

## **Kinetic Mechanism of 2,3,3,3-Tetrafluoropropene (HFO-1234yf) Combustion**

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Short communication

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## Kinetic Mechanism of 2,3,3,3-Tetrafluoropropene (HFO-1234yf) Combustion

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### Abstract

A kinetic model for 2,3,3,3-tetrafluoropropene (HFO-1234yf) high temperature oxidation and combustion is proposed. It is combined with the GRI-Mech-3.0 model, ~~with~~ the previously developed model for 2-bromo-3,3,3-trifluoropropene (2-BTP), and ~~with~~ the NIST C<sub>1</sub>-C<sub>2</sub> hydrofluorocarbon model. The model includes 909 reactions and 101 species. Combustion equilibrium calculations indicate a maximum combustion temperature of 2076 K for an HFO-1234yf volume fraction of 0.083 in air for standard conditions (298 K, 0.101 MPa). Modeling of flame propagation in mixtures of 2,3,3,3-tetrafluoropropene with oxygen-enriched air demonstrates that the calculated maximum burning velocity reproduces the experimentally observed maximum burning velocity ~~within about~~ reasonably well. However, the calculated maximum is observed in lean mixtures in contrast to the experimental results showing the maximum burning velocity shifted to the rich mixtures of HFO-1234yf.

**Keywords:** R-1234yf; ~~r~~Refrigerant flammability; ~~b~~Burning velocity; ~~l~~ow ODP/GWP refrigerants; kinetic model.

### 1. Introduction

In accord with the Montreal Protocol many of the ozone-depletion potential (ODP) chlorofluorocarbons and hydrochlorofluorocarbons (CFCs and HCFCs) have been largely phased out [1]. The replacement agents, mostly hydrofluorocarbon compounds (HFCs), have zero ODP. However, they have a large global warming potential (GWP) and are the subject to new restrictions via the 2016 addendum to the Montreal Protocol, and their use will be phased down. Replacement compounds with lower GWP have been developed but unfortunately the changes to the molecules that reduce the GWP (addition of double bonds or hydrogen atoms) also make them more flammable. For example, the hydrofluoroolefin (HFO) compound 2,3,3,3-tetrafluoropropene (CH<sub>2</sub>CFCF<sub>3</sub>, HFO-1234yf) has received considerable attention as one of the promising low-GWP alternative refrigerants [2, 3], having an atmospheric lifetime of 10.5 days [4] and a GWP<sub>100yr</sub> value < 1 [4,5], as compared to typical HFC refrigerants (e.g. R-410A, a 50/50 mass blend of CH<sub>2</sub>F<sub>2</sub> (R-32) and C<sub>2</sub>HF<sub>5</sub> (R-125), with a GWP<sub>100</sub> of 1924 [5]. However, it has been found that HFO-1234yf 2,3,3,3 tetrafluoropropene is weakly flammable [3,6,7].

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The aim of the present work is the development of a kinetic model of combustion of 2,3,3,3-tetrafluoropropene in air to be used in simulation studies of its flammability and combustion behavior. A kinetic model has been developed based on previous work for halogenated fire suppressants added at low concentration to hydrocarbon-air flames, and the combustion behavior of fire suppressants [8]. These include kinetic models for C<sub>1</sub>-C<sub>2</sub> fluorocarbon chemistry [9] and for the structurally similar compound, 2-bromo-3,3,3-trifluoropropene (2-BTP) [10,11]. For new species in the present model, the thermochemical parameters were estimated, and based on equilibrium concentrations of the intermediate radical species, the possible flame reactions of the new species with radicals were considered. Premixed flame simulations were used to further refine the reaction set, and were then analyzed to understand the mechanism of reaction of the fuel species and to compare predicted burning velocity with available experimental burning velocity data. To our knowledge, the first kinetic model of combustion of 2,3,3,3-tetrafluoropropene was recently developed by P. Papas et al. [12]. In the present work, we suggest an alternative mechanism of 2,3,3,3-tetrafluoropropene decomposition in a flame based on a different set of considered intermediate species and reactions.

## 2. Kinetic model

The complete kinetic model was assembled from four distinct blocks of reactions. The first block represents the hydrocarbon oxidation reactions, for which GRI-Mech-3.0 [13] was incorporated, providing description of high temperature oxidation of hydrocarbons up to C<sub>3</sub> species. The second block is from the NIST C<sub>1</sub>-C<sub>2</sub> hydrofluorocarbon model [9] with modifications [8, 14]. The third, for C<sub>3</sub>-hydrofluorocarbon reaction, is from the models developed for flame inhibition by heptafluoropropane (FM-200) [15] and 2-bromo-3,3,3-trifluoropropene, 2-BTP [10,11]. The fourth block, for the combustion of 2,3,3,3-tetrafluoropropene (HFO-1324yf), was developed in the present work as described below.

Table 1 contains the list of additional species considered in the mechanism with their enthalpy of formation  $\Delta H_f^\circ$ , standard entropy  $S_o$ , and heat capacity at constant pressure  $C_{p,o}$  (all at 298.15 K). Thermochemical data for the species CF<sub>3</sub>CCF and CHCFCF<sub>3</sub> were estimated using the group additivity approach, while data for the other species were taken from the literature [11, 16]. Table 2 lists the Arrhenius rate parameters (in Chemkin format [17, 18]) for the proposed

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decomposition reactions of 2,3,3,3-tetrafluoropropene down to species already present in the previously developed kinetic models. Flame equilibrium calculations and preliminary burning velocity simulations provided rough estimates of the intermediate species concentrations, which were used to evaluate the possible reactions. Rate constants were estimated by analogy with similar reactions and using empirical correlations. The complete model contains 909 reactions with 101 species. The Chemkin set of programs [17-19] was used for combustion equilibrium calculations and for modeling of laminar flame propagation in mixtures of 2,3,3,3-tetrafluoropropene in air of various oxygen volume fractions,  $X_{O_2}$ . 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 may be made once a variety of experimental data and theoretical results are available for testing the mechanism. Also, the mechanism is intended for combustion of pure HFO-1234yf in air, where reactions with H and OH are expected to be of lower importance.

### 3. Results and discussion

**3.1. Flame equilibrium calculations.** Figure 1 presents the results of flame equilibrium calculations performed for mixtures 2,3,3,3-tetrafluoropropene with air at normal conditions (298 K, 0.101 MPa), showing the variation in major fluorine-containing species volume fraction and temperature with mixture composition. The maximum combustion temperature of 2076 K corresponds approximately to the 8.3 % of 2,3,3,3-tetrafluoropropene in air. Nonetheless, in accord with the stoichiometric equation suggested by Takizawa et al. [3],  $CF_3CFCH_2 + 2.5O_2 = 2CO_2 + CF_2O + 2HF$ , we adopt a stoichiometric volume fraction of 0.0775 for the fuel. For equivalence ratios  $\phi$  of 0.5 to about 1.7, HF is the major product, followed by  $CF_2O$ . The maximum equilibrium volume fraction of F atom is very high, about 4 % by volume at 7.4 % of 2,3,3,3-tetrafluoropropene. The F/H ratio of 2,3,3,3-tetrafluoropropene is 4/2, so the combustion should be dominated by fluorine-containing radicals [8], and a promotion effect of water vapor would be ~~is~~ expected [20, 21] (via through the reaction  $F + H_2O = HF + OH$ ).

**3.2. Flame propagation.** The calculated burning velocities of premixed flames of 2,3,3,3-tetrafluoropropene were compared with the experimental data of Takizawa et al. [3]. To avoid uncertainties associated with flame stretch and radiation heat losses, which become more important

at lower burning velocity, data selected for comparison are those having measured burning velocities above 8 cm/s, corresponding to  $X_{O_2}=0.39$  and  $X_{O_2}=0.50$  in air. Figure 2 shows the measured (symbols) and calculated (lines) burning velocity as a function of the equivalence ratio (defined above) using the present kinetic model with dry air. Also shown is the adiabatic flame temperature (upper curves, right scale). The peak burning velocity is predicted reasonably well (within 10 %), and the variation with  $\phi$  is mild, and much less than for hydrocarbons. The simulations do, however, predict a peak burning velocity near an equivalence ratio of 0.7, while the experiments predict the peak near 1.15. Previous measurements and modeling of HFC burning velocities using the C<sub>1</sub>-C<sub>2</sub> fluorocarbon model (e.g. R-32 [22]) also show a peak burning velocity for rich mixtures in the experiments and lean mixtures in the modeling results. This is unusual given that in both the R-32 and HFO-1234yf systems the temperature peak is close to the stoichiometric conditions, as indicated in Figure 2. Additional studies are required to clarify sources of observed discrepancies of modeling results with experimental data.

Figure 3(a,b) shows profiles of the main species concentrations and temperature in the reaction zone of a stoichiometric flame, with enriched air ( $X_{O_2} = 0.39$ ). The measured burning velocity for this flame is 9.9 cm/s [3]. The flame reaches a high temperature in the main reaction zone (about 2130 K), but also has a long after-burning zone with slow conversion of CO and CF<sub>2</sub>O to the equilibrium products (Fig.3a), reaching a final temperature of 2289 K. Figure 3b shows the major radical species of the 2,3,3,3-tetrafluoropropene flame, which are F, CF<sub>2</sub>, CF<sub>3</sub>, CF<sub>2</sub>O, O, OH and H.

**3.3. Reaction pathways.** Figure 4 shows the main reaction pathways for the consumption of 2,3,3,3-tetrafluoropropene, which reacts essentially with radicals: F, CF<sub>3</sub>, O, OH, and H in the proportions: 0.58, 0.21, 0.08, 0.02, and 0.02. Consumption is mostly (80 %) via reactions with fluorine-containing species, with the radical pool species typical for hydrocarbon flames (H, O, and OH) playing a minor role. The species CHCF<sub>2</sub>CF<sub>3</sub> is a major intermediate, accounting for almost half of the CH<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub> consumption, and quickly decomposing to C<sub>2</sub>HF and CF<sub>3</sub>. The latter is also a major radical intermediate formed by more than 80 % of the reactions consuming CH<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>. The other major products of CH<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub> reaction are the fluorinated ethenes CH<sub>2</sub>CF<sub>2</sub>, CHFCHF(z), and CHF<sub>2</sub>CF<sub>2</sub> (formed from CF<sub>3</sub>CHF). These intermediates and the subsequent ones are consumed via decomposition reactions or reactions with radicals (primarily fluorine-

containing). Even in these flames with high F/H ratio, H and OH reach superequilibrium levels with the peak values (in the main reaction zone of the flame-) that are about a factor of 900 and 300 higher than the final, for H and OH, respectively in the main reaction zone of the flame. The slow after-burning region of the flame starts where their concentrations are greatly reduced. In this slow burning region, about two-thirds of the total consumption of  $\text{CF}_2\text{O}$  occurs primarily via thermal decomposition to CFO and F, and about half of the total consumption of CO occurs primarily via  $\text{CO}+\text{O}_2$  and  $\text{CO}+\text{O}+\text{M}$ , contributing to slow temperature rise. As in the equilibrium calculations, the volume fraction of F atom was very high, near 1% in the main reaction zone, and about 10% in the products for stoichiometric conditions and oxygen enriched air.

In contrast to the present work, the reaction pathway diagram presented in [12] demonstrates shows that HFO-1234yf is largely consumed in the reactions with radicals (H, O, OH) to form the  $\text{CHCF}_2\text{CF}_2$  radical, which further reacts with O or OH to form CHCFO or  $\text{CF}_2\text{CFCHO}$ , respectively. As described above, the present work shows HFO-1234yf to be consumed largely (80 %) via reactions with F and  $\text{CF}_3$ , with only minor contributions (about 13 %) from reactions with H and O. Moreover, only about 44 % of the HFO-1234yf forms  $\text{CHCF}_2\text{CF}_2$ , with most of the HFO-1234yf decomposition reactions forming  $\text{CHFCHF}(\text{Z})$  and  $\text{CH}_2\text{CF}_2$  (19 % and 19 %, both via reaction with F) and  $\text{CHF}_2\text{CF}_2$  (9 % via reaction with O). Hence, there are important differences in the predictions of the two models, warranting further work with subsequent the formation of the  $\text{CHCF}_2\text{CF}_2$  radical in accord with the results [12]. Further reaction of this radical through decomposition leads to the formation of the  $\text{CHCCF}_3$  species. The reaction of  $\text{CHCF}_2\text{CF}_2$  radical with the O atom leads to the formation of the CHCFO species and the reaction with the OH radical leads to the formation of the  $\text{CF}_2\text{CFCHO}$  species. As discussed above, our analysis of reaction pathways using the present suggested model (Fig. 4) demonstrates, as discussed above, that the major radical reactions leading to the  $\text{CHCF}_2\text{CF}_2$  radical are the reactions of F and  $\text{CF}_3$  radicals, accounting for approximately 44% of the HFO-1234yf consumption, with only minor contributions of reactions with O and OH radicals accounting approximately 44% of CHFO-1234yf consumption. In the present work, approximately 38 % of 2,3,3,3-tetrafluoropropene is consumed in reactions with F atom to with formation of  $\text{CH}_2\text{CF}_2$  and  $\text{CHFCHF}(\text{Z})$  species, and 9 % of CHFO-1234yf 2,3,3,3-tetrafluoropropene reacts with O atom forming the  $\text{CH}_3\text{CHF}$  radical. Thus, the main differences between the suggested mechanism and

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the model [12] are the initial stages of 2,3,3,3-tetrafluoropropene decomposition considered in the models.

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#### 4. Conclusions

A kinetic mechanism for flames of 2,3,3,3-tetrafluoropropene in oxygen/nitrogen systems was proposed. Combined with the hydrocarbon combustion model GRI-Mech-3.0, and fluorine-species flame inhibition models (NIST C<sub>1</sub>-C<sub>2</sub> hydrofluorocarbon model, Williams et al. HFC-227ea model, and NIST 2-BTP model), the model was used to describe flames of the refrigerant HFO-1234yf (2,3,3,3-tetrafluoropropene) in air with variable oxygen content. The overall kinetic model includes 909 reactions with 101 species.

Combustion equilibrium calculations have been performed for mixtures of 2,3,3,3-tetrafluoropropene with air, and indicate an adiabatic flame temperature near 2100 K at 2,3,3,3-tetrafluoropropene volume fraction of 0.083. The equilibrium calculations showed a very high volume fraction, about 4 %, for atomic fluorine in the equilibrium products for mixtures close to stoichiometric composition. Modeling of flame propagation in mixtures of 2,3,3,3-tetrafluoropropene with oxygen enriched air demonstrates reasonable agreement of calculated burning velocities with available experimental data. The major pathways of reaction of HFO-1234yf have been investigated.

#### Acknowledgements

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### Figure captions

Figure 1. Dependencies of the combustion temperature and F-containing equilibrium products (volume fraction) on CH<sub>2</sub>CF<sub>3</sub> volume fraction in air (initial conditions: 298 K, 0.101 MPa).

Figure 2. Burning velocity of CH<sub>2</sub>CF<sub>3</sub> as a function of equivalence ratio (initial conditions: 298 K; 0.101 MPa; solid line, calculations for air with 50 % of O<sub>2</sub>, dashed line, calculations for air with 39 % of O<sub>2</sub>; symbols, experimental data of Takizawa et al. [3]).

Figure 3 (a,b). Flame structure of stoichiometric CH<sub>2</sub>CF<sub>3</sub>-air flame (initial conditions, 298 K, 0.101 MPa; X<sub>O<sub>2</sub></sub> = 0.39).

Figure 4. Reaction pathways for stoichiometric CH<sub>2</sub>CF<sub>3</sub>-air flame (298 K, 0.101 MPa, X<sub>O<sub>2</sub></sub>=0.39). The number next to the reaction partner is the fraction (%) of the consumption of the parent species by that route.

Table 1. Thermodynamic properties of additional species considered in the HFO-1234yf combustion model.

Species	$\Delta H_f^0(298\text{ K})$ kJ/mol	$S_o(298\text{ K})$ J/mol/K	$C_{po}(298\text{ K})$ J/mol/K	Reference
CH <sub>2</sub> CFCF <sub>3</sub> (HFO-1234yf)	-813.2	327.5	101.2	[16]
CFCCF <sub>3</sub>	-531.2	333.4	96.6	estimate, [23]
CHCFCF <sub>3</sub>	-567.6	332.1	99.9	estimate
CF <sub>3</sub> CHCH <sub>2</sub>	-631.2	319	90.7	[16]
CF <sub>3</sub> CCH <sub>2</sub>	-375.0	325	91.1	[16]
CF <sub>3</sub> CCH	-428.5	314	88.3	[11]
CF <sub>3</sub> COCH <sub>3</sub>	-837.3	357	108.5	[11]

Table 2. Arrhenius parameters for 2,3,3,3-Tetrafluoropropene decomposition model ( $AT^n \exp(-E/RT)$ ), units: mole, K, s, cm, kJ).

Reaction	A	n	E
CH <sub>2</sub> CFCF <sub>3</sub> (+M) => CF <sub>3</sub> +CH <sub>2</sub> : CF (+M)	7.9E+15	0.	451.9
LOW /5.40E18	0.0	108700.0/	
H <sub>2</sub> O/9.00/ CH <sub>4</sub> /2.00/ CO/1.50/ CO <sub>2</sub> /2.00/ C <sub>2</sub> H <sub>6</sub> /3.00/			
CH <sub>3</sub> F /6.00/ CH <sub>2</sub> F <sub>2</sub> /6.00/ CHF <sub>3</sub> /6.00/ HF /2.00/			
CF <sub>3</sub> CCH <sub>2</sub> + F = CH <sub>2</sub> CFCF <sub>3</sub>	2.0e14	0.	0.
CH-CFCF <sub>3</sub> + H = CH <sub>2</sub> CFCF <sub>3</sub>	2.0e14	0.	0.
CH <sub>2</sub> CFCF <sub>3</sub> + H = CH-CFCF <sub>3</sub> + H <sub>2</sub>	2.5e13	0.	66.9
CH <sub>2</sub> CFCF <sub>3</sub> + H = CH <sub>2</sub> :CHF + CF <sub>3</sub>	1.5e13	0.	25.1
CH <sub>2</sub> CFCF <sub>3</sub> + OH = CH-CFCF <sub>3</sub> + H <sub>2</sub> O	2.e13	0.	28.5 *
CH <sub>2</sub> CFCF <sub>3</sub> + OH = CH <sub>3</sub> + CF <sub>3</sub> COF	7.5e11	0.	1.0 **
CH <sub>2</sub> CFCF <sub>3</sub> + O = CH-CFCF <sub>3</sub> + OH	1.2e12	0.7	62.8
CH <sub>2</sub> CFCF <sub>3</sub> + O = CF <sub>3</sub> -CHF + HCO	1.3e7	1.83	0.
CH <sub>2</sub> CFCF <sub>3</sub> + O = CH <sub>2</sub> F + CO + CF <sub>3</sub>	6.5e6	1.83	0.

$\text{CH}_2\text{CFCF}_3 + \text{CF}_3 = \text{CH-CFCF}_3 + \text{CHF}_3$	2. e13	0.	58.6
$\text{CH}_2\text{CFCF}_3 + \text{F} = \text{CH-CFCF}_3 + \text{HF}$	5. e13	0.	30.1
$\text{CH}_2\text{CFCF}_3 + \text{F} = \text{CH}_2:\text{CF}_2 + \text{CF}_3$	5. e13	0.	30.1
$\text{CH}_2\text{CFCF}_3 + \text{F} = \text{CHF:CHF}[\text{Z}] + \text{CF}_3$	5. e13	0.	30.1
$\text{CH-CFCF}_3 = \text{CF}_3 + \text{C}_2\text{HF}$	2. 1e13	0.	179.9
$\text{CH-CFCF}_3 + \text{O}_2 = \text{H}_2\text{O} + \text{CFCCF}_3$	2. e13	0.	129.7
$\text{CH-CFCF}_3 + \text{H} = \text{CF}_3 + \text{CH}_2:\text{CF}$	2. e13	0.	20.9
$\text{CH-CFCF}_3 + \text{H} = \text{H}_2 + \text{CFCCF}_3$	1. e13	0.	12.6
$\text{CH-CFCF}_3 + \text{H} = \text{HF} + \text{CF}_3\text{CCH}$	1. e13	0.	8.4
$\text{CH-CFCF}_3 + \text{OH} = \text{H}_2\text{O} + \text{CFCCF}_3$	2. e13	0.	0.
$\text{CH-CFCF}_3 + \text{CH}_3 = \text{CH}_4 + \text{CFCCF}_3$	1. e13	0.	33.5
$\text{CFCCF}_3 + \text{H} = \text{CF}_3 + \text{C}_2\text{HF}$	5. e13	0.	31.4
$\text{CFCCF}_3 + \text{O} = \text{CF}_3 + \text{CFO}$	1. 1e13	0.	0.
$\text{CFCCF}_3 + \text{OH} = \text{CF}_3 + \text{CHFO}$	3. e13	0.	20.9
$\text{CFCCF}_3 + \text{F} = \text{CF}_3 + \text{C}_2\text{F}_2$	1. e13	0.	29.3

\*) [24] ; \*\*) [25]

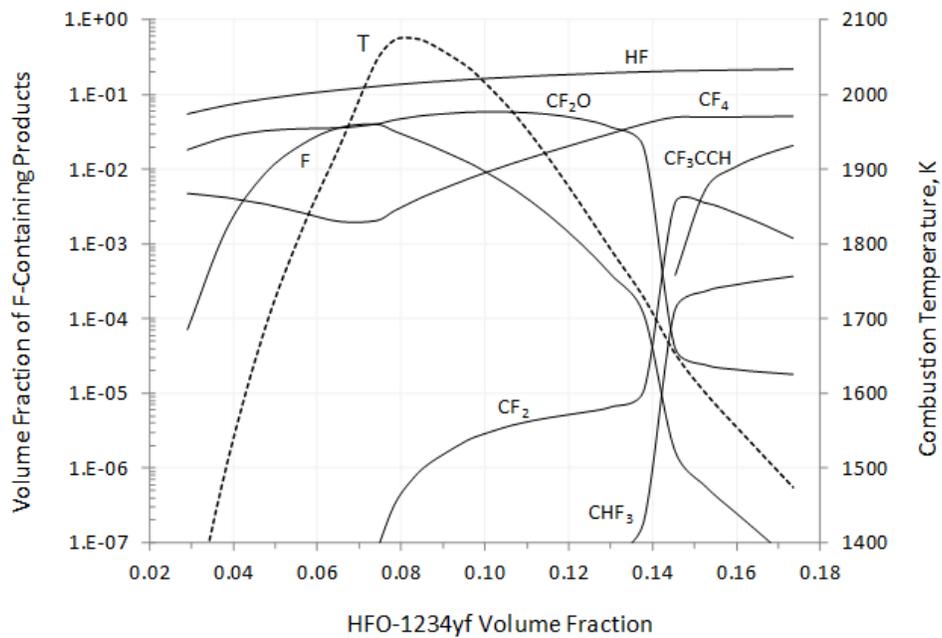


Figure 1. Dependencies of the combustion temperature and F-containing equilibrium products (volume fraction) on  $\text{CH}_2\text{CFCF}_3$  volume fraction in air (initial conditions: 298 K, 0.101 MPa).

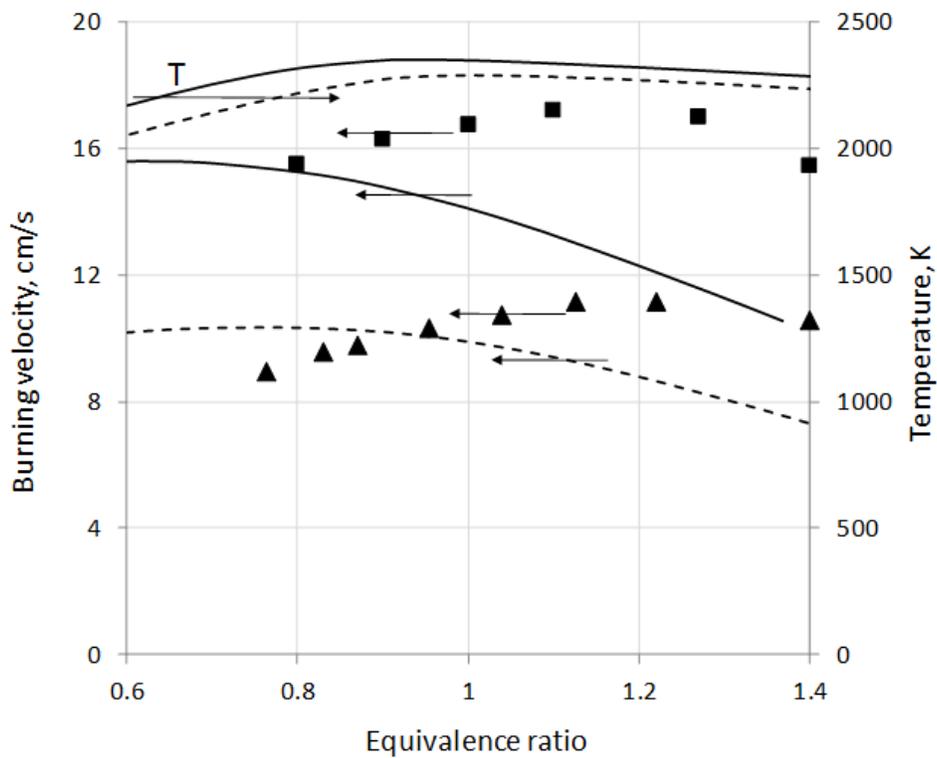
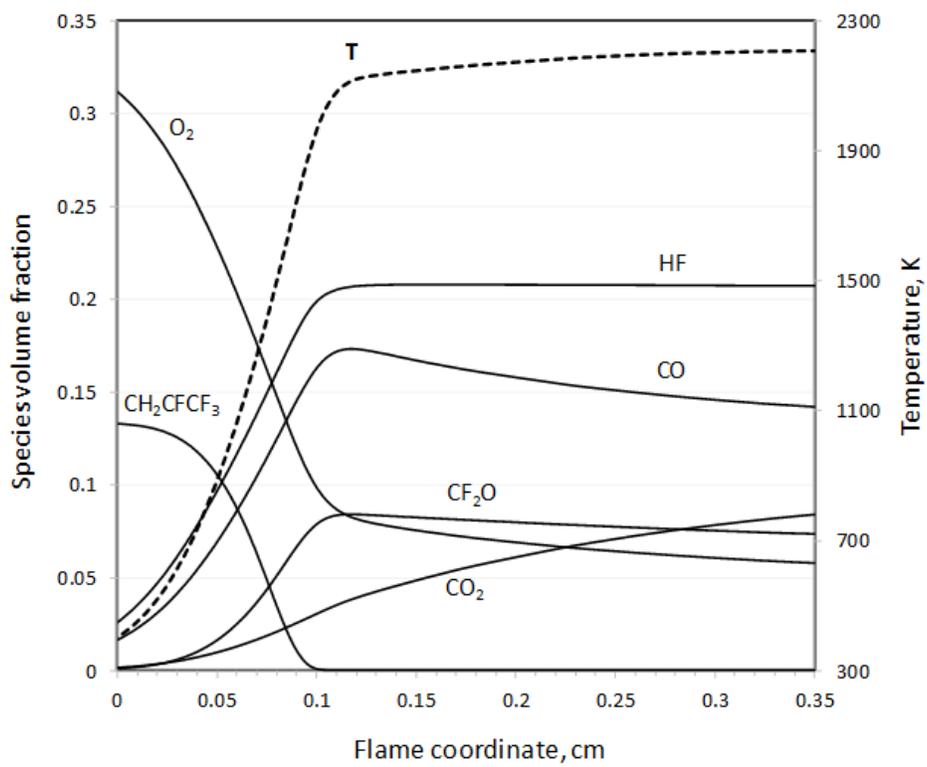


Figure 2. Burning velocity (lower curves and symbols) and adiabatic temperature (upper curves) of CH<sub>2</sub>CFCF<sub>3</sub> as a function of equivalence ratio (initial conditions: 298 K; 0.101 MPa; solid line, calculations for air with 50% of O<sub>2</sub>, dashed line, calculations for air with 39 % of O<sub>2</sub>; symbols, experimental data of Takizawa et al. [3]).

a)



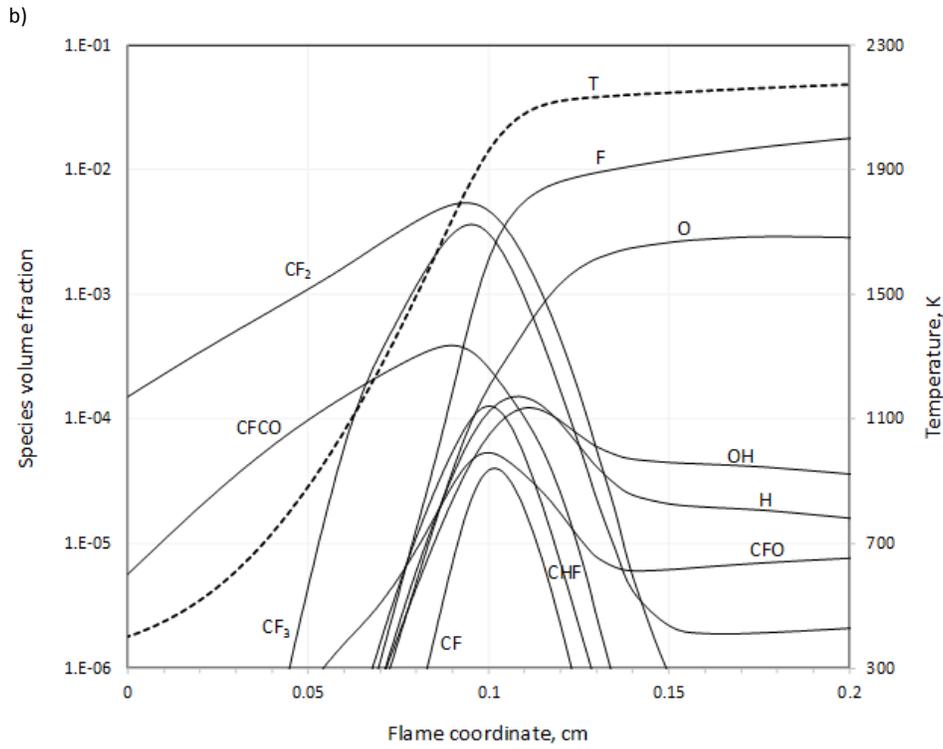


Figure 3 (a,b). Flame structure of stoichiometric  $\text{CH}_2\text{CF}_3$ -air flame (initial conditions, 298 K, 0.101 MPa;  $X_{\text{O}_2} = 0.39$ ).

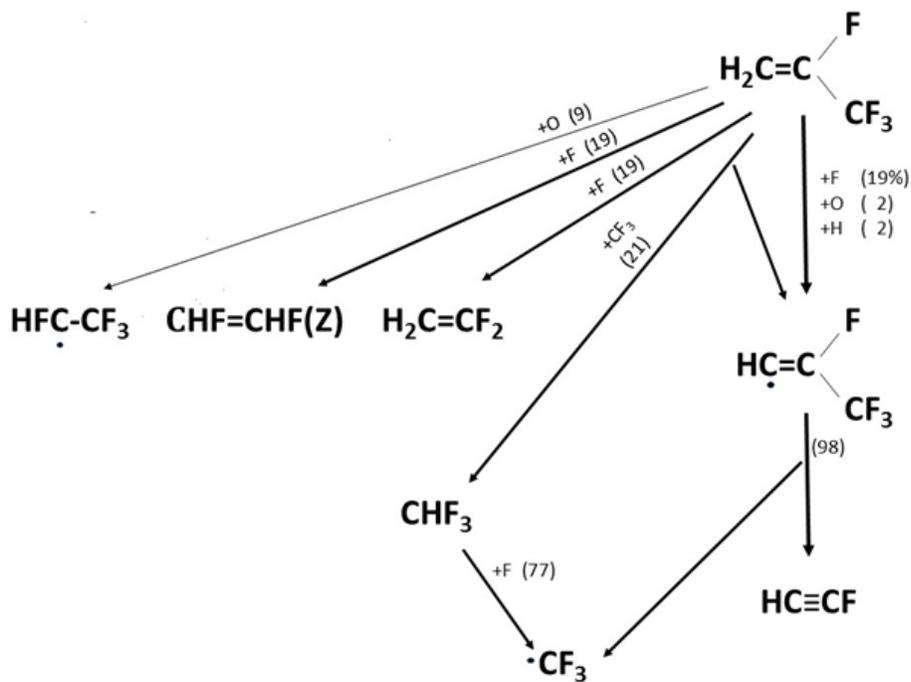


Figure 4. Reaction pathways for stoichiometric  $\text{CH}_2\text{CFCF}_3$ -air flame (initial conditions: 298 K, 0.101 MPa,  $X_{\text{O}_2}=0.39$ ). The number next to the reaction partner is the fraction (%) of the consumption of the parent species by that route.