_2-air-TMP/DMMP/CF_3I detonations. (c) Thermicity and temperature profiles for H_2-air detonations with (10000 ppmv) and without inhibitors.

The induction length increases with the increasing inhibitor concentration, as shown in Fig. 1b. At lower concentrations, the inhibition effect of all the inhibitors is nearly the same, but a significant difference can be observed at higher concentrations. For TMP and DMMP, the induction length increased significantly at concentrations above 10000 ppm. TMP caused the largest increase in the induction length, followed by DMMP and then CF_3I. Thus, TMP is a better inhibitor than DMMP and CF_3I. The location of the thermicity peak shifts away from the leading shock front in the presence of TMP and DMMP. The shift in thermicity peak is greater for TMP than DMMP, as shown in Fig. 1c. The maximum thermicity and the temperature in the reaction zone are also reduced with the addition of TMP and DMMP. These compounds decrease and delay the energy release by interfering with the chemical kinetics in the reaction zone.

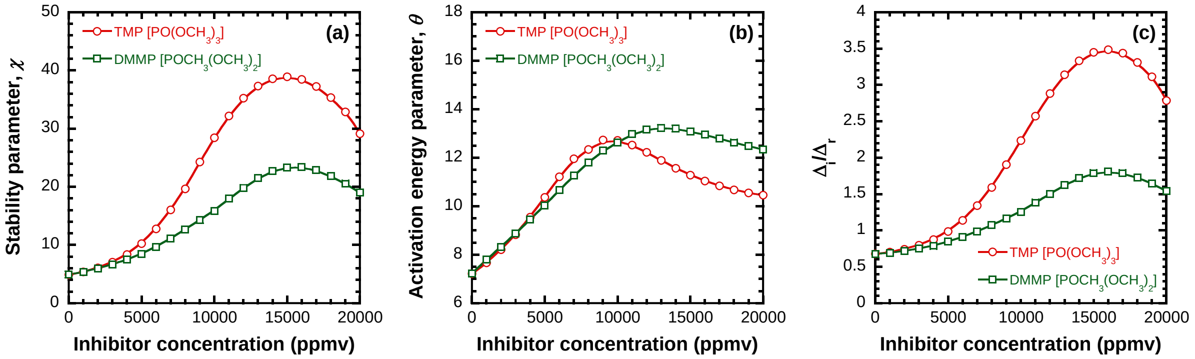

Figure 2: Effect of varying inhibitor concentration on the (a) stability parameter (χ), (b) activation energy parameter (θ), and (c) the ratio Δ_i/Δ_r, for stoichiometric H_2-air-TMP/DMMP mixtures.

The inhibition effects of TMP and DMMP are mainly due to their interactions with key combustion radicals in the reaction zone. Chemically active flame inhibitors such as TMP and DMMP alter flame chemistry by catalytic recombination of key flame radicals, especially H, O, and OH radicals. H atoms are particularly important in flame propagation since the principal chain branching reaction in hydrogen and hydrocarbon flames is $H + O_2 \rightarrow OH + O$. TMP and DMMP act by catalyzing the recombination of H atoms into relatively non-reactive molecules or stable products, where they lower the overall rate of chain branching by reducing the available radical pool [11]. Fast elementary reactions interconnect these small radical species, and the removal of a given species through recombination reduces their concentrations correspondingly. The inhibition effect of TMP and DMMP is primarily due to the catalytic recombination of these active combustion radicals through the reactions R1-R4.

$$PO_2 + H + M \rightarrow HOPO + M \qquad (R1)$$

$$HOPO + H \rightarrow H_2 + PO_2 \qquad (R4)$$

$$PO_2 + OH\ (+M) \rightarrow HOPO_2\ (+M) \qquad (R3)$$

$$HOPO_2 + H \rightarrow H_2O + PO_2 \qquad (R4)$$

These reaction pathways act as termination reactions, converting highly reactive H and OH radicals to intermediate species (HOPO, PO_2, $HOPO_2$, H_2) and stable products (H_2O). The only distinction between different organophosphate inhibitors is how rapidly these catalytic cycles are established [11].

The one-dimensional stability parameter (χ) was evaluated based on the definition given by Ng et al. [16]. The variation of the stability parameter with TMP and DMMP addition is presented in Fig. 2a. The stability parameter initially increases up to ~ 15000 ppmv and then shows a slight decrease. For small values of χ, the power pulses originating from neighboring particles will overlap, thus leading to a coherence in energy release and stable detonation. On the other hand, if the parameter χ is large, the power pulses will not be coherent, which can lead to gas dynamic instabilities in the reaction zone structure [16]. Thus, the one-dimensional stability analysis indicates that hydrogen-air detonations become unstable with the addition of TMP and DMMP up to ~15,000 ppmv. Beyond this concentration, the observed decrease in χ suggests a stabilizing effect. The stability parameter is influenced by both the activation energy parameter (θ) and the ratio Δ_i/Δ_r which together govern its dependence on inhibitor concentration. The activation energy parameter increases with the addition of inhibitors and then decreases at higher concentrations. The initial increase in θ, is due to the consumption of reactive radicals (O, H, and OH). However, ZND computations also reveal that the peak concentration of CH_3 radicals within the reaction zone increases with increasing inhibitor concentration. Thus, the increase and decrease in θ is a result of the competition between the consumption and production of reactive radicals in the reaction zone. The addition of inhibitors also significantly increases the induction length of hydrogen-air detonations (refer to Fig. 1b). The reaction zone length (Δ_r) also increases in the presence of inhibitors. However, the increase in induction length is more pronounced, leading to an overall rise in Δ_i/Δ_r. The ratio, Δ_i/Δ_r attains a maximum at 16000 ppmv and then starts to decrease, as shown in Fig. 2c. The observed reduction is due to a disproportionately larger increase in the reaction zone length compared to the induction length. The reaction zone length increases substantially at higher inhibition concentrations. A large reaction zone has a stabilizing effect as it spreads out the energy release and reduces the impact of gas dynamic instabilities. Thus, the results of the one-dimensional stability analysis for hydrogen-air-TMP/DMMP detonations highlight the complex interplay of mechanisms that influence detonation stability.

3.2 Effect of TMP and DMMP on radical generation

The species profiles for H_2-air, H_2-air-TMP, and H_2-air-DMMP detonations provide further insights into the chemical kinetics within the reaction zone. The presence of TMP and DMMP leads to a reduction in the concentrations of key radicals (H, O, and OH) compared to the hydrogen-air detonation without inhibitors (refer to Fig. 3). This reduction indicates the inhibition effect of TMP and DMMP. These inhibitors, through their phosphorus-containing groups, interact with radicals in the reaction zone (through reactions R1-R4) and are responsible for the scavenging of radical species like H, O, and OH. The formation of intermediate species, such as HOPO and PO, is also observed in significant amounts in both H_2-air-TMP and H_2-air-DMMP detonations. The catalytic recombination of the reactive radicals results in the formation of these intermediate species. The presence of these intermediate species in the reaction zone is indicative of the chemical pathways through which TMP and DMMP exert their inhibition effects.

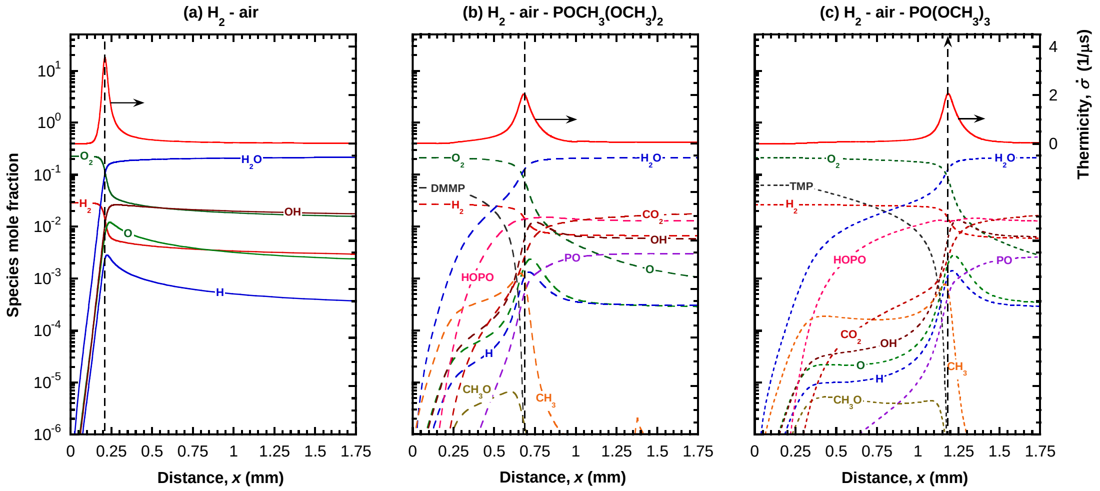

Figure 3: Mole fraction profiles of key species in the presence of inhibitors at 10000 ppmv. (a) H_2 – air, (b) H_2 – air – DMMP, and (c) H_2 – air – TMP.

3.3 Effect of varying equivalence ratio on inhibition efficacy of TMP and DMMP

The effect of the equivalence ratio (ϕ) on the inhibition efficacy of TMP and DMMP was evaluated by varying ϕ, from ultra-lean (0.4) to fuel-rich (2.2) conditions. The induction length increased with increasing inhibitor concentration (for most equivalence ratios), which was consistent with the general inhibition mechanism. However, under ultra-lean conditions (ϕ = 0.4), the induction length decreased as the inhibitor concentration increased (refer to Fig. 4) for both TMP and DMMP mixtures. This suggests that TMP and DMMP may act as promoters rather than inhibitors under ultra-lean conditions. The reduction in induction length at ϕ = 0.4 implies that the inhibitors contribute to the reaction kinetics in a way that promotes detonation. This phenomenon can be explained by the fuel content present in TMP and DMMP. In ultra-lean mixtures, where the fuel availability is low, the introduction of TMP and DMMP likely provides additional fuel. This supplementary fuel reacts with the available oxidizer and produces the promotion effects, compensating for the inhibitory effects typically associated with these compounds. For near stoichiometric and fuel-rich mixtures, the induction length consistently increased with inhibitor concentration. The dominant inhibition mechanism in these conditions involves the depletion of radicals (H, O, and OH), which lowers the rate of chain-branching reactions. The contrasting behavior under ultra-lean conditions highlights the dual role of TMP and DMMP.

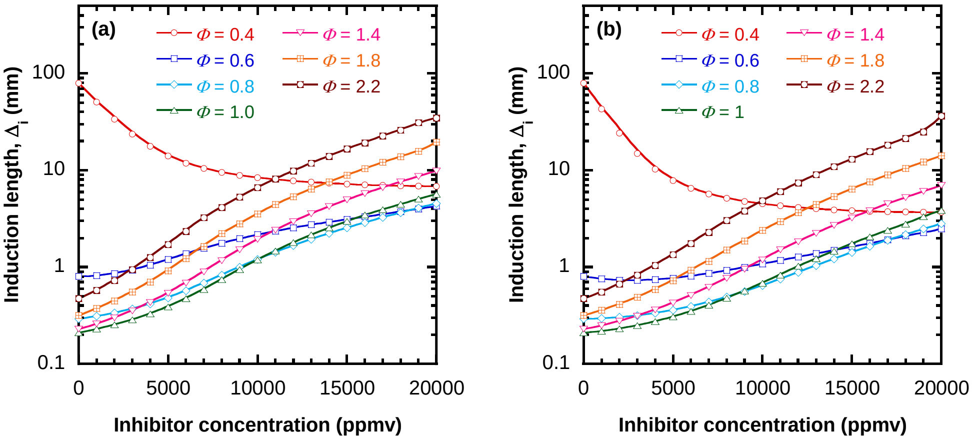

Figure 4: Effect of varying inhibitor concentration on the induction length over a range of equivalence ratios. (a) H_2-air-TMP, and (b) H_2-air-DMMP detonations.

The chemical composition of these inhibitors enables them to act as both inhibitors and promoters, depending on the concentration and mixture conditions. This dual nature highlights the complexity of their interaction with the reaction kinetics and emphasizes the need for a detailed understanding of their chemical pathways under various initial conditions.

4 Conclusions

The current work systematically investigated the inhibition of hydrogen-air detonations using organophosphorus compounds (TMP and DMMP). ZND computations and detailed chemical kinetic models were used to evaluate the effect of these inhibitors on hydrogen-air detonations. The results showed that TMP and DMMP exhibit superior inhibition efficiency compared to CF_3I, resulting in a larger increase in the induction length at the same concentration levels. The inhibition mechanism primarily involves the scavenging of active radicals such as H, O, and OH, coupled with the formation of stable intermediate species. The consumption of reactive radicals in the reaction zone disrupts the chain-branching reactions, thereby suppressing detonation. The fuel content of TMP and DMMP was found to influence detonation dynamics under specific conditions, particularly at lower inhibitor concentrations, where the detonation velocity increased due to an increase in the energy content of the reactant mixture. The study also investigated the effect of the equivalence ratio (ϕ) on the inhibition efficacy of TMP and DMMP. The equivalence ratio significantly impacted the inhibition effectiveness of TMP and DMMP. Under ultra-lean conditions (ϕ=0.4), these inhibitors acted as promoters, thereby reducing the induction length.

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