Hydrocarbon Flame Inhibition by C₆F₁₂O (Novec 1230): Unstretched Burning Velocity Measurements and Predictions^{*}

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Abstract

This study experimentally and numerically determined the unstretched laminar burning velocity of premixed CH_4 -air and C_3H_8 -air flames with added $\text{C}_6\text{F}_{12}\text{O}$ (Novec 1230). High-speed shadowgraphy of spherically expanding flames provided the burning velocity as a function of stretch, which was extrapolated to zero-stretch conditions using non-linear methods. Unstretched burning velocities predicted using a recently assembled kinetic mechanism were generally in good agreement with the measurements, but tended to have poorer agreement for highly-inhibited very lean flames. To benchmark the performance of $\text{C}_6\text{F}_{12}\text{O}$, measured burning velocities were compared to previously measured burning velocities of premixed flames inhibited by CF_3Br (Halon 1301). The two agents provided similar reductions in the burning velocity of rich flames, whereas CF_3Br provided greater reductions when added to stoichiometric and lean flames. Lastly, experiments and simulations showed the influence of water vapor on the burning velocity of lean C_3H_8 -air flames with added $\text{C}_6\text{F}_{12}\text{O}$. The presence of water vapor in the oxidizer increased the burning velocity by up to 23 % when the fluorine to hydrogen ratio of the reactant mixture was greater than unity.

1. INTRODUCTION

The clean agent fire suppressant $\text{C}_6\text{F}_{12}\text{O}$ ($\text{C}_2\text{F}_5\text{COC}_3\text{F}_7$; FK-5-1-12; Novec 1230) has an ozone depletion potential (ODP) of zero and a global warming potential (GWP) of one, and consequently has already replaced CF_2BrCl (Halon 1211) in many total flooding applications. It may have the potential to replace CF_3Br (Halon 1301) in remaining critical-use applications; however, when tested by the Federal Aviation Administration in the Aerosol Can Test (FAA-ACT), sub-inerting concentrations of $\text{C}_6\text{F}_{12}\text{O}$ caused the pressure rise to more than double compared to the uninhibited case [1, 2]. The behavior of C_2HF_5 and $\text{C}_3\text{H}_2\text{F}_3\text{Br}$ was similar. The FAA-ACT simulates the explosion of an aerosol can during a fire in an aircraft cargo bay. In the test, a suppressant is premixed with air in a 10 m^3 cylindrical pressure vessel (cargo bay simulator) and the typical contents of an aerosol can (ethanol/water/propane, molar ratio: 5.87/5/2.05) are released impulsively across high-voltage arcing electrodes near the center of the chamber [3]. Among the many unique aspects of this test, water constitutes a significant portion of the impulsively released “fuel”.

In previous work, thermodynamic and kinetic models for the decomposition of $\text{C}_6\text{F}_{12}\text{O}$ in hydrocarbon-air systems have been assembled and used to interpret the over-pressure in the FAA-ACT and to study the general effect of $\text{C}_6\text{F}_{12}\text{O}$ [11]. Equilibrium calculations showed that addition of $\text{C}_6\text{F}_{12}\text{O}$ to lean fuel-air systems can increase the adiabatic flame temperature (compared to the uninhibited system), and perfectly stirred reactor calculations showed that agent addition can increase the overall reaction rate. In further work [12], numerical simulations for pure $\text{C}_6\text{F}_{12}\text{O}$ -air at 400 K predicted a premixed, laminar, unstretched burning velocity S_u^0 of 0.367 cm/s for stoichiometric conditions. Although this was significantly lower than typically required for stable flames, and lower than the calculated burning velocity of most of the other pure agent-air blends considered in that study [12] (i.e., CF_3H , $\text{C}_2\text{F}_5\text{H}$, $\text{C}_3\text{F}_7\text{H}$, $\text{C}_3\text{H}_2\text{F}_3\text{Br}$, etc.), the equilibrium simulations [11] together with the dynamics of the FAA-ACT test suggested that in that test, regions of pure $\text{C}_6\text{F}_{12}\text{O}$ -air reacted and contributed to the pressure rise.

In later work [13], the pressure rise and burning velocity were measured in a constant-volume device for stoichiometric and lean ($\Phi = 0.6$) CH_4 -air flames with added $\text{C}_6\text{F}_{12}\text{O}$. When sub-inerting concentrations of $\text{C}_6\text{F}_{12}\text{O}$ were added to the stoichiometric flame, the pressure rise increased slightly before decreasing at higher concentrations, whereas the burning velocity

decreased steadily to about 20 % of the uninhibited flame speed at a $C_6F_{12}O$ volume fraction X_a of 0.03. In contrast, when added to the lean flame ($\Phi = 0.6$), the pressure rise nearly doubled and the burning velocity increased by 30 % at $X_a = 0.02$ before decreasing below the uninhibited value at higher concentrations, consistent with the full-scale results in the FAA-ACT.

The measured burning velocities previously reported in ref. [13] were determined from the pressure rise method and subsequently were not corrected for potential stretch effects and could have been effected by flame-front cellular instabilities (since the flames were not imaged). For these reasons, these data are not well-suited for comparison with predicted burning velocities of 1-D planar flames [14], especially since the response of these inhibited flames to stretch and thermal-diffusive instabilities is unknown. Furthermore, recent research [15] has shown the importance of stretch in the behavior of flames inhibited by halogenated fire suppressants.

The first objective of the present study is to provide unstretched burning velocities for flames with added $C_6F_{12}O$, and to compare them with numerical predictions for 1-D planar unstretched flames as a first step in verifying the performance of the $C_6F_{12}O$ kinetic sub-model. Verification and further development of the kinetic model for $C_6F_{12}O$ -fuel-air combustion will allow use of the model for understanding and predicting the behavior of $C_6F_{12}O$ as a fire suppressant added to premixed and diffusion flames. The second objective is to compare the inhibition performance of $C_6F_{12}O$ to CF_3Br for a wider range of premixed flame conditions and inhibitor concentrations than previously considered in ref. [13] to further identify conditions and scenarios for which $C_6F_{12}O$ could be used as an effective replacement. The third objective is to experimentally and numerically study the effect of water vapor on the flame propagation with added $C_6F_{12}O$.

Water vapor in air can influence the reaction rates of fluorinated hydrocarbons. Wider flammability limits and higher heats of combustion have been reported [4-6], and the importance of water vapor as an additional source of H-atoms in the radical pool during combustion of highly fluorinated compounds has been described [7-10]. Moreover, an influence of relative humidity of the ambient air for flames with added $C_6F_{12}O$ or pure $C_6F_{12}O$ -air flames has been observed numerically [11]. Hence, the present experiments and simulations are used to explore the role of water vapor in the reactivity of the $C_6F_{12}O$ -fuel-air system.

To accomplish the three objectives, high-speed shadowgraph imagery of outwardly propagating spherical flames provide data on the flame location as a function of time. Post processing of the data incorporating non-linear extrapolations yields the unstretched burning velocities and allows comparison to the results of 1-D planar premixed simulations. Experiments and simulations are performed with $C_6F_{12}O$ added to CH_4 - and C_3H_8 -air mixtures over a range of equivalence ratio. The numerical results are used to interpret the reaction of $C_6F_{12}O$ and its decomposition products.

2. EXPERIMENTAL

The experiment and the data reduction techniques are outlined below, with more details available in ref. [15]. The visually accessible 30 L spherical chamber and z-type shadowgraph system for high-speed video recording (schematics shown in Fig. 1) are based on the design of Faeth and coworkers [16-19] and Takizawa et al. [20]. Mixtures are prepared in the chamber via the partial pressure method, circulated for 3 minutes (using a metal bellows pump) to ensure complete mixing, then given 10 minutes to settle. The sample reactants are CH_4 (Matheson Tri-Gas, 99.97 % purity), C_3H_8 (Scott Specialty Gases, 99.0 % purity), $C_6F_{12}O$ (3M, > 99 % purity), de-ionized house water, and house air that is filtered, dried, and conditioned with a $0.01\ \mu m$ filter, a carbon filter, and a desiccant bed to remove small aerosols, organic vapors, and water vapor. A capacitive discharge system generates a spark (with an estimated energy of 0.05 mJ to 500 mJ) near the center of the chamber to initiate combustion. For each test, the ignition energy is gradually increased until ignition occurs, ensuring that the supplied energy is within an order of magnitude of the minimum ignition energy (MIE).

Fig. 1: Schematic diagram of the experiment (left) and the shadowgraph system (right).

For each test, flame propagation is captured via a high speed camera, and post-processing of the images (using custom-developed software) yields the flame radius R_f as a function of time t . For slow flames (burning velocity ≈ 10 cm/s or lower), buoyancy affects the burned gas velocity and the local stretch rate. To minimize the influence, the flame radius as a function of time for all tests is determined by tracking the flame progression in the two horizontal directions [20-22]. The temporal evolution of the flame radius R_f yields the stretched burned gas velocity as a function of flame radius, which is related to the stretch rate K (s^{-1}) [23] as

$$K = \frac{2}{R_f} \frac{dR_f}{dt} = \frac{2}{R_f} S_b \quad (1)$$

Extrapolation to zero-stretch conditions is done using the non-linear equation derived by Ronney and Sivashinsky [24], and formulated by Kelley and Law [25],

$$\left(\frac{S_b}{S_b^0}\right)^2 \ln\left(\frac{S_b}{S_b^0}\right)^2 = -2 \frac{L_b K}{S_b^0} - 2 \frac{L_b}{S_b^0} \frac{dS_b}{dR_f} \quad (2)$$

where S_b^0 is the unstretched burned gas velocity and L_b is the burned gas Markstein length, which is a measure of the response of the flame to stretch. Eq. 2 has been shown to work well for mixtures with Lewis numbers $Le \geq 1$ [25-27]. The expanded form of Eq. 2,

$$\frac{S_b}{S_b^0} \left[1 + \frac{2L_b}{R_f} + \frac{4L_b^2}{R_f^2} + \frac{16L_b^3}{3R_f^3} + o^4 \left(\frac{L_b}{R_f} \right) \right] = 1 \quad (3)$$

is considered to avoid the difficulty in applying Eq. 2, which is unstable. Lastly, the integrated form of Eq. 3 is used to eliminate errors associated with numerical differentiation,

$$S_b^0 t + c = R_f + 2L_b \ln R_f - 4 \frac{L_b^2}{R_f^2} - \frac{8}{3} \frac{L_b^3}{R_f^3} \quad (4)$$

where the variable c is an integration constant. The variables S_b^0 , L_b , and c in Eq. 4 are determined by fitting the equation to the experimental data (flame radius as a function of time). From conservation of mass across the flame sheet, the unstretched unburned gas velocity S_u^0 is then obtained:

$$S_u^0 = \frac{\rho_b}{\rho_u} S_b^0 \quad (5)$$

where ρ_u and ρ_b are the unburned and burned gas densities. The burned gas is assumed to be in chemical equilibrium and is taken from a constant-pressure, constant-enthalpy calculation

described below. Validation of the experimental results and the post-processing and data reduction methods has been described previously [15].

The initial conditions are 296 ± 2 K and 1.01 bar, and tests are repeated twice for each mixture. Fitting coefficients generated from the right and left side tracking are averaged and then results from the two tests are averaged. As described in ref. [15], the maximum expanded relative uncertainty in the measured burning velocity is 13 %. Experimental validation described in ref. [15] showed that measured burning velocities were well within the scatter of previously reported data for CH₄-air and C₃H₈-air mixtures.

3. NUMERICAL METHODS

Equilibrium adiabatic flame temperatures are calculated using the Sandia EQUIL code [28], for constant pressure, constant enthalpy conditions. Planar adiabatic freely propagating flame structures are calculated using the Sandia PREMIX code [29-31]. Simulations are performed at 298.15 K and 1.01 bar with air composed of 21 % O₂ and 79 % N₂. The Soret effect is included and molecular diffusion is accounted for using mixture-averaged coefficients. The GRAD and CURV parameters are each set to 0.05, resulting in 350 to 550 grid points.

The kinetic model (previously assembled in ref. [11]) is composed of the following sub-models. The hydrocarbon model is from the USC Mech, Version II [32] for H₂/CO/C1-C4 compounds. The C1-C2 hydrofluorocarbon model is based on the original NIST HFC mechanism [33, 34], with updates as summarized in refs. [35, 36] (including new rate data for reactions involving atomic fluorine). The reactions of C3 fluorocarbons are from inhibition studies of C₃F₇H [37]. The decomposition reactions of C₆F₁₂O and its products down to C3 and smaller species are described using the model presented in ref [11] and summarized in Table 1.

Table 1: Sub-mechanism describing the decomposition reactions of $C_6F_{12}O$ ($C_2F_5COC_3F_7$) and its products.

Reaction	A (cm, mol, s)	E (J/mol)	Notes
$C_2F_5COC_3F_7 \rightarrow C_3F_7 + C_2F_5CO$	8.5E+16	288,700	[38]a
$C_2F_5COC_3F_7 + H = C_2F_5CHO + C_3F_7$	2.0E+12	20,900	b
$C_2F_5COC_3F_7 + OH = C_2F_5CO + C_3F_7OH$	5.0E+12	25,100	
$C_2F_5COC_3F_7 + O = C_2F_5CO + C_3F_7O$	5.0E+12	33,500	
$C_2F_5CHO + H = C_2F_5CO + H_2$	4.0E+13	16,700	c
$C_2F_5CHO = C_2F_5 + HCO$	4.0E+16	334,700	d
$C_2F_5CHO + CF_3 = CHF_3 + C_2F_5CO$	1.3E+11	28,000	[39]
$C_2F_5CHO + CF_3 = CH_4 + C_2F_5CO$	7.9E+12	41,000	[39]
$C_2F_5CO = C_2F_5 + CO$	2.2E+13	33,500	[40, 41]e
$CF_3COF + CF_3 = CF_3CO + CF_4$	2.0E+12	37,700	
$CF_3COF + C_2F_5 = CF_3CO + C_2F_6$	3.0E+11	58,600	
$C_2F_6 + CF_3 = CF_4 + CF_3O$	3.0E+12	47,300	
$CF_3CO + F = CF_3 + CF_3O$	3.0E+12	0	
$CF_3CO + F = CF_4 + CO$	5.0E+12	0	

^a Analogy with decomposition of perfluoroacetone [38]. Activation energy adjusted for enthalpy change.

^b Similar to the displacement reaction of perfluoroacetone [38].

^c Similar to the $CF_3CHO + H$ reaction.

^d Similar to CF_3CHO [38].

^e Analogy with decomposition of CF_3CO [40]; adjustment with the use of data in [41].

4. RESULTS AND DISCUSSION

4.1 Comparison of experimental data with previous measurements

Fig. 2 compares the present measurements with data of ref. [13], which were determined with a different experimental approach (i.e., from pressure rise in a constant volume, 2 L chamber) and were not stretch corrected (hence the y-axis is labeled S_L). At nearly all conditions, the present and previous measurements agree within 4 %, except at $\Phi = 0.6$ and $X_a = 0.03$ where the present burning velocity is lower by 20 %.

Fig. 2: Comparison of measured burning velocities for CH_4 -air with added $C_6F_{12}O$. Square symbols are the present measurements and diamonds are the measurements reported in ref. [13].

4.2 Comparing suppression effectiveness of $C_6F_{12}O$ and CF_3Br

Laminar burning velocities of CH_4 -air and C_3H_8 -air flames with added $C_6F_{12}O$ are compared to those with added CF_3Br measured in previous work [15]. Fuel-air equivalence ratios Φ of 0.6, 0.8, 1.0, and 1.2 are considered, with agent addition up to $X_a = 0.03$, or to the concentration that prevents ignition (the values of which are specific to our configuration and available ignition energy and technique). Reported equivalence ratios are based on the uninhibited mixtures, with the reported fuel-air ratio held constant as agent is added. Fig. 3 shows the unstretched burning velocities S_u^0 (left axes) and equilibrium adiabatic flame temperatures T_{ad} (right axes) of CH_4 -air (left frames) and C_3H_8 -air (right frames) as a function of agent volume fraction. Rich flames ($\Phi = 1.2$) are shown in the top frames, with descending frames showing data at progressively leaner conditions.

Fig. 3: Measured burning velocity S_u^0 (symbols) and calculated adiabatic flame temperature T_{ad} (lines) of CH₄-air (left frames) and C₃H₈-air (right frames) with added CF₃Br (Δ) and C₆F₁₂O ($\circ$). For clarity, lines connect the experimental data points (and do not represent numerical predictions). Data at $S_u^0 = 0$ represent points of unsuccessful flame propagation or non-ignition and are not intended to signify flammability limits.

Rich flames ($\Phi=1.2$)

When adding $C_6F_{12}O$ or CF_3Br to rich flames, $C_6F_{12}O$ provides a greater reduction in the adiabatic flame temperature, but the two agents provide similar reductions in burning velocity. For rich CH_4 -air mixtures, addition of $C_6F_{12}O$ at $X_a = 0.03$ lowers T_{ad} by about 340 K compared to the uninhibited conditions, whereas CF_3Br only slightly lowers it by about 75 K when added at the same concentration. The behavior for the rich C_3H_8 -air mixtures is similar. For the burning velocity of the rich CH_4 -air mixture, similar reductions occur when adding the two agents at low volume fractions (e.g., $X_a = 0.01$); however, at $X_a = 0.02$, CF_3Br prevents ignition while flame propagation occurs with $C_6F_{12}O$ (S_u^0 of 5.8 cm/s). For C_3H_8 -air mixtures, the two agents yield a very similar reduction in burning velocity for the values of X_a tested (0.01, 0.02, and 0.03). For CF_3Br , the lower reduction in T_{ad} but comparable reduction in S_u^0 illustrates its superior catalytic radical recombination action as compared to $C_6F_{12}O$, which acts much like a blend of C_2HF_5 and C_3HF_7 [11].

Stoichiometric flames

For the stoichiometric flames, the reduction in flame temperature with agent addition is similar to that in the rich flames; however, the reduction in burning velocity is greater for CF_3Br addition than with $C_6F_{12}O$ addition. Note that for the case of $C_6F_{12}O$ addition to the C_3H_8 -air mixtures, there is a kink in the curve for T_{ad} vs. X_a , near $X_a = 0.026$ (at which value the slope of the curve becomes steeper). At this value of X_a , the fluorine to hydrogen ratio ($[F]/[H]$) in the mixture is unity. Above this agent loading, the system is hydrogen deficient, and cannot form the most stable product of fluorinated species (HF), and instead forms partially oxidized species (such as COF_2 and CF_4), so that the heat release is less and T_{ad} cannot reach as high a value. Note that for stoichiometric CH_4 -air mixtures, $[F]/[H] = 1$ occurs at $X_a > 0.03$, so the change in the slope of T_{ad} vs X_a is not observed in the figure.

Lean flames ($\Phi = 0.8$ and 0.6)

At $\Phi = 0.8$, CF_3Br addition again slightly decreases the adiabatic flame temperature, whereas $C_6F_{12}O$ addition steadily increases it (compared to the uninhibited case) for X_a up to about 0.02 before starting to reduce it at higher concentrations. For both CH_4 - and C_3H_8 -air flames, T_{ad} begins to fall once $[F]/[H] = 1$, as was the case for the stoichiometric C_3H_8 -air flame. For flame

speed reduction, CF_3Br is about three (two) times as effective as $\text{C}_6\text{F}_{12}\text{O}$ when added to CH_4 -air (C_3H_8 -air) flames at $\Phi = 0.8$; moreover, at $X_a = 0.02$, addition of CF_3Br prevents ignition of both CH_4 and C_3H_8 whereas addition of $\text{C}_6\text{F}_{12}\text{O}$ yields a flame with S_u^0 of about 15 cm/s.

At the leanest conditions considered ($\Phi = 0.6$), CF_3Br addition again decreases the adiabatic flame temperature of CH_4 -air and C_3H_8 -air, whereas $\text{C}_6\text{F}_{12}\text{O}$ increases it by as much as 340 K. For these lean CH_4 - and C_3H_8 -air mixtures, the $[\text{F}]/[\text{H}]$ ratio when adding $\text{C}_6\text{F}_{12}\text{O}$ reaches unity at $X_a = 0.02$ and $X_a = 0.016$ respectively; thus T_{ad} increases up to these values of X_a . For burning velocity, addition of the two agents to the leanest flames is quite different: CF_3Br prevents ignition of both the CH_4 - and C_3H_8 -air flames at $X_a = 0.005$, whereas $\text{C}_6\text{F}_{12}\text{O}$ increases the burning velocity of the CH_4 -air flame at $X_a = 0.01$ and 0.02 as previously observed in ref. [13].

The adverse effect when adding $\text{C}_6\text{F}_{12}\text{O}$ to lean flames is the result of the exothermic reaction of the molecule with oxygen and the fuel, which increases T_{ad} , even for X_a for which $[\text{F}]/[\text{H}]$ is considerably higher than unity depending on the initial equivalence ratio. The increased T_{ad} increases the rate of the chain-branching step $\text{H} + \text{O}_2 = \text{OH} + \text{O}$, increasing chain-branching radical volume fractions, and this effect dominates over the chain-terminating reactions of the fluorinated species with radicals; nonetheless, at higher loading, the temperature enhancement decreases and the radical trapping by the fluorinated species increases, leading to more effective flame inhibition.

4.1 $\text{C}_6\text{F}_{12}\text{O}$ model verification

To test the performance of the $\text{C}_6\text{F}_{12}\text{O}$ model, the measured burning velocities are compared to predictions, as shown in Fig. 4 for CH_4 -air (left frame) and C_3H_8 -air (right frame) flames with $\Phi = 0.6, 0.8, 1.0$, and 1.2, and $\text{C}_6\text{F}_{12}\text{O}$ added up to a volume fraction $X_a = 0.03$. The different symbols (measurements) and line styles (predictions) represent data at different Φ . As indicated, for the CH_4 -air flames, the measured and predicted burning velocities agree very well (generally within 6 % to 11 % of each other), except for the case of the very lean flame ($\Phi = 0.6$) of CH_4 -air. In that condition, the largest discrepancy occurs for the uninhibited flame, for which the measured value is 2.8 cm/s lower than the prediction, and about 0.7 cm/s to 1.6 cm/s lower for the other values of X_a .

For the C_3H_8 -air flames, the predictions are generally good (within about $\pm 15\%$) for the rich and stoichiometric flames. For $\Phi = 0.8$, predictions are within 5 % for $\text{C}_6\text{F}_{12}\text{O}$ loadings up to $X_a = 0.02$, whereas at $X_a = 0.03$ the predicted burning velocity is about 80 % higher than the measured result (8.0 cm/s compared to 4.8 cm/s). At $\Phi = 0.6$, the uninhibited burning velocity prediction is 14.4 cm/s and compares well to the measured value of 13.6 cm/s, but with added $\text{C}_6\text{F}_{12}\text{O}$, the model under-predicts suppression performance: predicted burning velocities are 13 % to 130 % higher for $0.01 \leq X_a \leq 0.03$, with the discrepancy increasing as the concentration increases. It is too early to conclude if the discrepancy is due to shortcomings in the kinetic model, or to errors due to buoyancy and radiation heat losses, which become more important for the slower flames, as has been discussed in the literature [22, 42-44], but even for these very lean flames near the flammability limit, the simulations capture the main features of the inhibited flames.

Fig. 4: Comparison of experimental (symbols) and numerical (lines) S_u^0 for $\text{C}_6\text{F}_{12}\text{O}$ inhibited CH_4 -air (left frame) and C_3H_8 -air (right frame) flames at $\Phi = 0.6, 0.8, 1.0$, and 1.2 .

4.2 Equilibrium product species

For stoichiometric CH_4 -air flames, Fig. 5 (left frame) shows the equilibrium product species volume fractions as a function of $\text{C}_6\text{F}_{12}\text{O}$ volume fraction, while for CH_4 -air flames with $\text{C}_6\text{F}_{12}\text{O}$ added at $X_a = 0.03$, Fig. 5 (right frame) shows the equilibrium product species as a function of

equivalence ratio. As indicated, the peak value of HF volume fraction is 0.27 (at $\Phi = 1.0$ and $X_a = 0.03$). Unity $[F]/[H]$ ratio occurs near $X_a = 0.03$ for $\Phi = 1.0$. At higher agent loadings (left frame), COF_2 and CF_4 form and have volume fractions of around 5 % when $X_a = 0.06$.

Fig. 5: Calculated equilibrium product species volume fractions as a function of $\text{C}_6\text{F}_{12}\text{O}$ volume fraction when $\Phi = 1.0$ (left frame) and as a function of equivalence ratio when $X_a = 0.03$ (right frame).

4.3 Sensitivity analysis

The first-order sensitivity coefficients of the burning velocity with respect to reaction rate pre-exponential factors A_i ($\delta \ln S_u / \delta \ln A_i$) are shown in Fig. 6 for C_3H_8 -air flames at $\Phi = 1.0$ and 0.6 and with $\text{C}_6\text{F}_{12}\text{O}$ added at a volume fraction of 3%. For these flames, the burning velocity is most sensitive to the chain branching reaction $\text{H} + \text{O}_2 = \text{O} + \text{OH}$, followed by reactions involving fluorinated intermediates which either increase or decrease the concentration of H and O. Reactions of CF_2O , CF_3 , and CF_2 with H or O to form HF have negative sensitivities (i.e., they add to the heat release and increase burning velocity). Reactions with fluorinated intermediates that form the chain branching radicals H and O have positive sensitivities. In general, the burning velocity of the lean C_3H_8 -air flame with added $\text{C}_6\text{F}_{12}\text{O}$ is more sensitive than is the stoichiometric flame to rates of reactions involving fluorinated species.

Fig. 6: Sensitivity coefficients for stoichiometric and lean ($\Phi=0.6$) C_3H_8 -air with $C_6F_{12}O$ addition at a volume fraction of 3%.

4.4 Influence of H_2O on the effectiveness of $C_6F_{12}O$

Previous numerical simulations [10] of CH_4 -air flames with added C_2HF_5 have shown that added water vapor either increases or decreases the burning velocity depending on whether the fluorine to hydrogen ratio $[F]/[H]$ is greater than or less than unity. To explore the influence of $[F]/[H]$ for flames with added $C_6F_{12}O$, burning velocities are measured and calculated for lean C_3H_8 flames ($\Phi = 0.6$) in air at a relative humidity of 0 % and 100 % (at 23 °C) with added $C_6F_{12}O$. The lean flame is considered for consistency with the conditions of the FAA-ACT [11], for which water vapor was calculated to have a large effect, and to ensure that the burning velocities can be measured for a range of $[F]/[H]$ ratios (i.e., at higher Φ , it becomes difficult to ignite mixtures with $C_6F_{12}O$ added at concentrations needed to achieve $[F]/[H]>1$).

Fig. 7 presents burning velocity measurements (symbols) and predictions (lines), along with calculated equilibrium adiabatic flame temperatures as a function of the added $C_6F_{12}O$ volume fraction, for C_3H_8 flames at $\Phi = 0.6$ in saturated (solid lines) and dry (dashed lines) air. The dotted vertical lines represent the $C_6F_{12}O$ concentration for which the $[F]/[H]$ ratio of the dry and humid flames is unity ($X_a = 0.016$ and 0.02). The burning velocity predictions are consistently higher than the measurements (as is discussed above for this value of Φ), but they exhibit similar trends as the concentration of $C_6F_{12}O$ increases. When the $C_6F_{12}O$ concentration is less than

about 0.013 ($[F]/[H] < 0.8$), H_2O acts as a suppressant, as can be observed in the adiabatic flame temperature, which is 10 K lower for the moist flame as compared to the dry flame. At higher $C_6F_{12}O$ concentrations ($[F]/[H] > 0.8$), the water in the oxidizer enhances the burning velocity in both the experiments and simulations. As observed in ref. [10], the enhancement begins when the $[F]/[H]$ ratio is close to but slightly less than unity, and increases as $[F]/[H]$ increases, but then decreases as the fluorine-radical (F) driven flame propagation becomes insensitive to relatively low values of $[H]$. The model somewhat under-predicts the enhancement by H_2O for $[F]/[H] > 1$, but generally captures the enhancement effect observed in the experiments.

Fig. 7: Measured and predicted burning velocities (lower symbols and curves, respectively) and equilibrium adiabatic flame temperatures (top curves) for C_3H_8 -air at $\Phi = 0.6$ in dry (solid lines and Δ symbols) and humid air (dashed lines and $\square$ symbols), as a function of added $C_6F_{12}O$ volume fraction.

To further understand the influence of water vapor on reactivity, Fig. 8 shows the equilibrium and peak H and OH concentrations as a function of $C_6F_{12}O$ volume fraction for the humid and

dry C_3H_8 -air flames. For $X_a \leq 0.015$ ($[\text{F}]/[\text{H}] < 1$), water vapor has little effect on the equilibrium and peak concentrations. Near $X_a = 0.015$, however, the equilibrium and peak volume fractions reach a maximum value at a slightly higher $\text{C}_6\text{F}_{12}\text{O}$ concentration for moist air. This is because, with water vapor, the fluorine to hydrogen ratio reaches unity at a higher $\text{C}_6\text{F}_{12}\text{O}$ concentration as a result of the additional H from the H_2O in the air. Similarly, in Fig. 7, a shift in the peak and a higher value of T_{ad} occurs with humid air, leading to a higher burning velocities for the humid flame when X_a is between 0.015 and 0.03. Although adiabatic flame temperatures are similar at $X_a \geq 0.03$, the model and experiment continue to yield a higher burning velocity when water vapor is present because (as shown in Fig. 8) peak radical concentrations remain higher for the humid flame. As discussed in ref. [10], the rate of the reaction $\text{H}_2\text{O} + \text{F} = \text{HF} + \text{OH}$ increases as the concentration of H_2O increases. Not only is this reaction exothermic, it also forms the active flame radical OH, and this additional reaction pathway for the formation of OH is responsible for the increased burning velocity when the $\text{C}_6\text{F}_{12}\text{O}$ concentration is larger than $X_a \geq 0.03$.

Fig. 8: H and OH radical volume fractions, peak (upper curves) and equilibrium (lower curves) for C₃H₈-air at $\Phi = 0.6$ in dry (solid lines) and humid air (dashed lines), as a function of added C₆F₁₂O volume fraction.

5. CONCLUSIONS

The clean agent fire suppressant C₆F₁₂O has replaced Halon 1211 in many total flooding applications and has potential to replace Halon 1301 in others. A kinetic mechanism for its inhibition of hydrocarbon-air flames has been presented in the literature, but the mechanism has not been tested against experimental data. As a first step in model validation, premixed flame

unstretched burning velocities were measured and calculated and compared with each other. CH₄-air and C₃H₈-air mixtures ranging in equivalence ratio were considered (at 296 K and 1.01 bar), with C₆F₁₂O added at volume fractions up to $X_a = 0.03$. In some cases, the relative humidity of the air was varied. Considering the early stage of development of the C₆F₁₂O mechanism, the measured and predicted burning velocities were generally in good agreement, but tended to have poorer agreement for highly-inhibited very lean flames. Improvements to the model may be necessary to eliminate the discrepancy between predictions and measurements when adding higher concentrations of C₆F₁₂O to lean C₃H₈-air flames.

As a benchmark, the burning velocities of similar flames with added CF₃Br were compared to those with C₆F₁₂O. The two suppressants provided similar reductions in the burning velocity of rich flames, whereas CF₃Br provided greater reductions when added to stoichiometric and lean flames. When added to lean flames at moderate loading, C₆F₁₂O increased both the final flame temperature and the burning velocity (i.e., the system became more reactive). This effect is responsible for the switching of the relative performance of C₆F₁₂O as compared to CF₃Br for rich and lean flames, and is consistent with the overpressure observed in the FAA Aerosol Can Test (which used to screen potential halon replacements for aircraft cargo bay fire suppression).

The influence of water vapor on the effectiveness of C₆F₁₂O in the FAA Aerosol Can Test postulated in previous work has been demonstrated experimentally and numerically for premixed flames. Experiments and calculations were performed for lean C₃H₈ in dry and humid air ($\Phi = 0.6$) with added C₆F₁₂O. Water vapor in the oxidizer either suppressed or enhanced the burning velocity depending on the ratio of fluorine to hydrogen in the system. When there was less fluorine than hydrogen ($[F]/[H] < 0.8$) the added water vapor acted as a diluent. When the system contained more fluorine than hydrogen (i.e., at higher C₆F₁₂O concentrations), added water vapor increased the burning velocity. The reaction $F + H_2O = OH + HF$ or increased final temperature (depending upon the value of $[F]/[H]$) were primarily responsible for the enhanced burning velocity.

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