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Combustion and flammability chemistry for the refrigerant HFO-1234yf (2,3,3,3-tetrafluroropropene)

Craig D. Needham, Phillip R. Westmoreland*

Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, USA

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ABSTRACT

A comprehensive chemical mechanism has been developed to describe combustion of the refrigerant HFO-1234yf (2,3,3,3-tetrafluroropropene, YF), revealing the dominant pathways for its stoichiometric combustion with O_2. This novel mechanism is a quantum-chemistry-based extension to a previous mechanism developed at NIST for small fluorinated hydrocarbons. The new reactions were proposed by analyzing the YF molecule for potential unimolecular and bimolecular destruction routes, including chemical-activation channels. Kinetic parameters and thermochemistry were calculated using computational quantum chemistry or were developed by analogy to similar reactions or species. The new mechanism was compared favorably to experimental adiabatic-flame-speed data for stoichiometric YF/(35% O_2/65% N_2) flames at different initial temperatures. Analyses of these predictions revealed the key YF-destruction step at this H-starved condition to be F addition, producing CH_2CF_2+CF_3 via chemically activated $(\bullet CH_2CF_2CF_3)^*$.

1. Introduction

HFO-1234yf (or YF) has been shown to be a desirable, low-environmental-impact alternative to the more common HFC-134a as a refrigerant [1–5]. However, YF is mildly flammable, so there is interest in its flammability characteristics. A few experimental studies have been conducted [4–6], but more comprehensive analysis of the behavior of YF in flames is desirable. Although some attempts have been made in the past to measure reaction rates of YF with certain radicals [1,7], no comprehensive chemical mechanism has been proposed until this work and the recent work of Papas et al. [8].

A reaction mechanism is developed here to describe YF combustion, serving as a useful aid for exploring the refrigerant's flammability behavior. By building on the previously developed NIST mechanism describing the combustion of small, fluorinated hydrocarbons [9–11], the only new reactions that need to be described are those that break YF down into smaller molecules.

2. Methods

Thermochemical properties of the new species and the reaction rate parameters for the new reactions were calculated using Gaussian 09 [12], ChemRate including unimolecular RRKM/Master-Equation solutions [13] and, in a few cases, with estimations using Bimolecular Quantum-RRK [14].

The energies, optimized geometries, and harmonic frequencies were calculated for new species and transition states using the CBS-QB3 method [15,16] implemented in Gaussian 09 [12]. Simmie and Somers [17] have analyzed predictions from six high-level methods including CBS-QB3, compared to literature data for 45 C/H/O molecules, and found $2\sigma = 3.1$ kcal/mol for $\Delta_f H^\circ_{298}$ from CBS-QBS. Most transition states were calculated using the quadratic synchronous transit method QST3 [18,19], which uses structural estimates of the reactant(s), transition state, and products(s). Transition-state identities were confirmed by Intrinsic Reaction Coordinate calculations. These results were used with ChemRate to generate rigid-rotor, harmonic-oscillator ideal-gas thermochemistry for species with hindered internal rotor corrections where deemed appropriate by Gaussian hindered-rotor analysis, fitted to the seven-parameter NASA format for temperature dependence [20].

ChemRate was also used to generate high-pressure-limit rate parameters, drawing data for all involved species from literature values or Gaussian geometry-optimization output files. For pressure-dependent kinetics for simple decomposition reactions and chemically activated association-stabilizations, the collision model was assumed to be exponential-down with an energy-dependent energy-transfer parameter, α, of $70 + 0.003E$ cm^{-1} for each species [21]. Lennard-Jones parameters were either taken

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* Corresponding author.
E-mail address: prwestmo@ncsu.edu (P.R. Westmoreland).

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Table 1
Steric factors for radical species used in collision-theory rate coefficients.

Species	β_i	Sources
H	1.00	Ref. [23]
O	0.69	Ref. [23]
F	0.64	Analogy to OH.
CF_3	0.38	Ref. [22]
CH_2CF	0.42	Analogy to C_2H_3 in [23]
E- or *Z*-$CHCFCF_3$	0.40	Slightly lower than allyl [22]
CH_3CFCF_3	0.25	Analogy to iC_3H_7 [22]

from the CHEMKIN Transport database [22] or were estimated by analogy to similar species. Transition-state data were extracted from the corresponding output file in a similar manner to the reactant and product species. The reactants, products, and transition state were then linked together as a reaction. To compute the rate coefficient, ChemRate master-equation analysis was applied at temperatures varying from 300 to 2300 K, the temperature window of most interest.

Bimolecular Quantum-RRK calculations were used to estimate the competition between stabilization vs. decomposition products for possible chemically activated association-decomposition reactions (well-skipping reactions). This simple method indicates whether stabilization or chemically activated decomposition dominates, as opposed to their both being significant, in which case subsequent master-equation calculations are indicated. After the rate-coefficent calculations were completed, appropriated Arrhenius or modified Arrhenius expressions were fitted.

As input to ChemRate and Bimolecular Quantum-RRK for reactions having no electronic barriers in the CBS-QB3 model chemistry, such as radical combinations, rate coefficients were derived using collision-rate theory $k(A+B\rightarrow AB)=\beta_A\beta_B Z_{coll} g_{AB}/g_A g_B$, where β_i is a fitted molecular steric factor; Z_{coll} is the collision-frequency rate constant; and g_i is the electronic degeneracy of *i* [23,24]. The steric factor β_i for each species involved in a reactive collision, determined from analysis of multiple reactions or by analogy, is summarized in Table 1.

The resulting Chemkin-format mechanism is provided as supplementary material. To evaluate this mechanism after it was assembled, adiabatic freely propagating flame simulations were carried out using CHEMKIN-Pro [25]. The CHEMKIN-Pro tool for reaction-path analysis was used to analyze the dominant reaction routes and to check for any unrealistic behavior of the mechanism.

3. Mechanism development

3.1. Determining possible reaction pathways

The first step to creating a mechanism for YF combustion was to analyze the molecule and enumerate the different routes by which it could decompose into species already described by the NIST small-fluorocarbon combustion mechanism [9–11]. Figure 1 is a schematic showing the different destruction routes that were included.

There are three different classes of reactions by which the YF molecule can be destroyed: Unimolecular decomposition (denoted by *u* reactions), hydrogen abstraction (denoted by *a* reactions), and radical addition of H, O, OH, and F (denoted by *b, c, d,* and *e* reactions, respectively). These reaction classes and the specific reactions included in each class are discussed below.

3.2. Unimolecular decomposition reactions

Of the unimolecular routes considered, five are homolytic bond scissions and the other three are concerted, four-centered eliminations. Chemically activated decomposition of the radical-product recombinations also occur on this potential energy surface.

Most of the bonds in the YF molecule are very strong and are unlikely to undergo homolytic scission on their own. However, the C_d–C single bond between the double-bonded carbon and the CF_3 group has a bond energy of only 109 kcal/mol vs. 116 for C_d–H and 125 for C_d–F, meaning that it is the most likely to break homolytically. This thermal, collisionally mediated reaction is shown as reaction u_1. Given the nature of homolytic bond scission, this reaction is electronically barrierless, so pure ab initio calculations cannot locate a transition state. Rather than applying a variational analysis, the reverse rate (i.e., the rate for radical recombination) was estimated using collision-rate theory.

Energy barriers are lowest for the YF molecule to undergo concerted pericyclic 1,2-eliminations of HF, where the fluorine on carbon 2 enters a four-centered transition state with the hydrogen on carbon 1 (the other side of the double bond), breaking away from the molecule. CF_3H can eliminate similarly. Eliminations of HF and CHF_3 are represented by reactions u_2 and u_3, respectively. Figure 2 shows a representation of the electron movements involved in u_2.

Heats of formation are shown in Fig. 3 for the species and transition states involved in unimolecular reactions of YF. For all energy diagrams, each plateau represents the heat of formation at 298 K of the reactants, the products, or the transition state of each reaction. The transition state is labeled according to which reaction it represents, and reactant or product species are shown near the energies to which they correspond.

Reaction u_1 has the highest rate constant among the unimolecular reactions. It has the second lowest energy barrier but, with its loose transition state, a much higher Arrhenius pre-exponential factor than for the concerted reactions u_2 and u_3. Both u_1 and u_2 contribute in the combustion modeling, so only they were included in the final mechanism (Supplemental data). Notably, u_2 produces stable HF, giving the least endothermic products.

The reverses of the unimolecular steps u_1–u_7 are association reactions that form chemically activated YF*, which can yield other product channels than forming thermal YF. Energy-removing third-body collisions completely stabilize YF* to thermal YF only in the high-pressure limit. Thermalized YF can react with other species, while, in contrast, chemically activated YF* is so short-lived that it will not ordinarily undergo any bimolecular reactions.

Most importantly, the YF* from radical combination of $CH_2{=}CF+CF_3$ rapidly decomposes almost instantly to $CF_3CCH+HF$ (a chemically activated association-decomposition, shown as an arrow from the u_1 products to the u_2 products). In such a case, YF is not detectable as a product, and the reaction is effectively $CH_2{=}CF+CF_3\rightarrow CF_3CCH+HF$. As the high-pressure limit is approached, both stabilization and association-decomposition can occur, although the total rate cannot exceed the high-pressure limit of the radical combination.

3.3. Hydrogen abstraction reactions

The two vinylic hydrogens in YF are most easily abstracted from the YF molecule, given the greater strength of the carbon–fluorine bonds. The abstracting species considered are H, O, OH, CH_3, F, and CF_3 radicals and O_2. Abstraction via either reaction a_1 or a_2 produces 2,3,3,3-tetrafluoropropenyl radical with a single H remaining, either *trans* to the F (denoted as *E*-$CHCFCF_3$ in the mechanism, route a_1) or *cis* to it (denoted as *Z*-$CHCFCF_3$, route a_2). Figure 4 shows the energy surfaces for the five abstractors with computed transition states: H, OH, CH_3, F, and CF_3. Parameters for abstraction by O are estimated from the rate given in Tsang [26] for propene. Parameters for abstraction by O_2 are estimated as half of the rate