

EFFECT OF HALOGENATED FLAME INHIBITORS ON C₁-C₂ ORGANIC FLAMES

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The influence of CF₃Br, CF₃I, CF₄, CHF₃, C₂F₆, and C₂HF₅ on laminar flame propagation in mixtures of CH₄, CH₃OH, C₂H₆, and C₂H₄ with air has been determined by numerical simulations. Comparisons are made with experimental results and earlier calculations. Flame velocities as a function of inhibitor concentration and equivalence ratio have been determined. For all the organic fuels, the ranking of inhibitive efficiency is CF₃Br, CF₃I > C₂F₆ > C₂HF₅ > CHF₃ > CF₄. The bromine and iodine compounds are clearly the most efficient flame suppressants. They are of equal effectiveness except in methanol, where CF₃I is superior. The retardants are more effective for rich mixtures than for lean. With 1% inhibitor concentration, the decrease in burning velocity is most pronounced for unsaturated fuels. The general ordering is consistent with calculational results on flame thickness and radical concentrations. Reaction pathway analysis demonstrates the importance of the regeneration of reactive scavengers. Relative contributions from physical and chemical effects are estimated.

Introduction

With the discovery of the deleterious effects on stratospheric ozone from brominated fire suppressants, intensive research studies have been undertaken to find effective replacements. The focus of the present work is on the comparative behavior of potential suppressants in combustion systems. Numerical simulations will be used in establishing a ranking of inhibitor efficiency. Comparisons with the literature are made to establish the basis for such efforts and to develop useful correlations. Key pathways for chemical inhibition are determined and the relative importance of physical and chemical effects estimated. Note that the physical effects of concern here are those of heat capacity (thermal) and dilution.

The numerical study of flame inhibition processes involving bromine-containing organic compounds, with detailed chemical kinetics, was initiated by Dixon-Lewis et al. [1-2] and Westbrook [3-4]. The first studies described the effect of HBr, CF₃Br, CH₃Br, CH₃I, and so forth on hydrocarbon flames. The importance of catalytic cycles for the reduction

of H-atom concentration by bromine compounds was demonstrated. Westbrook showed that the fluorocarbon part of the retardant molecule can also make contributions in scavenging active species, thus enhancing the efficiency of CF₃Br as a flame suppressant [4]. Westbrook's calculations indicated that the flammability limits for methanol in the presence of CF₃Br are similar to those for hydrocarbon systems [4]. This is in disagreement with experimental results summarized by Ford [5] and is a significant concern since in actual fire situations methanol may well be a more representative fuel. CF₃I is included in this study because of the recent interest in its use as a substituent for CF₃Br.

This is a numerical study of the influence of CF₃Br, CF₃I, CHF₃, CF₄, C₂HF₅, and C₂F₆ on laminar flame propagation in air mixtures of methane, methanol, ethane, and ethylene. The aim is to generalize the results of the earlier investigations by covering a larger variety of molecules and conditions and to relate the results to the analysis of inhibition mechanisms. A full set of elementary reactions [6,7] for fluorine-containing C₁/H/O and C₂/H/O species has been developed recently and used [7,8] for the prediction of the influence of CF₂H₂, CHF₃, and CF₄ additives on methane/air flames. With the addition of appropriate organic bromine and iodine species, the database was used to deduce the influence of CF₃Br and CF₃I on combustion behavior in

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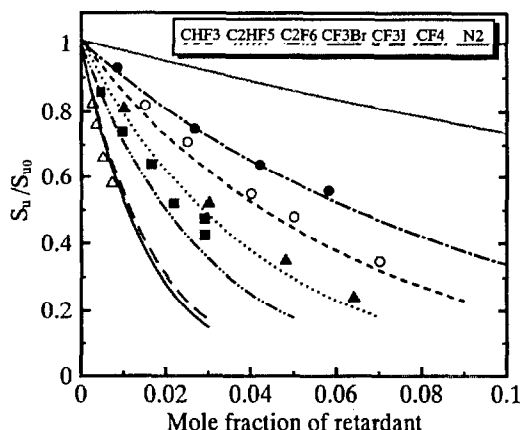


FIG. 1. Relative burning velocity as a function of additive concentration for stoichiometric CH_4/air flame. Lines are calculated results based on a model that yield $S_{u0} = 42.1$ cm/s. Points represent experimental data: circle, CHF_3 ; solid triangle, C_2HF_5 [20]; solid square, C_2F_6 [18]; solid circle, CF_4 [8]; triangle, CF_3Br [20].

plug-flow and perfectly stirred reactors [9,10] for methane/air combustion systems.

Kinetic Model and Simulation Techniques

Calculations of burning velocity and structure of freely propagating flames were carried out using the Sandia CHEMKIN PREMIX code [11]. (Certain commercial materials and equipment are identified in this paper to specify adequately the procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the material or equipment is necessarily the best for the purpose.) Reaction pathways were analyzed with a NIST interactive graphical postprocessor.

The database on the C/H/O/F system, described previously [6], formed the basis of this work. The subset of C_1 - C_2 oxidation chemistry is from existing kinetic models [12-15]. Some rate constants were updated to match experimental dependencies of burning velocities of air mixtures of H_2 , CH_4 , CH_3OH , C_2H_6 , C_2H_4 , and C_2H_2 on equivalence ratio. Kinetic submodels for bromine- and iodine-containing species were the same as in our earlier work [9]. Calculations were carried out at atmospheric pressure and an initial temperature of 298 K.

Validation

Validation of the kinetic data was made by comparison with experimental measurements. These included comparisons of ignition delay and species his-

tory from the oxidation of H_2 , CH_4 , CH_3OH , and C_2H_6 in the presence and absence of CHF_3 , CH_3Br , CF_3Br , and CH_3I [9,10]. The calculated burning velocities were in substantial agreement with measurements at various equivalence ratios for a number of C_1 - C_2 hydrocarbon compounds [13-14,16-17]. Comparisons with experimental measurements of burning velocity of methane/air flames doped with CHF_3 , CH_2F_2 , CF_4 , CF_3Br , C_2HF_5 , and C_2F_6 can be found in Fig. 1 [8,18-20] and are illustrative of the match between experiments and calculations. Calculated structures of the methane flame with CF_3Br at low pressures were also in substantial agreement with measurements [20]. The database should be expected to predict with reasonable accuracy the general trends regarding the influence of these inhibitors on flame properties. An important issue is the relevance of such results to actual fire situations. This is also the case for laboratory determinations; real fire tests, which are very expensive, are only applicable to the specific situation tested. Numerical and laboratory tests in conjunction with field study validation will ultimately yield procedures that lead to an understanding permitting the selection of the most effective fire inhibitor for a given scenario.

Results and Discussion

Burning Velocity under Stoichiometric Conditions

Figures 1 and 2 contain calculated burning velocities of stoichiometric air mixtures of CH_4 , CH_3OH , C_2H_6 , and C_2H_4 with various amounts of additives and demonstrate a monotonic decrease in calculated flame velocity with increasing inhibitor concentration. Burning velocities at 1% inhibitor concentration levels (on a mole basis) under stoichiometric conditions are summarized in Table 1. Also included in Table 1 are data on CH_3Br , HBr , HI , and C_2H_2 (products from inhibition and fuel decomposition reactions), which give an indication of their possible contributions. The general ranking for suppressant capability is CF_3I , $\text{CF}_3\text{Br} > \text{C}_2\text{F}_6 > \text{C}_2\text{HF}_5 > \text{CHF}_3 > \text{CF}_4$ and is relatively invariant with respect to fuel type. These results coincide with cup burner experiments for heptane flames [21] and other measurements [22]. The effectiveness of CF_3Br and CF_3I as retardants is similar. CF_3Br is a more effective retardant than CF_3I for stoichiometric methane and acetylene flames but less effective for methanol.

The relative magnitudes (in terms of the ratio of flame velocities in the presence and absence of retardants) obtained here for methane and ethylene in the presence of CF_3Br are in excellent agreement with the results tabulated by Westbrook [4]. In the case of methanol, CF_3Br is less effective as a retardant than in methane. This is in agreement with ex-

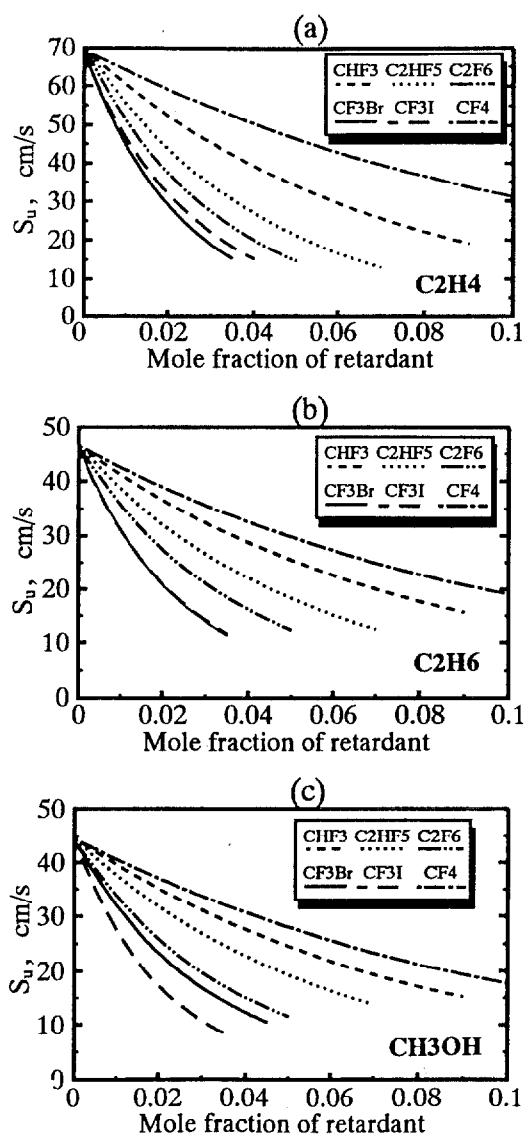


FIG. 2. (a) Burning velocity as a function of additive concentration for stoichiometric C₂H₄/air flame. (b) Burning velocity as a function of additive concentration for stoichiometric C₂H₆/air flame. (c) Burning velocity as a function of additive concentration for stoichiometric CH₃OH/air flame.

perimental observations and confirms Westbrook's suggestion [4] that the database he used for his calculations may be incomplete. Suppression effects from the compounds that do not contain either bromine or iodine are conspicuously smaller. It will be demonstrated later that the small contributions from CF₄ are due mostly to thermal contributions. Assuming that the differences in calculated velocities

characterize relative inhibition efficiency, one may conclude that a given inhibitor is more effective as the degree of unsaturation is increased. Table 1 shows that for both CF₃I and CF₃Br, the changes in flame velocities from the pure mixtures increase for the sequence of molecules C₂H₆, C₂H₄, and C₂H₂. This can also be attributed to the decrease in the hydrogen content of the fuel. It is consistent with experimental observation [23] in which the results were for chlorine- and bromine-containing additives in the combustion of hydrogen, *n*-hexane, and benzene. In the present work, the concentration of the inhibitor is small (1%). Thus, the overall stoichiometry is not greatly affected. The variation of flame speeds with inhibitor concentration (see Figs. 1 and 2) certainly indicates that the H/F ratio is another important variable.

Dependence of Burning Velocity on Equivalence Ratio

Burning velocities were calculated for equivalence ratios ranging from 0.8 to 1.4. Typical results for C₂H₄ with different additives are given in Fig. 3. All of the retardants appear to be more effective for rich mixtures than for lean. These results are in agreement with those from the literature [24–25]. CF₃I is more effective in rich mixtures than CF₃Br. In lean mixtures, CF₃Br is more effective than CF₃I in CH₄ and C₂H₄. The change of burning velocities with equivalence ratio did not affect the relative ordering of the effectiveness of the retardants.

Flame Thickness

The flame thickness is defined as follows: the cold boundary of the flame zone is taken as a temperature of 400 K and the hot boundary is defined as the location where 95% of the fuel has been consumed. For rich mixtures, the 95%-consumption boundary is defined as the value of the fuel concentration needed for total consumption of oxygen as dictated by the reaction stoichiometry. At this position, the reaction rate is at its maximum, the conversion to CO is mostly complete, and CO transformation to CO₂ has begun. It is clear that the flame thickness δ is increased with retardant concentration. This increase is directly related to the decrease in the burning velocity as follows from the well-known simple dependence of the characteristic thickness of the flame zone or

$$\delta = \lambda / (C_p \rho S_u)$$

where λ is the coefficient of heat conductivity; C_p , the heat capacity; and ρ , the mixture density [26]. Figure 4 is a plot summarizing all the calculations from this study. The universality of this curve arises from the relative invariance of the physical parameters that govern these organic flames. However, the

TABLE 1
Computed burning velocities (cm/s) with 1% retardant (stoichiometric mixtures, 1 atm, 298 K)

Retardant	CH ₄	CH ₃ OH	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂
none	42.1	44.4	46.1	69.1	132
CF ₄	38.5	40.1	42.5	64.1	—
CHF ₃	36.0	39.9	41.0	59.8	—
C ₂ HF ₅	34.4	37.1	39.4	56.6	—
C ₂ F ₆	29.9	33.5	36.6	51.9	—
CH ₃ Br	29.4	—	—	—	—
HBr	27.0	—	—	—	—
HI	26.4	—	—	—	—
CF ₃ I	23.3	27.5	30.3	43.7	96.4
CF ₃ Br	22.5	30.1	31.5	45.0	90.5

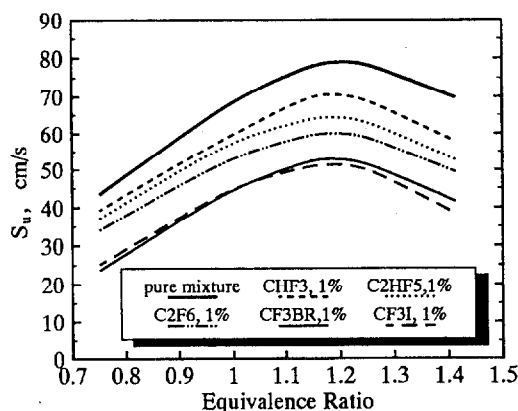


FIG. 3. Burning velocity as a function of equivalence ratio for C₂H₄/air flame.

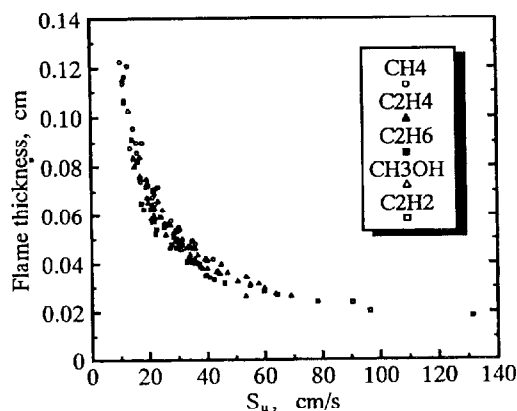


FIG. 4. Flame thickness as a function of burning velocity (including results with retardants).

correlation implied by the flame thickness-flame speed relation given previously (using C_p and p as determined here), leads to flame thicknesses that are smaller than those calculated by factors of 5–10. This is in accord with experimental observations [27] in which differences of a factor of 5–8 have been noted. Nevertheless, the important consequence is that the functional relation is obeyed. This general result is independent of the definition of the flame thickness. Physically, the observed effect is a manifestation of the decrease in heat-release rate as a result of the addition of the inhibitor.

Chain Carrier Concentrations in the Flame Zone

Table 2 contains a summary of the calculated data for H-atom concentrations at the hot boundary for the fuels that have been studied with 1% retardant. It can be seen that the results are compatible with a rank ordering similar to that of the flame velocities. The absolute values of the hydrogen concentrations are consistently lower in the methanol and ethane systems than in methane and ethylene. Results for OH and O are similar to those for the H atom described here, except that the sensitivity to changes in retardant concentration is less.

Thermal and Chemical Effect of Retardants

The relative importance of physical and chemical effects can be made clearer by carrying out simulations with and without the set of reactions of a particular inhibitor. Results for methane are summarized in Fig. 5. The fractional chemical contribution is defined as $(S_{uc} - S_{ui}) / (S_{uo} - S_{ui})$ and the subscripts ui , uc , and uo refer to calculations with and without inhibition chemistry and without inhibitor, respectively. An advantage of simulation experiments is precisely this capability of examination. In this case, the numerator represents the change in flame velocity brought about solely by chemistry, while the de-

TABLE 2
Mole fraction of H-atom concentration for stoichiometric air/fuel mixtures with 1% retardant, 1 atm and 298 K

Retardant	CH ₄	CH ₃ OH	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂
none	3.6×10^{-3}	1.3×10^{-3}	2.5×10^{-3}	5.4×10^{-3}	7.6×10^{-3}
CF ₄	3.2×10^{-3}	1.2×10^{-3}	2.3×10^{-3}	5.4×10^{-3}	—
CHF ₃	2.8×10^{-3}	1.1×10^{-3}	2.1×10^{-3}	4.4×10^{-3}	—
C ₂ HF ₅	2.6×10^{-3}	1.0×10^{-3}	1.9×10^{-3}	3.9×10^{-3}	—
C ₂ F ₆	2.1×10^{-3}	8.3×10^{-4}	1.7×10^{-3}	3.6×10^{-3}	—
CH ₃ Br	2.4×10^{-3}	—	—	—	—
HBr	2.3×10^{-3}	—	—	—	—
HI	2.0×10^{-3}	—	—	—	—
CF ₃ I	1.7×10^{-3}	7.0×10^{-4}	1.3×10^{-3}	3.6×10^{-3}	5.5×10^{-3}
CF ₃ Br	1.4×10^{-3}	5.9×10^{-4}	9.1×10^{-4}	3.0×10^{-3}	5.0×10^{-3}

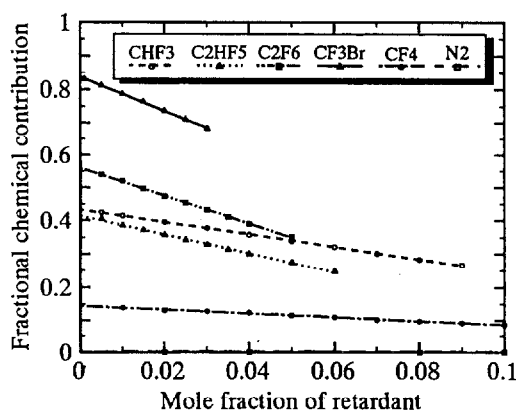


FIG. 5. Fractional chemical contribution to flame retardation ($S_{uc}-S_{ui}/S_{uo}-S_{ui}$) as a function of additive concentration for stoichiometric CH₄/air flames. For definition of symbols, see text.

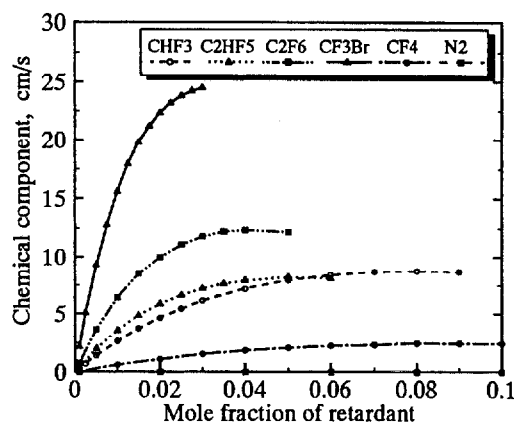


FIG. 6. Chemical contribution to flame retardation ($S_{uc}-S_{ui}$) as a function of additive concentration for stoichiometric CH₄/air flames. For definition of symbols, see text.

nominator is the total change. The large chemical component for inhibition by CF₃Br and smaller contributions for the other suppressants are clearly displayed. These results are in accord with the conclusions of Sheinson et al. [28] regarding the contributions from thermal and chemical effects in suppressant action of CF₃Br. An additional consequence of this treatment is that there appears to be a maximum value for the chemical contribution to inhibition. This can be seen in Fig. 6.

Reaction Mechanisms

The mechanisms for the oxidation of CH₄, CH₃OH, C₂H₆, and C₂H₄ have been discussed in detail and our analysis confirms those of the earlier studies [13-14,17]. Fluorinated retardants such as CHF₃, C₂F₆, and C₂HF₅ have some capacity to scav-

enge chain carriers and thus affect flame propagation. CF₄ behaves to a large extent as an inert compound. The main differences between the scavenging capabilities of the fluorinated compounds arise from the relative concentrations of the fluorinated radicals that are the reaction intermediates. Reaction pathway analysis demonstrated that the initial intermediates from the decomposition of the fluorinated inhibitors are CF₃ and CHF₂. Decomposition of C₂F₆ and CHF₃ leads to the production of mainly CF₃. C₂HF₅ decomposition generates CHF₂ and CF₃ radicals. The difference in the reactivity of these radicals is connected with the effectiveness of the fluorinated compounds as inhibitors. Although CHF₂ is more easily oxidized to CO₂ than CF₃, the observed ordering suggests that CF₃ is a more effective scavenger than CHF₂. The detailed sequence of reactions for the decomposition of these fluorinated radicals has been given in an earlier pa-

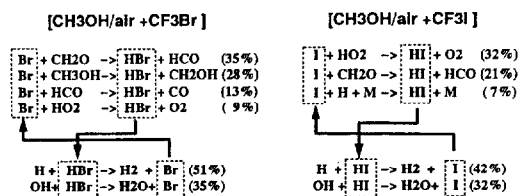
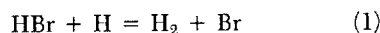


FIG. 7. Regeneration cycles for the inhibition of stoichiometric CH_3OH flames with CF_3Br and CF_3I additives (2%). Figures in parentheses represent the contributions toward the consumption of Br , HBr , I , and HI , respectively. These are derived from results with 2% CF_3Br and CF_3I , respectively. The reaction fluxes are integrated until all fuel has been destroyed (maximum concentration of H atoms).

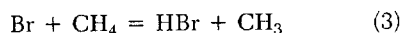
per [8]. Note that there are no effective pathways for the regeneration of the inhibiting species.

CF_3Br and CF_3I can inhibit flames via two mechanistic pathways. The fluorinated part of the molecule inhibits via the scavenging of hydrogen atoms by CF_3 radicals and following the pathways outlined previously. The main inhibition channel involves hydrogen iodide and hydrogen bromide. They remove H atoms through reactions

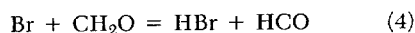


This is in contrast to HF , since the reaction of $\text{H} + \text{HF}$ is highly endothermic. Particularly important is the capability of bromine and iodine atoms to participate in catalytic cycles. This enhances inhibition effects through regeneration of the scavenging species. The individual reactions are, however, different.

In the case of methane, aside from the reaction used by Westbrook

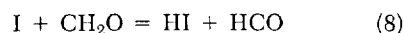
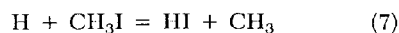
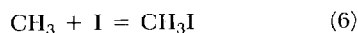


we find that the reactions



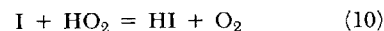
also make contributions. The last is in fact a termination process. An important difference between this and earlier work [1-4] is the conclusion that the processes $\text{H} + \text{Br} + \text{M} = \text{HBr} + \text{M}$ and $\text{Br} + \text{Br} + \text{M} = \text{Br}_2 + \text{M}$ followed by $\text{H} + \text{Br}_2 = \text{HBr} + \text{Br}$ are relatively unimportant as channels for the formation of HBr .

The weakness of the $\text{H}-\text{I}$ bond means that HI is not readily formed by I attack on methane. Instead, the presence of radicals can lead to combination with the iodine atom through the following reactions:



The reactions $\text{I} + \text{I} + \text{M} = \text{I}_2 + \text{M}$ and $\text{H} + \text{I}_2 = \text{HI} + \text{I}$ do not make appreciable contributions to inhibition because of the weakness of the $\text{I}-\text{I}$ bond. Reactions of H atoms with initial compounds CF_3I and CF_3Br also contribute to the scavenging effect.

Catalytic cycles of bromine and iodine species in methanol combustion are presented in Fig. 7. As with methane, HBr regeneration is partly effected through bromine attack on the methanol molecule. In the case of HI , however, quadratic termination or disproportionation is an important process:



The HO_2 radical is formed through the chain propagation reaction



Thus, removal of HO_2 from the system has significant inhibitory effects. These general tendencies, and a series of processes that ultimately lead to the regeneration of the hydrogen halide, are repeated for all the other systems considered.

Summary

1. The influence of CHF_3 , CF_4 , CF_3I , CF_3Br , C_2F_6 , and C_2HF_5 on laminar flame propagation in air mixtures of CH_4 , CH_3OH , C_2H_6 , and C_2H_4 was studied. The ordering of suppressant efficiency in terms of decreasing burning velocities was found to be CF_3I , $\text{CF}_3\text{Br} > \text{C}_2\text{F}_6 > \text{C}_2\text{HF}_5 > \text{CHF}_3 > \text{CF}_4$. This trend was followed generally by the other measures tested. The relative effectiveness of CF_3I and CF_3Br is dependent on the nature of the fuel and the physical conditions.
2. Methane flames appear to be inhibited more easily than methanol and ethane. At a given concentration of retardants, inhibitive efficiency is increased with equivalence ratio.
3. Inhibition is brought about largely through the scavenging of hydrogen atoms. A distinction is made between scavenging with and without regeneration of the scavengers; fluorinated fragments belong in the latter category. In the presence of iodine and bromine, regeneration of the hydrogen halides is brought about by various cycles. These involve not only radical attack on the fuel, the inhibitor, and their breakdown products, but equally important (particularly for iodine), processes initiated by radical reaction with the halogen atom. For methanol, with CF_3I as the

inhibitor, a particularly important reaction is $I + HO_2 \Rightarrow HI + O_2$, which regenerates HI while removing HO_2 radicals in the flame zone.

4. With the chemical mechanism, it is possible to distinguish between chemical and physical aspects of inhibition. There appears to be a saturation effect for chemical inhibition.

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