

ACID GAS PRODUCTION IN INHIBITED DIFFUSION FLAMES

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Abstract

The proposed replacements to halon 1301, mainly fluorinated and chlorinated hydrocarbons, are expected to be required in significantly higher concentrations than CF_3Br to extinguish fires. At these higher concentrations the by-products of the inhibited flames may include correspondingly higher portions of corrosive gases, including HF and HCl. To examine the chemical and transport-related mechanisms important in producing these acid gases, a series of inhibited flame tests have been performed with several types of laboratory-scale burners, varying agent type and concentration, and fuel type. A wet-chemistry analysis of the final products of the flames using ion-selective electrodes for F^- and Cl^- provided an experimental basis for quantitative understanding of the HF and HCl production. Production rates were measured for co-flow laminar and turbulent diffusion flames. Systematic selection of the agent concentrations, burner type, and air flow rates allowed an assessment of the relative importance of agent transport and chemical kinetics on the acid gas production rates. These experimental results were then compared to a model which estimates the maximum HF and HCl production rates based on stoichiometric reaction to the most stable products. The results demonstrate the relative significance of F, Cl, and H in the inhibitor and fuel, as well as the effect of different burner configurations.

Introduction

Although the corrosiveness and toxicity of candidate fire suppressants have always been recognized as important, it has also been observed that since the most effective flame suppressants are not chemically inert the properties of their decomposition by-products are also important. Halogenated hydrocarbons are widely used and effective flame suppressants; however, the production of the most effective of these (for example halon 1301 CF_3Br and 1211 CF_2ClBr) has been discontinued. The proposed alternatives to these halons, primarily fluorinated and chlorinated hydrocarbons, are required in much higher concentrations. Consequently, they have the potential to have correspondingly higher proportions of decomposition by-products. Since most hydrocarbon-based compounds at flame temperatures typically undergo both thermal decomposition and decomposition by radical attack, the formation of products other than the inhibitor itself is highly probable. The acid gases hydrofluoric (HF) and hydrochloric acid (HCl) are believed to be the most corrosive products. The objective of this research project is to obtain an understanding of the chemical and physical process of acid gas formation in inhibited flames in order to predict the amount of acid gas formed in suppressed fires, allowing a comparison of the relative amounts of acid gases formed by alternative suppressants.

Background

The halogen acid or hydrogen halide HX (where X represents the halogen) is a thermodynamically stable product in mixtures containing hydrogen and halogen atoms. Formation of acid gases in inhibited hydrocarbon flames has been studied for many years. The research can be categorized as

either global measurements of HF produced in suppressed fires, or detailed flame structure measurements. Burdon *et al.* (1955) ignited mixtures of fuel, air, and CH_3Br in flasks, analyzed the products and found copious amounts of HBr. Numerous premixed low pressure flame studies (e.g. Wilson, 1965; Biordi *et al.*, 1973; Safieh *et al.*, 1982; and Vandooren *et al.*, 1988) used mass spectroscopy to measure the profiles of hydrogen halides and other products in hydrogen, carbon monoxide, and hydrocarbon flames inhibited by CH_3Br , CF_3Br , and CF_3H . These studies indicated conversion efficiencies of the halogens in the inhibitor into halogen acids on the order of unity. Acid gas formation in hydrocarbon-air pool fires suppressed by CF_3Br has been studied by Sheinson *et al.* (1981, 1982). These studies, in test volumes of 1.7 and 650 m^3 , stressed the difficulties in probe sampling for acid gases. The latter study described an in situ IR absorption method for measuring HBr and HF. To overcome these limitations and also provide time-resolved acid gas concentration data, Smith *et al.* (1993) developed a new HX sampling technique and obtained HX and inhibitor concentrations as functions of time for discharge of CF_3Br into a 56 m^3 space. In a series of experiments with a variety of fuels and halogenated inhibitors, Yamashika (1973) showed that the extinction time for a compartment fire sprayed with inhibitor is dependent upon the discharge rate and room volume. He then showed (Yamashika, 1974) that the amounts of hydrogen halides and carbonyl halides are also dependent upon the discharge rate. Using a simple model of acid gas formation based on the steady-state rates, he developed a model of transient acid gas formation to explain his results.

In more recent studies, Ferreira *et al.* (1992a,b) injected CF_3Br , C_3HF_7 , and C_4F_{10} into an enclosure fire and measured the HF produced using ion-selective electrodes. Di Nenzo *et al.* (1993) introduced halon alternatives into compartment fires and measured the HF, HCl, and COF_2 produced using Fourier transform infrared spectroscopy. These studies again confirmed the importance of injection rate and fuel consumption rate on the amount of acid gas produced. Filipczak (1993) introduced CF_2ClBr and CF_3Br into a methane flame and measured the O_2 , CO_2 , H_2O , HF, HCl, HBr, and unreacted inhibitor using a mass spectrometer. Hoke and Herud (1993) are currently developing a fast-response ion-selective electrode for measuring HF and HCl produced in extinguished fires in crew compartments of combat vehicles.

Previous research related to understanding acid gas formation in inhibited flames can be seen to include both detailed flame structure measurements and global measurements of HF produced in suppressed fires. The inhibited low-pressure premixed flame studies provide detailed data on the concentration profiles of major species as a function of position in the flame for inhibition by CH_3Br , CF_3Br , and CF_3H . These results provide the basis for obtaining a good understanding of the underlying chemical kinetics of the formation of acid gases. The second category of experiments is global measurements of the amount of acid gas formed in suppressed diffusion flames. These studies provide important information on the magnitude of the acid gases produced and allow a comparison of the relative amount of acid gases formed by new halon alternatives. In addition, progress has been made (Yamashika, 1974; Smith *et al.*, 1993) in developing engineering models of acid gas formation in suppressed flames. There remains a need to develop a fundamental basis for interpreting the data on acid gas formation in flames suppressed by halon alternatives and to understand the chemical kinetic rates of acid gas formation in flames inhibited by these alternative agents. In particular, there exists a need to understand the relationship between fuel and inhibitor type, flame characteristics, agent transport rates, and the concentrations of by-products formed.

Approach

The formation of toxic and corrosive by-products in flames suppressed by halogenated hydrocarbons may be controlled by transport rates of the inhibitor into the flame, chemical kinetic rates, and equilibrium thermodynamics. These phenomena in turn will be affected by the fuel type, local

stoichiometry, inhibitor type and concentration, and the characteristics of the flow field (mixing rates, strain, and stabilization mechanisms). The approach in this research is to study the influence of key parameters (including the fuel type, inhibitor type and concentration, rate of inhibitor injection, and flame type) through systematic experiments on laboratory-scale flames. The results of four specific sets of experiments are presented in this article along with a fundamentally-based model which provides an estimate of the amounts of acid gases formed.

The first set of experiments involve steady-state measurements of the HF production rate for inhibitors added to the air stream of a propane-air cup burner diffusion flame; in the second set, the inhibitor was instead added to the fuel stream. The third set of experiments were also conducted with propane-air diffusion flames (at the same flow rates as the cup burner), but with a co-flow jet burner which produced either laminar or turbulent flames, so that the effect of turbulent mixing could be studied. These first three sets of experiments were all conducted with twelve alternative agents. In the fourth set of experiments, again with the propane-air cup burner at the same fuel and air flow rates, the concentration of C_2HF_5 in the air stream was increased from zero to 125% of the extinction concentration, and the amount of HF produced in the transient suppression was measured.

Experiments

Steady-State Cup Burner Experiments: Inhibitor Addition to Fuel or Air Stream

The experiments were performed with a propane-air co-flow diffusion flame modelled after the cup burner described by Booth *et al.* (1973) and Bajpai (1974). The experimental arrangement is shown in Figure 1. The burner consists of a 28 mm diameter pyrex cup positioned concentrically in a 12 cm diameter 45 cm tall chimney at about 15 cm from the base. In these experiments with propane, the cup burner was modified for use with a gaseous fuel. The cup was filled with glass beads and covered with a stainless steel screen. The air used was shop compressed air (filtered and dried) which was passed through an 0.01 micron filter to remove aerosols and particulates, a carbon filter to remove organic vapors, and a desiccant bed to remove water vapor. The fuel gas was propane (Matheson, CP grade¹) at flow rate of 0.114 ± 0.005 l/min at 21 ± 1.5 °C. Gas flows were measured with rotameters (Matheson 1050 series) which were calibrated with bubble and dry (American Meter Co. DTM-200A and DTM-325) flow meters. Inhibitor gases were of different purities from various suppliers.

Before measuring HF in the product gases, the concentration of inhibitor in the air stream necessary to extinguish the flame was determined. The inhibitor was then added to the co-flowing air stream at a concentration of either 50 or 90% of the extinguishing concentration, and the product gases were sampled for acid gas. A wet chemistry technique was used to measure the HF and HCl concentrations in the exhaust gases from the co-flow diffusion flames. A glass funnel was placed over the chimney and the exhaust gases passed through the 4.0 cm diameter neck. A quartz probe, centered in the neck, extracted a measured fraction of the product gases (approximately 0.5%), and directed the gases through polyethylene sample lines to a polyethylene impinger filled with water which trapped the acid gases. The sample flow was continued for a total collection time of sixty seconds. The sample was tested for F⁻ and Cl⁻ using ion-selective electrodes (Orion models 96-09 and 96-17B). It should be noted that since COF_2 is known to hydrolyze rapidly in the presence of water, this technique for acid gas measurement includes F⁻ from both HF and COF_2 . To reduce the effects of sampling losses reported by other investigators, a quartz probe and polyethylene sample lines were used, the

¹Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment are necessarily the best available for the intended use.

distance from the chimney top to the impinger was kept small (~ 10 cm) and the interior of the probe and sample lines were rinsed with water (which was returned to the impinger) immediately after the sample was collected. The burner was operated for sixty seconds whereupon the inhibitor was added and the gas sampling started. After sixty more seconds the gas sampling flow was stopped and the burner shut down. The tests were conducted with the agents CF_3Br , C_2F_6 , C_3F_8 , C_4F_8 , C_4F_{10} , C_2HF_5 , C_2HClF_4 , C_3HF_7 , $\text{C}_3\text{H}_2\text{F}_6$, $\text{C}_2\text{H}_2\text{F}_4$, CHF_2Cl , and $\text{CH}_2\text{F}_2/\text{C}_2\text{HF}_5$.

For these twelve agents, the inhibitor was also added to the propane rather than the air stream. This served two purposes. In order to understand the formation rate of HF from inhibitor decomposition, one must know the mass flux of the inhibitor into the reaction zone of the flame. For agent addition to the air stream, it is possible to estimate this flux; however, addition of the agent to the fuel stream removes the uncertainty in this estimation. Addition of the agent to the fuel stream also changes the chemical environment seen by the agent. Since the species profiles are distinctly different on the air side compared to the fuel side of a diffusion flame, agent addition to the fuel side may provide a different chemical route leading to HF formation.

Steady-State Jet Burner Experiments: Inhibitor Addition to Air Stream

In order to produce a turbulent jet diffusion flame, the propane-air cup burner apparatus was modified by changing only the burner. The one inch diameter cup with glass balls and the stainless steel screen was replaced with a 25 cm long pyrex tube with a 0.50 mm diameter opening positioned concentrically and with its tip at the same height as the top of cup burner. The cold flow Reynolds number based on the exit velocity in the tube was 10,500. This second burner, referred to here as the jet burner, was designed to provide turbulent mixing of the inhibitor in the air stream with the fuel. The burner was also tested at 50 and 90% of the extinction concentration for inhibitor in the air stream.

Transient Cup Burner Experiments

To gain a basic understanding of the physical and chemical system in the inhibited diffusion flames described above, it was first necessary to study simple systems in a steady-state mode as described above. However, when HF is formed during suppression of an actual fire, the process is transient. The propane-air cup burner co-flow diffusion flame was used to study the effect of transient addition of inhibitor to the air stream. In these experiments, a computer-operated mass flow controller (described below) ramped the inhibitor flow linearly in time to a flow rate which produced an inhibitor concentration in the air stream 25% above the extinction concentration. The same gas sampling system described above was used to extract the product gases, except that two impingers in series were used with no filter, and the sampled flow rate represented about 8% of the total flow (about eighteen times higher than for the steady-state experiments). The effective ramp time varied from 6 to 15 seconds and the product gases were sampled for 60 seconds. The wet chemistry technique described above was used for determining the F concentration in the impinger.

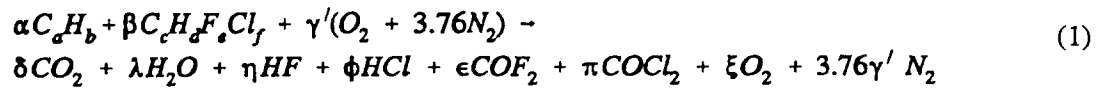
Model for Acid Gas Formation

A model for the amount of acid gas formed in an inhibited diffusion flame can be developed in a manner analogous to the determination of the local equivalence ratio and structure for diffusion flames. In the classic Burke-Schumann analysis (Burke and Schumann, 1928), the chemical reaction is assumed to occur at a sheet. This location serves as a sink for the fuel and oxidizer which are assumed to diffuse there in stoichiometric proportions based on complete reaction to the most stable products (i.e., HF formation is assumed to be controlled by equilibrium thermodynamics rather than chemical kinetics). This model will be referred to as the stoichiometric model. In the case of a flame

inhibited by halogenated hydrocarbons, a thermodynamic analysis shows that in equilibrium, the inhibitor readily breaks down to CO₂, HX, and H₂O. Consequently, the inhibitor is assumed to be consumed like a fuel and form the most stable products. The assumptions used in the model are:

1. complete reaction of the inhibitor molecule with fuel and air to the most stable products;
2. no destruction of the inhibitor through interaction with the post-combustion flame gases;
3. no loss of acid gases to the chimney walls; and
4. perfect mixing of the product gases.

An equation for the reaction of an arbitrary hydrocarbon with air and an arbitrary halogenated hydrocarbon inhibitor is:



In this equation α is specified as is β when inhibitor is present only in the fuel stream or for a premixed flame. For inhibitor present in the air stream, β is determined by the concentration of inhibitor in the air stream and the ratio of the diffusion rates for oxygen and inhibitor by the equation

$$\beta = \frac{\alpha(a+b/4)}{1/(\rho r) - [c+1/4(d-e-f)]} \quad (2)$$

where ρ is the ratio of the binary diffusion coefficient of the inhibitor in nitrogen to that of oxygen with nitrogen and r is the ratio of the concentration of inhibitor to oxygen in the air stream. For simplicity, the diffusion rate of the inhibitors was assumed initially to be equal to that of O₂ in N₂ (i.e. $\rho=1.0$). To account for the large molecular weights of the inhibitors relative to oxygen, an improved estimate was also obtained by using the molecular weight correction factor

$$\sqrt{\frac{W_i + W_{N_2}}{W_{N_2} W_i}} / \sqrt{\frac{W_{O_2} + W_{N_2}}{W_{O_2} W_{N_2}}} \quad (3)$$

where W is the molecular weight and the subscripts N₂, O₂, and i refer to nitrogen, oxygen, and inhibitor. An atom balance for all species provides all of the unknown coefficients, and an estimate of the amount of acid gas formed per mole of fuel $(\eta + \phi)/\alpha$ is then readily found.

Results

Three of the experiments described above involved steady-state diffusion flames: the cup burner with agent addition to the air stream, the same burner with agent addition to the fuel stream, and the jet burner with agent addition to the air stream. In all of these experiments, the fuel was propane at a flow rate of 0.114 ± 0.005 l/min with co-flowing air at 20.7 ± 0.8 l/min. These results are discussed first, followed by the transient cup burner tests.

Steady-State Diffusion Flame Results

The acid gases produced were measured at inhibitor concentrations of 50 and 90% of the extinction concentration for agent addition to the air stream for the cup and jet burners, and at 70% of the extinction concentration for inhibitor added to the propane stream for the cup burner. Table 1 lists

the extinction concentrations for each agent for inhibitor added to the air stream of both burners, and the ratio of the inhibitor flow to the fuel flow for inhibitor added to the fuel stream of the cup burner.

As the table indicates, the jet burner flame typically requires about 50% less inhibitor in the air stream to extinguish the flame than the cup burner, even for identical fuel and air flows, although there are notable exceptions: CF_3Br , which required about one fifth as much inhibitor in the jet burner than in the cup burner, and C_2HF_5 and the $\text{CH}_2\text{F}_2/\text{C}_2\text{HF}_5$ mixture which had nearly the same extinction concentrations. In addition to providing the necessary extinction conditions for specification of inhibitor flows at 50 and 90% of extinction, these results also demonstrate the sensitivity of the extinction conditions to the burner geometry.

Table 1 - Extinction conditions for halon alternatives added to the air or fuel of co-flow propane-air cup burner and jet burner flames.

Inhibitor	Extinction Concentration in Air (mole percent)		Ratio of Inhibitor to Fuel Flow
	jet	cup	cup (agent in fuel)
CF_3Br	0.8 (\pm 0.02)	4.3 (\pm 0.1)	0.88 (\pm 0.08)
$\text{C}_3\text{H}_2\text{F}_6$	4.0 (\pm 0.1)	7.2 (\pm 0.2)	3.5 (\pm 0.3)
$\text{CH}_2\text{F}_2/\text{C}_2\text{HF}_5$	15.5 (\pm 0.5)	15.2 (\pm 0.5)	11.8 (\pm 1)
C_4F_{10}	3.2 (\pm 0.1)	5.0 (\pm 0.2)	1.6 (\pm 0.1)
C_2HClF_4	4.2 (\pm 0.1)	8.6 (\pm 0.3)	2.6 (\pm 0.2)
$\text{C}_2\text{H}_2\text{F}_4$	9.5 (\pm 0.3)	11.1 (\pm 0.3)	5.6 (\pm 0.5)
C_2HF_5	6.2 (\pm 0.2)	10.2 (\pm 0.3)	3.1 (\pm 0.3)
CHClF_2	6.7 (\pm 0.2)	13.8 (\pm 0.4)	4.3 (\pm 0.4)
C_3HF_7	4.2 (\pm 0.1)	7.6 (\pm 0.2)	2.2 (\pm 0.2)
C_2F_6	3.8 (\pm 0.1)	9.4 (\pm 0.3)	2.5 (\pm 0.2)
C_3F_8	3.8 (\pm 0.1)	7.5 (\pm 0.2)	2.0 (\pm 0.2)
C_4F_8	5.1 (\pm 0.2)	7.6 (\pm 0.2)	2.2 (\pm 0.2)

The measured HF for these diffusion flames is presented in Figures 2 and 3 which show the HF produced (moles/min) for each inhibitor for the four burner/inhibitor combinations. The total flow was about 1 mole/min. The figures indicate that the amount of HF varies with the flame type by about a factor of two and with inhibitor type by about a factor of ten. Hydrogen chloride was also measured in these experiments and the results are qualitatively the same as for HF. For clarity of presentation, only the HF results are reported.

In order to provide insight into the controlling parameters in inhibited diffusion flames, the data of Figures 2 and 3 are presented in an alternative form in Figures 4 to 15. In these figures, the amount of HF produced is plotted as a function of the inhibitor concentration in air. The symbols represent the experimental data, while the lines marked F and H represent estimates of the fluxes of fluorine and hydrogen into the reaction zone based on the stoichiometric model described above.

Figure 4 shows the measured and estimated HF production rates in a propane-air diffusion flame for C_2F_6 in the cup and jet burners. We concentrate first on the solid lines which present the estimated fluxes of fluorine and hydrogen into the reaction zone. The curve labeled F in Figure 4 is the maximum fluorine atom mass flux into the reaction sheet of the diffusion flame calculated using

the stoichiometric model described above. The curve labeled F' in Figure 4 is the fluorine mass flux when the diffusion rate of the inhibitor relative to oxygen is modified to account for preferential diffusion of oxygen relative to the inhibitor as in Eq. 3. The fluorine and hydrogen fluxes are estimated based on actual experimental flows which vary slightly from run to run. These variations in flows cause the discontinuities in the F and H curves as in Figure 12.

Qualitatively, the curves F and F' in Figure 4 are seen to increase with increasing inhibitor concentration in air, and the mass flux of inhibitor into the reaction zone is lower when a lower rate of diffusion is used for the inhibitor. The curves labeled H and H' (coincident for C₂F₆) show the estimated hydrogen atom flux into the reaction zone as a function of inhibitor concentration in the air stream. Since this inhibitor does not contain hydrogen, all of the hydrogen is from the propane, and increasing inhibitor in the air stream does not increase the hydrogen flux into the flame. One would expect that the HF production rate would not be greater than the estimated flux of F or H into the reaction zone. For this inhibitor, the flame appears to be hydrogen limited above about 5% C₂F₆ in the air stream; however, when there is not enough hydrogen, the most stable product is COF₂, which is known to hydrolyze rapidly in the presence of water, and would also appear as F in the impinger. Consequently, it appears that as the ratio of the fluorine to hydrogen fluxes into the flame increase above unity, HF² is not forming at greater rates.

Also shown in the figure are the experimentally measured HF production rates for the jet and cup burners (labeled j and c respectively) at 50 and 90% of the extinction concentration of C₂F₆. As indicated, the measured quantities of HF are lower than both the fluorine and hydrogen limits, and the measured values are closer to the estimated limits when the effects of preferential diffusion are included.

Although the cup and jet burner results are plotted together, the phenomenological behavior of jet burner is distinctly different from that of the cup burner. Because the flame of the jet burner first stabilizes as a co-flow diffusion flame anchored at the outlet of the jet, the heated gases have a much lower Reynolds number, keeping the flow laminar. As inhibitor is added to the air stream, the flame grows in length (as it would in increasing the fuel flow rate). Eventually, the flame lifts off the burner surface by about 5 cm to form a lifted turbulent jet diffusion flame. With further inhibitor addition, the flame eventually blows off. These concentrations are referred to as the extinction concentrations (see Table 1) and are found to be much lower (about half) of the values determined for the cup burner. In the tests at 50% extinction, the flow was laminar, whereas at 90% of extinction, the flow was turbulent and the flame was lifted. Transport of the agent into the flame is estimated in the stoichiometric model assuming molecular diffusion. The goal of these experiments was to compare the model's prediction of HF formation for a diffusion flame where turbulent mixing occurs, and identify if the enhanced mixing increases the HF production. Figures 4 to 15 show that HF production in the turbulent burner is higher (except for C₂F₆ and C₄F₈) but that it is still not above the estimate of the fluorine flux based on equal transport for O₂ and the inhibitor (the curve labeled F).

When viewed in this manner, the behavior of the alternative inhibitors falls into three categories. In the first category are those inhibitors (C₂F₆, C₃F₈, C₄F₁₀, C₃F₈, C₂HF₅, and C₃HF₇; Figures 4 to 8) where, at the highest inhibitor concentration tested (cup burner at 90% of extinction), the estimated hydrogen flux into the reaction zone is lower than the fluorine flux, and is not a strong function of the inhibitor concentration. For these inhibitors, the HF produced does not increase significantly when the inhibitor concentration in the air stream increases above that necessary for a hydrogen/fluorine ratio in the reaction zone of about unity (the region of where the lines marked F and H or F' and H' cross in

²In the discussion below the species HF is used for brevity; however, in all cases it refers to any species which would form fluoride ion when the product gases are bubbled through a distilled water bath (which is the case for HF and COF₂).

Figures 4 to 15). The second category includes those inhibitors ($C_2H_2F_4$, C_2HClF_4 , $C_3H_2F_6$, and CH_2F_2/C_2HF_5 ; Figures 10 to 13) for which the estimated H and F fluxes are about equal. For these inhibitors, the amount of HF produced increases with increasing inhibitor concentration in the air, but the highest concentration tested corresponds roughly to a unity F/H ratio in the reaction zone. The last category consists of CF_3Br and $CHClF_2$ (Figures 14 and 15) for which the estimated hydrogen flux is much higher than fluorine flux, and there is estimated always to be more hydrogen than fluorine in the reaction zone. For these inhibitors, the HF produced is always increasing with higher agent concentration in the air stream.

Although the stoichiometric model is very simple and is only expected to provide an estimate of the upper limit on the amount of HF formed, it is instructive to investigate the possible reasons that the measured HF production rates might be lower than the estimates. Lower HF may be measured in the experiments due to experimental difficulties, for example: loss of HF to the chimney walls, loss in the sampling system, HF undetected by the ion-selective electrodes, or imperfect mixing in the product gases. Based on parametric tests, these loss mechanisms were found to be of secondary importance. The predicted values of the HF production do not include chemical kinetic limitations, and the estimates of transport rates into the reaction zone are only approximate. One simple test to remove the uncertainty associated with agent transport into the flame is to add the agent to the fuel stream in a diffusion flame, or to add the agent with the fuel and air in a premixed flame. Addition of the agent to the fuel stream in a diffusion flame is discussed next; the premixed experiments are still in progress.

The results for the inhibitor addition to the fuel stream in the cup burner (labeled f) are plotted at an inhibitor concentration of zero so that they can be included in Figures 4 to 15. The agents make 37 to 57% of the maximum HF they could based on the flow rates (in this case measured) of H and F into the flame, except for $C_3H_2F_6$ and C_2HF_5 which make slightly lower (about 33%) and CF_3Br which makes essentially all the HF it can (Br was not measured). Clearly there are kinetic limitations to HF formation when the inhibitor is added to the fuel stream in a diffusion flame.

Transient Suppression of Cup Burner Diffusion Flames

As described above, the concentration of C_2HF_5 in the air stream of the propane cup burner flame was increased linearly in time to a value 25% above the extinction concentration so that the flame extinguished; the fluoride formed during this transient process was measured. The inhibitor concentration in the air stream was increased at different rates. Figure 16 shows the measured mass of F⁻ collected as a function of the effective ramp time (determined as the time from when the inhibitor reaches the flame to flame extinction) for these ten experiments. Also shown is the predicted fluoride mass based on the stoichiometric model. Since the inhibitor concentration increases linearly in time, the HF production rate at each concentration of inhibitor in the air stream can be estimated from the steady-state results shown in Figure 8. For these predictions, the steady-state HF concentration in the product gases is assumed to be the equilibrium value at each inhibitor concentration up to a concentration 5% (which corresponds to a unity F/H ratio in the flame) whereupon the HF production rate is held constant at the value predicted for F/H = 1 (refer to Figure 8). As Figure 16 indicates, the agreement is reasonable considering the simplicity of the model.

Conclusions

1. The formation rate of HF in diffusion flames is strongly influenced by the mass flux of inhibitor into the flame sheet. For diffusion flames with the inhibitor added to the air stream, there appear to be kinetic limitations to the rate of HF formation for most but not all of the agents tested which increase as the inhibitor concentration in the air stream increases. Many of the agents (for example $C_2H_2F_4$, C_2HClF_4 , $C_3H_2F_6$, CH_2F_2/C_2HF_5 , CF_3Br and $CHClF_2$) produced HF at rates

within about 25% of that given by equilibrium thermodynamics in the diffusion flames tested. Most of the perfluorinated agents tested (C_2F_6 , C_3F_8 , and C_4F_{10}) and the agents C_4F_8 , C_2HF_5 and C_3HF_7 produced 0 to 35% less than the equilibrium values except when the estimated fluorine to hydrogen flux into the flame goes above unity when they show no further increase with increasing inhibitor concentration in the air stream.

2. Co-flow diffusion flames with inhibitor added to the fuel stream show HF production rates about 50% of the values given by equilibrium thermodynamics, clearly implying kinetic limitations.
3. Formation of HF during transient suppression of a diffusion flame can be predicted based on the steady-state results from a range of inhibitor concentrations in the air stream. The results have been verified for concentration ramps of six to fifteen seconds and are expected to be valid for much shorter (less than a second) or much longer (up to any length) times.
4. Further research is needed to understand the reasons for and implications of the kinetic limitations to the HF formation rate in flames with high fluorine loading, and to determine the fate of the fluorine which does not go to HF.

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Figure Captions

Figure 1 - Experimental apparatus for co-flow diffusion flame studies of acid gas formation in inhibited propane-air flames.

Figures 2 and 3 - Measured HF production rates in co-flow propane-air diffusion flames. Data are shown for cup and jet burners at 50 and 90% of the extinction concentration for agent added to the air stream, and at 70% in the fuel stream in the cup burner. Note that in Figure 3 the curves for CF_2H_2 /- C_2HF_5 and $C_2H_2F_4$ are reduced by a factor of 4.

Figures 4 to 15 - Moles of HF produced as a function of the inhibitor concentration in the air stream for the cup (c) and jet (j) burners at 50 and 90% of extinction, and with inhibitor addition to the fuel stream (f) of the cup burner at 70% of extinction. The squares are the experimental data. The lines show the estimated fluorine (F) and hydrogen (H) flux into the reaction zone using the stoichiometric model, based on equal rates of diffusion for O_2 and inhibitor (un-primed) and with binary diffusion coefficients corrected for molecular weight variations (primed). The estimated error bars on the HF measurements are $\pm 10\%$. Figures 4 to 15 provide the results for C_2F_6 , C_3F_8 , C_4F_{10} , C_4F_8 , C_2HF_5 , C_3HF_7 , $C_2H_2F_4$, C_2HClF_4 , $C_3H_2F_6$, CF_2H_2/C_2HF_5 , CHF_2Cl , and CF_3Br respectively.

Figure 16 - Milligrams of fluoride produced (points) during suppression of a cup burner propane-air diffusion flame by addition of C_2HF_5 to the air stream as a function of the inhibitor ramp time (the time necessary for the inhibitor concentration to reach the extinction value). The solid line presents the predicted amount of fluoride produced using the stoichiometric model.

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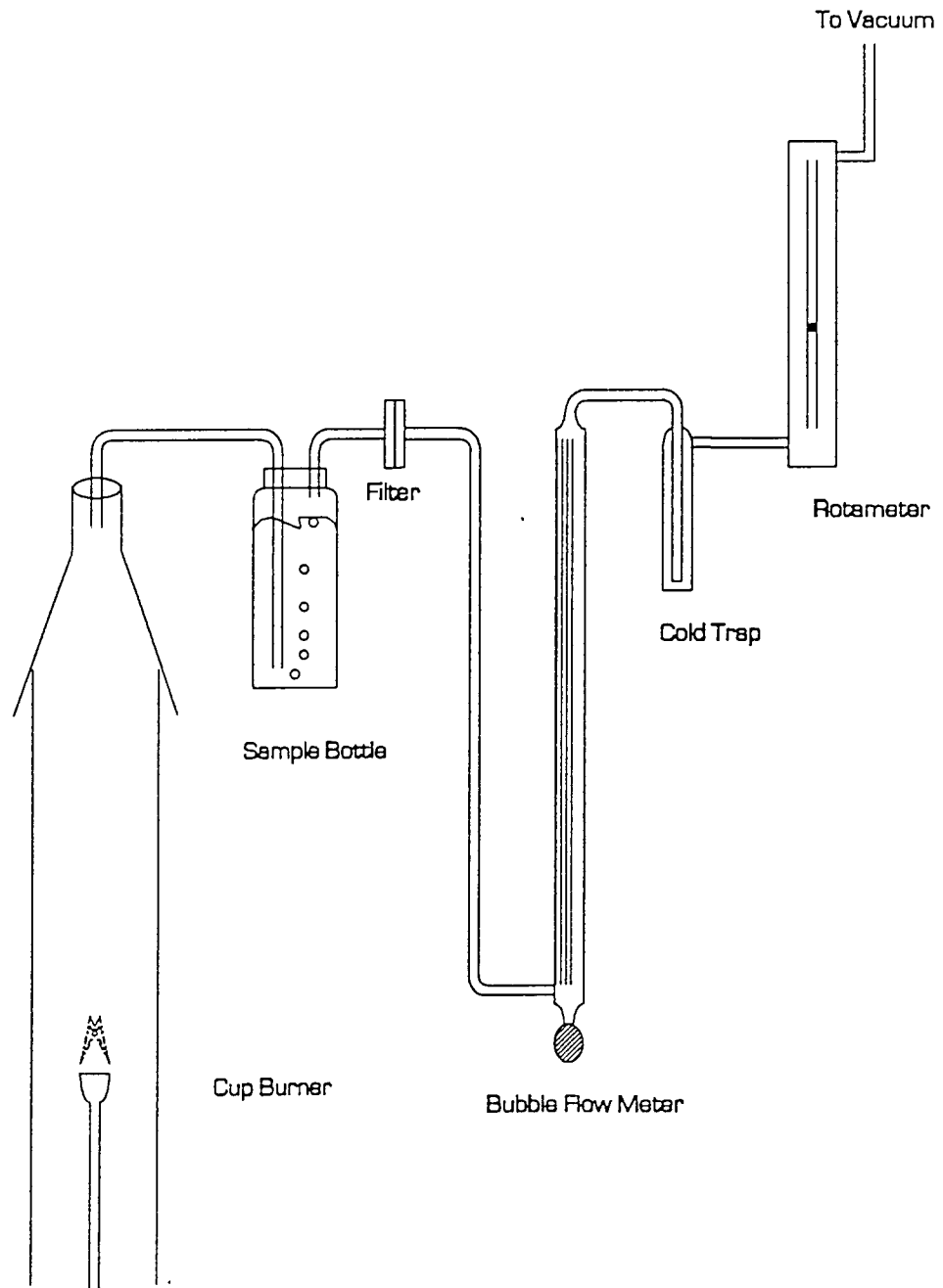


Figure 1

Figure 2

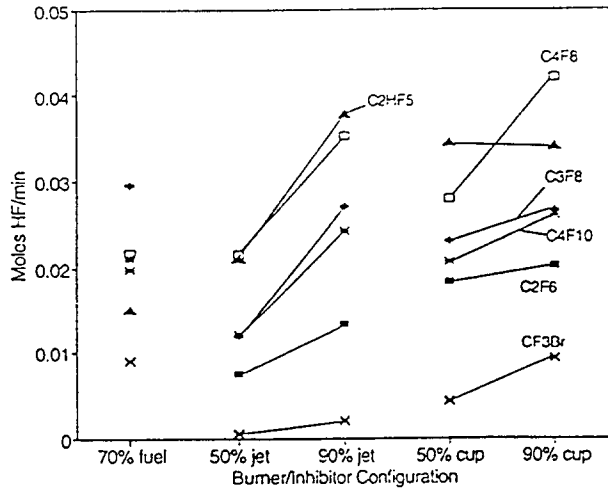


Figure 3

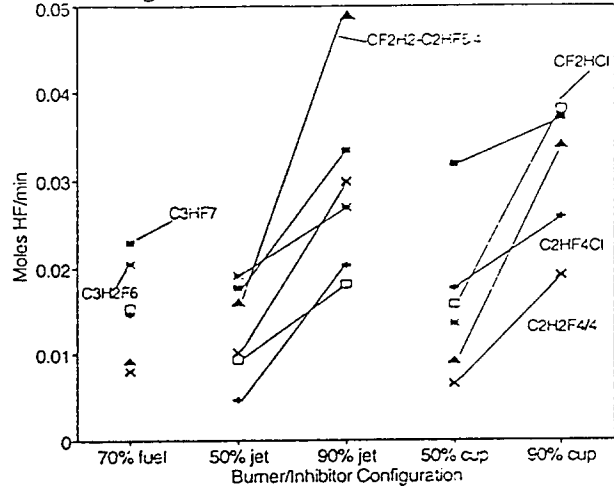


Figure 4

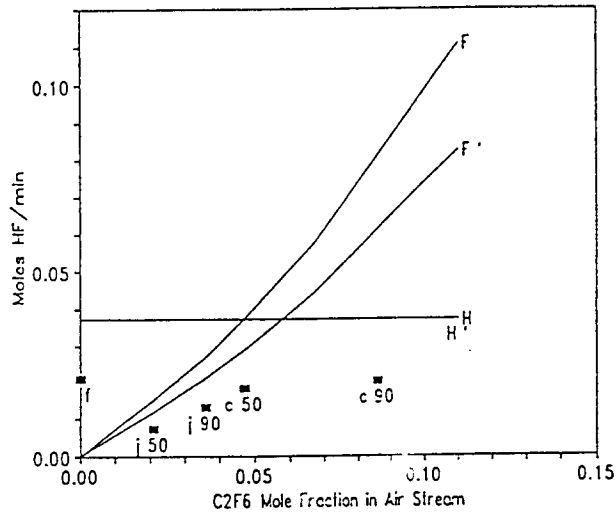


Figure 5

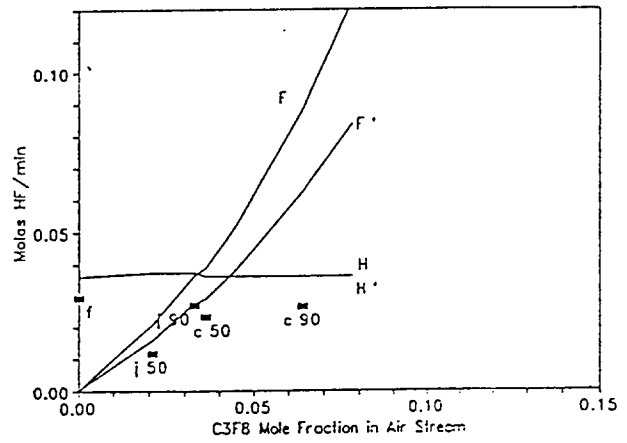


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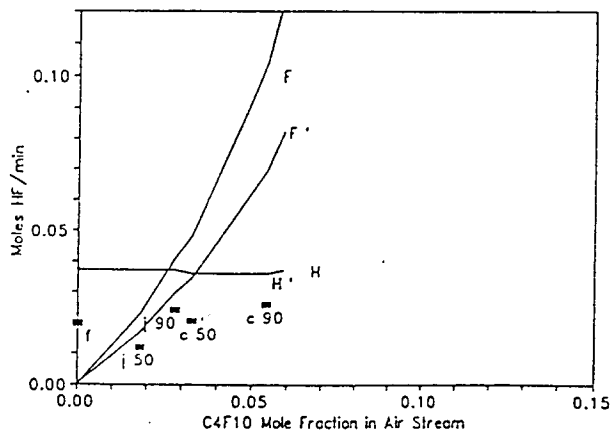


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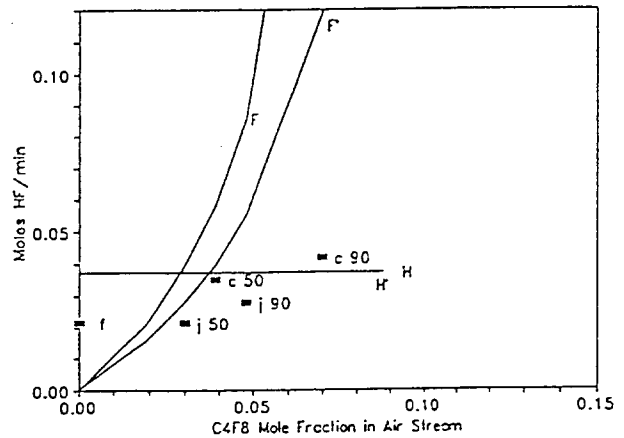


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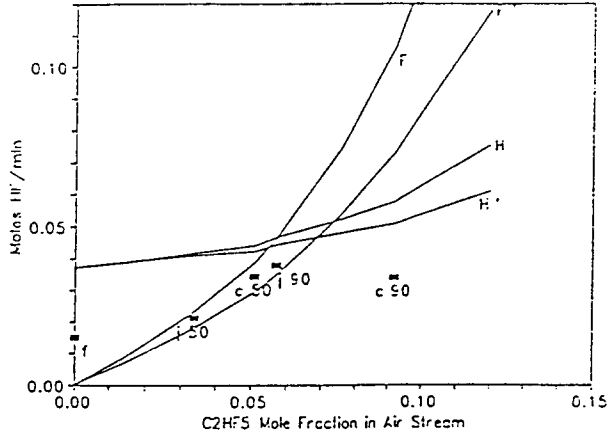


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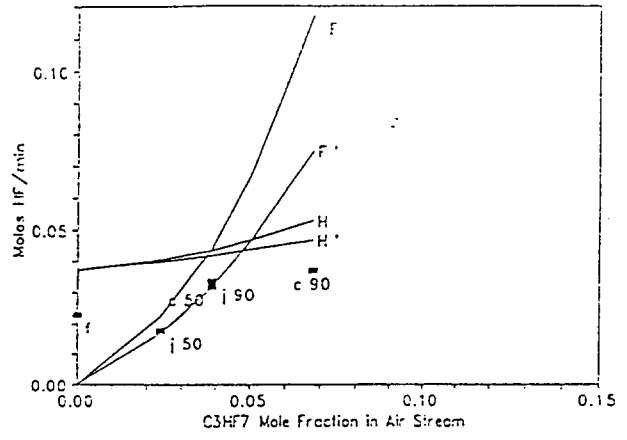


Figure 10

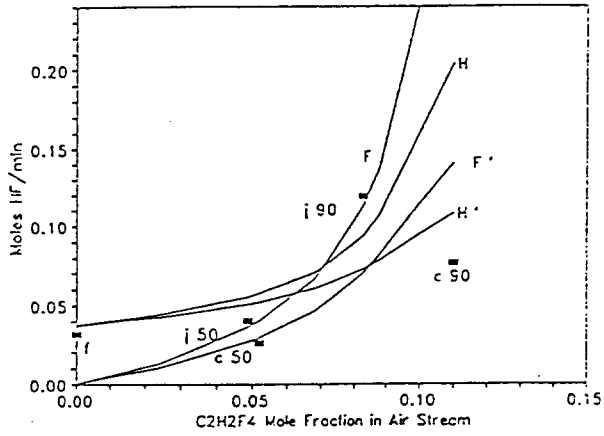


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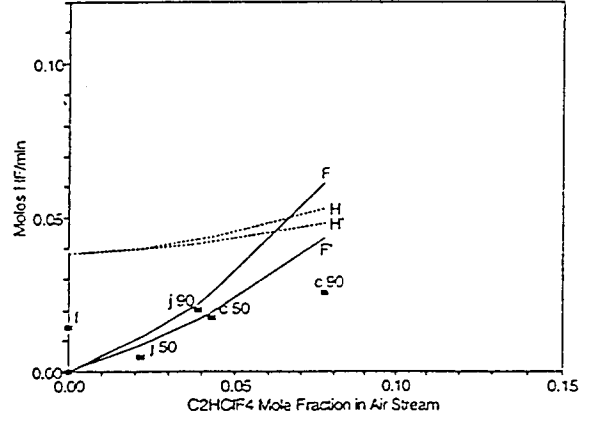


Figure 12

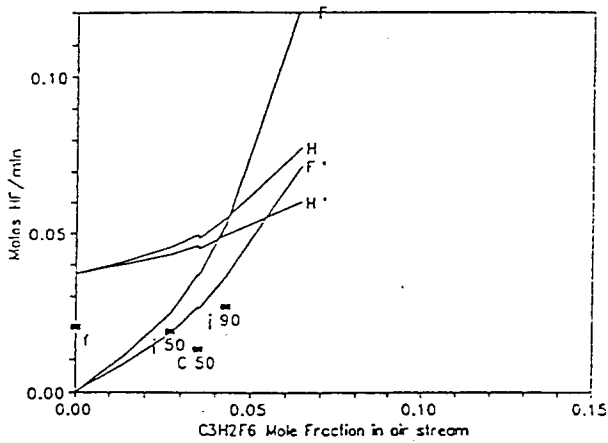


Figure 13

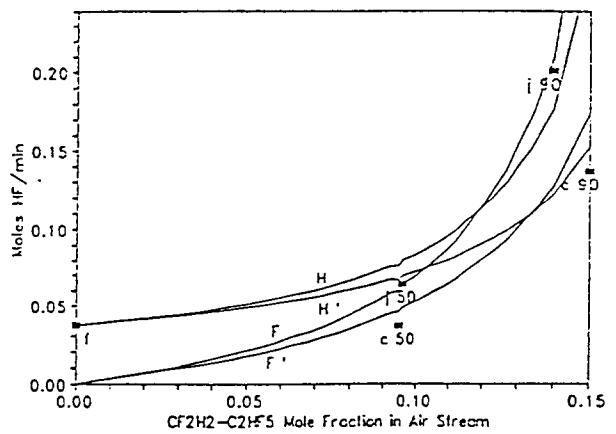


Figure 14

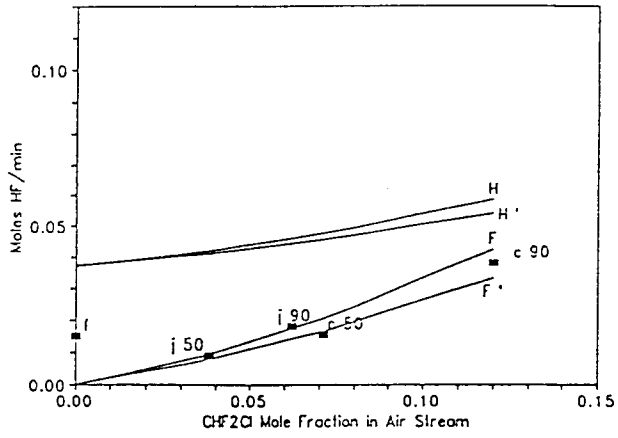


Figure 15

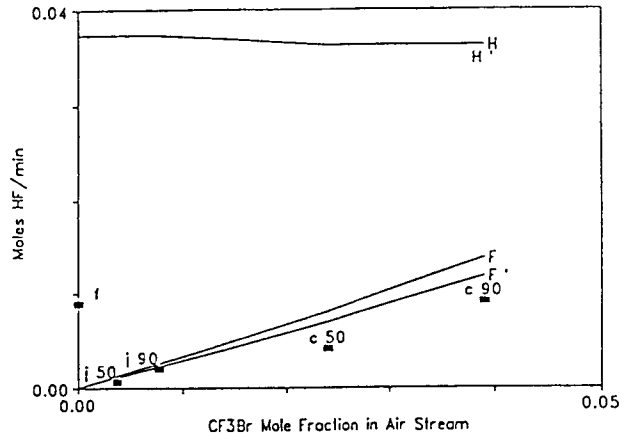


Figure 16

