# A Kinetic Mechanism for CF<sub>3</sub>I Inhibition of Methane-Air Flames<sup>1</sup>

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## A Kinetic Mechanism for CF<sub>3</sub>I Inhibition of Methane-Air Flames<sup>2</sup>

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#### Abstract

The influence of CF<sub>3</sub>I on the burning velocity of methane-air flame is experimentally and numerically studied. Experimental results demonstrate that the inhibition effectiveness of CF<sub>3</sub>I is very close to that of CF<sub>3</sub>Br. A detailed kinetic model of flame inhibition by CF<sub>3</sub>I is presented, based on an updated version of a previous model. The kinetic model contains 1072 reactions with 115 species including 10 iodine-containing species. Modeling results demonstrate good agreement with experimental data, and both experiments and calculations show that CF<sub>3</sub>I is only slightly less effective at reducing the burning velocity than CF<sub>3</sub>Br. The flame structure predicted from numerical simulations is analyzed and shows that main reactions of the inhibition cycle of CF<sub>3</sub>I are: H+HI=H<sub>2</sub>+I; H+I+M=HI+M; I+I+M=I<sub>2</sub>+M; H+I<sub>2</sub>=HI+I; I+CH<sub>3</sub>+M=CH<sub>3</sub>I+M; H+CH<sub>3</sub>I=CH<sub>3</sub>+HI; I+HCO=HI+CO; HI+OH=H<sub>2</sub>O+I and O+HI=I+OH.

## Introduction

Halon 1301, CF<sub>3</sub>Br, is a highly effective flame inhibitor but has a very high Ozone Depletion Potential (ODP) and hence has been banned for terrestrial applications. Iodotrifluoromethane, CF<sub>3</sub>I, is also an effective flame inhibitor (Tapscott et al., 1995, Babushok and Tsang, 2000, Su and Kim, 2002, Westbrook, 1982, Moore et al., 1994), but is reactive in the troposphere and hence has a negligible ODP. Recently, because of an improved outlook regarding its toxicity, CF<sub>3</sub>I has gained increased consideration as replacement for CF<sub>3</sub>Br in aircraft fire suppression, for which CF<sub>3</sub>Br is still being used. In addition, CF<sub>3</sub>I is being considered as a component of refrigerant blends (Bell and McLinden, 2020, Lv et al., 2021), since it has both favorable thermodynamic properties and can reduce the flammability of new, low Global Warming Potential GWP hydrofluorocarbon HFC refrigerants, which become more flammable as their GWP decreases.

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The effectiveness of CF<sub>3</sub>I has been described previously. Trees et al. (1995) using counterflow and co-flow burners to rank various halon alternatives, concluded that on a mass basis the effectiveness of CF<sub>3</sub>I is close to that of CF<sub>3</sub>Br. Dlugogorski et al. (2002) measured the flammability limits of different hydrocarbons and their mixtures in the presence of fire suppressants and found that CF<sub>3</sub>Br and CF<sub>3</sub>I behaved similarly. Sanogo et al. (1996) and Mathieu et al. (2015) experimentally studied the influence of CF<sub>3</sub>I on burning velocity of methane-air flames and found that burning velocity reduction by CF<sub>3</sub>Br and CF<sub>3</sub>I are very close.

Kinetic models of hydrocarbon flame inhibition by  $CF_3I$  have been developed (Westbrook, 1982, Babushok et al., 1996, Battin-Leclerc et al., 1997, Luo et al., 2008b). These models have been used to predict the influence of  $CF_3I$  on the ignition delay (Babushok et al., 1996, Mathieu et al., 2015), burning velocity (Luo et al., 2008a, Mathieu et al., 2015, Noto et al., 1996, Noto et al., 1998) and on the reaction proceeding in the jet-stirred reactor (Battin-Leclerc et al., 1997). Simulation studies demonstrate that under combustion conditions,  $CF_3I$  molecules decompose readily to form  $CF_3$  and I radicals. Iodine radicals and HI form catalytic inhibition cycles which scavenge the typical hydrocarbon chain-propagating radicals (H, O, and OH), reducing their concentrations and hence the overall reaction rate. The main radical scavenging reactions were identified, such as H+HI=H<sub>2</sub>+I, O+HI=OH+I, OH+HI=H<sub>2</sub>O+I, which together with various HI regeneration reactions (e.g., H+I+M=HI+M, I+I+M=I<sub>2</sub>+M, H+I<sub>2</sub>=HI+I) form the radical termination cycle.

In this work we present previously unpublished data on the effect of  $CF_3I$  on burning velocity of premixed methane-air flames and provide an updated kinetic mechanism for  $CF_3I$  hydrocarbon flame inhibition. The present mechanism is based on that developed at NIST 25 years ago (Babushok et al., 1996), and since that time, a rather large amount of new kinetic data on the reactions of iodine-containing species has been published. Hence, in the present work we update the kinetic model to include new reactions and recent kinetic data. The thermodynamic data for fluorine-containing species were also updated to include recent determinations. Calculated burning velocities using the updated mechanism are then compared with experimental data in the literature as well as with the previously unpublished burning velocity measurements from our laboratory. Finally, the flame structure of  $CF_3I$ -inhibited flames is presented along with analysis of the important reaction pathways for the catalytic radical recombination cycles in  $CF_3I$  flame inhibition.

## Measurements of burning velocity

The experimental data for CF<sub>3</sub>I flame inhibition were collected at the same time as previously reported results of Linteris and Truett (1996) for CF<sub>3</sub>H, CH<sub>2</sub>F<sub>2</sub>, and CF<sub>4</sub>, and the experimental apparatus, data collection, and analysis are identical to those presented previously. The experimental arrangement, also used in subsequent work (Linteris et al., 2000), is described briefly here for convenience. A Mache–Hebra nozzle burner  $(1.0 \text{ cm} \pm 0.05 \text{ cm} \text{ diameter})$  produced a premixed Bunsen-type flame about 1.3 cm tall with a straight sided schlieren image that was captured by a video frame-grabber board in a personal computer. Digital mass flow controllers, under computer control, held the equivalence ratio and the flame height constant while maintaining the inlet mass fraction of the inhibitor at the desired value. The average burning velocity was determined from the reactant flows and the schlieren image using the total area method. The fuel gas was methane (Matheson UHP, 99.9%), and CF<sub>3</sub>I was from Great Lakes. House compressed air (filtered and dried) is used after it has been additionally cleaned by passing it through an 0.01 µm filter, a carbon filter, and a desiccant bed to remove small aerosols, organic vapors, and water vapor. Water vapor relative humidity in the inlet air was typically less than 2 % (Pagliaro et al., 2016). Gas flows are measured with digital mass flow controllers (Sierra Model 860) calibrated for each gas such that their uncertainty is  $\pm 2$  %. For CF<sub>3</sub>I, however, the heating by-pass section of the mass flow controllers caused CF<sub>3</sub>I to decompose, so a calibrated rotameter, set manually for each flow condition, was used for the small CF<sub>3</sub>I flows (with uncertainty of  $\pm 5\%$ ). For all flames, the equivalence ratio (in the absence of inhibitor) was 1.0, and the agent volume fraction was calculated relative to the total reactant flow.

The burning velocity in Bunsen-type flames is known to vary at the tip and base of the flame and is influenced by heat loss and stretch (as compared to the planar burning velocity). These effects are most important over small regions of the flame, so their effect on the average burning velocity is lessened. The low conductivity of the uncooled quartz nozzle results in low heat loss to the burner, and the low strain and curvature of the flame facilitate comparisons with calculations for a one-dimensional adiabatic flame. To minimize the uncertainty in the burning velocity in the present arrangement, the burning velocity of the inhibited flames is normalized by the uninhibited burning velocity, and the uncertainty in the normalized burning velocities was about 5%.

## Kinetic model and modeling procedure

The complete suggested mechanism for  $CF_{3}I$  flame inhibition is presented in the Supplementary Materials. The kinetic model used here was assembled from the three blocks of reactions. The first block represents the hydrocarbon oxidation reactions, for which FFCM-1 (Smith G.P. et al., 2016) was incorporated, providing description of high temperature oxidation of  $C_1$ - $C_2$  hydrocarbons. The second block is from the NIST  $C_1$ - $C_2$  hydrofluorocarbon model (Burgess et al., 1995) with modifications suggested in more recent work, as summarized in (Linteris et al., 2012, Babushok et al., 2015). The third block of reactions representing flame inhibition by  $CF_3I$  is based on our previous model (Babushok et al., 1996). All kinetic data were updated using recent experimental and theoretical results and several new reactions were added. Table 1 lists the Arrhenius parameters for the reactions of the iodine-containing species in the mechanism.

The important changes in the mechanism from our previous model pertaining to iodine-containing species were updated rate expressions for the following reactions:

H + I + M = HI + M	(Lifshitz et al., 2008)
$CF_{3}I(+M) = CF_{3} + I(+M)$	(Zaslonko et al., 1990)
$CH_3I + M = CH_3 + I + M$	(Yang et al., 2009)
$CH_3I + H = CH_3 + HI$	(Marshall et al., 1997)
$HI + CH_3 = I + CH_4$	(Marshall et al., 2011)
$\mathbf{CF}_{3}\mathbf{I} + \mathbf{CH}_{3} = \mathbf{CF}_{3} + \mathbf{CH}_{3}\mathbf{I}$	(Berry and Marshall, 1998)
$HCO + HI = CH_2O + I$	(Becerra et al., 1997)
HCO + I = CO + HI	(Friedrichs et al., 2002), est. $\frac{1}{2} k(HCO + H = CO + H_2)$

The thermodynamic data for iodine containing species are mostly from the database of Burcat and Ruscic (2021), with one value (CH<sub>2</sub>I) from Sander et al. (2011). Transport data for the iodine-containing species were obtained from the literature or estimated using molecular weight correlations or by analogy. Thermodynamic, transport, and kinetic data in Chemkin format are presented in the Supplementary Materials.

In the present work, laminar burning velocity calculations are made with python scripts employing Cantera (Goodwin et al., 2016), an open-source suite of object-oriented software tools for problems involving chemical kinetics, thermodynamics, and transport processes. The equations of mass, species, and energy conservation are solved numerically for the initial gas compositions, temperature, and pressure corresponding to those in the experiments. The solution assumes isobaric, adiabatic, steady, planar, one-dimensional, laminar flow and neglects radiation and the Dufour effect, but includes thermal diffusion. Molecular diffusion is modeled with the multicomponent transport equations using the Hirschfelder approximation. The boundary conditions, corresponding to a freely propagating flame, are inlet mass fractions, velocity and temperature, and vanishing gradients downstream from the flame. The number of active grid points was selected to assure that the solutions were grid-independent.

#### **Results and discussion.**

Figure 1 presents the burning velocity of methane-air flames as a function of the volume fraction of added flame inhibitor. Experimental data (symbols) are shown for CF<sub>3</sub>I for the present data (filled circular symbols) as well as those of Sanogo et al. (1996)(closed circular symbols). The two sets of experimental data for CF<sub>3</sub>I agree reasonably well. As shown, CF<sub>3</sub>I is a very effective flame inhibitor, reducing the burning velocity by 47 % at an inhibitor volume fraction of 1 %. For comparison, data are also shown for CF<sub>3</sub>Br (filled triangles) for the same experimental conditions (Linteris et al., 2000), and as indicated, CF<sub>3</sub>Br is slightly more effective, reducing the burning velocity by 52 % at a volume fraction of 1 %. The data for CF<sub>3</sub>Br are in agreement with those of Sanogo et al. (1996) (open triangles), which are also shown on the figure.

Also shown in Figure 1 are the results of the burning velocity calculations for  $CF_3I$  and  $CF_3Br$ , given by the solid and dashed lines, respectively. The modeling for  $CF_3Br$  was performed using the  $CF_3Br$  mechanism described previously (Babushok et al., 2015), but incorporating the same hydrocarbon and fluorine sub-mechanisms as in the present work. As indicated, the simulations accurately reproduce the experimental results, and hence, provide some confidence that the mechanisms can be used to understand the effects of these agents on the flames.

Employing the results of the numerical flame simulations for methane-air flames, Figures 2(a,b) show the flame structure of the present methane-air flame inhibited by CF<sub>3</sub>I. In this figure and all subsequent figures and discussions, the inlet conditions of the simulations are: 298 K, 101kPa, CF<sub>3</sub>I volume fraction 0.91 %, and unity equivalence ratio. The inhibitor decomposes rather fast, forming the iodine-containing species I, HI and I<sub>2</sub>. The main iodine-containing species

in the combustion products is the iodine atom, which reaches a final volume fraction of 0.87%; i.e., very close to the initial CF<sub>3</sub>I loading. The concentration of HI in the combustion products constitutes about 2% of the added iodine species. A relatively large maximum concentration of CH<sub>3</sub>I is observed, 0.06 %, and it is formed via reactions of CH<sub>3</sub> with CF<sub>3</sub>I or I.

Figure 3 shows the flux of iodine through the major iodine containing species in the flames. As in the catalytic inhibition cycle of Br, the typical inhibiting species, the hydrogen halide, HI, reacts primarily (about 60%) with H and OH radicals to form I. To regenerate the HI, the I atom reacts with the I, H, and CHO radicals to reform HI, or with I to form I<sub>2</sub>, followed by I<sub>2</sub> reaction with H to form HI. A regeneration channel also exists via I reaction with CH<sub>3</sub> to form CH<sub>3</sub>I, followed by CH<sub>3</sub>I reaction with H to reform HI. Although this reaction route appears to be minor, the burning velocity is quite sensitive to the rate of this reaction. All steps in this cycle consume radicals, which together with the high concentrations of the relevant inhibiting species in the flame, lead to the efficient catalytic cycle.

Figure 4 shows the dependence of maximum hydrogen atom concentration in the flame on the CF<sub>3</sub>I volume fraction. Also shown on the figure is the calculated burning velocity. Increasing CF<sub>3</sub>I concentration leads to decreasing peak H atom volume fraction, with addition of 1% of CF<sub>3</sub>I leading to a decrease in the peak H atom volume fraction by about a factor of two. The fractional decrease in the peak H atom volume fraction is close to, but greater than the decrease in the burning velocity. The peak H atom volume fraction reaches the equilibrium value at a burning velocity of around 1 cm/s. The reactions of the iodine-containing species with H atom sum to about 15% of the total consumption of H atom in the flame.

Figure 5(a,b) presents the reaction pathways of CF<sub>3</sub>I decomposition, showing the reaction pathways for conversion of fluorine species. Arrows connect reactants and products, with the reaction partner next to the arrow, and the number in parentheses is the fraction (in %) of the total consumption of the reactant through the indicated pathway. When the reaction partner is not indicated, the number corresponds to the contribution of the decomposition reaction. The reaction fluxes were determined by integration of reaction rates through the flame zone. To avoid clutter in the figures, only 80 % to 90 % of the consumption of each species is covered, and the decomposition of the intermediate species 1,1-difluoroethylene,  $CH_2CF_2$ , is presented in Figure 5 b. Also, in that figure, the conversion of fluoroethylene,  $CH_2CHF$ , is not presented. For the most part, the reactions of  $CH_2CHF$  with H, O and OH radicals lead to the formation of CHFCH(Z),

 $CH_2F$ , CFO and  $CH_2CF$  radicals. Overall, only about 3.5 % of the flux of  $CF_3$  goes through formation of  $CH_2CHF$ , so its neglect in the figure is reasonable. Note that species denoted with an asterisk appear multiple times in the figure. Having them only appear once with connecting lines would lead to too much clutter.

Figure 5a shows that 79 % of the CF<sub>3</sub>I is consumed via the decomposition reaction to form CF<sub>3</sub> and I, followed by 17 % consumption via its reaction with hydrogen atom (17%) to form HI and CF<sub>3</sub>. The reaction path for consumption of CF<sub>3</sub> radical is presented in Figure 5(a,b) essentially tracking the fluorine flux (not carbon) down to HF. The flux of iodine containing species is outlined above in the context of the flame inhibition cycle. The main reactions of iodine species which decrease radical pool concentrations and thus decrease the burning velocity are presented below. First, the major reactions of I atom are listed; the number in the parentheses is the fraction of total I consumption in the entire flame by that reaction.

$I+I+M = I_2 + M$	(0.27)
CH3+I+M=CH3I+M	(0.22)
H+I+M=HI+M	(0.21)
I+HCO=HI+CO	(0.08)

The species HI and CH<sub>3</sub>I also react with chain-carrying radicals to reduce their peak concentrations, and also reform I atom, completing the catalytic cycle. The major reactions and their fraction, in parentheses, of total HI consumption are:

H+HI=I+H <sub>2</sub>	(0.33)
OH+HI=H <sub>2</sub> O+I	(0.28)
H+I2=HI+I	(0.12)
CH <sub>3</sub> +HI=CH <sub>4</sub> +I	(0.063)
O+HI=OH+I	(0.053)
H+CH <sub>3</sub> I=CH <sub>3</sub> +HI	(0.03).

## **Conclusions.**

In this work we present experimental results on the influence of CF<sub>3</sub>I on burning velocity of stoichiometric methane flame and an updated kinetic model for flame inhibition by CF<sub>3</sub>I. In comparison with our previous model (Babushok et al., 1996) many rate constants are updated and additional reactions with iodine-containing species are included. Thermodynamic data for the iodine-containing species are based on the new version of the database of Burcat and Ruscic (2021). The main results of this work are as follows:

1. The new data on the burning velocity of stoichiometric methane flame with CF<sub>3</sub>I addition agree acceptably well with previous measurements.

2. The measured flame inhibition effectiveness of CF<sub>3</sub>I is very high and only slightly less than that of CF<sub>3</sub>Br.

3. The updated CF<sub>3</sub>I kinetic model (10 iodine-containing species), when combined with a hydrocarbon sub-mechanism and fluorine-species sub-mechanism (total: 1027 reactions with 114 species), accurately predicts the burning velocity reduction in stoichiometric methane-air flames caused by CF<sub>3</sub>I when added at up to about 1 % volume fraction in the reactants.

4. The mechanism of CF<sub>3</sub>I flame inhibition is analyzed and the reaction pathways for CF<sub>3</sub>I consumption are studied. The main reactions of inhibition cycle, which include radical scavenging reactions and reactions regenerating the scavenging agent, HI, are: H+HI=H<sub>2</sub>+I, H+CH<sub>3</sub>I=HI+CH<sub>3</sub>, H+I+M=HI+M, H+I<sub>2</sub>=HI+I, I+I+M=I<sub>2</sub>+M, HI+O=OH+I, I+HCO=HI+CO and I+CH<sub>3</sub>+M=CH<sub>3</sub>I+M.

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Zhang, S., Strekowski, R. S., Monod, A., Bosland, L. & Zetzsch, C. 2012. Temperature-Dependent Kinetics Study of the Reactions of OH with C2H5I, n-C3H7I, and iso-C3H7I. *The Journal of Physical Chemistry A*, 116, 9497. Table 1. Kinetic data for reactions with iodine-containing species (AT<sup>n</sup>e<sup>-E/RT</sup>; mol, cm, s, kJ, K)

No	Reaction	Α	n	Ε	Reference
1	I2 + M = I + I + M	8.24E13	0.	126.775	(Baulch et al., 1981)
2	H + I + M = HI + M	2.9E21	-1.8	70.	(Lifshitz et al., 2008)
	H2/2.00/ H20/8.00/ CH4/2.	.50/ CO/2.00/	/ CO2,	/3.00/ C2H6/	'3.00/ AR/0.70/
3	CF3I (+M) = CF3 + I (+M)	2.51E14	0.	220.329	(Zaslonko et al., 1990)
	LOW/4.22E14 0. 28810	9./			
4	CH3I + M = CH3 + I + M	6.04E50 -9	9.52	298.989	(Yang et al., 2009)
	H2/2.00/ H20/8.00/ CH4/2	.50/ CO/2.0/	CO2/	3.00/ C2H6/3	3.00/ AR/0.70/
5	C2H5I = C2H4 + HI	1.27E14	0.	220.915	(Yang and Conway, 1965)
6	C2H5I = C2H5 + I	4.50E13	0.	209.200	(Yang and Conway, 1965)
7	C2H3 + I = C2H3I	4.4e12	0.	4.184	(Lifshitz et al., 2008)
8	I + I + H2 = HI + HI	6.65E13	0.	22.217	(Sullivan, 1967)
9	H + HI = H2 + I	4.74E13	0.	2.745	(Baulch et al., 1981)
10	H + I2 = HI + I	4.31E14	0.	1.803	(Baulch et al., 1981)
11	H + CH3I = HI + CH3	1.29E09	1.66	2.510	(Marshall et al., 1997)
12	H + CH3I = H2 + CH2I	7.56E07	1.9	45.815	(Sullivan, 1967)
13	H + C2H3I = HI + C2H3	3.47E14	0.	20.910	(Westbrook, 1982)
14	H + C2H5I = HI + C2H5	6.6E13	0.	5.899	(Yuan et al., 1997)
15	H + CF3I = CF3 + HI	4.04E13	0.	3.807	(Yuan et al., 1998)
16	HI + O = I + OH	2.82E13	0.	8.326	(Singleton and Cvetanović, 1978)
17	HI + OH = I + H2O	1.81E13	0.	0.	(Atkinson et al., 1992)
18	I + HO2 = HI + O2	9.00E12	0.	9.121	(Atkinson et al., 1992)
19	I + CH3I = I2 + CH3	2.57e08	1.9	85.646	(Skorobogatov et al., 1994)
20	HI + CH3 = I + CH4	1.63E05	2.38	-5.314	(Mečiarová et al., 2011)
21	CH3 + C2H5I = CH3I+C2H5	7.94E11	0.	30.920	(Sidebottom and Treacy, 1984)
22	CH3 + C2H3I =CH3I+C2H3	2.00E12	0.	50.208	(Babushok et al., 1996)
23	CH3+C2H3I=C3H6 + I	2.00E11	0.	33.472	*
24	CF3 + CH3I = CHF3 + CH2I	3.98E10	0.	31.380	(Kondratiev, 1972)
25	CF3I + CH3 = CF3 + CH3I	5.0e05	2.18	15.564	(Berry and Marshall, 1998)
26	CF3 + C2H5I = CF3I+C2H5	1.00E12	0.	33.472	(Babushok et al., 1996)
27	CF3 + C2H3I =CF3I+C2H3	2.00E12	0.	41.840	(Babushok et al., 1996)

28	IO + CH3O = CH2O + IOH	2.40E13	0.	0.	(Shah et al., 2001)
29	HI + CH2OH = I + CH3OH	1.63E12	0.	-4.800	(Seetula and Gutman, 1992)
30	I2 + C2H3 = I + C2H3I	1.00E13	0.	0.	(Westbrook, 1982)
31	I2 + C2H5 = I + C2H5I	1.00E13	0.	0.	(Westbrook, 1982)
32	HI + C2H5 = I + C2H6	2.71E12	0.	-3.192	(Seetula et al., 1990)
33	CH3I + F = HF + CH2I	4.34E13	0.	0.	(Sehested et al., 1994)
34	CH3I + F = I + CH3F	4.82E11	0.	13.807	(Denisov and Azatyan, 2003)
35	I + CF3I = I2 + CF3	7.59E12	0.	78.994	(Skorobogatov et al., 1991)
36	I + CHF3 = CF3 + HI	3.98E13	0.	151.879	(Kondratiev, 1972)
37	I + H202 = HI + H02	1.00E12	0.	75.312	(Babushok et al., 1996)
38	CH3F + I = CH2F + HI	2.00E14	0.	128.867	(Pickard and Rodgers, 1983)
39	HI + F = HF + I	4.10E13	0.	0.	(Baulch et al., 1981)
40	C2H3 + HI = C2H4 + I	4.37e12	0.	-3.180	(Seetula, 1991)
41	I + HCO = HI + CO	5.00E13	0.	0.	(Friedrichs et al., 2002)
42	I + C3H8 = nC3H7 + HI	1.1E14	0.	99.788	(Knox and Musgrave, 1967)
43	I + C3H8 = iC3H7 + HI	7.59E14	0.	123.888	(Knox and Musgrave, 1967)
44	OH + CH3I = CH2I + H2O	1.64E00	3.9	97 -3.740	(Sullivan, 1967)
45	OH + CH3I = IOH + CH3	6.04E12	0.	19.330	(Sullivan, 1967)
46	O + CH3I = CH2I + OH	1.30E13	0.	31.798	(Babushok et al., 1996)
47	CH3 + CH3I = CH4 + CH2I	6.31E11	0.	50.618	(Saito et al., 1980)
48	HO2 + CH3I = CH2I + H2O2	1.00E11	0.	62.760	(Babushok et al., 1996)
49	IO + CH3I = CH2I + IOH	4.00E11	0.	50.208	(Babushok et al., 1996)
50	CH2I + HI = CH3I + I	1.02E12	0.	-1.600	(Seetula and Gutman, 1991)
51	CH2I + CH2O = CH3I + HCO	1.0E12	0.	41.840	(Babushok et al., 1996)
52	CH2I + C2H6 = CH3I + C2H2	5 3.0E12	0.	50.208	(Babushok et al., 1996)
53	CH2I + HO2 = CH2O + OH + I	1.0E13	0	0.	(Babushok et al., 1996)
54	CH2I + CH3 = C2H5I	3.15E13	0.	0.	(Saito et al., 1980)
55	CH2I + CH3 = C2H5 + I	4.00E13	0.	0.	(Saito et al., 1980)
56	0 + I2 = I0 + I	7.53E13	0.	0.	(Atkinson et al., 2007)
57	0 + CF3I = I0 + CF3	7.00E12	0.	0.	(Herron, 1988)
58	0 + CH3I = CH3 + I0	2.00E13	0.	83.680	(Babushok et al., 1996)
59	IO + HO2 = IOH + O2	8.43E12	0.	-4.477	(Atkinson et al., 2007)
60	0 + I0 = I + 02	8.43E13	0.	0.	(Atkinson et al., 2007)

61	OH + IO = I + HO2	1.00E13	0.	0.	(Babushok et al., 1996)
62	IO + IO = I + I + O2	6.00E13	0.	0.	(Babushok et al., 1996)
63	IO + CO = CO2 + I	2.41E05	2.0	43.765	(Louis et al., 2003)
64	IO + CH4 = CH3 + IOH	7.8E03	2.71	45.982	(Louis et al., 2001)
65	IO + CH2O = HCO + IOH	1.20E13	0.	46.442	*
66	IO + H2O2 = IOH + HO2	3.00E12	0.	20.920	*
67	IO + C2H4 = CH2I + CH2O	3.00E12	0.	27.196	*
68	IO + C2H4 = CH3 + HCO + I	1.00E10	0.	33.472	(Babushok et al., 1996)
69	IO + H = OH + I	1.00E13	0.	0.	(Babushok et al., 1996)
70	IO + CF3 = I + CF3O	3.85e12	0.	0.	(Vipond et al., 2002)
71	OH + CF3I = CF3 + IOH	1.75E05	1.5	7.991	(Berry et al., 1998)
72	OH + I2 = IOH + I	1.26E07	1.9	12.008	(Xerri et al., 2012)
73	HI + OH = H + IOH	9.00E05	2.28	103.596	(Xerri et al., 2012)
74	H + IOH = IO + H2	9.60E00	3.64	17.991	(Xerri et al., 2012)
75	H + IOH = I + H2O	6.00E08	1.55	13.096	(Xerri et al., 2012)
76	I + IOH = HI + IO	2.20E06	2.29	119.411	(Xerri et al., 2012)
77	O + IOH = OH + IO	6.00E12	0.	18.410	(Babushok et al., 1996)
78	OH + IOH = H2O + IO	2.20E-3	4.41	19.916	(Xerri et al., 2012)
79	IOH (+ M) = OH + I (+M)	3.00E15	0.	213.384	(Babushok et al., 1996)
	LOW/5.70E09 0. 46400	./			
80	CH3CO + HI = CH3CHO + I	2.00E11	0.	6.276	(Babushok et al., 1996)
81	H2 + I2 = HI + HI	1.94E14	0.	171.444	(Baulch et al., 1981)
82	HI + CH3I = I2 + CH4	2.00E14	0.	139.746	(Kondratiev, 1972)
83	HI + C2H5I = I2 + C2H6	5.01E13	0.	124.863	(Kondratiev, 1972)
84	I + O + M = IO + M	3.00E13	0.	0.	(Babushok et al., 1996)
85	IO + H = O + HI	1.00E12	0.	0.	(Babushok et al., 1996)
86	CH2I + 0 = CH20 + I	7.00E12	0.	0.	(Babushok et al., 1996)
87	CH2I + OH = CH2O + HI	2.00E10	0.	41.840	(Babushok et al., 1996)
88	CH2I + HO2 = CH3I + O2	2.00E12	0.	0.	(Babushok et al., 1996)
89	I + CH3O = HI + CH2O	5.10E13	0.	0.	(Shah et al., 2001)
90	C2H5I + 0 = C2H5 + I0	1.00E13	0.	46.024	(Babushok et al., 1996)
91	C2H3I + OH = C2H3 + IOH	1.00E13	0.	125.520	(Babushok et al., 1996)
92	C2H5I + OH = C2H5 + IOH	3.34E12	0.	6.904	(Zhang et al., 2012)

93  HCO + IO = CO + IOH	5.00E12	0.	0.	(Babushok et al., 1996)
94 CH3 + IO = CH2O + HI	1.00E13	0.	0.	(Babushok et al., 1996)
95 HCO + HI = CH2O +I	1.86e12	0.	0.837	(Becerra et al., 1997)

\* Estimation



Figure 1. Dependence of burning velocity of stoichiometric methane-air flame on the CF3I volume fraction (101 kPa, 298 K; CF3I : • - this work,  $\circ$  - data of Sanogo et al. (1996), —— calculation; CF3Br:  $\blacktriangle$  - data of Linteris et al. (2000),  $\Delta$  - data of Sanogo et al. (1996), ----- calculation.



Figure 2(a,b). Flame structure of methane flame inhibited by CF<sub>3</sub>I (298 K, 101 kPa, stoichiometric methane flame, 0.91% of added CF<sub>3</sub>I)



Figure 3. Reaction flux diagram of major iodine-containing species.



Figure 4. The dependence of peak hydrogen volume fraction and equilibrium value (left axis) on  $CF_3I$  concentration, together with the normalized burning velocity (right axis) (298 K, 101 kPa, stoichiometric methane/air flame).



a.)



b.)

Figure 5(a,b). Reaction pathways of CF<sub>3</sub>I decomposition (101 kPa, 298 K, stoichiometric air/methane flame, 0.91 % CF<sub>3</sub>I).

## Supplementary Materials

Thermodynamic Data in Chemkin Format

Transport Data in Chemkin Format

Reaction Data in Chemkin Format