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FLAME INHIBITION BY CF_3CHCl_2 (HCFC-123)

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A kinetic model is suggested for hydrocarbon/air flame propagation with addition of hydrochlorofluorocarbon (HCFC) fire suppressant, encompassing the combined chemistry of fluorine- and chlorine-containing species. Calculated burning velocities using the kinetic model are in good agreement with available experimental burning velocity data for CF_3Cl , CF_2Cl_2 , or CFCl_3 added to $\text{CO}/\text{H}_2/\text{O}_2/\text{Ar}$ flames. The agent CF_3CHCl_2 is more effective than C_2HF_5 , and reaction pathway analysis shows that the inhibition effect of chlorine reactions is greater than that of fluorine. The main reactions of the chlorine inhibition cycle are $\text{H}+\text{HCl}=\text{H}_2+\text{Cl}$, $\text{OH}+\text{HCl}=\text{H}_2\text{O}+\text{Cl}$, $\text{Cl}+\text{CH}_4=\text{HCl}+\text{CH}_3$, $\text{Cl}+\text{HCO}=\text{HCl}+\text{CO}$, and $\text{Cl}+\text{CH}_2\text{O}=\text{HCl}+\text{HCO}$. The inhibition effect of CF_3CHCl_2 is largely the result of competing reactions of chlorine-containing species with hydrogen (and other radical pool) species, decreasing the rate of the chain-branching reaction $\text{H}+\text{O}_2$, with additional effects from substitution of the reactive chain-branching radicals for less reactive fluorine- and chlorine-containing radicals.

Keywords: CF_3CHCl_2 ; Fire suppressants; Fire suppression; Flame inhibition; HCFC-123; Kinetic model; R123

INTRODUCTION

Because of its high ozone depletion potential (ODP), the effective fire suppression agent CF_3Br (halon 1301) has largely been removed from use in terrestrial applications. Nonetheless, it is still used in aircraft, and it is desirable to find replacements for use there. Unfortunately, all of the proposed replacements have failed one particular Federal Aviation Administration (FAA) qualification test, the Aerosol Can Test (FAA-ACT), which is part of the FAA Minimum Performance Standard (Reinhardt, 2005) for the use of fire suppressants in cargo bays. The FAA-ACT is designed to simulate the rupturing of an aerosol can located in luggage during a cargo-bay fire. In the test, a two-phase spray of fuel (simulating the aerosol can contents: $\text{C}_2\text{H}_5\text{OH}$, C_3H_8 , and water) passes an igniter into ambient air, forming an explosion in a large (11.4 m^3) pressure vessel. By repeating the test with added suppressant premixed with the air, the volume fraction of agent required to suppress

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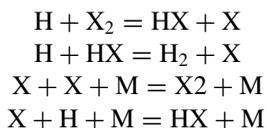
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the explosion is determined. For the halon replacement agents C₂F₅H, C₃F₇COC₂F₅, and 2-bromo-3,3,3-trifluoropropene (2-BTP), however, it was also found that when added at sub-inerting volume fractions, these agents all produce higher pressure rise in the chamber than with no agent. In contrast, CF₃Br (halon 1301) did not show this tendency, lowering the explosion pressure at all volume fractions. Using thermodynamic (Linteris et al., 2011) and kinetic (Linteris et al., 2012a, 2012b) simulations, the enhanced pressure rise and suppression have been analyzed for the FAA-ACT results.

The agents tested to date have included hydrofluorocarbons (HFCs) and fluoroketones. There is reason to believe, however, that hydrochlorofluorocarbon (HCFC) compounds may reduce the overpressure tendency (even in the absence of suppression), and recent thermodynamic calculations have verified this tendency (Linteris et al., 2011). In order to predict and interpret the potential of the HCFC agents to suppress the explosion, it is desired to perform kinetic simulations of the various HCFC agents together with FAA-ACT fuel with air, for various flames and reaction environments. To that end, we have developed the first kinetic mechanism for describing the flame inhibition by mixed fluorine- and chlorine-containing hydrocarbons. The mechanism has been validated through comparison with available data in the literature, and it is used in flame simulations to gain insights into the inhibition by the agent CF₃CHCl₂ (R-123, HCFC-123).

The inhibition of combustion by chlorine-containing compounds has been analyzed in previous work. The basic mechanism of flame inhibition by halogen species was outlined by Rosser et al. (1959), and further elucidated by Butlin and Simpson (1968), Wilson et al. (1969), Day et al. (1971), and Dixon-Lewis and Simpson (1976), followed by detailed numerical modeling of flames and detonations by Westbrook (1982). The order of effectiveness of the halogens is F < Cl < Br ≈ I. It was suggested that the difference in inhibition effectiveness is due to differences in the rate of the reaction H + HX = H₂ + X (in which X is a halogen), which is often controlled by the thermodynamic equilibrium relation. The inhibition includes the reactions:



Later detailed modeling work supported these findings. Chang et al. (1987) simulated chlorine inhibition of a hydrogen-catalyzed CO flame, and showed the burning velocity to be sensitive to the rates of H and OH reactions with HCl, as well as to the rate of the recombination reaction H+Cl+M=HCl+M. Roesler et al. (1992) analyzed the influence of HCl on moist carbon monoxide oxidation in a flow reactor at ≈1000 K, and found that moist CO oxidation was sensitive to HCl when present at volume fractions as low as 75 μL/L. The oxidation of CO was inhibited by the reaction H+Cl+M=HCl+M, as well as by the reactions of H and OH with HCl, and the reaction Cl+HO₂=HCl+O₂. Also using a flow reactor at around 1000 K, Ho et al. (1992) studied the effects of CH₂Cl₂ added to a hydrogen/oxygen/argon mixture. Carbon monoxide oxidation was inhibited through the competition of the reaction OH+HCl=Cl+H₂O with OH+CO=CO₂+H. Casias and McKinnon (1996) investigated combustion quenching by chlorine in a well-stirred reactor. It was found that termolecular reactions, H+Cl+M=HCl+M and Cl+Cl+M=Cl₂+M, have a relatively insignificant influence on flame inhibition. Wang and Barat (1995) analyzed the inhibitory effect of CH₃Cl addition to rich methane flame. They indicated that HCl

competes with O_2 for hydrogen atoms. The fast reaction $H+HCl=H_2+Cl$ was possibly the cause of lower O_2 consumption in the presence of the chlorinated hydrocarbon.

A number of HCFC agents have been studied for use as fire suppressants. Van Tiggelen and coworkers (DaCruz et al., 1988) used a Mache–Hebra nozzle burner to measure the burning velocities of $CO/H_2/Ar/O_2$ flames with added CF_3Cl , CF_2Cl_2 , and $CFCl_3$. Moore et al. (1996) used a cup-burner to determine the minimum extinction concentration for CF_3CHCl_2 (7.1% for heptane), which is similar to the value found by Kim (2002) (7.1% to 7.8%). Su and Kim (2002) studied suppression of heptane pool fires by C_3HF_7 , $C_3H_2F_6$, CF_3I , and Halotron I (about 95% CF_3CHCl_2), and found Halotron I to be more effective than the HFCs. Holmstedt et al. (1994) used a propane/air coflow diffusion flame to measure changes in the heat release rate as the concentration of different halogenated agents in the fuel stream was increased to the extinction value. They found that the heat release rate increased with addition of any HFC, but did not increase for addition of CF_3CHCl_2 or CF_3Br (and decreased for CF_3Br at low concentration). In general, given the superior action of Cl over F, and the lack of increased heat release with addition of HCFC as opposed to HFC (Holmstedt et al., 1994), it is expected that CF_3CHCl_2 should perform better than C_2HF_5 in the FAA aerosol can test.

The purpose of the present work is to study the effect of the chlorine- and fluorine-containing agent CF_3CHCl_2 on laminar flame propagation, and compare its effect with those of C_2F_5H and CF_3Br . To this end we have developed a kinetic model of hydrocarbon/air flame inhibition by CF_3CHCl_2 . As a first step in validation of the model we compare calculated burning velocities with experimental values available in the literature for other HCFCs (data are not yet available for CF_3CHCl_2 itself). We have analyzed the inhibition mechanism of CF_3CHCl_2 and the reaction pathways of its consumption. Finally the relative flame inhibition ranking of several HCFCs, considered as possible halon replacements in the literature, is estimated using the empirical group additivity approach suggested by Fristrom and Van Tiggelen (1978).

KINETIC MODEL AND MODELING PROCEDURE

The kinetic model consists of four sub-mechanisms: (1) hydrocarbon combustion (Linteris et al., 2012a, 2012b; Wang et al., 2007), (2) C_1 – C_2 fluorocarbon inhibition of hydrocarbon flames (Linteris et al., 2012a, 2012b), (3) C_1 – C_2 chlorocarbon flame chemistry, and (4) reactions related to mixed F- and Cl-containing species. The hydrocarbon model is the C_1 – C_4 model of Wang et al (2007). This model has been validated through comparisons with experimental ignition delays from shock tubes; species profiles from shock tubes, flow reactors, and flames; and laminar flame speeds. To reduce computation time, the reactions with C_5 – C_7 species were not considered (they have a minor effect in the present work). The mechanism to describe hydrofluorocarbon reactions in hydrocarbon flames is from Burgess et al. (1995), including modifications noted in the recent work (Linteris et al., 2012b). The sub-mechanism describing chemistry of C_1 – C_2 -chlorine containing species is from Leylegian et al. (1998a, 1998b), which has been used for modeling hydrochlorocarbon/air flames and hydrocarbon/air flames with chlorine-containing additives (Leylegian et al., 1998a, 1998b; Linteris and Babushok, 2000; Shin et al., 2006). Note that the rate constant of reaction $Cl+HCO=HCl+CO$ was modified to be consistent with available kinetic data for reactions of bromine and iodine atoms with HCO radical (Poulet et al., 1984). The block of reactions with C_1 – C_2 -species containing chlorine and fluorine atoms, and describing the interaction between fluorine and chlorine parts of the model, is

Table 1 List of Cl- and F-containing species considered in the model

Species	Enthalpy of formation at 298 K, kJ/mol	Entropy at 298 K, J/(mol K)	Heat capacity at 298 K, J/(mol K)	Reference
CF ₃ CHCl ₂	-757.5	352.5	102.6	Goos et al., 2012
CF ₃ CCl ₂	-562.3	364.0	101.7	Wang et al., 2010
CF ₃ CCl ₃	-759.1	376.5	120.6	Goos et al., 2012
CFCl ₂	-105.0	298.9	59.1	Goos et al., 2012
CF ₂ Cl	-275.1	287.4	55.2	Goos et al., 2012
CF ₃ Cl	-710.0	285.4	66.9	Goos et al., 2012
CF ₂ Cl ₂	-495.8	300.9	72.5	Goos et al., 2012
CFCl ₃	-290.7	309.8	78.1	Goos et al., 2012
CHF ₂ Cl	-482.8	280.9	55.9	Goos et al., 2012
CHFCl ₂	-284.9	293.2	61.0	Goos et al., 2012
CFCIO	-412.8	276.9	52.4	Goos et al., 2012
FCI	-55.7	217.9	32.1	Goos et al., 2012
CFCl	25.8	259.2	43.0	Goos et al., 2012
C ₂ F ₃ Cl	-515.1	322.3	83.9	Gurvich et al., 1993

the topic of the present work. For modeling of flame propagation with CF₃Br additives, the kinetic model from Babushok et al. (1996, Submitted) was used.

Table 1 lists the chlorine- and fluorine-containing species considered in the present model. Of the C₁-HCFC species, the list includes all stable C₁ species, except the two hydrogen atom containing species, CH₂FCl, and the corresponding radical CHFCl. These two species were not considered because they are not expected to play important roles: the hydrogen atom should be abstracted first, and the formation of CH₂-mixed species should be relatively small. Thermochemical data, except for C₂F₃Cl and CF₃CCl₂, are from the database of Goos et al. (2012). Chemkin thermodynamic polynomials for CF₃CCl₂ and C₂F₃Cl species were generated using data from Wang et al. (2010) and Gurvich et al. (1993).

A list of plausible reactions with Cl- and F-containing species was considered. They include reactions of CF₃CHCl₂ decomposition, reactions of CF₃CHCl₂ and its products with the important radicals (H, OH, O, F, Cl, CF₃, CF₂, and CCl₃), and reactions of the main hydrocarbon species (CH₄, C₂H₆, C₃H₈, CH₂O) with radicals formed from mixed hydrochlorofluorocarbons (CF₂Cl, CFCl₂, CF₃CCl₂). Based on thermochemical considerations and estimation of species equilibrium concentrations, this list was reduced to that in Table 2. Rate constants were taken from literature data reviews, when available. For reactions with no data in the literature, rates were estimated using empirical correlations and similar reactions.

The model also includes reactions of COFCl, which has been experimentally observed as a product in low temperature oxidation and decomposition of HCFC compounds (Francisco and Li, 1989; Wu and Carr, 1992). The formation is included through the recombination of CFO with Cl and CClO with F; however, we do not include formation through reactions of CFCl₂ with O₂ leading to CFCl₂O with fast decomposition to COFCl. Rough estimates indicate that the activation energy of reaction with O₂ is very high (more than 125 kJ/mol). For the reaction CF₃Cl+H=CF₃+HCl, available data are those of Bradley et al. (1976) in the temperature range 538 K to 676 K. Their rate expression was modified (by decreasing the pre-exponential factor by a factor of five) to obtain agreement between the simulated burning velocity and available experimental data for H₂/CO/Ar/O₂ flames inhibited by CF₃Cl (DaCruz et al., 1988).

Table 2 Reactions of Cl- and F-containing species*

Reaction	A	n	E	Reference
$\text{CF}_3\text{CCL}_2\text{H} + \text{OH} = \text{CF}_3\text{CCL}_2 + \text{H}_2\text{O}$	4.4e06	1.7	3.10	Cohen and Westberg, 1991
$\text{CF}_3\text{CCL}_2\text{H} + \text{H} = \text{CF}_3\text{CCL}_2 + \text{H}_2$	7.e12	0.0	25.10	est
$\text{CF}_3\text{CCL}_2\text{H} + \text{O} = \text{CF}_3\text{CCL}_2 + \text{OH}$	5.e12	0.0	29.29	est
$\text{CF}_3\text{CCL}_2\text{H} + \text{F} = \text{CF}_3\text{CCL}_2 + \text{HF}$	4.93e08	1.35	1.00	Wang et al., 2010
$\text{CF}_3\text{CCL}_2\text{H} + \text{Cl} = \text{CF}_3\text{CCL}_2 + \text{HCl}$	2.65e12	0.0	14.56	Atkinson et al., 2001
$\text{CF}_3\text{CCL}_2\text{H} + \text{CF}_3 = \text{CF}_3\text{CCL}_2 + \text{CHF}_3$	1.26e11	0.0	34.10	CF ₂ C(H)FCl; Quick and Whittle, 1972
$\text{CF}_3\text{CCL}_2\text{H} = \text{CF}_3 + \text{CHCl}_2$	2.0e16	0.0	372.38	est
$\text{CF}_3\text{CCL}_2\text{H} = \text{C}_2\text{F}_3\text{Cl} + \text{HCl}$	2.0e14	0.0	292.88	est
$\text{C}_2\text{F}_3\text{Cl} + \text{H} = \text{CF}_2 + \text{CF} + \text{HCl}$	4.e5	2.5	37.66	est
$\text{C}_2\text{F}_3\text{Cl} + \text{O} = \text{CF}_2 + \text{CFClO}$	5.0e9	1.0	2.09	est
$\text{C}_2\text{F}_3\text{Cl} + \text{F} = \text{CF}_2 + \text{CF}_2\text{Cl}$	5.5e12	0.0	18.83	est
$\text{C}_2\text{F}_3\text{Cl} + \text{F} = \text{CF}_2 + \text{CF}_2 + \text{Cl}$	2.e13	0.0	41.84	est
$\text{C}_2\text{F}_3\text{Cl} = \text{CFCl} + \text{CF}_2$	2.e16	0.0	351.46	est
$\text{CFCl} + \text{Cl} = \text{CFCl}_2$	1.6e13	0.0	0.	est
$\text{CFCl} + \text{H} = \text{CF} + \text{HCl}$	2.e13	0.0	0.	est
$\text{CFCl} + \text{O}_2 = \text{CFClO} + \text{O}$	2.e13	0.0	110.88	est
$\text{CFCl} + \text{OH} = \text{CF} + \text{HCl}$	2.5e13	0.0	0.	est
$\text{CFCl} + \text{O} = \text{CF} + \text{Cl}$	3.e13	0.0	0.	est
$\text{CF} + \text{Cl} = \text{CFCl}$	2.e13	0.0	0.	est
$\text{CF}_3\text{CCL}_2 + \text{HCO} = \text{CF}_3\text{CCL}_2\text{H} + \text{CO}$	2.e12	0.0	6.28	est
$\text{CF}_3\text{CCL}_2 = \text{CF}_3 + \text{CCL}_2$	3.e15	0.0	330.54	est
$\text{CF}_3\text{CCL}_2 + \text{CH}_4 = \text{CF}_3\text{CCL}_2\text{H} + \text{CH}_3$	3.e11	0.0	62.76	est
$\text{CF}_3\text{CCL}_2 + \text{CH}_2\text{O} = \text{CF}_3\text{CCL}_2\text{H} + \text{HCO}$	2.e11	0.0	37.66	est
$\text{CF}_3\text{CCL}_2 + \text{C}_2\text{H}_6 = \text{CF}_3\text{CCL}_2\text{H} + \text{C}_2\text{H}_5$	3.e11	0.0	50.21	est
$\text{CF}_3 + \text{CCL}_3 = \text{CF}_3\text{CCL}_3$	1.4e13	0.0	0.	CF ₃ +CF ₃
$\text{CF}_3\text{CCL}_2 + \text{Cl} = \text{CF}_3\text{CCL}_3$	1.e13	0.0	0.	est

$\text{CF}_3\text{CCL}_2 + \text{CL}_2 = \text{CF}_3\text{CCL}_3 + \text{CL}$	1.26e12	0.0	24.35	Cullison et al., 1973
$\text{CF}_3\text{CCL}_3 + \text{H} = \text{CF}_3\text{CCL}_2 + \text{HCL}$	3.e12	0.0	16.74	est
$\text{CF}_3\text{CCL}_3 + \text{O} = \text{CF}_3\text{CCL}_2 + \text{CLO}$	2.e12	0.0	50.21	est
$\text{CF}_3\text{CCL}_3 + \text{OH} = \text{CF}_3\text{CCL}_2 + \text{HOCL}$	2.e12	0.0	96.23	est
$\text{CF}_3\text{CCL}_3 + \text{CH}_3 = \text{CF}_3\text{CCL}_2 + \text{CH}_3\text{CL}$	7.94e11	0.0	40.58	Sidebottom and Treacy, 1984
$\text{CF}_3\text{CCL}_3 + \text{CF}_3 = \text{CF}_3\text{CCL}_2 + \text{CF}_3\text{CL}$	6.31e12	0.0	53.14	Quick and Whittle, 1972
$\text{CF}_3\text{CCL}_2 + \text{O} = \text{COCL}_2 + \text{CF}_3$	1.1e13	0.0	0.	Similar to F-containing species
$\text{CF}_3\text{CCL}_2 + \text{H} = \text{CF}_3\text{CCL}_2\text{H}$	1.12e47 -	10.8	17.15	Similar to F-containing species
$\text{CF}_3\text{CCL}_2 + \text{H} = \text{CF}_3 + \text{CHCL}_2$	4.4e16	-0.746	18.24	Similar to F-containing species
$\text{CCL}_4 + \text{CF}_3 = \text{CF}_3\text{CL} + \text{CCL}_3$	1.44e12	0.0	33.35	Olleta and Lane, 2002
$\text{CF}_3\text{CL} + \text{CL} = \text{CF}_3 + \text{CL}_2$	1.9e14	0.0	131.38	Amphlett and Whittle, 1967
$\text{CF}_3\text{CL} + \text{H} = \text{CF}_3 + \text{HCL}$	3.4e12	0.0	36.82	Bradley et al., 1976(x0.2)
$\text{CF}_3\text{CL} (+\text{M}) = \text{CF}_3 + \text{CL} (+\text{M})$	7.24e19	-1.10	385.30	Kumaran et al., 1996b
LOW / 7.81e24 - 10.83 101000./				
$\text{CF}_3\text{CL} + \text{F} = \text{CF}_4 + \text{CL}$	1.5e12	0.0	71.13	est
$\text{CHCL}_3 + \text{CF}_3 = \text{CF}_3\text{CL} + \text{CHCL}_2$	1.82e11	0.0	44.69	Olleta and Lane, 2002
$\text{CH}_3\text{CCL}_3 + \text{CF}_3 = \text{CF}_3\text{CL} + \text{CH}_3\text{CCL}_2$	3.16e11	0.0	40.58	Quick and Whittle, 1972
$\text{CF}_2\text{CL}_2 + \text{CF}_3 = \text{CF}_3\text{CL} + \text{CF}_2\text{CL}$	2.34e11	0.0	56.23	Olleta and Lane, 2002
$\text{CF}_2\text{CL}_2 + \text{CH}_3 = \text{CH}_3\text{CL} + \text{CF}_2\text{CL}$	1.26e12	0.0	47.32	Sidebottom and Treacy, 1984
$\text{CF}_2\text{CL}_2 + \text{M} = \text{CL} + \text{CF}_2\text{CL} + \text{M}$	8.07e16	0.0	263.59	Kumaran et al., 1995
$\text{CF}_2\text{CL}_2 + \text{OH} = \text{HOCL} + \text{CF}_2\text{CL}$	6.03e11	0.0	29.92	DeMore et al., 1997
$\text{CF}_2\text{CL}_2 + \text{F} = \text{CF}_2\text{CL} + \text{FCL}$	1.58e13	0.0	69.83	Foon and Tait, 1972b
$\text{CF}_2\text{CL}_2 + \text{H} = \text{CF}_2\text{CL} + \text{HCL}$	5.e12	0.0	39.75	est
$\text{CF}_2 + \text{CL}_2 = \text{CF}_2\text{CL}_2$	3.21e8	0.0	8.83	Melnikovich and Moin, 1986
$\text{CF}_2\text{CL} + \text{CL}_2 = \text{CF}_2\text{CL}_2 + \text{CL}$	7.76e11	0.0	7.99	Timonen et al., 1986
$\text{CF}_2\text{CL} + \text{CF}_2\text{CL} = \text{CF}_2\text{CL}_2 + \text{CF}_2$	2.06e16	0.0	39.50	Majer et al., 1969
$\text{CL} + \text{CF}_2 + \text{M} = \text{CF}_2\text{CL} + \text{M}$	3.6e17	0.0	0.	Codnia and Azcarate, 2006

(Continued)

Table 2 (Continued).

Reaction	A	n	E	Reference
$F + CCl_2 + M = CFCl_2 + M$	1.5E17	0.0	0.	est
$CHFCl_2 + O = CFCl_2 + OH$	1.0e13	0.0	30.75	Herron, 1988
$CHFCl_2 + Cl = CFCl_2 + HCl$	3.1e12	0.0	13.97	Talhaoui et al., 1996
$CHFCl_2 + F = CFCl_2 + HF$	1.57E13	0.0	7.07	Louis and Sawerysyn, 1998
$CHFCl_2 + H = CFCl_2 + H_2$	5.66e06	2.03	27.82	Louis and Sawerysyn, 1998
$CHFCl_2 + OH = CFCl_2 + H_2O$	9.08e06	1.7	5.06	Cohen and Westberg, 1991
$CFCl_3 + H = CCl_3 + HF$	4.e12	0.0	41.84	est
$CFCl_3 + H = CFCl_2 + HCl$	3.e13	0.0	20.92	est
$CFCl_3 + OH = CFCl_2 + HOCl$	6.0e11	0.0	30.33	Atkinson et al., 2001
$CFCl_3 + CF_3 = CF_3Cl + CFCl_2$	8.51e11	0.0	45.65	Olleta and Lane, 2002
$CFCl_3 + CH_3 = CH_3Cl + CFCl_2$	2.e11	0.0	44.77	Sidebottom and Treacy, 1984
$CFCl_3 = CFCl_2 + Cl$	1.7e16	0.0	219.49	Kumaran et al., 1996a
$CFCl_2 + Cl_2 = CFCl_3 + Cl$	8.32e11	0.0	13.97	Timonen et al., 1986
$CF_2 + HCl = CHF_2Cl$	6.6e11	0.0	50.63	Melnikovich et al., 1984
$CF_2Cl + H = CHF_2Cl$	2.5e13	0.0	16.69	Yu et al., 2005 (x0.5)
$CF_2Cl + F = CF_3 + Cl$	7.2e13	0.0	0.	Burkovskaya et al., 1978
$CFCl_2 + F = CF_2Cl + Cl$	2.e13	0.0	12.55	est
$CHF^2Cl + Cl = CF^2Cl + HCl$	3.19e12	0.0	20.21	Talhaoui et al., 1996
$CHF^2Cl + O = CF^2Cl + OH$	7.0e12	0.0	34.94	Herron, 1988
$CHF^2Cl + F = CF^2Cl + HF$	1.45e13	0.0	8.66	Louis and Sawerysyn, 1998
$CHF^2Cl + H = CHF^2 + HCl$	1.87e08	1.66	38.28	Louis et al., 2004
$CHF^2Cl + H = CF^2Cl + H^2$	6.62e06	2.05	37.57	Louis et al., 2004
$CHF^2Cl + OH = CF^2Cl + H^2O$	4.89e06	1.8	9.79	Cohen and Westberg, 1991
$CHF_2Cl + CF_3 = CF_2Cl + CHF^3$	2.0e11	0.0	45.06	Leyland et al., 1970
$CHF_2Cl + CH_3 = CF_2Cl + CH_4$	1.0e12	0.0	41.84	Nikisha et al., 1976
$CH_3Cl + F = CH_2Cl + HF$	4.97e13	0.0	3.51	Wang et al., 2005
$CH_2Cl_2 + F = CHCl_2 + HF$	4.4e12	0.0	0.67	Foon and McAskill, 1969
$CHCl_3 + F = CCl_3 + HF$	1.02e13	0.0	4.56	Louis and Sawerysyn, 1998
$CH_3Cl + CF_3 = CH_2Cl + CHF_3$	2.63e11	0.0	41.71	Olleta and Lane, 2002
$CH_3Cl + CF_3 = CH_3 + CF_3Cl$	1.9e11	0.0	60.63	Olleta and Lane, 2002

$\text{CH}_2\text{Cl}_2 + \text{CF}_3 = \text{CHCl}_2 + \text{CHF}_3$	8.51e10	0.0	27.41	Olleta and Lane, 2002
$\text{CH}_2\text{Cl}_2 + \text{CF}_3 = \text{CH}_2\text{Cl} + \text{CF}_3\text{Cl}$	7.94e10	0.0	53.72	Olleta and Lane, 2002
$\text{CHCl}_3 + \text{CF}_3 = \text{CCl}_3 + \text{CHF}_3$	7.41e10	0.0	27.82	Olleta and Lane, 2002
$\text{CH}_3\text{F} + \text{Cl} = \text{CH}_2\text{F} + \text{HCl}$	1.02e13	0.0	9.67	Atkinson et al., 2001
$\text{CH}_2\text{F}_2 + \text{Cl} = \text{CHF}_2 + \text{HCl}$	9.03e12	0.0	13.14	Atkinson et al., 2001
$\text{CHF}_3 + \text{Cl} = \text{CF}_3 + \text{HCl}$	5.e12	0.0	41.84	est
$\text{CH}_3\text{F} + \text{CCl}_3 = \text{CH}_2\text{F} + \text{CHCl}_3$	5.e11	0.0	58.58	est
$\text{CH}_2\text{F}_2 + \text{CCl}_3 = \text{CHF}_2 + \text{CHCl}_3$	5.e11	0.0	60.67	est
$\text{CF}_2\text{Cl} + \text{O} = \text{CF}_2 + \text{ClO}$	1.8e13	0.0	0.	Wu and Carr, 1992
$\text{CF}_2 + \text{ClO} = \text{Cl} + \text{CF}_2\text{:O}$	4.e12	0.0	0.	Wu and Carr, 1992
$\text{CF:O} + \text{Cl} + \text{M} = \text{CFClO} + \text{M}$	1.e16	0.0	0.	est
$\text{CClO} + \text{F} + \text{M} = \text{CFClO} + \text{M}$	1.e16	0.0	0.	est
$\text{CF:O} + \text{Cl}_2 = \text{CFClO} + \text{Cl}$	3.e12	0.0	20.92	est
$\text{CFClO} + \text{H} = \text{CF:O} + \text{HCl}$	3.e12	0.0	37.66	est
$\text{CFClO} + \text{CF}_3 = \text{CF:O} + \text{CF}_3\text{Cl}$	2.e12	0.0	46.02	est
$\text{CFClO} + \text{O} = \text{CF:O} + \text{ClO}$	3.e12	0.0	83.68	est
$\text{CF:O} + \text{HOCl} = \text{OH} + \text{CFClO}$	2.e12	0.0	29.29	est
$\text{CClO} + \text{CF:O} = \text{CFClO} + \text{CO}$	3.e12	0.0	8.37	est
$\text{CFClO} = \text{CF:O} + \text{Cl}$	3.e14	0.0	347.27	Francisco and Li, 1989
$\text{CFCl}_2 + \text{O} = \text{CFClO} + \text{Cl}$	1.5e13	0.0	0.	est
$\text{CFCl}_2 + \text{OH} = \text{COCl}_2 + \text{HF}$	7.0e12	0.0	0.	est
$\text{CFCl}_2 + \text{H} = \text{CCL}_2 + \text{HF}$	1.e13	0.0	16.74	est
$\text{CFCl}_2 + \text{HCO} = \text{CO} + \text{CHFCl}_2$	1.5e13	0.0	0.	est
$\text{CF}_2\text{Cl} + \text{H} = \text{CF}_2 + \text{HCl}$	2.e13	0.0	4.18	est
$\text{CFCl}_2 + \text{CH}_3 = \text{CH}_3\text{F} + \text{CCL}_2$	3.e12	0.0	50.21	est
$\text{CF}_2\text{Cl} + \text{CH}_2 = \text{CH}_3\text{Cl} + \text{CF}_2$	3.e12	0.0	20.92	est
$\text{HCO} + \text{Cl} = \text{CO} + \text{HCl}$	1.7e14	0.0	0.	Br
$\text{C}_2\text{H}_5\text{OH} + \text{Cl} = \text{CH}_3\text{CHOH} + \text{HCl}$	6.1e13	0.0	0.	Seakins et al., 2004

(Continued)

Table 2 (Continued).

Reaction	A	n	E	Reference
$C_2H_5OH + F = CH_3CH_2O + HF$	3.8e13	0.0	0.	Khatoon et al., 1989
$C_2H_5OH + F = CH_3CHOH + HF$	1.5e13	0.0	0.	Khatoon et al., 1989
$C_2H_5OH + F = CH_2CH_2OH + HF$	2.3e13	0.0	0.	Khatoon et al., 1989
$C_2H_5OH + CF_3 = CH_3CHOH + CHF_3$	4.e11	0.0	40.58	est
$C_3H_8 + Cl = nC_3H_7 + HCl$	6.75e13	0.0	1.76	Tschuikow-Roux et al., 1985
$C_3H_8 + Cl = iC_3H_7 + HCl$	4.9e13	0.0	0.71	Tschuikow-Roux et al., 1985
$C_3H_8 + F = nC_3H_7 + HF$	3.5e13	0.0	0.	Fettis et al., 1960
$C_3H_8 + F = iC_3H_7 + HF$	4.1e13	0.0	0.	Fettis et al., 1960
$C_3H_8 + CF_3-CF_2 = nC_3H_7 + CF_3-CHF_2$	3.9e11	0.0	32.64	Whytock et al., 1972
$C_3H_8 + CF_3-CF_2 = iC_3H_7 + CF_3-CHF_2$	3.3e11	0.0	25.52	Whytock et al., 1972
$C_3H_8 + CF_3 = nC_3H_7 + CHF_3$	5.4e11	0.0	35.73	Arican et al., 1973
$C_3H_8 + CF_3 = iC_3H_7 + CHF_3$	1.8e11	0.0	27.28	Arican et al., 1973
$HCl + F = HF + Cl$	2.51e13	0.0	1.46	Wagner et al., 1976
$HOCl + F = FCl + OH$	7.2e12	0.0	0.	Vogt and Schindler, 1993
$F + Cl_2 = FCl + Cl$	5.5e14	0.0	5.86	Warmatz et al., 1971
$CF_3Cl + F = CF_3 + FCl$	3.15e13	0.0	87.32	Foon and Tait, 1972b,(x0.5)
$CF_2Cl_2 + F = CF_2Cl + FCl$	1.58e13	0.0	69.87	Foon and Tait, 1972b
$CFCl_3 + F = CFCl_2 + FCl$	2.88e12	0.0	54.31	Foon and Tait, 1972a
$CCL_4 + F = CCL_3 + FCl$	1.0E13	0.0	42.63	Foon and Tait, 1972b
$FCl + H = HF + Cl$	6.9e12	0.0	0.	Bykhalo et al., 1994
$FCl + H = HCl + F$	1.7e13	0.0	0.	Bykhalo et al., 1994
$FCl + M = F + Cl + M$	3.0e14	0.0	240.58	Blauer et al., 1971
$FCl + O = F + ClO$	5.e11	0.0	37.66	est

*Rate constants were provided in the form $AT^n \exp(-E/RT)$, (mole,cm,kJ,s); est – Estimate or taken by analogy. Additionally included are the reactions of propane and ethanol (components of FAA aerosol can test mixture) with F- and Cl-containing radicals.

Overall the block of reactions includes 120 reactions with fluorine- and chlorine-containing species (Table 2). The Sandia Chemkin suite of programs is used to model 1-D premixed laminar flames and to calculate the adiabatic combustion temperatures (Kee et al., 1986, 1989, 1991; Sandia, 1988). The present model is expected to be applicable to hydrocarbon/air combustion systems with added HCFC agents, in a temperature range of 1100–2300 K.

Although CF_3CHCl_2 is the molecule of main interest in the present work, to our knowledge there are no available data on the effect of CF_3CHCl_2 on burning velocity, ignition delay, or flame structure. Hence, to validate the kinetic model of combined fluorine- and chlorine-containing species, the experimentally determined effects of CF_3Cl , CF_2Cl_2 , and CFCl_3 on burning velocity were compared with simulations. Figures 1a–1c show the calculated and experimental burning velocities of $\text{CO}/\text{H}_2/\text{Ar}/\text{O}_2$ flames with added CF_3Cl , CF_2Cl_2 , and CFCl_3 (DaCruz et al., 1988). These calculations employ the kinetic model of Dryer and co-workers (Li et al., 2007), which was developed for modeling of combustion of $\text{CO}/\text{CH}_2\text{O}/\text{CH}_3\text{OH}$ mixtures, since it provides better agreement with experimental data on the burning velocities for the system without inhibitors than does the kinetic model of Wang et al. (2007). The difference in burning velocities between the two models (for the present $\text{CO}/\text{H}_2/\text{Ar}/\text{O}_2$ flames) is about 10–15%. Figures 1a–1c (solid lines) show that the present model provides reasonable agreement with the experimental data on burning velocity. In Figure 1c, the burning velocity reduction in the absence of the rate adjustments for the reaction $\text{CF}_3\text{Cl} + \text{H} = \text{CF}_3 + \text{HCl}$ is shown by the dashed line for CF_3Cl addition (the rate of this reaction has no effect for CFCl_3 or CF_3Cl addition). It should be noted that the present kinetic model should be considered as a starting point for further development and refinement. Numerous changes to both the rates and the reactions incorporated may be made once a variety of experimental and theoretical data are available for testing the mechanism.

RESULTS AND DISCUSSION

Burning Velocity Dependence on CF_3CHCl_2 Concentration

The dependence of burning velocity on inhibitor concentration is often used for estimation of its inhibition effectiveness and for inhibition mechanism studies. Figure 2 shows the calculated burning velocity of methane/air flames with CF_3CHCl_2 addition. For comparison, results for CF_3Br and $\text{C}_2\text{F}_5\text{H}$ are also included. CF_3CHCl_2 is less effective than CF_3Br , but more effective than $\text{C}_2\text{F}_5\text{H}$. As with most flame inhibitors, the marginal reduction in burning velocity decreases as the volume fraction of agent increases (Noto et al., 1998). In the absence of experimental burning velocity data with added CF_3CHCl_2 , we can compare the numerical predictions of Figure 2 with existing flame extinction data as follows: a burning velocity of 5 cm/s has been correlated (Egerton and Thabet, 1952) with flammability limits measured in typical tests, and this criterion has been used by others to provide an estimate of a flame extinction value from calculated premixed burning velocities. (For example, Westbrook (1983) used this criterion with calculated premixed CH_4 -, CH_3OH -, and C_2H_4 -air flames with added HCl , CH_3Cl , and $\text{C}_2\text{H}_5\text{Cl}$.) In the present work, the 5 cm/s criterion for a stoichiometric methane/air flame corresponds to volume fractions of 0.061, 0.067, and 0.031, for CF_3CHCl_2 , $\text{C}_2\text{F}_5\text{H}$, and CF_3Br . For comparison, the minimum extinction concentration (MEC) in coflow diffusion flames, is ≈ 0.075 , 0.094, and 0.029, respectively, or 24%, 42%, and –10% higher (cup-burner configuration with

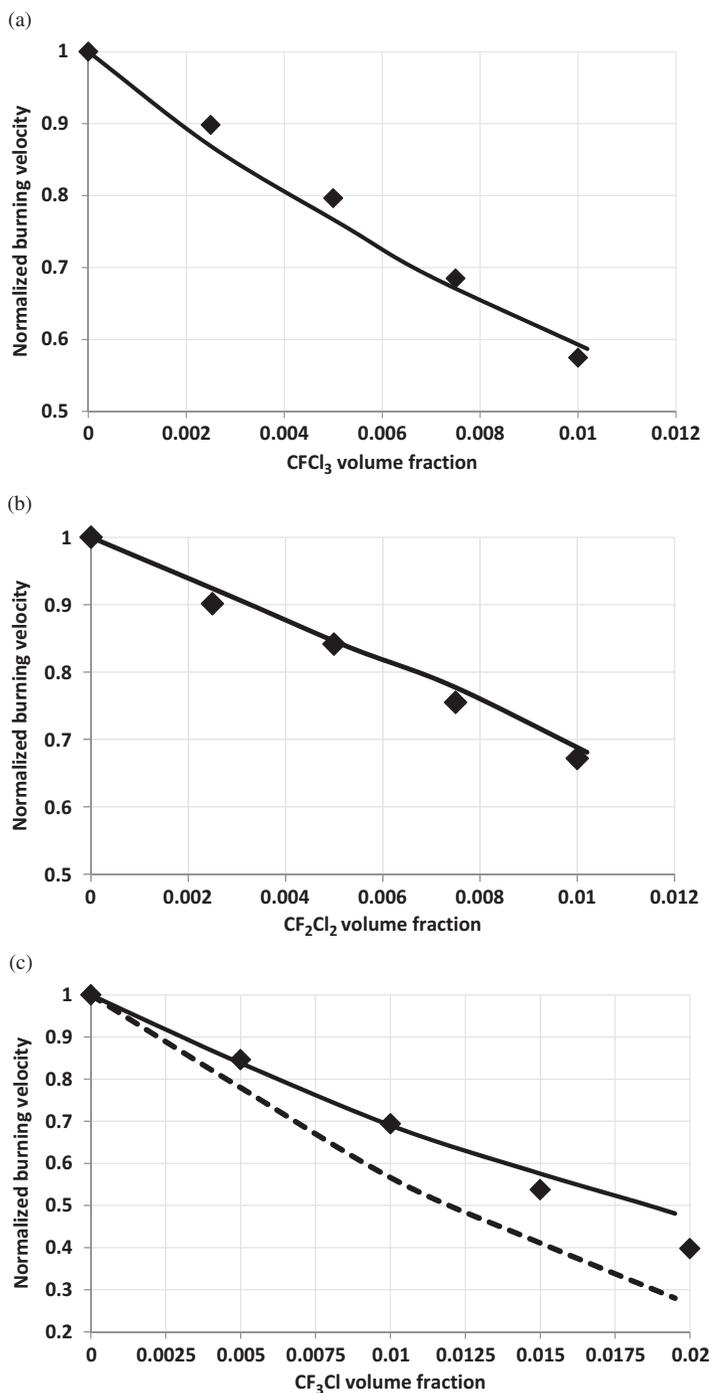


Figure 1 Burning velocity of CO/H₂/O₂/Ar mixtures (1 bar, 298 K, $\alpha=X_{Ar}=0.5$, $\phi=(CO+H_2)/2O_2=1$, $\beta=H_2/(CO+H_2)=0.05$), with added (a) CFCl₃, (b) CF₂Cl₂, or (c) CF₃Cl; symbols: experimental data (DaCruz et al., 1988); lines: modeling result (dashed line: unmodified rate constant for CF₃Cl+H=CF₃+HCl; solid line: pre-exponential factor lowered by a factor of five). In the absence of additive, the calculated burning velocity is 58.1 cm/s, while the experimental values (DaCruz et al., 1988) are (a) 60.9 cm/s, (b) 64.9 cm/s, and (c) 63.1 cm/s.

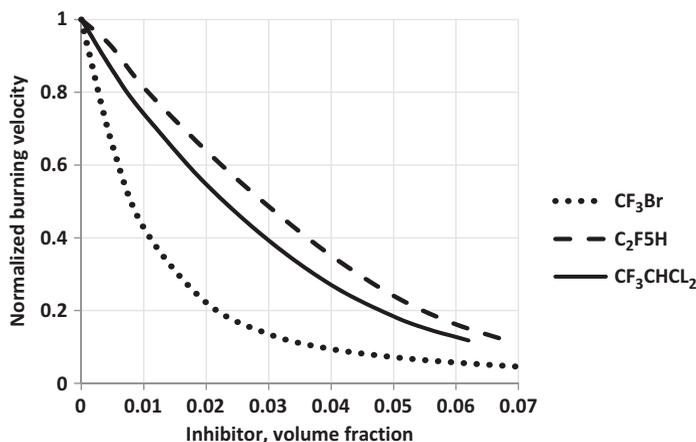


Figure 2 Normalized burning velocity of stoichiometric methane/air mixture (1 bar, 298 K) with added CF_3CHCl_2 , CF_3Br , or $\text{C}_2\text{F}_5\text{H}$ (calculated burning without additive is 39.7 cm/s; volume fraction of additive is based on all reactants).

heptane fuel and agent added to the air; Kim, 2002; Moore et al., 1996). Additionally, the MEC of cup-burner flames has recently been numerically calculated for these agents with the fuel of the FAA Aerosol Can Test (alcohol, propane, water) (Takahashi et al., 2013). The predicted MEC was about 25% lower for this fuel than the reported heptane/air cup-burner values, for addition of either CF_3CHCl_2 or CF_3Br . While the above comparisons indicate reasonable performance of the kinetic mechanism for CF_3CHCl_2 , clearly, additional data (e.g., burning velocity, flame structure, or flow reactor data) for combustion systems inhibited by CF_3CHCl_2 would be most useful for refining and validating the mechanism.

Mechanism of Flame Inhibition

The flame structure of a methane flame with CF_3CHCl_2 added at a volume fraction of 1.1% is shown in Figure 3. Consumption of CF_3CHCl_2 occurs in parallel to the consumption of methane, and most of the agent is consumed prior to the point of maximum rate of heat release in flame. The main chlorine-containing species in the reaction zone (and downstream) are chlorine atom and hydrogen chloride. Hydrogen chloride experiences a slight intermediate maximum in the reaction zone, which is related to the consumption of methane and CF_3CHCl_2 . Thus sources of additional formation of HCl disappear, and its concentration starts to be mostly determined by the equilibrium relationship between Cl atom and HCl, and temperature. The chlorine atom concentration corresponds approximately to those of the radical pool species H, OH, and O in the flame zone, while the concentration of the CF_3 radical is more than an order of magnitude less.

Reaction pathways for CF_3CHCl_2 consumption in the flame zone are presented in Figure 4a, which shows routes to formation of CF_3 , CF_2 , CFO , CF , HCl , and Cl , which are the main species participating in the inhibition reactions. Figure 4b shows the consumption routes of the CF_3 , CF_2 , CFO , and CF species down to the combustion product HF. To simplify the presentation of reaction pathways, the consumption of C_2F_3 is not presented on Figure 4b (its formation represents about 8% of the destruction of HCFC-123). About 74%

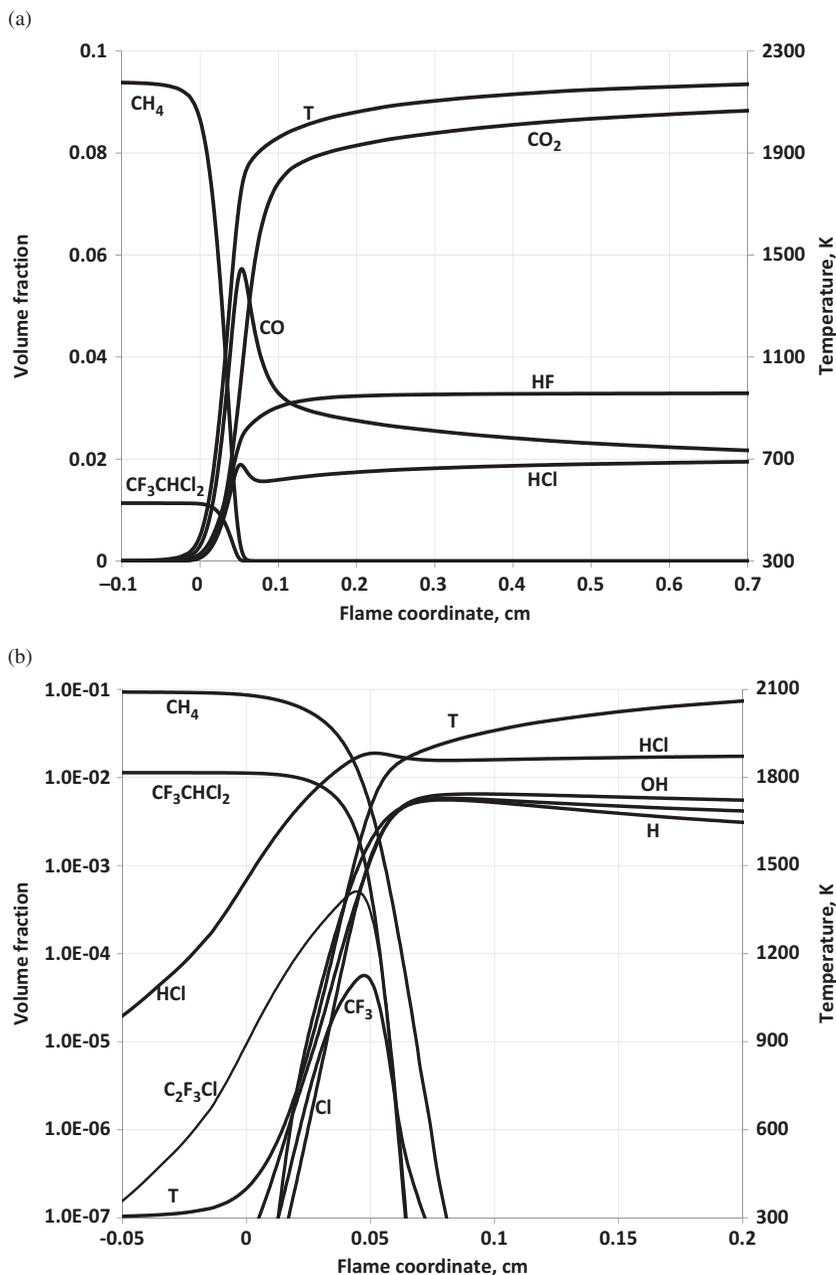


Figure 3 Structure of methane/air stoichiometric flame (1 bar, 298 K) with CF_3CHCl_2 added at a volume fraction (in the fuel/air mixture) of 1.12%.

of the CF_3CHCl_2 is consumed in decomposition reactions ($\text{CF}_3\text{CHCl}_2 = \text{C}_2\text{F}_3\text{Cl} + \text{HCl}$ and $\text{CF}_3\text{CHCl}_2 = \text{CF}_3 + \text{CHCl}_2$), and 23% in the reactions with radicals (H , OH , O , Cl) to form $\text{C}_2\text{F}_3\text{Cl}$ (of course, the distribution between different consumption routes is influenced by various assumptions in the reaction model). The decomposition product $\text{C}_2\text{F}_3\text{Cl}$

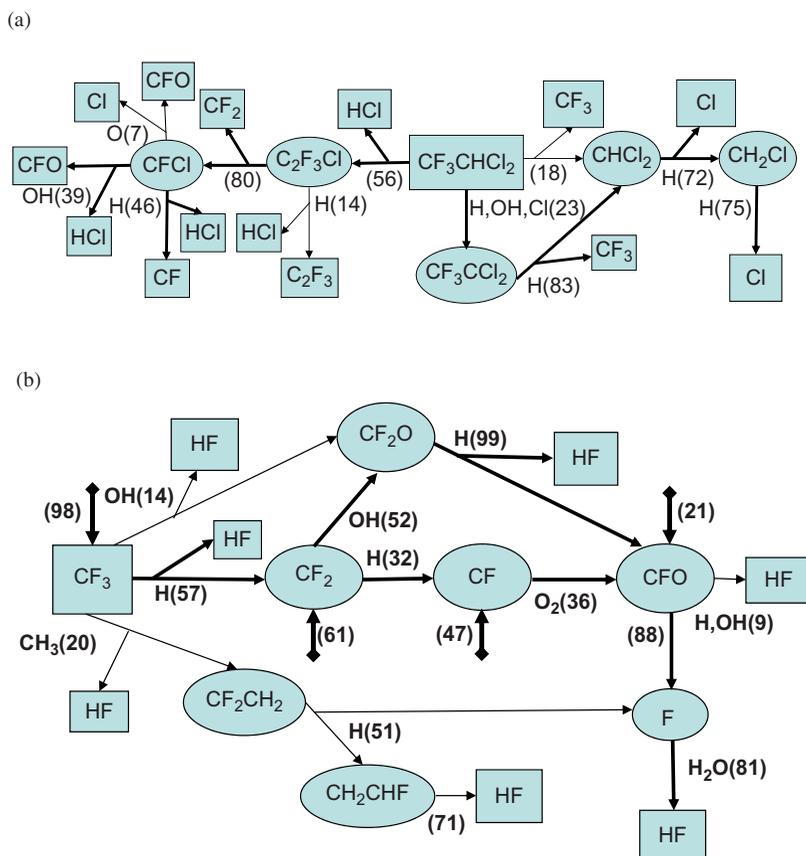
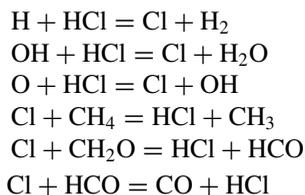


Figure 4 The main decomposition pathways of (a) CF_3CHCl_2 and (b) fluorinated species in the flame of Figure 3 (integrated for the position of maximum overall reaction rate, corresponding to a temperature of 1250 K to 1850 K). Arrows connect the reactants and products of a reaction, while the species next to the arrow is the reaction partner. The number next to the reaction partner is the fraction (in %) of the overall consumption rate of the first reactant in that reaction. The main reaction path is shown by heavier arrows (initial reactants and the products are shown in squares; intermediate species are shown in ovals).

also primarily undergoes thermal decomposition to form CF_2 and CFCI . The product of radical attack on the CF_3CHCl_2 , CF_3CCl_2 , is consumed mostly via the reaction with hydrogen atom. Further reactions of intermediate chlorine-containing species eventually lead to formation of CF_3 , CF_2 , CFO , Cl , and HCl .

Once Cl and HCl are formed, they participate in the reaction cycle:



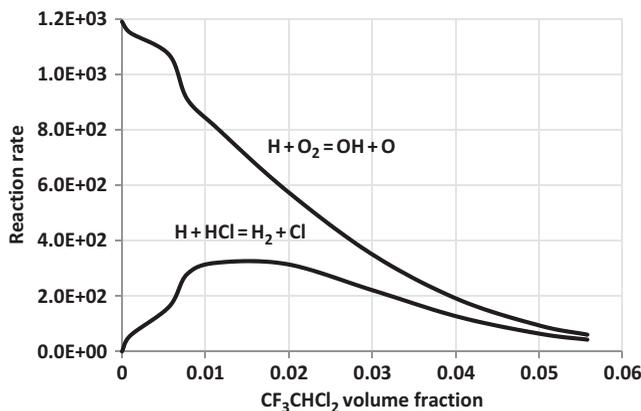


Figure 5 Maximum rate of chain-branching reaction, $\text{H} + \text{O}_2 = \text{OH} + \text{O}$, as compared to the maximum rate of inhibiting reaction $\text{H} + \text{HCl} = \text{H}_2 + \text{Cl}$, as a function of the CF_3CHCl_2 volume fraction in a stoichiometric methane/air flame (1 bar, 298 K); reaction rate is presented in (volume fraction)/s.

The net effect of this HCl-Cl cycling sequence is to compete with the chain-branching reaction ($\text{H} + \text{O}_2 = \text{OH} + \text{O}$) by providing parallel channels for consumption of H and other radicals. Thus, there are two mechanisms of radical reduction: decomposition routes of CF_3CHCl_2 (and the intermediate species), which require radicals, and the cycling sequence of reactions of Cl and HCl species. Figure 5 shows, for a stoichiometric methane/air flame with added CF_3CHCl_2 , the maximum rate of the chain-branching reaction as compared to the maximum rate of the reaction $\text{H} + \text{HCl} = \text{H}_2 + \text{Cl}$. For CF_3CHCl_2 addition up to a volume fraction 1.5%, the rate of $\text{H} + \text{HCl}$ reaction rate increases while the $\text{H} + \text{O}_2$ reaction rate decreases. Above 1.5% loading, the rate of the reaction $\text{H} + \text{HCl} = \text{H}_2 + \text{Cl}$ decreases because H atom concentration and temperature are becoming lower.

The main reactions responsible for the production and consumption of chlorine atoms are shown in Figure 6a, while Figure 6b shows the termolecular chain termination reactions involving Cl, together with the contribution of the disproportionation reaction $\text{Cl} + \text{HO}_2 = \text{HCl} + \text{O}_2$. The termolecular recombination reactions are about 60–70 times less important than the $\text{Cl} + \text{CH}_4 = \text{HCl} + \text{CH}_3$ reaction, and are not a significant sink for Cl radicals. Note that in the post-flame zone, the recombination reactions, $\text{H} + \text{Cl} + \text{M} = \text{HCl} + \text{M}$ and $\text{Cl} + \text{Cl} + \text{M} = \text{Cl}_2 + \text{M}$, are becoming dominant in the consumption of chlorine atom.

The recycling reactions involving HCl listed above allow CF_3CHCl_2 to be more effective than C_2HF_5 , but less effective than CF_3Br . For example, estimation of a regeneration factor (average number of cycles of the above reaction sequence per molecule of HCl) (Noto et al., 1998) leads to the value of 2.3 for CF_3CHCl_2 , as compared to 7 for CF_3Br (Noto et al., 1998) (integration was performed from the beginning of flame zone to a temperature of approximately 2000 K). In the case of C_2HF_5 (as well as for the fluorinated species formed from CF_3CHCl_2 , e.g., CF_3 , CF_2 , FCO), the intermediates react with (i.e., trap) H atoms to form the stable species HF (and thereby reduce H concentration and chain branching), but do not enter into recycling reaction sequences.

The difference between inhibiting reactions of bromine- (iodine) and chlorine-containing species can be inferred. The reaction rate of the hydrogen atom with HBr is faster than with HCl (due to the stronger bond of HCl). On the other hand, regeneration reactions of the Cl atom to form HCl are much faster than those for HBr regeneration

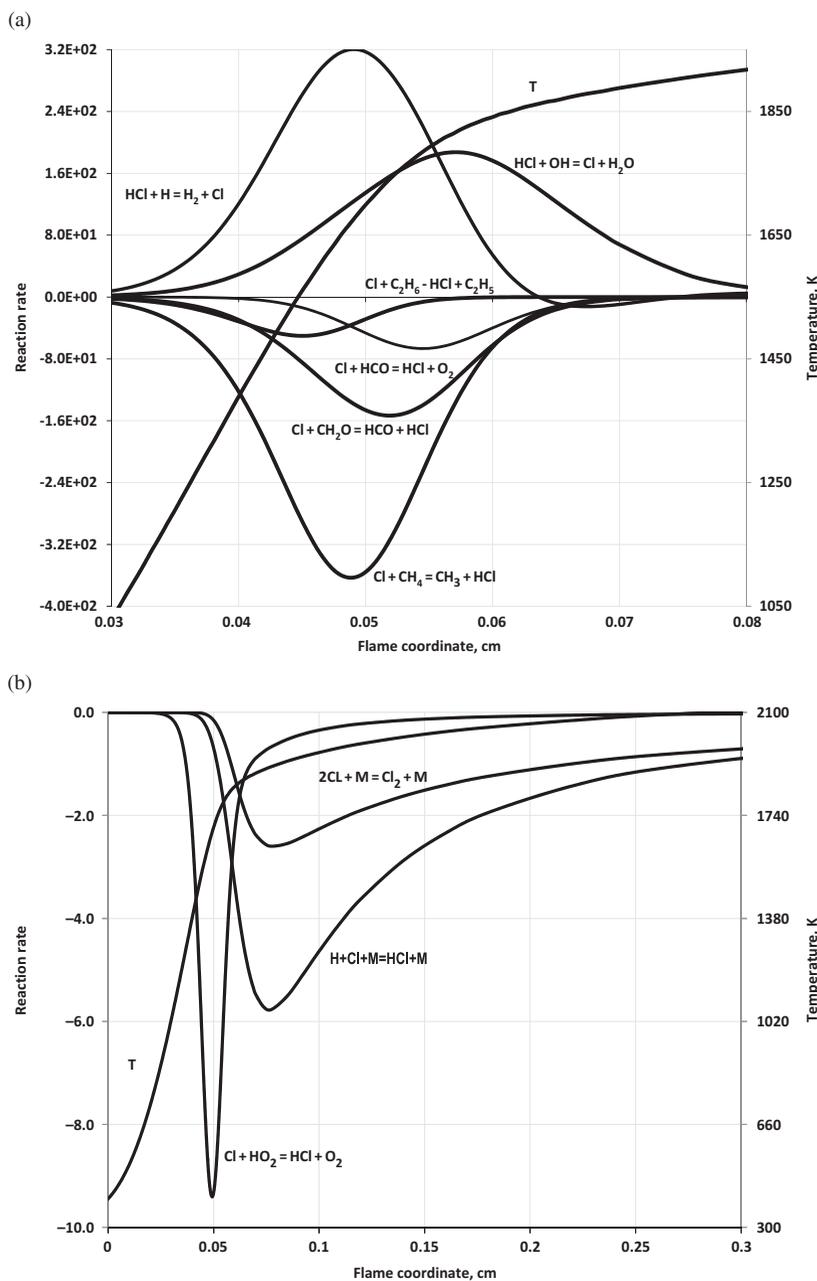


Figure 6 Rates of the (a) main formation and consumption reactions of chlorine atom, and (b) termination reactions for Cl consumption, in a stoichiometric air/methane flame (1 bar, 298 K) with CF_3CHCl_2 added at a volume fraction of 1.12% (reaction rate is in (volume fraction)/s).

(since bromine and iodine atoms are relatively unreactive in comparison to the chlorine atom). For example the activation energy of the chlorine atom reaction with CH_4 is about 10 kJ/mole in contrast to that for bromine atom (75 kJ/mol) and iodine atom

(142 kJ/mol). Since the reactions of hydrocarbons with halogen atoms are much faster for Cl (HCl formation) than for reaction with Br or I (HBr or HI formation), the recombination steps ($\text{Cl} + \text{H} + \text{M} = \text{HCl} + \text{M}$, $\text{Cl} + \text{Cl} + \text{M} = \text{Cl}_2 + \text{M}$) are relatively less important (compared to those of Br and I) in the cycling sequence (Figure 6). Since the recombination steps are termination steps in the inhibition reaction cycle, they have a large effect on the radical recombination efficiency of the overall cycle. Note that for chlorine inhibition of ethylene combustion in a well-stirred reactor, Casias and McKinnon (1996) also found that the recombination steps make only a small contribution to the inhibition effect.

Inhibition Effectiveness of Chlorinated Agents

To estimate the effectiveness of HCFC agents considered as halon replacements in the literature (Table 3), but for which experimental data do not yet exist, the different chlorinated compounds can be compared using an empirical scaling procedure (Fristrom and Van Tiggelen, 1978; Noto et al., 1998). An inhibition parameter, Φ , is defined as

$$\Phi = \{(S_0 - S_u) / S_0\} (C_{O_2} / C_{in}) \quad (1)$$

in which C_{O_2} is the initial concentration of oxygen in mixture, C_{in} is the inhibitor concentration (CF_3CHCl_2), and S_0 and S_u are the burning velocities without and with inhibitor, respectively. Hence, Φ represents the normalized reduction in the burning velocity at a given inhibitor loading. As presented by Fristrom and Van Tiggelen (1978), the value of Φ can be estimated for a new flame inhibitor based on indices (ϕ_i) for constituent groups and atoms in the HCFC molecule: $\Phi = \sum n_i \phi_i$, where n_i is the number of the corresponding atoms or groups constituting the molecule. The inhibition index of the Cl atom can be estimated from the calculated burning velocity data for CF_3CHCl_2 addition, which yields a value of 1.4 (using the modified index definition of Noto et al., 1998). This is relatively

Table 3 HCFC compounds considered as halon replacements for fire suppression

Agent name	Formula	Inhibition parameter
HCFC-22; Chlorodifluoromethane	CHF_2Cl	5.2
HCFC-124; FE-241; 1-Chloro-1,2,2,2-tetrafluoroethane	CF_3CHFCl	8.2
HCFC-123; R-123; 1,1,-Dichloro-2,2,2-trifluoroethane	CF_3CHCl_2	9.1
HCFC Blend A (blend of HCFC-123, HCFC-22, HCFC-124, and d-limonene)		
HCFC Blend B (blend of HCFC-123, CF_4 , and Ar); Halotron I		9.0
HCFC Blend C (blend of HCFC-123, HCFC-124, HFC-134a)		
HCFC Blend D		
HCFC Blend E (blend of HCFC-123, $\text{C}_2\text{F}_5\text{H}$, and $\text{C}_{10}\text{H}_{16}$)		
HCFC-123a; 1,2-Dichloro-1,1,3-trifluoroethane	$\text{CF}_2\text{ClCHFCI}$	9.1
HCFC-124a; 1-Chloro-1,1,2,2-tetrafluoroethane	$\text{CF}_2\text{ClCF}_2\text{H}$	8.2
HCFC-132; 1,2-Dichloro-1,2-difluoroethane	CHFClCHFCI	8.3
HCFC-225ca; 1,1-Dichloro-2,2,3,3,3-pentafluoropropane	$\text{CF}_3\text{CF}_2\text{CHCl}_2$	12.1
HCFC-225cb; 1,3-Dichloro-1,1,2,2,3-pentafluoropropane	$\text{CF}_2\text{ClCF}_2\text{CHFCl}$	12.1
HCFC-235cb; 1-Chloro-2,2,3,3,3-pentafluoropropane	$\text{CF}_3\text{CF}_2\text{CH}_2\text{Cl}$	10.4
HCFC-226cb; 1-Chloro-1,1,2,2,3,3-hexafluoropropane	$\text{CF}_2\text{ClCF}_2\text{CF}_2\text{H}$	11.15

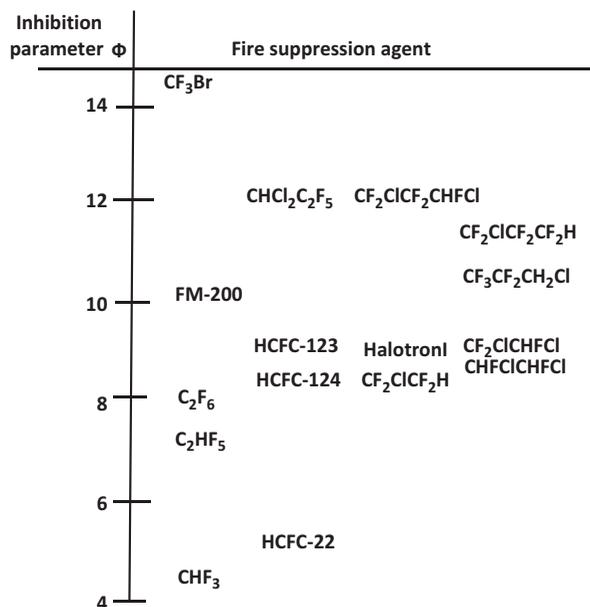


Figure 7 Flame inhibition effectiveness of HCFC compounds that have been considered as halon replacements (Table 1).

close to the inhibition index of 1.9 as determined by Fristrom and Van Tiggelen (1978) from experimental results for different compounds at similar conditions.

Figure 7 illustrates the approximate relative ranking of the HCFC compounds presented in Table 3 with the use of inhibition indices from (Fristrom and Van Tiggelen, 1978). For comparison, the inhibition parameters of C_3HF_7 , C_2F_6 , $\text{C}_2\text{F}_5\text{H}$, CHF_3 , and CF_3Br are also included. While exponential-type indices (Noto et al., 1998) may also be used for comparison, we used the linear indices (Fristrom and Van Tiggelen, 1978) since only these were available for Cl-containing compounds. As discussed by Fristrom and Van Tiggelen (1978), replacing fluorine atoms by chlorine atoms makes an inhibitor more effective. Note that the inhibition indices do depend upon the fuel and the equivalence ratio, but have relatively small variations for different hydrocarbon fuels. The ranking using the parameter Φ typically is based on low agent loadings, where the saturation effect is small. At the suppression concentration, the differences in inhibition effectiveness might be reduced.

CONCLUSIONS

To study the hydrocarbon/air flame inhibition by HCFC-123 (CF_3CHCl_2), a new kinetic model has been developed for mixed F- and Cl-containing species, and the model has been used to understand the premixed laminar methane-air flame inhibition by CF_3CHCl_2 . The following results are obtained in this work:

1. A kinetic model for flame inhibition by CF_3CHCl_2 is suggested. A block of reactions with Cl-F-containing species and describing the interaction between fluorine- and chlorine sub-models was added to the previously developed kinetic model (Linteris et al., 2012a, 2012b) for hydrocarbon/air flames inhibited by fluorinated hydrocarbons with

- added reactions of C₁–C₂-chlorine-containing species from (Leylegian et al., 1998a, 1998b).
2. The kinetic model is tested against experimental burning velocity data (DaCruz et al., 1988) for a CO/H₂/O₂/Ar flame with added Cl-F-containing inhibitors (CF₃Cl, CF₂Cl₂, and CFCI₃). The modeling results agree reasonably well with the experimental data.
 3. The agent CF₃CHCl₂ is more effective than C₂HF₅, but less effective than CF₃Br, in reducing the calculated burning velocity of a methane/air flame.
 4. The reaction pathways of CF₃CHCl₂ in a simulated methane/air flame are determined. The main radical scavenging reactions in a flame zone are due to the chlorine-inhibition cycle: H+HCl=H₂+Cl, OH+HCl=H₂O+Cl, Cl+CH₄=CH₃+HCl, Cl+CH₂O=HCl+HCO, and Cl+HCO=HCl+CO. This cycle, together with reactions of radicals with the inhibitor itself, competes with the chain-branching reaction H+O₂=OH+O and decreases the overall reaction rate and burning velocity. For CF₃CHCl₂ in a stoichiometric methane/air flame, the estimated regeneration factor, showing the average number of cycles of the inhibition reactions per agent molecule, is 2.3 (evaluated at an agent volume fraction of 1.1%). Moreover, the contribution of recombination reactions H+Cl+M and Cl+Cl+M to the inhibition effect of the compound is small in comparison with the chain propagation steps of inhibitor species.
 5. The flame inhibition effectiveness (based on burning velocity reduction) of several HCFC compounds, which have been proposed as possible halon replacements, is estimated, and is found to be slightly higher than for the corresponding HFC agents.

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