

# Influence of $\text{CF}_3\text{I}$ , $\text{CF}_3\text{Br}$ , and $\text{CF}_3\text{H}$ on the High-Temperature Combustion of Methane

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The effects of a number of flame retardants ( $\text{CF}_3\text{I}$ ,  $\text{CF}_3\text{Br}$ , and  $\text{CF}_3\text{H}$ ) on the high-temperature reactions of methane with air in a plug flow reactor are studied by numerical simulations using the Sandia Chemkin Code.<sup>1</sup> The dependence of (a) the ignition delay and (b) time for substantially complete reaction as a function of temperature and additive concentrations are calculated. In agreement with experiments, the ignition delay can be increased or decreased by the addition of retardants. The reaction time is always increased by additives. The mechanism for these effects has been examined. It is concluded that the ignition delay is controlled by the initial retardant decomposition kinetics, which releases active species into the system. These species can either terminate or initiate chains. The reaction time is largely a function of the concentrations of the active radicals H, OH, and O that are formed during the combustion process. It is shown that their concentrations, particularly those of H atoms, are lowered in the presence of the retardants. We find that the chemical mechanism governing reaction time is very similar to that which controls the flame velocity and a correlation between decreases in flame velocity and H-atom concentration is demonstrated. The calculations suggest that relative reaction time and H-atom concentrations should be effective measures for the estimation of retardant effectiveness. Copyright © 1996 by The Combustion Institute

## BACKGROUND

In an earlier paper [1] we analyzed through chemical kinetic simulations the effects of a number of candidate fire suppressants on ignition delay in a plug flow reactor. Our conclusion was that the commonly measured time to ignition for the fuels studied did not appear to be a satisfactory single measure of suppressant power of the compounds that we analyzed. Indeed, in many situations a number of the candidate fire suppressants can decrease the time to ignition and thus act as an initiator. A search of the literature showed that there is ample experimental verification of such effects [2–24]. The data are summarized in Table 1.

This paper has a threefold objective. First, to determine additional parameters of the combustion system that may be more suitable for expressing suppression power. Specifically, we will consider time for destruction of (a) fuel, (b) oxidant, and (c) maximum temperature increase. Second, to obtain some insight into the characteristics of  $\text{CF}_3\text{I}$  as a fire suppressant. Third, to understand, on a more fundamental basis, the chemistry that is involved in ignition delay and time of destruction, paying particular attention to the lack of correlation and indeed an opposite effect between fire retardancy and ignition delay as summarized in Table 1. Toward these ends, we have investigated the combustion behavior of stoichiometric air–methane mixtures in the presence and absence of  $\text{CF}_2\text{I}$ ,  $\text{CF}_3\text{Br}$ , and  $\text{CF}_3\text{H}$ . The choice of methane as the fuel is dictated by the availability of a very complete and validated database for its combustion. In addition, the fluorinated hydrocarbon database that is used is at present restricted to one and two carbon systems. Thus, although a fuel such as propane may be more realistic, the database for its inhibited decomposition is much less complete.

Earlier modeling studies of a premixed flame by Westbrook [25, 26] have established the flame velocity as a parameter that is lowered

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<sup>1</sup> Certain commercial materials and equipment are identified in this paper in order to specify the experimental procedure adequately. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the material or equipment is necessarily the best available for the purpose.

TABLE I  
Data on the Promotion of Combustion by Halogenated Flame Suppressants

Combustion Process	Fuel	Promotion Additives	References		
Slow oxidation, spontaneous combustion	C <sub>2</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>8</sub> , C <sub>4</sub> H <sub>10</sub> isobutyl chloride, isobutyl bromide, <i>n</i> -propyl bromide, <i>n</i> -butyl bromide, 2,3-dimethyl butane, isobutan, isopentane, toluene, ethylbenzene, cumene, naphthenes	HBr	2		
		Isobutane	HBr	3	
		Acetaldehyde, diethylether, isopentane, ethane, benzene, formaldehyde, cumene	HBr, CH <sub>3</sub> Br, CH <sub>2</sub> Br <sub>2</sub> , CH <sub>2</sub> BrCl, CF <sub>2</sub> Br <sub>2</sub>	4	
		Hydrogen	I <sub>2</sub>	5	
		Hydrogen	C <sub>2</sub> H <sub>5</sub> Br, C <sub>2</sub> H <sub>5</sub> I	6	
		Hydrogen	HBr (modeling)	7	
		Carbon monoxide	CH <sub>2</sub> F <sub>2</sub> , CH <sub>3</sub> F	8	
		C <sub>3</sub> H <sub>8</sub>	CF <sub>3</sub> Br, CH <sub>2</sub> ClBr, C <sub>2</sub> F <sub>3</sub> Cl <sub>3</sub>	9	
		Two-stage ignition	Cyclohexane <i>n</i> -heptane	C <sub>2</sub> H <sub>5</sub> Br, CH <sub>3</sub> I C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub> , C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	10
		Hot wire ignition	CH <sub>4</sub> , C <sub>3</sub> H <sub>8</sub>	CCl <sub>4</sub> , SiCl <sub>3</sub> H, PCl <sub>3</sub> , Cl <sub>2</sub> , BBr <sub>3</sub>	11
		Initiation of detonation (exploding wire)	C <sub>2</sub> H <sub>2</sub> decomposition H <sub>2</sub>	SO <sub>2</sub> , CF <sub>3</sub> Br, CH <sub>3</sub> Cl CF <sub>3</sub> Br, C <sub>2</sub> Br <sub>2</sub> F <sub>4</sub> , Cl <sub>2</sub> , CCl <sub>4</sub> , CHCl <sub>3</sub>	12 13
		Flame propagation	CH <sub>4</sub>	CF <sub>3</sub> Br	14
		Ignition behind shock waves	H <sub>2</sub>	CF <sub>3</sub> Cl	15
CH <sub>4</sub>	CF <sub>3</sub> Br, CH <sub>3</sub> Br		16		
CH <sub>4</sub>	CH <sub>3</sub> Cl, CH <sub>3</sub> Br		17		
CH <sub>4</sub>	CF <sub>3</sub> Cl		18		
CH <sub>4</sub>	CH <sub>3</sub> Br		19		
CH <sub>4</sub>	CH <sub>3</sub> Cl, CH <sub>3</sub> I, CH <sub>3</sub> Br		20		
Coal particles	CH <sub>3</sub> Cl, CH <sub>3</sub> I		21		
Detonation	H <sub>2</sub>	CF <sub>3</sub> H, CF <sub>3</sub> , CF <sub>3</sub> Br	22, 23		
	C <sub>2</sub> H <sub>4</sub>	CF <sub>3</sub> Br, CHF <sub>2</sub> Cl	22		
	C <sub>2</sub> H <sub>4</sub>	CHF <sub>3</sub>	24		

by the presence of a fire retardant such as CF<sub>3</sub>Br. It has also been shown that this decrease is monotonic with retardant concentration. Unlike the induction time, which is largely affected by the initial chemistry, the flame velocity is strongly driven by the overall chemistry. Our choice of a time period for substantial conversion of oxidant, fuel, or temperature increase was dictated by the need to consider the subsequent chemistry of the system after

ignition. Certainly, if ignition behavior is not a manifestation of inhibitory power, then the subsequent reactions must control the fire phenomena. In the type of simulations that are carried out, all the fuels are ultimately converted to their thermodynamic endpoint. Thus, over time, all the exothermic energy is released into the system. However, the rate of energy release should have drastic effects on the character of combustion. This is the rationale for

the choice of the test variables. Westbrook has also made a very perceptive analysis of the reaction mechanism. Much of his analysis is consistent with the present study, even though a number of the rate constants have been changed. Thus the results from the study on  $\text{CF}_3\text{Br}$  are qualitatively similar to those of the earlier work.

The use of a plug premixed flow reactor model for simulation for most of this work was dictated by the ease with which such calculations can be carried out. Running times on a typical workstation are on the order of a few minutes. This is in contrast with flame velocity calculations, which may take several days. We are thus able to examine in much greater detail the chemistry that is driving the reaction. Since our model does not contain transport, it may be considered to be less realistic. All the calculations were carried out with 1% mixtures of the prospective retardants; thus chemical effects, as opposed to those from heat capacity, are optimized. However, an actual fire situation is very poorly defined. Different computational models emphasize different aspects of the phenomenon. Real understanding can only come through a careful examination of all the possibilities and ultimately, through comparison with experiments. It should be noted that we have also carried out some flame velocity calculations. These are for the purposes of calibrating our results with those of Westbrook [25, 26] and of comparing calculated radical concentrations with decreases in flame velocities when retardants are added.

The present results for reaction time are carried out at an initial temperature of 900 K. This value has been selected because self-ignition can occur after a reasonable time. Although there are some changes in the reaction time at temperatures above this value, the relative scales in terms of retardant effectiveness do not change appreciably. This is to be expected since once rapid fuel and oxidant consumption occurs, the conditions are largely driven by the exothermicity of the reaction.

Due to the effects of  $\text{CF}_3\text{Br}$  on the ozone layer, the Montreal protocol has mandated a ban on the production of this chemical. Currently,  $\text{CF}_3\text{H}$  and  $\text{CF}_3\text{I}$  are among the candidates being considered as alternative fire sup-

pressants. The latter appears to be especially attractive, since it has a very low ozone depletion potential and in a number of tests [27] has been found to have approximately the same fire suppressant characteristics as  $\text{CF}_3\text{Br}$ .

## MODELING TECHNIQUES AND KINETIC MODEL

It is possible to think of the combustion phenomenon as roughly divided into three time periods. These are (1) the induction period (ignition delay), where active radicals are generated, (2) the reaction period, where a considerable amount of the reactant is consumed and is characterized by large temperature increases, and (3) relaxation toward the equilibrium state or completion of reaction. We will be concerned with the first two periods. It is highly improbable that the third time period should have much influence on the combustibility of a mixture. In our earlier work [1], we also noted interesting effects in cases where large quantities of suppressants are present. These results reflect differences in the pyrolysis kinetics of these compounds. In the present study we will be directly concerned with dilute retardant concentrations.

Ignition delay was characterized in terms of the following times: (1) time of achievement of maximum concentration of OH; (2) time for temperature rise of  $100^\circ\text{C}$ ; (3) the time for the achievement of the maximum rate of increase in the temperature and rate of decrease in concentration of initial reactants; (4) time for increase in temperature for one characteristic temperature rise ( $RT_0^2/E$ , as from thermal explosion theory), where  $E$  is the global activation energy of the ignition process (decrease of fuel). The uncertainty in the calculated ignition delays from such determinations has been found to be between 10 and 30%. The limits to such studies arise at high temperatures, where the reaction time is comparable to the ignition delay.

There are a number of alternative definitions of the characteristic reaction time. The general situation can best be seen from Fig. 1, which represents a temporal history of fuel, oxygen, and temperature. The main problem is the separation of the ignition delay from the

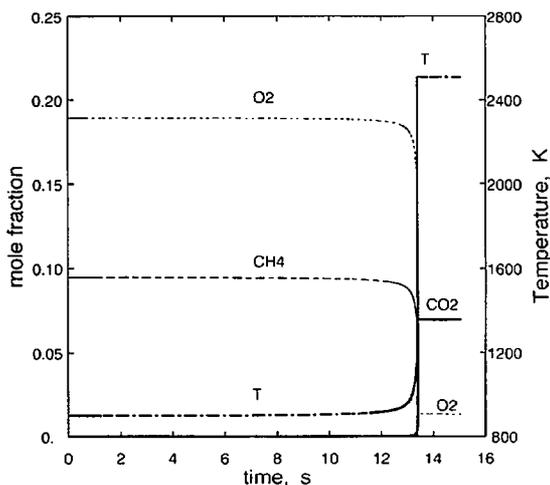


Fig. 1. Temporal history of  $\text{CH}_4$ ,  $\text{O}_2$ , and temperature during ignition of a stoichiometric methane-air mixture at 1 atm pressure and initial temperature of 900 K.

time where the main combustion process is occurring. Figure 2 is an alternative way to plot the data and it includes the parameters used to define the reaction time. There is an element of arbitrariness in this procedure and indeed, depending on the variable chosen, there can be wide variations in this parameter. Nevertheless, the use of any single parameter should

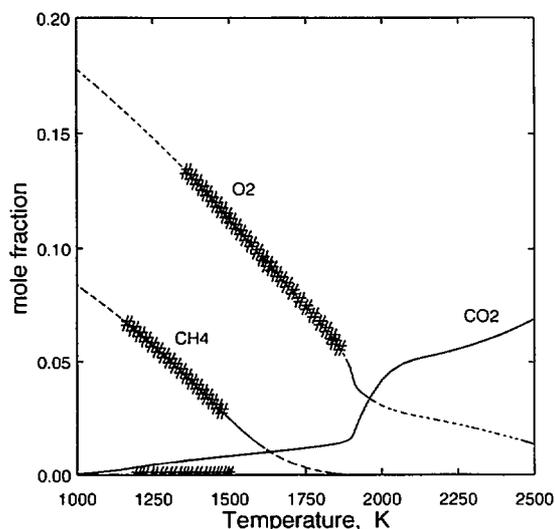


Fig. 2. Mole fractions and temperatures covered during reaction time. Reaction time is defined such that methane and oxygen are consumed from 30 to 70% and the temperature increases from  $T_0 + 300$  K to  $T_0 + 600$  K. The periods are marked by shadowed range ( $T_0 = 900$  K, stoichiometric  $\text{CH}_4$ -air mixture; 1 atm).

provide a common basis for making comparisons between different inhibitors. For the present purposes, we have considered reaction "times" as defined by the time required for the consumption of methane and oxygen from 30 to 70% of the initial concentrations and where the temperature increases from  $T_0 + 300$  to  $T_0 + 600$ . From Fig. 1 it can be seen that the variables of concern are changing rapidly with time; thus experimental determinations may have to be carefully carried out if high accuracy is desired. On the other hand, this is not a serious problem from a calculational point of view.

Most of the calculations were carried out on the basis of a plug flow reactor at constant (1 atm) pressure using the Sandia Chemkin code SENKIN [28] and analyzed with a NIST interactive graphics postprocessor. For purposes of comparison, the influence of inhibitors on laminar flame propagation has also been calculated using the Chemkin code PREMIX.

The simulation results are from the kinetic database described in earlier works [1, 29] with the addition of the set of reactions involving iodine; it contains reactions involving species with C, H, O, F, Br, and I atoms. Table 2 contains a summary [30-59] of the reactions with iodine- and bromine-containing species that have been added to the C, H, O, and F database. The backward rates were calculated from thermodynamic equilibrium. Thermodynamic data are derived from the earlier report [29] and the Chemkin database. Table 3 contains a summary [60-66] of the thermodynamics of the new species that are considered. The iodine reaction subset is constructed by analogy with that from the bromine kinetic mechanism. Thus a similar set of reaction species— $\text{CF}_3\text{I}$ ,  $\text{CH}_3\text{I}$ ,  $\text{CH}_2\text{I}$ ,  $\text{HI}$ ,  $\text{I}_2$ ,  $\text{I}$ ,  $\text{C}_2\text{H}_3\text{I}$ ,  $\text{C}_2\text{H}_3\text{I}$ ,  $\text{IO}$ , and  $\text{IOH}$ —is used. Information about kinetic parameters is extracted from the works of Westbrook [25, 26], the NIST database [67], the handbooks of Kondratiev [46] and Kerr et al. [68], and original references. For some rate constants, estimates are made. Westmoreland et al. [69] used an earlier version of the C-H-O-F database to calculate the effect of  $\text{CF}_3\text{H}$ ,  $\text{CF}_2\text{H}_2$ , and  $\text{CF}_4$  on flame velocities. Differences from the newer version used here are not significant.

TABLE 2

Reactions of Bromine- and Iodine-Containing Species (Chemkin Format Presentation; mole, s, cm, cal)

No.	Reaction	<i>A</i>	<i>n</i>	<i>E</i>	Comment, <sup>a</sup> Ref.
1	BR + BR + M = BR2 + M BR2/14./CF3BR/3./CH4/1.5/ CO2/2.3/CO/1.15/O2/1.15/H2O/5.4/	1.92E14	0.	-1,700.	30
2	H + BR + M = HBR + M	4.78E21	-1.963	510.5	30, fit
3	CF3BR = CF3 + BR	2.00E13	0.	6,2800.	31
4	CH3BR = CH3 + BR	1.58E13	0.	7,1700.	16
5	H + HBR = H2 + BR	1.26E10	1.05	160.	32
6	H + BR2 = HBR + BR	2.28E11	1.	440.	30
7	H + CH3BR = HBR + CH3	5.11E13	0.	5,840.	30
8	H + C2H3BR = HBR + C2H3	1.00E14	0.	6,000.	24, e
9	H + C2H5BR = HBR + C2H5	1.00E14	0.	5,000.	24, e
10	H + CF3BR = CF3 + HBR	1.41E14	0.	9,340.	30
11	HBR + O = BR + OH	3.97E12	0.	3,060.	33
12	HBR + OH = BR + H2O	6.62E12	0.	0.	34
13	BR + HO2 = HBR + O2	8.43E12	0.	1,170.	34
14	BR2 + CH3 = BR + CH3BR	1.21E13	0.	-390.	35
15	HBR + CH3 = BR + CH4	9.46E11	0.	-380.	36
16	CH3 + CF3BR = CH3BR + CF3	5.75E12	0.	4200.	37
17	CH3 + BR = CH2 + HBR	1.10E14	0.	22,968.	38
18	BR + HCO = HBR + CO	1.70E14	0.	0.	e
19	BR2 + CF3 = BR + CF3BR	1.21E12	0.	240.	39
20	CF3 + HBR = CHF3 + BR	2.63E11	0.	2,560.	40
21	HBR + CH2OH = BR + CH3OH	5.24E11	0.	-880.	41
22	BR2 + C2H3 = BR + C2H3BR	3.02E13	0.	-477.	39
23	BR12 + C2H5 = BR + C2H5BR	1.57E13	0.	-820.	35
24	HBR + C2H5 = BR + C2H6	1.02E12	0.	-1,000.	36
25	C2H5 + BR = C2H5BR	2.00E13	0.	0.	e
26	F + HBR = HF + BR	3.30E13	0.	1,000.	42
27	BR + H2O2 = HBR + HO2	6.03E12	0.	5,960.	43
28	BR + CH2O = HBR + HCO	1.02E13	0.	1,600.	34
29	CH3OOH + BR = HBR + CH3OO	1.58E12	0.	3,199.	44
30	CH3F + BR = CH2F + HBR	7.20E12	0.	14,800.	45
31	CH2F2 + BR = HBR + CHF2	2.34E13	0.	16,580.	46
32	C2H3 + BR = C2H3BR	3.00E13	0.	0.	e
33	BR + C2H4 = C2H3 + HBR	5.00E12	0.	25,000.	e
34	C2H5BR + CH3 = C2H5 + CH3BR	1.00E13	0.	6,000.	e
35	C2H3BR + CH3 = C2H3 + CH3BR	1.00E13	0.	11,000.	e
26	OH + CH3BR = H2O + CH2BR	7.60E07	1.3	994.	47
37	O + CH3BR = CH2BR + OH	2.00E13	0.	7,750.	48
38	CH3 + CH3BR = CH4 + CH2BR	1.26E12	0.	10,100.	46
39	CH3BR + HO2 = CH2BR + H2O2	1.00E13	0.	16,700.	e
40	CH3BR + BRO = CH2BR + BROH	3.00E11	0.	10,700.	b
41	BR + CH3BR = HBR + CH2BR	1.00E14	0.	16,310.	46
42	BR + CH2BR = BR2 + CH2	5.00E09	0.	10,200.	46
43	CH2BR + CH2O = CH3BR + HCO	3.60E11	0.	6,200.	b
44	CH2BR + C2H6 = CH3BR + C2H5	1.00E12	0.	8,500.	b
45	CH2BR + C2H4 = C2H3 + CH3BR	2.00E12	0.	12,000.	b
46	CH2BR + HO2 = CH2O + OH + BR	1.00E13	0.	0.	b
47	CH2BR + CH3 = C2H5BR	3.10E11	0.	-4,300.	b
48	CH2BR + CH3 = C2H4 + HBR	5.40E12	0.	1,400.	b
49	CH2BR + CH3 = C2H5 + BR	1.00E13	0.	7,000.	b
50	CH2BR + H2 = CH3BR + H	2.00E12	0.	13,100.	b
51	O + BR2 = BRO + BR	1.00E13	0.	0.	33
52	O + CF3BR = BRO + CF3	9.00E12	0.	13,510.	48
53	CH3BR + O = CH3 + BRO	1.00E13	0.	13,500.	45

TABLE 2 (Continued)

Reactions of Bromine- and Iodine-Containing Species (Chemkin Format Presentation; mole, s, cm, cal)

No.	Reaction	<i>A</i>	<i>n</i>	<i>E</i>	Comment, <sup>a</sup> Ref.
54	BRO + HO2 = BROH + O2	2.00E13	0.	0.	b
55	BRO + O = BR + O2	1.02E13	0.	-520.	49
56	BRO + OH = BR + HO2	1.00E13	0.	0.	b
57	BRO + BRO = BR + BR + O2	2.40E12	0.	380.	49
58	BRO + BRO = BR2 + O2	2.52E10	0.	-1,320	49
59	BRO + CO = CO2 + BR	6.00E11	0.	7,400.	b
60	CH4 + BRO = CH3 + BROH	1.40E13	0.	15,000.	b
61	CH2O + BRO = HCO + BROH	3.20E13	0.	11,100.	b
62	H2O2 + BRO = BROH + HO2	5.00E12	0.	2,000.	b
63	C2H4 + BRO = CH2BR + CH2O	5.00E12	0.	0.	b
64	BRO + H2 = H + BROH	6.00E11	0.	14,100.	b
65	H + BRO = OH + BR	1.00E13	0.	0.	e
66	H + BRO = HBR + O	1.00E12	0.	0.	b
67	CH3BR + OH = CH3 + BROH	1.00E13	0.	13,500.	45
68	OH + BR2 = BROH + BR	2.52E13	0.	0.	49
69	H + BROH = HBR + OH	9.50E13	0.	7,620.	b
70	BR + BROH = HBR + BRO	7.00E12	0.	100.	b
71	O + BROH = OH + BRO	6.00E12	0.	4,400.	b
72	OH + BROH = H2O + BRO	2.00E12	0.	1,000.	b
73	BROH(+M) = OH + BR(+M) LOW/6.0E09 0. 46000./	3.00E15	0.	50,000.	b
74	I2 + M = I + I + M	8.24E13	0.	30,300.	30
75	H + I + M = HI + M	1.20E13	1.	0.	23
76	CF3I(+M) = CF3 + I(+M) LOW/4.22E14 0. 28810./	2.51E14	0.	52,660.	50
77	CH3I = CH3 + I	2.57E13	0.	54,700.	51
78	C2H5I = C2H4 + HI	1.27E14	0.	52,800.	52
79	C2H5I = C2H5 + I	4.50E13	0.	50,000.	51
80	C2H3I = C2H3 + I	4.17E15	0.	66,500.	51
81	H + HI = H2 + I	4.74E13	0.	656.	30
82	H + I2 = HI + I	4.31E14	0.	431.	30
83	H + CH3I = HI + CH3	3.47E14	0.	4,500.	23
84	H + C2H3I = HI + C2H3	3.47E14	0.	5,000.	23
85	H + C2H5I = HI + C2H5	3.47E14	0.	3,500.	23
86	H + CF3I = CF3 + HI	5.00E13	0.	1,000.	53
87	HI + O = I + OH	2.82E13	0.	1,990.	54
88	HI + OH = I + H2O	1.81E13	0.	0.	34
89	I + HO2 = HI + O2	9.00E12	0.	2,180.	34
90	I2 + CH3 = I + CH3I	1.00E13	0.	0.	30
91	HI + CH3 = I + CH4	2.70E12	0.	-290.	55
92	CH3 + C2H5I = CH3I + C2H5	5.00E11	0.	10,000.	e
93	CH3 + C2H3I = CH3I + C2H3	2.00E12	0.	12,000.	e
94	CF3 + CH3I = CHF3 + CH2I	3.98E10	0.	7,500.	46
95	CF3 + CH3I = CF3I + CH3	3.88E09	0.	3,300.	46
96	CF3 + C2H5I = CF3I + C2H5	1.00E12	0.	8,000.	e
97	CF3 + C2H3I = CF3I + C2H3	2.00E12	0.	10,000.	e
98	HI + CH2OH = I + CH3OH	1.63E12	0.	-1,147.	41
99	I2 + C2H3 = I + C2H3I	1.00E13	0.	0.	23
100	I2 + C2H5 = I + C2H5I	1.00E13	0.	0.	23
101	HI + C2H5 = I + C2H6	2.71E12	0.	-763.	55
102	I + CF3I = I2 + CF3	7.59E12	0.	18,880.	56
103	I + CHF3 = CF3 + HI	3.98E13	0.	36,300.	46
104	I + H2O2 = HI + HO2	1.00E12	0.	18,000.	e
105	I + CH2O = HI + HCO	8.32E13	0.	17,430.	46
106	CH3F + I = CH2F + HI	2.00E14	0.	30,800.	57

TABLE 2 (Continued)

Reactions of Bromine- and Iodine-Containing Species (Chemkin Format Presentation; mole, s, cm, cal)

No.	Reaction	A	n	E	Comment, <sup>a</sup> Ref.
107	I = HCO = HI + CO	1.00E13	0.	0.	e
108	HI + F = HF + I	4.10E13	0.	0.	30
109	I + C2H4 = HI + C2H3	1.00E12	0.	1,500.	e
110	OH + CH3I = H2O + CH2I	1.87E12	0.	2,226.	34
111	O + CH3I = CH2I + OH	1.30E13	0.	7,600.	e
112	CH3 + CH3I = CH4 + CH2I	6.31E11	0.	12,098.	58
113	HO2 + CH3I = CH2I + H2O2	1.00E11	0.	15,000.	e
114	IO + CH3I = CH2I + IOH	4.00E11	0.	12,000.	e
115	CH2I + HI = CH3I + I	1.02E12	0.	-382.	59
116	CH2I + CH2O = CH3I + HCO	1.00E12	0.	10,000.	e
117	CH2I + C2H6 = CH3I + C2H5	3.00E12	0.	12,000.	e
118	CH2I + HO2 = CH2O + OH + I	1.00E13	0.	0.	e
119	CH2I + CH3 = C2H5 + I	4.00E13	0.	0.	e
120	CH2I + H2 = CH3I + H	1.00E12	0.	10,000.	e
121	CH2I + CF3 = CF3 - CH2 + I	2.00E13	0.	0.	e
122	O + I2 = IO + I	8.43E13	0.	0.	34
123	O + CF3I = IO + CF3	7.00E12	0.	0.	48
124	O + CH3I = CH3 + IO	2.00E13	0.	22,000.	e
125	IO + HO2 = IOH + O2	3.85E13	0.	0.	34
126	O + IO = I + O2	1.81E13	0.	0.	34
127	OH + IO = I + HO2	1.00E13	0.	0.	b
128	IO + IO = I + I + O2	6.00E13	0.	0.	e
129	IO + CO = CO2 + I	2.00E14	0.	24,000.	e
130	IO + CH4 = CH3 + IOH	1.40E13	0.	15,000.	b
131	IO + CH2O = HCO + IOH	3.20E13	0.	11,100.	b
132	IO + H2O2 = IOH + HO2	5.00E12	0.	2,000.	b
133	IO + C2H4 = CH2I + CH2O	5.00E12	0.	0.	b
134	IO + C2H4 = CH3 + HCO + I	1.00E10	0.	8,000.	e
135	IO + H2 = H + IOH	6.00E11	0.	14,100.	b
136	IO + H = OH + I	1.00E13	0.	0.	e
137	OH + CH3I = CH3 + IOH	1.80E12	0.	2,200.	e
138	OH + CF3I = CF3 + IOH	1.80E12	0.	2,200.	e
139	OH + I2 = IOH + I	1.08E14	0.	0.	34
140	H + IOH = HI + OH	3.00E13	0.	4,000.	e
141	I + IOH = HI + IO	3.00E13	0.	18,000.	e
142	O + IOH = OH + IO	6.00E12	0.	4,400.	b
143	OH + IOH = H2O + IO	1.00E12	0.	0.	e
144	IOH(+M) = OH + I(+M) LOW/6.0E09 0. 46000. /	3.00E15	0.	50,000.	b
145	CH3CO + HI = CH3CHO + I	2.00E11	0.	1,500.	e
146	H2 + I2 = HI + HI	1.94E14	0.	40,976	30
147	HI + CH3I = I2 + CH4	2.00E14	0.	33,400.	46
148	HI + C2H5I = I2 + C2H6	5.01E13	0.	29,800.	46

<sup>a</sup>e denotes estimation; b denotes chlorine analogy.**MODEL VALIDATION**

The results of comparisons with experimental measurements of our simulations are contained in an earlier publication [1]. These results include not only ignition delay, but also species concentration as a function of time for

different systems (oxidation of H<sub>2</sub>, CH<sub>4</sub>, CH<sub>2</sub>O, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>6</sub>, and additives CF<sub>3</sub>H, CH<sub>3</sub>Br, and CF<sub>3</sub>Br). The important point is that the main physical characteristics of the system are reproduced with reasonable accuracy. Unfortunately, there are not many high-temperature experimental kinetic and ignition

TABLE 3  
Enthalpy of Formation for Some Iodine- and  
Bromine-Containing Species<sup>a</sup>

Species	$\Delta H_f^0$ (298 K) (kcal/mol)	Ref.
BrO	30.10	60
HOBR	-19.00	61
CH <sub>3</sub> BR	-9.10	62
CH <sub>2</sub> BR	41.50	63
C <sub>2</sub> H <sub>5</sub> BR	-15.30	62
C <sub>2</sub> H <sub>3</sub> BR	18.73	62
CF <sub>3</sub> BR	-155.1	64
IO	31.03	65
HOI	-18.1	e
CH <sub>3</sub> I	3.43	64
CH <sub>2</sub> I	54.42	e
C <sub>2</sub> H <sub>5</sub> I	-2.0	62
C <sub>2</sub> H <sub>3</sub> I	31.03	66
CF <sub>3</sub> I	-140.60	65

<sup>a</sup>e denotes estimation.

delay measurements involving iodine-containing species. Indeed, there does not appear to be any experimental data on CF<sub>3</sub>I itself. Takahashi et al. reported on the effect of CH<sub>3</sub>I on the ignition of diluted CH<sub>4</sub>- and C<sub>2</sub>H<sub>6</sub>-air mixtures behind shock waves (1.4–3 atm and 1200–2000 K) [20]. Our numerical simulations demonstrate good agreement with this data. Westbrook [25, 26] has summarized the experimental data on the effect of bromine-containing compounds on methane flames. With the present database, these dependences of flame velocity with suppressant concentrations can be reproduced with satisfactory accuracy.

## RESULTS

### Effect of Temperature

#### a. Ignition Delay

Figure 3 contains results on the dependence of the ignition delay on the initial temperature for methane with air in stoichiometric mixtures at 1 atm pressure in the absence and presence of 1% CF<sub>3</sub>Br, CF<sub>3</sub>I, and CF<sub>3</sub>H, respectively. The simulations show that CF<sub>3</sub>Br and CF<sub>3</sub>H always act as promoters; that is, they decrease the ignition delay. CF<sub>3</sub>I is an exception in that it increases the ignition delay at 900 K. However, as the initial temperature increases, the effect decreases until at 1000 K the trend is

reversed. Subsequently, CF<sub>3</sub>I decreases the ignition delay. At practically all temperatures, CF<sub>3</sub>Br is a more effective promoter than CF<sub>3</sub>H. With increasing temperature, the ignition delays become closer to each other. These results are consistent with the observed promotion effect for CF<sub>3</sub>Br by Suzuki et al. [16] from their shock tube study. At 1500 K all the additives decrease the ignition delay and CF<sub>3</sub>I becomes, in fact, the most effective promoter.

#### b. Reaction Time

Figure 4 contains results on the temperature dependence of the reaction time under the same conditions as those used in Fig. 3. It provides an excellent comparison of the reaction times for the data in Fig. 3. The key observation is that regardless of the measure used, inhibition is the predominant behavior. The extent of this inhibition, however, decreases with increasing temperature. The brominated and the iodinated compounds are clearly better inhibitors than CF<sub>3</sub>H. However, the results are somewhat ambiguous with regard to the ranking of these two compounds. Furthermore, as will be seen subsequently, there are dramatic effects with respect to concentration dependencies.

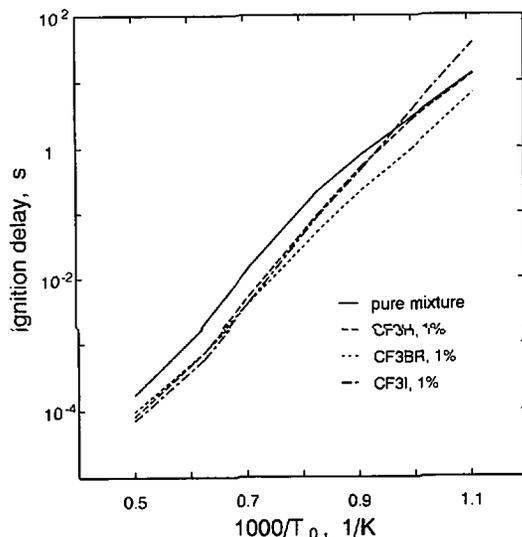


Fig. 3. Temperature dependence of ignition delay (time for increase of 100 K) for stoichiometric methane-air mixture without and with 1% CF<sub>3</sub>H, CF<sub>3</sub>Br, and CF<sub>3</sub>I; 1 atm.

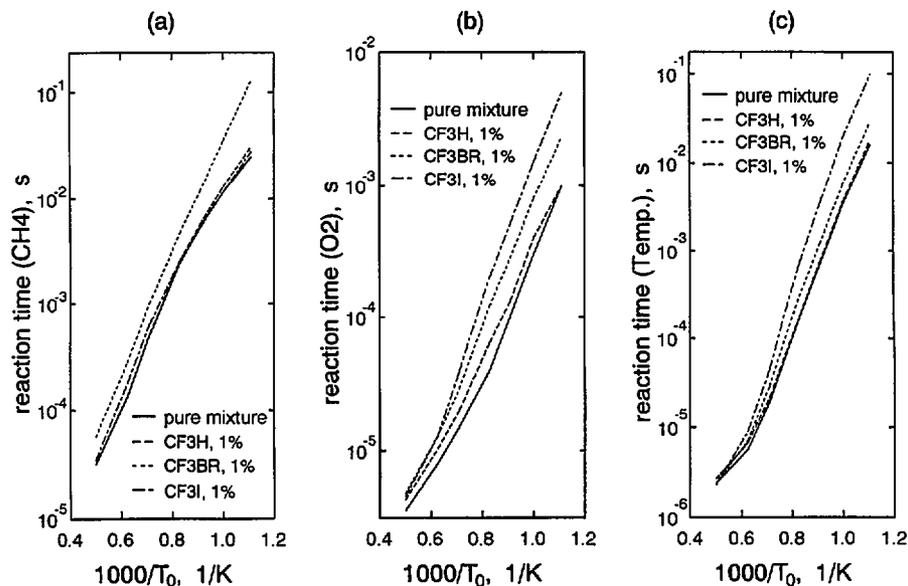


Fig. 4. Temperature dependence of reaction time for stoichiometric methane-air mixture without and with 1%  $\text{CF}_3\text{H}$ ,  $\text{CF}_3\text{Br}$ , and  $\text{CF}_3\text{I}$ ; 1 atm. Reaction time is defined according to the consumption of methane (a) and oxygen (b) from 30 to 70% and temperature increase from  $T_0 + 300$  K to  $T_0 + 600$  K (c).

## Effect of Additive Concentrations

### a. Ignition Delay

The ignition delay simulations for stoichiometric mixtures of methane with varying quantities of  $\text{CF}_3\text{I}$ ,  $\text{CF}_3\text{Br}$ , and  $\text{CF}_3\text{H}$  are presented in Fig. 5. The change in the ignition delay is nonmonotonic. For  $\text{CF}_3\text{Br}$  and  $\text{CF}_3\text{H}$ , the ignition delay is decreased initially. At concentrations from 0.5 to 4% there is a minimum or, equivalently, an optimum concentration for promotion. Subsequently, there is a continual increase in the ignition delay. This is connected with a decrease in the heat release rate and may be due to the pyrolysis of the additive. As mentioned earlier, we will not consider this case at present.

C-Br is the most labile bond in  $\text{CF}_3\text{Br}$ . Its cleavage and the resulting formation of bromine atoms in the methane combustion system lead to rapid formation of HBr. Thus it is not completely surprising that effects similar to those for the parent molecule were observed for HBr at small concentrations (Fig. 6). At additive concentrations less than 0.2%, promotion of methane ignition is observed at 900 K. The rate of reaction is very sensitive to traces

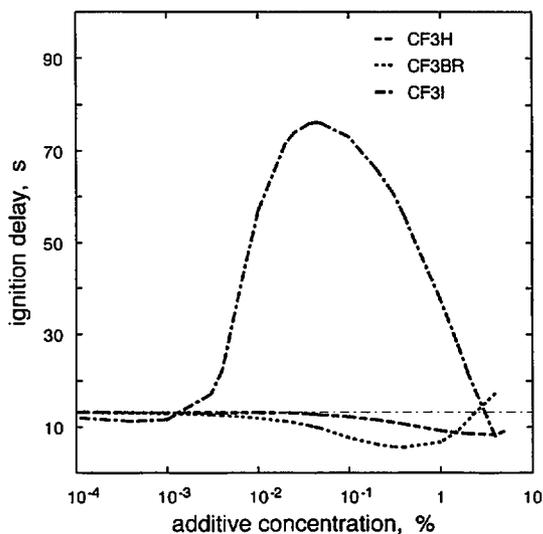


Fig. 5. Additive concentration ( $\text{CF}_3\text{H}$ ,  $\text{CF}_3\text{Br}$ , and  $\text{CF}_3\text{I}$ ) dependence on ignition delay (time for increase of 100 K) for stoichiometric methane-air mixture at 900 K and 1 atm. The horizontal line corresponds to ignition mixture without additives.

of HBr. For example, the addition of 1 ppm HBr changes the ignition delay approximately 5%. Maximum decrease of the ignition delay is observed at  $[\text{HBr}] \sim 400$  ppm. Increasing the concentration from 0.2% of HBr leads to a

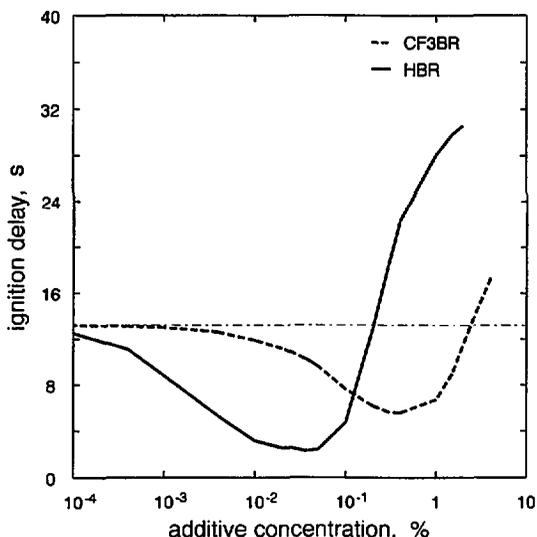


Fig. 6. Additive concentration (HBr and  $\text{CF}_3\text{Br}$ ) dependence of ignition delay (time for increase of 100 K) for stoichiometric methane-air mixture at 900 K and 1 atm. The horizontal line corresponds to ignition mixture without additives.

sharp increase of the delay. At 1% HBr, the ignition delay is about 28 s.

The data on  $\text{CF}_3\text{I}$  are very different than those for the other compounds. This can be seen in Fig. 5. Particularly striking are effects at very low concentration. At levels as low as 1 ppm there is a slight promotive effect. However, as the concentration increases, this is converted to an inhibitive effect and achieves a maximum at levels of 450 ppm. This then swings over to more typical behavior as the concentration is further increased. The general trends are very similar for  $\text{CH}_3\text{I}$  and HI additives.

### b. Reaction Time

A different situation occurs when one plots the reaction time relative to the concentration of inhibitors. It can be seen from Fig. 7 that there are large effects with inhibitor concentrations.  $\text{CF}_3\text{I}$  and  $\text{CF}_3\text{Br}$  are clearly more inhibiting than  $\text{CF}_3\text{H}$ . Note that for the first two compounds,  $\text{CF}_3\text{I}$  appears to be a better suppressant than  $\text{CF}_3\text{Br}$  if the reaction time is defined in terms of the  $\text{O}_2$  concentrations. From the data in Fig. 4 it can be seen that if the other measures are selected, the results will not be so clearcut, at least at the 1% level. It can be seen from Fig. 2 that the onset of reaction time as defined in this work is different for  $\text{O}_2$  and

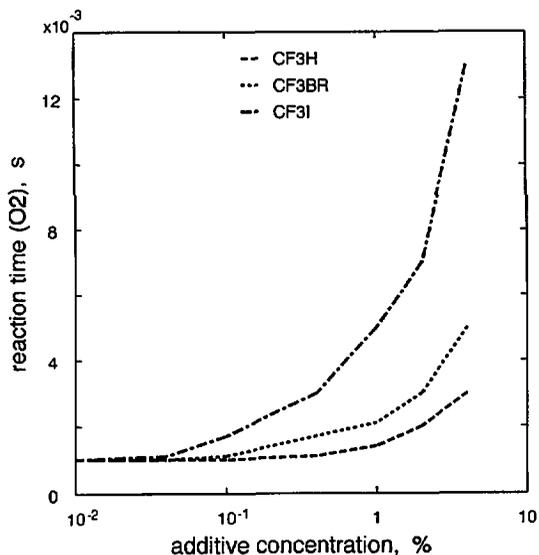


Fig. 7. Additive concentration ( $\text{CF}_3\text{H}$ ,  $\text{CF}_3\text{Br}$ , and  $\text{CF}_3\text{I}$ ) dependence of reaction time for stoichiometric methane-air mixture (900 K, 1 atm). The reaction time is defined according to consumption of oxygen from 30 to 70%.

$\text{CH}_4$ . For most of the simulations,  $t(30\% \text{CH}_4) < t(T_0 + 300) < t(30\% \text{O}_2)$ . Since the selected endpoints in time are not far apart, the reaction time defined for  $\text{O}_2$  is generally a minimum value. The reaction is thus proceeding at its maximum rate. This may be the most appropriate value for the description of the reaction time. In terms of the chemistry, the methane consumption (at the 30% concentration) is influenced by the  $\text{HO}_2$  radical and the transient kinetics between induction and reaction periods. Note that in the range covered, the reaction time varied by almost an order of magnitude.

## MECHANISMS

### a. Retardant Influence on Ignition Delay

Figure 8 shows the differences in the kinetics of additive destruction during ignition delay for stoichiometric mixtures at 1% additive concentration. It can be seen that  $\text{CF}_3\text{I}$  is decomposed extremely rapidly and that its lifetime is only a small part of the ignition delay.  $\text{CF}_3\text{H}$ , on the other hand, is barely consumed until the end of the ignition delay. As was discussed earlier,  $\text{CF}_3\text{Br}$  represents an intermediate case

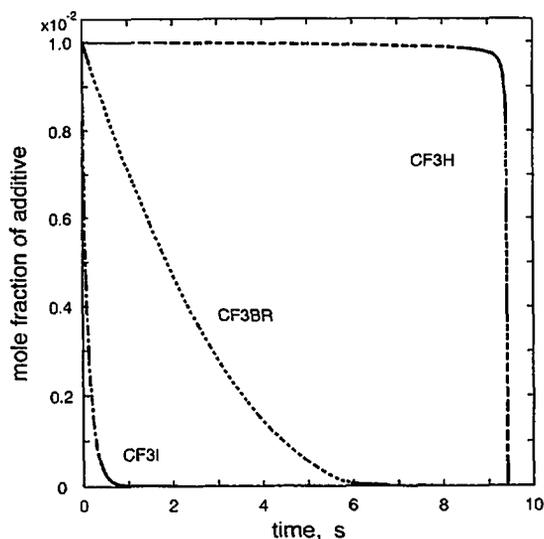
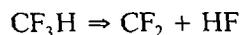
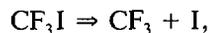
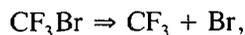


Fig. 8. Consumption kinetics of  $\text{CF}_3\text{H}$ ,  $\text{CF}_3\text{Br}$ , and  $\text{CF}_3\text{I}$  additives during ignition delay. Stoichiometric methane-air mixture at 1 atm and 900 K.

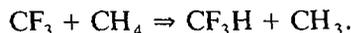
where the lifetime coincides with the ignition delay.

An analysis of reaction pathways demonstrates that when promotion of ignition occurs, the decomposition of the additive is an important cause. This is easily illustrated by excluding from the set of reactions the initial unimolecular decomposition reactions



of the additives in systems where they are present and observing a corresponding increase in the calculated ignition delay. We now discuss the specific pathways responsible for perturbing methane decomposition in turn.

With  $\text{CF}_3\text{Br}$  as the additive, a key process is the  $\text{CH}_3$  radical-catalyzed transformation of  $\text{CF}_3\text{Br}$  to  $\text{CF}_3\text{H}$  via the reactions



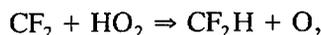
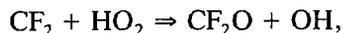
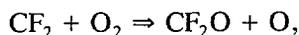
The rates of these reactions are much higher than the other processes involved in  $\text{CH}_3$  consumption and formation. The chain of transformations ( $\cdots \text{CH}_3 \Rightarrow \text{CF}_3 \Rightarrow \text{CH}_3 \Rightarrow \cdots$ ) results in the consumption of the  $\text{CF}_3\text{Br}$  inhibitor and the transformation of methane to

$\text{CF}_3\text{H}$  and  $\text{CH}_3\text{Br}$ . It appears that the induction time does not end until the  $\text{CF}_3\text{Br}$  is consumed.

The situation is completely different from  $\text{CF}_3\text{H}$  as the additive. Hardly any of the  $\text{CF}_3\text{H}$  is consumed during ignition delay. This is because the rate constants for  $\text{CF}_3\text{H}$  decomposition at 900 K are an order of magnitude smaller than those for  $\text{CF}_3\text{Br}$ . Furthermore, rate constant  $k(\text{CH}_3 + \text{CF}_3\text{H} \rightarrow \text{CH}_4 + \text{CF}_3) = 0.1k(\text{CH}_3 + \text{CF}_3\text{Br} \rightarrow \text{CH}_3\text{Br} + \text{CF}_3)$ . The consequence is that, unlike the situation with 1%  $\text{CF}_3\text{Br}$ , where the rate of destruction of methane is about the same as with the inhibitor, in the presence of  $\text{CF}_3\text{H}$  the rates of methane decomposition are now 10–20 times that of  $\text{CF}_3\text{H}$  destruction. Thus unlike  $\text{CF}_3\text{Br}$ ,  $\text{CF}_3\text{H}$  does not directly participate in the initial decomposition process. As a result, the levels of  $\text{CF}_3$  radical concentration are high when  $\text{CF}_3\text{Br}$  is the additive. The main decomposition channel for  $\text{CF}_3\text{H}$  begins with the initiation reaction

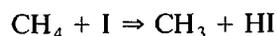


followed by reactions involving the  $\text{CF}_2$  radicals,

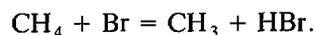


where the first reaction is the main source of oxygen atoms during the initial stage of the ignition period. Thus the key chemical differences between  $\text{CF}_3\text{Br}$  and  $\text{CF}_3\text{H}$  are the presence of Br in the former and the release of  $\text{CF}_2$  from the latter. As we have noted earlier, much of the  $\text{CF}_3\text{Br}$  is in fact converted to  $\text{CF}_3\text{H}$ . In this sense the effect of  $\text{CF}_3\text{Br}$  is really a combination of  $\text{CF}_3\text{H}$  as well as HBr and Br chemistry.

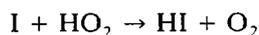
The differences in the effect of  $\text{CF}_3\text{I}$  and  $\text{CF}_3\text{Br}$  on the induction time are connected with the wide variation in the rate constants for the abstraction of hydrogen by the halide from methane. The rate constants for the reaction



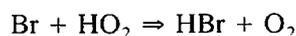
are much smaller than those for the process



Similarly, the rate constant for I-atom attack on formaldehyde is much smaller than the comparable reaction with Br. The consequence is that the I atom can remove HO<sub>2</sub> from the reactive system via the reaction



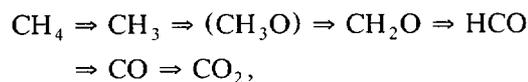
and thus serves as a termination process. This is the reason for the initial inhibitory effect observed upon addition of CF<sub>3</sub>I. In contrast, when CF<sub>3</sub>Br is the additive, the greater reactivity of Br atoms means that its concentration is much lower; thus, the analogous chain termination reaction



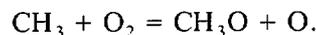
is much less important.

### b. Reaction Time

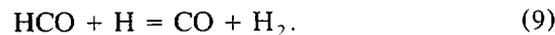
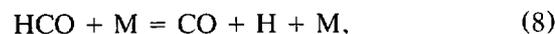
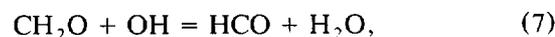
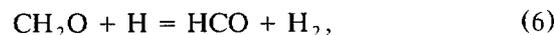
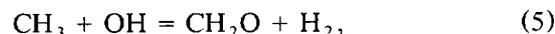
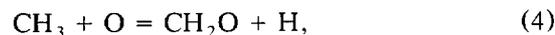
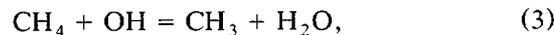
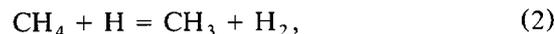
An analysis of the mechanism of methane decay shows that the main reaction pathway is, as could have been expected,



where the methoxy radical is from the process



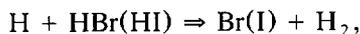
This process is most important during ignition delay and at lower temperatures. The main reactive species are H, O, and OH species, and the important reactions are



Reactions 2, 3, 6 and 7 represent chain transfer. They are precisely the processes that are known to destroy organic molecules in combustion systems. Reactions 4, 5, and 9 are

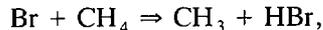
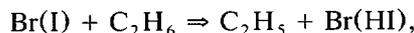
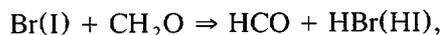
termination steps. These terminations counteract the well-known branching process  $H + O_2 \Rightarrow OH + O$ . The  $O + H_2 \Rightarrow OH + H$  reaction is unimportant in the present study due to the low concentrations of H<sub>2</sub>.

Upon addition of CF<sub>3</sub>Br or CF<sub>3</sub>I, an important channel for H-atom consumption is introduced into the system, that is, interaction with HBr or HI,

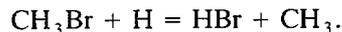
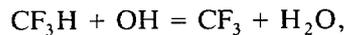
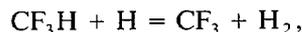


and competes with the branching reaction 1. This reaction leads to a decrease not only of the hydrogen atom concentration, but also leads to some decreases in the OH and O concentration. This can be seen in Figure 9a-d where we have plotted the H, OH, and O concentration with and without additives.

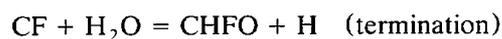
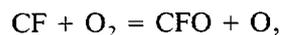
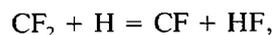
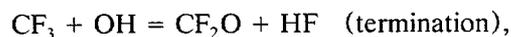
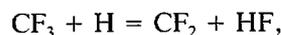
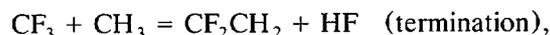
Regeneration of HBr or HI occurs through the reactions of Br or I atoms with the hydrogen atoms in the fuel or its intermediate products



where in the first two cases the contributions from the reactions are larger due to the more favorable thermochemistry. The existence of the stable intermediate products CH<sub>3</sub>Br (smaller amounts of CH<sub>3</sub>I) and CF<sub>3</sub>H leads also to additional scavenging of active species through the reactions



The overall effect is to introduce alternative channels through the reactions of the less active species. Thus the following reactions of the CF<sub>3</sub> radical also contribute:



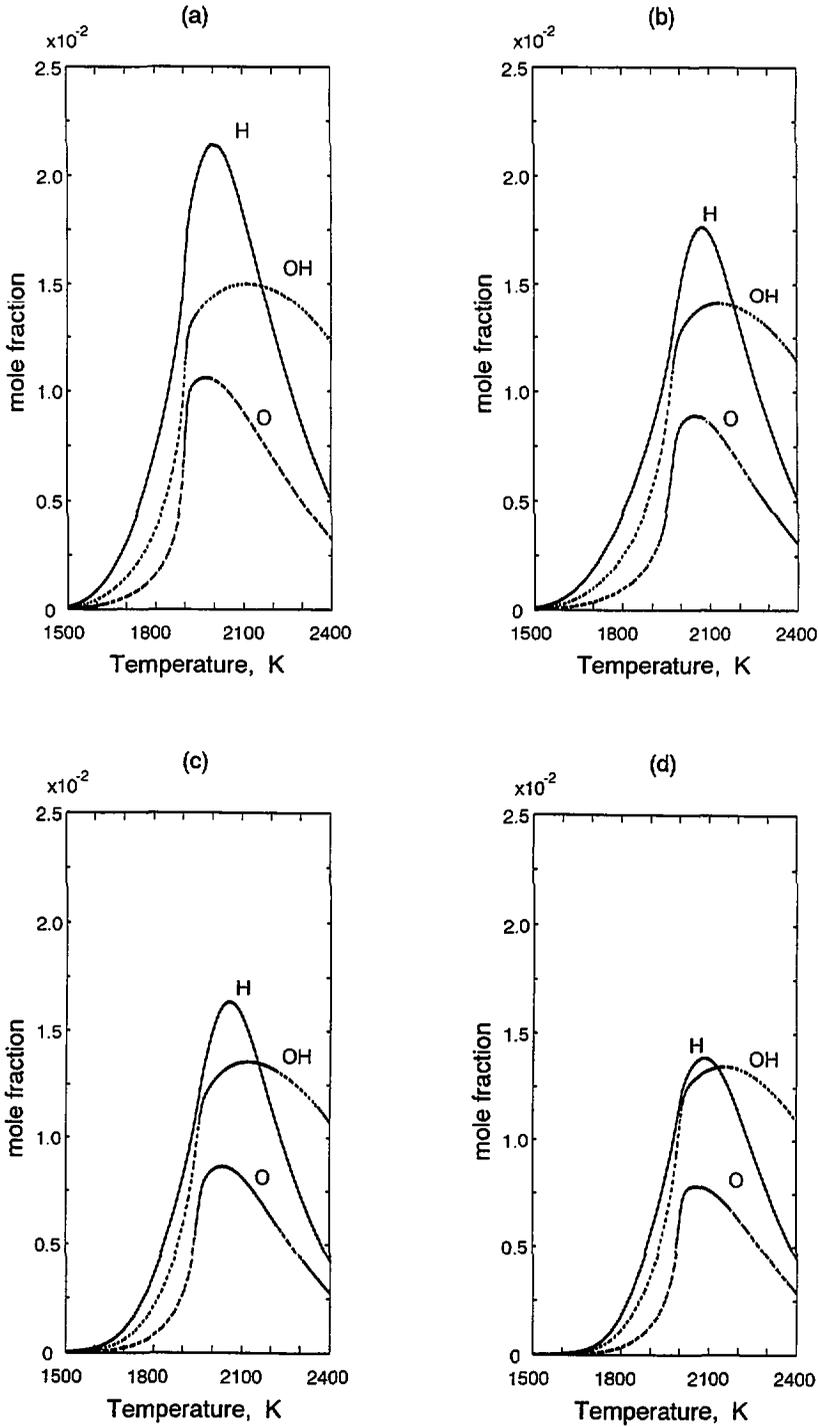


Fig. 9. Concentration of H, OH, and O as a function of reaction temperature without (a) and with 1% additive  $\text{CF}_3\text{H}$  (b)  $\text{CF}_3\text{Br}$  (c), and  $\text{CF}_3\text{I}$  (d). Initial conditions, stoichiometric methane-air mixture at 1 atm and 900 K.

It is seen that regeneration of HBr and HI is realized through chain propagation steps. The main inhibitive action involves the consumption of H atom and thus limits its contributions during the branching process [25, 26, 70].

At high temperatures (for example, 1900 K), the high concentrations of H and Br lead to the formation of sufficient concentrations of HBr through the reaction



so that HBr can take part in further inhibitive cycles.

The conversion pathways of  $\text{CF}_3\text{H}$  have been discussed earlier [69]. To a considerable extent they are a subset of the processes discussed in the foregoing text for  $\text{CF}_3\text{Br}$  and  $\text{CF}_3\text{I}$ .  $\text{CF}_3$  radical decomposition leads to the formation of  $\text{CF}_2$ ,  $\text{CF}_2\text{O}$ , and  $\text{CF}_2\text{CH}_2$ . Under the conditions covered in this investigation, approximately half of the  $\text{CF}_3$  is converted to  $\text{CF}_2$ . With decreasing equivalence ratio, contributions from the  $\text{CF}_2\text{O}$  formation channel are increased. Increasing fuel concentration leads to the formation of  $\text{CF}_2\text{CH}_2$ .

## DISCUSSION

The present analysis is in excellent accord with the general picture of the main processes in combustion. Specifically, there is an initial induction period where reactive radical concentrations are increasing and a reaction period where much of the fuel is destroyed by the attack of the reactive radicals such as OH, H, and O on the fuel. The entire process is aided by a slow initial increase in temperature and a very large temperature increase as most of the latent energy of the fuel is released. Our model shows that the chemical role of the additives is to influence the concentration levels of these radicals. The situation is particularly complex during the initial reaction stage. This is because the decomposition of the additive can generate active species that promote reaction. On the other hand, the additive and its decomposition products can react with the reactants generated from the fuel and oxidant and thereby, in some cases, lead to increases in the ignition delay. The sensitivity analysis shows

that particularly important intermediates are formaldehyde and the hydroperoxyl radical.

A particularly interesting result from these simulations is the confirmation of experimental evidence (Table 1) that ignition delay can be decreased with the addition of certain flame inhibitors. Thus this parameter cannot be used as a measure of inhibitive power. We have also investigated the possibility that  $\text{HO}_2$  may play an important role in the induction time. The results can be seen in Fig. 10. This does not appear to be the case. Only initially does the  $\text{HO}_2$  concentration track the observed induction time tendencies.

On the other hand, the reaction time is always increased with the addition of the suppressants and the general trends are in agreement with what is known about the flame suppression powers of the compounds studied. Since in all cases the fuel is always destroyed, it is clear that it is the rate of the overall reaction that is key parameter that is effected by flame inhibitors. This is consistent with a model of chemistry supplying the driving force in terms of temperature and reactive radicals with the flame spread being effected by physical factors such as mass and heat transfer.

These results are suggestive of a possible general procedure for screening compounds

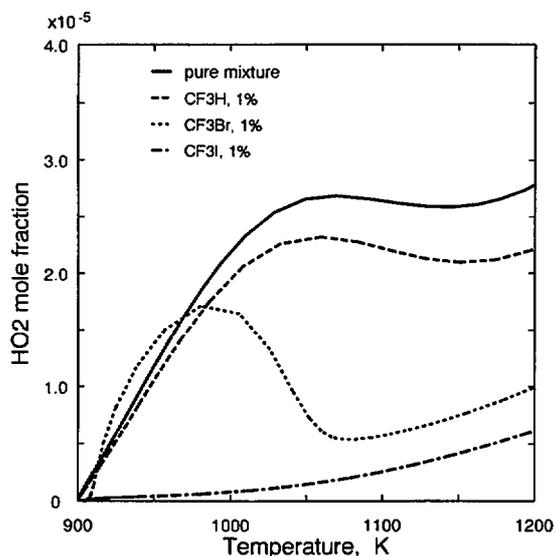


Fig. 10. Dependences of the  $\text{HO}_2$  radical on current temperature without additives and with 1% additives  $\text{CF}_3\text{H}$ ,  $\text{CF}_3\text{Br}$  and  $\text{CF}_3\text{I}$ . Stoichiometric methane-air mixture at 1 atm and 900 K.

for retardation efficiency. This will involve the levels of reactive radicals that may be present in the presence and absence of the retardant. It will, however, be important to see whether there are some unique features of a stoichiometric methane combustion system. It would be interesting to study other fuels such as methanol and larger hydrocarbons such as propane. It should be emphasized that once we believe in the validity of the data and the model, the simulations can be used to predict many other properties of the combustion system. Indeed, a particularly crucial test is the accuracy of the predictions regarding the concentrations of specific compounds. Thus, with the current interest in toxic chemicals, the model can be used to predict their rates of production and destruction in high-temperature environments. For example, we are currently using the model to predict the yields of HF for equivalent flame retarding power.

The preceding discussion stresses the importance of the three reactive radicals in contributing the fuel decomposition. One would expect that the fire retardants will affect their concentrations. Figure 9a shows the yields of the three radicals with no retardant. This can be compared with the situation with retardants in Fig. 9b-d. It can be seen that it is the hydrogen atom concentration that is most drastically lowered, while the concentration of OH and O atoms are affected to a much smaller extent. Dependence of the maximum H-atom concentrations on the amount of additives is presented in Fig. 11. The general trends clearly establish a suppressant ranking of  $\text{CF}_3\text{H} < \text{CF}_3\text{Br} \leq \text{CF}_3\text{I}$ . Particularly interesting is the much larger sensitivity of maximum H-atom concentration. As a further check of these suggestive results, we compare the maximum mole fraction of H atoms at the flame front with the calculated flame velocity for various additive concentrations. The results can be seen in Fig. 12. There is a clear correlation between calculated H-atom concentrations and burning velocities. This can be considered to be a demonstration of the importance of the former as a measure of flame suppression propensity.

These calculations suggest that  $\text{CF}_3\text{I}$  is clearly as good, if not a better, inhibitor than

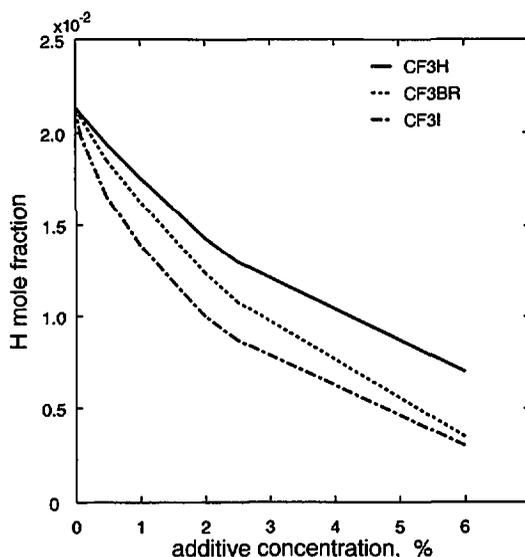


Fig. 11. Maximum concentration of H as a function of inhibitor concentration from plug flow reactor calculations. Initial conditions, stoichiometric methane-air mixture at 1 atm and 900 K.

$\text{CF}_3\text{Br}$ . It is interesting that it even shows inhibitory powers under certain conditions for ignition delay. This latter is clearly due to the relative inertness of the iodine atom. Iodine atoms are not able to abstract hydrogen atoms as rapidly as bromine atoms. Reactive radical

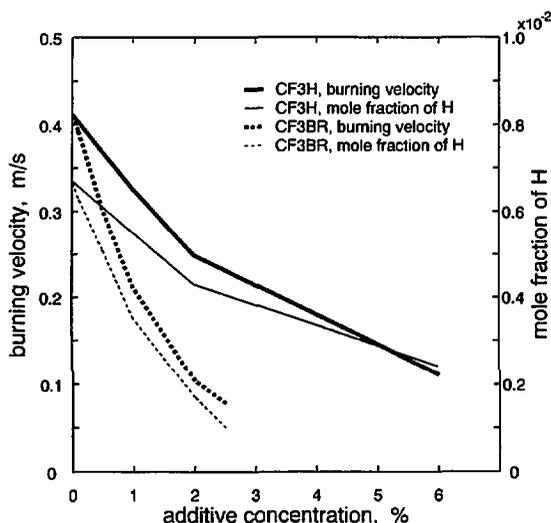


Fig. 12. Comparison of the dependence of flame velocity and maximum H-atom concentration on retardant ( $\text{CF}_3\text{H}$ ,  $\text{CF}_3\text{Br}$ ) concentration in the flame zone. Flame velocity calculations with stoichiometric methane-air mixture at 1 atm and 298 K. Calculations were conducted by Sandia Chemkin code PREMIX.

concentrations must therefore be lower. Furthermore, the rate constants for low activation energy processes such as disproportionation and combination for bromine and iodine atoms are similar. Thus contributions from termination processes remain unchanged.

## CONCLUSIONS

The present analysis has demonstrated that two new parameters can be used as a measure of the effectiveness of inhibition. These are the times for substantially complete reaction and the maximum hydrogen atom concentration. We demonstrate that the differences in maximum hydrogen concentration between systems with and without retardant track those deduce from differences in flame velocity. It is unfortunate that there is no simple way to directly measure hydrogen atom concentrations in combustion systems. On the other hand, it should be possible to devise techniques to measure the times necessary for substantial reaction just as readily as the flame velocity. It would appear that simulations can provide a very simple way of making a first-cut estimate regarding suppression power or inhibition efficiency of candidate compounds. For similar applications,  $\text{CF}_3\text{I}$  is predicted to be at least as good a retardant as  $\text{CF}_3\text{Br}$ ; it has the added benefit of being able to inhibit ignition at lower temperatures.

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