Intermediate Species Profiles in Low Pressure Premixed Flames Inhibited by Fluoromethanes

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We have investigated premixed 10 torr methane/oxygen flames containing CH₃F, CH₂F₂, CHF₃, and CF₄. Profiles of temperature and CH⁺ chemi-luminescence were acquired, and laser-induced fluorescence (LIF) was used to obtain profiles of the intermediate species H, OH, CH, CF, CHF, CF₂, and CF₂O. The fluoromethanes were added in amounts such that each flame had the same flux of fluorine atoms. In the flames containing CH₃F, CH₂F₂, and CHF₃, the methane flow was adjusted to give an equivalence ratio of 1.07 for all three inhibited flames. The experimental intermediate profiles were compared to predicted profiles calculated from a hydrofluorocarbon kinetic mechanism recently developed at NIST. No fluorinated intermediates were detectable in the CF₄ inhibited flame, indicating that this agent does not react significantly under the flame conditions studied. The temperature profiles, H atom profiles, and OH profiles for the other three fluoromethane inhibited flames are nearly identical, indicating that flames containing different fluorocarbon compounds, but identical proportions of fluorine atoms, have similar structures. The kinetic model correctly predicts the location of the reaction zone in the flames containing CH₂F₂ and CH₃F. In the CHF₃ flame, however, the location of the reaction zone is predicted to be too far above the burner surface, and concentrations of H and OH are too low. The discrepancy appears to be due to pressure dependence and third body efficiencies of the agent thermal decomposition. Furthermore, relative amounts of CF, CH, CF₂, and CHF in the different flames are not very well predicted. In general, partially fluorinated methyl and methylene radicals appear to have a greater than predicted propensity to lose hydrogen atoms rather than fluorine. We propose modifications to the fluorine mechanism to correct the discrepancies observed in the low pressure experiments, while simultaneously achieving good agreement with atmospheric pressure flame speed data in CH₄/air/CHF₃ flames, and, except in rich conditions (φ > 1.25) CH₄/air/CH₂F₂ flames. © 1999 by The Combustion Institute

INTRODUCTION

The global ban on production of stratospheric ozone-depleting halons (bromine-containing fluorocarbons) has necessitated a search for alternative fire suppressants [1]. Hydrofluorocarbons (HFCs) are currently used in many instances where fire protection was previously provided by halons [2]. Since hydrofluorocarbons lack bromine, primarily responsible for both the fire suppression [3] and ozone depletion properties [1] of halons, HFCs must be employed in larger quantities to provide protection for an equivalent fire threat [4, 5]. Owing to space and weight limitations in many applications, HFC-based fire protection systems often must operate with smaller safety factors than halon systems. Safe and efficient use of HFCs thus requires greater understanding of their flame chemistry than was needed for the bromine based fire suppressants.

Recently, a chemical kinetic mechanism has been developed at the National Institute of Standards and Technology (NIST) to describe the relevant flame chemistry of C₁ and C₂ HFCs [6–9]. Studies of HFC kinetics are relatively sparse in comparison to the analogous hydrocarbon reactions, especially in view of the large (~600 reactions involving fluorine species) reaction set. Therefore, kinetic mechanism development has had to rely extensively on computational modeling of reaction dynamics, and on analogies with equivalent hydrocarbon reactions [7]. The mechanism has been used to predict the behavior of hydrofluorocarbon inhibited flames in a variety of laboratory scale experiments [7, 10–13] with the eventual goal of modeling suppression of larger scale fires.

Comparison of model predictions with experimental data is necessary to validate and refine the current understanding of HFC combustion chemistry. To date, the effect of HFCs on
flames has been investigated primarily by measuring global parameters such as burning velocity, HF and CF$_2$O production, extinction strain rate, and flame temperature [11–18]. The detailed kinetics of hydrofluorocarbons in combustion environments, by contrast, has not been subject to extensive experimental investigation. There have been two studies that have reported species profiles in fluorocarbon inhibited flames by mass spectrometry [19, 20]. Vandooren et al. [19] compared several species in a CO/H$_2$/O$_2$/Ar flame inhibited by CHF$_3$ to those in an inhibited flame and one inhibited by CF$_3$Br. The profiles of the stable hydrocarbon species as well as the radical species H, O, and OH, and the fluorinated species CHF$_3$, HF, and CF$_2$O were reported. Kinetic modeling was not performed; however, the authors concluded that the reactions

\[
\begin{align*}
\text{CHF}_3 + H &\rightarrow \text{CF}_3 + H_2 \quad (R1) \\
\text{CF}_3 + \text{OH} &\rightarrow \text{CF}_2\text{O} + \text{HF} \quad (R2)
\end{align*}
\]

are primarily responsible for the reduction in concentration of the radicals H, O, and OH. It was also observed that CF$_2$O was a relatively stable product under the flame conditions used. Since the fluorine/hydrogen ratio was 1.5, the authors concluded that the low concentration of atomic hydrogen present in their flame was responsible for the persistence of carbonyl fluoride.

Sanogo et al. [20] studied a 31.5 torr (4.2 kPa) stoichiometric CH$_4$/O$_2$/Ar flame inhibited with 1% C$_2$F$_6$. Profiles were recorded for several fluorinated species, including the radical species CF$_3$ and CF$_2$. Kinetic modeling was performed, using a different reaction set than the NIST mechanism. Agreement between the model and experiment was good for most species, but poor for CF$_2$ and CF$_3$, possibly due to the necessity of using a low electron impact energy in the mass spectrometer to avoid ion fragmentation [20].

Previous modeling studies have predicted the reaction pathways of fluoromethanes in low pressure flames [7]. Fluoromethanes are thought to react in flames through hydrogen atom abstraction by either OH radical or H atom attack. Since CF$_4$ does not have this pathway available to it, it is nearly inert in most flame environments [7]. The fluoromethyl radicals CF$_3$, CHF$_2$, and CH$_2$F produced, respectively, from CHF$_3$, CH$_2$F$_2$, and CH$_3$F, can react with H atoms, causing removal of either an H or an F atom to produce the methylene radicals CH$_2$, CHF, and CF$_2$.

Alternately, the CHF$_3$ radicals can react with O or OH to form the carbonyl compounds CH$_2$O, CHFO, and CF$_2$O. CF$_2$O, carbonyl fluoride, is of particular interest because it is a relatively stable compound and is the only fluorine product besides HF likely to exit the combustion zone [7]. The kinetics of the CF$_2$O removal reactions assumed by the NIST mechanism, by reactions with H atoms and H$_2$O [5], have not been thoroughly characterized experimentally.

Here we present experimental data on intermediate species profiles in 10 torr methane/oxygen flames containing the series of fluoromethanes. It should be noted in making comparisons between experimental data and modeling predictions that the model was constructed primarily for use at atmospheric pressure [8], and most fluorocarbon association reactions included in the NIST mechanism are assumed to be in the high pressure limit. Intermediate species profiles in premixed flames are one of the best ways of verifying proposed kinetic pathways in a chemical mechanism but are only practical at reduced pressures. The situation is thus not ideal in that these experimental tests of the mechanism can only be performed outside its stated range of applicability. Nevertheless, many important features of the kinetic pathways (for instance, branching ratios of bimolecular reactions) should not be pressure dependent.

Because much of the development of the HFC kinetic mechanism has relied on analogies with the much better understood hydrocarbon flame chemistry, comparisons between molecules with differing degrees of fluorine substitution are a good way to investigate the fluorine kinetics. We therefore study a complete series of fluoromethanes. CHF$_3$ and CF$_4$ are used as fire suppressants, while CH$_2$F$_2$ is being considered as a replacement for chlorofluorocarbons in refrigeration applications [21]. CF$_4$ is thought to be inert in most flame environments because its only possible reaction pathway is the removal of a fluorine atom either by thermal dissociation
The CHF, CHF, and CHF flames contain equal amounts of H, F, C, and O. The mass flow of CF was chosen such that the F flux was equivalent to the other fluorine containing flames. All flames were operated at 10 ± 0.05 torr. The uncertainty of the flows is ±1% of the flow.


CF only fluorine product considered in equilibrium calculation.

Equilibrium distribution of fluorine products (predominantly HF).

<table>
<thead>
<tr>
<th>TABLE 1</th>
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<tbody>
<tr>
<td>Flame conditions used in experiment*</td>
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<tr>
<td>---------------------------------------------</td>
</tr>
<tr>
<td>Flow rates (cm³/min @ 0°C)</td>
</tr>
<tr>
<td>Agent</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>none</td>
</tr>
<tr>
<td>CH₃F</td>
</tr>
<tr>
<td>CH₂F₂</td>
</tr>
<tr>
<td>CHF₃</td>
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<tr>
<td>CF₄</td>
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</table>

* The CHF, CHF, and CHF flames contain equal amounts of H, F, C, and O. The mass flow of CF was chosen such that the F flux was equivalent to the other fluorine containing flames. All flames were operated at 10 ± 0.05 torr. The uncertainty of the flows is ±1% of the flow.


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or by abstraction, both of which have exceedingly slow kinetics [22]. Comparison of the CF inhibited flame with other fluoromethane inhibited flames highlights the changes to the flame structure resulting from chemical activity as opposed to physical effects (oxygen dilution and increased heat capacity) of the agent [14].

The fluorinated intermediates CF, CF, CHF, and CF were monitored by laser-induced fluorescence (LIF), as were the species H, OH, and CH. The profiles and relative concentrations of these intermediates can be used to infer the reaction pathways followed by the different fluorocarbons, along with their effect on the overall structure of the methane flame. Comparison of experimental radical profiles and kinetic modeling calculations in premixed flames can provide a more definitive indication of areas of kinetic mechanisms which need revision than can global parameters such as flame speed or extinction conditions.

EXPERIMENTAL

Flame Conditions

Table 1 shows the gas flow conditions of the five flames studied in this experiment. The following gases were used as received from the suppliers: CH₃, Air Products, 99.99%; O₂, MG Industries, 99.9%; Ar, MG Industries, 99.9%; CH₃, PCR, 98%; CH₂F₂, PCR, 98%; CHF₃, Dupont, 99.9%; and CF₄, Air Products, 99.97%. The uninhibited flame was a stoichiometric methane/oxygen flame without any diluent gas. The four other flames each contained one of the compounds CH₃, CH₂F₂, CHF₃, and CF₄. The mole fraction of CHF₃ added to the methane/oxygen mixture was about one third of the amount needed to blow the flame off the burner under the flow and pressure conditions used in our experiment. The relative amounts of the fluoromethanes were chosen such that all four inhibited flames contained equal numbers of fluorine atoms. The flow rates of methane and oxygen in the CHF₃ and CF₄ inhibited flames were the same as in the uninhibited flame. For the flames containing CH₃ and CH₂F₂, the methane flow rate was reduced to maintain the same equivalence ratio and concentrations of fluorine, carbon, and hydrogen as the flame containing CHF₃. These three flames (CH₃, CH₂F₂, and CHF₃) are predicted to produce nearly identical concentrations of all final products, and the heat releases are nearly the same. The equivalence ratios for all the flames with added agent were slightly fuel rich (φ = 1.07) with the exception of the flame containing CF₄, which had an equivalence ratio of unity.

The premixed flames were stabilized on a water-cooled burner (McKenna Products) enclosed in a vacuum chamber [23]. Flows were controlled using mass flow controllers (Sierra Instruments), with an accuracy of 1% of full scale. The premixed fuel, oxygen, and fluorocarbons flowed through a 6 cm diameter sintered
Fluorescence was collected at right angles to the laser beam using a two lens collection system, which imaged a 0.25-1 cm section of the probe volume near the center of the burner. Filters were used to isolate the spectral region of interest, and the fluorescence was detected by a photomultiplier (Hamamatsu R1477). Resolved emission from the inhibited flames was characterized by replacing the emission filters with a 0.5 m monochromator (Jarrell-Ash).

The fluorescence signal was analyzed by a boxcar integrator, with a short gate (25 ns) set to the peak of the fluorescence decay. Where laser scatter interfered with the fluorescence signal, the boxcar gate was delayed some 30 ns from the peak PMT signal. Collision-induced quenching is minimized by these experimental protocols but is not removed entirely. Since the primary objective in the present study is to make relative measurements of species mole fraction between different inhibited flames, quenching only affects the overall result if the quenching environment is appreciably different between the various flames, or changes dramatically with location in a particular flame. The quenching environment should be similar for the flames studied, since they have similar concentrations of most major flame species. The quenching rates of the fluorinated radical species monitored in this study have not been extensively investigated. CF, CF₂, and CF₃O all have fluorescence lifetimes (radiative + predissociation) of 60 ns or less, so quenching should have little effect on the fluorescence signals of these species.

Changes in the excitation energy were monitored by UV-VIS spectrophotometry and measured by attaining spectral resolution with optical density using a high intensity light source.

Flame temperature T(x) was measured by a point pyrometer.
SPECIES PROFILES IN FLUOROMETHANE-INHIBITED FLAMES

The chemical structures of the inhibited flames were modeled using the Sandia PREMIX and related codes [26-28]. The kinetic mechanism and thermodynamic database used for the H/C/O chemistry for one-carbon and two-carbon species was the Gas Research Institute GRI-Mech 2.11 [29], with nitrogen chemistry deleted. The NIST HFC mechanism is used for the thermodynamics and reactions of the fluorinated species [6-9]. The NIST mechanism has received some updates from that given in ref. [8]; the changes are listed in Table 3. This mechanism is referred to below as the base mechanism. Further adjustments to the mechanism were performed as discussed below.

The NIST mechanism includes nearly all one- and two-carbon species containing hydrogen, fluorine, and oxygen. The total reaction set includes 81 species and 759 reactions. Calculations of the experimental burner-stabilized flames were performed using the experimental temperature profiles as input. Multicomponent viscosities were used for species transport, and thermal effects on diffusivities were considered for the species H and Hz. The computational domain extended from the burner surface to 5 cm. Catalytic recombination of atomic hydrogen on the burner surface was not considered in the calculation. In both the experimental and calculated profiles, the H atom concentration is greatly reduced near the burner in the inhibited flames relative to the uninhibited methane/oxygen flame. Therefore the influence of burner surface chemistry on the structure of the inhibited flames will be less than on the uninhibited flame, where it has been found to have a rather minor influence [30]. Mesh refinement tolerances (local/global variation) for the species concentrations were set to 0.1 for the species concentrations (the GRAD parameter in the PREMIX code) and to 0.25 for the concentration gradients (CURV parameter). The final grids for the uninhibited and CF4 inhibited flames contained approximately 80 mesh points, while the solutions for the other three inhibited flames contained approximately 110 mesh points.

RESULTS

Temperature Profiles

Figure 1 shows the measured temperatures and the fitted functions. The flame containing CF4...
TABLE 3
Changes in Base Fluorine Mechanism From That Given in [8]

<table>
<thead>
<tr>
<th>Reaction added:</th>
<th>Arrhenius parameters $k = A T^a \exp(-E_a/RT)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A$ (cm, mol, s)</td>
</tr>
<tr>
<td>1. CH3OH + CH2F = CH3O + CH3F</td>
<td>1.44E+01</td>
</tr>
<tr>
<td>2. CH3OH + CHF2 = CH3O + CH2F2</td>
<td>1.44E+01</td>
</tr>
<tr>
<td>3. CH3OH + CF3 = CH3O + CHF3</td>
<td>1.44E+01</td>
</tr>
<tr>
<td>4. CH3OH + CH2F = CH2OH + CH3F</td>
<td>3.20E+01</td>
</tr>
<tr>
<td>5. CH3OH + CHF2 = CH2OH + CH2F2</td>
<td>3.20E+01</td>
</tr>
<tr>
<td>6. CH3OH + CF3 = CH2OH + CHF3</td>
<td>3.20E+01</td>
</tr>
<tr>
<td>7. CF + CH2O = &gt;CHF + HCO</td>
<td>1.00E+13</td>
</tr>
<tr>
<td>8. CF + HCO = &gt;CHF + CO</td>
<td>1.00E+13</td>
</tr>
<tr>
<td>9. CF:O + CF:O = CO + CF2:O</td>
<td>2.23E+13</td>
</tr>
<tr>
<td>10. CH3 - CHF + CH2O = CH3 - CHF2 + HCO</td>
<td>5.50E+03</td>
</tr>
<tr>
<td>11. CH3 - CF2 + CH2O = CH3 - CHF2 + HCO</td>
<td>5.50E+03</td>
</tr>
<tr>
<td>12. CH2F - CH2 + CH2O = CH3 - CHF2 + HCO</td>
<td>5.50E+03</td>
</tr>
<tr>
<td>13. CH2F - CF2 + CH2O = CH2F - CHF2 + HCO</td>
<td>5.50E+03</td>
</tr>
<tr>
<td>14. CH2F - CF2 + CH2O = CH2F - CHF2 + HCO</td>
<td>5.50E+03</td>
</tr>
<tr>
<td>15. CH2F2 - CHF + CH2O = CH2F2 - CHF2 + HCO</td>
<td>5.50E+03</td>
</tr>
<tr>
<td>16. CH2F2 - CF2 + CH2O = CH2F2 - CHF2 + HCO</td>
<td>5.50E+03</td>
</tr>
<tr>
<td>17. CF3 - CH2 + CH2O = CH3 - CF3 + HCO</td>
<td>5.50E+03</td>
</tr>
<tr>
<td>18. CF3 - CF2 + CH2O = CH3 - CF3 + HCO</td>
<td>5.50E+03</td>
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<tr>
<td>19. CF3 - CF2 + CH2O = CHF2 - CF3 + HCO</td>
<td>5.50E+03</td>
</tr>
<tr>
<td>20. CF3 - CF2 + CH2O = CHF2 - CF3 + HCO</td>
<td>5.50E+03</td>
</tr>
<tr>
<td>21. HCO + F = CHF + CO</td>
<td>3.00E+13</td>
</tr>
<tr>
<td>22. CFCO + F = CF2 + CO</td>
<td>3.00E+13</td>
</tr>
<tr>
<td>23. C2H3 + F = CH2F + HF</td>
<td>2.00E+13</td>
</tr>
<tr>
<td>24. CHF:CF[Z] + F = CHF + CF2</td>
<td>1.00E+13</td>
</tr>
<tr>
<td>25. CF2:CF + F = CF2 + CF2</td>
<td>2.00E+13</td>
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</tbody>
</table>

Reaction numbers below refer to [8].


New parameters:

- MA32. HCO + CH2F = CH2CO + HF
- MA33. HCO + CF3 = CF2CO + HF
- MA34. HCO + CF3 = CF2CO + HF
- PP10. CF3O + HCO = >CF2:O + HF + CO
- NN20. CHF + O = CO + HF
- NN42. CF + OH = CO + HF
- GG50. CH3 - CF2 + OH = CH2:CF2 + H2O

had nearly the same temperature profile as the uninhibited flame; the flames containing the other fluoromethanes all had higher peak temperatures (attained slightly further above the burner surface) than the uninhibited flame, with the monoo- and di-fluoromethane having slightly higher peak temperatures than the trifluoromethane flame. The temperature rise in the flames containing CF4, CHF3, and CH2F2 appeared to be pushed slightly (≈0.5 mm) further away from the burner surface, although the size of this effect was of the same magnitude as the uncertainty in the burner position (0.2 mm reproducibility uncertainty and 0.5 mm beam diameter).

Flame Emission Profiles

The uninhibited flame becomes noticeably brighter upon addition of CHF3, CH2F2, or CH3F. In the uninhibited flame, all of the structured emission in the 300-600 nm spectral region is due to OH*, CH*, and C2* [31]. No
additional spectral features appear upon addition of CHF₃, but the existing band systems increase in intensity by a factor of 1.25 in the case of OH⁺, and by a factor of approximately 3–4 for both CH⁺ and C₂⁺. The bottom panel of Fig. 2 shows CH⁺ emission profiles at 430 nm for the uninhibited flame, the flames inhibited by the fluoromethanes, and an uninhibited flame with an equivalence ratio of 1.1, slightly greater than that of the inhibited flames. The flames containing CH₃F, CH₂F₂, and CHF₃ are all more than twice as luminous as the φ = 1.1 flame, indicating that increased emission in the inhibited flames is not primarily an effect of richer stoichiometry. The luminous zone in these three flames moves approximately 2 mm further from the burner than its location in the uninhibited flame. The flame containing CH₃F produced the most CH⁺ luminescence, followed by the CH₂F₂ flame, and then the CHF₃ flame. CF₄, in contrast, produces little change in the CH⁺ emission profile.

Recently, the reaction
\[ \text{C}_2\text{H} + \text{O} \leftrightarrow \text{CH}^+ + \text{CO} \]  (R3)
has been identified as the primary source of CH⁺ chemiluminescence in hydrocarbon flames [32]. Assuming a similar quenching environment for the different flames, the CH⁺ emission profile can be expressed as
\[ I_{\text{CH}^+} = k_{\text{R3}}(T)[\text{C}_2\text{H}][\text{O}]. \]  (2)

The overall reaction C₂H + O → products is written in the GRI mechanism as being temperature independent. The rate of the CH⁺ channel has only been measured at room temperature [32]. If we assume that the branching ratio is temperature independent, the CH⁺ emission intensity is then given by the product of the C₂H and O atom concentration profiles. The product of the calculated profiles for the various flame conditions is plotted in the top panel of Fig. 2.
The predicted O atom concentrations in the various flames vary by less than a factor of two, so the CH* emission intensity will be governed chiefly by the C2H profile. The formation of C2 species in the flames containing fluoromethanes is predicted to be dominated by methyl + fluoromethyl recombination reactions:

\[ \text{CH}_3 + \text{CH}_2\text{F}_3 \rightarrow \text{CH}_2 = \text{CH}_2 \text{F}_2 + \text{HF}. \]

The CH* emission profiles give an indication (albeit an indirect one) of the importance of the C2 chemistry in the inhibited flames. Evidently the recombination of fluorinated methyl radicals with CH3 is more facile than the recombination of two methyl radicals.

**Intermediate Species Profiles**

**H**

Calculated and measured H profiles are shown in Fig. 3. Hydrogen atoms were detected by a two-step excitation process involving a two photon absorption at 243 nm (150 μJ focused with a 35 cm focal length lens) from the 1s to 2s state, followed by a single photon excitation at 486 nm (5-10 μJ, unfocused) to the 4p state [33, 34]. Fluorescence was detected at 486 nm. The intensity of the 486 nm beam was adjusted to be near the saturation intensity, while the LIF signal exhibited a quadratic dependence on the 243 nm laser energy. Interference presumably from CF3 was noted in the flames inhibited by CH2F2 and CHF3; the interference signal depended only on the presence of the 243 nm light. There was also a small amount of laser scatter at 486 nm. To correct for these complications, the fluorescence signal was recorded with each of the two beams blocked, and these profiles were subtracted off the profile recorded with both beams present.

The peak H mole fractions in all the flames are nearly identical, although the CHF3, CH2F2, and CH3F inhibited flames have higher peak temperatures, which would normally tend to increase the radical's mole fraction. The position of the H concentration rise in the CHF3, CH2F2, and CH3F inhibited flames is moved further away from the burner.

**OH**

Calculated and measured OH profiles are shown in Fig. 4. LIF profiles of the hydroxyl radical were recorded by exciting the R1(8) line of the A-X (1,0) band. Fluorescence was detected both on the (1,1) and (0,0) bands [35]. Typical laser energies were 30 μJ for recording profiles. For temperature measurements, the probe energy was attenuated to 2 μJ in an unfocused beam of approximately 0.01 cm2 cross section to avoid saturation of the transition.

The OH profiles have many features in common with the H atom profiles, which is to be expected given the fast equilibrium between the two species [36]. As with the H atoms, the OH profiles are almost identical for the uninhibited and the CF4 inhibited flames. The peak OH mole fractions of the CHF3, CH2F2, and CH3F inhibited flames were similar to that of the uninhibited.
Fig. 4. Calculated (top) and measured (bottom) OH profiles. Predictions using the revised mechanism are indicated by solid lines, the prediction using the base mechanism for the CHF₃ flame is shown in dashed lines. Predictions for the other inhibited flames using the base mechanism were similar to those using the modified mechanism.

The profiles of ground state CH show much less sensitivity to the addition of the agents than do the profiles of CH⁺ emission. The peak CH mole fraction is increased in all of the inhibited flames; the effect is greatest in the flame inhibited by methyl fluoride, in which the peak CH mole fraction increases by some 70%. The CH mole fraction profile is slightly increased (by about 10%) in the flame inhibited by CF₄.

CF₂

Calculated and measured CF₂ profiles are shown in Fig. 6. The CF₂ radical was detected by exciting at a wavelength of 250 nm, roughly in the middle of the A-X transition, which at room temperature extends from 270 to 220 nm [25]. Typical pulse energies were 60 μJ, unfocused. Fluorescence was collected at 334 nm, using a 20 nm bandpass filter. The fluorescence signal was extremely strong, and the light had to be attenuated so that the PMT could operate in a region of linear response.

The flame excitation spectrum of CF₂ is essentially a continuum due to substantial populations in numerous excited ro-vibrational levels at combustion temperatures. Since the rotational transition(s) probed are unknown, we
have corrected the LIF profiles only for density variations in the flame. The lack of distinct spectral features makes it difficult to prove that CF₂ is indeed the source of the LIF signal. The observed fluorescence decay time of ~60 ns, however, matches the reported value for CF₂. Also, the signal is present in the flames containing CHF₃ and CH₂F₂, but not CH₃F, strongly suggesting that the source must have two fluorine atoms. The intense fluorescence from CF₂ interferes with the detection of other species such as CF, OH, H, and CF₂O. The structureless interference due to CF₂ may be easily subtracted off from profiles of OH, CF, and H atoms, which have well structured spectra. For larger molecules such as CF₂O, interference from CF₂ inherently limits the detection sensitivity.

CF₂ is slightly more abundant in the CHF₃ flame than in the CH₂F₂ flame. CF₂ appears later in the CHF₃ flame than in the CH₂F₂ flame, indicating that the reaction pathway CHF₃ \rightarrow CF₃ \rightarrow CF₂ occurs more slowly than the analogous pathway CH₂F₂ \rightarrow CHF₂ \rightarrow CF₂.

The CF₂ concentrations in the CH₃F and CH₂F₂ inhibited flames are less than 1% that of the CHF₃ flame. No CF₂ signal was observed in the CF₄ inhibited flame even when the CF₄ flow was quadrupled.

### CHF

Calculated and measured profiles of CHF are shown in Fig. 7. CHF was excited on the most intense bandhead of the (0,3,0)-(0,0,0) band of the A-X transition near 492 nm [25, 38]. CHF represents an intermediate case between the strongly fluorescent CF₂ molecule, and CH₂, which can only be detected in flames with extreme difficulty [39]. We chose the (0,3,0)-(0,0,0) band to attempt to detect CHF because it has a shorter radiative lifetime than the bands...
at longer wavelengths and fluoresces in a region relatively free from interference [38]. A significant fluorescence signal from CHF is observed in the flames containing CH₃F and CH₂F₂ but not CHF₃ or CF₄. Since CHF₃ is thought to react predominantly by abstraction of the hydrogen atom, the observed pattern is consistent with the assignment of CHF as the source of the LIF signal and also the model's prediction of the reaction pathways of the fluoromethanes in flames.

A rotational analysis has not been carried out for this band, making it difficult to convert the LIF profiles into mole fractions. Unlike the CF₂ spectrum, the CHF spectrum displays appreciable structure, so temperature corrections to the spectrum are probably more significant. We have estimated the temperature influence on the LIF signal by assuming a ground state rotational energy of 300 cm⁻¹. The rotational energy of the spectral feature used for monitoring is unknown but is probably fairly low since room temperature spectra of CHF also display prominent band heads. The major influence on the temperature correction is the rapid increase in the molecular partition function due to population of higher rotational and vibrational states. The converted profiles are shown in the bottom panel of Fig. 7. The exact shape and peak location is only approximate due to the large and uncertain temperature correction. Furthermore, in the luminous zones of the flames (>8 mm above the burner), there was some saturation of the photomultiplier due to background luminescence, resulting in a baseline drift. Although the locations of the calculated peak CHF concentrations disagree by about 3 mm with the experimental values, this is not necessarily significant in light of the uncertainties in the data analysis. The data does indicate that CHF peaks slightly earlier and at a ≈30% lower mole fraction in the CH₃F flame than in the CH₂F₂ flame.

**CF**

Calculated and measured CF profiles are shown in Fig. 8. CF was excited on the overlapping resonance lines Q₂(21.5), P₁(26.5), and Q₁(19.5) of the A-X (1,0) band at 223.299 nm [40]. Fluorescence was detected on the (1,4) and (1,5) bands [41] using a 15 nm bandpass filter centered at 255 nm. Typical pulse energies were 200 µJ in an unfocused beam. Since CF is one of the few fluorine species which has a well-defined spectrum at flame temperatures, interference from CF₂ was corrected for by tuning the laser just off the CF line and subtracting this background signal from the profiles. The fluorescence lifetime was approximately 20 ns, consistent with previous determinations [41]. There was essentially no scattered light transmitted by the filter, so the boxcar gate was set to the peak of the laser pulse. CF was produced in detectable amounts from all the agents except for CF₄.

**CF₂O**

Carbonyl fluoride is detectable by LIF but has a rather weak signal and a broad featureless spectrum at flame temperatures. We attempted to record profiles of CF₂O in the inhibited flames but were unsuccessful due to very weak signals,
Fig. 9. LIF Profiles of CF₂O. A profile of CF₂O was obtained from a C₂F₄/O₂ flame [25, 42]. The signal obtained from fluoromethane inhibited CH₄/O₂ flames is many times weaker and may be complicated due to interference from CF₂ and vibrationally excited O₂.

as well as interference from other species, including CF₂ and vibrationally excited O₂. We were, however, able to set an upper bound on the amount of carbonyl fluoride which could be present in the inhibited flames, based on comparison with the C₂F₄/O₂ flame where CF₂O is a stable product and is produced in abundance [42]. Figure 9 shows profiles recorded at an excitation wavelength of 211.03 nm in the HFC inhibited CH₄/O₂ flames, as well as in a 20 torr C₂F₄/O₂ flame identical to the 35% fuel case of Douglass et al. [42]. The signal in the C₂F₄ flame is primarily due to CF₂O, especially in the region above 1.5 cm. Time-resolved fluorescence decays can distinguish fluorescence contributions from CF₂ and oxygen observed closer to the burner; the lifetime of CF₂ is 60 ns, the lifetime of O₂ is less than 15 ns (limited by the laser pulse width), while that of CF₂O is 30 ns [25].

The signal level in the inhibited methane flames is many times weaker than that of the C₂F₄/O₂ flame. In the C₂F₄/O₂ flame studied for comparison, the partial pressure of CF₂O at 20 torr is predicted to be 6 torr in the post-flame zone [42]. The LIF signal is at least 80 times weaker in the post-flame zone (x = 3.0 cm) of the inhibited methane/oxygen flames under the same excitation and detection conditions. This indicates that CF₂O has a mole fraction of less than 0.01 in the inhibited methane/oxygen flames; less than 10% of the F atoms in the flames studied exit the reaction zone as CF₂O. This upper bound to the CF₂O mole fraction is consistent with the prediction of the chemical kinetic mechanism for these flames. Evidently interferant species contribute to the fluorescence as an appreciable LIF signal is observed in the reaction zone in the uninhibited as well as the inhibited flames. It is not clear how much of the fluorescence is due to CF₂O.

Analysis and Mechanism Refinement

Calculations using the base mechanism are shown in dashed lines in Figs. 3–8. For the CHF₃ flame the predicted location of the reaction zone (as indicated by any of the intermediate species monitored here) is several mm too far from the burner. Furthermore, the relative concentrations of the intermediate species for the different agents are not always well predicted. The concentrations of the fluorinated intermediates CF and CF₂ are overpredicted in the trifluoromethane flame relative to the flames containing the other agents. CHF is underpredicted in the CH₃F flame relative to the CH₂F₂ flame. The CH mole fraction is overpredicted in the CH₂F₂ flame compared to all the other flames. CH⁺ emission based on the product of the C₂H and O atom profiles is overpredicted in the CH₃F and CH₂F₂ flames.

To remedy these deficiencies, we carried out a sensitivity and reaction path analysis and adjusted selected rates of reactions involving fluorinated species in an iterative process. Our goal was to improve predictions of our low pressure data, while simultaneously achieving good agreement with published data on atmospheric pressure flame speeds for methane/air flames containing CHF₃ and CH₂F₂. In addition to constructing a better validated model, we also hoped to identify individual reactions which may require further experimental or theoretical investigation.

Recently, Saso et al. [12] have recommended adjustments to the reactions of CHF₃ and FCO with H, as well as FCO thermal decomposition,
We have added falloff behavior to all other decomposition reactions, which, according to the base mechanism, were predicted to be important for our conditions. The reactions $\text{CF}_2 \leftrightarrow \text{CF} + \text{F}$ and $\text{CF}_2 \leftrightarrow \text{CF} + \text{F}$ were converted to bimolecular rates. For $\text{CF}_4$, the decomposition...
reaction, along with F atom abstraction by H, is the only possible destruction mechanism. Sensitivity analysis showed that the CF$_2$ thermal decomposition reaction was predicted to have a significant influence on the propagation speed of the trifluoromethane flame, at least when it was written as being unimolecular. After being converted to a bimolecular rate, the influence of this reaction was greatly reduced. Also, the decomposition reactions of fluoroethylenes to eliminate HF were predicted to dominate destruction of CF$_2$=CH$_2$ and CHF=CH$_2$, which are formed in the CHF$_3$ and CH$_2$F$_2$ flames, respectively, by the reactions:

$$\text{CF}_3 + \text{CH}_3 \rightarrow \text{CH}_2=\text{CH}_2 + \text{HF}, \quad \text{(R6)}$$

$$\text{CHF}_2 + \text{CH}_3 \rightarrow \text{CHF}=\text{CH}_2 + \text{HF}. \quad \text{(R7)}$$

Reactions (R6) and (R7) are predicted to be the dominant route to formation of C$_2$ species under our conditions. The thermal decomposition of the resulting fluoroethylenes has only been investigated above 4 atmospheres, where it appears to be in the high pressure limit [45, 46]. We have added falloff behavior to these reactions, assuming that the transition between high pressure and falloff occurs somewhere in the vicinity of atmospheric pressure.

Another issue is the third body efficiencies of flame species for these decomposition reactions. The NIST mechanism includes no third body efficiencies for the CHF$_3$ decomposition reaction; all the shock tube studies on CH$_3$F and CHF$_3$ decomposition [43, 44] were performed in argon. We have assumed third body efficiencies for these reactions equal for most species to those given in the GRI mechanism for methane dissociation, along with efficiencies of 2 for HF, 9 for water, and 6 for the fluoromethanes. The low pressure A factors in the decomposition reactions have been divided by 0.7 (the relative third body efficiency used in GRI-mech for Ar for most decomposition reactions). The net result is that the overall third body efficiency in the flame reaction zones is increased by a factor of six relative to argon. In methane/air flames, the effect is much less significant since N$_2$, which by definition is assigned a relative third body efficiency of unity, has a mole fraction of approximately 70% throughout the flame.

H$_2$ vs. HF Elimination in Chemically Activated Decompositions

Reaction pathway analysis indicates that the greatly overpredicted peak CH mole fraction in the CH$_2$F$_2$ flame is due to the reaction

$$\text{CHF} + \text{H} \leftrightarrow \text{CH} + \text{HF}. \quad \Delta H_f = -21 \text{ kJ} \quad \text{(R8)}$$

The kinetic parameters for this reaction in the HFC mechanism are based on the study of Tsai and McFadden [47], which measured the total disappearance rate of CHF. The alternate channel,

$$\text{CHF} + \text{H} \leftrightarrow \text{CF} + \text{H}_2. \quad \Delta H_f = -92 \text{ kJ} \quad \text{(R9)}$$

is lower in energy, but was not included in the HFC mechanism. Tsai and McFadden detected both CF and CH products but were unable to determine a branching ratio due to secondary reactions and uncertainties in detection efficiency. The lack of a significant increase in the CH concentration in the difluoromethane flame relative to the other inhibited flames indicates that the CF channel is the dominant one. We have put in a branching ratio of approximately 70% for Reaction (R9) while keeping the total rate of reactions (R8) and (R9) fixed to the measured value.

The reaction

$$\text{HF} + \text{CH} \rightarrow \text{CF} + \text{H}_2, \quad \text{(R10)}$$

which according to the base mechanism was predicted to be quite important, is essentially equivalent to a redistribution of the branching ratio between reactions (R8) and (R9). The rate in the base mechanism was set to the upper limit suggested by RRKM calculations. Adding reaction (R9) to the mechanism allowed this rate to be lowered by one third to better match the peak CH concentrations in the flames inhibited by CH$_3$F, CH$_2$F$_2$, and CHF$_3$ relative to the uninhibited flame.

The product channels of the fluoromethyl reactions with atomic hydrogen

$$\text{CH}_3\text{F}_{3-i} + \text{H} \rightarrow \text{CH}_3\text{F}_{2-i} + \text{HF} \quad \text{(R11)}$$

$$\text{CH}_3\text{F}_{2-i} + \text{H} \rightarrow \text{CH}_{i-1}\text{F}_{3-i} + \text{H}_2 \quad \text{(R12)}$$
is another area of the mechanism to which the experimental data suggests some modifications. The base mechanism predicts that the HF channel overwhelmingly dominates (>96% branching ratio for both mono- and di-fluoromethyl radicals), largely on the basis of a lower energy barrier assuming the reaction proceeds through a chemically activated fluoromethane intermediate. The H2 channel could also proceed via a direct abstraction as well as by elimination from a complex, whereas abstraction of a fluorine atom would occur at an extremely slow rate.

In the methyl fluoride flame, the base mechanism predicts that CH2F radicals are nearly all converted to CH2 by the reaction by atomic hydrogen. Very little CHF is predicted to be formed in this flame relative to the CH2F2 flame. Formation of CF in the CH2F flame is predicted to occur almost exclusively via the CH + HF reaction. In the difluoromethane flame, formation of CF2 is predicted to occur primarily through the disproportionation reaction with methyl radicals:

\[
\text{CHF}_2 + \text{CH}_3 \rightarrow \text{CF}_2 + \text{CH}_4. \quad \text{(R13)}
\]

This reaction causes a slight overprediction of CF2 in the CH2F2 flame relative to the CHF3 flame when kinetics of the fluoromethane decomposition reactions are placed in the falloff regime.

The rate of (R13) has been reduced to correctly predict the ratio of CF2 between the difluoromethane and trifluoromethane flames. The kinetics of the CHF2 + H reactions have not been altered in our modification. It is conceivable that H atoms, rather than CH3 radicals, constitute the primary reaction partner leading to CF2 formation from CHF2, although our data provide no information on this issue. One study [48] at room temperature reported that CF2 and CHF were produced in comparable amounts from the H + CHF2 reaction. For the CH2F + H reaction, we have increased the branching ratio of the CHF + H2 channel to better predict the CHF and CF profiles. In the reactions of CHF, CH2F, and CHF2 with H atoms, formation of H2 is in all cases the lowest energy product channel, and it seems plausible that the branching ratios may be higher than the base mechanism predicts. Further investigation of the product channels of these reactions would be extremely useful.

Relative Importance of H, O, and OH Reaction Partners With Hydrofluorocarbon Radicals

The fluoromethyl and fluoromethylene radicals can react with atomic hydrogen as described above, or with O or OH to form the oxidized species CF2O, CHFO, FCO, and HCO. In the base mechanism, reaction with H is predicted to be the dominant path in most cases. Since the O and OH reactions produce different products than the H reactions, the relative reaction rates with the different partners will influence the net yield of, for instance, CF from CF2. These reactions will thus affect the profiles of the species we have detected, although unfortunately none of the oxygen containing products are sufficiently amenable to LIF diagnostics to obtain a direct measurement of their profiles. CHFO and HCO both have transitions in the vicinity of 250 nm, but interference from CF2 would preclude their detection at these wavelengths for our conditions. Some kinetic studies have been performed on O atom reactions with the hydrofluorocarbon radicals, but the OH reaction rates have, in most cases, never been directly measured. In the HFC mechanism, the OH kinetics are largely based on the analogous O atom reactions.

Kinetic rates of the reactions of CF2 with H and O atoms have been measured at room temperature by Tsai and McFadden [49, 50], while the reaction rate with OH has only been inferred from kinetics modeling of flames inhibited by CF3Br performed by Biordi et al. [51, 52]. The base mechanism assumes that the reaction rates with O and particularly with H increase with temperature, the result being that at flame temperatures, CF2 is almost quantitatively converted to CF by the reaction with H atoms. The base mechanism greatly overpredicts the amount of CF in the trifluoromethane flame relative to the mono- and di-fluoromethane flames. The only way to reasonably bring the predicted CF concentrations into agreement with the experiment is to assume that CF2 has reaction rates with O and/or OH comparable to those with H under flame conditions. We have made the rates temperature independent and set the rate with OH to four times the value for O.

The rate of the reaction CHF2 + OH → CHFO + HF was reduced by a factor of two to
better fit the CHF and CF profiles in the difluoromethane flame. The reaction $\text{CF} + \text{OH} \rightarrow \text{CO} + \text{HF}$ has been increased to move the CF concentration peak closer to the burner. Even in the revised mechanism, the CF profiles in all the flames remain about 2 mm too far from the burner, even though the H, OH, CH, and CF$_2$ profile maxima are all predicted to within 1 mm of the experimental value for all the flames. Since the reaction zone as a whole is predicted to occur in the right place, the problem seems to be that either the CF formation or removal kinetics are too slow. Since CF is produced primarily from CHF in the methyl fluoride flame (in the revised mechanism) and from CF$_2$ in the trifluoromethane flame, there is not a single CF formation reaction that can be responsible for the late CF peak in all three flames. Concerning the removal kinetics, the reaction rates of CF with H and O have been measured at room temperature only [49, 50, 53], while the rate with OH has not been measured. The recent measurement of Van Hoeymissen et al. [53] for the $\text{CF} + \text{O}$ reaction measured a value three times larger than did the study of Tsai and McFadden [50], from which the kinetic parameters in the base mechanism have been taken. We have increased the rates by a factor of two at high temperatures for the H and O reactions while maintaining the same rates as in the base mechanism at 300K and increased the rate with OH. These changes moved the CF profile slightly toward the burner but not enough to obtain good agreement with the experimental profiles. It is also conceivable that the rate of $\text{CF} + \text{O}_2$ should be increased at high temperature, since $\text{O}_2$ is the most important reaction partner in CF removal. The preexponential factor assumed in the base mechanism, $2 \times 10^{13} \text{cm}^3/\text{mol-s}$, however, is already fairly high for a radical reaction with a closed shell species, and approaches that of the analogous reaction for CH, which is generally observed to be more reactive than CF [53].

The recombination rates of the fluoromethyl radicals CH$_2$F and CHF$_2$ with CH$_3$

$$\text{CH}_2\text{F} + \text{CH}_3 = \text{C}_2\text{H}_4 + \text{HF}, \quad (\text{R14})$$

$$\text{CHF}_2 + \text{CH}_3 = \text{CHFCH}_2 + \text{HF} \quad (\text{R15})$$

have been lowered by 30% from the base mechanism. The base mechanism predicts that the C$_2$H concentration (and by extension the amount of CH* emission) should be three times as high in the mono- and di-fluoromethane flames as in the trifluoromethane flame, whereas the experimental ratio of the CH* emission profiles is slightly less than a factor of 2. Sensitivity analysis for C$_2$H concentrations found that the reactions above had the highest sensitivities of any reactions involving fluorine because they constitute the principal route to formation of C$_2$ species in these flames. Even with the revisions, the ratio of predicted CH* emission is still too high. Further adjustment of the rates is probably not warranted based on the emission profiles. Both the temperature dependence of the $\text{C}_2\text{H} + \text{O} \rightarrow \text{CH}^*(A^2\Delta) + \text{CO}$ reaction and detailed validation of the C$_2$ hydrocarbon and fluorocarbon kinetics leading to C$_2$H formation require further investigation.

**Reaction Pathways and Profile Comparisons With Experiment**

Reaction pathways of the fluorinated agents in the burner stabilized flames were determined by integrating the chemical production rates across the flame zone and summing individual rates with all possible reaction partners. The results for the base mechanism are shown in Figs. 10, 12, and 14, for the flames containing CH$_3$F, CH$_2$F$_2$, and CHF$_3$, respectively. Predictions for the revised mechanism are shown in Figs. 11, 13, and 15. Arrow thicknesses are proportional to the flux of carbon atoms integrated over the flame zone. Next to each reaction path, the reaction partner(s) are written in decreasing order of importance.

For the small fraction of agent which is predicted to react in the flame containing CF$_3$, the reaction pathways of the CF$_3$ radical are similar to those in the CHF$_3$ inhibited flame in most respects. The one exception was that very small amounts of C$_2$ hydrofluorocarbons were produced, due to most of the agent consumption taking place after the methyl radical had disappeared, giving the reaction

$$\text{CH}_3 + \text{CF}_3 = \text{CH}_2\text{CF}_2 + \text{HF}, \quad (\text{R16})$$
The modifications made to the mechanism are summarized in Table 4. The revised mechanism gives very good predictions of profiles and relative concentrations for most species. The profiles of CHF appear about 3 mm later than the experiment indicates; however, the experimental difficulties of spectral interference and temperature correction make this disagreement of marginal significance. The calculated CF profiles are about 2 mm too far from the burner. Since the CF spectrum is well characterized and has little interference, this discrepancy is statistically significant. Additional data on the formation and removal kinetics of CF at high temperatures are probably needed to correct this disagreement.

The H atom profiles deviate from the prediction in the postflame zone (>2 cm above the burner). Specifically, the experimental H atom mole fraction begins to decrease while the calculation predicts an increase over the entire computational region.
This behavior is generally seen in this type of burner geometry [33, 54, 55] in all types of flame systems and therefore does not depend on the fluorine chemistry. It may be a consequence of preferential lateral diffusion depleting the H atom mole fraction when the height above the burner becomes comparable to the burner radius. This phenomenon is not likely due to radial spread of the flame with height above the burner, since the mole fraction of OH (which has a much lower diffusivity) is quite accurately predicted by the model up to 5 cm.

**Flame Speed Validation of Revised Mechanism**

The HFC mechanism has already been shown to accurately predict the propagation speed of atmospheric pressure methane/air flames containing CH$_2$F$_2$ under most conditions [11]. Furthermore, the modifications of Saso et al. produced good agreement with experimental data for methane/air flames containing CHF$_3$. Since our proposed changes to the kinetics have been dictated by low pressure experiments, it is necessary to make sure that these changes maintain agreement with the atmospheric pressure flame speed data. Several of the reactions we have adjusted were identified in the study of Linteris and Truett as having significant sensitivities for flame speeds.

We performed calculations to compute burning velocities of freely propagating atmospheric pressure flames containing di- or tri-fluoromethane for eight representative conditions for which experimental data are available. The reactant mixtures were composed of methane, air, and inhibitor with ratios of methane/oxygen of 0.45, 0.5, and 0.55, corresponding to equivalence ratios of 0.9, 1.0, and 1.1 for the uninhibited flames. The mixtures contained the agents CH$_2$F$_2$ or CHF$_3$ at up to 7% mole fraction.

The flame speed calculations were performed on a domain extending 25 cm from the flame on the cold boundary and 60 cm on the hot boundary. The calculations used multicomponent viscosities, thermal diffusivities for H and H$_2$, and windward differencing on the convective term. The initial temperature of the fresh gases was set to 298.2K. Meshes were refined until tolerances of 0.1 and 0.2, respectively, for GRAD and CURV, were satisfied, or until a maximum of 150 grid points was reached. The final meshes contained approximately 120 grid points for the uninhibited methane/air flames and >140 grid points for the inhibited flames.

Results of the atmospheric pressure flame speed calculations are summarized in Table 5. In Figs. 16 and 17, the calculated flame speeds for CH$_4$/O$_2$/CHF$_3$ and CH$_4$/O$_2$/CH$_2$F$_2$ mixtures,
shown to speed of speed of speed of mes con- 

is quite 5 cm.

Table 5. The speeds mixtures,
respectively, are plotted normalized by the uninhibited flame speed at the same CH$_4$/O$_2$ ratio. The experimental data of Linteris and Truett [11] and of Saso et al. [12] are plotted for comparison. The agreement of the calculations with the experimental data is very good for CHF$_3$. The agreement is less good for the flames containing CH$_2$F$_2$ under some conditions. At 6% CH$_3$F$_2$ with a methane/oxygen ratio of 0.50, and 5% CH$_2$F$_2$ with a methane/oxygen ratio of 0.55, flame speeds were underpredicted by about 25%. In contrast, the calculated speeds of flames with CH$_4$/O$_2$ = 0.50 with 5% CH$_2$F$_2$, and CH$_4$/O$_2$ = 0.45 with 5% CH$_2$F$_2$,

were in good agreement with the measurements of Linteris and Truett.

The two conditions for which the mechanism gave poor predictions of the flame speed were both substantially fuel rich, having equivalence ratios of approximately 1.3 (taking into account the effect of the agent on the flame stoichiometry). By contrast, the CHF$_3$ inhibited flames for which burning velocity data is available all have equivalence ratios less than 1.2. The source of the difficulty in predicting the difluoromethane

\begin{table}
\centering
\caption{Continued}
\label{table4}
\begin{tabular}{lcccc}
\hline
Reaction & Arrhenius Parameters $k = AT^b \exp(-E_a/RT)$ & \\
 & A & b & $E_a$ & Remarks \\
 & (cm, mol, s) & & (cal/mol) & \\
\hline
JD3. & CHFCHF[Z] & & & \\
 & (+M) = C$_2$HF + HF (+M) & & & \\
High-pressure limit: & 2.50E+14 & 0.0 & 78,000. & \\
Low-pressure limit: & 9.00E+15 & 1.0 & 78,000. & \\
Third body efficiencies: & H$_2$:2.0 & & & \\
 & H$_2$O:1.5 & & & \\
 & CO:1.5 & & & \\
 & CO$_2$:2.0 & & & \\
 & C$_2$H$_6$:3.0 & & & \\
JD4. & CHF = CF$_2$ (+M) = C$_2$F$_2$ + HF & & & \\
 & (+M) & & & \\
High-pressure limit: & 2.50E+14 & 0.0 & 100,000. & \\
Low-pressure limit: & 9.00E+15 & 1.0 & 100,000. & \\
Third body efficiencies: & H$_2$:2.0 & & & \\
 & H$_2$O:1.5 & & & \\
 & CO:1.5 & & & \\
 & CO$_2$:2.0 & & & \\
 & C$_2$H$_6$:3.0 & & & \\
\hline
\end{tabular}
\end{table}

\begin{table}
\centering
\caption{Test Cases for Flame Speed Calculations Using Revised Mechanism [8] modified according to Tables 3 and 4}
\label{table5}
\begin{tabular}{lcccc}
\hline
Agent & CH$_4$/O$_2$ & Agent mole & Equivalence & Flame speed & \\
& ratio & fraction & ratio & (cm/s) & \\
\hline
None & 0.45 & — & 0.90 & 35.25 & \\
None & 0.50 & — & 1.00 & 39.37 & \\
None & 0.55 & — & 1.10 & 40.11 & \\
CHF$_3$ & 0.45 & 4.04% & 1.01 & 21.57 & \\
CHF$_3$ & 0.50 & 5.00% & 1.11 & 19.20 & \\
CHF$_3$ & 0.50 & 7.11% & 1.15 & 13.85 & \\
CHF$_3$ & 0.55 & 5.19% & 1.20 & 16.27 & \\
CHF$_3$ & 0.45 & 5.05% & 1.10 & 22.37 & \\
CHF$_3$ & 0.50 & 5.00% & 1.24 & 18.13 & \\
CHF$_3$ & 0.50 & 6.00% & 1.29 & 12.88 & \\
CHF$_3$ & 0.55 & 5.00% & 1.33 & 11.86 & \\
\hline
\end{tabular}
\end{table}
flame speeds must involve fluorine chemistry, since both the study of Linteris and Truett and the validation tests of the GRI mechanism found good agreement with experimentally measured flame speeds for methane/air (uninhibited) flames at these equivalence ratios.

Our modifications did not substantially alter the mechanism's performance for the CH₂F₂ flames from that reported by Linteris and Truett, who also observed substantial underpredictions of flame speeds for rich conditions. Sensitivity analysis of the flame speed for the flame with the methane/oxygen ratio of 0.55 and 5% CH₂F₂ found that the fluorinated reactions having the highest sensitivity coefficients for the flame speed were the agent thermal decomposition and reactions with H and OH, the same as for leaner stoichiometries. Reactions involving fluoromethyl + (fluoro)methyl including recombination and hydrogen disproportionation had sensitivities about an order of magnitude lower (absolute values of 0.005 compared to 0.05 for the difluoromethane removal reactions; the H + O₂ = OH + O reaction has a sensitivity of 0.5, the highest value in the inhibited as well as the uninhibited flames). For a reaction having a sensitivity coefficient of X for the flame speed, a 1% increase in the reaction's kinetic rate will cause an X% change in the flame speed, a positive sensitivity coefficient corresponding to an increased flame speed. The recombination of two (fluoro)methyl radicals to form an ethylene with HF elimination had a positive sensitivity coefficient, while hydrogen disproportionation to form a (fluoro)methane and a (fluoro)carbene had a negative sensitivity coefficient. Alterations to the kinetics of the C₂ reactions are probably needed to correctly predict flame speeds under rich conditions, but such changes cannot be validated without additional data. Species profiles for rich stoichiometries (ideally comprising some C₂ species as well as those monitored here) are needed to ascertain which aspects of the kinetics need attention.

Conclusions

We have obtained profiles for a number of intermediate species in methane/oxygen flames containing C₁ hydrofluorocarbons and propose chemically plausible adjustments to selected reactions in the HFC mechanism. This revised mechanism provides good agreement with both our low-pressure profile data and, except for rich stoichiometries, atmospheric pressure flame speeds. In making changes to the kinetic mechanism, it must be emphasized that because of the large number of kinetic parameters, which could conceivably be modified and the rather limited range of data, there is not a unique set of adjustments that will adequately reproduce the experimental results. Having information on oxygen containing fluorine species and on C₂ species would be very useful in diagnosing further uncertainties in the mechanism, which include the relative reactivities of the fluorinated radicals with O, H, and OH, and the rather poor prediction of flame speeds under rich stoichiometries. Flame speed data on methane/air/CH₃F mixtures, while not of practical importance for fire suppression, would add to the data needed to interrogate hydrofluorocarbon kinetics. The profiles obtainable for the CHF radical could benefit from investigation of alternative wavelengths for a fluorescence diagnostic and especially from an improved temperature correction. Individual reactions in the HFC mechanism, which, based on our study, appear to require attention include the product...
channels of atomic hydrogen reactions with fluorinated radicals (H₂ vs HF product), and the falloff behavior and particularly the third body efficiencies of flame species for thermal decomposition reactions.

We thank Phillip Westmoreland and Don Burgess for helpful discussions. This work was funded by the U.S. Naval Sea Systems Command.

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Received 2 October 1997; revised 17 August 1998; accepted 27 August 1998.