MODELING OF HYDROGEN FLUORIDE FORMATION FROM FLAME SUPPRESSANTS DURING COMBUSTION

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ABSTRACT

We have completed an initial computational study related to acid gas formation for two of the leading near-term Halon substitutes, FE-13 (CF_3H) and HFC-125 (C_2F_5H), and compared these results with Halon 1301(CF_3Br). Our goal is to determine whether we can identify conditions under which HF production can be minimized for the same inhibiting power, a result that could have significant practical implications. Our approach is based on investigating possible differences in the kinetics of HF formation under different agent loading scenarios using premixed flame codes with CH_4/air as the combusting system. We consider the situation where suppressants are mixed with inert compounds such as N_2 and CO_2 and deduce the commensurate decreases in hydrogen fluoride yields to obtain the same degrees of suppressant capability. This work clearly illustrates the great potential of computational simulations as a tool for identifying specific agent configurations for maximized performance. Other areas of possible future application of simulations are indicated.

BACKGROUND

Significant acid gas formation is one of the major problems that has been identified during testing of near-term candidate Halon replacement agents and which is limiting the potential utility of such agents. Recent work at NIST (discussed below) has demonstrated that experimentally measured acid gas concentrations in cup burner tests can be somewhat lower than those predicted on the basis of thermodynamic considerations. This finding suggests that there may be a possible kinetic effect that is responsible for this behavior. Due to the practical importance of the acid gas generation problem, and having reached the point of considerable confidence in the flame mechanisms that we are using in our combustion models, we felt that we could study this problem via a concerted flame modeling effort. In particular, we hypothesized that there may be optimal conditions of mixtures of agents with inert gases which may give the same level of inhibition, but a minimum amount of acid gas generated. This paper summarizes the results we achieved while testing this hypothesis.

Our approach is to use flame modeling to determine yields of HF for comparable suppression power for a pre-mixed system. This is an ideal use for the detailed simulations. It is well known that simulations, with complete chemistry, have the potential of yielding much information regarding the temporal behavior of all of the chemical species that may be present. For direct applications, such as fire suppression, much of this detailed information may not be necessary. However, once this preliminary work is done, there is the capability of making detailed estimates bearing on many specific process related issues. The production of toxic chemicals such as hydrogen fluoride is an obvious and probably the simplest extension of such work. However, note that if some means can be found to reduce its yield, one must then consider the formation of fluorinated organics. Currently, the results of simulations cannot be considered to be predictive. Instead, it is probably a very useful supplement to experimental work or equivalently, as a means of expanding such observations. This will become clear in the course of the subsequent discussion.

This work is based on the earlier studies of Westbrook[1] who showed through computer simulations that the addition of CF_3Br into a combustion mixture leads to a decrease in flame velocity and identified this as an appropriate parameter for considering fire suppression. Experimentally this is of course well established [2]. Systematic development of this relationship through simulations have only become possible through the development of a chemical kinetic data base [3]. The slow progress is also a reflection of the long running times necessary for the calculation of this parameter. With increasing computational power, this is now much more reasonable. Even now however, the results we are presenting are those from three work stations operating virtually full time for a number of weeks. These long running times make difficult any attempt at carrying out sensitivity analysis; leading to simplification of mechanisms so as to permit quantitative .identification of key reactions and suggest alternative approaches.

In this respect, we have recently demonstrated that equivalent results in terms of scales of suppression power can be obtained from modeling the time for reaction or hydrogen atom yields in plug flow reactors[4]. The advantage of this approach is that results can be obtained in a few minutes as opposed to the many hours of computation time required for flame velocity determinations. However, because the flame velocity approach is more established and indeed the paper on the plug flow simulations is still in preparation we have followed this procedure in the present work.

Linteris[5] has reported on the effect on flame velocities upon the addition of a number of additives in stabilized methane-air flames. The results are summarized in Figure 1. From these studies he obtained results that could be interpreted in terms of a ranking of the inhibition power of various retardants. They are in accord with the results from the cup tests [3] which are summarized in Table 1. There have been a number of studies [6-8] on the yields of hydrogen fluoride in combustion systems where retardants are added to air or fuel streams. Large quantities of this compound are formed. Clearly, substantial

Table 1. Percent of Agent in Oxidizer Stream At Extinction in Heptane Cup Burner Flames

Compound	Volume Percent	Mass Percent
CF_3Br	3.1	14
CF_3CF_2H	8.7	29
CF_3H	12	25
CO,	23	32
N_2	32	31

portions of the the fire retardant are being destroyed and these products must contribute to the chemistry of the decomposition process. However, the measurements, which 'are difficult to carry out, indicate that not all the available fluorine are converted into hydrogen fluoride or easily hydrolyzed compounds such as carbonyl fluoride. Due to the complexity of the combustion process the interpretation of results are never clearcut. The conclusion of Linteris is that there are kinetic limitations that lower the amount of hydrogen fluoride formed in diffusion flames. Table 2 contains a summary of results for CF_3Br and CF_3CF_2H. It is interesting to note that the large differences in HF yields arise from the differences in inhibition strengths of the two retardants and that when normalized on this basis yields of HF are not that much different. This of course leads to minimum yields when CF_3Br is used.

Figure 1. Normalized flame velocity measurements versus retardant concentrations for stabilized methane-air premixed flames

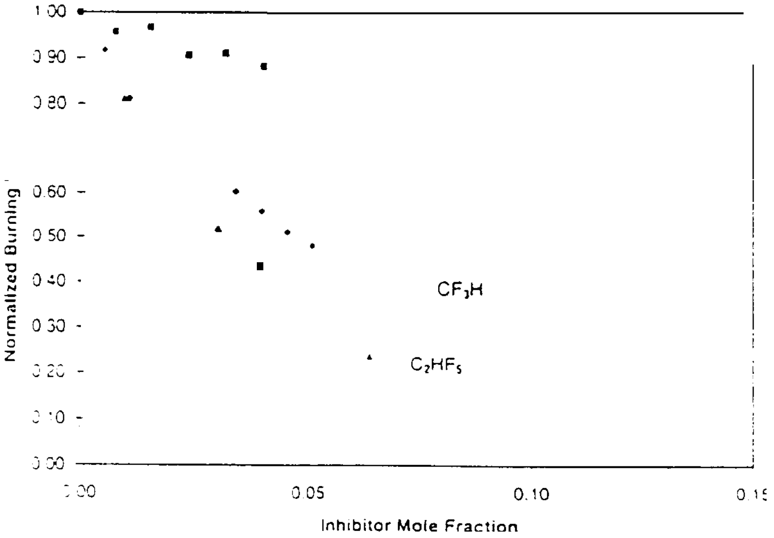


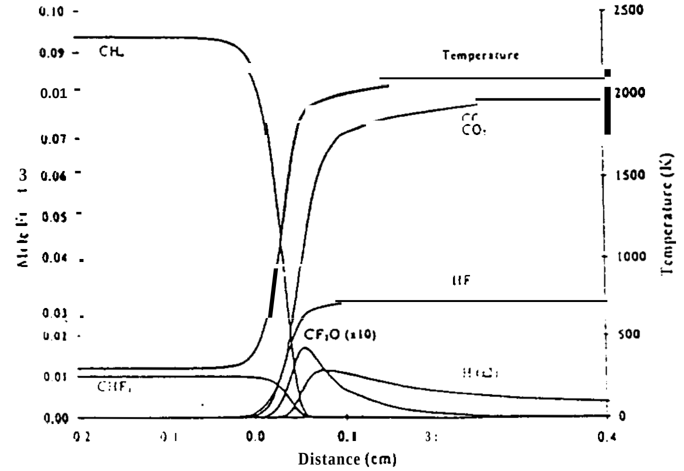
Table 2. Extinction conditions and acid fluorine collected with agent added to fuel or oxidizer

Inhibitor	Extinction Concentration (mol %)		H/X Ratio in flame at 70% ext.		Fraction of possible F- collected	
	fuel	air	fuel	air	fuel	air
CF_3Br	0.88	4.2	4.4	3.7	0.38	0.69
C_2F_5H	3.1	10.2	.94	.96	0.35	0.64

PROCEDURE

Our approach is to calculate the flame velocity for stoichiometric and near stoichiometric methane-air flames with varying amounts of CF_3Br, CF_3H and CF_3CF_2H respectively. This is the intermediate case from the experimental results in Table 2, for cup burner diffusion flames with retardants added to the fuel and air, separately. We show that this decrease in flame velocity is correlatable with the results from cup tests and then use this as a measure of inhibition power. The ratio of the concentration of two retardants that leads to equal decreases in flame velocity is then defined as the inverse of the relative suppression power. From our calculations we can deduce the relative amounts of HF that is produced when achieving the same amount of inhibition. Flame velocity calculations end where equilibrium conditions are attained. For the fluorinated compounds of concern thermodynamic calculations dictate that all the fluorine atoms are converted to HF. Thus

Figure 2: Calculated concentrations of reactants and products for stoichiometric methane-air flame with 1%CF_3H.



the ratio of HF produced for the same degree of inhibition can be directly determined from the ratio of concentrations and the number of fluorines on the retardant. The simulations also lead to predictions of the concentration of hydrogen fluorides produced at various stages of fuel decomposition. Comparison of the situation with the various retardants can be regarded as possible deviations from the equilibrium results. It will thus be possible to draw conclusions regarding the rate of hydrogen fluoride release during the combustion of premixed gases. Finally, we wish to investigate the situation where inert gases are mixed with suppressants. This introduces additional dilution and heat capacity effects. Although we know that the consequences are generally smaller than the purely chemical effect from CF_3Br, we are interested in the trade offs as far as hydrogen fluoride formation is concerned. There may, of course, also be synergestic effects which are not intuitively obvious.

The computer simulations were carried out with the Chemkin[9] program and with the NIST numerical graphical post-processor. The data base that is used has been developed at NIST for studying fire retardancy and has been largely validated by reproducing a wide variety of high temperature phenomena[10]. These include ignition delay for onset of rapid temperature, or pressure or concentration increase of OH as well as concentration measurements of the various stable products formed in static, flow and shock tube experiments. They have now provided a very satisfactory description of the chemical basis for fire suppression. Although we cannot be certain of the exact correctness of all the elements of the data base, we believe our data base substantially captures the chemistry that is occurring. Finally, note that all the results are normalized to those from systems where CF_3Br is the retardant. For these simulations this has the great advantage that much of the possible errors in the data base may cancel. Thus the results may have much higher degrees of validity than absolute values from each compound. This is especially true for a major product such as HF.

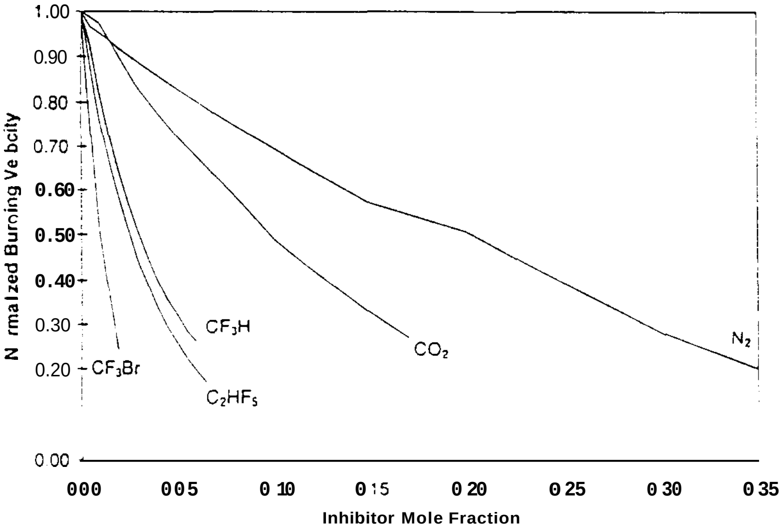


Figure 3: Normalized flame velocities as a function of retardant concentrations.

RESULTS

Figure **2** describes the behavior of the species of importance during the combustion of a stoichiometric methane-air flame with 1.0% CF_3H as a function of position from the flame front. This is typical of the results that have been obtained. They demonstrate the rapid disappearance of the reactants and intermediates at the flame front and the rapid production of hydrogen fluoride. Except for perfluoromethane, it is expected that this will be the general picture for all the fluorinated organics. We have not plotted the yields of the intermediates since their concentrations are extremely low. The final products such as CO_2 and hydrogen fluoride reach their equilibrium values fairly rapidly or at positions near the flame front. Their concentrations at the regions of maximum energy release are about a factor of *two* less than their final (equilibrium) concentrations. This is clearly a kinetic phenomena and presumably, this is the region where hydrogen fluorine reduction can be effected. This also establishes a limit for how much hydrogen fluoride can be reduced.

Figure **3** contains a summary **of** the simulation results for stoichiometric methane-air flames in terms of the dependence of flame speed on retardant concentration. The compounds covered are CF_3Br, CF_3H, C_2F_5H, CO_2, and N_2. All of the results show the expected decrease in flame velocity with increasing retardant concentration. Although the curves are monotonic, they are not linear. **As** one approaches low flames speeds, there is a flattening of the curves. For the present purposes however, cursory inspection demonstrates clearly that CF_3Br is the most effective retardant and the general ordering are in conformity with the observations summarized in Tables **1** and **2.** The CO, and N, in Figure **3** demonstrate the situation where only the dilution and heat capacity effects are of importance. They clearly do not decompose and indicate that these essentially physical effects do not have as strong consequences as those that arise from chemistry. It is nevertheless important to remember that the curves for all the fluorinated compounds also contain contributions from dilution and heat capacity effects. These effects must be removed if one looks for the effects arising from chemistry alone. These results can be directly used to establish an upper limit for the increased amount of HF that is produced from the two retardants when equivalent fire suppression power is achieved. **As** noted earlier the end point of flame velocity calculations is the equilibrium state. For the systems under consideration this leads inevitably to complete conversion to hydrogen fluoride. Thus from Figure **3,** one can immediately deduce the relative concentration of retardants that will achieve equivalent suppression effects. This leads to a rough linear relation. With this ratio, one need only know the number of fluorines in the retardant to determine the maximum number of hydrogen fluoride that will be formed if one assumes that the final equilibrium state is reached.

In Figures 4(a-b) we examine more closely the release of hydrogen fluoride into the system. For this purpose we calculate the ratio of concentration of hydrogen fluoride at every position with those at the equilibrium or complete conversion point. The concentration of the retardants are set so that they have equivalent suppression power as defined in terms of equal decreases in flame velocity. It can be seen that despite the change

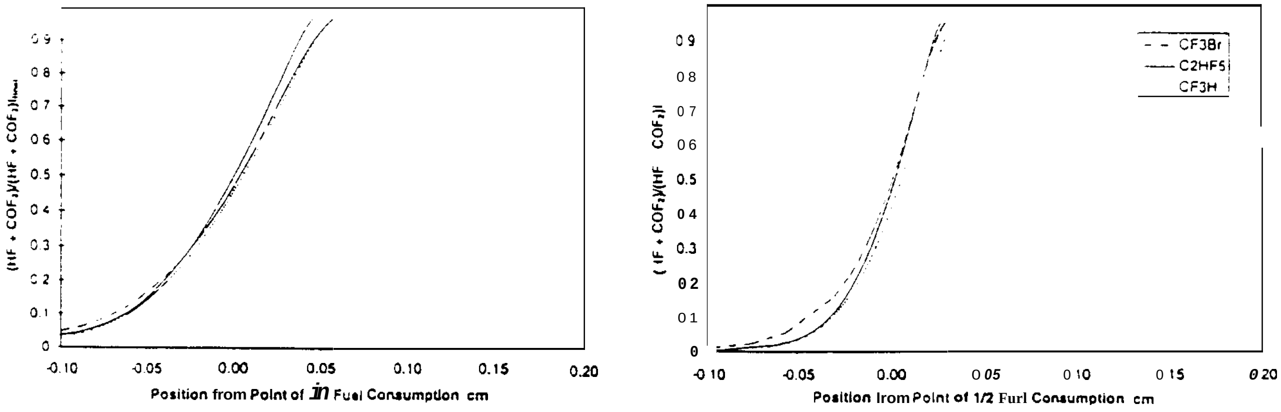


Figure 4: Normalized yields of hydrogen fluoride at equivalent suppression power €or stoichiometric mixture. Flame velocity = 10 cm/sec at left and 20 cm/sec at right

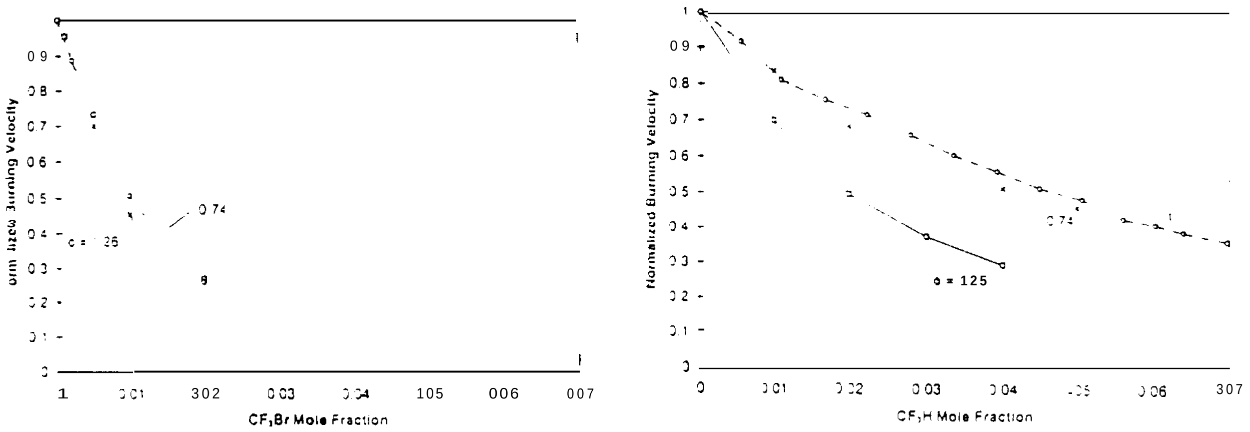


Figure 5: Flame velocity versus retardant concentration for fuel rich and lean mixtures €or CF_3Br and CF_3H. Points are results of calculations

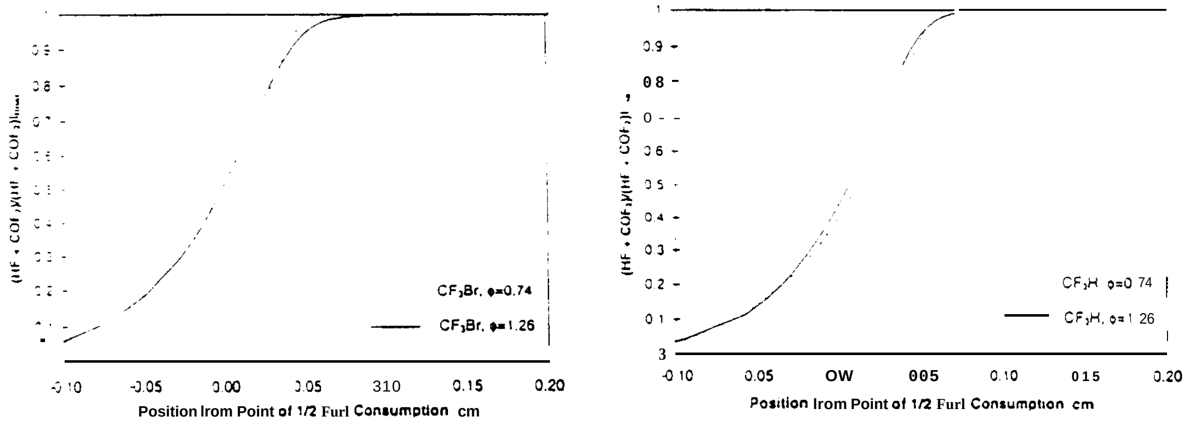


Figure 6: Normalized hydrogen fluoride yields as a function of position from flame €or fuel rich and fuel lean mixtures

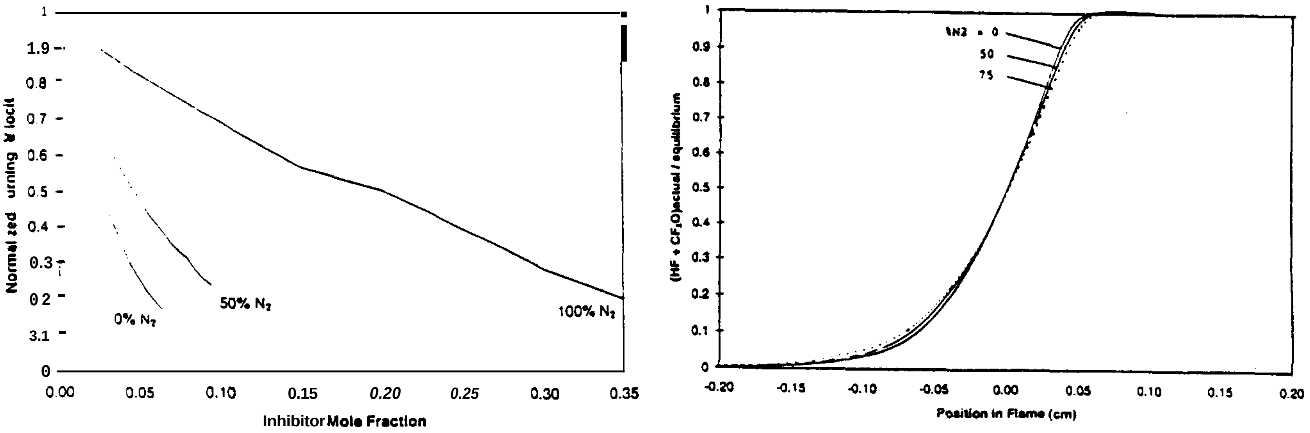


Figure 7: (a) Flame velocity versus CF_3CF_2H concentration with N_2 addition. (b) Normalized hydrogen fluoride yields

in the retardants and the consequent differences in the absolute quantities in hydrogen fluoride the shape of the curves are very similar. Note that for comparative purposes it is necessary to consider concentrations at the same position at the flame. Due to the steep rise in hydrogen fluoride concentration near the flame front differences are minimized. It is very tempting to interpret these results in the context of Linteris' observations on hydrogen fluoride yields. However, the different physical configurations suggest that considerable care must be exercised.

Figure 5 contains data on the dependence of flame velocities on retardant in slightly rich and lean methane air mixtures for CF_3Br and CF_3H. The general situation is very similar to that described earlier for the stoichiometric mixtures: there is a monotonic decrease in flame velocities as the amount of the retardants are increased but the rate of decrease is slowed at very low flame speeds. The ordering of the compounds are also relatively unchanged. It does appear that the inhibitor is more effective in the fuel rich region. Note that in these cases the initial flame speed are different.

Figure 6 is a plot relative HF yields from the runs carried out for Figure 5 and is analogous to those in Figure 4. As in Figure 4 the characteristic shapes of the HF yields as a function of position are not changed.

In Figure 7 we show typical results for the cases where the fluorinated agents have been mixed with an inert compound, in this case N_2. The general shape of the curves are the same as above. In the case of CF_3Br, suppression power is so large in comparison to that of N_2 the result is only due to its dilution. However as one goes to less efficient fire suppressants the effect of inerts which only contribute via dilution and heat capacity effects becomes somewhat more important. As before we plot the ratio of the concentration of hydrogen fluoride at any position with the equilibrium value in Figure 7b. This shows that adding of inerts can make some contribution. However it would appear that we should be working with larger molecules and thus heat capacities.

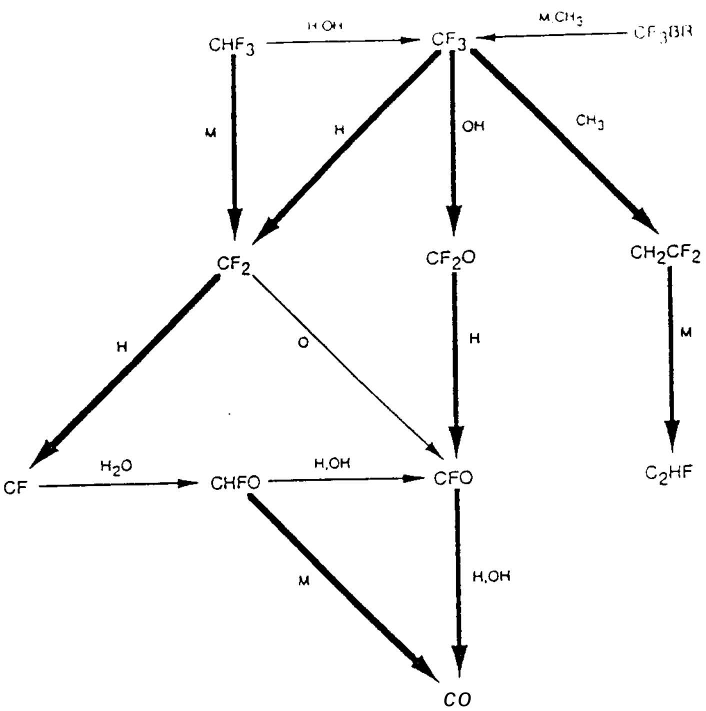


Figure 8: Mechanism for CF_3H and CF_3Br decomposition in methane-air flame. Solid lines refer to pathways that lead to HF formation.

DISCUSSION

The mechanism that is responsible for the production of hydrogen fluoride from the retardants is outlined in Figure 8 (where the bold arrows ultimately lead to hydrogen fluoride formation). This leads directly to the results summarized in Figure 2. It is very encouraging that the calculated inhibition rankings are very much in accord with the existing experimental numbers. Note that the present results are for a premixed flame while the experimental results are for diffusion flames. Our results clearly indicate the lessened suppression capability of the two halon substituents. A necessary consequence is the formation of larger quantities of HF in order to obtain the same suppression power. It should be noted that for the systems under consideration the only stable alternative product is CF_2O and since it is very easily hydrolyzed to HF, there are no particular advantage in converting hydrogen fluoride to this compound. Indeed, as seen in the figure legends when wet chemical methods are used, the total fluorines are always the sum of hydrogen fluoride and carbonyl fluoride. In fuel rich systems it may well be that some of the fluorine may appear as unsaturated organic fluorides. Although these may not be an acid gas, they have their own characteristic toxic properties. When they are present, kinetic modeling will be necessary to elucidate formation routes and amounts formed.

For this application, what is really desirable is a retardant that is chemically stable. Hence our attempt to substitute inerts. However, our results demonstrate that small compounds such as N_2 or CO_2 do not produce substantial effects. Clearly the need is for larger polyatomics. The number of possibilities are severely restricted in terms of the need for non-flammable and non-toxic substances. This inevitably leads to the large saturated perfluorinated compounds. We ignore unsaturated fluorinated compounds due to their possible toxic properties. However, except for perfluorinated methane most of these compounds, although more stable than the retardants we have studied, will be decomposed upon passage through the flame front. Thus, they will also contribute to the acid gas budget. However, in real systems decomposition of retardants can also occur outside the flame region. For these cases the more stable saturated perfluorinated compounds will yield less acid fluorides. One of the problems with these larger molecules is their lower vapor pressure and hence methods of delivery must be considered. Indeed, one is almost driven inevitably into consideration of multiphase systems.

The results from this study suggests that the next step in this program must be to use the model to derive a hypothetical molecule that has a sufficient heat capacity so that one could obtain the fire suppression capability of CF_3Br without yielding any hydrogen fluoride at all. It is likely that this will not lead to any realistic gas phase molecule. However, it may well be the beginning of modeling the situation where particulates are introduced. It is true that Chemkin is designed for homogeneous gas phase reactions only. Nevertheless, from the thermodynamic properties of a particulate and heat transfer capabilities one may well be able to construct a "virtual" molecule to serve this purpose. This will of course give us information on the nature and quantity of the particulate that will serve this purpose. A particular advantage of this approach is that it will be possible to use the existing data base. An additional improvement will probably be the use of a more realistic fuel than methane. A higher hydrocarbon such as propane or some mixture may well be more appropriate. This is well within our capabilities.

It should be emphasized that the results of the type of simulations are crucially dependent upon the accuracy of the chemical kinetic data base. Furthermore, they are not truly predictive except in the case where the model in strictly applicable. A real fire situation is, of course, extremely complex and the premixed system under consideration here must be regarded as an apptoximation. Thus, there is the need for constant checks with experiments. It should be noted that the laboratory experiments themselves are approximations to the actual situation. However, with increasing experience one is emboldened to use the existing models in more creative manners. Indeed, it can be regarded as another testing method. Hence, our suggestion for using the models to obtain desired properties and then finding molecular or particulate systems that will match them. Certainly, in terms of the cost saving it may be almost mandatory to carry out simulations before large scale testing so as to optimize the information that can be obtained.

ACKNOWLEDGEMENT

This work was sponsored by the Strategic Environmental Research and Development Program (SERDP)

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