A Modeling Study of Flame Quenching by CF_3Br using Detailed Chemical Kinetic Mechanisms

C.R. Casias and J.T. McKinnon
Department of Chemical Engineering and Petroleum Refining
Colorado School of Mines, Golden, CO 80401

This paper presents the methodology and results of research undertaken to identify how halogens interact with flames and to isolate the chemical kinetics and physical phenomena associated with flame quenching mechanisms. The specific interest in the *study* of Halon 1301 is to further understand how CF_3Br functions as an effective flame suppressant *so* that this information can be used to identify alternative suppression agents. For the first time, both the ways in which CF_3Br molecules directly participate in flame inhibition and the contributions of the Br and CF_3 fragments have been identified. The predominant mechanisms including: (1) trapping of H atoms diffusing in the direction opposite to the flow of convection, (2) consumption of the free-radicals, H and HO_2, and (3) reduced rate of heat release as a result of endothermic reaction, are ranked and described.

INTRODUCTION

The work associated with this paper expands on the earlier evaluations of flame inhibition mechanisms (Casias and McKinnon, 1996) and focuses on halons and fluorocarbons. Of particular interest is a better or improved understanding of the fundamental mechanisms by which CF_3Br (Halon 1301) functions as an effective flame suppressant. This information will be invaluable in identifying alternative flame suppression agents.

Experimental observations and model predictions (Walravens et al, 1995; Sheinson et al, 1989; Linteris and Truett, 1996) demonstrate the effectiveness of CF_3Br as a flame inhibitor, even under low concentrations such as a 1% (mole basis) addition used in this *study*. However, the specific pathways by which inhibition occurs are not yet fully understood.

In this paper, the pathways are analyzed by evaluation of specific elementary chemical kinetic reactions hypothesized as having predominant roles in flame inhibition. These reactions are part of a set of elementary reactions in which predicted flame speeds were compared to experimental data and determined to be in excellent agreement for the inhibitors CH_2F_2 and CF_4 (Linteris and Truett, 1996).

Walravens et al (1995) performed analyses based on a continuous flow stirred reactor in order to evaluate the influence of the addition of brominated compounds on the conversion of methane in helium/methane/oxygen mixtures. Walravens et al demostrated that a maximum inhibiting efficiency existed at around 1073 K as a result of the brominated compounds reacting though the cycle,

$$HBr + CH, \rightarrow Br + CH_4 \qquad (1)$$

$$Br + CH, \rightarrow CH_3Br \qquad (2)$$

$$CH_3Br + H \rightarrow HBr + CH, \qquad (3)$$

which results in the net termination reaction,

$$CH_3 + H \rightarrow CH_4 . \qquad (4)$$

The termination *step,* reaction 4, was noted for competing directly with the principal chain branching reaction.

$$H + O_2 + OH \ + O . \qquad (5)$$

Reaction 5 was qualified as being less important at lower temperatures relative to the degenerate branching reaction,

$$H_2O_2 + M \rightarrow 2OH + M \qquad (6)$$

which was influenced in the presence of bromine due *to* the production of peroxide though the reaction,

$$HO_2 + HBr \rightarrow H_2O_2 + Br \qquad (7)$$

In the work presented herein, the termination reaction 4 is not identified as having as significant of a role in flame inhibition. Although, similar interpretations concerning the influence of reaction 5 were made, it will become evident that other reactions are important (particularly when considering flame structure) within the preheat and reactions zones of a flame.

In other work, Sheinson et al (1989) defined the effectiveness of CF_3Br for suppressing air/hydrocarbon fires as being *20%* physical, *25%* chemical due to CF_3, and *55%* chemical due to Br. Sheinson et al developed a physical predictive model which allowed for determining the contribution from physical effects and for isolating and calculating of the purely chemical suppression contribution of agents. However, the model did not reveal any direct mechanisms that CF_3Br molecules may play in chemical suppression.

In the work presented herein, in addition to analyzing the roles of CF3 and Br fragments, flame inhibition effects associated directly with CF_3Br molecules are also evaluated. As a presage to the following sections, the role of CF_3Br molecules in trapping H atoms and endothermically decomposing have been evaluated and determined to account significantly to CF_3Br effectiveness in flame suppression.

MODEL

In this study, numerical simulations were conducted using PREMIX (Kee et al, 1990) for a number of different cases in an attempt to identify the mechanism or mechanisms associated with flame inhibition of hydrocarbons in the presence of CF_3Br. Inhibition effects are evaluated based on the addition of an inhibiting agent in the amount of 1% (mole basis) and are compared to an uninhibited case, referred to as the reference case. The reference case assumes an adiabatic flame configuration for a stoichiometric C_2H_4/air mixture burning at atmospheric pressure. The parameter used for comparison of uninhibited to inhibited flames is the adiabatic laminar flame *speed,* S_L. For the base case, S_L was computed to be equal to 73.2 cm/s. A reduction in the flame *speed* is an indication that an introduced agent acts as an inhibitor, and the magnitude of change in the flame speed is an indication of the relative effectiveness of the agent

The elementary chemical reactions used is this study was compiled from three sources: Bowman et al (1996), Miller and Melins (1992), and Burgess et al (1996). These elementary reactions were selected based on their applicability to this research in accounting for: general hydrocarbon combustion, singlet and triplet methylene reactions, and fluorocarbon, bromofluorocarbon, and iodofluorocarbon chemistry.

RESULTS

A number of cases were modeled where the specific conditions selected for each case were based on the desire to isolate the individual inhibition effects that are hypothesized to occur from CF_3Br addition. The more significant cases analyzed and results are presented in Table 1. The table lists the specific fuel mixture used in each case, along with a brief description of the criteria and restrictions to the chemical kinetics. Resulting adiabatic laminar flame speeds and adiabatic flame temperatures are also presented.

Comparison of Reference Case to CF_3BR Cases

Initially, the reference case was compared to two CF_3BR addition cases: CF_3Br addition in which no restrictions were placed on the chemical kinetics, Case CF_3Br; and CF_3Br addition in which the agent was not allowed to react, and thus, functions merely as an inert gas, Case CF_3Br-NR. Comparison of the reference case to the CF_3Br case allows definition of the conditions without and with inhibition effects from 1% (mole basis) addition of CF_3Br. Inclusion of the CF_3Br-NR case allows isolation of any heat capacity effects that may influence the flame. Figure 1 depicts the temperature profiles for the reference and CF_3Br cases. The rate of change in temperature as a function of axial distance is shown in Figure 2 for the reference and CF_3Br cases.

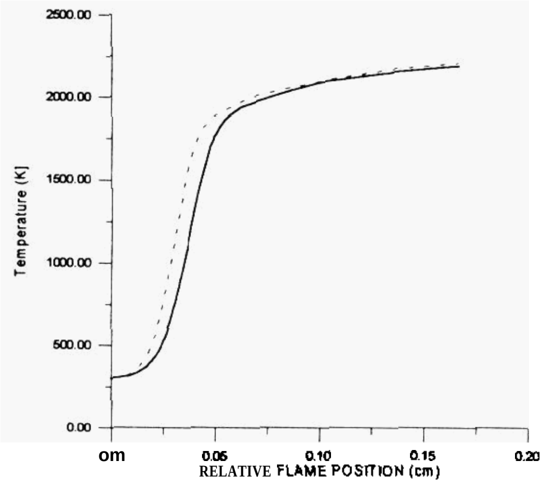


Figure 1. Temperature profiles for the reference (dotted line) and CF_3Br (solid line) cases. The pints at which the rate of change in temperature attains its maximum value are defined as the inflection points on the curves.

Table **1**

Comparison of Adiabatic Flame Speeds for C_2H_4/Air and C_2H_4/Inhibitor/Air Mixtures[a].

Fuel Mixture	CASE IDENTIFIER and Comments	S_L[b] (cm/s)	T[c] (K)
C_2H_4/air	Reference Case - $\Phi = 1.0$	13.2	2386
C_2H_4/CF_3Br/air	**CF_3BR - No restrictions on** chemical kinetics.	53.1	2368
C_2H_4/CF_3Br/air	**CF_3BR-HTRAP** - CF_3Br is allowed to decompose only through the given reaction in order to test the importance of H-atom trapping from back diffusion of H atoms. $H + CF_3Br = CF_3 + HBr$	51.6	2368
C_2H_4/CF_3Br/air	**CF_3BR-ENDO** - CF_3Br is allowed to decompose only through the given reaction in order to test the importance of this endothermic dissociation process. $CF_3Br = CF_3 + Br$	59.5	2391
C_2H_4/CF_3Br/air	**CF_3BR-NR** - CF_3Br is not allowed to react	68.0	2391
C_2H_4/HBr/air	**EIBR - No restrictions on** chemical kinetics. The direct addition of HBr allows for the independent evaluation of bromine kinetics since HBr rapidly dissociates in the early stages of flame development.	60.2	2368
C_2H_4/CF_3H/air	**CF_3H - No restrictions on** chemical kinetics. The direct addition of CHF_3 allows for the independent evaluation of CF_3 kinetics since the H atom is rapidly abstracted from CHF_3 in the early stages of flame development.	63.5	2389
C_2H_4/CF_4/air	**CF_4 - No** restrictions on chemical kinetics.	67.1	2312
C_2H_4/CF_4/air	**CF_4-NR** - CF_4 is not allowed to react.	61.6	2359

a: 1% inhibitor (male fraction) added to the base reference case C_2H_4/air fuel mixture, for which the fuel equivalence ratio, Φ, is qual to 1.0. b S_L is the adiabatic laminar flame velocity. c: T is the adiabatic flame temperature at a distance of 10 cm above the flame origination point.

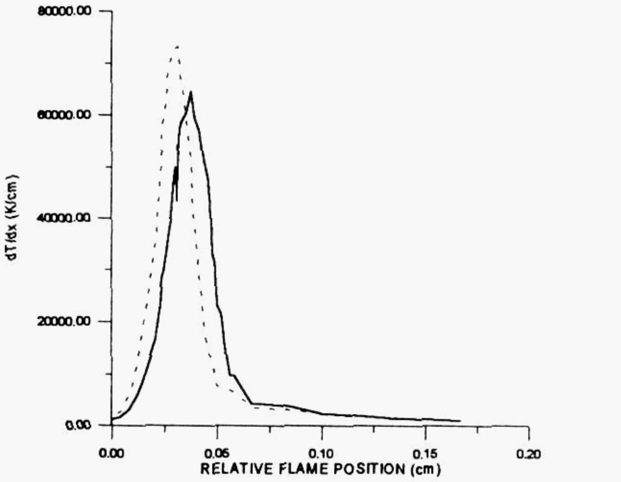


Figure 2. Rate of change in temperature as a function of axial position for the reference (dotted line) and CF_3Br (solid bold line) cases. The points at which the rate of change in temperature attains its maximum value are defined as the points where dT/dx is a maximum..

For all subsequent comparisons, the axial positions of the flames are adjusted so that the points at which the rates of the change in temperature attain their maximum value coincide. In Figure 1, these points are defined as the inflection points In Figure 2, these points are identified as the points of maximum change in temperature as a function of axial position (dT/dx). In Figure 1, the area from approximately 0.0 to 0.035 cm (the location of the inflection point) is defined at the preheat zone, and the area from approximately 0.035 to 0.075 cm is defined at the reaction zone.

Based on these adjustments to the flame positions, axial concentrations (mole fractions) of H, OH, O, and HO_2 were plotted and compared to each other for the cases: reference, CF_3Br, and CF_3Br-NR. These plots of mole fraction versus relative flame position are shown in Figure 3. For clarity, the positions at which HO_2 attains a maximum are also shown by the vertical line that extends from the text to the x-axis on the H atom, OH, and O atom concentration plots.

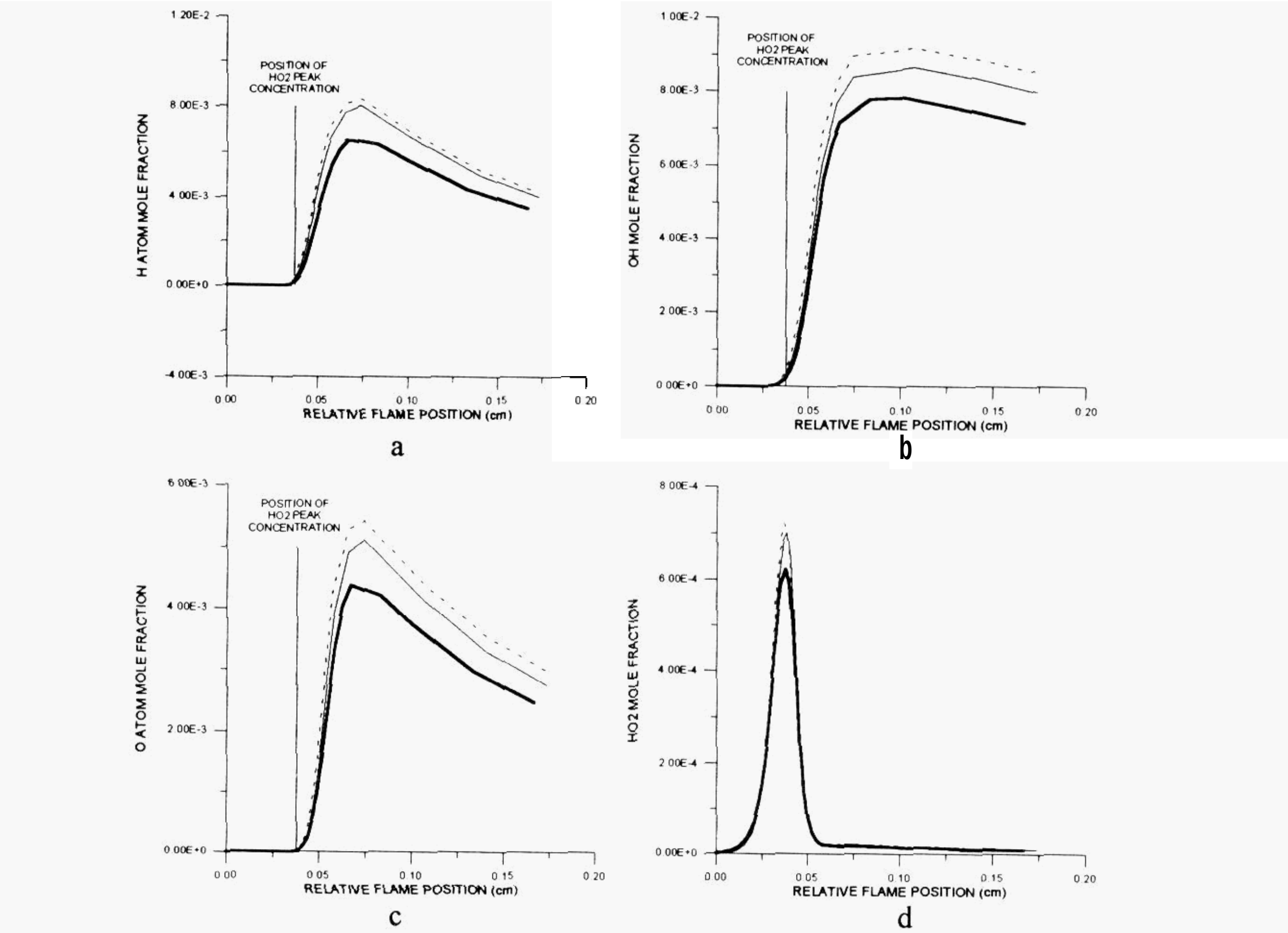


Figure 3. H, OH, O, and HO_2 concentration profiles for the reference (dotted lines), CF_3Br (solid bold lines), and CF_3Br-NR (solid lines) cases. The relative flame position at which the HO_2 concentrations attain a maximum value is also shown on the H, OH, and O diagrams.

In Figure 3, it is apparent that the concentrations of H, OH, O, and HO_2 are reduced when the inhibitor is introduced, This effect can been Seen in going from the reference case, to the CF_3Br-NR case, and then to the CF_3Br case. Minimal inferences as to the reasons for reduction in these concentrations will be made at this time; however, it should be noted that the relative position at which the HO_2 concentrations peak in the flame zone is of specific interest. HO_2 is considered 'to be an important precursor to flame development within the preheat zone and readily forms because of the lower temperature through the reaction,

$$H + O_2 + A4 = HO_2 + M. \tag{8}$$

Although H atoms are not generated within the preheat zone, this reaction occurs as a result of H atoms diffusing from the high-temperature reaction zone, against the convective flow, into the preheat zone (Glassman, 1987).

In comparing the reference case to the CF_3Br-NR case (see Table 1), it can be shown that heat capacity effects (although present) are minimal. As expected, the addition of CF_3Br as an inert does not result in the characteristic flame speed reduction observed in the fully inhibited case, Case CF_3Br.

In Figure 4, the principal CF_3Br decomposition reactions and rates for the CF_3Br case are shown. Negative reaction rates on the diagram indicate that CF_3Br is being consumed, and positive reaction rates indicate that CF_3Br is being produced. The primary CF_3Br reactions are,

$$H + CF_3Br = CF_3 + HBr\ , \tag{9}$$

and

$$CF_3Br = CF_3 + Br\ , \tag{10}$$

where reaction 9 is an H-atom consumption reaction and reaction 10 is an endothermic dissociation reaction. As a first cut in isolating CF_3Br inhibition effects, simulations were conducted eliminating all CF_3Br reactions, except for reactions 9 and 10. Given that the rates of these two reactions are significantly greater than those of other CF_3Br decomposition reactions, the predominant CF_3Br inhibition effects should be exhibited by inclusion of only these two reactions. Table 2 compares the resulting flame speed of the fully inhibited case, Case CF_3Br, to that of the case (identified as Case CF_3Br-R2) in which the only CF_3Br reactions allowed to occur are reactions 9 and 10.

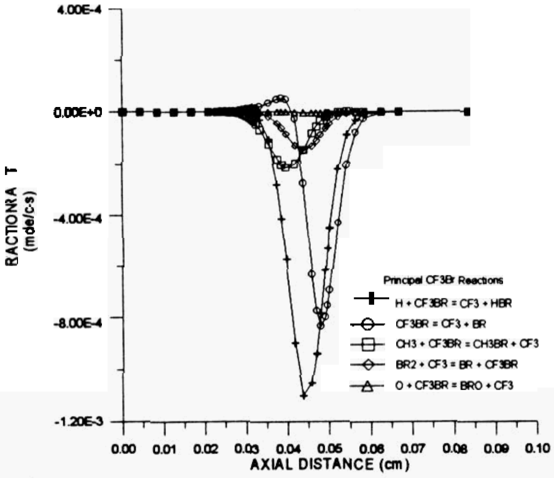


Figure 4. Principal CF_3Br reactions and rates. Negative reaction rates indicate that CF_3Br is being consumed. Positive reaction rates indicate that CF_3Br is being produced.

Table 2
Comparison of Flame Sped and Flame Temperature Between the Fully Inhibited Case, Case CF_3Br, and the Case in which CF_3Br is Allowed to React only through the Reactions,
$H + CF_3Br = CF_3 + HBr$ and $CF_3Br = CF_3 + Br$

Operative Reaction(s)	Adiabatic Flame Speed, S_L (cm/s)	Adiabatic Flame Temperature at 10 cm (K)
CASE CF_3Br	53.1	2368
$H + CF_3Br = CF_3 + HBr$ $CF_3Br = CF_3 + Br$ $CH_3 + CF_3Br = CH_3Br + CF_3$ $Br_2 + CF_3 = Br + CF_3Br$ $O + CF_3Br = BrO + CF_3$		
CASE CF_3Br-R2	53.5	2366
$H + CF_3Br = CF_3 + HBr$ $CF_3Br = CF_3 + Br$		

CF3Br-HTRAP and CF3Br-ENDO Cases

To test which reaction (reaction **9** or **10**) may play a greater role in reducing the flame ***speed*** a series of numerical simulations were conducted in which ***only*** these two CF_3Br reactions were included in the reaction mechanism. Inclusion of only the two predominant reactions results in flame inhibition effects for which the flame *speed* and flame temperature are nearly identical to those of the fully inhibited case, Case CF_3Br. Based on this setup, the following analysis focuses on evaluating effects based only on these two predominant reactions. Secondary effects, which may occur as a result of the products of these reactions (CF_3, Br, and HBr) further reacting, were also isolated. This was accomplished by allowing these products to be either reactive or non-reactive. Tables **3** and **4** illustrate the effects on the flame ***speed*** and adiabatic flame temperature. Table **3** presents the results from modeling in which only reaction **9** was allowed to occur. Table **4** presents the results from modeling in which only reaction 10 was allowed to occur. In both tables, reaction **products** with square brackets [] indicate that the product is not allowed to further react once produced.

Table 3
Evaluation of the Reaction, $H + CF_3Br = CF_3 + HBr$,
Case CF_3Br-HTRAP.

Subcase, Operative Reaction, and Restrictions[a]	Adiabatic Flame Speed, S_L (cm/s)	Adiabatic Flame Temperature at 10 cm (K)
A. $H + CF_3Br = [CF_3] + [HBr]$	58.1	2336
B. $H + CF_3Br = CF_3 + [HBr]$	58.7	2385
C. $H + CF_3Br = [CF_3] + HBr$	50.4	2320
D. $H + CF_3Br = CF_3 + HBr$	51.6	2368

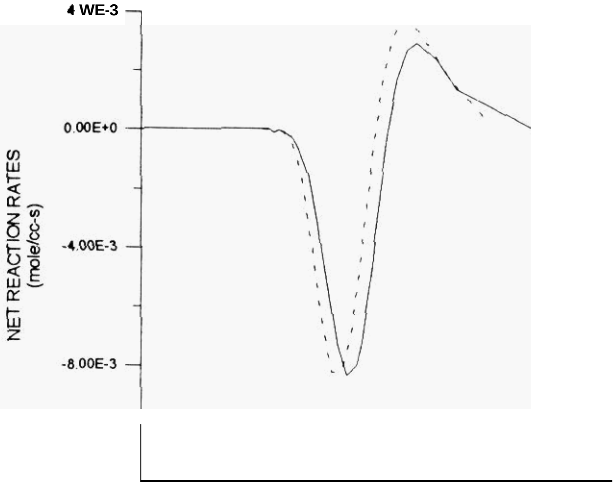
a: Square brackets [] around the reaction products indicate that the product is not allowed to further read once produced

For Case CF_3Br-HTRAP, effects to the flame speed are significant under all scenarios evaluated. The importance of the reaction **9** and its role in flame inhibition, particularly within the reaction zone, **is** best demonstrated by consideration of the information contained in Figure **5**.

Table4
Evaluation of the Reaction $CF_3Br = CF_3 + Br$, Case CF_3Br-ENDO

Subcase, Operative Reaction, and Restrictions[a]	Adiabatic Flame Speed, S_L (cm/s)	Adiabatic Flame Temperature at 10 cm (K)
A. $CF_3Br = [CF_3] + [Br]$	62.5	2318
B. $CF_3Br = CF_3 + [Br]$	61.0	1372
C. $CF_3Br = [CF_3] + Br$	61.4	2327
D. $CF_3Br = CF_3 + Br$	59.5	2377

a: Square brackets [] around the reaction products indicate that the product is not allowed to further react once produced



In Figure **5**, the net rates of H-atom production for the reference and CF_3Br cases shown were calculated by summing the rates all H-atom producing and H-atom consuming reactions. The main point of Figure **5** is to illustrate that, within the preheat, the net rate of H-atom production is negative. Therefore, in order for the reactions (i.e., H-atom consumption reactions in the preheat zone) to proceed, H atoms must diffuse opposite to the direction of convective **flow** from the high-temperature reaction zone (where the rate of H-atom production is positive) into the preheat zone. Thus, the term "H-atom trapping" was derived based on this phenomenological process in which it is hypothesized that H atoms are trapped (by reaction with CF_3Br) as they attempt to diffuse into the preheat zone.

For Case CF_3Br-HTRAP, Subcase A in Table 3, when neither of the products (CF_3 or HBr) is allowed to react, once formed, the flame speed is reduced from 73.2 cm/s (reference case) to 58.1 cm/s. This case is illustrative of the significance of H-atom trapping since the only other reaction occuring, compared to the non-inhibited reference case, is reaction 9.

In Case CF_3Br-HTRAP, Subcase B, the flame speed increases slightly to a value of 58.7 cm/s when the reactant CF_3 is allowed to react, as compared to a value of 58.1 cm/s when the reactant CF_3 is not allowed to react. The reason for this increase is that most subsequent reactions involving CF_3 are exothermic and thus function slightly as flame promoters rather than flame inhibitors. This is evident by comparison of the adiabatic flame temperature, which also increases when CF_3 is allowed to react. In Case CF_3Br-HTRAP, Subcase C, where CF_3 is not allowed to react and HBr is allowed to react, it can be seen that the flame speed is reduced even further to a value of 50.4 cm/s. Thus, HBr can be considered to be an effective flame inhibitor. At this point in the discussion, analysis of flame inhibition effects from HBr will be deferred. A more detailed discussion of the role that HBr plays in flame inhibition is presented in the following section, *HBr Case.* Lastly, in Case CF_3Br-HTRAP, Subcase D, again the flame speed increases slightly to a value of 51.6 cm/s when the reactant CF_3 is allowed to react, as compared to a value of 50.4 cm/s when the reactant CF_3 is not allowed to react. Again, because the majority of the subsequent reactions involving CF_3 are exothermic, CF_3 functions slightly as a flame promoter. As before, this is evident by comparison of the adiabatic flame temperature of this subcase to Subcase C, which also increases when CF_3 is allowed to react.

For Case CF_3Br-ENDO, Subcase A, when neither of the products (CF_3 or HBr) is allowed to react, once formed, the flame speed is reduced from 73.2 cm/s (reference case) to 62.5 cm/s as shown in Table 4. Although, the flame speed is not reduced to the same degree as it was in the CF_3Br-HTRAP case, this case is illustrative of the significance of endothermic dissociation of CF_3Br through reaction 10.

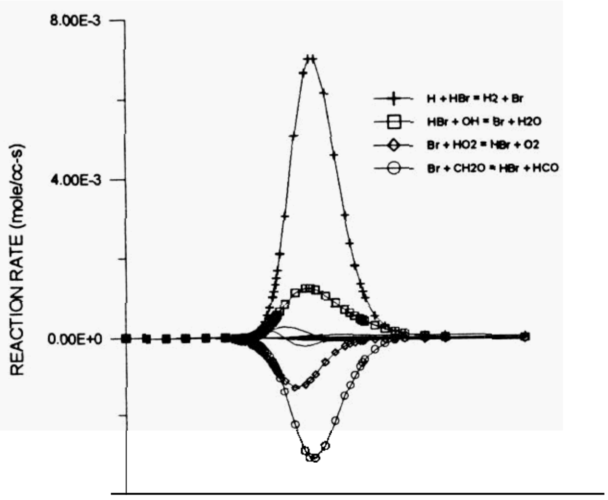
In Case CF_3Br-ENDO, Subcase B and D, the flame speeds decrease slightly to values of 61.0 and 59.5 cm/s when the reactant CF_3 is allowed to react, as compared to values of 62.5 and 61.4 cm/s, respectively, when the reactant CF_3 is not allowed to react. Previously (Case CF_3Br-HTRAP, Subcases B and D), CF_3 was attributed as functioning slightly as a flame promoter, as evidenced by the slight increase in flame speed, due to the fact that all subsequent reactions involving CF_3 were exothermic. However, in this case, CF_3 acts slightly as a flame inhibitor due to the subsequent reaction,

$$H + CF_3 = CF_2 + HF, \qquad (11)$$

becoming relatively important as a H-atom consumption reaction; recall that for this general case, CF_3Br-ENDO, reaction 9 is not allowed to occur. In Subcases C and D, where Br atom was allowed to react (as compared to Subcases A and B, where Br atom was not allowed to react), the flame speeds were not affected to the same degree as they were in the CF_3Br-HTRAP case, where similar restrictions were placed on HBr. The roles that Br and HBr play in flame inhibition require a greater level of analysis and, thus, are discussed separately in the following section.

HBr Case

With the direct addition of HBr in the inlet feed, it was possible to evaluate inhibition effects associated with bromine's chemical kinetics independent of those effects attributed to CF_3Br consumption. In Figure 6, the predominant reactions involving Br atom are shown. Negative reaction rates (on the figure) indicate that Br-atom is being consumed, and positive reaction rates indicate that Br-atom is being produced.



As can be seen, the predominant reaction (in terms of the magnitude of the rate) is the reaction,

$$H + HBr = H_2 + Br\cdot \qquad (12)$$

Reaction 12 is effective in directly reducing the H atom concentration. Williams **(1985)** identitied this reaction as being responsible for removing "the very active H atom, replacing it with the less active Br atom, thereby reducing the overall rate of heat release." It is evident that the rate of heat release is reduced when HBr is allowed to react (by comparison of Subcases A and B to Subcases C and D of Case CF_3Br-HTRAP); however, reactions that consume H atom in the preheat zone as well as early in the reaction zone have a greater effect on flame inhibition. Recall that the H atom consumption channel (reaction **9)** was more effective in reducing the flame speed than was the endothermic dissociation channel (reaction 10) in the previous section.

The rate of the reaction,

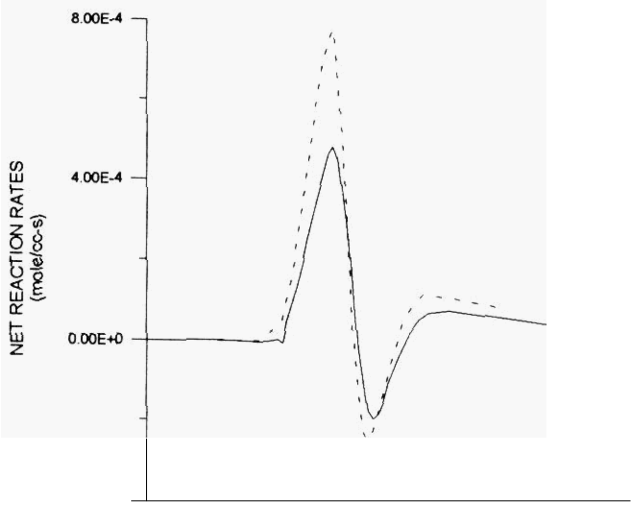
$$Br + HO_2 = HBr + O_2, \qquad (13)$$

is considerably lower than the rate of reaction **12;** however, reaction **13** is significant. Within the preheat zone and throughout the reaction zone, reaction **13** operates as a free-radical termination reaction *and* consumes HO_2. The direct impact that this reaction has on flame inhibition, due to the fact that it operates as a free-radical termination reaction, is obvious and will not be discussed any further; however, the role of this reaction in the consumption of HO_2 is of particular interest.

In Figure 3, it was shown that the production of HO_2 peaks in the preheat zone where the reaction,

$$H + O_2 + M = HO_2 + M \qquad (14)$$

is favorable due to the lower temperature. The maximum HO_2 concentration is well ahead of the peak concentrations of H, OH, and **O.** HO_2 subsequently forms peroxide, which does not dissociate at the temperatures in the preheat zone and is therefore convected into the reaction zone, where it forms OH radicals (Glassman, 1987). Under nominal conditions, where inhibition is not a factor, this process is effective in flame propagation. However, in the presence of bromine, the concentration of HO_2 in the preheat zone is significantly reduced **(as** shown in Figure **3)** by reaction with Br atoms through reaction **13.** Thus, the amount of HO_2 present for convection into the reaction zone is significantly lowered. Figure **7,** which compares the net rates of HO_2 production for the reference and CF_3Br cases, clearly illustrates the impact of bromine.



In addition to the effect of HO_2 consumption by bromine atom, the rate of production of HO_2 in the preheat zone via reaction **14** is also reduced in the presence of CF_3Br because a lower concentration of H atoms diffuse into the preheat zone. This phenomenon, defined as H-atom trapping, was previously presented in the section titled *CF_3Br-HTRAP* ***and CF_3Br-ENDO Cases.***

CF_3H, CF_4, and CF_4-NR cases

The purpose of Case CF_3H, as indicated in Table **1** was to independently evaluate the chemical kinetics associated with CF_3, since the H atoms of the CF_3H molecules are rapidly abstracted in the reaction zone. In fact, much of the independent analysis on CF_3 kinetics has already been accomplished in the section titled *CF_3Br-HTRAP* ***and CF_3Br-ENDO Cases. In*** the CF_3Br-HTRAP case, it was demonstrated that predominant CF_3 reactions are exothermic and act moderately as flame promoters. In the CF_3Br-ENDO Case, it has been shown that CF_3 kinetics also act to inhibit the flame. Overall, inhibition by the consumption of H-atoms is relatively more important than the ability of CF_3 reactions to act as flame promoters through exothermic channels given that the predominant CF_3 reaction consuming H atoms is reaction **11,** which also happens to be exothermic.

Case CF_3H is demonstrative of the role that CF_3 plays, primarily as a moderate flame inhibitor rather than as a flame promoter. In this case, the addition of CF_3H effectively increases the fuel equivalence ratio. Generally, an increase in the fuel equivalence ratio, for a fuel-lean flame, will result in an increase to the flame *speed;* however, in this case the flame speed is reduced from a value of **73.2** cm/s (reference case) to **63.5** cm/s. The **net** *effects* of the reactions associated with CF_3H oxidation is an exothermic process, as confirmed by the slightly higher adiabatic flame temperature in the post-flame zone. The **net** && of the reactions associated with CF_3H and CF_3 consumption in the reaction zone are **also** exothermic processes. Thus, the reduced flame speed observed for the CF_3H case must be attributed to free radical scavenging dominating over any compensating effects (that would act as flame promoters) from exothermic processes.

Case CF_4 and Case CF_4-NR *are* included to demonstrate the relative ineffectiveness of CF_4 as a flame inhibitor. **The** flame *speed* reductions from the reference case value of **73.2** cm/s to **67.7 cm/s** *(Case* CF_4) and **67.8** cm/s *(Case* **CF_4-NR)** *are* due almost entirely to heat capacity effects.

Flame Effects From Methane And Fluoromethanes

In Table **5**, the adiabatic flame speeds and flame temperatures are reported for two cases: the reference *case,* which is **a** stoichiometric mixture of **C_2H_4/air**, and the **C_2H_4-CH_4** *case,* in which 1% methane was added to the reference case. For the reference *case,* the resulting adiabatic flame speed and *flame* temperature are **73.2** cm/s and **2391 K**, respectively. **In** the **C_2H_4-CH_4** case, the flame speed and flame temperature increase to values of **76.9** cm/s and **2396 K**, respectively. These increases are due strictly to the change to the fuel equivalence ratio (Φ) when methane is added. The actual fuel equivalence ratio for the **C_2H_4-CH_4** case is equal to 1.15.

Table 5
Comparison of Adiabatic Flame Speed and Flame Temperature Fa Reference and C_2H_4-CH_4 Cases

Fuel Mixture	Fuel Equivalence Ratio (Φ)	Adiabatic Flame Speed, S_L (cm/s)	Adiabatic Flame Temperature at 10 cm (K)
C_2H_4/air	1.0	73.2	2391
C_2H_4/air/CH_4	1.15	16.9	2396

Based **on the known** behavior of laminar flame *speed* versus fuel equivalence ratio for fuel/air mixtures, as the fuel equivalence **ratio** is increased from a value of Φ equal to 1.0 to approximately 1.15 for a C_2H_4/air mixture, the laminar flame *speed* will also increase from a value of approximately **70** cm/s to **75** cm/s (Glassman, **1987).** Thus, the effect **Seen** here is strictly due to the fact that the mixture is a slightly fuel-rich **mixture,** and the flame *speed* is expected to be higher than that for the stoichiometric reference case. *As* the fuel-equivalence ratio is further increased, by the further addition of CH_4, the flame ***speed*** is now expected to decrease, and indeed it does **as** shown in Figure 8. **An** interesting point worth mentioning it that, conceptually, fuel-rich flames *can* be considered to be inhibited if the reduced flame speed is used as the indicator.

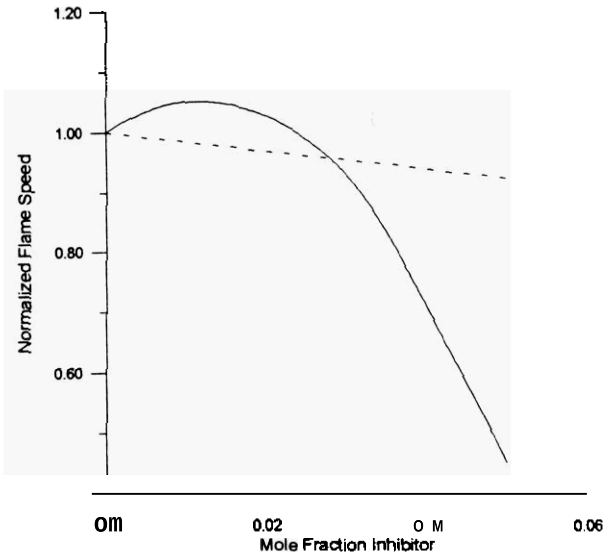


Figure 8. Comparison of normalized flame speed for C_2H_4/air/agent mixtures, where the agent is equal to N_2 (dotted line) and CH_4 (solid line).

Lastly, four C_2H_4/air/inhibitor mixtures were compared. The inhibitor agents evaluated were CH_4 (as previously presented), CH_3F, CH_2F_2, and CHF_3. The normalized flame speed versus mole fraction inhibitor results for **C_2H_4/air/inhibitor** mixtures are presented in Figure **9.** As the concentration of CH_4 is increased above approximately **5%** (mole basis), CH_4 becomes a more effective inhibitor than either CH_3F, CH_2F_2, or CHF_3. The reason for **this** is that **as** the mole **fraction** of inhibitor increases, the **fuel** equivalence ratio also increases (**this** is true in all cases); thus, the relative amount of oxygen present decreases.

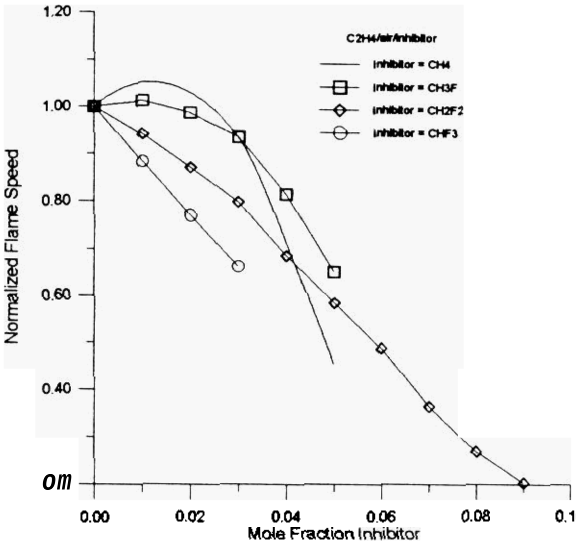


Figure 9. Comparison of normalized flame speed versus mole fraction inhibitor for CH_4, CH_3F, CH_2F_2, and CHF_3-fuel mixtures.

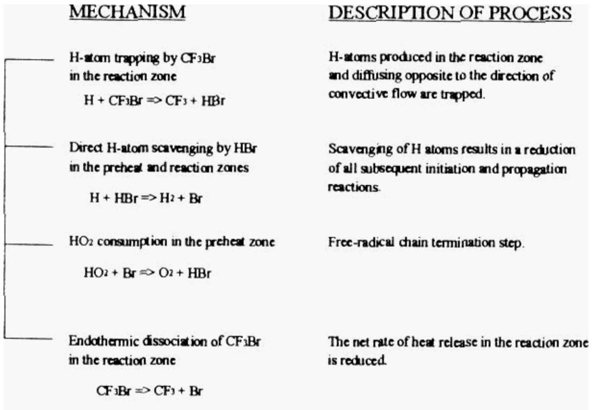
Specifically, for the C_2H_4/air/CH_4 fuel mixture, the reduced flame speed occurs as a result of an insufficient amounts of oxygen being available to carry out the "nod oxidation process (i.e., formation of CO and H_2O). On the other hand, in the fluoromethane cases, large amounts of other stable products of combustion can be formed (i.e., CF_2O and HF) which are significantly less dependent on oxygen. In effect, fluorine can act as a flame promoter under oxygen-deprived conditions.

In general, the rates at which hydrocarbons decompose are faster than those for the analogous fluorinated hydrocarbons. As a result, a relatively larger fraction of flnoromethane intermediates are convected further out in the flame prior to reacting. The inhibition effects observed from fluoromethanes are functions of the slower chemistry occurring within the reaction zone, with minimal dependency of the latter chemistry occurring in the post-flame zone,

For conditions in which oxygen deprivation is not an issue, as in the case where the inhibitor addition is less than approximately 4% (mole fraction), CHF_3 is the most effective flame inhibitor of the fluoromethanes. In this case, inhibition effected by H-atom consumption in the reaction zone through reaction 11, dominates over any flame promotion effects that might occur as a result of this reaction's exothermicity As the relative amount of CF_3 present decreases and the H-atom concentration increases (i.e., CF_2H_2 addition), the importance of reaction 11 is diminished. The addition of CH_3F further demonstrates the diminishing role of reaction 11, in that a 1% addition results in flame promotion. This effect is what would be expected when the fuel equivalence ratio is increased from a value of 1.0 to a higher value and chemical inhibition is not significant.

SUMMARY

Overall, the role of CF_3Br in flame inhibition has been presented. The predominant mechanism are presented in Figure 10 in relative order of importance. The results of this work provide an explanation of the mechanisms associated with flame inhibition by CF_3Br. Additionally, the results of this work provide a focal point from which experimental and other numerical studies can be based in order to test the general applicability of these mechanisms using other chemical species, particularly those being considered as alternative replacements to Halons.



MECHANISM	DESCRIPTION OF PROCESS
H-atom trapping by CF_3Br in the reaction zone $H + CF_3Br \Rightarrow CF_3 + HBr$	H-atoms produced in the reaction zone and diffusing opposite to the direction of convective flow are trapped.
Direct H-atom scavenging by HBr in the preheat and reaction zones $H + HBr \Rightarrow H_2 + Br$	Scavenging of H atoms results in a reduction of all subsequent initiation and propagation reactions.
HO_2 consumption in the preheat zone $HO_2 + Br \Rightarrow O_2 + HBr$	Free-radical chain termination step.
Endothermic dissociation of CF_3Br in the reaction zone $CF_3Br \Rightarrow CF_3 + Br$	The net rate of heat release in the reaction zone is reduced.

Figure 10. Identification of the predominant mechanisms, in relative order of importance, associated with flame inhibition by CF_3Br.

ACKNOWLEDGMENT

We are grateful lo the National Science Foundation National Young Investigator Program for financial support

REFERENCES

Bowman, C.T., R.K. Hanson, D.F. Davidson, WC. Gardiner Jr., V. Lissianski, G.P. Smith, DM. Golden. M. Frenlach, and M. Goldenberg (1996), World Wide Web. http://www.me.berkeley.edu/gri_mech/version21.

Burgess, D.R.F. Jr., M.R. Zachariah, W. Tsang, and P.R. Westmoreland (1996). Thermochemical and Chemical Kinetic Data for Fluorinated Hydrocarbons, World Wide Web, http://fluid.nist.gov/836.03/ckmech/Mechanism.html.

Casias, C R. and J.T. McKinnon (1996), Comb Sei Tech, 116117, 289-315.

Glassman. I. (1987). Combustion, 2ed, London, Academic Press, Inc.

Kee, R.J., J.F. Grcar, M.D. Smooke and Jd. Miller (1990), A Fortran Program for Modeling Steady Laminar One-Dimensional Premixed Flames, Sandia National Laboratories, Albuquerque. NM, SAND85-8240.

Linteris, G.T. and L. Truett (1996), Combust Flame, **105**, 15-27.

Miller, J.A., and C.F. Melius (1992), Combust Flame, **91**, 21-39

Sheinson. R.S., J.E., Penner-Hahn, and D. Indritz (1989), Fire Safety Journal, **15**, 437-450.

Walravens, B.. F. Battin-Leclerc, G.M. Come. and E Baronnet (1995), Combust Flame, **103**, 339-342.

Williams, F.A. (1985), Combustion Theory, 2ed, Addison-Wesley Publishing Company, Redwood, CA.