

# Development and Validation of a Mechanism for Flame Propagation in R-32/Air Mixtures

*Donald R. Burgess, Jr., Jeffrey A. Manion, Robert R. Burrell,  
Valeri I. Babushok, Michael J. Hegetschweiler, Gregory T. Linteris*

## **Abstract**

A mechanism for the combustion of the refrigerant R-32 (CH<sub>2</sub>F<sub>2</sub>) in air mixtures was developed and validated through comparisons with measured flame speeds for a range of equivalence ratios (0.9 to 1.4) and pressures (1 to 3 bar) using a constant-volume spherical flame method. Premixed flame calculations were performed and analyzed to identify primary species and reactions contributing to flame speeds and combustion. We found that there were only three HFC reactions that contributed significantly to flame speeds. Their rate constants were optimized within uncertainty limits and the model showed excellent agreement (<3 %) with measured flames speeds.

**Keywords:** Chemical kinetics, Refrigerant flammability, Burning velocity, Hydrofluorocarbons

## **1. Introduction**

The overall purpose of this work is to characterize the flammability of a set of fluoromethanes, fluoroethanes, and fluoropropenes, and their mixtures for use as refrigerant working fluids. Although it is possible to make measurements of the flammability of a single refrigerant under a limited set of conditions, it is not realistic to measure flammabilities of all possible formulations under a wide range of refrigerant-to-air ratios for different diluents, ambient temperatures, and humidity levels. The driving force for this work is the development of new refrigerant blends that simultaneously minimizes their global warming potentials (GWP) and flammabilities, while maximizing their refrigerant performance which is a function of thermodynamic and physical properties (e.g., critical temperature, vaporization enthalpy, thermal conductivity, saturation vapor pressure). The ability to have robust and accurate predictive tools that are benchmarked to high quality measurements of the flammability of these refrigerants for a set of specific mixtures under a range of conditions will allow industry to screen, optimize, and rank different blends to enable rapid development of new refrigerant formulations.

In the work reported here, the flammability of the refrigerant R-32 ( $\text{CH}_2\text{F}_2$ , difluoromethane) is studied using burning velocities (flame speeds). R-32 is a widely used refrigerant that is non-ozone depleting and has a moderate GWP. It, however, is mildly flammable, and is used with less flammable refrigerants in blends. This current work on R-32, a standard refrigerant, will provide a benchmark for extending flammability models based on elementary reaction kinetics to other refrigerants (both pure and blends) such as the HFC's R-125 (pentafluoroethane), R-134a (1,1,1,2-tetrafluoroethane), R-152a (1,1-difluoroethane), and the hydrofluoroolefins HFO-1234yf (2,3,3,3-tetrafluoropropene) and HFO-1234ze (1,3,3,3-tetrafluoropropene).

## 2. Methods

In this work, we developed and validated a chemical kinetic mechanism/model to predict the flammability of the refrigerant R-32 ( $\text{CH}_2\text{F}_2$ ). This requires understanding the chemistry on a microscopic level from the analysis of reaction pathways and comparison of the model predictions to measured flame speeds.

The full details of the measurements in this work are reported elsewhere [1] and are only summarized here. The flame speeds of R-32/air mixtures were measured using a constant-volume spherical-flame method. A spherical chamber about 15 cm diameter (~1.8 liters) was filled with R-32/air mixtures with equivalence ratios ranging from 0.9 to 1.4, and using different initial pressures on the order of (0.87 to 1.13) bar. The mixtures were then ignited by a spark at the center of the chamber, and the pressure rise (final pressures of about 7 to 11 bar) as a function of time was monitored. The final pressures were about 7 to 11 bar, but instabilities, interaction with the chamber wall, and other effects limited the reliable data to final pressures of about 1 to 3 bar. The pressure traces were then used to calculate flame radius, and thus flame speeds  $S_u(T,P)$ , using a thermodynamic spherical flame propagation model. In the data reduction procedures, corrections were made to account for thermal radiation of the burned gas [3] and flame stretch [4]. Buoyancy is unimportant for the present conditions [5] and was not considered.

In this work, the development and validation of a chemical kinetic mechanism (model) to predict the flammability of R-32 ( $\text{CH}_2\text{F}_2$ ) was iterative. An initial chemical kinetic mechanism was

developed based on compilations from the literature, updates to reflect more recent work, and an evaluation of reactions and their rate constants. Simulations were performed using the Sandia Premix code [6] and Cantera [7] and the results examined using reaction path analysis employing the graphics post-processor XSenkplot [8] to identify important species and reactions. The refined mechanism was used to simulate the flame speeds. Rough agreement between the computed and measured flames speeds was initially found, and the rate constants were then adjusted/optimized within their uncertainty limits (factors of about 1.3 to 2.0) to achieve best agreement.

### 3. Rate Constant Evaluation

We provide here a short discussion of the rate constants evaluated and utilized in this work. Key rate expressions are provided in Table 1. The rate expressions for hydrogen-oxygen chemistry and hydrocarbon/oxidized hydrocarbon chemistry were taken from GRI-Mech 3.0 [9], while those for H/O/F chemistry were based on our fits to rate constants reported in the literature [10-12].

The rate expression for  $\text{CH}_2\text{F}_2 \rightarrow \text{CHF} + \text{HF}$  was derived from the shock tube measurements for the analogous reaction  $\text{CHF}_3 \rightarrow \text{CF}_2 + \text{HF}$  by Schug and Wagner [13] and employing the very rough relative decomposition rates for  $\text{CH}_2\text{F}_2$  and  $\text{CHF}_3$  from the pyrolysis study of Politanskii and Shevchuk [14]. This scaled rate expression was then refined during our optimizations. It was found that the flame speeds could not be modeled with a pressure independent rate constant for this unimolecular reaction. It was necessary to use a pressure-dependent rate constant of the form  $\text{Rate} = k_0[\text{M}] + k_1$ , where the pressure dependent term  $k_0[\text{M}]$  dominated – suggesting that the reaction was approaching the low pressure limit under (P, T) conditions in the flame.

The rate expressions for H abstractions from  $\text{CH}_2\text{F}_2$  by the flame radicals H, O, OH, and F were evaluated in this work. In our evaluation, we utilized rate constants from the literature [15-21] and then fit them to extended Arrhenius rate expressions to provide rate constants over a wide range of temperatures. Depending upon the reaction, available data, and fitting procedures, we estimate uncertainty factors on the order of about (1.3 to 1.6) for these reactions.

The rate constants for  $\text{CHF}_2 + \text{O}_2 \rightarrow \text{CF}_2\text{O} + \text{OH}$  and  $\text{CHF} + \text{O}_2 \rightarrow \text{CHFO} + \text{O}$  were estimated by analogy to those for  $\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{OH}$  and  $\text{CF}_2 + \text{O}_2 \rightarrow \text{CF}_2\text{O} + \text{O}$ , respectively [22-23]. Both of the former reactions are significantly more exothermic ( $\sim 100 \text{ kJ mol}^{-1}$ ) than the reference reactions, and consequently should have much smaller barriers. For the  $\text{CHF}_2 + \text{O}_2$  and  $\text{CHF} + \text{O}_2$  reactions, we initially estimated activation energies on the order of (15 to 20)  $\text{kJ mol}^{-1}$  and (20 to 25)  $\text{kJ mol}^{-1}$ , but our optimizations compared to our measured flame speeds suggest somewhat smaller activation energies – on the order of (5 to 15)  $\text{kJ mol}^{-1}$  and (15 to 25)  $\text{kJ mol}^{-1}$ , respectively.

The rate expression for  $\text{CHF}_2 + \text{CHF}_2 \rightarrow \text{CHF}=\text{CF}_2 + \text{H}$  used in this work is from the earlier ab initio transition state and RRKM calculations by Burgess et al [24]. Although this is a primary pathway, this reaction has a small impact on flames speeds ( $< 3 \%$ ) and combustion – it simply provides a pathway to products. We utilized the rate expression for  $\text{CHF} + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{HF}$  from the ab initio transition state and RRKM calculations of Zachariah et al [25]. This reaction is a major destruction pathway for CHF and the primary pathway leading to the formation of  $\text{HO}_2$  ( $\text{CH}_2\text{O} + \text{OH} \rightarrow \text{CHO} + \text{H}_2\text{O}$ , followed by  $\text{CHO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$ ). This reaction, however, contributes a negligible amount ( $< 0.1 \%$ ) to changes in flame speeds – it is largely a conduit for establishing steady state concentrations during the pre-ignition process.

For the reactions  $\text{R}\cdot (\text{CHF}_2, \text{CF}_2, \text{CHF}) + \text{X} (\text{H}, \text{O}, \text{OH}, \text{F})$ , we utilized rate constants from the literature. These reactions are generally very fast and contribute negligible amounts to flame speeds and little to the combustion chemistry other than to provide pathways to complete combustion. Similarly, reactions involving CHFO,  $\text{CF}_2\text{O}$ , and CFO, contribute negligible amounts to changes in flame speeds, and provide pathways to combustion products.

**Table 1:** Rate parameters for elementary reactions employed in the model. The rate constants have the Arrhenius form  $k = Ae^{-E/RT}$  where A, E, and R are the pre-exponential, activation energy, and the gas constant, respectively. Units are mol, cm<sup>3</sup>, s, kJ. Note: these are only rate expressions developed as part of this work. Rate expressions for other reactions used in the model were taken from the literature (see text).

<b>Reaction</b>	<b>A</b>	<b>E</b>
CH <sub>2</sub> F <sub>2</sub> + M → CHF + HF + M	5.9E+17	295.0
CH <sub>2</sub> F <sub>2</sub> → CHF + HF	4.9E+11	272.0
CH <sub>2</sub> F <sub>2</sub> + H → CHF <sub>2</sub> + H <sub>2</sub>	2.5E+14	62.5
CH <sub>2</sub> F <sub>2</sub> + O → CHF <sub>2</sub> + OH	1.9E+14	56.3
CH <sub>2</sub> F <sub>2</sub> + OH → CHF <sub>2</sub> + H <sub>2</sub> O	1.7E+13	30.0
CH <sub>2</sub> F <sub>2</sub> + F → CHF <sub>2</sub> + HF	3.1E+14	19.4
CHF <sub>2</sub> + O <sub>2</sub> → CF <sub>2</sub> O + OH	4.9E+10	14.6
CHF + O <sub>2</sub> → CHFO + O	2.2E+13	20.9

#### 4. Results and Discussion

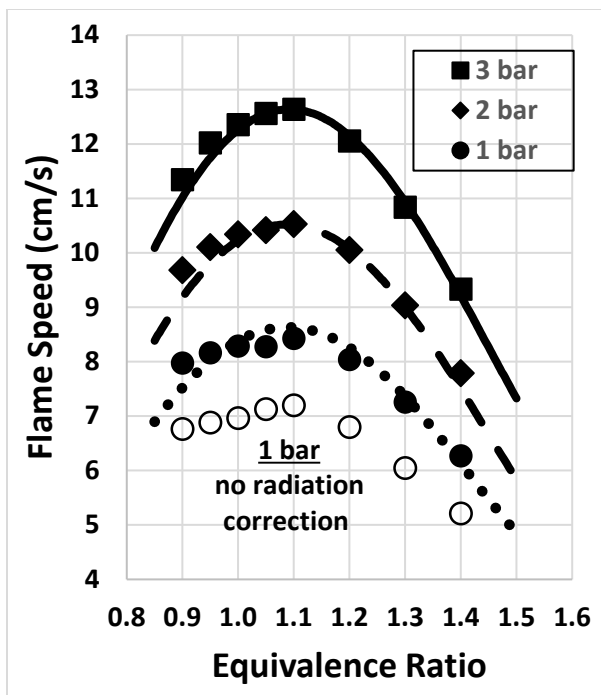
Figure 1 shows the experimentally-derived flames speeds (points) and the modeled flame speeds (curves). The solid symbols show the flame speeds corrected using an optically thin radiation model, while the open symbols show the uncorrected flames for 1 bar (2 and 3 bar data not shown for clarity). The deviations between the experimental flame speeds and the model predictions are on the order of (1 to 3) %. This is excellent agreement given that the uncertainties in the flames speeds are on the order of (10 to 20) % due to uncertainties in the rate constants which are multiplicative factors of about 1.5 to 2.0. As seen in Figure 1, the flame speeds are roughly linear with pressure suggesting the rate constant  $Rate = k_0[M] + k_1$  is approaching the low pressure limit.

The optically thin (limit) radiation model correction increases flames speeds by about (19±2) % relative to those computed using adiabatic flame temperatures (shown for 1 bar) and is independent (<1 %) of equivalence ratio. When estimated radiation absorption corrections are used for each major species, flame speeds decrease by about (8±3) % relative to those using the optically thin radiation model (not shown). Given the insensitivity of the corrections to equivalence ratio, the rate constants for the primary reactions contributing to flame speeds can be easily adjusted to correct for absorption of radiation. The correction using the optically thin radiation model translates into changes in the rate constants of about 40% (this is shown for 1 bar). This is lower than the uncertainties in the rate constants which have uncertainty factors of about 1.4 to 2.0.

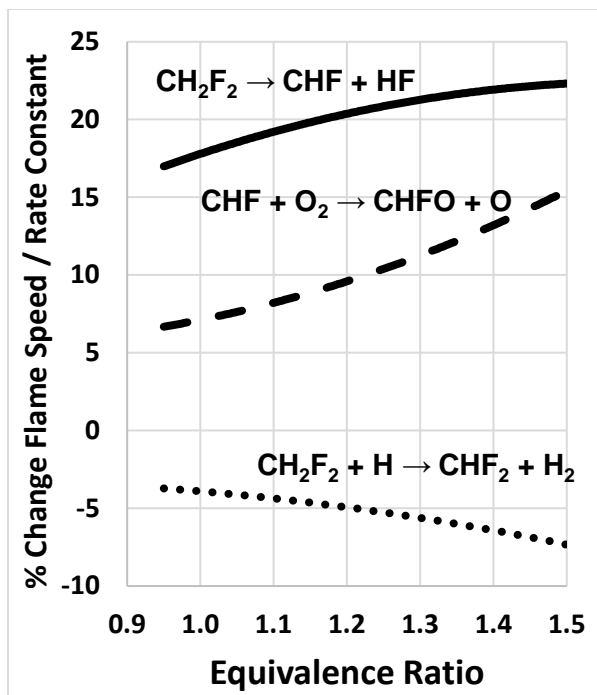
We note that under lean conditions (where flame stretch is most important) the measured flame speeds  $S_u(T,P)$  appear to be slightly higher (3 to 6) % than the modeled flame speeds. Recently, we have reprocessed the data better fitting the burning velocity / temperature-pressure curves  $S_u(T,P)$  and find lower burning velocities under lean conditions at 1 atm in good agreement (<3 %) with the model (these data are not shown, because we have not re-optimized model yet). In addition, we are currently in the process of optimizing the temperature and pressure dependencies of the rate constants by considering measurements that we have made using argon/O<sub>2</sub> mixtures (instead of air mixtures). The lower heat capacity of argon increases flame temperatures and thus increases flame speeds (by about a factor of 2). The refined experimental data and re-optimized rate constants are likely to provide better agreement between measured and model flame speeds.

Figure 2 shows the dependence of flame speeds for the three most important reactions as a function of equivalence ratio. The dependencies are on the order of (5 to 20) %, while all other reactions are less than 3 % and relatively independent of equivalence ratios. The quantity shown here is the percent change in flame speed relative to a change in rate constant. That is, a value of 20 % would mean increasing a rate constant by 10 % would result in an increase of 2 % in flame speed. The two most important reactions are the unimolecular decomposition of the refrigerant  $\text{CH}_2\text{F}_2 \rightarrow \text{CHF} + \text{HF}$  and the subsequent reaction of its decomposition product CHF with oxygen in the mixture  $\text{CHF} + \text{O}_2 \rightarrow \text{CHFO} + \text{O}$ . Both of these reactions contribute to increases in flame speeds. In contrast, H abstraction from the refrigerant  $\text{CH}_2\text{F}_2 + \text{H} \rightarrow \text{CHF}_2 + \text{H}_2$  causes a decrease in flame speeds – it inhibits the flame by consuming the radical H atom during pre-ignition that otherwise would be involved in radical chain branching leading to ignition.

Reaction pathway analysis and flame speed dependencies of rate constants show that burning of R-32 can be described by two quasi-separate reaction pathways. The first stage is pre-ignition driven by unimolecular decomposition of  $\text{CH}_2\text{F}_2$  forming CHF. The subsequent second stage is a combustion pathway driven by H abstraction by flame radicals H, O, OH, and F forming  $\text{CHF}_2$ . Both CHF and  $\text{CHF}_2$  then react quickly with the reactant  $\text{O}_2$  to form the fluorocarbonyls CHFO and  $\text{CF}_2\text{O}$ , respectively. The pre-ignition pathway is primarily responsible for generation of initial flame radicals and hence drives flame propagation, while the combustion pathway occurs after ignition, mediated by flame radicals, and drives the process to products. Interestingly, reactions in the combustion pathway actually inhibit ignition by consuming radicals needed for chain branching – tying up the chemistry in relatively stable intermediates that are slow to decompose.



**Figure 1:** Comparison between measured and model flame speeds for  $\text{CH}_2\text{F}_2/\text{air}$  mixtures.



**Figure 2:** Dependence of flame speeds on the three most important rate constants.



## 5. Conclusions

In this work, a mechanism for the combustion of the refrigerant R-32 ( $\text{CH}_2\text{F}_2$ ) in air mixtures was developed and validated through comparisons with measured flame speeds for a range of equivalence ratios (0.9 to 1.5) and pressures (1 to 3 bar) using a constant-volume spherical flame method. Premixed flame calculations were performed and analyzed to identify primary species and reactions contributing to flame speeds and combustion. We found that there were just three HFC reactions that contributed significantly to flame speeds. Their rate constants were optimized (within their uncertainty limits) and the model showed excellent agreement (<3 %) with measured flame speeds. Ongoing experiments and modeling will refine this model using other conditions such using Ar/O<sub>2</sub> mixtures (instead of air) to change flame temperatures and the addition of H<sub>2</sub>O and H<sub>2</sub> to change the concentration of flame radicals. The radiation parameters will also be improved. This work will be also extended to other refrigerants: the fluoroethanes R-125, R-134a, and R-152a and the hydrofluoroolefins HFO-1234yf (2,3,3,3-tetrafluoropropene) and HFO-1234ze (1,3,3,3-tetrafluoropropene).

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