# EFFECT OF HYDROFLUOROCARBONS AND PERFLUOROCABONS ON SUPPRESSION EFFICIENCY OF CF<sub>3</sub>I

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## ABSTRACT

The inhibition efficiency of mixtures of gaseous suppressants, containing CF<sub>3</sub>I blended with hydrofluorocarbons (HFCs), such as C<sub>3</sub>HF<sub>7</sub>, C<sub>2</sub>HF<sub>5</sub>, and CHF<sub>3</sub>, and perfluorocarbons (FCs), such as C<sub>2</sub>F<sub>6</sub>, is studied by examining the reduction in the laminar burning velocity. The calculations involve the use of the PREMIX code in conjunction with the detailed flame chemistry described by GRI-Mech 3.0, NIST HFC and updated NIST CF<sub>3</sub>I mechanisms. The inhibition effects are separated into physical and chemical phenomena, with the chemical suppression displaying a distinct saturation limit. The present investigation also involves reaction pathway analysis. This is performed to address the following focussing questions: (i) Does a less effective additive modify the saturation limit of the more effective agent? (ii) Are the combined physical and chemical effects linear or non-linear; i.e., are the combined effects of the two chemicals equal to the sum of the separate effects owing to the two suppressants? (iii) Does an additive alter the reaction pathways of the more efficient agent? The results indicate that a combination of physical effects of two mixed suppressants is a linear combination of the physical effects of each agent. The combination of chemical effects for mixtures of  $CF_3I$  with  $CHF_3$ ,  $CF_3I$  and  $C_2F_6$  is significantly increased in comparison to the summation of chemical effects of each agent. However, this effect is not observed for mixtures of CF<sub>3</sub>I with C<sub>2</sub>HF<sub>5</sub> and CF<sub>3</sub>I with C<sub>3</sub>HF<sub>7</sub>.

## INTRODUCTION

Similarly to CBrF<sub>3</sub>, CF<sub>3</sub>I displays excellent fire suppression properties. Both agents remove the chain-propagating radicals in flames (H, OH, HO<sub>2</sub>) by a means of well-known homogeneous catalytic cycles HBr  $\rightarrow$  H  $\rightarrow$  HBr and HI  $\rightarrow$  H  $\rightarrow$  HI, in addition to cooling down the flames and diluting flammable fuel-oxidiser mixtures. The latter (physical) effects are minor. In addition, the decomposition fragments of the suppressant molecules (CF<sub>3</sub>, Br, I) react with fuel molecules initiating their further decomposition in flames. This process activates fuel molecules.<sup>1</sup> Thus, the chemical inhibition efficiency of CBrF<sub>3</sub> and CF<sub>3</sub>I constitutes the resultant radical removal via catalytic cycles and fuel activation.

<sup>&</sup>lt;sup>1</sup> In practice, this effect has been found useful in converting surplus halons and CFC to other chemicals, especially to precursors for fluoroelastomer production (e.g. Uddin et al., 2003)

Generally,  $CF_3I$  activates fuel molecules less efficiently than  $CBrF_3$ , but  $CBrF_3$  is a better scavenger of radicals. Depending on the importance of these two effects, the relative performance of  $CBrF_3$  and  $CF_3I$  varies for different fuels (Luo et al., 2004).  $CF_3I$  is more effective against fires of some polar fuels, such as methanol, whereas  $CBrF_3$  is a better extinguishment agent against hydrocarbon flames. In spite of these differences, both agents display similar design concentrations against hydrocarbon fires (around 3% plus a safety factor), as determined from cup-burner tests.

Unfortunately, both agents also exhibit some undesirable properties.  $CBrF_3$  does not decompose in the troposphere, is transported to the stratosphere where it catalyses gas phase reaction that destroy ozone molecules. For this reason, the production of  $CBrF_3$  has been phased out in industrialised countries, with several countries also disallowing the use of the agent, except for a small number of critical applications. Lists of critical applications are frequently reviewed and updated in countries that have banned the use of halons.

On the other hand,  $CF_3I$  is a less stable molecule owing to a weaker C-I bond, in comparison to the C-Br bond in  $CBrF_3$ .  $CF_3I$  readily degrades in the troposphere with no opportunity for the agent to be transported to the ozone layer. However,  $CF_3I$  in concentrations higher than 0.4% can cause cardiac arrhythmia. Since this concentration is substantially smaller that the agent's design concentration, at present  $CF_3I$  can only be applied to protect equipment in unoccupied spaces. From this perspective, one can propose to formulate mixtures of  $CF_3I$  with hydrofluorocarbons (e.g.  $C_3HF_7$ ,  $C_2HF_5$ ) or perfluorocarbons ( $C_2F_6$ ) in such a way as not to compromise the limit of 0.4% imposed as a consequence of cardiac sensitisation by  $CF_3I$ .

There is yet another reason for us to embark on the present investigation. HFC, and especially FC, exhibit relatively high global warming potentials and long atmospheric lifetimes. For these reasons, the use of FC has been discontinued in fire suppression applications. Mixing of HFC and FC with  $CF_3I$  could substantially decrease the amount of HFC and FC needed for effective fire suppression, and therefore reduce the global warming impact of HFC and FC released from fire suppression installations. However, at present, no date exist to allow the estimation of the reduction in emissions of HFC and FC, should these agents be mixed with small amounts of  $CF_3I$ .

Thus, the objective of this paper is to determine whether  $CF_3I$ -HFC and  $CF_3I$ -FC mixtures offer advantages over single-component mixtures for mitigating hydrocarbon flames. Our approach is to compute the variation in the laminar burning velocity of  $CH_4$  flames doped with  $CF_3I$ , HFC and FC agents and their mixtures. We then correlate the results of numerical calculations using the phenomenological expression of Noto et al. (1998) that links the burning velocities, with ( $S_u$ ) and without ( $S_0$ ) suppressants, with the mole fraction of the inhibitor

$$\frac{S_u}{S_0} = e^{-bx} \,. \tag{1}$$

The inhibition index b is a fitted constant and x corresponds to mole fraction of an added inhibitor. Higher values of the inhibition index correspond to more effective extinguishment agents. Noto et al. reported that Equation 1 applies to both halogenated (e.g. HFC, halons) and

non-halogenated agents over a wide range of an agent's concentration. Typically, the inhibition index varies from about 10 for agents that rely on physical suppression to about 60 for agents exhibiting strong chemical extinguishment, such as  $CF_3I$ .

# COMPUTATIONAL DETAILS

The present calculations involve a hydrocarbon oxidation mechanism together with hydrofluorocarbon,  $CF_3I$  and  $C_3HF_7$  inhibition mechanisms. The GRI mechanism 3.0 of Smith et al. (2002) was adopted for characterising the hydrocarbon oxidation kinetics. Its thermodynamic database was used for both the kinetic and thermodynamic calculations. Reactions containing nitrogen species were removed from the mechanism. The National Institute of Standards and Technology (NIST) hydrofluorocarbon (HFC) mechanism by Burgess et al. (1995) with its database provided thermochemical constants characterising hydrofluorocarbon oxidation chemistry. In the HFC mechanism, we updated some of the reaction coefficients according to L'Esperance et al. (1995), Linteris and Truett (1996), Linteris et al. (1998). Additional modifications are listed in Table 1.

Reaction	A (orig.)	n (orig.)	$E_a$ (orig.)	A (modif.)	<i>n</i> (modif.)	$E_a$ (modif.)	Source
$CF_3 + H \rightarrow CF_2 + HF$	5.5×10 <sup>13</sup>	0	0	5.3×10 <sup>13</sup>	0	0	Takahashi et al. (1998)
$CF_2 + H \rightarrow CF + HF$	2.0×10 <sup>13</sup>	0	1250	4.0×10 <sup>13</sup>	0	0	Yamamori et al. (1999)
$\begin{array}{c} \text{CHFO} + \text{M} \rightarrow \text{CO} + \text{HF} + \\ \text{M} \end{array}$	2.5×10 <sup>25</sup>	-3.0	43000	5.5×10 <sup>14</sup>	0.0	35200	Saito et al. (1985)
$CO + F + M \rightarrow CFO + M$	3.1×10 <sup>19</sup>	-1.4	-487	-	-	-	NIST estimate
$CFO + M \rightarrow CO + F + M$	-	-	-	1.1×10 <sup>15</sup>	0.0	28200	Knyazev et al. (1997)

Table 1.Modifications to the NIST HFC inhibition mechanism (in units of cm, mol, cal,<br/>K and s).

For  $C_3HF_7$  inhibition mechanism, Williams et al.'s (2000) updated mechanism was adopted with the transport and thermodynamic properties of the relevant species provided by Professor Mackie in a private communication. The initial  $CF_3I$  inhibition mechanism was adopted from Babushok et al. (1996), with some elementary reaction rates updated using the values available in the literature; see Table 2 for details.

The commercially available PREMIX computer program, developed at Sandia National Laboratories, was employed to perform both the kinetic calculation and the sensitivity analysis (Kee et al., 1987). To save the CPU time, the calculations were performed for mixture-based transport properties and with no Soret diffusion. The effects of Soret diffusion and the multi-component thermal diffusion coefficients were examined. Their inclusion in the calculations was found to lead to insignificant differences in the results.

Deastion	Modified Arrhenius coefficients					
Reaction	A	п	$E_a$	Reference		
$2I + M \rightarrow I_2 + M$	2.36×10 <sup>14</sup>	0.0	$-1.50 \times 10^{3}$	Baulch et al. (1981)		
$\mathrm{HI} + \mathrm{I} \rightarrow \mathrm{I}_2 + \mathrm{H}$	$8.01 \times 10^{14}$	0.0	$3.72 \times 10^4$	Garrett and Truhlar (1979)		
$CF_3I + M \rightarrow CF_3 + I + M$	5.13×10 <sup>14</sup>	0.0	$2.98 \times 10^4$	Saito et al. (1984)		
$CF_3 + I \rightarrow CF_3I$	1.21×10 <sup>13</sup>	0.0	$4.91 \times 10^{2}$	Cobos and Troe (1985)		
$CH_3I + M \rightarrow CH_3 + I + M$	2.62×10 <sup>15</sup>	0.0	3.95×10 <sup>4</sup>	Kumaran et al. (1997)		
$H_2 + I \rightarrow H + HI$	2.72×10 <sup>14</sup>	0.0	3.39×10 <sup>4</sup>	Michael et al. (2000)		
$HI + CH_3 \rightarrow I + CH_4$	2.69×10 <sup>12</sup>	0.0	-27.7	Seetula (1991)		
$I + CH_4 \rightarrow HI + CH_3$	$1.48 \times 10^{14}$	0.0	3.30×10 <sup>4</sup>	Pardine and Martin (1983)		
$CF_3I + CH_3 \rightarrow CF_3 + CH_3I$	5.00×10 <sup>5</sup>	2.18	$3.72 \times 10^{3}$	Berry et al. (1998)		
$HI + OH \rightarrow I + H_2O$	2.17×10 <sup>17</sup>	-1.5	0.0	Campuzano-Jost and Crowley (1999)		

Table 2.Arrhenius coefficients for modified elementary reactions (in units of cm, mol, cal, K and s).

In several cases, to obtain a convergence, the parameter defining the frequency of calculating the Jacobian matrix (NJAC) was increased gradually from 5 to 40; i.e. the Jacobian matrix in Newtonian iteration was updated every NJAC (5 to 40) times. The effects of varying NJAC and TJAC were studied by varying NJAC from 40 to 5 and TJAC from 40 to 10, resulting in virtually unaltered solutions. Varying the effect of the absolute and relative tolerances on the Newtonian iterations and on the time steps (ATOL, RTOL, ATIM and RTIM) showed that while these parameters can affect the convergence, depending on the input (including the input kinetic mechanism), they had little influence on the resulting number of grid points. Furthermore, once a convergent solution was obtained, the continuation keyword (CNTN) was extensively employed to progress the solution to new conditions.

The choices of values for GRAD and CURV keywords define the number of grid points that ultimately determines the accuracy of the computed laminar burning velocity. The laminar burning velocity tends to decrease proportionally to the reciprocal of the number of grid points (Dlugogorski et al., 1998). In the current work, we set CURV and GRAD to 0.5 and 0.2, respectively. The effect of selecting relatively large values of these parameters, which were necessary owing to the CPU considerations, was factored out by reporting the laminar burning velocities of mitigated flames normalised with laminar burning velocity of non-mitigated stoichiometric flames.

The transport coefficients of some fluorinated or iodinated compounds, which were not readily available in published articles, were calculated by estimating  $\varepsilon/k_B$  and  $\sigma$  from the expressions proposed by Chung et al. (1984).

## **RESULTS AND DISCUSSION**

#### **Physical Inhibition**

To investigate the physical effects, such as heat capacity and dilution, we calculate the laminar burning velocity with the inhibition mechanisms turned off. Therefore the combustion kinetics is based solely on GRI-Mech 3.0. The combined physical effects, as a consequence of mixing of two agents, correspond to the sum of the physical effects of single agents. Hence, Equation 1 can be written as

$$\frac{S_u}{S_0} = e^{-(d_1 x_1 + d_2 x_2)} \tag{2}$$

where  $d_1$  and  $d_2$  are inhibition indices for the two suppressants in a mixture. Note that, we use symbol *d* to denote an inhibition index arising as a consequence of solely physical suppression, as opposed to symbol *b* included in Equation 1 that accounts for both physical and chemical suppression. Figure 1 presents a typical result for CF<sub>3</sub>I.



# Figure 1. Physical and chemical effects for stoichiometric methane-air flames inhibited by CF<sub>3</sub>I.

Table 3 lists the inhibition indices for the physical effects of CHF<sub>3</sub>, CF<sub>3</sub>I, C<sub>2</sub>HF<sub>5</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>HF<sub>7</sub> added to stoichiometric methane-air premixed flames. The ranking of inhibitors, considered in this study, according to the magnitude of their physical effects is as follows C<sub>3</sub>HF<sub>7</sub> > C<sub>2</sub>F<sub>6</sub> > C<sub>2</sub>HF<sub>5</sub> > CF<sub>3</sub>I > CHF<sub>3</sub>. It is also possible to express the effect of physical suppression as a fractional decrease in the laminar burning velocity,  $(S_0-S_u)/S_0 = 1 - S_u/S_0$ , owing to the addition of a suppression agent, as illustrated by the dash-dot line in Figure 2. However, the inhibition index is a simpler measure of the suppression effectiveness, as it does not depend on an agent's concentration.

Table 3.Inhibition indices for physical suppression. The error in the inhibition index d is<br/>estimated to be less than 0.3 for single agents, assuming an uncertainty of 1% in<br/>the computation of the laminar burning velocity.



Figure 2. The effect of saturation for chemical inhibition for CF<sub>3</sub>I.

### **Chemical Inhibition**

Similarly to Equation 2, the total suppression effectiveness of a mixture of two agents can be calculated from

$$\frac{S_u}{S_0} = e^{-(b_1 x_1 + b_2 x_2)} \tag{3}$$

where  $b_1$  and  $b_2$  are inhibition indices of single agents. However, if the two extinguishment agents interact then the calculated value of  $S_u/S_0$  would differ from that predicted by Equation 3. Table 4 summarises the inhibition indices for single agents, as obtained from the literature and from the present calculations. It can be seen that the inhibition indices derived from the present calculations are somewhat closer to the experimental values quoted by Noto et al. (1998), than the inhibition indices obtained from the previous calculations. This is especially true for CHF<sub>3</sub>,  $C_2HF_5$  and  $CF_3I$ , owing to fine tuning of the suppression mechanism, as described in the previous section. Only limited improvement was obtained for  $C_2F_6$  and  $C_3HF_7$ , indicating the need for further development of the relevant inhibition mechanisms. The saturation points presented in Table 4 are defined as the concentration of an additive for which the chemical suppression reaches the maximum. The effect of chemical suppression can be computed as the difference between the physical and total effects; see Figure 1 for an illustration. In case of a single agent, this is simply

$$F_{chem} = e^{-dx} - e^{-bx} \,. \tag{4}$$

Taking a derivative with respect to x and setting it to zero immediately yields

$$x_{sat} = \frac{\ln(\frac{b}{d})}{b-d}.$$
(5)

Additive	CF <sub>3</sub> I	CHF <sub>3</sub>	$C_2HF_5$	$C_2F_6$	$C_3HF_7$
<i>b</i> : Experiments from Noto et al. (1998)	69.3*	14.9	22.1	28.5	33.9
<i>b</i> : Calculated from Noto et al. (1998)	58.5	16.3	24.6	34.6	-
<i>b</i> : Present results**	65.2	15.7	21.6	33.6	37.9
Saturation point $x_{sat}$ (%)	3.3	8.5	5.4	4.2	3.4
$x_{\text{ext}}$ (%) when $S_{\text{u}}/S_0 = 0.1$	3.5	14.7	10.7	6.9	6.1

 Table 4.
 Overall inhibition effect of the agents considered in this study.

\* Fitted to the experimental measurements of Sanogo et al. (1996).

\*\* The error in the inhibition index *b* is in the order of 0.3 for single agents, assuming an uncertainty of 1% in the computation of the laminar burning velocity.

Figure 2 presents typical results for CF<sub>3</sub>I. For flames inhibited by a single additive, the results of Table 4 demonstrate that chemically active agents display lower saturation concentrations. Compare, for example, the inhibition index and saturation point for CF<sub>3</sub>I with those of C<sub>3</sub>HF<sub>7</sub>. In Table 4, we also estimate the extinguishment concentration for single agents, by assuming the extinguishment concentration to occur when the ratio  $S_u/S_0$  decreases to 0.1.

In the present work, we consider three types of binary mixtures, namely those resulting in: (i) 0.37% CF<sub>3</sub>I in the mixture of flammable gases together with varying amounts of CHF<sub>3</sub>, C<sub>2</sub>HF<sub>5</sub>, C<sub>2</sub>F<sub>6</sub>, and C<sub>3</sub>HF<sub>7</sub> (cases 1-4 in Table 5); (i) 1% CF<sub>3</sub>I in the mixture of flammable gases together with varying amounts of CHF<sub>3</sub>, C<sub>2</sub>HF<sub>5</sub>, C<sub>2</sub>F<sub>6</sub>, and C<sub>3</sub>HF<sub>7</sub> (cases 4-8); (iii) 1% CHF<sub>3</sub>, C<sub>2</sub>HF<sub>5</sub>, C<sub>2</sub>F<sub>6</sub>, and C<sub>3</sub>HF<sub>7</sub> in the mixture of flammable gases together with varying amounts of CF<sub>3</sub>I (cases 9 to 12).

In processing the simulation results for the cases listed in Table 5, we first calculated  $\exp(-b_1x_1)$ , using the inhibition index (Table 4) and the concentration of the first suppressant listed in column 2 (Table 5). Once the effect of the first suppressant was factored out, we fitted the inhibition index for the second suppressant according to Equation 3. If this index was substantially different from that included in Table 4 (and quoted for convenience in column 5 of Table 5) we concluded that there exists chemical interaction between the two agents composing the binary

mixture. Conversely, if the inhibition indices in columns 4 and 5 of Table 5 were similar, we conclude that there is little evidence of chemical interaction between the two agents.

It can be readily seen that binary suppressant mixtures, containing  $CF_3I$  and  $CHF_3$ , as well as  $CF_3I$  and  $C_2F_6$ , show a combined extinguishing effect that exceeds the effects of the single suppressants. In other words, these mixtures performed better than it would have been expected on the basis of the performance of pure agents. Sometimes, this effect is denoted in the fire suppression literature as a synergistic effect. On the other hand, addition of  $C_2HF_5$  and  $C_3HF_7$  to  $CF_3I$  does not result in an improvement of fire suppression properties of binary mixtures above those expected for pure agents. Figures 3 and 4 present the same information in a graphical form. Note that a minor deterioration in suppression properties is observed for mixtures containing  $C_3HF_7$ , in comparison with the effectiveness of pure  $C_3HF_7$  and  $CF_3I$  agents.

Table 5.Performance of binary mixtures of HFC-CF<sub>3</sub>I and PF-CF<sub>3</sub>I suppressants. The<br/>error in the inhibition index  $b_2$  is in the order of 0.6, assuming an uncertainty of<br/>1% in the computation of the laminar burning velocity.

No.	Binary agents	$\exp(-b_1x_1)$	$b_2$	$b_2$ (Table 4) (% diff)*	$x_{2, \text{ sat}}$ (%)	$x_{2, \text{ ext}}$ (%); $S_{\text{u}}/S_0 = 0.1$
1	0.37% CF <sub>3</sub> I+varying CHF <sub>3</sub>	0.79	21.6	15.7 (27.3)	5.5	9.6
2	0.37% CF <sub>3</sub> I+varying C <sub>2</sub> HF <sub>5</sub>	0.79	23.6	21.6 (8.5)	2.6	8.8
3	0.37% CF <sub>3</sub> I+varying C <sub>2</sub> F <sub>6</sub>	0.79	36.2	33.6 (7.2)	3.0	5.7
4	0.37% CF <sub>3</sub> I+varying C <sub>3</sub> HF <sub>7</sub>	0.79	34.6	37.9 (-9.5)	1.9	6.0
5	1% CF <sub>3</sub> I+varying CHF <sub>3</sub>	0.52	23.9	15.7 (34.3)	3.1	6.9
6	1% CF <sub>3</sub> I+varying C <sub>2</sub> HF <sub>5</sub>	0.52	23.7	21.6 (8.9)	-1.7	7.0
7	1% CF <sub>3</sub> I+varying C <sub>2</sub> F <sub>6</sub>	0.52	44.0	33.6 (23.6)	1.6	3.8
8	1% CF <sub>3</sub> I+varying C <sub>3</sub> HF <sub>7</sub>	0.52	38.9	37.9 (2.6)	0.0	4.3
9	1% CHF <sub>3</sub> +varying CF <sub>3</sub> I	0.85	73.2	65.2 (10.9)	3.0	2.9
10	1% C <sub>2</sub> HF <sub>5</sub> +varying CF <sub>3</sub> I	0.81	64.9	65.2 (-0.5)	3.2	3.2
11	1% C <sub>2</sub> F <sub>6</sub> +varying CF <sub>3</sub> I	0.72	70.8	65.2 (7.9)	2.9	2.8
12	1% C <sub>3</sub> HF <sub>7</sub> +varying CF <sub>3</sub> I	0.68	64.6	65.2 (-0.9)	3.1	3.0

\* Percent difference between the inhibition indices in columns 4 and 5.

By mixing CF<sub>3</sub>I with CHF<sub>3</sub> or C<sub>2</sub>F<sub>6</sub> one can save a substantial amount of CHF<sub>3</sub> or C<sub>2</sub>F<sub>6</sub>. It can be seen in Tables 4 and 5 that for binary agents containing 0.37 and 1.0% CF<sub>3</sub>I with varying concentration of CHF<sub>3</sub>,  $x_{ext}$  decreases from 14.7% to 9.6% and 6.9%, respectively. These values are in the same order as  $x_{ext}$  for C<sub>3</sub>HF<sub>7</sub> and C<sub>2</sub>F<sub>6</sub>. Furthermore, Tables 4 and 5 illustrate that for binary agents containing 0.37 and 1.0% CF<sub>3</sub>I with varying concentration of C<sub>2</sub>F<sub>6</sub>,  $x_{ext}$  changes from 6.9% to 5.7% and 3.8%, respectively, with the latter value being close to  $x_{ext}$  for CF<sub>3</sub>I.

For methane-air flames inhibited by a binary mixture of suppressants, Table 5 demonstrates that the saturation points of the suppressants generally decrease. Even in some cases the saturation points become negative. Mathematically, this follows by taking a derivative of Equation 6 with respect to  $x_2$ , keeping  $x_1$  constant and setting the results equal zero, to obtain Equation 7:



Figure 3. Comparison of the performance of binary mixtures of various HFC and FC agents mixed with CF<sub>3</sub>I: solid line – predicted from the performance of single agents using Equation 3; dash-dot line – calculated values for binary mixtures.



Figure 4. Comparison of the performance of binary mixtures of various HFC and FC agents mixed with CF<sub>3</sub>I: solid line – predicted from the performance of single agents using Equation 3; dash-dot line – calculated values for binary mixtures. Note that solid and dash-dot lines are essentially the same for mixtures containing C<sub>2</sub>HF<sub>5</sub> and CF<sub>3</sub>I, as well as C<sub>3</sub>HF<sub>7</sub> and CF<sub>3</sub>I.

Physically, this means that for all concentrations of  $x_2$ , the magnitude of chemical suppression decreases as the concentration of  $x_2$  increases. In general, strong coupling between the two suppression agents leads to a significant decrease in the saturation concentration. For example, for the combination of 1% CF<sub>3</sub>I with varying concentration of CHF<sub>3</sub>, the saturation point for CHF<sub>3</sub> decreases from 8.5 to 3.1%. Furthermore, addition of 1% CF<sub>3</sub>I to methane-air flames inhibited by CHF<sub>3</sub>, C<sub>2</sub>HF<sub>5</sub>, C<sub>2</sub>F<sub>6</sub> and C<sub>3</sub>HF<sub>7</sub> reduces the saturation point from 5.5, 2.6, 3.0, and 1.9% to 3.1, 0.0 (-1.7), 1.58, and 0.0%. This demonstrates that saturation points are very sensitive to the presence of another suppression agent.

Reaction pathway analysis, especially the integrated I atom flux for the thermal decomposition of CF<sub>3</sub>I by itself and in mixtures with CHF<sub>3</sub> and C<sub>2</sub>F<sub>6</sub>, shows that the thermal decomposition rates of CF<sub>3</sub>I are  $8.6 \times 10^{-6}$ ,  $1.6 \times 10^{-7}$  and  $6.2 \times 10^{-7}$  mol s<sup>-1</sup>, respectively. That is, the thermal decomposition rates of CF<sub>3</sub>I in the presence of CHF<sub>3</sub> and C<sub>2</sub>F<sub>6</sub> are much smaller than in the absence of these additives. This means that more CF<sub>3</sub>I is consumed by the reaction with H radicals, promoting the suppression efficiency of CF<sub>3</sub>I in mixtures with CHF<sub>3</sub> and C<sub>2</sub>F<sub>6</sub>.

The more effective coupling of CHF<sub>3</sub>, compared with  $C_2F_6$ , in binary mixtures with CF<sub>3</sub>I is a consequence of different decomposition pathways of CHF<sub>3</sub> and  $C_2F_6$ , as illustrated in Figure 5. Specifically, the decomposition of CHF<sub>3</sub> initiates via the removal of OH radicals rather than by the thermal degradation as is the case for  $C_2F_6$ :

 $CHF_3 + OH \rightarrow CF_3 + H_2O$ 

 $C_2F_6 + M \rightarrow CF_3 + CF_3 + M.$ 

# CONCLUSIONS

By employing the PREMIX program of the CHEMKIN kinetics package, we have successfully carried out a study on the chemical and physical interaction among HFC, FC and CF<sub>3</sub>I during suppression of premixed stoichiometric methane flames. The major conclusions that can be drawn from this work are as follow:

- Mixing of chemically active agents always affects the saturation concentration of the suppressants; i.e., the saturation concentration for agents in a mixture always decreases in comparison to pure agents.
- The physical suppression mechanisms, i.e., the effects of thermal capacity and dilution, are additive for components of binary suppression mixtures. Their magnitude can be predicted from Equation 2 in conjunction with the inhibition indices listed in Table 2.
- CHF<sub>3</sub> or C<sub>2</sub>F<sub>6</sub>, when added to CF<sub>3</sub>I, significantly improve the performance of CF<sub>3</sub>I. For example, the extinguishing concentration of these binary mixtures (CHF<sub>3</sub>-CF<sub>3</sub>I or C<sub>2</sub>F<sub>6</sub>-CF<sub>3</sub>I) is substantially lower than predicted from the behaviour of pure agents. However, there appears to be no or little chemical coupling when C<sub>2</sub>HF<sub>5</sub> or C<sub>3</sub>HF<sub>7</sub> is mixed with CF<sub>3</sub>I.
- Addition of small amounts of CF<sub>3</sub>I to HFC and FC substantially reduces the suppression concentration of HFC and FC. This means that less HFC and FC would be discharged in practical systems, based on binary CF<sub>3</sub>I/HFC and CF<sub>3</sub>I/FC mixtures, therefore reducing the impact of these agents on global warming.
- The chemical coupling between CHF<sub>3</sub> and CF<sub>3</sub>I and between C<sub>2</sub>F<sub>6</sub> and CF<sub>3</sub>I occurs as a consequence of lower thermal decomposition rates of CF<sub>3</sub>I, present in binary mixtures, in favour of CF<sub>3</sub>I reactions with H radicals. CHF<sub>3</sub> is more chemically active in mixtures with CF<sub>3</sub>I, than C<sub>2</sub>F<sub>6</sub>, owing to the initiation reactions of CHF<sub>3</sub> that involve mainly the interaction with OH radicals. For comparison, C<sub>2</sub>F<sub>6</sub> decomposes by thermal degradation to two CF<sub>3</sub> moieties.



Figure 5. Comparison of reaction pathways based on C atom flux for stoichiometric methane air premixed flames for binary mixtures of suppressants corresponding to (a) 1% CF3I, (b) 1% CF3I and 1% CHF3, (c) 1% CF3I and 1% C<sub>2</sub>F<sub>6</sub> in the flammable mixture.

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