CHEMICAL AND PHYSICAL INFLUENCES OF HALOGENATED FIRE SUPPRESSANTS

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ABSTRACT

The specific mechanisms by which fire suppressants influence flame properties have been determined on the basis of computer simulations. Attention is focussed on the relative contributions from physical and chemical processes. Chemical effects are most strongly manifested at **low** concentrations of suppressants. As their concentrations are increased, the chemical effects reach a maximum value, while the physical effects continue to increase. The use of a composite inhibitor composed of a mixture of an effective chemical inhibitor with a high heat capacity diluent may be beneficial. The relative contributions towards fire suppression from physical and chemical mechanisms are estimated near the flammability limits.

INTRODUCTION

Burning velocity, S_u, has been found to be an important parameter for the characterization of the inhibition efficiency of halogen-containing flame retardants. The direct observation is that flame velocity decreases as the suppressant concentration is increased. The exact mechanisms for this action has been a long standing issue. Considerable controversy has been focussed on the relative importance of physical mechanisms, where heat capacity and dilution effects dominate, and chemical mechanisms, where radical scavenging is important. Sheinson et al.[1] estimated the chemical and physical contributions of CF_3Br effect on heptane diffusion flames through an enthalpy balance and arrived at a value for the former of approximately 80%. In other works [2,3] it has been found that the overall effect of the retardant is to achieve an early maximum and then decreases with increasing additive concentration. In this paper we report on computer simulation studies on these issues. The great advantage of such work is that by adjustment of the input data one can tune in or out the contributions from physical or chemical sources, leading to clearer results that are not obtainable experimentally.

CALCULATIONAL PROCEDURE AND KINETIC MODEL

Most of the computations were conducted for stoichiometric laminar flames of methane, ethylene, ethane and methanol, respectively, at atmospheric pressure and adiabatic conditions. The initial temperature of the mixtures was 298K. The following halogenated retardants were considered: CF_3H, C_2HF_5, C_2F_6, CF„ CF_3Br, and CF_3I. The PREMIX code was used {4,5] in the calculations. Analyses of the numerical results were conducted using the NIST Interactive Graphics post processor Senkplot (http://www.nist.gov/cstl/div836/xsenkplot)

The data base used in the calculations for the C/H/O system has been used in an earlier study [6,7]. A comprehensive set {8} of elementary reactions for fluorine-containing C_1-C_2 species was folded into the larger data base (http://fluid.nist.gov/ckmech.html). The kinetic submodels for bromine and iodine containing species were the same as those in our earlier works {7,9}. Comparison of our numerical results showed that the burning velocities were in agreement with measurements for C,-C, hydrocarbon flames over wide ranges of the equivalence ratio. Comparisons with experimental measurements were also made for the burning velocities of methane-air flames with the additives: CF_3H, C_2HF_5, C_2F_6, CF„ and CF_3Br [lo-131. Good agreement is found between the measured and calculated burning velocities. In addition, our computational results were in close agreement with measurements of the burning velocity of methane-air flames with CF_3I as an additive [14] and ethylene-air flames with CH_3Br and CH_3I inhibitors {15} at atmospheric pressure. Thus, the data base could be expected to predict with reasonable accuracy the influence of inhibitors on flame propagation.

RESULTS and DISCUSSION

Physical and chemical action of flame retardants:

This study is concerned with the relative importance of the physical and chemical effects that are responsible for flame suppression. The particular approach used in the present work is illustrated in Figure 1. One begins with a plot of the calculated flame velocity as a function of the additive concentration (normalized to the situation where there is no additive). We note that this calculated line reproduces the experimental observation and thus represents the direct connection with flame inhibition effectiveness. We can now go through the data base and turn off the chemistry of the suppressant by arbitrarily setting all rate constants that involve it and its decomposition products to be zero. Thus the suppressant is treated as an inert polyatomic

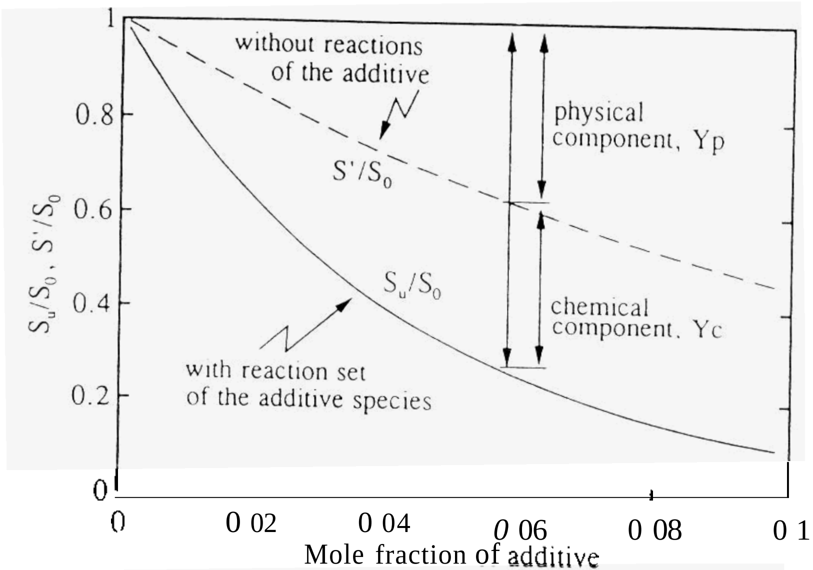

Fig 1. Definition of the physical Y_p and the chemical Y_c components **of** inhibitor influence.

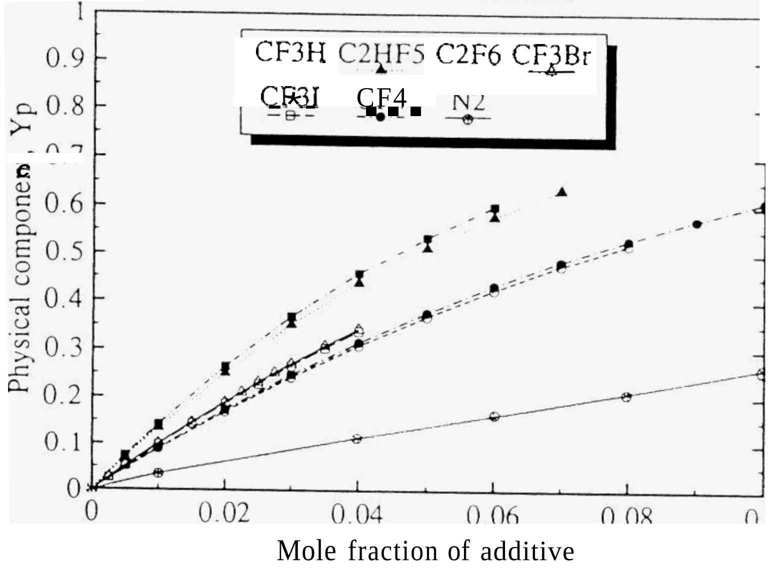

Fig 2. The physical component Y_p as a function of additive concentration in stoichiometric CH_4-air flames.

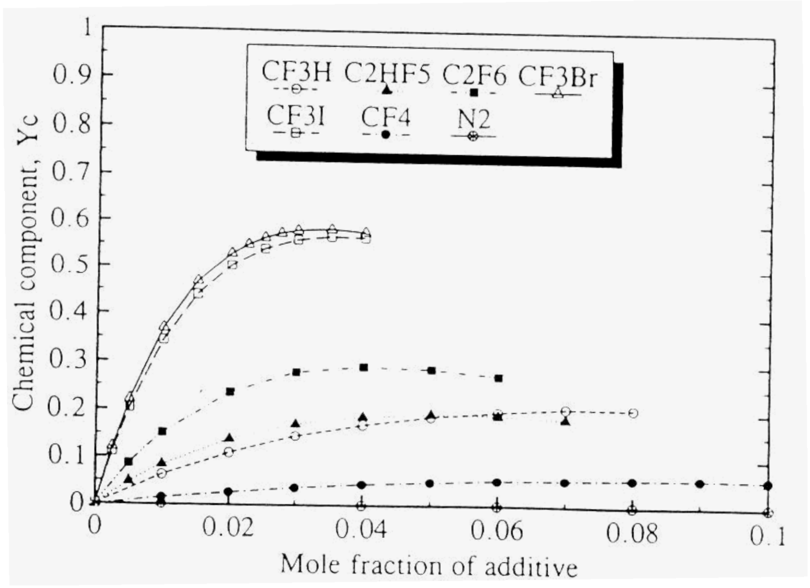

Fig 3. The chemical component Y_c as a function of additive concentration in stoichiometric CH_4-air flames.

molecule. This leads to the dashed line. The physical component, Y„ is defined as:

$$Y_p = 1-S_n/S_o$$

where S_o is the burning velocity calculated without additive. The chemical inhibition component(Y_c) is the difference between the physical component and the total inhibition effect:

$$Y_c = (S_n-S_u) / S_o$$

where S_u is the burning velocity calculated with the additive using the kinetic model including inhibitor reactions. The hypothetical nature of the situation where only physical effects have an influence should be emphasized. Implicit is the assumption that decomposition of the suppressant does not occur at all. Obviously any effect arising from decomposition must be classified as chemical in nature. In this sense it is probably the maximum possible contribution from physical effects.

Figure 2 shows the behavior of the physical component (Y,) as a function of additive concentration for a stoichiometric CH_4-air flame. The physical influence of the additives on flame speed is due to heat capacity and dilution effects. Halogenated compounds with approximately equal heat capacities such as (a) C_2HF_5 and C_2F_6, or (b) CF_3H, CF_3Br, CF_3I, and CF, have approximately equal physical effects. In addition it ***can*** be seen that the physical effect scales with the heat capacity of the added agent. For example, it requires approximately **6%**C_2F_6 and **10%**CF, to have a physical component **of *0.6*.** This correlates with the ratio of heat capacities of C_2F_6 and CF_4. **As** expected, the physical component of the inhibition action is increased with increasing additive concentration.

Figure **3** shows the dependence of the chemical component (Y_c) on additive concentration. Chemical effectiveness depends on the ability to reduce the concentration of chain carriers and the general observations are consistent with such processes. Nitrogen has no chemical contribution. The chemical effectiveness of C_2F_6 is almost twice that of CF_3H. One molecule of C_2F_6 produces two CF, radicals during the initial stage of decomposition, while the reactions involving the latter can lead to no more than one CF, radical. For C_2HF_5, the decomposition mechanism is dominated by the reaction: $C_2HF_5 => CHF_2 +$ CF,, and **the** chemical component ***can*** be considered to consist of the sum of the inhibition effects of CF, and CHF, radicals. The chemical action of CHF, is apparently less than **2/3** that of the CF, radical. The suppressant activity of CF_3Br arises mostly from chemical effects. The calculations show that this

additive	$S_u/S_o=0.5$		$S_u=5$ cm/s	
	Physical	Chemical	Physical	Chemical
CF_3H	64%	36%	79%	21%
C_2HF_5	67%	33%	81%	19%
C_2F_6	59%	41%	69%	31%
CF_3Br	22%	78%	35%	65%
CF_3I	23%	77%	36%	64%
CF_4	89%	11%	95%	5%

contributes to approximately 70-85% of the total decrease in the observed burning velocity. Comparison with CHF, results shows that the CF_3 part of a retardant molecule contributes approximately 20-30% to its chemical action. These estimates coincides closely with the conclusion of Sheinson[1]. For CF,, chemical contributions constitute only 10-15% of the suppressant action and physical effects are the predominant mode.

Chemical and Physical Action of Additives at Flammability Limits.

Table 1 contains a more detailed analysis of the results for stoichiometric methane/air flames summarized in Figures 2-4 at $S_u=5$ cm/s (the presumed extinction value [16]). Also, results are presented for $S_u/S_o=0.5$. As noted earlier, CF, acts mostly through physical mechanisms. Substitution of a hydrogen and a CF_3 group increases the chemical contribution. With bromine and iodine substitution chemical effects become predominant. Nevertheless there remains a significant physical component. Figure 4 shows the relative physical contribution, $100\times Y_p/(Y_p+Y_c)$, as a function of additive concentration. Physical contributions or dilution and heat capacity effects increase with additive concentration. Thus the influence of an inhibitor is dependent on concentration. The physical and chemical components of CF_3Br and CF_3I for C_2H_4, C_2H_6, and CH_3OH are presented in Table 2. In general, the physical contributions seem to be slightly larger than those for CH,.

Burning Velocity versus Flame Temperature for Air/Methane Mixtures with Inhibitors.

Calculated adiabatic flame temperatures as a function of the relative burning velocities for different additives in a methane air mixture are given in Figure 5. As before a velocity of

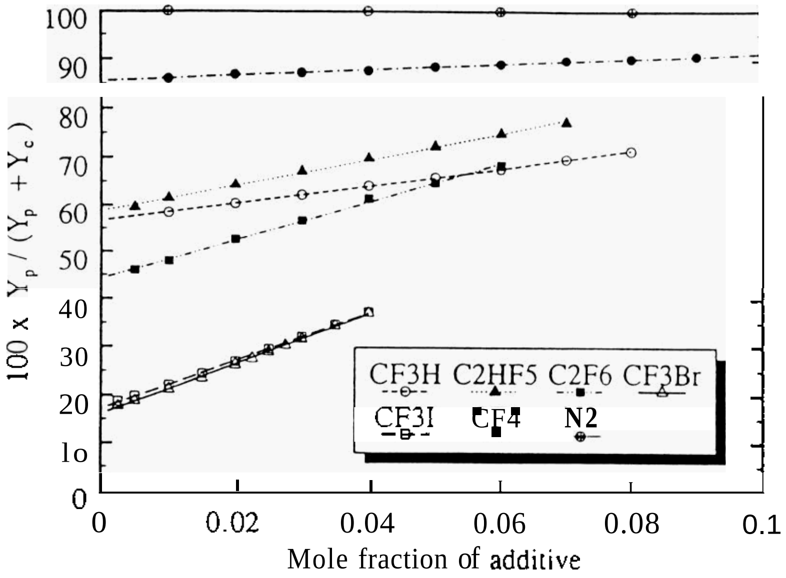

Fig 4. The fractional physical inhibition contribution, $Y_p/(Y_p+Y_c)$ **as** a function of additive concentration in CH_4-air flames.

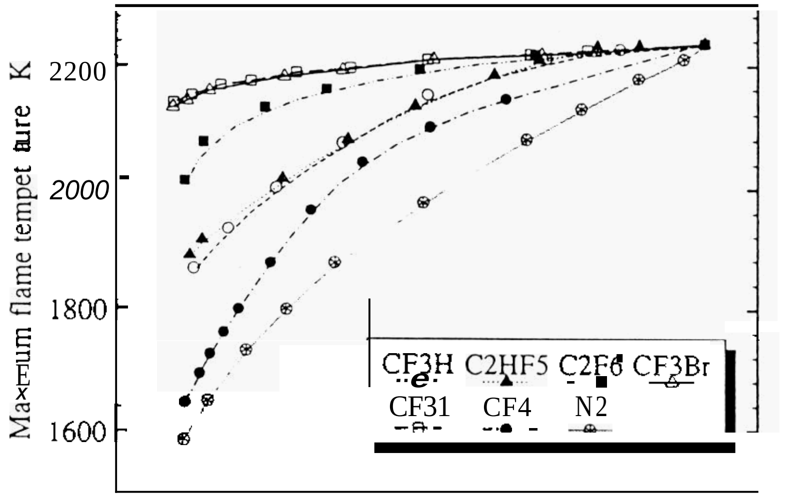

Fig.5. The relationship between the maximum flame temperature and the normalized burning velocity for methane-air flames with additives.

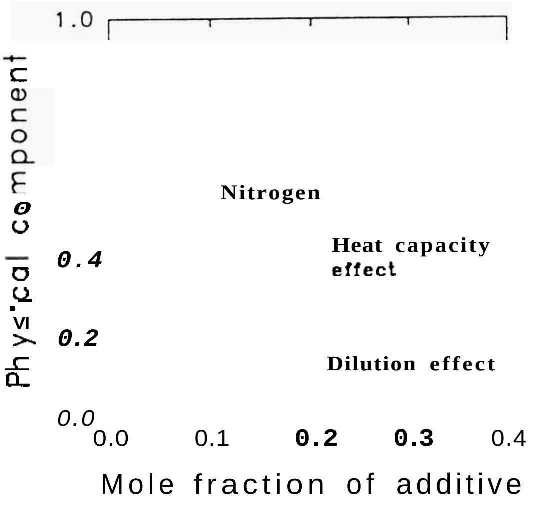

Fig.6. Contributions of heat capacity and dilution to physical effect of additive **action.**

Table 2: Physical and chemical contributions of CF_3Br and CF_3I at S_u=5 cm/s for C_1-C_2 toichiometric air flames

additive	CF_3Br			CF_3I		
	Mole Fraction for S_u=5 cm/s	Physical	Chemical	Mole fraction for S_u=5cm/s	Physical	Chemical
C_2H_6	0.056	41%	59%	0.057	43%	57%
C_2H_4	0.061	38%	62%	0.070	44%	56%
CH_4	0.035	35%	65%	0.036	36%	64%
CH_3OH	0.069	50%	50%	0.046	37%	63%

5 cm/s or a relative velocity of 0.12 is assumed to be the critical flame speed at extinction [16]. For nitrogen a flame temperature of approximately 1600K is obtained. This temperature has been considered to approximately represent the extinction limits for diffusion flames [1,17]. Use of chemical retardants such as CF_3Br, CF_3I, and other halogenated additives lead to larger values of the calculated adiabatic flame temperature (T_f) in comparison with inert additives for the same amount of S_u reduction. Large values of T_f represent increasing chemical influence of an additive.

Separation of Heat Capacity and Dilution Effects

The modeling procedure permits the direct evaluation of the contributions from heat and dilution effects. Dilution leads to decreases in the reactant concentration and the heat of reaction per unit of mixture and a corresponding decrease in the overall rates. "Pure" dilution effect can be calculated by using an artificial inert additive(A) with zero heat capacity. Results of such calculations for stoichiometric methane/air mixture with N_2 as an additive are presented on Fig.6. It is interesting that the contribution from dilution is less dependent on additive concentration than heat capacity.

Measures of Chemical and Physical Contributions of Inhibitor Influence.

In this paper the burning velocity is taken as an appropriate measure for differentiation of the chemical and physical contributions to inhibition. In addition, it is possible to use the additive concentrations calculated with or without additive reaction kinetics to obtain the same burning velocity reduction. Sheinson et al. [1] used the "concentration" measure to estimate the chemical and physical contributions to inhibition. The difference in the maximum flame

Measure	Physical Effectiveness	Chemical Effectiveness
Burning Velocity	35%	65%
Additive Concentration	17%	83%
Maximum Flame Temperature	15%	85%

temperatures calculated with and without reactions of additive species for the same burning velocity reduction represents another means to differentiate physical and chemical contributions. Table **3** shows the physical and chemical contributions to inhibition by CF_3Br determined by these different definitions. The 'concentration' and 'temperature' measures for physical and chemical contributions coincide and are fairly consistent with those of Sheinson et al. [1].

Saturation Effect

For the halogenated suppressants studied, the decrease in flame velocity with additive concentration from chemical contributions or a saturation effect becomes evident when the relative velocity (S_u/S_0) is approximately **0.2 to 0.4** (Fig. **3).** Subsequently, the contribution from chemical effects decreases with increasing additive concentration. This tendency is most pronounced for CF_3Br and CF_3I which are more effective retardants than the other fluorinated compounds. It is suggested that the phenomenon arises from the reduction in radical superequilibrium concentration to equilibrium levels as a result of reactions with the suppressant.

An analysis of reaction pathways for inhibition of methane flame by CF_3Br shows that the most important radical scavenging reactions for HBr consumption are the following:

$$H + HBr = H_2 + Br \qquad [R1]$$
$$OH + HBr = H_2O + Br \qquad [R2]$$

The relative importance of different reactions is determined through integral contributions of reaction rates: $\int w_I \, dt$, where w_I is the "i"th reaction rate and t is the reaction time [18]. Integration is carried out until a maximum **H** atom concentration is achieved. The integration interval corresponds to the flame zone, approximately. The contributions of R1 and R2 constitute more than 80% **of** the total consumption of HBr. For CF_3Br concentrations less than 0.02 **mole** fraction, HBr is mainly consumed by [R1]. For CF_3Br

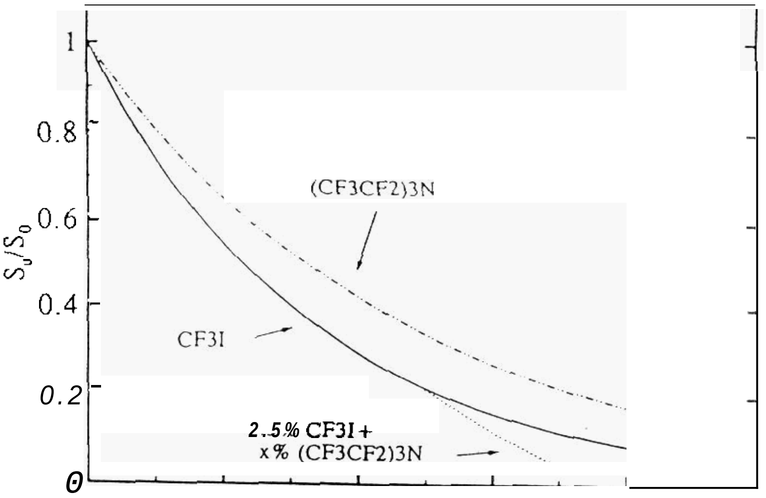

Fig.7. The burning velocity as a function of inhibitor concentration for an additive composed of CF_3I and $(CF_3CF_2)_3N$.

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works [20,21] combined effects of mixture of inert and chemical retardants are discussed. It was found that at flammability limits, "extinguishment" factors [20] show synergistic effects and the advantages of a composite inhibitor presented. We believe that such behavior are fully consonant with the explanation given here. An alternative possibility is a large organic molecule containing both bromine and iodine.

CONCLUSIONS

In this work, the chemical and physical effectiveness of halogenated flame retardants is analyzed. Premixed methane, ethylene, ethane, and methanol-air flames are considered. The chemical and physical contributions of retardant effect on flame propagation are determined. The main results are the following:

a. A procedure for the differentiating between physical and chemical contributions of halogenated additives to flame suppression is suggested. Although for the most effective chemical suppressants chemical effects are most important, physical mechanisms always make a contribution. We show that increasing additive concentrations lead to saturation of the chemical contributions. The subsequent increase of additive action is due to physical influence (heat capacity and dilution effects).

b. The utility of a "composite" inhibitor is suggested. Its constituents would be an effective chemical inhibitor and an inexpensive inert additive with a high heat capacity. The composition of a composite retardant should be determined by the "saturation" concentration of the chemical inhibitor and the peak concentration of the composite retardant.

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