KINETICS OF FLUORINE-INHIBITED HYDROCARBON FLAMES

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ABSTRACT

Numerical simulations of methane/air flames were used to evaluate the relative degree of effectiveness of potential fluorinated hydrocarbon replacements for Halon 1301 (CF_3Br). A comprehensive chemical mechanism was developed based on elementary reaction steps for the destruction of candidate agents, their participation in and influence on hydrocarbon flame chemistry, as well as for prediction of potential by-products of incomplete combustion. The reaction set consists of chemistry involving C_1 and C, stable and radical fluorinated hydrocarbon species, including partially oxidized species. Existing thermochemical data was compiled and evaluated. Where little or no data existed for potential species of interest, that data was estimated using both empirical methods (e.g., group additivity) and also through the application of *ab initio* molecular orbital calculations. Utilizing fluorinated species identified as potentially important, a grid of possible reactions was constructed. Existing rate data was compiled and evaluated. Where this data was available over limited temperature ranges and at different pressures, RRKM and QRRK methods were used to estimate the temperature and pressure dependencies of the rates and to predict relative rates where multiple product channels were possible. Where no rate data were available, the rate constants were estimated by analogy to other hydrocarbon reactions. For many important reactions, *ab initio* methods were used to calculate the geometries and energies of the transition states.

The reaction set was used to model the fluorinated hydrocarbon chemistry under a variety of conditions including different fuels, equivalence ratios, different agents, agent concentrations, and for different reactor geometries. Plug flow simulations were used to "debug" the mechanism and to test a variety of conditions. Adiabatic, freely-propagating, premixed flame simulations were performed to determine effects of agents on flame speed and extinction. Typically, fuel lean methane/air mixtures were simulated in order to be most sensitive to flame speed changes and, in a practical sense, since agents are added to the air supply. In addition to potential fluorinated hydrocarbon agents (CF_4, CF_3H, CF_2H_2, CF_3-CF_3, CF_3-CF_2H, CF_3-CFH,), other species were added to investigate the effects of heat capacity and heat release on changes in flame speed and temperature. These reference "agents" include N_2, H_2O, CO,, HF, and CH,. Of the various agents considered, only CF_3H was seen to have any chemical effect on flame suppression. Although flame temperature increased with CF_3H addition, flame speed decreased relative to inert molecule addition. These and other results will be discussed.

BACKGROUND

There has been a significant amount of work over many years investigating the effectiveness of halogenated fire suppressants [1-8], as well as other types of fire suppressants [9-12]. We will not review this body of work, but refer the reader to these and other relevant sources. A large part of our work is based on the pioneering work in this area by Biordi and coworkers [13] and Westbrook [6]. In earlier experiments on a range of candidates, CF_3Br was identified as being very effective for extinguishing flames. However, its mechanism was not understood. Biordi and coworkers use a flame-sampling molecular beam mass spectrometer to measure both stable and radical species in methane flames doped with CF_3Br. Many of the relevant elementary reactions describing the decomposition of CF_3Br, its chemistry, and its influence on hydrocarbon flames were determined in this work. Westbrook developed the first comprehensive chemical mechanism to describe in detail the chemistry of CF_3Br and modeled inhibition in hydrocarbon flames. As a result of this work, it is generally agreed that flame suppression by bromine-containing compounds is a result of catalytic destruction of H atoms by Br atoms. The ability of bromine to recycle in the chemical system in the flame is directly related to the weak molecular bonds formed by bromine.

There are a variety of ways in which fire suppressants act in inhibiting hydrocarbon flames. Most of these effects are intimately related. For example, a heat loss means a temperature decrease, which causes the chemistry to slow, which means fewer radicals leading to product formation, which means less heat generated, which results in a temperature decrease and so on. One can separate suppression effects into two general categories: physical and chemical (although there is overlap). One can define chemical effects as being directly related to the characteristics of the specific molecule (e.g., H, F, Cl substitution), while physical effects are not. For example, heat capacity is a physical effect, since it is largely a function of the number of atoms in the molecule and their connectivity, but not the identity of the molecule.

There are a number of different types of chemical effects. Most of these involve different competing factors. First, all of the fluorinated hydrocarbons will eventually decompose and then bum (forming CO_2, H_2O, and HF). This liberates heat and increases flame temperatures (which of course speeds flame chemistry). On the other hand, the agents are large molecules with many atoms. Consequently, their high heat capacities may result in a decrease in temperature in the flame prior to complete combustion (which of course slows flame chemistry). The competition between these two factors will be strongly dependent upon conditions; most important of which will likely be the mechanics of mixing of the fuel and oxidizer. Another set of competing effects involves fluorinated radicals produced by agent decomposition. These radicals are slower to burn than their pure hydrocarbon analogues, because the C-F bond is significantly stronger than the C-H bond. Consequently, reactions involving these radicals may effectively compete with analogous pure hydrocarbon chemistry by creating less "flammable" intermediates, thereby inhibiting combustion of the hydrocarbon fuel. For example, since the agents are added to the air stream, their immediate decomposition products (radicals) are formed in oxygen rich, relatively cold regions (preheat) of the flame. Consequently, these radicals may be involved in termination steps, such as $\bullet CHF_2 + HO_2\bullet \rightarrow CH_2F_2 + O$,, slowing radical chain reactions and inhibiting the flame. These radicals will compete with hydrocarbon radicals for important H, O, and OH radicals. On the other hand, these radicals can also react in the colder air stream with stable molecules (e.g., O_2), generating more radicals (e.g., O atoms) and thereby initiating chemistry or promoting combustion of the fuel.

SPECIES THERMOCHEMISTRY

We constructed a large comprehensive reaction set or "mechanism" for fluorinated hydrocarbon chemistry involving C, and C, stable and radical hydrocarbon species, including partially oxidized fluorinated hydrocarbons. Existing thermochemical data was compiled and evaluated. Where little or no data existed for potential species of interest (most of the radicals), we estimated that thermochemistry using both empirical methods, such as group additivity [14], and also through application of *ah initio* molecular orbital calculations [15-17]. For many of the radicals, we had to rely upon recent *ah initio* calculations of thermochemical data. This includes both *ab inirio* calculations done as part of this project and those done previously by other workers. Tschuikow-Roux and coworkers have calculated thermochemistry for the fluoroethyl radicals [18-21]. Melius has calculated thermochemistry for many stable and radical fluorinated species [22]. Nyden has used *ah initio* calculations to obtain thermochemical data for a number of the fluoroethanes and fluoroethyl radicals [23].

We used standard hydrogen/oxygen and hydrocarbon thermochemistry, most of which can be found in the JANAF tables [24], as can data for F, F,, HF, FO•, FOO•, FOF, and HOF. Thermochemical data for the fluoromethanes: CH_3F, CH_2F_2, CHF_3, and CF, can be found in the

JANAF tables and have been re-examined subsequently [25]. Heats of formation for CH_2F_2 and CF, are the best known, with levels of uncertainty of less than 1.5 kJ/mol and are derived from their heats of combustion. Heats of formation of CH_3F and CHF, have somewhat higher uncertainties of less than 10 kJ/mol, since they are indirect values derived from other measurements. Thermochemical data for the perfluoromethyl radical (•CF_3) can be found in the JANAF tables. More recent experimentally-derived values for the heat of formation of •CF_3 can be found elsewhere [26-28] suggesting a value about **4** kJ/mol higher. Experimentally-derived values for the other fluoromethyl radicals (•CH_2F, •CHF_2) can be found in two evaluated sources [27,29] with uncertainties of less than 5-10 kJ/mol. Thermochemical data for the fluoromethylenes, :CHF and :CF_2, can be found in the JANAF tables. Unfortunately (since :CHF and :CF_2 are important species), there are significant uncertainties in their heats of formation. The values for :CF_2 are the best (±10 kJ/mol) and are derived from a number of different measurements. The uncertainty in the heat of formation for :CHF is even greater (f30 kJ/mol) due to the lack of direct, reliable data (heat of reaction, kinetic, or otherwise).

Thermochemical data **for** most of the other possible C_1 fluorinated hydrocarbons can be found in the JANAF tables, including •CF, CHF=O, CF_2=O, and •CF=O. The biggest uncertainties here are for CHF=O (f20 kJ/mol) and •CF=O (±10 kJ/mol) where no direct experimental data are available and, consequently, their heats of formation were calculated using average bond dissociation energies from other related compounds. We have calculated heats of formation for these species using the BAC-MP4 and G2 *ab inirio* methods and can provide a better bracket on the uncertainties in their values. There is an experimentally-derived value for the heat of formation of CF_3O• [30]. However, we have used our BAC-MP4 *ab initio* value for the sake of consistency because we have relied solely on ***ab*** *initio* values for the other fluoromethoxy radicals and for a number of reactions involving CF_3O•.

Thermodynamic properties for many of the fluoroethanes are derived from experimental data. This **work** has been compiled and evaluated [31-32]. The heats of formation of CH_3-CH_2F and CH_3-CF_3 are the best known with uncertainties of less than 2 kJ/mol. There are also experimentally-derived heats of formation for CH_3-CHF_2, CHF_2-CF_3, and CF_3-CF_3 with uncertainties of 4-6 kJ/mol. For the other four fluoroethanes, one must rely upon values that have been estimated using group additivity or through other correlations and are only known to about 10 kJ/mol. There are experimentally-derived thermochemical data [26] for a few of the fluoroethyl radicals (CH_3-CH_2•, CF_3-CH_2•, CF_3-CF_2•) with uncertainties in heats of formation of about 5-10 kJ/mol. Thermochemistry for all of the fluoroethyl radicals have been calculated through the application of ***ab*** *initio* molecular orbital theory by Tschuikow-Roux and coworkers [18-21]. Thermochemistry for a number of the fluoroethyl radicals have also been calculated using the BAC-MP4 [22] and the G2 [23] *ab initio* methods. Thermochemistry for $CF_2=CF_2$ can be found in the JANAF tables and data for $CH_2=CHF$ and $CH_2=CF_2$ in DIPPR [32]. For the other fluoroethylenes, we have used thermochemistry from our ***ab*** *initio* calculations. There are not experimentally-derived thermochemical data (to our knowledge) for the fluorovinyl radicals. Consequently, we have used values calculated as part of this work using the BAC-MP4 *ab initio* method. The thermochemistry of the fluoroacetylenes (C_2HF, C_2F_2) can be found in the JANAF tables, however, with relatively large uncertainties: ±60 kJ/mol and ±20 kJ/mol in the heats of formation, respectively. Fluoroketenes and the fluoroketyl radical can be formed through a number of channels (analogous to simple hydrocarbon chemistry). To assess the importance of these species and relevant reactions, we have included these species in the mechanism. There are not experimentally-derived data for these species. Consequently, we have relied upon values calculated as part of this work using the BAC-MP4 *ab initio* method.

REACTION KINETICS

Utilizing the species identified as potentially important, a grid of possible reactions was constructed. Existing chemical rate data involving these fluorinated species was then compiled and evaluated. Where rate data were available, but only over limited temperature ranges or at different pressures (for unimolecular or chemically activated steps), RRKM and QRRK [33-34] methods were used to estimate the temperature dependencies (at 1 atmosphere pressure) of the rates and to predict relative rates where multiple product channels were possible. Where no rate data were available for potential reactions, the rate constants were estimated by analogy to other hydrocarbon or substituted hydrocarbon reactions. The rate constant prefactors were adjusted for reaction path degeneracy and the rate constant activation energies were adjusted empirically based on relative heats of reaction or relative bond energies (*i.e.*, Evans-Polanyi relationships).

The mechanism *is* too large to be described in any detail here. The C/H/O subset is derived from the Miller-Bowman mechanism [35] and consists of about 30 species and 140 reactions. The H/F/O subset consists of about *3* species and 8 reactions that are relatively well known, The C_1/H/F/O subset consists of about 15 species and 200 reactions. It includes all fluoromethane decompositions, both unimolecular and chemically-activated (e.g., $\bullet CF_3 + H \rightarrow :CF_2 + HF$), H atom abstractions from the fluoromethanes by H, O, and OH, chemically-activated fluoromethyl decompositions (e.g., $:CF_2 + H \rightarrow \bullet CF + HF$), and reactions of fluoromethyl radicals with O,, O, and OH to form carbonyl fluorides (e.g., $CF_2{=}O$) and other products. It also includes reactions of the fluorocarbenes (e.g., $:CF_2$) with O_2, O, and OH to form carbonyl fluorides and other products.

The C_2/H/F/O subset consists of about 40 species and 400 reactions and consists of reactions analogous to those in the C, subset (thermal decompositions, chemically-activated decompositions, and H atom abstractions) with a few exceptions (due to new types of product channels). Chemically-activated fluoroethane decompositions following combination of fluoromethyl radicals (e.g., $\bullet CH_3 + \bullet CF_3 \rightarrow CH_2{=}CF_2 + HF$) is one such important reaction class. Reactions involving the carbenes (e.g., $:CH_2$ + CF, → Products or $:CF_2$ + CH, → Products) is another potentially important type of reaction. **All** fluoroethyl and fluorovinyl radical reactions were estimated by analogy to the analogous hydrocarbon reactions. In a number of cases, it was identified that C_3 compounds might be formed (e.g., $CH_2{=}CH_2 + :CF_2 \rightarrow CHF_2\text{-}CH{=}CH_2$). In order to keep the number of species to a semi-manageable level, these type of reactions were not explicitly considered.

SIMULATIONS

Plug flow simulations were used extensively to refine the reaction set. Adiabatic, freely-propagating, premixed flame simulations [36] were performed to determine effects of agents on flame speed and extinction. Typically, fuel lean methane/air mixtures were simulated in order to be most sensitive to flame speed changes and, in a practical sense, since agents are added to the air supply. In addition to potential fluorinated hydrocarbon agents (CF,, CF_3H, CF_2H_2, CF_3-CF,, $CF_3\text{-}CF_2H$, $CF_3\text{-}CFH_2$), other species were added to investigate the effects of heat capacity and heat release on changes in flame speed and temperature. These reference "agents" include N_2, H_2O, CO,, HF, and CH,. The amount of added agent was varied in the range of 0-3%.

The effects of the various agents on flame temperature can be bracketed by addition of the inert molecules (decrease in flame temperature) and by addition of more fuel (large increase in flame temperature). The decrease in flame temperature upon addition of the inerts is due to dilution and increased heat capacity of the mixture. Addition of more fuel-like agents results in larger increases in flame temperatures. A range of effects on flame speed for the various added agents were also observed. For the inerts and the nearly inert fluorocarbons (CF,, CF_3-CF,), decreases in flame speed were observed (consistent with dilution of the mixture). On the other extreme, for CH, (the fuel) and CF_2H_2 (a slightly poorer fuel), increases in flame speed were observed. Of the various agents considered, only CF_3H was seen to have any chemical effect in flame suppression.

These simulations demonstrated that differences in the relative influence of candidate agents on hydrocarbon flames can be explained largely by differences in their relative heat capacities and relative amounts of heat release due to agent combustion. That is, flame extinction upon addition of each of the potential agents was mainly due to dilution of the flame by increased heat capacity of the mixture (consequently, reduced flame temperatures). For example, addition of 1% N_2 to a very lean methane/air flame with an equivalence ratio of 0.65 reduced the flame speed by about 0.8 cm/s, while addition of 1% CF, and 1% CF_3-CF_3 reduced the flame speed by about **2.4** and 3.8 cm/s, respectively (about 3 and 5 times more). However, CF, and CF_3-CF_3 have heat capacities (at 1500 K) of 105 and 175 J/mol/K, respectively, compared to 35 J/mol/K for N, (or about 3 and 5 times more).

Of the various agents considered, only CF_3H was seen to have any chemical effect in flame suppression. It was observed that although there is an increase in flame temperature upon CF_3H addition, there is also a <u>decrease</u> in flame speed relative to inert molecule addition. For example, addition of 1% CF_3H resulted in **a** decrease in flame speed of about 2.8 cm/s compared to 2.4 cm/s for addition of 1% CF, (same flame as mentioned above) or about 25% more effective when adjusting for the higher heat capacity of CF,. Inspection of reaction pathways for CF_3H and other agents reveals that a significant amount of decomposed CF_3H results in the formation of a relatively unreactive perfluorocompound, carbonyl fluoride (CF_2=O). Decomposition of CF_2=O occurs only very slowly via reaction with either H radicals (H addition + HF elimination) or with H_2O (through a hot fluoroformic intermediate). For all other agents, this CF_2=O bottleneck is avoided.

Our simulations predominantly focussed on the influence of added agents on premixed, lean methane/air flames. Under other conditions (e.g., higher equivalence ratios, diffusion flames), the ranking of the various agents and the relative amounts of chemical inhibition versus dilution may be different. We have performed some simulations for near stoichiometric premixed flames, as well for diffusion flames. Our results indicate there are some distinct differences. However, these results are preliminary and need to be investigated further.

REACTION PATHWAYS

The fluoromethanes decomposed primarily through H atom abstraction by OH radicals in the premixed flame with H atom abstraction by H radicals the major secondary pathway (on the order of 10-20%). H atom abstraction by **O** radicals and unimolecular decomposition eliminating HF are the next important minor decomposition channels (generally contributing less than 10%). These minor pathways only begin to contribute as secondary channels at the highest temperatures in the premixed flame and the unimolecular decomposition channel at high temperatures/short residence times under plug flow conditions. It is likely that the unimolecular decomposition channel also plays a role in a diffusion flame due to the lack of fuel (and consequently H and OH radicals) in the preheat, oxygen side of the flame. Abstraction by methyl, fluoromethyl, and vinyl radicals are negligible in the premixed flame although they may be minor channels in plug flow or diffusion flames. Abstraction of F atoms by H radicals is negligible for CH_3F, CH_2F_2, and CHF,, since the H atom abstraction channel has a significant lower barrier (30-50 kJ/mol) than the F atom abstraction channel (120-160 kJ/mol). In the case of CF,, F atom abstraction by H radicals is the only possible abstraction channel. Similarly, since there is no HF elimination channel, the only possible unimolecular decomposition pathway for CF, is elimination of F atoms. However, our simulations indicate that the primary decomposition pathway for CF_4 in the flame is due to insertion of singlet $:CH_2$. Unfortunately, there are no experimental measurements of this rate constant (we have estimated a barrier-to-insertion of less than **20** kJ/mol).

There are two possible channels for production of fluoromethanes. The first involves the insertion of methylene ($:CH_2$) into HF (reverse reaction of the unimolecular decomposition) and the second is disproportionation between fluoromethyl radicals to form fluoromethanes and $:CF_2$. Although latter channel has significant experimental basis, there is some uncertainty with regard to this reaction, because there is also evidence to suggest that the reverse reaction or insertion of $:CF_2$ (a closed shell species) should have a modest barrier. Channels of the first type can contribute small amounts to "recycling" of F mass in the system. For example, CH_2F_2 can decompose via H atom abstraction reactions to form $\bullet CHF_2$, which can react with H radicals to create $:CHF$ and HF (by elimination from chemically activated CH_2F_2). The $:CHF$ formed via this pathway can then insert into HF (which is present in large concentrations in the system) and consequently reform CH_2F_2. However, in the cases we have tested, this channel contributes generally less than 10% to the net rate of reaction for CH_2F_2. On the other hand, this channel may be significant in predicting by-products of incomplete combustion. For example, CH_3F and the intermediates and products of its decomposition will always be formed in hydrocarbon flames irrespective of fluorocarbon starting material simply because the HF (always present in the fluorinated hydrocarbon-doped flame) will react with singlet methylene ($:CH_2$) (always present in hydrocarbon flames). The latter channel involving the disproportionation between fluoromethyl radicals to form fluoromethanes and $:CF_2$ should be investigated further.

There are three general channels for the destruction of the fluoromethyl radicals: (1) reaction with H radicals creating (fluoro)methylenes and HF - via chemically-activated fluoromethanes; (2) reaction with O and OH radicals creating elimination products (i.e., H, HF) and (fluoro)formaldehydes (CH_2O, $CHF{=}O$, CF, $=O$) - via both thermally- and chemically- activated fluoromethoxy radicals; and (3) reaction with $\bullet CH_3$ radicals creating (fluoro)ethylenes and HF - via chemically-activated fluoroethanes.

The relative importance of these three general channels depends upon fuel, agent, flame geometry, and other conditions. For example, under more realistic conditions in a diffusion flame where the agent is added to the air stream, the importance of the route involving combination with $\bullet CH_3$ radicals should be substantially diminished (as should the H atom combination route to some degree), because of the lack of fuel (mixed) in the air. On the other hand the OH combination route should significantly increase in importance due to its high dispersion in the flame due to the abundance of H_2O in the flame. Similarly, the O atom reaction route should decrease in importance. Furthermore, other otherwise minor oxidative routes such as $\bullet CH_2F+O_2$ and $\bullet CH_2F+HO_2$ may begin to contribute in the preheat, oxygen rich side of the flame. For ignition delays under plug flow conditions, these oxidative routes should be very important as contributors (like analogous reactions for pure hydrocarbons systems).

At high agent concentrations, combination of fluoromethyl radicals are contributing reactions. For $\bullet CF_3 + \bullet CF_3$, the HF elimination channel is not possible and consequently, CF_3-CF_3 is the sole product (at the highest temperatures this rate falls-off slightly). For $\bullet CHF_2 + \bullet CHF_2$, the elimination channel is diminished somewhat in importance, since CHF_2-CHF_2 with four heavy F atoms can effectively stabilize the heat of reaction and compete as a product channel.

Fluoromethyl radicals are primarily formed by H atom abstractions from the fluoromethane. However, there are several other channels which can contribute to their formation and should be discussed in detail with reactions classified as C_2 chemistry. For example, the reactions $CH_2=CHF + O \rightarrow \bullet CH_2F + HCO$ or $CHF_2\text{-}CF_2\bullet + H \rightarrow \bullet CHF_2 + \bullet CHF_2$ contribute to the formation of fluoromethyl radicals. Similarly, there ***are*** a number of other decomposition channels which can be classified as C_3 chemistry such as $\bullet CH_2F + C_2H_4 \rightarrow \bullet CH_2\text{-}CH_2\text{-}CH_2F$. These should be investigated further.

The $C_2/H/F/O$ subset of the mechanism consists of about 40 species and 400 reactions and consequently, cannot be described here in detail. Briefly, fluoroethane destruction pathways (like fluoromethanes) consist of thermally- and chemically-activated decompositions and H atom abstraction reactions. Fluoroethyl radicals can react with H radicals (like fluoromethyls) creating fluoroethylenes (via chemically activated fluoroethanes and HF elimination). Fluoroethyl radicals can also react with oxygen-containing species (O_2, O, OH) resulting in the formation of oxidized fragments (e.g., $CF_3\text{-}CF_2\bullet + O \rightarrow \bullet CF_3 + CF_2=O$). Fluoroethylenes (produced from thermally- and chemically-activated fluoroethane decompositions) are predominantly destroyed via reaction with O radicals resulting in the formation of oxidized fragments (e.g., $CH_2=CF_2 + O \rightarrow \bullet CH=O + \bullet CHF_2$). Fluoroethylenes are also destroyed to a lesser degree through H atom abstraction by radicals such as OH, resulting in formation of fluorovinyl radicals (e.g., $CH_2=CF_2 + OH \rightarrow CF_2=CH\bullet + H_2O$). Fluorovinyl radicals (like fluoromethyl and fluoroethyl radicals) are destroyed via reactions with H radicals, as well as with oxygen-containing species. However, it was observed that the fluorovinyl radicals established a dynamic equilibrium with the parent fluoroethylenes, irrespective of the specific creation and destruction pathways.

There are a number of key reactions that we have identified as important pathways for fluorinated hydrocarbons in the flame, but the experimental data for the rate constants either do not exist or are of a limited nature. We believe further development of a mechanistic description of fluorinated hydrocarbon flame chemistry would benefit greatly from measurements of kinetics of these reactions. (1) Fluoroethylenes + O. There are a few measurements at lower temperatures (300-500K). This is major decomposition pathway, so it would be useful to have higher temperature experimental values, especially since the H atom abstraction channel may begin to contribute. (2) Fluoroethylenes + OH. There are few scattered measurements here, generally room temperature. It would be useful to know if OH addition followed by 1,2 HF elimination competes with the H abstraction channel (e.g., $CH_2{=}CF_2$ + OH → $CF_2{=}CH\bullet$ + H_2O versus $CH_2{=}CF_2$ + OH → •CH2-C(O)F + HF). *(3)* Fluoromethanes + OH and (4) Fluoroethanes + OH. The only measurements are at low temperatures (200-500K). Transition state theory (TST) calculations of Cohen and Benson [37,38] extend the rate expression to higher temperatures using T" with $n=1.5\text{-}1.8$ (fluoromethanes) and $n=1.6\text{-}1.7$ (fluoroethanes). However, it would be useful to have experimental values at higher temperatures, since these are the major decomposition channels for the fluoromethanes and fluoroethanes in the flame. (5) Fluoroethylenes + H. Jones and coworkers [39] have made some measurements at higher temperatures (600-900K). The low barrier to addition makes any uncertainty here not very important. However, it would be useful to know relative branching for addition to one side versus another since this affects flow of chemistry. (6) Fluoroethanes + H and (7) Fluoroethanes + O. There are no measurements (to our knowledge). These are secondary channels (abstractions by OH are more important) in the flame. However, it would be useful to have one measurement for each to benchmark these reactions.

SUMMARY

The presentation will discuss the key species and important reactions in the fluorinated hydrocarbon chemistry. Emphasis will be placed on identification of those species and reactions with uncertain thermochemical and rate data that have the largest impact on the decomposition pathways and flame chemistry. Further refinement of the mechanism will require both flame measurements (i.e., flame speeds, flame temperatures, concentration profiles) and measurements of important, but uncertain rate constants.

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