Premixed flame inhibition by $C_2HF_3Cl_2$ and $C_2HF_5^*$

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Abstract

This study is the first to examine the inhibition effectiveness of $\text{C}_2\text{HF}_3\text{Cl}_2$ (HFC-123) on premixed hydrocarbon-air flames and is motivated by the eventual phase-out of CF_3Br (Halon 1301) used in civilian aircraft cargo compartments. To study the inhibition effectiveness, we measured the laminar burning velocity of CH_4 -air flames with added $\text{C}_2\text{HF}_3\text{Cl}_2$ in a spherical, constant-volume combustion vessel, over a range of inhibitor concentration and fuel-air equivalence ratio. Burning velocities at ambient ($T=298\text{ K}$; $P=1.01\text{ bar}$) and elevated ($T=400\text{ K}$; $P=3\text{ bar}$) conditions were compared to numerical predictions obtained using a newly-developed kinetic mechanism describing the decomposition of hydrochlorofluorocarbons (HCFCs) in hydrocarbon-air systems. The agreement was very good, considering the model parameters were not adjusted, and the present study was the first to test the mechanism against experimental data of a two-carbon HCFC. In addition to providing model validation, the effectiveness of $\text{C}_2\text{HF}_3\text{Cl}_2$ was compared to the analogous HFC compound C_2HF_5 to explore the advantages of Cl substitution for F. Experimental measurements of agent influence on burning velocity, as well as numerical modeling of premixed flame structures, demonstrated that $\text{C}_2\text{F}_3\text{Cl}_2\text{H}$ is a more effective flame inhibitor than $\text{C}_2\text{F}_5\text{H}$, particularly for very lean CH_4 -air mixtures. The reaction pathways and sensitivities were analyzed to interpret the differences in the inhibition mechanisms of $\text{C}_2\text{F}_5\text{H}$ and $\text{C}_2\text{HF}_3\text{Cl}_2$ and to prioritize elementary reactions for further study.

1. INTRODUCTION AND BACKGROUND

Because of its high ozone depleting potential (ODP), the fire suppressant Halon 1301 (CF_3Br) has been largely phased out. The civilian aircraft industry has received an exemption; however, the European Union is requiring replacement in new design aircraft by 2018, and existing aircraft by 2040. Cargo-bay fire suppression accounts for most of the Halon 1301 on aircraft (about 80 %), and is also proving to be the most difficult application for which to find replacements. For example, in a Federal Aviation Administration (FAA) - mandated test for cargo-bay fire suppression (the so-called Aerosol Can Test, abbreviated herein as the FAA-ACT), all of the proposed replacements so-far tested, HFC-125 (C_2HF_5), Novec 1230 ($\text{C}_6\text{F}_{12}\text{O}$), and 2-BTP ($\text{C}_3\text{H}_2\text{F}_3\text{Br}$) have failed [1-3]. The FAA-ACT simulates the explosion of an aerosol can caused by a fire in a cargo bay. In the test, a 10 m^3 pressure vessel replicates a section of a cargo bay; a fast-acting valve in the vessel releases a two-phase spray of the simulated contents of an aerosol can (alcohol, propane, and water), which flows past a 30 kV DC arc, and creates a fire ball. In the absence of suppressant, the pressure rise is about 1.8 bar, whereas at high enough agent concentration (the inerting concentration) in the air, the pressure rise is negligible. Unfortunately, when added at sub-inerting concentrations, all of the replacement agents created higher peak pressures than with no agent, failing the test. In contrast, CF_3Br reduced the peak pressure for all added concentrations.

Previous work analyzing the FAA-ACT [4-7] showed that the overpressure phenomenon depends upon the heat release from agent reaction (and consequent higher temperature), in competition with the slower reactivity of the halogen-inhibited, hydrocarbon-air systems. This competition was most apparent for very lean hydrocarbon-air flames and for pure suppressant-air flames (with predicted burning velocities of a few cm/s), which exist in the end gases of the FAA-ACT chamber. As described below, the agent $\text{C}_2\text{HF}_3\text{Cl}_2$ (CF_3CHCl_2 , HCFC-123) has been considered as a potential CF_3Br replacement [8-10] and has potential to overcome the enhanced overpressure in the FAA-ACT; hence, it is the subject of study in the present work. Because the agent C_2HF_5 has also been tested in the FAA-ACT, is the analogous HFC agent (to the HCFC $\text{C}_2\text{HF}_3\text{Cl}_2$), and is used as a halon replacement, it is analyzed in the present work for comparison.

Shebeko et al. [11] measured the flammability limits of many halogenated hydrocarbons and found the hydrochlorofluorocarbons, HCFCs, to require lower concentrations than the

hydrofluorocarbons, HFCs, for inertion of H_2 -air and CH_4 -air flames. Moore et al. [12], using an n-heptane co-flow diffusion flame (cup-burner), found minimum extinguishing values (MECs) of 0.094 and 0.071 for C_2HF_5 and $\text{C}_2\text{HF}_3\text{Cl}_2$, again illustrating superior performance for the HCFC relative to HFC. Variable strain rate opposed flow diffusion flame experiments [13], as well as turbulent spray diffusion flame experiments [14], indicated that among various HCFCs and HFCs, $\text{C}_2\text{HF}_4\text{Cl}$ required the lowest mass fraction (with the exception of CF_3Br) for flame extinction. The higher suppression effectiveness of chlorinated as compared to fluorinated compounds has been discussed [15-17]. Chlorine participates in catalytic recombination cycles, so that each Cl atom recombines a larger number of radicals, whereas fluorinated species essentially trap one radical per F atom, ultimately forming HF, which, due to its high stability does not enter into catalytic cycles [15]. Hence, kinetically, the agent $\text{C}_2\text{HF}_3\text{Cl}_2$ should lower the reactivity more so than C_2HF_5 , since two of the F atoms are replaced by Cl atoms.

Another benefit of HCFCs over HFCs is a potentially lower heat release with added agent. Holmstedt et al. [18] performed co-flow diffusion flame experiments with HFC, HCFC, and Halon 1301 suppressants premixed in the *fuel* stream (propane), and found that Halotron I (about 95% $\text{C}_2\text{HF}_3\text{Cl}_2$) was the only agent tested, besides CF_3Br , that did not increase the heat release rate. Takahashi et al. [10] performed simulations of co-flow diffusion flames stabilized on a cup burner, and found that at volume fractions just below those for extinguishment, C_2HF_5 increased the total heat release in the flame by 158 %, whereas $\text{C}_2\text{HF}_3\text{Cl}_2$ increased it by only 37 %. Similarly, Shebeko et al. [11] found that CHF_3 widened the lean flammability limit (of CH_4 -air flames), whereas CHF_2Cl did not. Babushok et al. [9] developed a kinetic reaction mechanism for $\text{C}_2\text{HF}_3\text{Cl}_2$, and using it, predicted that $\text{C}_2\text{HF}_3\text{Cl}_2$ should provide greater burning velocity reduction than C_2HF_5 when added to stoichiometric premixed CH_4 -air flames. Initial tests of the performance of the mechanism were conducted using experimental data available in the literature (burning velocity data for $\text{CO-H}_2\text{-O}_2\text{-Ar}$ mixtures with the added one-carbon HCFCs: CFCl_2 , CF_2Cl_2 , and CF_3Cl) [19]; however, no experimental data exist for the inhibition effectiveness of $\text{C}_2\text{HF}_3\text{Cl}_2$ when added to premixed hydrocarbon-air flames, and many of the previous studies did not consider $\text{C}_2\text{HF}_3\text{Cl}_2$ itself.

The present work provides initial tests of the accuracy of the newly developed HCFC kinetic model [9] for predicting burning velocity of CH_4 -air flames with added $\text{C}_2\text{HF}_3\text{Cl}_2$. For

comparison, experiments and simulations are also performed for the analogous HFC compound C_2HF_5 . A laboratory-scale, constant volume combustion device [20] provides the laminar burning velocity of CH_4 -air flames (for a range of equivalence ratios) with added $\text{C}_2\text{HF}_3\text{Cl}_2$ and C_2HF_5 , for ambient (298 K; 1.01 bar) and elevated (400 K; 3 bar) conditions. The experimental results are compared to the numerical predictions obtained using the newly-developed kinetic mechanism. The results are used to explore the advantages of chlorinated hydrocarbons over fluorinated as flame inhibitors.

Although the Montreal Protocol classifies $\text{C}_2\text{HF}_3\text{Cl}_2$ as a controlled substance (due to its ozone depletion potential, ODP), it is permitted for use in the United States and in the EU as a halon replacement [21]. $\text{C}_2\text{HF}_3\text{Cl}_2$ has low ODP (0.02) and GWP (77) and is one of several HCFCs that could offer improved performance in the FAA-ACT. Thus, in addition to examining the performance of $\text{C}_2\text{HF}_3\text{Cl}_2$, the generic value of Cl substitution for F is examined here to provide a basis for exploring new low-ODP halon replacements that may currently exist or may be developed (e.g., halogenated ketones or alkenes).

2. EXPERIMENTAL

2.1. Apparatus

The constant volume combustion device, used in past work [20], is illustrated in Fig. 1. The spherical stainless steel chamber has an inner diameter of 15.24 cm, volume of 1.85 L, and wall thickness of 2.54 cm (similar to previous designs [22-26]). Sensors include an absolute pressure gage, a dynamic pressure sensor, and a thermocouple, so that the experiment can provide directly the flammability limits, temperature rise, explosion pressure, and rate of pressure rise. Further processing of the pressure data (outlined below) yields the instantaneous laminar burning velocity (1-D spherical) as a function of pressure and temperature.

Fig. 1: Schematic diagram of the experimental apparatus.

The partial pressure method provides the initial mixture composition, via injection of liquid ($\text{C}_2\text{HF}_3\text{Cl}_2$), followed by gaseous, reactants. The partial pressure of each mixture component is determined with an Omega PX811 absolute pressure transducer that is periodically calibrated against a Baratron 627D (claimed accuracy of 0.12% of reading). Liquid suppressants ($\text{C}_2\text{HF}_3\text{Cl}_2$) are injected using a syringe via a gas-tight septum (which is separated from the chamber by a ball valve to ensure leak-free operation during the explosion event). The reactants are CH_4 (Matheson Tri-Gas, 99.97% purity), $\text{C}_2\text{HF}_3\text{Cl}_2$ (American Pacific Corp., > 99% purity), and C_2HF_5 (Allied Signal Chemicals, 99.5% purity). The air is house compressed air (filtered and dried) that is additionally conditioned with a $0.01\ \mu\text{m}$ filter, carbon filter, and a desiccant bed to remove small aerosols, organic vapors, and water vapor. The measured relative humidity of the air (at room temperature), is less than 2% for all tests. The reactant mixture is given 10 minutes to settle, after which combustion is initiated at the center of the chamber. A capacitive discharge ignition system (based on the work of Shepherd et al. [27], and described in detail in ref. [20]), provides a controlled spark with an estimated energy range of 0.05 mJ to 500 mJ. Two tungsten electrodes form an adjustable gap (typically 2 mm) in the center of the chamber, and thin electrodes (diameter of 0.4 mm) ensure minimal heat loss from the flame. The explosion pressure is recorded at 4000 Hz using a dynamic pressure sensor, with a claimed accuracy of 0.1% of full scale.

2.4. Burning velocity from the pressure trace

Laminar burning velocity is determined from the pressure trace using a thermodynamic model [22-24, 28-32], summarized briefly below, with more details available in ref. [20]. The contents of the chamber are divided into burned and unburned zones separated by an infinitely

thin flame sheet. Flame propagation is assumed to be spherical and smooth, creating a spatially uniform pressure rise. All gases are considered ideal and semi-perfect (variable specific heats), with the unburned gas frozen at its initial composition, and the burned gas composition represented by thermodynamic equilibrium products of a constant-volume, constant-energy process (calculated using CEA2 [33]). Both zones are adiabatic, and the unburned gas is compressed isentropically as the flame expands. With these assumptions, the instantaneous flame radius r_f and laminar burning velocity S_L are expressed in terms of known variables as in Eqs. 1 and 2 (more details in refs. [22, 32]),

$$r_f = R[1 - (1 - x_b)(P_0/P)^{1/\gamma_u}]^{1/3} \quad (1)$$

$$S_L = R/3(R/r_f)^2(P_0/P)^{1/\gamma_u}(dx_b/dt) \quad (2)$$

where R the chamber radius, x_b the mass fraction of burned gas, P the instantaneous pressure, P_0 the initial pressure, and γ_u the specific heat ratio of the unburned gases. The thermodynamic model relates the mass fraction of burned gas x_b to the instantaneous pressure P . The mass and energy conservation equations are solved simultaneously for the chamber contents (burned and unburned gases), using Eqs. 3 and 4.

$$\frac{V}{M} = \int_0^{x_b} v_b dx + \int_{x_b}^1 v_u dx \quad (3)$$

$$\frac{E}{M} = \int_0^{x_b} e_b dx + \int_{x_b}^1 e_u dx \quad (4)$$

where V is the chamber volume and E and M are internal energy and mass of the initial contents, e and v are the internal energy and specific volume of the gas, and the subscripts b and u refer to the burned and unburned gas.

Polynomial coefficients (for the major reactant and product species) are taken from GRI-mech 3.0 [34] for hydrocarbon-air species (CH_4 , O_2 , N_2 , CO_2 , H_2O , CO , NO , OH , H_2 , and O), the NIST HFC mechanism [35, 36] for fluorinated species (C_2HF_5 , F , HF , CF_4 , and CF_2O), and from Burcat et al. [37, 38] for chlorinated species ($\text{C}_2\text{HF}_3\text{Cl}_2$, Cl , and HCl) to describe the thermodynamic properties of the burned and unburned gas. The instantaneous unburned gas temperature is related to the pressure through isentropic compression:

$$T_u = T_{u0} \left(\frac{P}{P_0} \right)^{(\gamma_u - 1)/\gamma_u} \quad (5)$$

in which T_{u0} is the initial unburned temperature. The unburned gas properties v_u and e_u in Eqs. 3 and 4 are calculated at each pressure increment from the unburned gas composition and temperature T_u , reducing the model to two equations and two unknowns (T_b and x_b). The remaining unknowns in the conservation equations (v_b , e_b , and x_b) are found using a non-linear optimization routine that iterates on T_b (v_b and e_b are functions of temperature) and x_b at each pressure increment, until the proper values of T_b and x_b are obtained. Once $x_b(P)$ is known, the burning velocity $S_L(P, T_u)$ is determined over the experimental range of pressure and temperature using Eq. 2.

2.5. Data reduction

When the flame radius r_f is small, the propagation rate can be affected by flame stretch and by excess energy deposited during the ignition process; whereas when r_f is large, it can be affected by heat loss to the chamber walls. Therefore, only a portion of the pressure data from each experiment is used (typically the central 75% of the data points) in the present study to calculate burning velocity. Spherically expanding flames are subject to stretch rates that are inversely proportional to r_f [39],

$$\kappa = \frac{2}{r_f} \frac{dr_f}{dt} \quad (6)$$

where κ is the stretch rate and dr_f/dt is the flame front velocity. The effects of stretch and ignition are reduced by neglecting data when the flame radius r_f is less than 50% of the chamber radius R , as proposed by Elia [40]. Additionally, only data up to dP/dt_{max} (i.e., the inflection point in the $P(t)$ curve) are considered, eliminating data affected by heat loss to the walls [41].

The pressure data from an individual test are used to determine the burning velocity at each combination of unburned gas pressure and temperature occurring during the test. Tests are performed at $T_0=296\pm 2$ K, and at $P_0=0.868$ bar, 1.01 bar, and 1.13 bar to increase the number of combinations. The results of multiple tests (repeated twice for each initial pressure) are fit to Eq. 7 [33] to decouple the influences of pressure and temperature on S_L ,

$$S_L = S_{L,0} \left(\frac{T}{T_0} \right)^\alpha \left(\frac{P}{P_0} \right)^\beta \quad (7)$$

where S_L is the laminar burning velocity, P_0 is the initial pressure, T_0 is the initial temperature, $S_{L,0}$ is the laminar burning velocity at the initial conditions; α , β , and $S_{L,0}$ are the fitting parameters. In discussions following, S_L is presented at two conditions: ambient ($P=1.01$ bar and $T=298$ K), and compressed ($P=3$ bar and $T=400$ K) as obtained from Eq. 7. Note that the presented results are interpolations, or small extrapolations, from the experimental data, eliminating the need to control the ambient initial conditions during experiments (as done in ref. [24]).

Spherical flame propagation is a critical condition for reliable calculation of S_L from the pressure trace. In the presence of gravity, buoyancy can distort the symmetry of the flame front. For fast flames, buoyancy effects are negligible because of the short amount of time available for the hot gases to accelerate upward before the flame sheet reaches the chamber walls. For slower flames (i.e., inhibited flames) with long propagation times, buoyant forces are not negligible; therefore, to reduce experimental inaccuracies, only flame speeds that are greater than 6 cm/s are reported, as recommended in refs. [24, 42]. Cellular instabilities, which also invalidate the spherical flame assumption, are monitored through inspection of the S_L data of individual test runs. The onset of cellular instabilities is detected via a distinct increase in the burning velocity [29, 43], which did not occur in any of the data in the present study.

To validate the experimental facility and data reduction methods, burning velocities were determined for uninhibited CH₄-air flames over a range of equivalence ratios ($0.6 \leq \Phi \leq 1.3$) as described in ref. [20]. At ambient conditions (298 K; 1.01 bar), acceptable agreement was observed with published results using: the same technique [24, 26], the stretch-corrected spherically propagating technique [44-46], and the stretch-corrected counter-flow flame technique [47, 48]. At compressed conditions (400 K; 3 bar), burning velocities for the entire range of CH₄-air equivalence ratios were in excellent agreement with results using the same measurement technique [24, 26]. In addition, measurements with the present constant-volume technique agree within experimental error with those of a constant-pressure spherically propagating flame experiment [49, 50] for CH₄-air flames inhibited by CF₃Br, C₆F₁₂O, and C₃H₂F₃Br (within $\pm 12\%$ for $\Phi=1.0$ and 0.6 with agents added at concentrations up to 3% by volume).

2.6. Uncertainties

Individual uncertainty components and root-sum-of-squares (RSS) components are determined based on the procedure outlined in ref. [51], with uncertainties in the measured parameters presented as expanded uncertainties ku_c from a combined standard uncertainty (estimated standard deviation) u_c , and a coverage factor $k=2$ (level of confidence approximately 95%). Relative uncertainties ku_c/X are reported, with X being the measured value of the parameter under consideration. Uncertainties in initial temperature and pressure, dynamic pressure rise, agent volume fraction, equivalence ratio, and burning velocity calculation and fitting to Eq. 7 are considered. The expanded relative uncertainties related to reactant mixture preparation are 1.0% for the equivalence ratio, 0.3% for the volume fraction of air, and 0.8% for the volume fraction of CH_4 . Uncertainty in the volume fraction of agent ranged from 4% at low concentrations ($X_a=0.01$) to <1% at higher concentrations ($X_a=0.05$). Relative uncertainties for the dynamic pressure rise, initial pressure, and initial temperature are 1.3%, 0.7%, and 1.0% respectively. Thus, the maximum expanded relative uncertainty (ku_c/X) for the reported experimental burning velocities is 12%.

3. NUMERICAL METHODS

A comprehensive reaction mechanism is used to model CH_4 -air flames with added C_2HF_5 or $\text{C}_2\text{HF}_3\text{Cl}_2$. Hydrocarbon-air reactions are modeled with the C1-C4 mechanism of Wang et al. [52] (111 species and 784 reactions). Reactions involving C1-C3 hydrofluorocarbons are modeled with an updated NIST HFC mechanism [35, 36] (51 species and 600 reactions). Recent updates to the original NIST HFC mechanism are summarized in refs. [5, 53]. The C1-C2 chlorocarbon chemistry is described using the mechanism of Leylegian et al. [54, 55] (50 species and 333 reactions). Reactions involving chlorofluorinated C1-C2 species are modeled using the newly developed mechanism of Babushok et al. [9] (14 species and 127 reactions). The complete kinetic mechanism for $\text{C}_2\text{HF}_3\text{Cl}_2$ addition to CH_4 -air contains 226 species and 1918 reactions (the mechanism for C_2HF_5 addition contains 212 species and 1791 reactions). It should be emphasized that the mechanism adopted for the present study is considered only as a starting point. Changes to both the rates and the reactions incorporated may be made once more experimental and theoretical data are available to test the mechanism, especially the portion containing chlorofluorinated species reactions.

Thermodynamic equilibrium calculations are carried out using the EQUIL subroutine [56]. The equilibrium product species and their thermodynamic state are determined for a constant-pressure, constant-enthalpy process. The planar adiabatic premixed flame structure is calculated using the Sandia PREMIX flame code [57-59]. The equations of mass, species, and energy conservation are solved for initial temperatures and pressures corresponding to the ambient (298 K and 1.01 bar) and compressed (400K and 3 bar) conditions. Thermal diffusion is considered and molecular diffusion is modeled using mixture-averaged coefficients. The mixture-averaged diffusion model significantly reduces computational time while producing less than a 1.5% relative error in calculated burning velocities (when compared to the multicomponent model) for n-heptane-air over a range of equivalence ratios and at 1 atm [60]. We performed a similar analysis for CH₄-air and C₃H₈-air burning velocities and found the relative error to increase with decreasing fuel molecule size (up to 3% for CH₄-air). Therefore, the largest error associated with the mixture-averaged model should occur at uninhibited conditions and decrease as the large molecule agents are added. Computations are carried out on a 100 cm domain with gradient (GRAD) and curvature (CURV) values of 0.05. During simulation, the number of grid points ranged from 330 to 450, with the final 100 point grid refinement (GRAD and CURV from 0.1 to 0.05) resulting in less than a 2% change in calculated burning velocities (the change is typically much less and is largest for slow burning mixtures with $S_L \sim 6\text{cm/s}$). This level of convergence is acceptable considering the uncertainty in the measured S_L values.

4. RESULTS AND DISCUSSION

4.1. Kinetic model validation

To validate the kinetic model for HCFCs, the experimentally measured burning velocities of CH₄-air flames with added C₂HF₃Cl₂ or C₂HF₅ are compared to numerical predictions. For the HFC sub-mechanism, validations have been performed previously [61-66]. The recent upgrades, mentioned in the numerical modeling section, mostly involve reactions of F atom, and are only important for mixtures of pure agent in air (not inhibited hydrocarbon-air flames, in which [F] is low) [7]; hence, the previous validation studies are still valid. Nonetheless, a comparison of measured and numerically predicted burning velocities is first made for CH₄-air

flames inhibited by C_2HF_5 to illustrate performance of the HFC sub-mechanism and to test it at leaner conditions than previously considered.

Fig. 2 shows the present experimental burning velocities for CH_4 -air flames at $\Phi=0.6$ and $\Phi=1.0$ (Δ and $\square$ symbols, respectively) with added C_2HF_5 ($0 \leq X_a \leq 0.07$) at ambient (298 K; 1.01 bar) conditions, together with numerical predictions (lines). Experimental burning velocities from other researchers [62, 67, 68] are also shown (X, *, and + symbols). (The reported equivalence ratios Φ are based on the uninhibited mixtures prior to agent addition: as agent is added, proportional amounts of CH_4 and air are displaced.) For $\Phi=1.0$, the present experimental measurements compare reasonably well with published results using the stretch-corrected spherically propagating flame method [68] and the total area method [62, 67].

For the initially stoichiometric flames ($\Phi=1.0$) the calculated burning velocities agree well with the present experimental results for the entire range of agent loading considered ($X_a \leq 0.06$). At $X_a < 0.04$ the predicted S_L is within the experimental uncertainty (about the size of the symbols) of the data, while at higher X_a , it is up to 12% lower. For $\Phi=0.6$, agreement is poor for uninhibited flames and at low agent loading (as discussed below), but improves as X_a increases. For example, at $X_a=0$, the predicted S_L (11.3 cm/s) is 43% higher than the measured value (8.3 cm/s), while at $X_a \geq 0.05$, agreement improves to within 3%.

Fig. 2: Laminar burning velocity of CH₄-air flames at equivalence ratios Φ of 0.6 and 1.0 as a function of C₂HF₅ concentration (initial condition: 298 K and 1.01 bar).

Fig. 3 presents similar comparisons for the compressed initial conditions (400 K; 3 bar). The accuracy of the numerical predictions is again very good for stoichiometric flames (at all agent loadings), and for lean flames at high agent loading, but poor for lean flames at low C₂HF₅ loading. Reasons are discussed below.

Fig. 3: Laminar burning velocity of CH₄-air flames at equivalence ratios Φ of 0.6 and 1.0 as a function of C₂HF₅ concentration (initial condition: 400 K and 3 bar).

The largest discrepancy between measured and predicted burning velocity occurs at lean uninhibited conditions ($\Phi=0.6$ and $X_a=0.0$). The hydrocarbon-air portion of the mechanism [52] has been extensively validated for a wide range of fuels and flame conditions (with the exception of very lean flames), suggesting that the disagreement between calculated and measured S_L for $\Phi=0.6$ and low agent loading may be due to experimental considerations (such as flame stretch, buoyancy, and/or radiative heat loss). Although flame stretch effects are not fully eliminated using the present experimental method, they seem not to be the cause of discrepancy. For example, for uninhibited CH₄-air at $\Phi=0.6$, the present results agree well with stretch-corrected spherically propagating flame results [44, 46, 69, 70]. Buoyancy is unlikely the cause of discrepancy since results obtained in microgravity for CH₄-air at $\Phi=0.6$ [71, 72] are ~20% lower (and further from the numerical prediction) than the present experimental result. Also, in a

previous study [42] with the present experimental technique, the influence of buoyancy was found to be negligible when measuring burning velocities greater than 6 cm/s. Investigating the possible causes for the disagreement between numerical and experimental S_L of lean CH_4 -air mixtures ($0.5 \leq \Phi \leq 0.65$), Chen [73] showed that radiation and compression of the unburned gases result in lower measured burning velocities when using the spherically expanding flame technique. In the present study, compression effects are not of concern because the pressure trace is used to determine S_L , not flame-front tracking (which assumes constant-pressure during the observed propagation). Chen [73] found that burning velocities of lean mixtures were more strongly affected by radiative losses because the relative reduction of flame temperature was greater for mixtures with lower adiabatic flame temperatures (or alternatively, the radiative heat loss rate is a higher fraction of the total heat release rate at the low reaction rate of the lean flames). This may explain the improved performance of the numerical prediction at higher X_a in the lean flames (adding agent to a lean CH_4 -air increases the heat release; for example, adding C_2HF_5 increases the adiabatic flame temperature from 1629 K at $X_a=0$ to 2003 K at $X_a=0.05$).

To validate the chlorine-species portion of the kinetic model, measured values of S_L for CH_4 -air flames with added $\text{C}_2\text{HF}_3\text{Cl}_2$ are compared with model predictions. Fig. 4 presents the experimental S_L (symbols) with the numerical predictions (lines) for addition of $\text{C}_2\text{HF}_3\text{Cl}_2$ to flames with four different initial equivalence ratios ($\Phi=0.6, 0.9, 1.0, 1.1$), at agent volume fractions X_a of 0 to 0.05 (different symbol and line styles present data at different initial equivalence ratios). Overall, model predictions agree very well with the experimental results; predicted burning velocities are within 7% for all agent loadings at $\Phi=1.0, 0.9$, and 1.1 (with the exception of $X_a=0.04$, $\Phi=1.1$, where the prediction is 15% higher). At leaner conditions ($\Phi=0.6$), agreement is less satisfactory, although as with C_2HF_5 , it improves as the $\text{C}_2\text{HF}_3\text{Cl}_2$ concentration increases. The discrepancy for the uninhibited lean flame ($\Phi=0.6$) is again likely a consequence of the radiative heat loss. Nonetheless, with $\text{C}_2\text{HF}_3\text{Cl}_2$ addition ($0.01 \leq X_a \leq 0.05$), agreement at $\Phi=0.6$ is better than with C_2HF_5 addition.

Fig. 4: Laminar burning velocity of CH_4 -air flames at equivalence ratios Φ of 0.6, 0.9, 1.0, and 1.1 as a function of $C_2HF_3Cl_2$ concentration (initial condition: 298 K and 1.01 bar).

Fig. 5 shows the burning velocities with $C_2HF_3Cl_2$ addition to CH_4 -air flames at the compressed conditions (400 K; 3 bar). The agreement is somewhat better than for the flames at the initially ambient conditions (Fig. 4), with the largest discrepancies again occurring at the uninhibited conditions. At $\Phi=0.9-1.1$ and $\Phi=0.6$ S_L predictions of inhibited mixtures are within 7% and 14% of the measured values, respectively (again with the exception of $X_a=0.04$, $\Phi=1.1$, where the prediction is 12% higher). The overall agreement between numerical and experimental results is very good considering the early stage of development of the kinetic mechanism for the mixed fluorine/chlorine/hydrocarbon system.

At compressed conditions, adding $C_2HF_3Cl_2$ to lean ($\Phi=0.6$) CH_4 -air mixtures no longer reduces the experimentally measured burning velocity for all X_a . For example, at $X_a=0.02$, the burning velocity is 3% higher than the uninhibited case, while at higher loading ($X_a \geq 0.04$), the burning velocity is once again reduced compared to $X_a=0$. The lower inhibition effectiveness of $C_2HF_3Cl_2$ at 400 K and 1.01 bar is consistent with previous findings [20], in which reduced effectiveness was observed for C_2HF_5 , $C_3H_2F_3Br$, and $C_6F_{12}O$ at compressed initial conditions.

Fig. 5: Laminar burning velocity of CH_4 -air flames at equivalence ratios Φ of 0.6, 0.9, 1.0, and 1.1 as a function of $\text{C}_2\text{HF}_3\text{Cl}_2$ concentration (initial condition: 400 K and 3 bar).

4.2. Comparing agent influence on S_L

Fig. 6 presents the burning velocities (bottom curves) for premixed CH_4 -air flames with added $\text{C}_2\text{HF}_3\text{Cl}_2$ (triangles), C_2HF_5 (circles), or CF_3Br (squares) for stoichiometric ($\Phi=1.0$, closed symbols) and lean ($\Phi=0.6$, open symbols) flames at 298 K and 1.01 bar. The adiabatic flame temperatures are shown in the top curves for $\text{C}_2\text{HF}_3\text{Cl}_2$, C_2HF_5 , and CF_3Br by solid, dashed, and dotted lines (CF_3Br data are included for reference). As Fig. 6 shows, at stoichiometric conditions, $\text{C}_2\text{HF}_3\text{Cl}_2$ provides a larger reduction in S_L , than does C_2HF_5 . For example, at an agent volume fraction $X_a=0.01$, $\text{C}_2\text{HF}_3\text{Cl}_2$ and C_2HF_5 reduce S_L to 25.2 cm/s and 28.2 cm/s, respectively. As more agent is added, the marginal reduction of S_L is nearly the same, illustrated by similar slopes in Fig. 6 once $X_a \geq 0.02$. As the upper curves in Fig. 6 show, the adiabatic flame temperatures for the two agents (at $\Phi=1.0$) are similar for the range of X_a considered, with the largest difference occurring at $X_a=0.05$, where T_{ad} is 24 K lower with $\text{C}_2\text{HF}_3\text{Cl}_2$ addition than with C_2HF_5 addition. The greater reduction in S_L with $\text{C}_2\text{HF}_3\text{Cl}_2$ (while T_{ad} is similar) suggests that chlorine substitution improves the inhibition performance via a kinetic mechanism rather than thermal. Burning velocities and adiabatic flame temperatures are shown in Fig. 6 for CF_3Br added at $X_a \leq 0.02$. For the stoichiometric flame, CF_3Br is more

effective (on a per mole basis) that C_2HF_5 or $C_2HF_3Cl_2$, reducing S_L to about 2/5 and 1/5 the speed of the uninhibited flame when added at $X_a=0.01$ and 0.02.

At lean conditions, sub-inerting concentrations of C_2HF_5 slightly increase burning velocity (up to 6%), as described previously [20], whereas similar concentrations of $C_2HF_3Cl_2$ reduce S_L by 7%-30% (at 298 K and 1.01 bar). The adiabatic flame temperatures increase with addition of either agent, and while the values are similar for addition of either agent, there is a slight difference between them that increases as X_a increases (up to a 45 K difference at $X_a=0.05$). Interestingly, for each agent, the burning velocity of the stoichiometric and lean systems are very close to each other (within 0.6 cm/s) at $X_a=0.05$ (and the adiabatic flame temperatures are also roughly equal at that agent loading). When adding CF_3Br at $X_a=0.005$, the flame is suppressed, illustrated by a burning velocity of zero in Fig. 6, and the adiabatic flame temperature is 5 K lower than the uninhibited flame.

Fig. 6: Burning velocity (lower data, left axis) and equilibrium flame temperature (upper data, right axis) for $C_2HF_3Cl_2$ (triangles), C_2HF_5 (circles), or CF_3Br (squares) added to stoichiometric (closed symbols) and lean (open symbols) CH_4 -air. The solid, dashed, and dotted lines represent the flame temperatures with added $C_2HF_3Cl_2$, C_2HF_5 , or CF_3Br (for clarity, lines connect the experimental data points and do not represent predictions).

4.3. Equilibrium and peak chain-carrier radical concentrations

Burning velocity is known to be correlated with the peak radical (particularly OH) concentration in flames [74-76]. Hence, equilibrium and peak concentrations of chain-carrier radicals (H, OH, and O) are examined to compare the kinetic inhibition effectiveness of $C_2HF_3Cl_2$ and C_2HF_5 . Fig. 7 presents the chain-carrying radical volume fractions for $C_2HF_3Cl_2$ (solid lines) and C_2HF_5 (dotted lines) added to stoichiometric (left frames) and lean (right frames) CH_4 -air flames. For uninhibited flames at stoichiometric conditions, the peak values of [H], [OH], and [O] are 0.006, 0.008, and 0.003, or about 16, 3, and 14 times the equilibrium values. As either agent is added, the equilibrium radical concentrations decrease similarly as X_a increases. The peak values decrease as either agent is added, however, all peak radical volume fractions decrease less rapidly than do the equilibrium values with C_2HF_5 addition, but more rapidly with $C_2HF_3Cl_2$ addition. That is, addition of $C_2HF_3Cl_2$ causes the peak radical volume fractions to approach the equilibrium values, while addition of C_2HF_5 causes them to diverge from the equilibrium values. This is consistent with the stronger reduction in burning velocity with addition of $C_2HF_3Cl_2$ as seen in Fig. 6. (and with the catalytic cycle described for Cl [15], which drives the radical volume fractions to equilibrium values)

At lean conditions (right frames), the uninhibited flames ($X_a=0$) have peak radical volume fractions somewhat lower than (but close to) those of stoichiometric flames (volume fractions of 0.0005, 0.0025, and 0.0011 for H, OH, and O, or about 12, 3, and 2.5, times lower than the stoichiometric flames). Moreover, the equilibrium radical volume fractions are much lower than the peak values in the lean flames, about 1,960, 9, and 130 times, leading to greater radical super-equilibrium for the neat lean flames at $\Phi=0.6$ than at $\Phi=1.0$. The effect of addition of either agent on the equilibrium radical volume fractions is very similar at low concentrations ($X_a \leq 0.05$), increasing the equilibrium value by a factor of about 15, 5, and 10 (at $0.05 \leq X_a \leq 0.06$ as compared to $X_a=0$) for H, OH, and O, and then decreasing it rapidly for $X_a > 0.05$ (C_2HF_5) and $X_a > 0.06$ ($C_2HF_3Cl_2$).

For the equilibrium radical volume fractions, the behavior above $X_a=0.05$ is different for C_2HF_5 and $C_2HF_3Cl_2$, with [H] and [OH] dropping off earlier and faster for C_2HF_5 addition, but [O] dropping faster for $C_2HF_3Cl_2$ addition above $X_a=0.06$. This behavior is related to the ratio of halogen $[X]=[F]+[Cl]$ in the system to hydrogen [H] ($[X]/[H]$), and the difference in equilibrium

product species formed when adding the two agents. $[X]/[H]$ is equal to 1 at the same value of X_a (0.05) for the two agents; when C_2HF_5 is added above $X_a=0.05$, there is not enough hydrogen to form the stable product HF. There is, however, some available hydrogen, in the form of H_2O , when $C_2HF_3Cl_2$ is added slightly above $X_a=0.05$ (for which $[X]/[H]$ is slightly greater than 1) because a substantial amount of Cl is present in the equilibrium products ($X_{Cl} = 0.015$), whereas with added C_2HF_5 , $[F]$ is much lower ($X_F \approx 10^{-5}$). When adding either C_2HF_5 or $C_2HF_3Cl_2$, once hydrogen is no longer available, the resulting product species change, affecting both the final temperature and the equilibrium radical volume fractions. Thus, with added C_2HF_5 , equilibrium $[H]$ and $[OH]$ start to drop off earlier than with added $C_2HF_3Cl_2$, because of formation of the very stable species HF. Regardless, despite the slower drop-off in equilibrium $[H]$ and $[OH]$ with added $C_2HF_3Cl_2$, the peak $[H]$ and $[OH]$ (as well as peak $[O]$) drop more rapidly because the chlorine catalytic radical recombination cycle drives the radical toward equilibrium more effectively than does the radical trapping mechanism of C_2HF_5 . This is illustrated in the reaction flux analyses described below.

For the stoichiometric case, the unity hydrogen to halogen ratio ($[X]/[H]=1$) occurs at $X_a=0.08$ for both agents, so the radical volume fractions decrease at a relatively steady slope in Fig. 7; i.e., because $[X]/[H]$ is less than 1 for the entire range of X_a shown.

The peak radical volume fractions are affected differently with addition of the two agents in the lean flames as compared to addition to the stoichiometric flames. For example, in the stoichiometric flames (left frames, upper curves in each frame of Fig. 7), both agents tend to lower peak radical volume fractions at increasing X_a , but the effect is somewhat stronger for $C_2HF_3Cl_2$ addition. For $\Phi=0.6$ (right frame, upper curves of Fig. 7) the peak radical volume fractions decrease mildly for $X_a<0.06$ and sharply at $X_a>0.06$ (at which $[X]/[H] \approx 1$). In fact, for C_2HF_5 addition below $X_a \approx 0.06$, the peak radical volume fractions all *increase* in concentration. The reasons for this behavior become clearer after examination of the flux of reactions producing and consuming radicals, described below.

Fig. 7: Equilibrium and peak radical concentrations ($[H]$, top; $[OH]$, middle; $[O]$, bottom) in CH_4 -air flames ($\Phi=1.0$, right frames; $\Phi=0.6$, left frames) with added $C_2HF_3Cl_2$ (solid lines) and C_2HF_5 (dotted lines).

4.4. Rate of production analysis

Fig. 8 and Fig. 9 present the halogenated reactions involved in the production and consumption of $[H]$, $[OH]$, and $[O]$ in stoichiometric (left frame) and lean (right frame) CH_4 -air with $C_2HF_3Cl_2$ (Fig. 8) and C_2HF_5 (Fig. 9) added at $X_d=0.05$. The rates of production (left axes,

units: mol/cm³-s) are shown as a function of position in the flame. Only the most important halogenated reactions are shown, with $\text{H}+\text{O}_2=\text{O}+\text{OH}$ included for reference and scaled by a factor of 2.5 to improve clarity. The overall generation rate of radicals is lower with $\text{C}_2\text{HF}_3\text{Cl}_2$ compared to C_2HF_5 (as a result of the chlorine catalytic cycle). Consequently, the peak rates of production/consumption by radical reactions with halogenated species are also lower with $\text{C}_2\text{HF}_3\text{Cl}_2$ (note the different scales in Fig. 8 and Fig. 9).

We consider first the stoichiometric flames. With added $\text{C}_2\text{HF}_3\text{Cl}_2$, the primary production/consumption reactions for H, OH, and O involve HCl, with smaller contributions from reactions of CF, CF_2 and CFCl , which form $\text{CF}_2\text{:O}$ and HF and regenerate HCl. When adding either $\text{C}_2\text{HF}_3\text{Cl}_2$ or C_2HF_5 , the primary reactions containing fluorinated species responsible for radical consumption are $\text{CF}_2+\text{H}=\text{CF}+\text{HF}$, $\text{CF}_2+\text{OH}+\text{CF}_2\text{:O}+\text{HF}$, and $\text{CF}_2+\text{O}=\text{CF}+\text{O}+\text{F}$. The rates of these reactions are only roughly a factor of 3 lower than the branching reaction $\text{H}+\text{O}_2=\text{OH}+\text{O}$, showing the dominant role of the halogen reactions in the flame chemistry. At this loading of either agent, F atom attacks water, abstracting an H atom to form HF and OH, with a rate similar to that of the halogenated reactions reducing chain-carrier radical concentrations.

Fig. 8: Rate of production/consumption of chain-carrier radicals ($[H]$, top; $[OH]$, middle; $[O]$, bottom) in CH_4 -air flames ($\Phi=1.0$, right frames; $\Phi=0.6$, left frames) with $C_2HF_3Cl_2$ added at $X_a=0.05$.

Fig. 9: Rate of production/consumption of chain-carrier radicals ($[H]$, top; $[OH]$, middle; $[O]$, bottom) in CH_4 -air flames ($\Phi=1.0$, right frames; $\Phi=0.6$, left frames) with C_2HF_5 added at $X_a=0.05$.

For the lean flames ($\Phi=0.6$), the primary production/consumption reactions are similar to those observed for the stoichiometric case, although the peak rates are lower. The reaction $\text{HCl}+\text{H}=\text{H}_2+\text{Cl}$, which mostly consumes H in the stoichiometric flames, behaves differently in the lean flames. There, the net effect is neutral: in the preheat zone of the flame zone the reaction consumes H atom, and then as the temperature increases, the reaction produces nearly the same amount of H atom (illustrating the shift in equilibrium with temperature for this key reaction in the Cl inhibition mechanism). Since the temperature of the lean and stoichiometric flames are about the same at $X_a=0.05$, the forward rate is favored in the stoichiometric flames due to the much higher [H] which also causes the peak rate of [H] consumption by $\text{HCl}+\text{H}=\text{H}_2+\text{Cl}$ to be factor of 3 higher at stoichiometric conditions (compared to $\Phi=0.6$). At lean conditions, the primary chlorinated reaction reducing [H] is $\text{Cl}_2+\text{H}=\text{HCl}+\text{Cl}$, which has a broad profile that tracks [H]. Peak consumption of [H] by reaction with CFCl and CF_2 are also lower at lean conditions, with $\text{CF}_2+\text{H}=\text{CF}+\text{HF}$ absent as a primary reaction. The reactions important for production/consumption of [OH] and [O] are similar to those for stoichiometric conditions, with consumption mainly through reactions involving HCl and CFCl and CF_2 .

To quantify the overall effect of the chlorinated-species reactions vs. fluorinated-, the rates of production are integrated across the primary flame zone. The percentage of total consumption of radicals by reactions with chlorinated, fluorinated, and chlorofluorinated species are provided in Table 1. For $\text{C}_2\text{HF}_3\text{Cl}_2$ addition, reactions involving chlorinated species account for the largest reduction in radical concentration. Overall, reactions with halogenated species account for about 45 % of the H and OH destruction at stoichiometric and lean conditions, and 36 % and 73 % of O destruction, for stoichiometric and lean conditions, respectively. Of these, reactions with chlorinated species are about three times more important than reactions with only fluorinated species. For C_2HF_5 addition, the halogen reactions (F species only) account for a lower fraction of the total radical consumption (roughly 20 to 40%) as compared to $\text{C}_2\text{HF}_3\text{Cl}_2$ addition, for both stoichiometric and lean conditions, which is consistent with the lower peak radical concentrations and higher burning velocity seen in Fig. 6 and Fig. 7 at $X_a=0.05$.

Table 1: Percentage of H, OH, and O radical consumption by reactions containing halogenated species (agent volume fraction of 0.05).

Agent Rxn Group	% of H Cons.		% of OH Cons.		% of O Cons.	
	$\Phi=1.0$	$\Phi=0.6$	$\Phi=1.0$	$\Phi=0.6$	$\Phi=1.0$	$\Phi=0.6$
C₂HF₃Cl₂						
Cl rxns	20	24	30	30	25	59
F rxns	16	13	12	13	7	9
F-Cl rxns	10	6	5	6	4	5
Halogen rxns	46	42	46	48	36	73
C₂HF₅						
F rxns	34	40	19	26	14	32

There are competing effects when a suppressant containing a hydrocarbon portion is added to a lean flame [16, 53, 62]. The suppressant can react with excess oxygen, increasing the heat release and temperature, which in turn increases the overall reactivity of the system. The suppressant simultaneously introduces halogen atoms to the flame-zone reducing chain-carrier radical concentrations through chain-terminating reactions. When adding C₂HF₅ to the lean CH₄-air flame, the increase in heat release dominates, resulting in increased peak radical concentrations and S_L seen in Fig. 6 and Fig. 7. At a higher temperature (resulting from exothermic reaction of the suppressant), the main chain branching reaction, $H+O_2=OH+O$, proceeds at a higher rate, producing more chain-carrier radicals than consumed by the chain-terminating reactions involving fluorine. With C₂HF₃Cl₂, the improved radical recombination ability of chlorine outweighs the increased rate of chain branching caused by the additional heat release, hence the reduction in peak radical concentrations and S_L for all X_a added to the lean flame. Also, because of the formation of Cl and Cl₂ in the products, the final flame temperature of the lean flames is lower with C₂HF₃Cl₂ addition than with C₂HF₅ addition. Thus, the C₂HF₃Cl₂ inhibited flames have less heat release (i.e., enhancement) and more inhibition (due to the effectiveness of the Cl cycle), making C₂HF₃Cl₂ a more effective inhibitor than C₂HF₅.

4.5 Sensitivity analysis

Normalized sensitivity coefficients, in the form of logarithmic derivatives ($\delta \ln S_u / \delta \ln A_i$), are determined for stoichiometric and lean ($\Phi=0.6$) CH₄-air flames with C₂HF₅ and C₂HF₃Cl₂ added at $X_a=0.05$ (for a positive sensitivity, increasing the Arrhenius pre-exponential factor A of that reaction increases S_L). In Fig. 10, the halogenated reactions with highest absolute sensitivities are shown (with $H+O_2=O+OH$, scaled by 2.5, included for reference) for

stoichiometric (black bars) and lean (dashed bars) flames with added C_2HF_5 (left frame) and $C_2HF_3Cl_2$ (right frame). Reactions involving fluorinated species are grouped at the top of each frame, followed by reactions with chlorinated species.

Fig. 10: Sensitivity coefficients for stoichiometric and lean ($\Phi=0.6$) CH_4 -air flames with C_2HF_5 (left frame) and $C_2HF_3Cl_2$ (right frame) addition at a volume fraction of 5%.

With addition of C_2HF_5 , S_L of the stoichiometric flame is generally increased by increasing rates of the fluorinated reactions $CF+O_2=CF:O+O$, $CO+F+M=CF:O+M$, $CHF_2+O_2=CF_2O+O+H$, and $CF_2+OH=CF_2O+H$, which have comparable sensitivities, with the first the most important for stoichiometric flames, and all roughly equally important for lean. The first and third reactions are exothermic and chain-branching; the second is exothermic, and the fourth terminating but exothermic. The three fluorinated-species reactions with negative sensitivities all consume radicals (with $CHF_2+H=CHF+HF$ and $CF_2O+H=CF:O+HF$ being roughly thermally neutral and $CF+OH=CO+HF$ exothermic), and hence inhibit the flame, so increasing their rate decreases the overall reactivity. In general, S_L of the lean CH_4 -air flame is slightly more sensitive than the stoichiometric flame to reactions containing fluorinated species.

For addition of $C_2HF_3Cl_2$, Fig. 10 (right frame) shows that the burning velocity is generally less sensitive to the fluorine-species reactions, with a few exceptions (e.g., $CF+O_2=CF:O+O$ and $CF_2+OH=CF_2:O+H$ have 30% higher sensitivities). Of the chlorine-species reactions, S_L is sensitive to three reactions of the initial breakdown of the inhibitor (which was not the case for C_2HF_5 addition), as well as two of the reactions in the catalytic radical recombination cycles ($HCl+OH=Cl+H_2O$, and $Cl+HCO=CO+HCl$). Conversely, the burning velocity is not sensitive to the rate of the reaction $H+HCl=H_2+Cl$, which is responsible for most of the H atom recombination (consistent with previous studies with CH_3Cl , CH_2Cl_2 , $CHCl_3$, and CCl_4 added to CH_4 -air flames [54, 55, 77]). The burning velocity of the lean ($\Phi=0.6$) inhibited CH_4 -air flame is sensitive to the important termination reaction for the catalytic cycle $Cl+Cl+M=Cl_2+M$; at stoichiometric conditions the sensitivity is about a factor of 4 lower. Lastly, both the lean and stoichiometric flames exhibit a negative sensitivity to the reaction $CH_3Cl=CH_3+Cl$ (which increases $[Cl]$ in the flame zone).

5. CONCLUSIONS

For reducing the undesirable heat release and over-pressure due to agent reaction in the FAA Aerosol Can Test, hydrochlorofluorocarbons (HCFCs) may have advantages over hydrofluorocarbons (HFCs) as fire suppressants. To understand the difference between these compounds, burning velocity measurements and numerical simulations with detailed chemistry were performed for CH_4 -air flames with added $C_2HF_3Cl_2$ or C_2HF_5 . Comparisons of the experimental and numerical results also served as first steps in validating a newly-developed HCFC model.

Constant-volume combustion chamber experiments provided the burning velocity of CH_4 -air mixtures at ambient (298 K; 1.01 bar) and compressed (400 K; 3 bar) conditions, with addition of C_2HF_5 or $C_2HF_3Cl_2$. For stoichiometric flames, both agents reduced the burning velocity by about a factor of three at an agent loading of $X_a=0.05$ (with somewhat faster inhibition by $C_2HF_3Cl_2$ at lower agent loadings). For lean flames ($\Phi=0.6$) the same agent loading ($X_a=0.05$) had the opposite effect for the two agents: increasing S_L by about 10% for C_2HF_5 , and reducing it about 10% for $C_2HF_3Cl_2$. Hence, unlike the HFC, the HCFC did not show the enhanced burning when added to the lean flame at ambient conditions.

For model validation, experiments with CH₄-air flames at equivalence ratios of 0.6, 0.9, 1.0, and 1.1 and C₂HF₃Cl₂ or C₂HF₅ at volume fractions up to around 5% provided data for comparison with numerical simulations. For the near-stoichiometric flames, agreement was generally very good. At lean conditions ($\Phi=0.6$), agreement was good for C₂HF₃Cl₂ loading above about 2%, and C₂HF₅ loading above about 5%; while at low agent loading (and for uninhibited flames), the model over-predicted the burning velocity by about 3.5 cm/s (and the reason is believed to be radiative heat loss in the experiment, which is a higher fraction of the total heat release rate at the lean condition).

The numerical simulations provided flame structure data useful for understanding the action of the two agents. Addition of either agent to a stoichiometric flame reduced both the equilibrium and peak volume fraction of the chain-carrying radicals (H, OH, and, O), with a somewhat greater reduction in peak radical concentrations for addition of C₂HF₃Cl₂ than addition of C₂HF₅. Chlorine is more effective in reducing peak H, OH, and O radical concentrations; hence, the greater reduction in burning velocity with added C₂HF₃Cl₂. For the lean flames at agent volume fractions below about 0.05, C₂HF₅ addition increased the peak radical volume fractions, whereas C₂HF₃Cl₂ reduced it, foretelling the results of the burning velocity. A reaction flux analysis highlighted the key reactions in the C₂HF₃Cl₂ inhibited system responsible for the greater reduction in peak [H], [OH], and [O] compared to C₂HF₅. The lower peak radical concentrations are the result of improved radical consumption by reactions containing chlorinated and chlorofluorinated species. In addition, a sensitivity analysis showed that, unlike the case for C₂HF₅ addition, the burning velocity is particularly sensitive to the rates of the initial C₂HF₃Cl₂ decomposition reactions.

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