Premixed flame inhibition by CF$_3$Br and C$_3$H$_2$F$_3$Br (2-BTP)*

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Abstract

The un-stretched burning velocities and Markstein lengths of premixed CH$_4$- and C$_3$H$_8$-air flames with added C$_3$H$_2$F$_3$Br (2-BTP) or CF$_3$Br (Halon 1301), have been studied experimentally and numerically. For CF$_3$Br flame inhibition, the un-stretched burning velocities, predicted using a recently updated kinetic model for CF$_3$Br flame inhibition, were in excellent agreement with the experimental results over a range of fuel-air equivalence ratio and CF$_3$Br loading. For C$_3$H$_2$F$_3$Br flame inhibition, the un-stretched burning velocities predicted using a recently developed kinetic mechanism were in good agreement with the experimental results for most of the equivalence ratios tested; nonetheless, for very lean flames approaching the flammability limit, model predictions differed by up to 25 %, even for uninhibited flames. The influence of inhibitor on the flame response to stretch and susceptibility to instabilities was examined through consideration of the measured burned gas Markstein lengths. Markstein lengths were very large, leading to large stretch effects on the flame stability after ignition, and flame wrinkling during explosion tests, greatly increasing the rate of pressure rise. The influence of stretch with regard to flame inhibitor effectiveness is discussed.
1. INTRODUCTION

CF$_3$Br (Halon 1301) is an effective fire suppressant that has been largely phased out (by the Montreal Protocol) because of its high ozone depletion potential. Although a critical use exemption has been granted for use in commercial aircraft, the European Union is requiring replacement in new aircraft by 2018 and in existing aircraft by 2040. As a result of the expected phase-out, the Federal Aviation Administration (FAA) developed a minimum performance standard for the use of fire suppressants in cargo bays [1, 2] and tested three potential drop-in alternatives (C$_2$HF$_5$, C$_6$F$_{12}$O, and C$_3$H$_2$F$_3$Br). During the test (the Aerosol Can Test, FAA-ACT), a mixture of propane, ethanol, and water (simulating an exploding aerosol can) is impulsively released in the direction of a 15 kV DC arc that is 91.4 cm downstream of the release and near the center of a 11.4 m$^3$ chamber containing premixed ambient air and suppressant at specified concentrations. The test was designed to determine the minimum inerting concentration of a suppressant and to examine the consequences of adding sub-inerting concentrations. When sub-inerting concentrations of CF$_3$Br were added, the pressure rise was always lower than the pressure rise of the uninhibited case, whereas when sub-inerting concentrations of the proposed alternative C$_3$H$_2$F$_3$Br (2-BTP) were added, the pressure rise was about three times larger than the uninhibited case (the pressure rise was about two times larger when adding sub-inerting concentrations of C$_2$HF$_5$ and C$_6$F$_{12}$O) [2, 3].

Recent work [4-6] performed equilibrium and perfectly-stirred reactor simulations with detailed chemistry to understand how CF$_3$Br, C$_2$HF$_5$, and C$_6$F$_{12}$O impact the total heat release and reactivity in the FAA-ACT. Exothermic reaction of the alternative agents (C$_2$HF$_5$ and C$_6$F$_{12}$O) was found to add energy to the system, which not only increased the total heat release (and hence, the overpressure), but the reactivity as well (this was not the case with added CF$_3$Br). The analysis was later extended to include C$_3$H$_2$F$_3$Br [7]; Burgess et al. [8] developed the first kinetic mechanism describing the decomposition of C$_3$H$_2$F$_3$Br in hydrocarbon-air systems (down to C$_2$ bromine-containing species). During parallel work [9], the CF$_3$Br mechanism reported in ref. [10] (which is used as a sub-mechanism to describe C$_3$H$_2$F$_3$Br decomposition in the present work) was updated to include more accurate reaction rate data (Arrhenius coefficients) made available in literature since the original model was developed.
The objective of the present study is to provide experimental data for verification of the updated CF₃Br sub-model and the new C₃H₂F₃Br sub-model, and to compare the inhibition performance of C₃H₂F₃Br to CF₃Br for a wider range of premixed flame conditions and inhibitor concentrations than previously considered in ref. [11]. Laminar burning velocity is selected as a first step in model verification. Using high-speed shadowgraph images of spherically expanding flames, the burning velocity as a function of stretch is measured, from which the un-stretched laminar burning velocity and flame response to stretch (characterized by the Markstein length) are determined. Experiments are performed with CF₃Br and C₃H₂F₃Br added to premixed CH₄- and C₃H₈-air flames, at ambient temperature and pressure (296 ± 2 K, 101 kPa), with initial equivalence ratios $\Phi$ of 0.6, 0.8, 1.0, and 1.2, and inhibitors added at volume fractions up to 3% in the total reactant mixture. To test the kinetic mechanism, the flames are modeled as 1-D laminar flames using the Sandia PREMIX code and the predicted burning velocities are compared to the experimental values.

2. EXPERIMENTAL

2.1 Apparatus and procedure

The experiment developed for the present investigations (Fig. 1) is based on those of Faeth and coworkers [12-15] and Takizawa et al. [16]. A small spark-ignited spherically propagating flame develops in premixed gases contained in a larger chamber, and high-speed shadow graph images provide the flame speed. The spherical test chamber has an inner diameter of 380 mm, a volume of 30 L, and a wall thickness of 6.4 mm. The apparatus has vertical electrodes, an absolute pressure gauge, a dynamic pressure sensor, a thermocouple, and a mixing pump. Visual access is provided by two windows (102 mm in diameter and 25.4 mm thick) along the centerline of the chamber. The windows are polycarbonate (instead of quartz) to better resist the halogenated acids formed as product species in the present tests.
Fig. 1: Schematic diagram of the experiment (left) and shadowgraph setup (right).

The premixed reactants are prepared in the chamber via the method of partial pressures. First, a vacuum pump (Alcatel rotary vane) reduces the pressure below 100 Pa. Gaseous reactants are then added in order of lowest to highest concentration, with the partial pressure of each determined by an absolute pressure transducer (Omega PX409, which is periodically calibrated against a Baratron 627D pressure gage, claimed accuracy of 0.12 % of reading).

Liquid reactants (e.g., C₃H₂F₃Br) are injected into the chamber via a syringe and leak free septum (that is separated from the chamber by a ball valve that is closed prior to ignition). The desired mass is first obtained gravimetrically (using a Mettler PE 360 scale; 0.001g resolution), and after injection, the partial pressure is used for verification. A bellows pump (Parker Hannifin Model MB602XP) and external loop circulate the reactant gases for 3 min. (≈ 8 volume changes), after which the gases are allowed to settle for 10 min. The reactants are CH₄ (Matheson Tri-Gas, 99.97 % purity), C₃H₈ (Scott Specialty Gases, 99.0 % purity), CF₃Br (Great Lakes Chemical Corp., 99.6 % purity), and C₃H₂F₃Br (American Pacific Corp., > 99 % purity). To provide the ambient air for the tests, in-house compressed air is filtered, dried, and conditioned with a 0.01 µm filter, a carbon filter, and a desiccant bed to remove small aerosols, organic vapors, and water vapor. The relative humidity of the air is less than 2 % for all tests according to measurements with a humidity gage (TSI Velocicalc 8386).

The reactant mixtures are centrally ignited with a capacitive discharge spark. Two vertical tungsten wire electrodes (0.8 mm diameter) form a 2 mm gap in the center of the chamber. A capacitive discharge system (similar to that of ref. [17]), consisting of a power supply (Acopian model PO15HP2, 1-15 kV) and a bank of interchangeable capacitors (1-100 nF), provides variable...
ignition energies estimated to range from 0.05 mJ to 500 mJ. For most tests, the ignition energy is gradually increased until flame propagation occurs, ensuring the deposited energy is within an order of magnitude of the minimum value. For certain strongly-inhibited mixtures, higher ignition energies are required for the flame to propagate through the entire viewing window (because of the competing effects of stretch and the ignition energy [18], as described below).

The optical system for capturing the flame images is shown in Fig. 1. A z-type shadowgraph system, based on the recommendations of Settles [19], creates a shadow image of the flame, highlighting variations in the second derivative of the index of refraction. A 100 W mercury lamp creates a diverging beam that reflects off a parabolic mirror (f = 940 mm) creating a collimated beam that passes through the chamber. The beam then reflects off an identical parabolic mirror to a lens (Nikkor SLR, with a 135 mm focal length) attached to a high-speed camera ( Phantom v7.0, operated at up to 7200 frames/s, monochrome images with a spatial resolution of 143 μm). Fig. 2 shows the recorded shadowgraph images of a stoichiometric CH₄-air flame with CF₃Br added at an agent volume fraction \( X_a = 0.01 \).

Fig. 2: Shadowgraph images of a propagating stoichiometric CH₄-air flame with 1 % CF₃Br.

In addition to visually recording flame propagation, a dynamic pressure sensor (PCB Piezotronics, 101A06; claimed accuracy of 0.1 % of reading) records the instantaneous pressure rise. After each test, the chamber is quickly vented and purged with nitrogen to reduce heat transfer from the product gases to the chamber. External fans cool the chamber to ambient temperature
(296 K ± 2 K) while it is purged with air, and then subjected to vacuum three times to ensure all products are removed before the next test.

2.2 Data reduction

The experiment provides an image of the flame as a function of time. Image analysis software (developed in-house) tracks the flame position (at the top, bottom, left, and right edge) as the location of the maximum positive gradient in light intensity when approaching the outer edge from the center (i.e. the hot gas boundary of the flame sheet [20]). For slow burning flames, which are of interest in this study, the influence of buoyancy is reduced by considering flame propagation in the horizontal direction only, as suggested in previous studies [16, 21-23]. The temporal evolution of the flame radius $R_f$ yields the stretched flame speed, which is further processed to determine the burning velocity as a function of the stretch rate, as well as the un-stretched value (determined from extrapolations, as described below).

Following recommendations in the literature [23-30], the range of flame radii included in data reduction is limited in order to accurately capture the relationship between burning velocity and stretch rate (the change in burning velocity as the radius changes can also be effected by confinement, radiation, ignition, instabilities, etc.). The upper bound $R_{fU}$ is fixed at 3.5 cm for all tests, which is less than 25% of the chamber radius as recommended in ref. [24] to avoid confinement effects. An $R_{fU}$ smaller than 25% of the chamber radius was chosen to minimize the use of data affected by radiation [23, 25, 26], which occurs more so for slow burning flames with product gases of high emissivity (which are of interest in this study). For example, some of the flames described below have burning velocities near 4 cm/s, and produce high concentrations of HF and COF₂, which are strong radiators in the IR. Finally, larger flames can be more prone to have a cellular structure, which can greatly increase the burning velocity. By selecting an upper bound of 3.5 cm, all flame images post-processed to provide propagation rates were free from any cellularity.

The lower bound of flame radii ($R_{fL}$) to be included in data analysis excludes data potentially influenced by the ignition event or extreme nonlinearity during the early stages of flame propagation (the latter was shown to occur for mixtures with Lewis numbers significantly greater than unity and found to not be adequately captured by current extrapolation methods, leading to considerable errors in un-stretched results [26, 29]). Thus, $R_{fL}$ ranges between 0.5 and 2.0 cm, and
is determined for each mixture by estimating (visually from a plot of $R_f$ vs time, as in Fig. 3) $R_f$ above which the curve is nearly linear. Fig. 3 illustrates two cases with varying degrees of non-linearity early on, for which an $R_{fL}$ of 1.0 cm and 2.0 cm were selected. Note that in a select number of cases where high ignition energies (relative to our ignition capabilities) were required to generate sustained propagation, $R_{fL}$ was set to 1.5 cm, a value slightly more conservative than those chosen in previous investigations (e.g. refs [26-29], with a 0.6 cm to 1.1 cm range).

![Fig. 3: Illustration of lower bound on flame radius used to eliminate non-linearity during the early stages of propagation.](image)

For spherically symmetrical flame propagation, the flame speed in the laboratory frame of reference corresponds to the burned gas velocity $S_b$,

$$S_b = \frac{dR_f}{dt}$$  \hspace{1cm} (1)

and is a function of the stretch rate, defined [31] as

$$K = \frac{1}{A_f} \frac{dA_f}{dt} = \frac{2}{R_f} \frac{dR_f}{dt}$$  \hspace{1cm} (2)

where $K$ is the stretch rate ($s^{-1}$), $A_f$ is the flame surface area, and $t$ is time. As seen in Eq. 2, the stretch rate decreases as the flame radius increases.

For kinetic model verification, the un-stretched burning velocity can be compared to the burning velocity predicted by numerical simulations of planar 1-D laminar flames. For this comparison, the measured burning velocities need to be extrapolated to un-stretched conditions (i.e., infinitely large flame radii), and various extrapolation procedures have been discussed in the
literature [30, 32-34]. In the present work, both linear and non-linear methodologies are considered.

*Linear extrapolation*

We use the linear relationship between burning velocity and stretch rate first employed by Markstein [35] and later expressed in the present form by Clavin [36],

\[ S_b = S_b^0 - L_b K \]  

(3)

where \( S_b^0 \) is the un-stretched burned gas velocity and \( L_b \) is the burned gas Markstein length, which is a measure of the response of the flame to stretch. This functional form was derived for weakly stretched flames with near unity Lewis number \( Le \) (defined as the ratio of the mixture thermal diffusivity \( D_T \) to the mass diffusivity of the deficient reactant \( D_i \)). For the present inhibited mixtures, however, the controlling Lewis number is not obvious. Correlations exist for bi-component fuel mixtures [37], but a major assumption is that the two fuels independently react with the oxidizer and do not interact, which is not the case for the chemically active suppressants. For example, \( \text{C}_3\text{H}_2\text{F}_3\text{Br} \) is both a fuel and oxidizer, and its decomposition products react with the fuel and its decomposition products, as well as oxygen; moreover, as noted by Babushok et al.[9], for \( \text{CH}_4\)-air flames inhibited by \( \text{C}_3\text{H}_2\text{F}_3\text{Br} \), the fuel decomposition chemistry is intimately connected to the brominated species chemistry. Table 1 provides calculated \( Le \) values for lean (\( \Phi = 0.8 \)) and rich (\( \Phi = 1.2 \)) mixtures in \( \text{CH}_4\)-air or \( \text{C}_3\text{H}_8\)-air flames with \( \text{C}_3\text{H}_2\text{F}_3\text{Br} \) added at a volume fraction of 2% (assuming reactants are at 298 K). Clearly, significant departure from unity Lewis number is expected for the mixtures of interest (especially lean \( \text{C}_3\text{H}_8\)-air flames with added \( \text{C}_3\text{H}_2\text{F}_3\text{Br} \)), thus non-linear extrapolation is also performed as outlined below.

Table 1: Examples of fuel/agent/air mixture Lewis numbers at 2% agent volume fraction. \( Le \) calculated as the ratio of the mixture thermal diffusivity (\( D_T \)) of the considered blend to the binary diffusion coefficient (\( D_i \)– reference species \( \text{N}_2 \)) of either: i) the deficient species (either fuel or agent) for the lean cases, or ii) \( \text{O}_2 \) for the rich cases.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Agent</th>
<th>( Le_{\text{fuel}} )</th>
<th>( Le_{\text{agent}} )</th>
<th>( Le_{\text{O}_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_4 )</td>
<td>( \text{CF}_3\text{Br} )</td>
<td>0.93</td>
<td>1.70</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>( \text{C}_3\text{H}_2\text{F}_3\text{Br} )</td>
<td>0.89</td>
<td>2.92</td>
<td>0.96</td>
</tr>
<tr>
<td>( \text{C}_3\text{H}_8 )</td>
<td>( \text{CF}_3\text{Br} )</td>
<td>1.84</td>
<td>1.60</td>
<td>0.91</td>
</tr>
</tbody>
</table>

9
Non-linear extrapolation

Non-linear extrapolation is performed using the equations derived by Ronney and Sivashinsky [38] (for highly stretched flames with large \( Le \)), as formulated by Kelley et al. [39],

\[
\left( \frac{s_b}{s_b^0} \right)^2 \ln \left( \frac{s_b}{s_b^0} \right)^2 = -2 \frac{L_b K}{s_b^0} - 2 \frac{L_b d s_b}{s_b^0} d R_f
\]  

(4)

Note that Eq. 4 is similar to the commonly used non-linear equation proposed in the earlier works of Kelley and Law [33],

\[
\left( \frac{s_b}{s_b^0} \right)^2 \ln \left( \frac{s_b}{s_b^0} \right)^2 = -2 \frac{L_b K}{s_b^0}
\]  

(5)

It should be noted that while the non-linear methods generally provide more accurate results compared to the linear one, Wu et al. [34] recently showed that none of the existing extrapolation methods capture the true non-linear relationship between flame speed and stretch rate when \( Le \) is considerably lower than unity (\( L_b < 0 \)).

In applying Eq. 4 for data reduction, an expanded form, suggested in ref. [39]

\[
\frac{s_b}{s_b^0} \left[ 1 + \frac{2L_b}{R_f} + \frac{4L_b^2}{R_f^2} + \frac{16L_b^3}{3R_f^3} + \cdots \right] = 1
\]  

(6)

is applied because it is more numerically stable. Finally, using integrated forms of Eqs. 3 and 6 (as in [39-41]) reduces uncertainty resulting from the numerical differentiation required to solve Eqs. 3 and 6. Thus, the equations used to reduce the raw data and extract the un-stretched burning velocity \( s_b^0 \) and Markstein length \( L_b \) become

\[
R_f = S_b^0 t - 2L_b \ln R_f + c_1
\]  

(7)

\[
S_b^0 t + c_2 = R_f + 2L_b \ln R_f - 4 \frac{L_b^2}{R_f^2} - \frac{8 L_b^3}{3 R_f^3}
\]  

(8)

where the variables \( c_1 \) and \( c_2 \) are integration constants. The variables \( s_b^0, L_b, c_1, \) and \( c_2 \) are determined using a non-linear least squares optimization routine that fits Eqs. 7 and 8 to the experimentally measured flame radius versus time \( R_f(t) \). From conservation of mass across the flame sheet, the un-stretched unburned gas velocity \( s_u^0 \) is then obtained:
\[ S_{u}^{0} = \frac{\rho_{b}}{\rho_{u}} S_{b}^{0} \]  

(9)

where \( \rho_{u} \) and \( \rho_{b} \) are the unburned and burned gas densities. The burned gas is assumed to be in chemical equilibrium and \( \rho_{b} \) is taken from a constant-pressure, constant-enthalpy calculation at the initial temperature and pressure of each test using the CEA2 routine of Gordon and McBride [41].

Thermodynamic data for these calculations are from the NASA database [42] (included in CEA2), the NIST (National Institute of Standards and Technology) HFC mechanism [43], and the \( \text{C}_{3}\text{H}_{2}\text{F}_{3}\text{Br} \) mechanism [8] (the latter two sources are described in more detail below).

Tests are performed at 296 K ± 2 K and 1.01 bar and are repeated twice for each mixture. For each test, the extrapolation equations are fit to the \( R_{f} \) vs. \( t \) data from the left and right side flame tracking locations. The fitting parameters (\( S_{b}^{0} \), \( L_{b} \), and \( c \)) from the two sides are then averaged. Lastly, the results of the multiple tests are averaged to produce the burning velocities and burned gas Markstein lengths reported in the present study, which have standard deviations that are generally around 0.3 cm/s and 0.15 mm, with maximum values of 0.9 cm/s and 0.7 mm.

Fig. 4 shows the average \( S_{b} \) from the left and right tracking locations of select \( \text{CF}_{3}\text{Br} \)-inhibited \( \text{C}_{3}\text{H}_{8} \)-air tests (symbols) as a function of stretch rate, along with the linear extrapolation to zero-stretch conditions (dotted lines). For clarity, data with Markstein lengths greater than, less than, and nearly equal to unity are labeled. Note that elsewhere in the present paper, the reported values of \( S_{u}^{0} \) and \( L_{b} \) are from the non-linear fit of \( R_{f} \) vs. \( t \), as mentioned above. In Fig. 4, \( \frac{dR_{f}}{dt} \) (i.e., \( S_{b} \)) are extrapolated to \( S_{b}^{0} \) using the linear and non-linear methods (Eqs. 3 and 4) strictly for illustrating the extrapolation to zero-stretch conditions and the differences in the flame response to stretch, characterized by \( L_{b} \). As the figure shows, for these conditions there is no discernable difference in the value of un-stretched burning velocity from using either the linear or non-linear extrapolation methods.
Fig. 4: Burned gas velocity versus stretch rate for CF$_3$Br-inhibited C$_3$H$_8$-air mixtures at $\Phi=1.2$. The symbols are the experimental data, the dashed lines are the linear extrapolation (Eq. 3), and the dotted lines are the non-linear extrapolation (Eq. 4) to zero-stretch conditions.

2.5 Uncertainties and measurement accuracy

The uncertainties in experimental burning velocity are reported as expanded uncertainties $U = k u_c$ determined from a combined standard uncertainty $u_c$ and a coverage factor $k = 2$ corresponding to a level of confidence of 95 %. The combined standard uncertainty is determined using the root-sum-of-squares (RSS) method of combining individual uncertainty components, as outlined in ref. [44]. As described by Chen [26], uncertainties in the initial conditions can be propagated to uncertainties in the burning velocities. Using his estimations based on numerical modeling, uncertainties in the initial temperature, pressure, mixture equivalence ratio, and inhibitor concentration, of 3 K, 1.3 kPa, 1 %, and 0.3 % result in a maximum expanded relative uncertainty of 13 % in $S_u^0$, which occurs at lean conditions when the uncertainty in the equivalence ratio has the largest effect on the reported data.

Measurement uncertainty is not the only cause of inaccuracy in the reported data. Buoyancy, radiation, and non-linear stretch effects can cause the measured result to differ from the speed of the ideal 1-D planar adiabatic flame or even the true speed of a spherically propagating flame (this is particularly important when comparing experimental data to numerical predictions). Higher inaccuracy exists for slow burning flames most affected by buoyancy and radiation. In addition, higher uncertainty is expected for mixtures with Lewis numbers far from unity (i.e. $Le$
because, for highly non-equidiffusive mixtures, the extrapolation methods fail to fully capture the non-linearity between the burning velocity and stretch rate, as demonstrated in ref.[34]. While these factors cannot be eliminated in the present study, their influence was minimized by using only the portion of the $R_f$ vs. $t$ data described above.

3. NUMERICAL METHODS

Equilibrium product species and their thermodynamic state are calculated for a constant-pressure, constant-enthalpy process using the EQUIL subroutine [45] (reactants at 298.15 K and 1.01 bar). Planar adiabatic freely propagating premixed flame structures are calculated using the Sandia PREMIX code [46-48]. The mass, species, and energy conservation equations are solved for each reactant mixture at an initial temperature and pressure of 298.15 K and 1.01 bar, with air modeled as N$_2$ and O$_2$ at volume fractions of 0.79 and 0.21. The Soret effect is considered and molecular diffusion is modeled using the mixture-averaged formulation. Large computational domains are used with final gradient (GRAD) and curvature (CURV) parameters set to 0.05. As such, the number of grid points ranged from 310 to 420, with the final adjustment of the GRAD and CURV parameters adding about 100 grid points, and yielding a burning velocity change of less than 2 % (the change was typically much less and decreased as the burning velocity increased).

A comprehensive reaction mechanism previously assembled in ref. [9], and included here as supplementary material, is used to model CH$_4$- and C$_3$H$_8$-air flames with added CF$_3$Br or C$_3$H$_2$F$_3$Br. The complete mechanism is composed of several sub-mechanisms. Hydrocarbon-air reactions are modeled with the C1-C4 mechanism of Wang et al. [49]. C1-C3 hydrofluorocarbon reactions are modeled with an updated version of the NIST HFC mechanism [43, 50], with the updates summarized in refs. [5, 9]. Decomposition reactions of brominated C1 species in the presence of hydrocarbon-air are modeled with an updated version of the original CF$_3$Br mechanism of Babushok et al. [10], as described in ref.[9]. Lastly, reactions involving the larger brominated species of C$_3$H$_2$F$_3$Br decomposition have been developed by Burgess et al. [9]. It should be emphasized that the mechanism assembled for the present verification study is considered only as a starting point. Numerous changes to both the rates and the reactions included may be made once additional experimental and theoretical data become available (this is particularly true for the new C$_3$H$_2$F$_3$Br decomposition sub-mechanism).
4. RESULTS AND DISCUSSION

4.1 Experimental validation

To validate the accuracy of the present experimental system and data reduction methods, the un-stretched, unburned gas burning velocity $S_{u0}$ of CH$_4$- and C$_3$H$_8$-air flames over a range of fuel-air equivalence ratios are presented and compared with other data in the literature. (In these comparisons and others, the non-linear extrapolation method was used to reduce the present data, unless otherwise stated). Fig. 5 compares the present CH$_4$-air ($0.6 \leq \Phi \leq 1.3$) measurements to spherically propagating flame [28, 51-53] and counterflow flame [54, 55] datasets, as well as numerical predictions using the Wang mechanism [56]. For each experimental dataset, the inclusion of an (L) or (NL) in the figure legend specifies whether linear or non-linear extrapolation was performed. Burning velocities are in excellent agreement with the previous results and agree well with predictions, except for $\Phi \leq 0.8$, where measured $S_{u0}$ is 10 % to 25 % lower. For $\Phi \geq 0.9$, measured $S_{u0}$ is within 3 % of the predictions. At lean conditions, previously determined experimental burning velocities are in general lower than the predictions, with the exception of refs. [53, 55]. The agreement between the present data and previously published data show that the new experiment provides accurate burning velocity measurements for CH$_4$-air mixtures.

![Fig. 5: Burning velocity of premixed CH$_4$-air flames at 298 K and 101 kPa as a function of equivalence ratio, together with previously published results (symbols) and 1-D planar adiabatic simulation (dashed line).](image-url)
Fig. 6 compares burning velocities for C₃H₈-air flames against spherically propagating [15, 56], counterflow [54, 57], and heat flux-stabilized [58] flame datasets, along with numerical predictions with the Wang mechanism [49]. As in Fig. 5, the use of linear or non-linear extrapolation is specified for each dataset by an (L) or (NL). At lean conditions, the present $S_u^0$ results are in excellent agreement with the previous experiments and with the numerical predictions. For rich conditions ($\Phi > 1.0$), the present data are on the lower end of the experimental scatter, but exhibit reasonable agreement with the model predictions.

![Graph](image_url)

**Fig. 6:** Burning velocity of premixed C₃H₈-air flames at 298 K and 101 kPa as a function of equivalence ratio, together with previously published results (symbols) and 1-D planar adiabatic simulation (dashed line).

We further validate the experimental results by comparing burned gas Markstein lengths $L_b$ for CH₄-air flames to results in the literature. Fig. 7 presents the linearly (left frame) and non-linearly (right frame) extracted results according to Eq. 7 and Eq. 8, along with previous experimental [28, 51-53, 59] and computational [27] datasets. Similar to what was seen in the above $S_u^0$ comparison, the present $L_b$ values fall within the scatter of previously published data for the entire range of equivalence ratio. Non-linearly extracted $L_b$ values are in excellent agreement with the results of refs. [28, 59] and linearly extracted $L_b$ values are closest to the results of ref. [28]. Moreover, at lean conditions, the $L_b$ values obtained by the linear and non-linear method are similar, whereas at rich conditions the linear method yields $L_b$ values that are considerably larger. The larger scatter in linearly-extracted Markstein lengths (compared to non-linearly extracted...
ones) has been demonstrated [26] to be the result of higher sensitivity to the lower and upper radius bounds considered during extrapolation.

![Burned gas Markstein lengths of premixed CH₄-air flames as a function of equivalence ratio, together with previously published results. Linear method: left frame; non-linear method: right frame.](image)

Fig. 7: Burned gas Markstein lengths of premixed CH₄-air flames as a function of equivalence ratio, together with previously published results. Linear method: left frame; non-linear method: right frame.

Fig. 8 provides Markstein lengths $L_b$ of C₃H₈-air flames as a function of equivalence ratio. The present linearly and non-linearly extrapolated experimental data are plotted together (because fewer data are available in the literature) and compared to previous spherically expanding experimental [60-62] and numerical [63] data (linear and non-linear extrapolations are noted by the dashed and circle symbols respectively). For rich conditions, present and previously reported Markstein lengths are all in good agreement regardless of the extrapolation method. At leaner conditions, the scatter becomes larger, with the linearly extracted Markstein lengths generally higher. As observed for the CH₄-air flames, the present non-linear $L_b$ values are in excellent agreement with the non-linear data reported by Varea [62].
Fig. 8: Burned gas Markstein lengths of premixed C₃H₈-air flames as a function of equivalence ratio, together with previously published results.

4.2 Influence of CF₃Br and C₃H₂F₃Br on $S_u^0$

Fig. 9 presents the burning velocities (bottom curves in each frame) for premixed CH₄-air (left frames) and C₃H₈-air (right frames) flames with added CF₃Br (triangles) or C₃H₂F₃Br (circles), for $S_u^0$ determined using the non-linear extrapolation method. Computed equilibrium adiabatic flame temperatures are shown by the lines without symbols for CF₃Br and C₃H₂F₃Br. The upper, middle, and lower frames provide data for equivalence ratios of 1.2, 1.0 and 0.8 (based on the uninhibited mixture prior to agent addition).

**Rich cases ($\Phi = 1.2$)**

As shown in Fig. 9, C₃H₂F₃Br provides a larger reduction in both $S_u^0$ and $T_{ad}$ as compared to CF₃Br (top left frame). At $X_a = 0.02$, the computed $T_{ad}$ for the C₃H₂F₃Br-inhibited mixture is 147 K lower than for the CF₃Br case and both agents are found to prevent ignition. Similar results are seen when adding the agents to the rich C₃H₈-air flames (top right frame). For instance, C₃H₂F₃Br lowers the burning velocity 38 % and 56 % more than CF₃Br at $X_a = 0.01$ and 0.02. For the same conditions, the reduction in $T_{ad}$ is 74 K and 142 K larger with C₃H₂F₃Br. At $X_a = 0.03$, $\Phi$ = 1.2

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1 The phrase “prevent ignition” and term “non-ignition” are used throughout to identify conditions where a flame was either not observed or did not propagate throughout the entire viewing window when applying the maximum available ignition energy. We avoid “extinction” and “limits” because the concentrations for which non-ignition occurs are both vessel specific and based on the available ignition energy range in the present study. We do not claim the concentrations causing non-ignition to be representative of flammability or ignition limits.
non-ignition occurs with C$_3$H$_2$F$_3$Br, whereas flame propagation was observed for the CF$_3$Br case with $S_u^0 = 6.8$ cm/s.

**Stoichiometric cases**

For the stoichiometric CH$_4$-air mixture (middle left frame), CF$_3$Br and C$_3$H$_2$F$_3$Br provide similar reductions in burning velocity. While the flame adiabatic temperatures are similar for $X_a < 0.01$, the decrease of $T_{ad}$ is larger with C$_3$H$_2$F$_3$Br addition when $X_a > 0.01$. For example, at $X_a = 0.03$ $T_{ad}$ is 170 K lower with C$_3$H$_2$F$_3$Br than with CF$_3$Br, and both agents prevent ignition. Similar trends are again observed when adding agents to C$_3$H$_8$-air flames (middle right frame), although for C$_3$H$_8$-air flames, C$_3$H$_2$F$_3$Br seems more efficient at reducing $S_u^0$ at higher agent loadings ($X_a > 0.02$).

**Lean cases ($\phi = 0.8$)**

At lean conditions, CF$_3$Br provides a larger reduction in the burning velocity (as compared to richer cases) at all agent concentrations considered. For example, for $\phi = 0.8$, addition of 2% CF$_3$Br is found to prevent ignition of both CH$_4$-air and C$_3$H$_8$-air flames (bottom frames), whereas addition of 3% C$_3$H$_2$F$_3$Br still allows stable flames, with corresponding burning velocities of 5.8 cm/s and 8.7 cm/s. Note that for CF$_3$Br addition to the lean flames, $T_{ad}$ decreases mildly with $X_a$ increase, as it was for the case for the rich and stoichiometric flames. In contrast, the addition of C$_3$H$_2$F$_3$Br to either CH$_4$- or C$_3$H$_8$-air flames increases the adiabatic flame temperature, by up to 200 K at $X_a = 0.018$, and then the increase is reduced as $X_a$ increases.
Fig. 9: Laminar burning velocity $S_u^0$ and adiabatic flame temperature $T_{ad}$ of CH$_4$-air (left) and C$_3$H$_8$-air (right) with added CF$_3$Br and C$_3$H$_2$F$_3$Br. For clarity, lines connect the experimental data points (and do not represent predictions). Data at the highest value of $X_a$ and $S_u^0=0$ represent points of unsuccessful flame propagation or non-ignition.

The differences in the behavior of added CF$_3$Br and C$_3$H$_2$F$_3$Br to lean and rich flames is worthy of discussion. It has been shown [64, 65] that the chemical inhibition by halogen-containing agents results from reduction of active flame radical (H, OH, O) concentrations by halogenated intermediates, which lowers the overall flame reactivity. Since the atomic concentrations of fluorine and bromine are identical for CF$_3$Br or C$_3$H$_2$F$_3$Br addition (at the same $X_a$), the mechanisms of reduction in the chain-carrying radical concentrations due to radical
trapping and radical recombination cycles are not expected to differ significantly. Rather, the change in the effective stoichiometry due to the fuel component \((C_xH_y^-)\) of the \(C_3H_2F_3Br\) (as compared to \(CF_3Br\)) is likely the cause.

To illustrate the effect of \(C_3H_2F_3Br\) on the overall stoichiometry, an overall equivalence ratio \(\Phi_{overall}\) can be defined that incorporates the agent fuel effect. The balance equation for the fuel/agent/air system can be written as:

\[
\rho C_a H_b + \alpha C_c H_d F_e Br_f + \gamma [0.21O_2 + 0.79N_2] = \beta CO_2 + \lambda HF + \mu H_2O + \delta Br + \eta N_2
\]

Note that when fluorine is present, the main combustion products are dependent on the ratio of hydrogen to fluorine atoms ([F]/[H]). For the present inhibited mixtures, [F]/[H] is always less than unity, so that only the fluorinated product HF need be considered (unlike cases with [F]/[H] > 1, for which CFO₂ and CF₄ formation must be considered). The stoichiometric proportion of air \(\gamma_{stoic}\) is found by performing balances on C, H, F, Br, and O atoms:

\[
\gamma_{stoic} = \rho(a + b/4) + \alpha(c + d/4 - e/4)
\]

so that \(\Phi_{overall}\) is expressed as:

\[
\Phi_{overall} = \left(\frac{(\rho + \alpha)/(\gamma_{actual})}{(\rho + \alpha)/(\gamma_{stoic})}\right)
\]

Fig. 10 shows the change in \(\Phi_{overall}\) with agent addition (\(C_3H_2F_3Br\) or \(CF_3Br\)) to \(C_3H_8\)-air at initial equivalence ratios of 0.8, 1.0 and 1.2. When \(CF_3Br\) is added, there is minimal change in the overall equivalence ratio. Conversely, as \(C_3H_2F_3Br\) is added, the overall equivalence ratio is shifted considerably toward rich conditions. For instance, the initially lean \(C_3H_8\)-air flame at \(\Phi = 0.8\) reaches stoichiometry when \(C_3H_2F_3Br\) is added at \(X_a \approx 0.015\). The results observed in Fig. 10 are consistent with the relative inhibitor efficiencies observed in Fig. 9. For the lean flame, the peak temperature with added \(C_3H_2F_3Br\) occurs near the concentration corresponding to \(\Phi_{overall} = 1\) \((X_a \approx 0.018)\). At lean conditions, \(CF_3Br\) has a lesser impact on \(T_{ad}\) and \(\Phi_{overall}\) (compared to \(C_3H_2F_3Br\)) and reduces burning velocity more effectively. At rich conditions, the higher inhibition efficiency of \(C_3H_2F_3Br\) is likely the result of the larger shift in \(\Phi_{overall}\) toward even richer conditions.
Fig. 10: Overall equivalence ratio as C$_3$H$_2$F$_3$Br (dashed lines) or CF$_3$Br (solid lines) is added to C$_3$H$_8$-air flames at different initial equivalence ratios.

The stoichiometry of the flame affects the radical trapping by fluorinated intermediates (e.g., CF$_3$, CF$_2$, etc.) and catalytic radical recombination by Br-species. For example, Fig. 11 shows the peak (solid lines) and equilibrium (dashed lines) OH volume fraction as a function of the volume fraction of added C$_3$H$_2$F$_3$Br or CF$_3$Br, for $\Phi=0.53$, 1.0, and 1.33. (Note that the response for OH is approximately the average of the response for O and H, so that the net radical behavior is approximated by that of OH.) The first thing to note is that the equilibrium OH volume fraction is strongly affected by addition of C$_3$H$_2$F$_3$Br, but minimally by CF$_3$Br. For example, with addition of C$_3$H$_2$F$_3$Br, the equilibrium OH volume fraction is increased (non-monotonically) by a factor of 21 for lean flames (at $X_a=0.03$) but reduced by a factor of about 9 and 11 for stoichiometric and rich flames (at $X_a=0.02$, and more at higher $X_a$). For CF$_3$Br addition, the equilibrium OH volume fraction decreases monotonically about the same amount (36 % to 60 % reduction at $X_a=0.02$) for the lean and stoichiometric flames, respectively. The behavior of the peak OH volume fraction is also different for the two agents: CF$_3$Br always drives the OH towards equilibrium (i.e., the catalytic radical recombination effect), and the catalytic efficiency is lower for richer flames (i.e., higher agent loadings are required for the peak OH volume fraction to reaches the equilibrium value for richer flames). The agent C$_3$H$_2$F$_3$Br also drives the OH to equilibrium relatively efficiently for the lean flame, but poorly (i.e., little catalytic effect) for the initially stoichiometric
and rich flames. That is, with C\textsubscript{3}H\textsubscript{2}F\textsubscript{3}Br addition, most of the radical reduction in the stoichiometric and rich flames occurs due to reduction in the equilibrium value. Moreover, for the lean flame, the equilibrium value increases rapidly with C\textsubscript{3}H\textsubscript{2}F\textsubscript{3}Br addition (due to the increase in peak flame temperature), so that catalytic radical recombination cycle, while working, does not help reduce burning velocity. Thus, C\textsubscript{3}H\textsubscript{2}F\textsubscript{3}Br is a more effective agent than CF\textsubscript{3}Br for rich and stoichiometric flames because it reduces the equilibrium radical concentrations more so than does CF\textsubscript{3}Br.

Fig. 12: Overall equivalence ratio as C\textsubscript{3}H\textsubscript{2}F\textsubscript{3}Br (dashed lines) or CF\textsubscript{3}Br (solid lines) is added to C\textsubscript{3}H\textsubscript{8}-air flames at different initial equivalence ratios.

4.3 CF\textsubscript{3}Br model verification

As a check of the updated C1 brominated-species sub-mechanism, the experimentally measured burning velocities are compared to numerical predictions of CF\textsubscript{3}Br-inhibited flames. Fig. 13 presents experimental values of \( S_u^0 \) (symbols) together with numerical predictions (lines), for flames of CH\textsubscript{4}-air (left frame) and C\textsubscript{3}H\textsubscript{8}-air (right frame). The separate curves shows results at a given value of the initial, uninhibited, equivalence ratio \( \phi = 0.6, 0.8, 1.0, \) and \( 1.2 \). The open symbols denote values of \( S_u^0 \) determined using non-linear extrapolation (described above) while the bars (-) show values obtained using linear extrapolation. As indicated, for nearly all data collected (except the two circled conditions), the difference between the two extrapolation methods is very small. The agreement between the predicted and measured values of \( S_u^0 \) is also very good, typically within about 7 %, which is much less than the estimated maximum uncertainty in \( S_u^0 \) (± 13 %). Moreover, the present burning velocities agree well with previously reported values for CF\textsubscript{3}Br-inhibited stoichiometric CH\textsubscript{4}-air flames [11, 66, 67], as illustrated in Fig. 14. For C\textsubscript{3}H\textsubscript{8}-air flames (right frame in Fig. 13), the agreement between measured and predicted \( S_u^0 \) is similar to
that observed for the inhibited CH$_4$-air flames: numerical predictions slightly over-predict inhibition, but by less than 8% for most conditions, with the exception of $\Phi = 1.0$ and $X_a = 0.03$ where the model over-predicts inhibition by 18%. When adding CF$_3$Br to CH$_4$- and C$_3$H$_8$-air flames, the marginal reduction in $S_{u0}$ decreases as the agent concentration increases in both experiments and predictions, as has been discussed previously [68, 69]. Although no burning velocity data could be collected for inhibited flames at very lean conditions ($\Phi = 0.6$), numerical predictions are provided to illustrate the expected inhibition. For both the CH$_4$-air and C$_3$H$_8$-air flames at $\Phi = 0.6$, non-ignition occurred at the lowest concentration tested ($X_a = 0.005$).

![Fig. 13: Comparison of experimental (symbols) and numerical (lines) $S_{u0}$ for CF$_3$Br-inhibited CH$_4$-air (left frame) and C$_3$H$_8$-air (right frame) at $\Phi = 0.6, 0.8, 1.0, \text{ and } 1.2$; open symbols are non-linearly extracted and bars are linearly extracted.](image-url)
Recently, Osorio et al. [67] compared measured burning velocities of CF\textsubscript{3}Br-inhibited CH\textsubscript{4}-
and C\textsubscript{3}H\textsubscript{8}-air flames with numerical predictions. A constant-pressure spherically expanding
flame experiment provided burning velocity as a function of stretch, which was extrapolated to zero-
stretch conditions using the linear method described above. These values of extracted \( S_u^0 \) were
then compared with predictions of the 1-D planar laminar burning velocity from the Sandia
PREMIX code, using the NUI-Galway mechanism (to describe hydrocarbon decomposition) [70]
and the CF\textsubscript{3}Br mechanism of ref. [10]. With CF\textsubscript{3}Br added at \( X_a = 0.005 \) or 0.01 and \( (0.8 \leq \Phi \leq 1.2) \), the burning velocity predictions were found to be consistently higher than the experimental
values. It was unclear whether the discrepancy was the result of inaccuracies in the original CF\textsubscript{3}Br
model [10] or bias associated with the linear method for extrapolating the burning velocity to unstretched
conditions (as described by other researchers [28, 32, 33]). Thus, to explore the source of the
discrepancies, tests were repeated for the conditions of their experiments, and the data were
reduced using the present linear and non-linear extrapolation methods. Finally, the values of \( S_u^0 \)
were predicted using PREMIX simulations using the present kinetic model.

The results from ref. [67] are compared to the present results in Fig. 15. Burning velocities
as a function of equivalence ratio are shown for flames of CH\textsubscript{4}-air (left frame) and C\textsubscript{3}H\textsubscript{8}-air (right
frame) with CF\textsubscript{3}Br volume fractions of 0, 0.005 and 0.01. The solid lines, solid bars, and solid
circles show the present predictions, linearly extrapolated data, and non-linearly extrapolated data. The dashed lines and open bars show the predictions and linearly extrapolated data from ref. [67]. As seen in the figure, the present experimental data are very close to each other when using either linear or non-linear extrapolations (except for the cases of rich CH₄-air and lean C₃H₈-air flames with CF₃Br volume fraction of 0.01). The present experimental data are also close to the experimental data of Osorio, generally within 7 % and with a maximum difference of 20 %. As seen in Fig. 15, burning velocity measurements from both studies are much closer to the present predictions using the updated CF₃Br mechanism proposed in ref [9] (as opposed to the older mechanism used by Osorio et al.). Overall, the predictions of ref. [67] are 4 % to 28 % and 13 % to 35 % higher than the present non-linearly extracted $S_{u0}$, while the present predictions fall within ±9 % of the non-linearly extracted values. Although the underlying hydrocarbon mechanisms are different, it appears that the updates² outlined in ref. [9] have significantly improved the accuracy of the CF₃Br model.

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Fig. 15: Comparison of present measured and predicted $S_{u0}$ with those of Osorio et al. [67] for CH₄-air (left) and C₃H₈-air (right) flames with added CF₃Br. Solid bars and circles represent the present linearly and non-linearly extracted $S_{u0}$; solid lines represent the present predictions; open bars and dashed lines are the linearly extracted and predicted $S_{u0}$ from ref. [67].

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² The improved performance of the updated model is the result of the inclusion of more accurate kinetic rate data made available in the literature since the original model was developed (and not based on the present measurements and predictions). As summarized in ref. [9], Arrhenius rate coefficient data was updated for 1/3 of the 100 reactions contained in the model.
4.4 C$_3$H$_2$F$_3$Br model verification

To validate the new C$_3$H$_2$F$_3$Br (2-BTP) kinetic model, measured $S_u^0$ for CH$_4$- and C$_3$H$_8$-air flames with added C$_3$H$_2$F$_3$Br are compared to predictions. For each fuel-air mixture, four different initial equivalence ratios are considered ($\Phi = 0.6, 0.8, 1.0, \text{ and } 1.2$). Fig. 16 presents the the present experimental $S_u^0$ (symbols) together with the numerical predictions (lines) for flames of CH$_4$-air (left frame) and C$_3$H$_8$-air (right frame). The open symbols and bars denote values of $S_u^0$ determined using the non-linear and linear extrapolation methods, and as seen for the CF$_3$Br-inhibited flames, nearly all the data (except for the circled condition) have very similar results using the two methods (well within the experimental uncertainty). In addition, burning velocities of C$_3$H$_2$F$_3$Br-inhibited CH$_4$-air flames (left frame) determined from the constant-volume spherically expanding method [11] (note that these data are not stretch corrected, but instead, extrapolated from experimental data at large flame radii when the stretch rate is small) are shown for $\Phi=1.0$ and $0.6$ (X symbols). The experimental data from the two methods agree within about 12 % and 7 % for $\Phi=1.0$ and $\Phi=0.6$.

For C$_3$H$_2$F$_3$Br added to CH$_4$-air, the model predictions are within 9 % of the experimental results for $\Phi = 1.0$ and 1.2, while for $\Phi = 0.8$, the inhibition performance is over-predicted in the range at low agent concentrations, with measured $S_u^0$ higher than predictions by up to 18 % (the discrepancy increases as $X_a$ increases). At $\Phi=0.6$, the model over-predicts inhibition performance by 25 % (which is close to the measurement accuracy of $\approx 2$ cm/s), but captures the non-monotonic behavior as the C$_3$H$_2$F$_3$Br concentration increases; the flame speed initially drops up to $X_a = 0.01$, before it increasing for $0.01 \leq X_a \leq 0.03$, and finally decreases as more C$_3$H$_2$F$_3$Br is added. Previous work with the BTP model [9] showed that the drop in $S_u^0$ at low concentrations, followed by the rise at higher concentrations, was the result of the competition between radical scavenging by the halogenated species (Br and F participate in chain terminating reactions) and the additional heat release associated with the decomposition of C$_3$H$_2$F$_3$Br in the lean CH$_4$-air environment.

For C$_3$H$_2$F$_3$Br added to C$_3$H$_8$-air, burning velocity predictions are within 7 % of the experimental results for the stoichiometric and rich flames, with the exception of the prediction for $\Phi = 1.2$ and $X_a = 0.02$ which is higher by 22 % (but still within the measurement uncertainty of $\approx 2$ cm/s). The model predictions are once again higher than the experimental values at the lean
conditions; at $\Phi = 0.8$, prediction accuracy decreases as $X_a$ increases, the relative error in $S_u^{\theta}$ at $X_a = 0.03$ being about 25%.

Fig. 16: Comparison of experimental (symbols) and numerical (lines) $S_u^{\theta}$ for C$_3$H$_2$F$_3$Br-inhibited CH$_4$-air (left) and C$_3$H$_8$-air (right) flames at $\Phi = 0.6$, 0.8, 1.0, and 1.2; open symbols are non-linearly extracted, bars are linearly extracted, and crosses are from ref. [11].

4.5 Sensitivity analysis

Normalized sensitivity coefficients in the form of logarithmic derivatives ($\delta \ln S_u / \delta \ln A_i$) are determined from the PREMIX simulations for CH$_4$-air flames with added CF$_3$Br and C$_3$H$_2$F$_3$Br to identify the brominated reactions that burning velocity is most sensitive to. In Fig. 17, the brominated reactions with the highest absolute sensitivities are shown for stoichiometric CH$_4$-air flames with CF$_3$Br (grey bars) and C$_3$H$_2$F$_3$Br (black bars) added at $X_a = 0.03$ (a positive normalized sensitivity coefficient indicates that an increase in the Arrhenius pre-exponential factor $A$ increases $S_u^{\theta}$, and vice versa). Burning velocities are found to be sensitive to numerous brominated reactions participating in both the recombination of H$_2$ and the generation of HBr. In general, the CF$_3$Br inhibited flame is more sensitive to the brominated reactions in Fig. 17, with higher sensitivity to the top three reactions because the concentrations of hydrocarbon fragments that serve as alternative paths for HBr and BR$_2$ formation are lower than in the C$_3$H$_2$F$_3$Br inhibited flame. In regard to the updates made to the CF3Br mechanism in ref. [9], reactions 6-9 in Fig. 17 are among the reactions for which more accurate rate coefficients were assigned.
Fig. 17: Sensitivity coefficients for stoichiometric CH$_4$-air flames with CF$_3$Br and C$_3$H$_2$F$_3$Br added at a volume fraction of 3%.

4.6 Flame stability and $S_u^0$

Referring back to Fig. 13, flames with higher predicted values of $S_u^0$ sometimes propagated less well than flames with lower values. For certain mixtures, applying near-minimum ignition energies established a flame that extinguished soon after. When this occurred, the experiment was repeated with a higher energy until the flame successfully propagated through the entire viewing window. For other tests, such as CH$_4$-air at $\phi = 1.2$ with 2% CF$_3$Br, the maximum available ignition energy initiated reaction, but did not produce sustained propagation. Hence, as shown for hydrocarbons [72], non-ignition of mixtures with added CF$_3$Br or C$_3$H$_2$F$_3$Br is not entirely controlled by $S_u^0$, but instead, dependent on other factors (i.e., in the present study non-ignition occurred over a range of predicted $S_u^0$, depending on the initial equivalence ratio). For example, flame propagation was observed for lean CH$_4$-air ($\phi = 0.8$) with 2% CF$_3$Br and not for rich CH$_4$-air ($\phi = 1.2$) with 2% CF$_3$Br although the predicted planar burning velocities were 4.3 cm/s and 6.6 cm/s, respectively. In other words, the mixture with the lower predicted burning velocity successfully propagated through the viewing window and the mixture with the higher predicted burning velocity did not. With added C$_3$H$_2$F$_3$Br, successful flame propagation could not be obtained for lean C$_3$H$_8$-air ($\phi = 0.6$) although it could for $\phi = 1.0, X_0 = 0.03$ and $\phi = 1.2, X_0 = 0.02$, for which $S_u^0$ which had burning velocities lower by $\sim$ 2 cm/s.
Similar observations were made by Qiao et al. [23] when measuring burning velocities of CH$_4$-air flames diluted with chemically passive suppressants (N$_2$, Ar, CO$_2$, and He). During their study, successful flame propagation was observed for stoichiometric CH$_4$-air flames diluted with N$_2$, Ar, and CO$_2$ with predicted $S_o$ around 5 cm/s. On the contrary, flame propagation was not observed for a He-diluted flame, even though the predicted $S_o$ was around 10 cm/s. For certain mixtures, the change in the response to stretch may cause stretch-induced quenching during the early stages of flame growth, as observed in ref. [23]. To interpret the influence of inhibitors on the flame response to stretch, Markstein lengths are examined in the following section.

### 4.7 Influence of agents on Markstein length and minimum ignition energy

Flame propagation speed and stability depend upon the flame’s response to stretch (which can be characterized by the Markstein length $L_b$) as well as the stretch condition of the particular configuration [73]. As described above, by considering flames of different radii, the present experiment provides the laminar burning velocity as a function of the stretch rate (from which the Markstein length $L_b$ can be determined, using either the linear or non-linear analysis of the data). For example, Fig. 18 shows the non-linearly extracted burned gas Markstein lengths $L_b$ for CH$_4$-air flames (left frames) and C$_3$H$_8$-air flames (right frames) as a function of the volume fraction of added CF$_3$Br (top) and C$_3$H$_2$F$_3$Br (bottom). The different symbols (with lines connecting the data) show results at different $\Phi$. As frequently reported in literature, the Markstein lengths of uninhibited CH$_4$-air and C$_3$H$_8$-air increase and decrease respectively as the equivalence ratio increases. (Opposite trends exist because the diffusivity of CH$_4$/C$_3$H$_8$ is higher/lower than the diffusivity of air [73].)

For CF$_3$Br addition, Fig. 18 shows that the influence on the flame response to stretch is not only dependent on the initial equivalence ratio and fuel type, but also on the volume fraction of added CF$_3$Br. For rich flames of CH$_4$, $L_b$ increases as the concentration of CF$_3$Br increases, while for lean flames, the opposite is true ($L_b$ becomes more negative) and for stoichiometric flames, $L_b$ is small, becomes slightly more positive up to $X_a = 0.005$, above which the effect is relatively neutral. For C$_3$H$_8$-air flames, the trends are generally opposite ($L_b$ for lean flames becomes more positive with added CF$_3$Br, etc.), although the influence is stronger and $L_b$ becomes more positive for stoichiometric flames as well. For the rich flames ($\Phi = 1.2$), $L_b$ first increases slightly then decreases and becomes negative. With added CF$_3$Br, the Markstein lengths are similar in
magnitude to the Markstein lengths for extremely rich (Φ ≈ 7) H₂-air flames [74], highlighting the strong sensitivity of the inhibited flame speeds to the stretch rate.

For C₃H₂F₃Br addition, (bottom frames of Fig. 18), the Markstein length is affected somewhat differently than with CF₃Br. In general, for C₃H₂F₃Br addition relative to CF₃Br addition, all of the curves in Fig. 18 are pushed down (for either CH₄- or C₃H₈-air flames); i.e. \( L_b \) increases less or decreases more with agent addition. Non-monotonic behavior for the \( L_b \), such as that shown in Fig. 18 for lean CH₄- and C₃H₈-air flames with added C₃H₂F₃Br, has also been observed for CH₄-air flames with added H₂ [75-77]; it was attributed to changes in the both the mixture Lewis number and overall activation energy as the concentration of H₂ increased [76].
The influence of inhibitors on the sensitivity of the flame response to stretch (as characterized by the Markstein length) can explain the non-ignition of some flames with higher values of the planar, un-stretched burning velocity $S^0_u$ than certain flames that successfully propagated. For spherically expanding flames with positive burned gas Markstein lengths, the burning velocity increases toward the planar 1-D burning velocity as the stretch rate decreases (i.e. as the flame radius increases). Hence, when $L_b$ is positive the flame propagation is slowest at small flame radii, and as $L_b$ gets larger, a critical flame radius must be reached for sustained propagation to occur [18, 78]. As detailed in the previous section, a well-established flame can form early on and then quickly extinguish because the supplied ignition energy is not sufficient to drive the flame to the critical radius. For example in Fig. 13, for the case of rich CH$_4$-air ($\Phi = 1.2$) with added CF$_3$Br at $X_a = 0.02$, partial flame propagation was observed (when applying the maximum available ignition energy). For this mixture, a flame propagated roughly 1.5 cm before extinction occurred. Apparently, the critical radius for these mixtures is larger than 1.5 cm, which is about a factor of 3 larger the critical radius determined for rich H$_2$-air flames ($\Phi = 5.1$ and $P = 101$ kPa) in ref. [18]. The same behavior was observed for lean ($\Phi = 0.8$) C$_3$H$_8$-air flames with added CF$_3$Br at $X_a = 0.02$. Both of these apparent anomalies can be explained by considering the effect of CF$_3$Br on $L_b$. As seen in Fig. 18 for the rich CH$_4$-air and lean C$_3$H$_8$-air flames with added CF$_3$Br, $L_b$ increases sharply as the concentration of CF$_3$Br increases; hence, the large positive value of $L_b$ makes the flames propagate faster at large radii. Excessive spark energy aids the flame propagation at small radii which is why initial flame propagation is observed; as the radius grows, the propagation speed increases, so that there is a critical flame radius required for the flame to self-propagate once the excess ignition energy is depleted.

4.8 Influence of agents on Markstein length and flame stability

The burned gas Markstein length not only shows how the propagation speed changes with the stretch rate, it is also a measure of the susceptibility of a flame to diffusional-thermal instability (i.e., flame transition to cellular structure) [73]. Kim et al. [79] added CF$_3$Br to H$_2$-air flames at equivalence ratios $\Phi = 0.8$, 1.0, and 1.8 and found that the flame stability decreased as the inhibitor concentration increased regardless of the fuel-air ratio, causing the flames to wrinkle and promoting transition from laminar to turbulent propagation. As the wrinkles grow, the surface area of the flame sheet increases which increases the mass burning rate. Thus, the reduced stability resulting from agent addition is undesirable and offsets the reduction in the mass burning rate that
occurs through chemical inhibition [79]. Currently, no data are available on how chemically active suppressants influence the stability of hydrocarbon-air flames, especially with added C$_3$H$_2$F$_3$Br.

If agent addition changes the Markstein length from positive to negative (or more negative) it makes the flame unstable and susceptible to flame wrinkling (a positive $L_b$ signifies a stable flame and vice versa). Referring to Fig. 18, adding CF$_3$Br or C$_3$H$_2$F$_3$Br can increase or decrease flame stability depending on the fuel, the initial equivalence ratio, and the agent concentration. CF$_3$Br addition promotes flame wrinkling for lean CH$_4$-air flames and rich C$_3$H$_8$-air flames; C$_3$H$_2$F$_3$Br addition has lesser effect for CH$_4$-air flames, but more strongly promotes wrinkling for rich C$_3$H$_8$-flames (or stoichiometric flames above $X_a = 0.005$). Thus, in contrast to what was observed in ref. [79] for H$_2$-air flames, the Markstein length, and hence flame stability, is not always reduced when inhibitor is added to hydrocarbon-air flames.

When an inhibitor significantly reduces flame stability ($L_b << 0$), laminar burning velocity may not be the only metric for ranking suppression effectiveness. The sign of $L_b$ suggests the expected flame dynamics for conditions beyond the small radii flames used to determine burning velocity in the present study. To illustrate this, the rate of pressure rise versus time (left frame) and the flame propagation speed versus stretch rate (right frame) are shown in Fig. 19 for rich ($\Phi = 1.2$) C$_3$H$_8$-air flames with 1 % C$_3$H$_2$F$_3$Br or 2 % CF$_3$Br. (Note that the stretched burning velocity data is extracted when the flame radii is small and the pressure is constant. The rate of pressure rise is extracted from the latter part of each test as the flame continues to propagate through the remaining chamber volume.) These mixtures (properties listed in Table 2) were chosen because they have similar un-stretched laminar burning velocities of 12.3 cm/s and 11.1 cm/s and similar adiabatic flame temperatures of 2002 K and 2144 K, but different Markstein lengths; the C$_3$H$_2$F$_3$Br-inhibited flame ($L_b = -4.15$ mm) is more unstable than the CF$_3$Br-inhibited flame ($L_b = 0.03$ mm). As seen in Fig. 19 (left frame), even though the burning velocities are similar (differing only by 1.2 cm/s), the peak rate of pressure rise $dP/dt_{\text{max}}$ is more than double for the C$_3$H$_2$F$_3$Br-inhibited mixture (164.7 bar/s compared to 73.4 bar/s), and the time of the onset of cellularity (determined from the video images, and illustrated in the figure by the black stars) occurs much earlier. Thus, the influence of the inhibitor on flame stability and response to stretch (described by the Markstein length) is significant and may influence the behavior of the suppressants in tests such as the FAA-ACT. Moreover, flammable mixtures containing new low-GWP refrigerants,
which are in many ways similar to the present hydrocarbon flames with added suppressant, may exhibit similar trends to those observed in the present work.

Table 2: Adiabatic flame temperature, un-stretched burning velocity, Markstein length, and peak rate of pressure rise for a rich C₃H₈-air flame inhibited by 1 % C₃H₂F₃Br and 2 % CF₃Br.

<table>
<thead>
<tr>
<th>Agent</th>
<th>C₃H₂F₃Br</th>
<th>CF₃Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xₐ</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Tₐd (K)</td>
<td>2002</td>
<td>2144</td>
</tr>
<tr>
<td>Sₜₐ° (cm/s)</td>
<td>12.34</td>
<td>11.11</td>
</tr>
<tr>
<td>Lₘ (mm)</td>
<td>-4.15</td>
<td>0.03</td>
</tr>
<tr>
<td>dP/dₜmax (bar/s)</td>
<td>164.7</td>
<td>73.4</td>
</tr>
</tbody>
</table>

Fig. 19: Rate of pressure rise versus time for combustion of rich C₃H₈-air (Φ=1.2) with 1 % C₃H₂F₃Br or 2 % CF₃Br added (the two mixtures have similar Sₜₐ° and Tₐd). The stars mark the instance when cellular flame structures were first observed in the videos.

5. CONCLUSIONS

Unexpected overpressures occurred in the FAA Aerosol Can Test when the fire suppressant C₃H₂F₃Br (2-BTP) was added. To aid in interpretation, previous researchers developed a kinetic model for inhibition by C₃H₂F₃Br and updated the model for CF₃Br. As a first step in model verification, burning velocity measurements and numerical simulations with detailed chemistry
were performed for CH$_4$-air and C$_3$H$_8$-air flames inhibited by these compounds. Comparison of the inhibited flame burning velocities highlighted differences in performance and the conditions for which each agent was most effective.

Experimentally measured spherically expanding flames provided the un-stretched burning velocity of premixed CH$_4$- and C$_3$H$_8$-air flames with addition of CF$_3$Br and C$_3$H$_2$F$_3$Br. For rich flames, C$_3$H$_2$F$_3$Br more effectively reduced the un-stretched burning velocity because, in addition to introducing halogenated radical scavengers, it shifts the overall equivalence ratio further away from stoichiometry (i.e. a fuel effect of the inhibitor). At stoichiometric conditions, the inhibitors caused a similar reduction (on a molar basis) in the burning velocity for both the CH$_4$- and C$_3$H$_8$-air flames. At lean conditions, CF$_3$Br was far more effective because C$_3$H$_2$F$_3$Br shifts the overall mixture toward stoichiometric proportions and increased the adiabatic flame temperature by about 200 K, whereas the calculated temperature remained nearly constant with added CF$_3$Br.

Experiments with CH$_4$- and C$_3$H$_8$-air flames at equivalence ratios of 0.6, 0.8, 1.0, and 1.2 with added CF$_3$Br or C$_3$H$_2$F$_3$Br at volume fractions up to $X_a = 0.04$ provided data for comparison with numerical models. Excellent agreement was observed for the CF$_3$Br-inhibited flames, highlighting the improved performance of the updated CF$_3$Br sub-model. Agreement was generally good for the C$_3$H$_2$F$_3$Br-inhibited flames at stoichiometric and rich conditions for both the CH$_4$- and C$_3$H$_8$-air mixtures. For lean conditions ($\Phi = 0.6$), predicted burning velocity was within 5 % to 25 % (which corresponds to a discrepancy of about 2 cm/s).

Both linear and non-linear extrapolation methods were used for determining the un-stretched laminar burning velocities $S_u^0$. The two approaches yielded values of $S_u^0$ very close to each other (i.e., within experimental error) for all conditions of the present work, except CF$_3$Br addition (at $X_a = 0.01$) to rich ($\Phi = 1.2$) CH$_4$-air flames or lean ($\Phi = 0.8$) C$_3$H$_8$-air flames (for which the linear value of $S_u^0$ was about 14 % and 11 % higher, respectively), and C$_3$H$_2$F$_3$Br addition (at $X_a = 0.01$) to rich ($\Phi = 1.2$) CH$_4$-air flames (for which the linear value of $S_u^0$ was about 40 % higher).

The experiments delineated the influence of inhibitor on the flame response to stretch in terms of the burned gas Markstein length $L_b$. The data show that $L_b$ is dependent on the inhibitor, fuel type, and initial equivalence ratio, with added CF$_3$Br or C$_3$H$_2$F$_3$Br increasing or decreasing $L_b$.
according to the conditions, sometimes non-monotonically. The influence of inhibitor on the flame response to stretch helped explain some conditions of non-ignition of mixtures with otherwise high enough values of $S_{u0}$. It would be worthwhile in future research to explore the influence of ignition energy and electrode gap on the flame propagation of the present mixtures. The results have significance with regard to halogenated hydrocarbon fire suppressants and new, mildly flammable refrigerants.

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