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Effect of C_2HF_5 and C_3HF_7 on methane and propane ignition and laminar flame speed: Experimental and numerical evaluation

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ABSTRACT

After the restriction on several ozone-depleting compounds, including the high efficiency fire suppressant Halon 1301(CF_3Br), several alternatives have been proposed. Among them, HFC-227-(C_3HF_7) and HFC-125 (C_2HF_5) represent two of the most-used fire suppressants in the industry because of their environmentally favorable properties. Due to their increasing demand, it is very important to understand their combustion properties to optimize their applications and to prevent undesirable events. To this end, the present work examined the effect of C_2HF_5 and C_3HF_7 on CH_4 and C_3H_8 laminar flame speeds and ignition delay times. The experimental techniques included freely propagating flames to obtain unstretched, laminar flame speed and a shock tube for the ignition delay times in fuel-O_2-suppressant mixtures highly diluted in Ar (~98%) using OH* emission near 307 nm. The laminar flame speed experiments were performed at 1 atm over a range of equivalence ratios from 0.7 to 1.3, and the shock-tube tests were done near 1.5 atm over a 1350–2200 K temperature range. A chemical kinetics mechanism was assembled using a HFC set of reactions together with a recently updated C_0-C_5 hydrocarbon mechanism and OH* chemistry. The results suggest that the tested agents may not be good alternatives as ignition preventers, although they can reduce the laminar flame speed, as a proof that they can be used as fire extinguishers. Comparisons between modeled and experimental data show that the HFC submechanism behaves well, however it can be improved. Surprisingly, a sensitivity analysis shows that many of the top reactions containing fluorinated compounds are classified as ignition-promoters, especially for the experiments with CH_4. This work presents some of the first fundamental ignition delay time and flame speed data for HFC-227 and -125, and the results can be used as the basis for future HFC-based chemical kinetics mechanism improvements and to further understand their impact on the combustion process.

1. Introduction

C_2HF_5 (HFC-125) and C_3HF_7 (HFC-227) represent two of the most-used Halon 1301 (CF_3Br) substitutes in the field of fire protection. Their wide acceptance is due to their low ozone-depleting potential, relatively low toxicity, low flammability, and good dispersion capabilities (Robin, 2012). In terms of Minimum Extinguishing Concentration (MEC), HFC-125 and HFC-227 have been shown to be more efficient than other clean alternatives on the market (Luo, 2010; Shmakov et al., 2008). Furthermore, some of their properties are similar to CF_3Br, leading to an easy re-use or adaptation of those installations from which Halon 1301 is removed. At the time of this publication, the Significant New Alternatives Policy (SNAP) program by the Environmental Protection Agency (EPA) includes HFC-227 and HFC-125 on the list of substitutes for Halon 1301 as a total flooding agent. There have been some concerns related to the high global warming potential associated with HFC molecules; however, the use of HFC-125 and HFC-227 for fire protection applications is minimal, and their impact on the climate change represents less than 0.01% of the impact of all greenhouse gas emissions (Robin, 2012). Thus, HFC-125 and HFC-227 are expected to remain as environmentally friendly Halon 1301 substitutes into the foreseeable future (Robin, 2012).

Based on this realization, the use of HFC-125 and HFC-227 has

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been suggested by several programs that search for potential alternatives, including the Halon Alternative Technology Development Program (TDP) by the U.S Department of Defense. Under the TDP, HFC-227 was identified as the best fire suppressant alternative applied in manned spaces of naval ships and critical command and control facilities, while HFC-125 represented the optimal compound used to suppress fires in engines. Consequently, the Next Generation Program by the National Institute of Standards and Technology found HFC-125 as the best single fire suppressant in airplane cabins and cargo bays; this finding shows that it is unlikely that a superior fluid that can be used for such purposes will be discovered (Gann, 2007). Currently, several industries use HFC-125 and HFC-227 as part of their fire suppression systems towards the protection of personal and valuable assets.

Undoubtedly, HFCs represent one of the best options as fire suppressants; however, these compounds have been associated with the promotion of combustion at certain conditions. Therefore, knowing the wide applicability of these substitutes, as well as their increasing demand, it is very important to better understand the combustion properties to provide safe, optimal applications. The following paragraphs provide background related to the flame inhibition mechanism of halogenated compounds and highlights the need for further understanding of the chemical kinetics of all fire suppressants.

Halogenated compounds have been shown to be good fire suppressants, especially when the flame is well established (i.e., after ignition). However, previous studies have demonstrated that they can also promote combustion at certain conditions (Babushok et al., 2012; Ohtani, 2004; Shebeko et al., 2000; Azatyan et al., 2007; Suzuki et al., 1991; Saso et al., 1998; Linteris and Truett, 1996; Hynes et al., 1998; Babushok et al., 1994; Gordon, 1975; Kondo et al., 2009; Gmurczyk and Grosshandler, 1994; Katta et al., 2006; Ural, 2003; Hamins and Borthwick, 1998; Osorio et al., 2013). For example, Osorio et al. (2013) and Suzuki et al. (1991) observed reduction of ignition delay times by the action of CF_3Br on methane mixtures, but the opposite effect was reported on systems containing ethane and propane. Hamins and Borthwick (1998) observed that CF_3Br and CF_3I are very efficient ignition retardants of hydrocarbon/air mixtures on a heated nickel surface, while C_3HF_7 can sometimes lead to a slight promoting effect on methane-air mixtures. On the other hand, Shebeko et al. (2000) used a closed vessel to study the effect of different fluorinated compounds on H_2 and CH_4 flames in air. By examining flammability regions, maximum explosion pressure, and maximum rate of explosion pressure, they concluded that some of these agents can promote combustion, especially in lean mixtures. They attributed this effect to the exothermic conversion of the inhibitor.

Gmurczyk and Grosshandler (1994) focused on the effect of different halomethanes on C_2H_4-air mixtures under highly dynamic situations. Their results showed that all the agents, except CHF_2Cl, can suppress turbulent flames and quasi detonations; they then concluded that the chlorine contained in the CHF_2Cl molecule may behave as a combustion enhancer by acting as an oxidizer. They also suggested that despite the fact that bromine and iodine are good flame inhibitors, they can still be part of both promoting and inhibition reactions; the final effect depends on the agent concentration. Among large-scale experiments, Reinhardt (2004) conducted aerosol can explosion tests involving C_2HF_5. Results showed that C_2HF_5 can increase the explosion overpressure if it is applied in concentrations below a critical value (i.e., the inerting concentration).

To better understand such phenomena, many studies have focused on the development and analysis of chemical kinetics mechanisms. One of the first fundamental works in this area was done by Westbrook (1983) who described a detailed mechanism for CF_3Br on hydrocarbon flames. By numerical analysis, Westbrook showed that the flame inhibition properties of the halogenated compounds are mainly due to their ability to scavenge highly reactive radicals such as H atoms. Also, he demonstrated that CF_3Br is slightly more efficient than CH_3Br and suggested that the fluorine contained in the CF_3Br molecule may be the cause of such an additional effect. This work has served as a basis for subsequent studies that focused on determining the role of specific fluorinated species in different scenarios. These included the study done by Westmoreland et al. (1994) who analyzed different fluoro-methane systems. They found that CF_4 and CF_2O act as inert diluents, while CH_2F_2 and CH_3F behave as fuels by increasing both the adiabatic flame temperature and the flame speed. CHF_3 was found to help the chain-terminating reactions, but at the same time, this species can contribute to increasing the adiabatic flame temperature through exothermicity. Then, the final effect depends on the competition between the HF (which contributes to chain termination reactions) and the production of H radicals from different oxidation mechanisms (Westmoreland et al., 1994). In general, the release of H radicals will be favored since the bond energy of C-F is higher than that for C-H. Nevertheless, this trend is not standard and will depend of the conditions and fuels involved.

Suzuki et al. (1991) suggested that in CH_4 systems the decomposition of the agent is prevalent leading to a promoting effect, while in C_2H_6-CF_3Br systems, the ignition is controlled by the fuel oxidation. Babushok et al. (1994) concluded that the agent can decompose on different active species that either promote or inhibit active radical formation. Osorio et al. (2013) conducted a sensitivity analysis on the ignition chemistry at high temperatures and found that fluorinated species play a significant role in ignition-retardant processes through the reactions ($CH_3 + CF_3 \rightleftarrows CH_2{:}CF_2 + HF$) and ($H + CF_3Br \rightleftarrows CF_3 + HBr$), but at the same time, CF_3 can promote the ignition of methane by activating the reaction $CF_3 + O_2 \rightleftarrows CF_3O + O$. Linteris et al. (2012) used detailed reaction kinetics and thermodynamic calculations, together with a perfectly stirred reactor model, to examine the promotion effects of C_2HF_5 on aerosol can explosions (reported by Reinhardt (2004)). From their analysis, it was concluded that an increment of the pressure can occur at certain concentrations of agent only if a large amount of oxygen is consumed. In other words, these effects are dependent on the stoichiometric fuel-oxidizer-agent proportions.

Katta et al. (2006) modeled the effects of CF_3H on cup burner flames and concluded that fluorinated species such CF_3H, CF_3, CF_2, CF, and CF_2O participate in termination reactions reducing radical concentrations in the flame and forming HF, which is a relatively more stable species. Nevertheless, in cup burner flames, CF_3H dilutes the oxidizer in the stream and also acts as a fuel requiring more oxygen. As a consequence, both the total heat released and the flame size become larger. Similar results were obtained from simulations conducted by Takahashi et al. (2013) who found an additional increment of heat release when C_2H_5F was added to microgravity cup-burner flames. These results are in agreement with Ural (2003) and Babushok et al. (2012) who indicated that halogenated agents possess their own heat release which can support the global combustion process.

Despite all of the extensive research related to HFC effects on flame chemistry, basic understanding of the relevant chemical kinetics still remains elusive. Further progress in this area requires well validated chemical kinetics mechanisms that can provide fundamental insights, and therefore to better predict the behavior of HFC-125 and HFC-227 at different conditions. Such models represent powerful tools that need to be compared against accurate measurements to address uncertainties in the mechanism. For this reason, experiments are particularly valuable, and there is a notable lack of fundamental data to suitably validate the kinetics of fire