INHIBITION EFFECTIVENESS OF HALOGENATED COMPOUNDS

by

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Inhibition Effectiveness of Halogenated Compounds*

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A numerical study of the inhibition efficiency of halogenated compounds was carried out for C_1–C_2 hydrocarbon–air laminar premixed flames. The inhibition efficiency of CF_3Br, CF_3I, CF_3H, C_2HF_5, C_2F_6, and CF_4 additives was interpreted using an additive group method. In agreement with measurements, the calculated burning velocity decreased exponentially with increasing additive concentration over a wide concentration range. The inhibition parameter Φ proposed by Fristrom and Sawyer indicating inhibition efficiency was modified to take into account the exponential dependence of burning velocity on inhibitor concentration. The inhibition indices for halogen atoms and groups important in the inhibition process were determined for stoichiometric conditions. The physical and chemical effects of the additives were studied. With increasing additive concentration, the chemical influence of an inhibitor saturates and the physical influence increases. Therefore, use of a composite inhibitor composed of a mixture of an effective chemical inhibitor with a high heat capacity diluent may be beneficial. The contribution of physical and chemical components on inhibitor influence are estimated near extinction. A procedure for determination of a regeneration coefficient, which indicates an effective number of catalytic cycles involving inhibitor during the combustion process, is suggested. The regeneration coefficient of HBr in stoichiometric methane–air flame with 1% CF_3Br added is approximately 7.

INTRODUCTION

The burning velocity, S_u, is an important parameter which characterizes the inhibition efficiency of halogen-containing flame retardants. As the inhibitor concentration increases, the burning velocity decreases due to increased inhibitor influence. Rosser et al. [1] studied experimentally the inhibition effect of different additives on methane flames. The burning velocity was found to decrease linearly with increasing additive concentration for concentrations less than 0.5% by volume, leading to the expression

$$S_u = S_0 - \Phi \cdot C_{in}, \tag{1}$$

where S_0 and S_u are the burning velocities for CH_4–air flames without and with additives, respectively, C_{in} is the additive mole fraction, and Φ is a constant. Rosser et al. [1] used the parameter Φ ($= dS_u/dC_{in}$) as a measure of inhibition efficiency. Halpern [2] reported that the flame speed is a linear function of inhibitor concentration for methane flames for small concentrations of CF_3Br, CF_2Br_2, CH_3Cl, CF_3Cl, and $CHFCl_2$ addition. Based on the linear dependence of S_u on additive concentration, Fristrom and Sawyer [3] suggested using a dimensionless inhibition parameter Φ_{FS} for evaluation of the inhibition efficiency of additives:

$$\Phi_{FS} = \left[(S_0 - S_u) \cdot C_{O_2}\right]/[S_0 \cdot C_{in}]. \tag{2}$$

Here, C_{O_2} is the initial concentration of oxygen in the mixture. Fristrom and Van Tiggelen [4] suggested that the parameter Φ_{FS} could be written as the sum of the inhibition indices ϕ_i for each atom constituting the additive molecule:

$$\Phi_{FS} = n_H \phi_H + n_C \phi_C + \sum n_x \phi_x. \tag{3}$$

Here, the subscript x indicates a halogen atom. Atomic indices were derived for a number of

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fuel systems. Table 1 shows atomic inhibition indices obtained by Fristrom and Van Tiggelen [4]. In addition to atomic indices, Da Cruz et al. [5] introduced some groups which improved the correlation. This procedure is similar to the group additivity method which is widely used for estimation of thermodynamic and other properties of chemical substances [6]. The group additivity procedure makes it possible to estimate the inhibition efficiencies of different compounds. Its application is restricted to small additive concentrations due to the assumption of a linear dependence of S_u. Another restriction is the absence of some atomic and group indices for fuel systems other than methane.

The assumption of a linear dependence of the burning velocity on inhibitor concentration (Eqs. 1 and 2) is, however, not consistent with other studies. Later, Rosser et al. [7] reported that the reciprocal of the square of the burning velocity was proportional to the inhibitor concentration for methane flames with additives such as BBr_3, PCl_3, $POCl_3$, and others. Parks et al. [8] showed that for CF_3Br addition over a wide range of additive concentrations and mixture compositions, the flame speed of premixed methane–air and propane–air flames decreased exponentially.

Some recent studies [9–12] have shown the nonlinear dependence of the burning velocity on additive concentration for methane–air premixed flames over a wide concentration range for CF_4, CF_3H, CF_2H_2, and other additives. We have computed the burning velocity for C_1–C_2 hydrocarbon–air premixed flames with halogenated additives, showing that the burning velocity decreases with additive concentration in a nonlinear fashion [13]. Specifically, to decrease S_u until flame extinction, relatively large amounts of additive are necessary.

The mechanisms of combustion inhibition and suppression are a long standing question. The mechanisms of retardant action can be split into two categories: physical mechanisms, when heat capacity and dilution effects dominate, and chemical mechanisms, where radical scavenging is important. Flame retardants are usually considered to behave both chemically and physically. Sheinson et al. [14] estimated the chemical and physical contributions of CF_3Br effect on heptane diffusion flames through an enthalpy balance. The chemical contribution of CF_3Br to obtain suppression was estimated as approximately 80%. Tucker et al. [15] studied flame extinction by the addition of inert gases and CF_3Br, and inferred that the chemical effect of the retardant decreased with increasing additive concentration.

The main focus of this work is to take into account the nonlinear dependence of burning velocity on additive concentration and to reconsider the group additivity procedure [6] for the evaluation of flame retardant efficiency. This is important because in actual practice a large concentration of inhibitor is usually applied. In addition, it is important to develop a

TABLE 1

Inhibition Indices Obtained by Fristrom and Van Tiggelen [4]

Fuel (λ)[a]	ϕ_H	ϕ_C	ϕ_F	ϕ_{Cl}	ϕ_{Br}	ϕ_I
H_2 (1.75)	0.34	0.33	0.25	0.25	1.22	*b*
CO (1)		*c*	0.60	1.2	7.0	*b*
CH_4 (1.06)	0.25	1	1	1.9	10.9	11.2
C_3H_8 (1)	0.5	0	*b*	1.6	10.6	8.8
C_6H_{14} (1)	0.3	0.4	*b*	1.1	4.4	*b*
C_2H_2 (1)	−0.3	1.6	*b*	1.3	5.1	*b*
C_2H_4 (1)	*d*	*d*	*b*	2.5	6.1	6.8
C_6H_6 (1)	*b*	*b*	*b*	1.3	5	*b*

[a] λ is the equivalence ratio.
[b] No data available.
[c] ϕ_C is assumed to equal 10.
[d] $\phi_{CH_3} \approx \phi_{CH_2}$.

simple predictive capability. The correlations derived here are based on both experimental and simulation results. An analysis of chemical and physical contributions of additive influence is also presented.

MODELING TECHNIQUES AND KINETIC DATA BASE

Computations were conducted mainly for stoichiometric laminar flames burning mixtures of air with methane, ethylene, ethane, and methanol at atmospheric pressure. The initial temperature of the mixtures was 298 K. The following halogenated retardants were considered: CF_3H, C_2HF_5, C_2F_6, CF_4, CF_3Br, and CF_3I. For the calculations, the PREMIX code was employed [16]. Thermal diffusion has been considered. The calculated burning velocities of stoichiometric premixed methane–air, ethane–air, ethylene–air, and methanol–air flames were 42.1, 46.1, 69.1, and 44.4 cm/s, respectively. Burning velocities were calculated by using the first order windward difference formula (WDIF) for the convective terms, in the PREMIX flame code [16], with the parameters GRAD (≈ 0.2) and CURV (≈ 0.3), and fewer than 100 grid points. Using the central difference formula (CDIF) with almost the same number of grid points, the accuracy of the calculations was improved and the values of the burning velocity were 40.9, 44.6, 67.1, and 40.6 cm/s, respectively. It is possible to obtain the same values by using WDIF with increasing the number of grid points to approximately 200. Since the calculations were performed with a large kinetic model (approximately 700 reactions and 80 species), central processing unit (CPU) time for calculations using CDIF were much longer than those using WDIF. Thus, we used WDIF to reduce the CPU time. Analyses of the numerical results were completed using the National Institute of Standards and Technology (NIST) interactive graphics postprocessor Senkplot.

The data base used for the C/H/O system was based on existing kinetic models [17–20] and has been employed in an earlier study [13, 21]. A comprehensive set [22, 23] of elementary reactions for fluorine-containing C_1–C_2 species was used. The kinetic submodels for bromine- and iodine-containing species were the same as that in our earlier work [13, 24]. Tables 2 and 3 contain the thermodynamic and transport properties of the bromine- and iodine-containing species. Comparison of our numerical results showed that the burning velocities were in agreement with measurements for C_1–C_2 hydrocarbon flames over a wide range of equivalence ratios [18, 19, 35, 36]. Favorable 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_4, and CF_3Br [9–12]. Good agreement is found between the measured and calculated burning velocities which differed less than 15% on average, as we showed in Fig. 1 of Ref. 13. In addition, our computational results were in close agreement with measurement of the burning velocity of methane–air flames with CF_3I addition [37] and ethylene–air flames with CH_3Br and CH_3I addition [38] at atmospheric pressure. Thus, the data base can be expected to predict with reasonable accuracy the influence of inhibitors on flame propagation. Although these comparisons cannot be considered a complete quantitative validation of the data base, they do indicate that the simulation results are compatible with existing experimental results and that confidence can be placed in their reliability.

RESULTS AND DISCUSSION

Burning Velocity Dependence on Additive Concentration

Figure 1 shows the relative burning velocity of a stoichiometric CH_4–air premixed flame as a function of additive concentration for CF_3H, CF_4, CH_2F_2, C_2HF_5, C_2F_6, C_3F_8, C_3HF_7, and CF_3Br. Figure 1a shows the experimental results [9–12] where the lines are least-squares best exponential fits to the experimental data. The mixture stoichiometry (the equivalence ratio) is determined without taking into account the properties of the inhibitor.

As previously mentioned, S_u was found to have a linear dependence on retardant concentration over a small range of agent concentration [1–3]. For inert compounds, a linear dependence is usually obtained over a relatively

TABLE 2

Thermodynamic Properties of Bromine- and Iodine-Containing Species

Species	ΔH_f° (298) (kcal/mol)	S° (298) [cal/(mol K)]	$c_p(T)$ [cal/(mol K)] 300	500	800	1000	1200	1500	2000	3000	Ref.
Br	26.73	41.80	4.97	4.97	5.03	5.11	5.21	5.32	5.42	5.42	24
Br_2	7.39	58.64	8.62	8.86	8.97	9.01	9.04	9.08	9.14	9.25	24
HBr	−8.71	47.46	6.96	7.04	7.42	7.72	7.98	8.29	8.63	8.98	24
BrO	30.10	56.80	7.70	7.93	8.10	8.21	8.32	8.48	8.70	8.95	25
BrOH	−19.00	59.20	9.00	9.50	10.10	10.42	10.73	11.20	11.97	13.32	26
CH_3Br	−9.01	58.76	10.19	13.56	17.23	19.04	20.38	21.77	23.00	23.75	27
CH_2Br	41.50	60.30	4.25	7.78	11.62	13.44	14.83	16.33	17.71	18.51	28
C_2H_5Br	−15.30	68.72	15.47	21.97	28.61	31.63	33.87	35.96	27.16	37.36	27
C_2H_3Br	18.73	65.84	13.30	18.06	22.51	24.45	25.84	27.26	28.45	29.10	27
CF_3Br	−155.10	71.18	16.78	20.54	23.49	24.13	24.49	24.93	25.41	25.62	29
I	25.49	43.15	4.96	4.96	4.96	4.96	4.97	5.00	5.09	5.30	30
I_2	14.03	62.22	8.81	8.94	9.03	9.08	9.15	9.31	9.66	9.96	29
HI	6.29	49.31	6.96	7.10	7.59	7.93	8.17	8.46	8.79	9.13	29
IO	31.03	57.17	7.86	8.56	9.30	9.62	9.81	9.89	9.91	9.73	30
IOH	−18.10	61.10	9.31	10.44	11.34	11.73	12.08	12.49	12.95	13.45	30
CH_3I	3.43	60.61	10.60	14.01	17.49	19.19	20.53	21.91	23.59	25.12	29
CH_2I	54.42	62.05	9.50	12.70	15.80	17.30	18.43	19.31	20.20	20.56	24
C_2H_5I	−2.00	70.83	15.80	22.10	28.70	31.70	33.72	35.25	37.21	39.82	31
C_2H_3I	31.03	68.03	13.60	18.40	22.70	24.58	26.03	27.56	29.46	31.38	32
CF_3I	−140.60	73.42	16.92	20.42	23.57	24.44	24.70	24.90	25.20	25.58	29

TABLE 3

Transport Properties of Bromine- and Iodine-Containing Species[a] (CHEMKIN Format Presentation)

Species	ϵ/k_b	σ	μ	α	Ref.
Br_2	507.9	4.296	0.2	7.02	6, 33
HBr	449.0	3.353	0.8	3.61	6, 33
Br	230.0	3.700	—	—	*e*
BrO	360.0	3.800	1.76	—	*e*, 33
BrOH	440.0	3.950	—	—	*e*
CH_3Br	449.2	4.118	1.82	5.87	6, 33
CH_2Br	449.0	4.100	—	—	*e*
C_2H_5Br	470.0	4.850	2.03	8.05	*e*, 33
C_2H_3Br	460.0	4.600	1.42	7.59	*e*, 33
CF_3Br	270.0	4.100	—	—	*e*
I_2	474.2	5.160	1.3	—	6
HI	288.7	4.211	0.5	5.4	6, 33
I	280.0	3.900	—	—	*e*
IO	420.0	4.100	2.45	—	*e*, 33
IOH	480.0	4.200	—	—	*e*
CH_3I	420.0	4.600	1.62	7.97	*e*, 33
CH_2I	410.0	4.500	—	—	*e*
C_2H_5I	440.0	5.000	1.91	10.0	*e*, 33
C_2H_3I	420.0	4.800	1.3	9.3	*e*, 33, 34
CF_3I	320.0	4.900	1.05	—	*e*, 33

[a] ϵ/k_b, the Lennard–Jones well depth (K); σ, the Lennard–Jones collision diameter (Å); μ, the dipole moment (De); α, the polarizability (Å^3); *e*, estimation.

wide range of concentrations. According to simple theoretical relations [39], the burning velocity is proportional to the square root of the reaction rate, which has an exponential dependence on the adiabatic flame temperature. The main effect of dilution by an inert is to approximately decrease the adiabatic flame temperature linearly. Thus, for inert additives, an exponential decay of the burning velocity is expected in contrast to a linear dependence.

As shown in Fig. 1a, a linear relationship between burning velocity and additive concentration becomes tenuous when a wide concentration range is considered. A best fit to the additive concentration for the burning velocity leads to an exponential dependence,

$$S_u/S_0 = \exp(-b \cdot C_{\text{in}}), \tag{4}$$

where b is a constant. The numerically obtained burning velocities, using the PREMIX code, are presented in Fig. 1b. The results of the numerical simulations also are well approximated by an exponential function.

The constant b in Eq. 4 reflects the efficiency of an inhibitor. In dimensionless form,

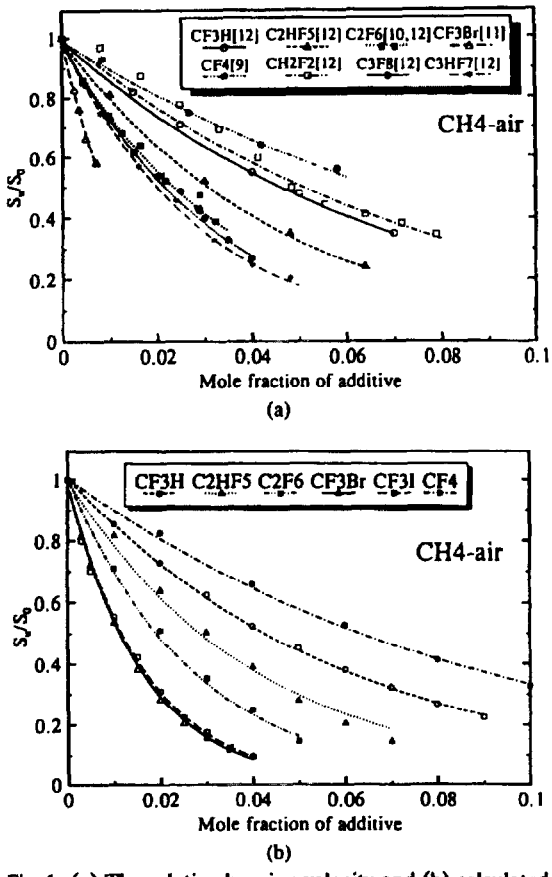

Fig. 1. (a) The relative burning velocity and (b) calculated relative burning velocity as a function of additive concentration for stoichiometric CH_4–air flames. Symbols represent (a) experimental data and (b) calculation results; lines are best exponential fits.

using the oxygen concentration C_{O_2} as a normalizing parameter [3], the inhibition parameter Φ is

$$\Phi = (C_{O_2}/C_{in}) \cdot \ln(S_0/S_u). \tag{5}$$

Here, Φ is modified from the form suggested by Fristrom and Sawyer [3], taking the exponential concentration dependence of S_u into account. The parameter Φ for the halogenated compounds considered here can also be represented as a sum of elementary indices

$$\Phi = n_F\phi_F + n_{CHF_2}\phi_{CHF_2} + n_{CF_4}\phi_{CF_4} + n_{Br}\phi_{Br} + n_I\phi_I. \tag{6}$$

It is assumed that $\phi_C = 0$ and $\phi_H = 0$. To obtain better fits to the burning velocity data, the groups CHF_2 and CF_4 are also used. This is a reflection of the fact that an atomic fluorine additivity scheme cannot fit the data due to the high stability of compounds such as CF_4 and CF_2O.

Table 4 presents both experimental and calculated values of the exponential constant b and the inhibition parameter Φ for different additives in stoichiometric CH_4–air premixed flames. Nitrogen is also presented as a reference basis in Table 4. The combination of inhibition indices for the fluorinated additives such as CF_3H, C_2HF_5, and C_2F_6 is based on

TABLE 4

Exponential Constant b and the Inhibition Parameter Φ for CH_4–Air Stoichiometric Flame with Halogenated Additives[a]

Additive	b_{exp}[b]	Φ_{exp}[c]	b_{cal}[b]	Φ_{cal}[c]	Indices for Φ
CF_3H	14.9	2.6	16.3	2.9	$3\phi_F$
C_2HF_5	22.1	4.0	24.6	4.5	$3\phi_F + \phi_{CHF_2}$
C_2F_6	28.5	5.2	34.6	6.3	$6\phi_F$
CF_3Br	78.6	14.0	60.9	11.1	$3\phi_F + \phi_{Br}$
CF_3I	—	—	58.5	10.7	$3\phi_F + \phi_I$
CF_4	10.3	1.8	11.1	1.9	ϕ_{CF_4}
CH_2F_2	13.7	2.4	—	—	$\phi_F + \phi_{CHF_2}$
C_3HF_7	33.9	6.2	—	—	—
C_3F_8	31.5	5.8	—	—	—
N_2	3.6[d]	—	3.6	—	—

[a] exp, experimental measurement; cal, calculation result.
[b] The constant b is derived from the equation $S_u/S_0 = \exp(-b \cdot C_{in})$.
[c] The constant Φ is derived from $\Phi = (C_{O_2}/C_{in}) \cdot \ln(S_0/S_u)$.
[d] The constant b is derived from data reported in Ref. 4.

the initial decomposition products. CF_3H and C_2F_6 decompose mainly to CF_3. Decomposition of C_2HF_5 generates CHF_2 and CF_3 radicals. CH_2F_2 decomposes to CHF_2 and CHF [22, 40]. Table 4 shows that there is reasonable agreement between the experimentally observed (b_{exp}) and the numerically obtained exponential constants (b_{cal}). A maximum difference between the experimental and computational exponential constants occurs for CF_3Br and is approximately 25%. Table 5 compares the inhibition indices for ϕ_F and ϕ_{Br} derived from the experimental measurements and the modeling, and the linear indices suggested by Fristrom and Van Tiggelen [4]. It is seen that the experimental linear indices [4] obtained in a small concentration range coincide with the "exponential" indices. For values of $\Phi \cdot C_{in}/C_{O_2} \leq 0.3$, the linear indices are approximately equal to the exponential indices.

Figure 2a–c shows calculations of normalized burning velocity for stoichiometric premixed C_2H_6–air, C_2H_4–air, and CH_3OH–air flames with additives. Table 6 shows the constant b and the inhibition parameter Φ for stoichiometric C_2H_6, C_2H_4, and CH_3OH flames with additives. The values of b and Φ follow similar trends. The constants b and Φ are largest for CF_3I and CF_3Br followed by C_2F_6, C_2HF_5, CF_3H, and CF_4, consistently for the three fuels.

The inhibition indices for F, Br, I, CHF_2, and CF_4 obtained from numerical modeling are shown in Table 7. Figure 3 shows a diagram of the inhibitor ranking for different halogenated additives estimated using inhibition indices. The index for the chlorine atom

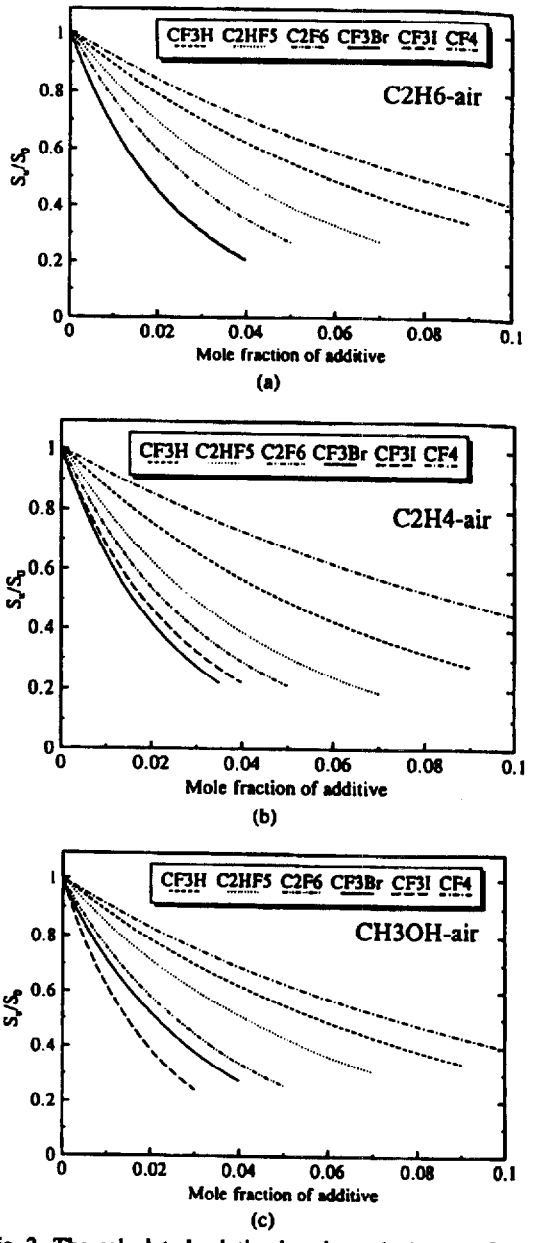

Fig. 2. The calculated relative burning velocity as a function of additive concentration for stoichiometric (a) C_2H_6–air, (b) C_2H_4–air, and (c) CH_3OH–air flames.

TABLE 5

Comparison of Inhibition Indices of Fluorine and Bromine Atoms Derived from Experimental Measurements, Calculation Results, and Those Suggested by Fristrom and Van Tiggelen [4]

Atomic Index	Inhibition Index			
	Exponential Dependence		Linear Dependence	
	Experiment	Calculation	Calculation	Ref. 4
ϕ_F	0.9	1.0	1.0	1.0
ϕ_{Br}	11.6	8.1	8.6	10.9

was assumed to be equal to the index given by Ref. 4. Note that the inhibition efficiencies in terms of decreases in flame velocity by halogenated compounds correspond approximately to experimental data [1, 9–12].

Figure 4 shows the relative burning velocity as a function of the ratio $\Phi \cdot C_{in}/C_{O_2}$ for stoi-

TABLE 6

Exponential Constant b and Inhibition Parameter Φ for C_2H_6–Air, C_2H_4–Air, and CH_3OH–Air Stoichiometric Premixed Flames with Additives of Halogenated Compounds CF_3H, C_2HF_5, C_2F_6, CF_3Br, CF_3I, and CF_4

System	b^a	Φ^b
C_2H_6–air + CF_3H	12.1	2.24
+ C_2HF_5	18.7	3.51
+ C_2F_6	26.4	5.01
+ CF_3Br	39.8	7.72
+ CF_3I	39.2	7.46
+ CF_4	8.91	1.63
C_2H_4–air + CF_3H	14.3	2.60
+ C_2HF_5	24.2	4.47
+ C_2F_6	31.3	5.85
+ CF_3Br	43.2	8.23
+ CF_3I	37.4	7.47
+ CF_4	8.02	1.45
CH_3OH–air + CF_3H	12.0	2.05
+ C_2HF_5	16.7	2.93
+ C_2F_6	26.9	4.76
+ CF_3Br	31.9	5.67
+ CF_3I	47.1	8.37
+ CF_4	9.21	1.57

[a] The constant b is derived from the equation $S_u/S_0 = \exp(-b \cdot C_{in})$.

[b] The constant Φ is derived from $\Phi = (C_{O_2}/C_{in}) \cdot \ln(S_0/S_u)$.

chiometric methane–air flames. This figure represents, in another form, that the burning velocity can be approximately described by a single exponential dependence for all additives using Eq. 5 over a wide range of additive concentrations. Also, it is seen that the ratio $\Phi \cdot C_{in}/C_{O_2}$ is a similarity parameter. The results of calculations for other equivalence ratios show that the inhibition indices are valid for equivalence ratios from 0.8 to 1.2 with an accuracy ±15%. For very lean or rich mixtures (< 0.8 and > 1.2), however, the inhibition efficiency of the additives may differ from near stoichiometric values.

Physical and Chemical Action of Flame Retardants

The mechanisms of a retardant's influence usually are divided into two categories: physical mechanisms, where heat capacity and dilution effects dominate, and chemical mechanisms, where radical scavenging is important. The burning velocity is reduced due to both physical and chemical influences of an additive. Figure 5 shows the calculated adiabatic flame temperature as a function of the relative burning velocity for different additives. The ratio $S_u/S_0 = 1$ corresponds to a flame without additives. A value of 5 cm/s is assumed as the critical flame speed at extinction [41]. This velocity is attained as the nitrogen concentration increases, at a flame temperature of approximately 1600 K. This temperature has been thought to approximately represent the extinction limits for diffusion flames [14, 42]. Use of chemical retardants such as CF_3Br, CF_3I, and other halogenated additives leads 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 [43].

A procedure for determination of the physical and chemical contributions of an additive is shown in Fig. 6. The physical influence of a retardant can be characterized by treating the additive as an inert compound and by calculating the burning velocity (S'), by turning off all reactions involving the inhibitor. The physical

TABLE 7

Inhibition Indices of Halogen Atoms (ϕ_F, ϕ_{Br}, ϕ_I) and Groups (ϕ_{CHF_2}, ϕ_{CF_3}) Composing the Inhibition Parameter Φ for C_1–C_2 Hydrocarbon–Air Stoichiometric Flames with Halogenated Compounds

Fuel	ϕ_F	ϕ_{CHF_2}	ϕ_{CF_3}	ϕ_{Br}	ϕ_I
CH_4	1.0	1.5	1.9	8.1	7.7
C_2H_6	0.8	1.1	1.6	5.3	5.1
C_2H_4	1.0	1.5	1.5	5.2	4.5
CH_3OH	0.7	0.8	1.6	3.6	6.3

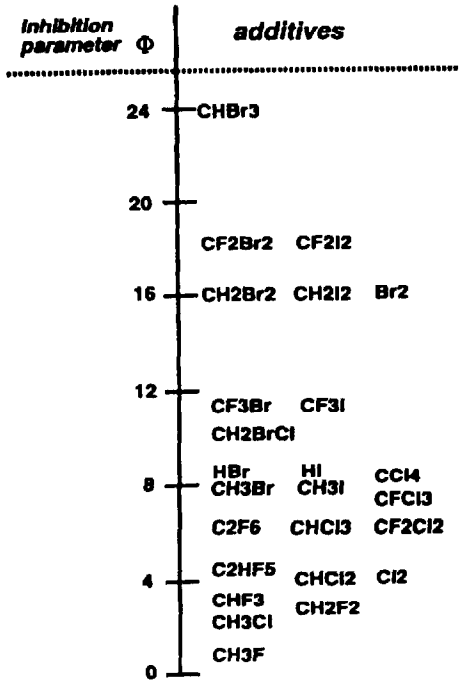

Fig. 3. The relative inhibition efficiency of halogenated additives according to inhibitor indices for stoichiometric methane–air flames.

component, Y_p, is defined as

$$Y_p = 1 - S'/S_0, \tag{7}$$

where S_0 is the burning velocity calculated without additives. The chemical inhibition component (Y_c) is the difference between the

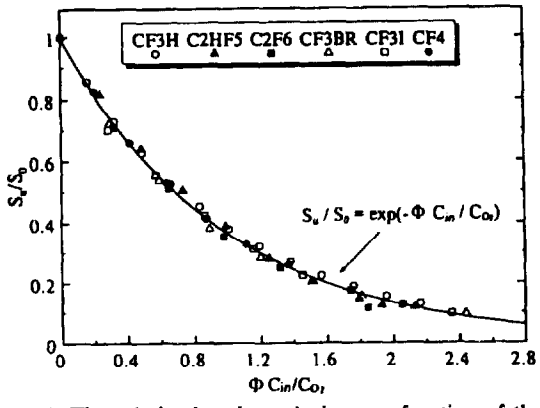

Fig. 4. The relative burning velocity as a function of the ratio $\Phi \cdot C_{in}/C_{O_2}$ for stoichiometric CH_4–air flames with additives.

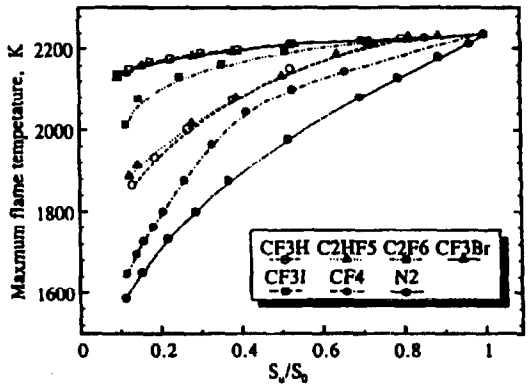

Fig. 5. The relationship between the maximum flame temperature and the normalized burning velocity for methane–air flames with additives.

physical component and the total inhibition effect,

$$Y_c = (S' - S_u)/S_0, \tag{8}$$

where S_u is the burning velocity calculated with the additive using the kinetic model including inhibitor reactions. Figure 7 shows the behavior of the physical component (Y_p) as a function of additive concentration for a stoichiometric CH_4–air flame. The physical influence of the additives on flame speed is mostly 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_4 have approximately equal physical effects. The physical

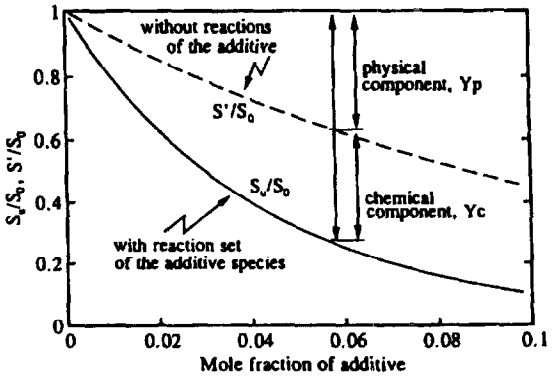

Fig. 6. Definition of the physical Y_p and the chemical Y_c components of inhibitor influence.

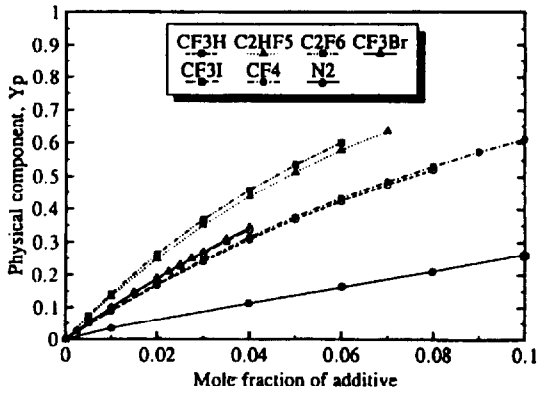

Fig. 7. The physical component Y_p as a function of additive concentration in stoichiometric CH_4–air flames.

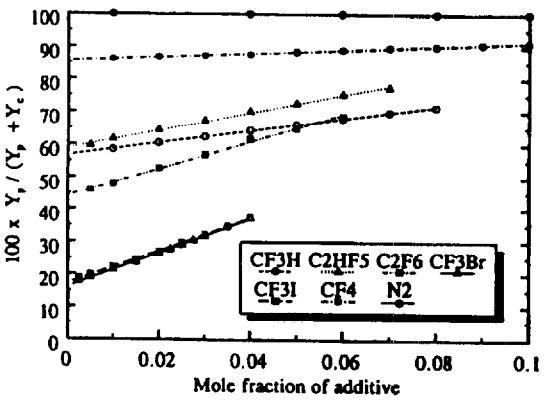

Fig. 9. The fractional physical inhibition contribution $Y_p/(Y_p + Y_c)$ as a function of additive concentration in CH_4–air flames.

component of the retardant influence increases with increasing additive concentration.

Figure 8 shows the dependence of the chemical component (Y_c) on additive concentration. As expected, nitrogen has no chemical contribution. Chemical effectiveness is thought to depend on the ability to reduce the concentration of chain carriers [44]. The chemical effectiveness of C_2F_6 is almost twice that of CF_3H. One molecule of C_2F_6 produces two CF_3 radicals during the initial stage of decomposition. For C_2HF_5, the decomposition mechanism is dominated by the reaction $C_2HF_5 \rightarrow CHF_2 + CF_3$, and the chemical component can be thought to consist of the sum of the inhibition effects of CF_3 and CHF_2 radicals. The chemical action of CHF_2 is less than 2/3 that of the CF_3 radical.

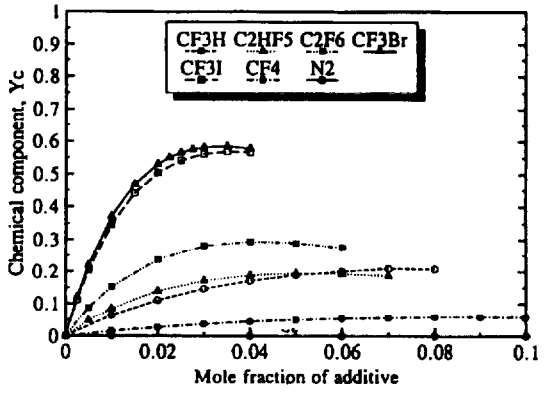

Fig. 8. The chemical component Y_c as a function of additive concentration in stoichiometric CH_4–air flames.

Table 8 shows the relative physical, $100 \times Y_p/(Y_p + Y_c)$, and the chemical, $100 \times Y_c/(Y_p + Y_c)$, components of inhibition for the additives in methane–air flames at $S_u = 5$ cm/s (the presumed extinction value [41]). Also, contributions are presented for decreasing S_u to half its value, where $S_u/S_0 = 0.5$.

TABLE 8

Physical and Chemical Contributions at $S_u/S_0 = 0.5$ and $S_u = 5$ cm/s for CH_4–Air Stoichiometric Flames

Additive	$S_u/S_0 = 0.5$		$S_u = 5$ cm/s	
	Physical Effectiveness (%)	Chemical Effectiveness (%)	Physical Effectiveness (%)	Chemical Effectiveness (%)
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

The physical contributions of the fluorinated compounds CF_3H and C_2HF_5 are 80% for $S_u = 5$ cm/s. CF_4 acts mostly through physical effect. On the other hand, physical inhibition components for CF_3Br and CF_3I are approximately 20% at $S_u/S_0 = 0.5$ and about 35% at extinction, respectively. Figure 9 shows the physical contribution percentage, $100 \times Y_p/(Y_p + Y_c)$, as a function of additive concentration. The physical contribution increases linearly with additive concentration. Figure 9 shows that as the additive concentration increases, dilution and heat capacity effects become relatively more important. The results indicate that the mode of influence of an inhibitor changes with its concentration. The physical and chemical components of CF_3Br and CF_3I for fuels other than CH_4 are presented in Table 9. For C_2H_4, C_2H_6, and CH_3OH, the percentage of the physical contribution of CF_3Br influence at $S_u = 5$ cm/s is 38, 41, and 50%, respectively. For the CH_3OH–air flame, physical and chemical factors for CF_3Br are nearly equal near extinction.

Different measures of chemical and physical contributions are possible. 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 and without reaction kinetics for the additive that yield the same burning velocity reduction. Sheinson et al. [14] used the "concentration" measure to estimate the chemical and physical contributions to inhibition. The difference in the maximum flame temperatures calculated with and without reaction kinetics for the additive yielding the same burning velocity reduction represents another means to differentiate physical and chemical contributions. Table 10 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 approximately consistent with those of Sheinson et al. [14].

Saturation Effect

For the halogenated compounds studied, when the additive concentration increases, the chemical contribution initially increases also. When the relative burning velocity (S_u/S_0) is approximately 0.2–0.4, saturation of chemical influence is observed (Fig. 8). In other words, the contribution of the chemical factor decreases with increasing additive concentration. This tendency is 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 concentration by the inhibitor.

TABLE 9

Physical and Chemical Contributions of CF_3Br and CF_3I at $S_u = 5$ cm/s for C_1–C_2 Stoichiometric Air Flames

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

TABLE 10

Physical and Chemical Contributions of the Influence of CF_3Br Determined at S_u = 5 cm/s for CH_4–air Stoichiometric Flame by Different Measures

Measure	Physical Effectiveness (%)	Chemical Effectiveness (%)
Burning velocity	35	65
Additive concentration	17	83
Maximum flame temperature	15	85

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 [13, 44]

$$H + HBr \Rightarrow H_2 + Br, \quad (R1)$$

$$OH + HBr \Rightarrow H_2O + Br. \quad (R2)$$

The relative importance of different reactions is determined through integral contributions of reaction rates, $\int w_i\, dt$, where w_i is the ith reaction rate and t is the reaction time [36]. Integration is carried out until a maximum H atom concentration is achieved. The integration interval approximately corresponds to the flame zone. Figure 10 contains the dependence of contributions of R1, R2, and the sum R1 + R2 to HBr consumption on CF_3Br concentration. 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 concentrations higher than 0.025 mole fraction, the importance of R2 increases. It is seen that the total effect of R1 and R2 saturates with retardant concentration. Saturation of HBr consumption is observed. The dependence of R1 + R2 contributions has a similar character as a chemical component of retardant influence (Fig. 8). In addition, an analysis of flame structure shows that the superequilibrium concentration of chain carriers [44] is reduced with increasing inhibitor concentration, resulting in a reduction in inhibitor effectiveness with further inhibitor addition.

After the saturation point, increase of additive concentration leads to preferentially less additional chemical influence, and thus, it is possible to consider the inhibitor as an inert gas. This leads us to suggest the use of a "composite" inhibitor which contains an effective chemical retardant and an additive with a high heat capacity. Its composition is determined by the saturation concentration of the retardant and the extinction concentration of the composite inhibitor. Figure 11 contains results of numerical modeling of CH_4–air flames when polyfluoroalkylamine $(CF_3CF_2)_3N$ [45] is added to 2.5% CF_3I which corresponds roughly to the saturation concentration. $(CF_3CF_2)_3N$ is treated as an inert. To achieve extinction, it may be advantageous to use a composite inhibitor consisting of an effective chemical inhibitor for rapid reduction of S_u and an inexpensive inert compound with a high heat capacity.

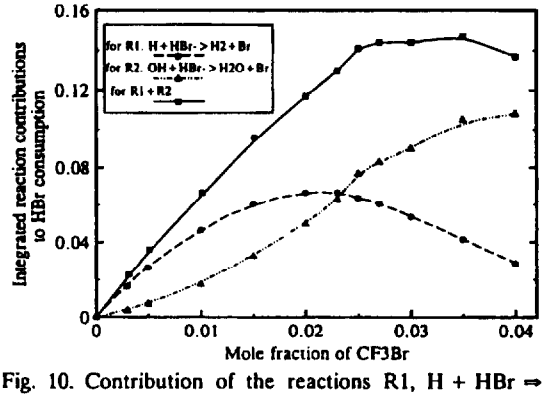

Fig. 10. Contribution of the reactions R1, H + HBr ⇒ H_2 + Br, and R2, OH + HBr ⇒ H_2O + Br, to HBr consumption as a function of CF_3Br mole fraction in stoichiometric CH_4–air flames.

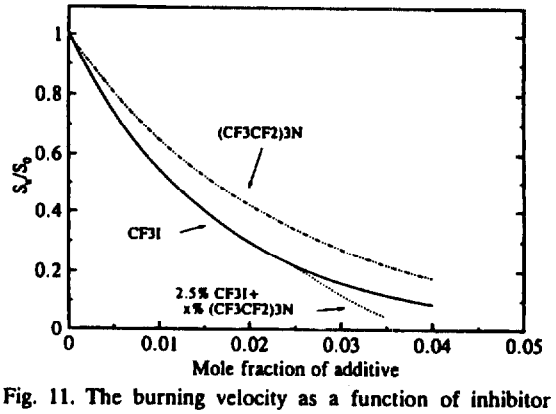

Fig. 11. The burning velocity as a function of inhibitor concentration for an additive composed of CF_3I and $(CF_3CF_2)_3N$.

Regeneration Coefficient

The scavenging of chain carriers by a flame inhibitor is increased due to reactions which regenerate the scavenging agent, or equivalently due to an increase of the "acting" concentration of an inhibitor [44]. The superior efficiency of CF_3Br and CF_3I as flame inhibitors, as compared to fluorinated hydrocarbons, is connected with the regeneration cycle associated with HBr and HI, respectively. It is possible to define a regeneration coefficient which indicates the effective number of catalytic cycles involving the inhibitor during the combustion process. The regeneration coefficient is determined by the ratio of the total concentration of scavenging agent (HBr, HI) consumed (or produced) to the initial concentration of this species which formed the agent:

regeneration coefficient

$$= [HBr]_{total}/[CF_3Br]_{initial}. \quad (9)$$

The total HBr consumed is determined by integration of the rates of reactions in which HBr is consumed until a maximum H atom concentration

$$[HBr]_{total} = \int \sum w_{HBr,i}\, dt. \quad (10)$$

The term $w_{HBr,i}$ is the reaction rate of the ith reaction consuming HBr. Figure 12 contains the concentration dependence of the regeneration coefficients of HBr and HI. The regeneration coefficient varies from 7 to 5 for CF_3Br concentrations from 0.5 to 4%. The regeneration coefficient of HI is approximately 4. The additional inhibition efficiency of CF_3I is due to an additional termination step, $CH_3 + I + M \Rightarrow CH_3I + M$, with the reaction $H + CH_3I \Rightarrow HI + CH_3$ [13].

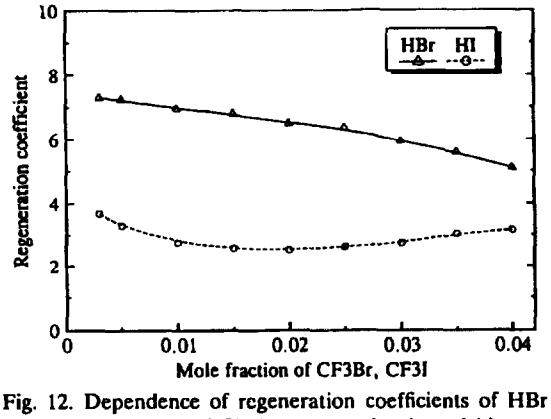

Fig. 12. Dependence of regeneration coefficients of HBr and HI on CF_3Br and CF_3I concentration in stoichiometric CH_4–air flames.

CONCLUSIONS

In this work, the inhibition effectiveness of halogenated flame retardants is analyzed by a modified additive group procedure [3, 4] taking into account the exponential dependence of burning velocity. Premixed methane, ethylene, ethane, and methanol–air flames are considered. Inherent in this treatment are assumptions regarding the nature of the decomposition products of the inhibitor during combustion. The chemical and physical contributions of retardant effect on flame propagation are determined. The main results are the following:

1. For the halogenated additives CF_3Br, CF_3I, CF_3H, C_2HF_5, C_2F_6, and CF_4, the burning velocity of C_1–C_2 hydrocarbons decreases exponentially with increasing additive concentration over a wide range of additive concentrations.
2. The inhibition parameter Φ proposed by Fristrom and Sawyer indicating inhibition efficiency is modified to the expression $\Phi = (C_{O_2}/C_{in}) \cdot \ln(S_0/S_u)$ to take into account the nonlinear dependence of burning velocity when a wide range of additive concentrations is considered. The inhibition indices for halogen atoms and groups were obtained for stoichiometric premixed C_1–C_2 hydrocarbon–air flames.
3. A procedure for the differentiation of physical and chemical contributions of additive effect is suggested. Increasing additive concentrations lead to saturation of the chemical contribution of additive effect. The subsequent increase of additive action is due to physical influence (heat capacity and dilution effects).
4. The utility of a "composite" inhibitor is suggested. Its constituents would be an effective chemical inhibitor and an inexpen-

sive 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.

5. The regeneration coefficient of an inhibition agent showing the number of regeneration cycles that occurred during combustion is determined. For atmospheric stoichiometric methane–air flames with 1% CF_3Br additive or 1% CF_3I additive, the regeneration coefficients are equal to approximately 7 and 4, respectively.

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