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Short Communication

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, the previously developed model for 2-bromo-3,3,3-trifluoropropene (2-BTP), and the NIST C_1-C_2 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 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.

1. Introduction

In accordance with the Montreal Protocol many of the high 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_2CFCF_3, 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 GWP100yr value < 1 [4,5], as compared to typical HFC refrigerants e.g. R-410A, a 50/50 mass blend of CH_2F_2 (R-32) and C_2HF_5 (R-125), with a GWP100 of 1924 [5]. However, it has been found that HFO-1234yf is weakly flammable [3,6,7].

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_1-C_2 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 descriptions of high temperature oxidation of hydrocarbons up to C_3 species. The second block is from the NIST C_1-C_2 hydrofluorocarbon model [9] with modifications [8,14]. The third, for C_3-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, was developed in the present work as described below.

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

Species	ΔH_f^0(298 K) kJ/mol	S_o(298 K) J/mol/K	C_{po} (298 K) J/mol/K	Reference
CH_2CFCF_3 (HFO-1234yf)	−813.2	327.5	101.2	[16]
$CFCCF_3$	−531.2	333.4	96.6	estimate, [23]
$CHCFCF_3$	−567.6	332.1	99.9	estimate
CF_3CHCH_2	−631.2	319	90.7	[16]
CF_3CCH_2	−375.0	325	91.1	[16]
CF_3CCH	−428.5	314	88.3	[11]
CF_3COCH_3	−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
CH2CFCF3 (+M) → CF3 + CH2CF (+M) LOW/5.40E18 0.0 108700.0/ H2O/9.00/CH4/2.00/CO/1.50/CO2/2.00/C2H6/3.00/ CH3F/6.00/CH2F2/6.00/CHF3/6.00/HF/2.00/	7.90E + 15	0	451.9
CF3CCH2 + F=CH2CFCF3	2.00E + 14	0	0
CHCFCF3 + H=CH2CFCF3	2.00E + 14	0	0
CH2CFCF3 + H=CHCFCF3 + H2	2.50E + 13	0	66.9
CH2CFCF3 + H=CH2CHF + CF3	1.50E + 13	0	25.1
CH2CFCF3 + OH=CHCFCF3 + H2O	2.00E + 13	0	28.5 *
CH2CFCF3 + OH=CH3 + CF3COF	7.50E + 11	0	1.0 **
CH2CFCF3 + O=CHCFCF3 + OH	1.20E + 12	0.7	62.8
CH2CFCF3 + O=CF3CHF + HCO	1.30E + 07	1.83	0
CH2CFCF3 + O=CH2F + CO + CF3	6.50E + 06	1.83	0
CH2CFCF3 + CF3=CHCFCF3 + CHF3	2.00E + 13	0	58.6
CH2CFCF3 + F=CHCFCF3 + HF	5.00E + 13	0	30.1
CH2CFCF3 + F=CH2CF2 + CF3	5.00E + 13	0	30.1
CH2CFCF3 + F=CHFCHF[Z]+ CF3	5.00E + 13	0	30.1
CHCFCF3=CF3 + C2HF	2.10E + 13	0	179.9
CHCFCF3 + O2=HO2 + CFCCF3	2.00E + 13	0	129.7
CHCFCF3 + H=CF3 + CH2CF	2.00E + 13	0	20.9
CHCFCF3 + H=H2 + CFCCF3	1.00E + 13	0	12.6
CHCFCF3 + H=HF + CF3CCH	1.00E + 13	0	8.4
CHCFCF3 + OH=H2O + CFCCF3	2.00E + 13	0	0
CHCFCF3 + CH3=CH4 + CFCCF3	1.00E + 13	0	33.5
CFCCF3 + H=CF3 + C2HF	5.00E + 13	0	31.4
CFCCF3 + O=CF3 + CFCO	1.10E + 13	0	0
CFCCF3 + OH=CF3 + CHFCO	3.00E + 13	0	20.9
CFCCF3 + F=CF3 + C2F2	1.00E + 13	0	29.3

*) [24].
**) [25].

Table 1 contains the list of additional species considered in the mechanism with their enthalpy of formation ΔH_f^0, standard entropy S_o, and heat capacity at constant pressure $C_{p,o}$ (all at 298.15 K). Thermochemical data for the species CF_3CCF and $CHCFCF_3$ 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 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_{O2}. 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

Fig. 1 presents the results of flame equilibrium calculations performed for mixtures 2,3,3,3-tetrafluoropropene with air at standard 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 accordance 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 ϕ 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 expected [20,21] (via 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 $X_{O2} = 0.39$ and $X_{O2} = 0.50$ in air. Fig. 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, and the variation with ϕ 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_1-C_2 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 indicted in Fig. 2. Additional studies are required to clarify sources of observed discrepancies of modeling results with experimental data. Note that the present simulations were conducted for dry reactants. The influence of water vapor should be examined in a future work.

Fig. 3(a,b) shows profiles of the main species concentrations and temperature in the reaction zone of a stoichiometric flame with enriched air ($X_{O2} = 0.39$). 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_2O to the equilibrium products (Fig. 3a), reaching a final temperature of 2289 K. Fig. 3b shows the major radical species of the 2,3,3,3-tetrafluoropropene flame, which are F, CF_2, CF_3, CFCO, O, OH and H.

3.3. Reaction pathways

Fig. 4 shows the main reaction pathways for the consumption of