Combustion properties of halogenated fire suppressants ☆

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ABSTRACT

Previous experimental studies have shown that some halogenated fire suppressant agents added to hydrocarbon–air systems can enhance the combustion. For example, their addition to the air stream can widen the flammability limits of lean mixtures, and increase the maximum explosion pressure for constant volume combustion. To explore the experimentally observed combustion enhancement, the combustion properties of pure mixtures of fire suppressants and air/oxygen were studied. Adiabatic combustion temperatures, ignition delays and burning velocities were calculated for several typical fluorinated fire suppressant agents (CF_3H, C_2F_5H, C_3F_7H and $C_3F_7COC_2F_5$) in mixtures with air, and CF_3Br and CF_3I in air and oxygen. Calculated burning velocities are in the range 0.37–2.5 cm/s at initial temperature 400 K (stoichiometric air mixtures of CF_3H, C_2F_5H, C_3F_7H, $C_3F_7COC_2F_5$, 1 bar). The results show that the fluorinated agents possess sufficient energy to participate in combustion processes, and can support combustion with burning velocities which should be measurable (for some of the systems) at slightly elevated initial temperatures. Simulated ignition delays for C_3F_7H and $C_3F_7COC_2F_5$ are shorter than for propane for the analyzed range of temperature (1000–1500 K), and those for C_2F_5H/air mixtures are comparable with propane in a lower temperature range (1000–1250 K).

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1. Introduction

It has been observed that halogenated fire suppressant agents may enhance combustion in laboratory and in large scale experiments under certain conditions. Ohtani [1], Shebeko et al. [2], Azatyan et al. [3] and Kondo et al. [4] reported wider flammability limits with suppressant addition for fuel lean conditions. Gmurczyk and Grosshandler [5,6] observed increased pressure ratio and wave propagation rate for high speed turbulent flames in a detonation/deflagration tube with the addition of various halogenated hydrocarbons to ethylene– and propane–air mixtures. Hamins and Borthwick [7] found a slight promotion effect of C_3F_7H and C_2F_5H on the hot surface ignition of methane and propane. In diffusion flame experiments, Holmstedt et al. [8] and Katta et al. [9] measured larger total heat release with hydrofluorocarbon (HFC) addition to the fuel or air stream of co-flow diffusion flames. Takahashi et al. [10], using direct numerical simulation, have recently calculated a larger heat release with C_2F_5H addition to the air stream of cup-burner flames of methane. Ural [11], Azatyan

et al. [3] and Lisochkin and Poznyak [12] indicated that halogenated agents possess their own heat release in the combustion process. Thus it should be expected that the contribution of additional heat to the hydrocarbon combustion system might sometimes lead to unexpected behavior.

In more applied, large-scale experiments involving suppression of fires in aircraft, Blake et al. [13] found ignition and flame propagation in the smoke layer (containing vitiated air and C_2F_5H) above bulk fires (cardboard boxes) in an aircraft cargo bay. In the Federal Aviation Administration (FAA) aerosol can test (FAA-ACT), Reinhardt [14] measured higher over-pressures in a simulated aerosol can explosion in a pressure vessel (simulating an aircraft cargo bay), in the presence of several fire suppressants. With the agents C_2F_5H, $C_3F_7COC_2F_5$, or 2-bromo-3,3,3-trifluoropropene (2-BTP) added to the air stream at sub-inerting concentrations, the pressure rise in the chamber was several times higher than with no agent. The agent CF_3Br (Halon 1301) did not show this tendency. In follow-up work Linteris et al. [15,16] used thermodynamic calculations and stirred-reactor modeling with full kinetics to investigate the conditions of FAA-ACT. They demonstrated that at sub-inerting concentrations of agent, the overpressures were controlled by thermodynamics and by the mixing of the fuel with oxidizer. Furthermore, for C_2F_5H, the implied burning velocities of the consumed mixtures were estimated to be as low as 1.7 cm/s. Note that the "enhancement" of the combustion in the FAA-ACT by the suppressant refers to the magnitude of the total pressure rise, not the

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Table 1
Combustibility of fire suppression agents.

Agent	Combustibility	Reference
CF_3Br	Self-ignition temperature 695 °C	[19]
	Some evidence of combustibility (while fighting big fires)	[11]
$C_2F_4Br_2$	Self-ignition temperature (air) 657 °C	[19]
	Self-ignition temperature (oxygen) 460 °C	
	Burning velocity (oxygen) 1.5 cm/s	
	Flammability limits (oxygen) 28.5–52% volume fraction	
CF_3I	Combustible (33.5–61.5% volume fraction in air, 1 bar, E_{ign} = 41–217 J)	[12]
C_3F_7H	Ignitability, 30.6 bar (444 psig), 298 K	[11]
	Flammable,<30.6 bar (450) psig	
	Some evidence of combustibility (while fighting big fires)	
C_2F_5H	Some evidence of combustibility (while fighting big fires)	[11]
	Combustible (8 bar, air, E_{ign} = 2.2 kJ)	[18]
CF_3CHCl_2 (R-123)	Self-ignition temperature 770 °C	[20]
	Combustible in air under pressure (strong ignition sources)	

rate of pressure rise; hence, even mixtures with low flame speeds can contribute to the pressure rise.

Since the mixtures in the FAA-ACT appeared to release energy (and have enhanced overpressure) even under conditions of low calculated burning velocity [17], and since those conditions are much closer to flames of the suppressant with air (having very little hydrocarbon), it is of value to examine the combustion properties of pure suppressants with air. It has been noted [1,3,11,12,18] that several fire suppressant agents themselves sustain combustion under specific conditions (elevated temperatures and pressures, large scale fires, oxygen atmosphere), as listed in Table 1. For example, Ural [11] experimentally observed the combustion of C_3F_7H at an initial temperature 295 K and pressure of 30.6 bar (444 psig, 12.6% agent volume fraction in air, closed spherical vessel with a volume of 20 L). Lisochkin and Poznyak [12,18] reported ignition of C_2F_5H–air and CF_3I–air mixtures.

The goal of the present work is to investigate the combustion properties of typical halogenated flame inhibitors (CF_3H, C_2F_5H, C_3F_7H, $C_3F_7COC_2F_5$, CF_3Br and CF_3I) mixed with air or oxygen (but with no hydrocarbon fuel), and to analyze thermodynamic and kinetic restrictions on the combustion of these systems. The following results are presented below. First, the adiabatic combustion temperatures are calculated for stoichiometric mixtures of some typical fire suppressant agents with air. Second, the 1-D adiabatic steady laminar flame is calculated for stoichiometric mixtures of CF_3H (HFC-23), C_2F_5H (HFC-125), $C_3F_7COC_2F_5$ (Novec 1230), C_3F_7H (FM-200, HFC-227a, CF_3CFHCF_3) with air and, CF_3Br and CF_3I with oxygen. Finally the ignition delay is calculated for the agents in air.

The flames of these pure halogenated hydrocarbon–air systems are somewhat exotic, and their burning velocities are low. Nonetheless, recent analyses have shown that for systems in which the residence time is very long [14], exothermic reaction of mixtures even with low overall reaction rate (i.e., burning velocities) must be considered [16].

2. Modeling procedure

Kinetic models of combustion of fluorinated compounds (CF_3Br, CF_3I, CF_3H, C_2F_5H, C_3F_7H, $C_3F_7COC_2F_5$) were taken from previous works [15,21,22]. GRI-Mech 3.0 [23] was used as the hydrocarbon part of the kinetic models. The previous development of the kinetic models for fluorinated inhibitors [24] was conducted assuming their addition in relatively low concentrations to near-stoichiometric hydrocarbon–air flames. Hence, the models have limitations when used for modeling combustion of air with the agents present

Table 2
Additional reactions.

Reaction	A (cm, mole, s)	E (J, mole)
$CF_3COF + CF_3 = CF_3CO + CF_4$	2.e12	37,700
$CF_3COF + C_2F_5 = CF_3CO + C_2F_6$	3.e11	58,600
$C_2F_6 + C_2F_5 = CF_4 + C_2F_5$	3.e12	47,300
$CF_3CO + F = CF_3 + CFO$	3.e12	0.0
$CF_3CO + F = CF_4 + CO$	5.e12	0.0

at large concentrations. For example, preliminary burning velocity simulations, performed in this work, indicated that for the pure agents with air, the radical pool consists mainly of F, CF_3, CF_2, C_2F_5, O and OH, with concentrations of fluoro-containing radicals substantially higher than those of O and OH radicals, which are much higher than concentration of H atoms. Hence, additional reactions were added to the National Institute of Standards and Technology (NIST) HFC mechanism as discussed in [15]. For $C_3F_7COC_2F_5$ combustion, burning velocities simulations showed stabilization of C_2F_6 and CF_3COF in the flame zone. Additional reactions of fluoro-containing radicals (F, CF_3 and C_2F_5) with these species were added to the mechanism as listed in Table 2. Rate constants were estimated by analogy with similar reactions and by using correlation of activation energies with reaction enthalpy changes.

The Sandia Chemkin programs EQUIL, PREMIX [25], and SENKIN [26] together with their chemical kinetics [27] and transport [28] interpreters were used to calculate equilibrium, laminar burning velocity and ignition delay. The NIST graphical post-processor SenkPlot [29] was used for post-processing.
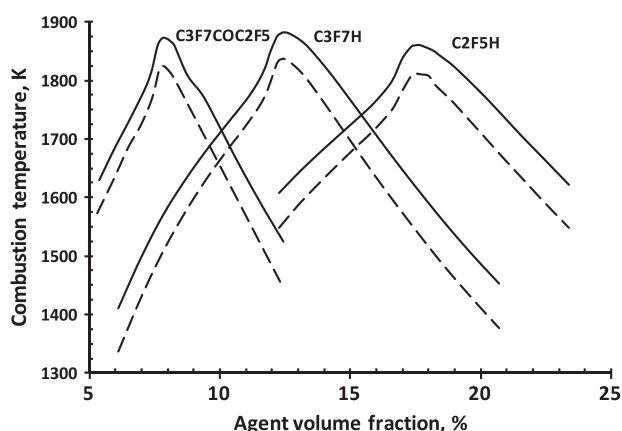
3. Results and discussion

3.1. Adiabatic combustion temperatures

Table 3 shows the calculated adiabatic combustion temperatures for stoichiometric mixtures of several fluorinated fire suppressants with air. The data are consistent with the results of Ural [11]. The halogenated agents have fuel-like properties, and when mixed with air might form combustible mixtures with heat release. Table 3 also includes results for stoichiometric mixtures of CF_3Br and CF_3I in oxygen atmospheres, at increased initial temperature and pressure (400 K and 3 bar). The calculated adiabatic temperatures are 1497 K and 1593 K. Earlier work [30–35] has shown that for hydrocarbon–air mixtures, the combustion temperature at the lean flammability limit is approximately constant at

Table 3
Adiabatic combustion temperatures of stoichiometric mixtures of fluorinated fire suppressants with air (1 bar, 300 K).

Fire suppressant	Stoichiometric concentration in air, % by volume	T (K)
C_2F_6	29.58	1381
C_3F_8	17.36	1552
C_4F_{10}	12.28	1743
CF_3H	29.57	1669
C_2F_5H	17.36	1809
C_3F_7H	12.28	1800
$C_3F_7COC_2F_5$	7.749	1823
CF_3Br	45.65	1248
CF_3Br, 1 bar, 400 K	45.65	1323
CF_3Br/O_2, 3 bar, 400 K	80 (oxygen atmosphere)	1497
CF_3I	45.65	1340
CF_3I, 1 bar, 400 K	45.65	1432
CF_3I/O_2, 3 bar, 400 K	80 (oxygen atmosphere)	1593

Table 4
Adiabatic burning velocities of fire suppressant/air stoichiometric mixtures (1 bar; heat losses were not considered).

Agent	Oxidizer	Initial temperature (K)	Burning velocity (cm/s)
CF_3H	Air	400	0.567
C_2F_5H	Air	400	1.56
C_3F_7H	Air	400	2.48
$C_3F_7COC_2F_5$	Air	400	0.367
CF_3I	Oxygen	500	1.33
CF_3Br (3 bar, maximum S_L at CF_3Br = 65% by vol.)	Oxygen	500	0.27

Fig. 1. Dependence of adiabatic combustion temperature on the agent concentration in the mixture with air (dashed line, 300 K; solid line, 400 K).

Fig. 2. Dependence of adiabatic burning velocity on C_3F_7H volume fraction in the mixture with air (1 bar, 400 K). Also included are burning velocities of stoichiometric air mixtures for $C_3F_7COC_2F_5$, C_2F_5H and CF_3H.

about 1500 K. Furthermore, for very low strain, well stabilized conditions (e.g., cup burner flames in microgravity), the temperature at flame extinguishment was calculated to be even lower, around 1250–1300 K [36]. Chen and Sohrab [33] estimated 1128 K as a limit temperature for lean counter-flow premixed methane/air flames. Thus, many of the stoichiometric mixtures listed in Table 3 could potentially support flames, depending upon the reaction kinetics, the stabilization, and the residence times.

Figure 1 shows the dependence of adiabatic combustion temperature on $C_3F_7COC_2F_5$, C_3F_7H and C_2F_5H concentrations in air at initial temperatures of 300 K and 400 K. Examination of the equilibrium species for the stoichiometric flames shows that CF_4, CF_2O, CO_2 and HF are the main products, depending on the equivalence ratio. It is of interest that combustion products contain rather large concentration of atomic F in the range between 0.1% and 1% by volume, while concentrations of O, OH and H are significantly smaller in comparison with concentration of F atom.
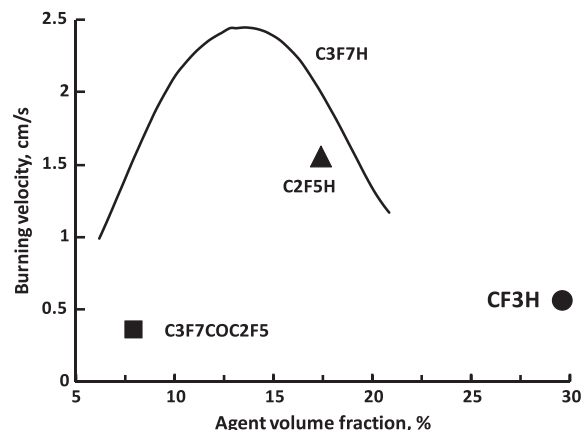
3.2. Burning velocities of premixed flames

The laminar burning velocity S_L was calculated for stoichiometric mixtures of the fire suppressants with air (Table 4, Fig. 2). Initial pressure was 1 bar, and the initial temperature was 400 K. Water vapor was present in the total mixture at a volume fraction of 0.001. The hydrofluorocarbons C_2F_5H and C_3F_7H had calculated burning velocities of about 1.6 cm/s and 2.5 cm/s, while those for CF_3H and $C_3F_7COC_2F_5$ were lower, around 0.5 cm/s. For C_3F_7H

which had the highest calculated burning velocity, solutions were also obtained over a range of stoichiometry, as indicated in Fig. 2. As with hydrocarbon–air flames, the maximum burning velocity of the C_3F_7H–air flames occurs in slightly rich mixtures. Since $C_3F_7COC_2F_5$ consists largely of a C_2F_5 fragment and C_3F_7 fragment, one might expect its behavior to be intermediate between C_2F_5H and C_3F_7H. As Fig. 2 shows, however, the burning velocity of $C_3F_7COC_2F_5$ is smaller than the average of burning velocities C_2F_5H and C_3F_7H. Apparently, the flame promotion effect of the hydrogen atoms is greater than that of the CO moiety. In addition, the calculated adiabatic burning velocities for stoichiometric mixtures of CF_3Br and CF_3I with oxygen are included in Table 4.

The flammability limits of fuel–air mixtures are known to be affected by the initial temperature and pressure, thus it is of interest to explore how they affect the burning velocity for the present agents. Figure 3 shows the effect of initial temperature on burning velocity of stoichiometric mixtures of air with $C_3F_7COC_2F_5$, C_2F_5H, and C_3F_7H. Increasing the initial temperature from 400 K to 500 K increases S_L by a factor of 3.84, 2.0, and 1.8, respectively. This is a much stronger temperature dependence than for hydrocarbons; for example, for CH_4–air flames, increasing T_0 from 400 K to 500 K increases S_L by a factor of about 1.4 [37,38]. Figure 4 shows the effect of initial pressure P_0 on the burning velocity. Increasing P_0 from 1 bar to 5 bar increases S_L by about 14% for C_3F_7H, whereas for $C_3F_7COC_2F_5$, it decreases S_L by about 42%. For C_2F_5H, increasing P_0 from 1 bar to 3 bar decreases S_L by about 14%. Hence, the effect of pressure on burning velocity depends on the agent and the magnitude of the effect is less than for a methane–air flame, for which increasing pressure from 1 bar to 5 bar decreases S_L by about 63% [38].

The calculated fluorocarbon/air flames correspond to a self-sustaining reaction proceeding with multiple zones of heat release
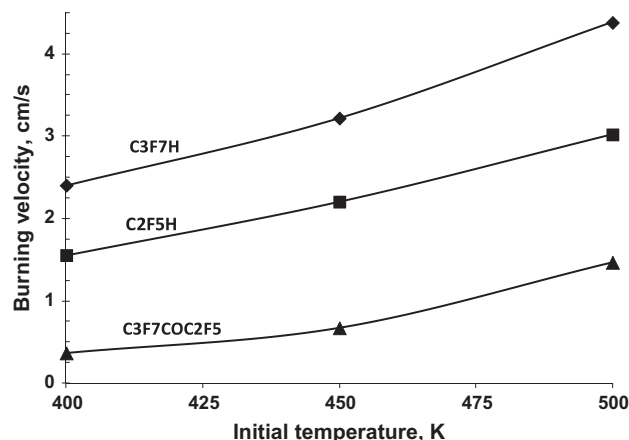
Fig. 3. Dependence of burning velocity on the initial temperature for stoichiometric air mixtures of C_2F_5H, C_3F_7H and $C_3F_7COC_2F_5$ (1 bar).
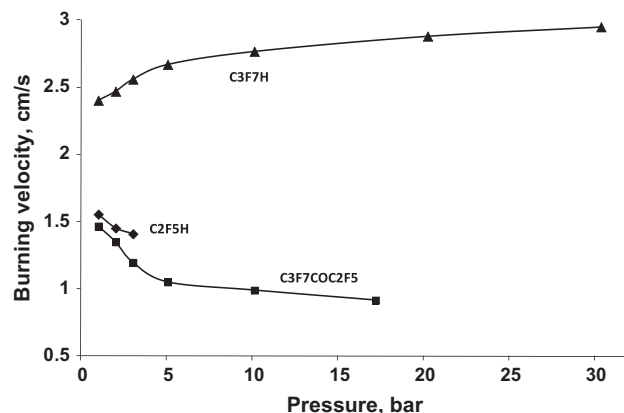

Fig. 4. Dependence of burning velocity on pressure for stoichiometric air mixtures of $C_3F_7COC_2F_5$ (500 K), C_3F_7H (400 K) and C_2F_5H (400 K).

(two for C_2F_5H and CF_3H, and three zones for $C_3F_7COC_2F_5$). It is of interest that two-stage combustion was observed for C_3F_7H/air mixtures by Ural [11]. Two pressure peaks were experimentally measured during combustion in a closed vessel at elevated pressures, with a rather large time interval between peaks. Figure 5 shows the flame structure of the C_2F_5H flame. As indicated in Fig. 5a for C_2F_5H, the first zone corresponds to the region with the main temperature increase and to the relatively fast oxidative decomposition of fluorinated agent, and CO formation. The second stage corresponds to relatively slow reaction of O_2 with CO, CF_4, and CF_2O, leading eventually to their flame equilibrium concentrations. The flame thickness for the low S_L flames of fluorinated compounds is large. The well-known correlation between flame thickness and burning velocity ($\delta \sim \lambda/(c_p \rho S_L)$, [39,40]) roughly corresponds for the level of calculated burning velocities (≈ 0.5–2.5 cm/s) to the thickness of the first stage, where most of the heat release occurs. It is of interest to note, that such large zones upon flame stabilization can provide additional opportunities for flame structure studies at moderate pressures.

Reaction pathways for the decomposition of the agent (and its byproducts) for the C_2F_5H–air flame are presented in Fig. 6. In the figure, arrows connect the reactant and product species of interest, with the specific reaction partner next to each arrow (and the fraction of the reactant going through that route in parentheses). The reaction fluxes are integrated over the entire reaction domain. The results demonstrate that the radical pool (responsible

for attack on the fuel and its fragments) consists primarily of F, CF_3, C_2F_5, O, OH and CF_2 radicals. The concentration of these radicals in a flame zone (first zone) is roughly an order of magnitude less than the concentration of the radical pool species (H, OH, O) in typical hydrocarbon/air flames. The decomposition of agent proceeds through straight-chain radical reactions rather than the typical chain-branching reaction proceeding in hydrocarbon–air systems. As a result, the present halocarbon–air systems are not particularly sensitive to the water vapor contents, as has been reported in systems with higher hydrogen content [41,42]. The compound $C_3F_7COC_2F_5$ does not contain a hydrogen atom in the molecule. Thus a dry $C_3F_7COC_2F_5$/air system might be sensitive to the presence of hydrogen containing additives. Nonetheless, for the agent $C_3F_7COC_2F_5$, preliminary calculations indicate that addition of water vapor just slightly increases burning velocity. For the other agents (CF_3H, C_2F_5H, C_3F_7H), trace water vapor addition decreases the burning velocity. However at large water vapor loadings exceeding 4–5% by volume, slight increase of burning velocity is observed. Note that the large water vapor volume fractions are possible because of the higher initial temperature of 400 K.

In the $C_3F_7COC_2F_5$/air flame, the agent decomposition occurs in the first zone with formation of the two stable intermediate fluorinated species C_2F_6 and CF_3COF, as well as CF_4, CF_2O, CO and CO_2. The two-carbon fluorinated species are consumed in the second flame zone after some induction period, implying that there exist some critical conditions for the consumption of C_2F_6 and CF_3CFO. The first temperature increase related to the consumption of $C_3F_7COC_2F_5$ is about 630 K, and the second increase related to C_2F_6 and CF_3CFO consumption is about 700–800 K. The duration of the first zone is determined by oxidized decomposition of $C_3F_7COC_2F_5$ to the more stable C2 (primarily) and C3 fluorinated species (to a lesser extent, since they mainly disappear in the first stage). As indicated above, the consumption of $C_3F_7COC_2F_5$ does not involve reactions with hydrogen containing species, which may explain why its burning velocity is lower as compared with the hydrogen containing fluorinated compounds.

The calculated flames are preheated, have thick, multistage reaction zones, and are slowly propagating and hence, might be thought of as somewhat exotic. Under normal conditions heat losses from the reaction zone and fluid dynamic disturbances extinguish such flames. For example under typical ambient conditions it is difficult to observe flames propagating with burning velocities below 0.5–3 cm/s [31,32,34,43–46], and 5 cm/s has sometimes been cited as the burning velocity at the flammability limit [30,47] (although this value is of course, device dependent). The staged behavior of these flames presents experimental challenges to their stabilization. Nonetheless, for large scale fires, completion of the latter stages of the reactions of these premixed systems could occur for systems with long residence times (on the order of tens of seconds).

The overall reaction rate with HFC-agent addition to the near stoichiometric hydrocarbon–air system is generally decreased [41]. Nonetheless, despite the reduction in the reactivity of the system, HFC agent addition creates the potential for higher heat release and an attendant higher pressure rise in a closed system. Whether the higher pressure rise will occur depends upon the rate at which reaction rate is increased by the higher temperature, versus the rate at which it is lowered due to slower kinetics of the fluorinated species system. Thus in spite of the use of effective flame inhibitors leading to substantial weakening the combustion system through the decrease of the reaction rate, the system may still have appreciable amount of additional heat release which increases the combustion temperature. Under typical conditions this is not a problem as the burning velocity is decreased to the level where the environment becomes able to remove the heat generated by the combustion process leading to extinguishment. Note,
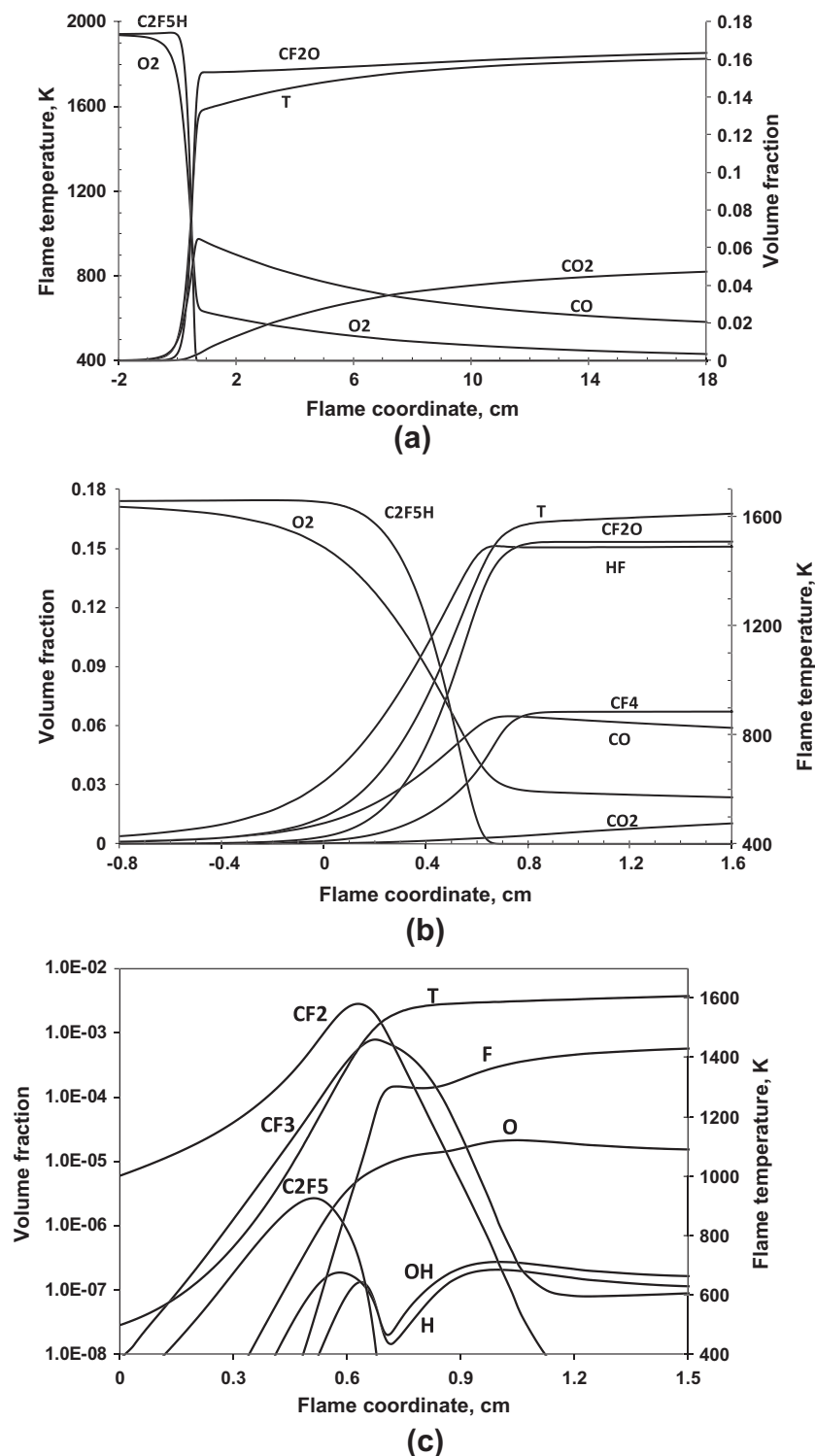
Fig. 5. (a–c) Flame structure of C_2F_5H/air flame (stoichiometric mixture, 1 bar, 400 K).

that some of the calculated burning velocities are possibly below a limit value determined by heat losses. The determination of the limit value of burning velocity represents a complex and separate problem [31,33,34,43–45,47]. However, it should be emphasized that under unfavorable conditions (large fires, extended times of process, elevated pressures and temperatures, etc.), where the environment is not able to remove the generated energy, the system itself may contain enough energy for sustaining combustion and as a result, unwanted combustion is observed.

3.3. Ignition delays

The ignition delay τ_i was determined for stoichiometric mixtures of the pure compounds (CF_3Br, CF_3I, CF_3H, C_2F_5H, C_3F_7H and $C_3F_7COC_2F_5$) with air at $P_0 = 1$ bar. The criterion for τ_i was defined as the time to reach a 100 K increase in temperature, which corresponds to the time for significant heat release. The simulations were performed for a range of initial temperatures as shown in Fig. 7. There were two complications in the determination of the
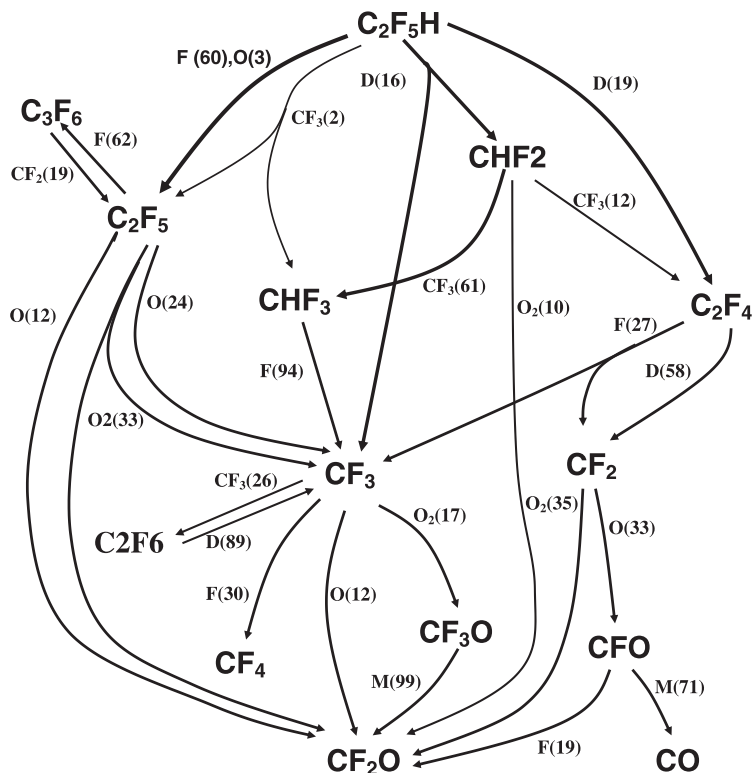
Fig. 6. Integrated overall reaction pathways of C_2F_5H decomposition in flame (stoichiometric mixture, 1 bar, 400 K); (b) Additional reaction pathways for consumption of CF_2 and CF_3 radicals (decomposition reactions are denoted by "D"; contributions of different reaction channels are shown in parenthesis as a percent of overall species consumption rate).
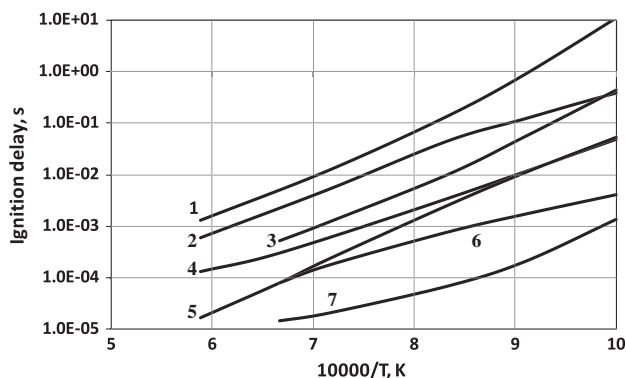
Fig. 7. Temperature dependence of ignition delay for stoichiometric air mixtures of CF_3Br (1), CF_3I (2), CF_3H (3), C_2F_5H (4), C_3H_8 (5), C_3F_7H (6) and $C_3F_7COC_2F_5$ (7) at 1 bar.

ignition delay. The first complication was the two-stage reaction behavior in the oxidation of CF_3I. The first stage corresponds to the relatively fast CF_3I decomposition with formation of C_2F_6 and with some heat release (approximately 5–10% of the total). The second reaction stage is related to the formation of reaction products CF_4 and CF_2O. The second reaction stage was used for the determination of the ignition delay. The second complication was a relatively large temperature decrease at the beginning of the induction period for CF_3H, C_2F_5H, C_2F_7H and $C_3F_7COC_2F_5$ due to endothermic decomposition of the agent, the magnitude of which increased with initial temperature. A similar temperature decrease is observed in the homogeneous autoignition of hydrocarbons; however it is substantially less pronounced than that for these fluorocarbons.

As indicated in Fig. 7, CF_3Br had the longest ignition delay, with the approximate ranking: $CF_3Br > CF_3H > CF_3I > C_2F_5H > C_3F_7H > C_3F_7COC_2F_5$. For comparison the ignition delay for a stoichiometric propane/air mixture was also calculated using C1–C4 kinetic model from Ref. [48]. Surprisingly, the agents C_3F_7H and $C_3F_7COC_2F_5$ have a shorter ignition time than propane for the temperature range of 1000–1500 K temperature range, while that for C_2F_5H is comparable to that of propane for 1000–1250 K.

There exists an experimentally determined self-ignition temperature of CF_3Br [19], (966 K as listed in Table 1), and this value can be approximately compared with the results of calculations. The critical condition of thermal explosion (self-ignition) is roughly determined by the relationship [49], $\tau_q = \tau_i$, where τ_q is the characteristic cooling time and τ_i is the adiabatic ignition delay time. The characteristic cooling time can be estimated using the relationship $\tau_q = c_p \rho V/(\alpha S)$, where c_p is the heat capacity; ρ, the mixture density; V, the reaction volume; α, the overall heat transfer coefficient, and S, the surface area of reaction vessel. The cooling time is roughly in the range 3–20 s for typical spherical reaction vessels (2–10 L). These characteristic cooling times can then be compared with the calculated ignition delay for CF_3Br at 966 K, $\tau_i \approx 37$ s, which is in approximate agreement with the cooling time. Note that the kinetic models were used without modifications, as described above, and additional reactions may be important for the region below 1000 K (e.g. reactions of the HO_2 radical).

It is of interest that extrapolating the ignition delay predictions for the fluorocarbons (Fig. 7) to the regime in which 3 s < τ_i < 20 s implies that self-ignition like phenomenon should be observed for all fluorocarbons, especially for C_3F_7H and $C_3F_7COC_2F_5$, at lower temperatures than for CF_3Br. These calculations indicate that the threshold for thermal stability of these fluorocarbons should be substantially decreased in mixtures with air. For example, the measured temperature threshold for thermal decomposition of

pure C_3F_7H, is approximately in the range 900–950 K [50], conversely the experimentally observed threshold of C_3F_7H decomposition in air was 500 °C, and decomposition of C_3F_7H was practically complete at 700 °C (C_3F_7H volume fraction of 0.05 in artificial air) [51].

The remarkably low values of ignition delays for C_3F_7H and $C_3F_7COC_2F_5$ in comparison to propane and the small reaction times, allow one to speculate that a sustainable detonation might be possible for these fluorinated compounds. In air mixtures, the heat release may be too low; however, in oxygen atmospheres, the energy release is larger, and the ignition time is much lower (five times lower for C_3F_7H at $T_0 = 1500$ K and twenty times lower at $T_0 = 1200$ K). Also, in the oxygen atmosphere, the initial temperature drop observed in air mixtures is substantially reduced.

4. Conclusions

Recent FAA (and other) tests have indicated that various fire suppression agents sometimes appear to enhance combustion. Consequently, to understand the phenomena, we have computationally studied the combustion properties of pure halogenated fire suppressant agents (CF_3H, C_2F_5H, C_3F_7H, $C_3F_7COC_2F_5$) in stoichiometric proportions with air. The adiabatic combustion temperature for the fluorinated agents is found to be 1669–1823 K, which is lower than that for hydrocarbons with air, but still in the range for which hydrocarbons are flammable. The calculated ignition delay for the initial temperature range (1000 K < T_0 < 1700 K) is predicted to be substantially shorter for several of the agents then for propane. Mixtures of the fluorinated agents with air demonstrate decreased thermal stability in comparison to the agent itself. A rough estimate of self-ignition temperature for CF_3Br agrees reasonably well with experimental data [19].

The calculated burning velocities are in the range of 0.37–2.5 cm/s at an initial temperature of 400 K (CF_3H, C_2F_5H, C_3F_7H, $C_3F_7COC_2F_5$). Hence, under certain conditions the mixtures of these compounds with air may be engaged in a self-sustained, exothermic reaction. For example, for systems in which the residence time is very long [14], exothermic reaction of mixtures even with low overall reaction rate (i.e., burning velocities) must be considered [16]. While it has been demonstrated previously [8–10,14,16] that HFC agents can augment the heat release when added to the air steam in a hydrocarbon fire, the present results indicate that it is possible for the pure agents themselves, in combination with slightly preheated air, to have measurable burning velocities. In future work, it would be of interest to measure the burning velocities of the pure agents with air, and to determine the practical conditions under which the potential flammability of these agents may be of significance.

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