



0360-1285(95)00009-7

THERMOCHEMICAL AND CHEMICAL KINETIC DATA FOR FLUORINATED HYDROCARBONS

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Abstract—A comprehensive, detailed chemical kinetic mechanism was developed and is presented for C_1 and C_2 fluorinated hydrocarbon destruction and flame suppression. Existing fluorinated hydrocarbon thermochemistry and kinetics were compiled from the literature and evaluated. For species where no or incomplete thermochemistry was available, these data were calculated through application of *ab initio* molecular orbital theory. Group additivity values were determined consistent with experimental and *ab initio* data. For reactions where no or limited kinetics were available, these data were estimated by analogy to hydrocarbon reactions, by using empirical relationships from other fluorinated hydrocarbon reactions, by *ab initio* transition state calculations, and by application of RRKM and QRRK methods. The chemistry was modeled considering different transport conditions (plug flow, premixed flame, opposed flow diffusion flame) and using different fuels (methane, ethylene), equivalence ratios, agents (fluoromethanes, fluoroethanes) and agent concentrations. This report provides a compilation and analysis of the thermochemical and chemical kinetic data used in this work.

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1. INTRODUCTION

1.1. Overview

The thermochemical and chemical kinetic data presented here were compiled as a part of flame-inhibition modeling work that was part of a large, short-term, intensive effort at NIST (A. Grosshandler *et al.*, 1994) that evaluated (for the U.S. Air Force, Navy, Army and Federal Aviation Administration) potential fluorinated hydrocarbons and other agents as replacements for Halon 1301 (CF₃Br). The modeling effort complemented the many experimental measurements in the overall NIST program, which characterized the effectiveness of various potential replacements. Our work focused on agent chemistry. This

report provides documentation of the thermochemical and chemical kinetic data used in the modeling work. Further details of the evaluation of the thermochemical and chemical kinetic data and the *ab initio* calculations will be provided elsewhere, as will the results of the simulations of flame inhibition.

Halon 1301 is very effective as a chemical extinguisher. However, it is also extremely effective for depleting stratospheric ozone. Consequently, its production and use are restricted. The major objective of the modeling part of the overall work was to provide a chemical basis for rationalizing the relative degree of effectiveness of each candidate agent. A fundamental understanding of the chemistry of these agents in hydrocarbon flames should facilitate identification of desired characteristics of effective agents.

That is, utilization of simple chemical concepts should enable screening and selection of potential agents with minimal time and human resources.

In order to accomplish this goal, it was necessary to develop a chemical mechanism based on elementary reaction steps for their destruction, their participation in and influence on hydrocarbon flame chemistry, as well as for prediction of potential by-products of incomplete combustion. However, neither a comprehensive mechanism nor a general review of the relevant chemistry existed prior to this study. Consequently, a significant effort was required simply in order to construct such a comprehensive mechanism prior to its use in any simulations. Further refinement of the mechanism requires experimental validation through comparisons with flame and flow reactor measurements. A few studies have already been completed (Westmoreland *et al.*, 1993; Burgess *et al.*, 1994; Westmoreland *et al.*, 1994; Babushok *et al.*, 1994; Daniel *et al.*, 1994; Burgess *et al.*, 1995; Babushok *et al.*, 1995; Linteris and Truett, 1995).

The focus of the mechanism development work was restricted to the chemistry involving only fluoromethanes and fluoroethanes. This includes the four candidate agents specifically being considered as replacements (i.e. CH_2F_2 , $\text{CF}_3\text{-CH}_2\text{F}$, $\text{CF}_3\text{-CHF}_2$, $\text{CF}_3\text{-CF}_3$), as well as all of the other possible fluoromethanes and fluoroethanes. Larger fluorinated hydrocarbon agents (e.g. C_3F_8) and chlorine-substituted agents (e.g. CHF_2Cl) were not explicitly considered in our study, because these additions significantly increase the complexity of the chemistry that must be considered. However, the effectiveness of each can be estimated to some degree by analogy to the other agents that were studied. This can be done by using the qualitative trends observed and the fundamental understanding of the chemistry developed by this and future work.

The complete sets of fluoromethanes and fluoroethanes were studied for two basic reasons. These are discussed below.

First, when the four specific candidate agents being considered decompose in the flame, they generate a pool of fluorinated hydrocarbon stable species and radicals, which results in the formation of many of the other fluoromethanes and fluoroethanes. Consequently, in order to adequately describe the decomposition of the four specific agents (and resultant chemistry), it is necessary to describe the chemistry of all of the intermediates and products that are created, including most of the other fluoromethanes and fluoroethanes. For example, the lowest energy and primary decomposition pathway for one of the candidate agents, $\text{CF}_3\text{-CF}_3$, involves dissociation of the C-C bond to form (two) $\cdot\text{CF}_3$ radicals. These $\cdot\text{CF}_3$ radicals will then react with methyl radicals, $\cdot\text{CH}_3$, which are present in significant concentrations in hydrocarbon flames. This radical-radical combination reaction has two decomposition channels whose relative importance is dependent upon temperature

and pressure. One channel results in the formation of a fluoroethylene, $\text{CH}_2\text{=CF}_2$ (and HF by-product). The other channel results in the formation of another fluoroethane, $\text{CH}_3\text{-CF}_3$. It is important that the mechanism adequately predicts the combustion products, the magnitude and rate of heat release in the flame, and ultimately the effectiveness of the added agent. Consequently, this requires that the mechanism is also able to describe correctly the decomposition of the two additional stable fluorinated hydrocarbon species ($\text{CH}_3\text{-CF}_3$, $\text{CH}_2\text{=CF}_2$). When one considers all decomposition channels for both the candidate agents and their decomposition products, one essentially must include all the chemistry describing almost all of the fluoromethanes and fluoroethanes.

Second, given that there are to date very little experimental data with which to make comparisons, it is imperative to provide a level of self-consistency to this purely modeling work by considering a range of modeling parameters, including different reactor/flame geometries, different fuels, different (potential) agents, and many other conditions. In doing so, it allowed us to develop confidence in the validity of the qualitative trends that we observed. Quantitative prediction of the absolute or even relative effectiveness of the specific agents will require successful comparison of the simulations with experimental measurements.

1.2. Background

There has been a significant amount of work over many years that has investigated the effectiveness of halogenated fire suppressants, as well as other types of fire suppressants (see references 574–643 for Section 6.12. Flame Inhibition: Halogens and references 644–689 for Section 6.13. Flame Inhibition: Non-Halogens). We will not review this body of work, but refer the reader to these and other relevant sources. A large part of our work is based on the pioneering work in this area by Biordi and co-workers, (e.g., Biordi *et al.*, 1973), Dixon-Lewis (e.g., Dixon-Lewis, 1979), Fristrom (e.g., Fristrom and Van Tiggelen, 1979) and Westbrook (1983). In earlier experiments on a range of candidates, CF_3Br was identified as being very effective for extinguishing flames. However, the mechanism for inhibition by CF_3Br was not understood. Biordi and co-workers measured both stable and radical species in methane flames doped with CF_3Br using a flame-sampling molecular beam mass spectrometer. Many of the relevant elementary reactions that describe the decomposition of CF_3Br , its chemistry, and its influence on hydrocarbon flames were determined in this work. Westbrook developed the first comprehensive chemical mechanism to describe in detail the chemistry of CF_3Br and modeled inhibition in hydrocarbon flames. As a result of this work, it is generally agreed

that flame suppression by bromine-containing compounds is a result of catalytic destruction of a hydrogen atom species by bromine atoms. The ability of bromine to recycle in the chemical system in the flame is directly related to the weak molecular bonds formed by bromine. Thus, bromine, when complexed in molecules such as CF_3Br , CH_3Br , HBr , and Br_2 , can regenerate bromine atoms through a number of reactions. It was also determined in these studies that $\cdot\text{CF}_3$, formed by decomposition of CF_3Br , also removes hydrogen atoms by competition with radicals important to combustion (e.g. H , O , OH , HO_2).

There are a variety of ways in which fire suppressants act to inhibit hydrocarbon flames. Most of these effects are intimately related. For example, heat loss means a temperature decrease, which causes the chemistry to slow, which means fewer radicals leading to product formation, which means less heat generated, which results in a further temperature decrease, and so on. One can separate suppression effects into two general categories: physical and chemical (although there is overlap). Chemical effects are directly related to the characteristics of the specific molecule (e.g. H , F , or Cl substitution), while physical effects, in general, are not. For example, the heat capacity of a molecule is a physical effect, since to a first approximation it is largely a function of the number of atoms in the molecule and their connectivity but not the identity of the molecule (i.e. its chemical composition).

There are a number of physical effects that relate to fluid mechanics, mass transport, and heat transport processes that were not specifically studied as a part of this modeling work. The physical effects which should be taken into account are, for example, PVT properties (pressure–volume–temperature), discharge dynamics, dispersion mechanics, as well as more complex flow reactor geometries than could be considered in this work. We will not discuss these physical effects in any detail here. However, it is necessary to understand the impact of these effects as they relate to our results in order to provide a framework for transfer of the results of our simulations to more realistic conditions. Some of the fluid mechanics and mass transport effects include dilution, turbulent mixing, diffusive mixing, thermal diffusion, and buoyancy. Heat-related effects, which cannot directly be addressed in the simulations, include the latent heat of vaporization and non-adiabatic effects, such as radiative cooling or heat losses for flames attached to a cold surface.

There are a number of different types of chemical effects. Most of these involve different competing factors. First, all of the fluorinated hydrocarbons will eventually decompose and then burn (forming CO_2 , H_2O , and HF). This liberates heat and increases flame temperatures (this speeds flame chemistry). On the other hand, the agents considered as replacements are large molecules with many atoms. Consequently, their high heat capacities may result

in a decrease in flame temperature prior to complete combustion (this slows flame chemistry). The competition between these two factors is strongly dependent upon conditions; most important of which is the mechanics of mixing fuel and oxidizer. Another set of competing effects involves fluorinated radicals produced by agent decomposition. These radicals are slower to burn than their pure hydrocarbon analogues, because the C-F bond is significantly stronger than the C-H bond. Consequently, reactions involving these radicals may effectively compete with analogous pure hydrocarbon chemistry by creating less flammable intermediates, thereby inhibiting combustion of the hydrocarbon fuel. For example, since the agents are added to the air stream, their immediate decomposition products (radicals) are formed in oxygen-rich, relatively cold regions of the flame. Consequently, these radicals may be involved in termination steps, such as $\cdot\text{CF}_3 + \text{HO}_2 \cdot \rightarrow \text{CHF}_3 + \text{O}_2$, slowing radical chain reactions and inhibiting the flame. These radicals also compete with hydrocarbon radicals for important H , O , and OH radicals. On the other hand, these radicals also react with stable molecules in the colder air stream (e.g. O_2), generating more radicals, such as oxygen atoms, and thereby initiating chemistry or promoting combustion of the fuel.

1.3. Mechanism Development

We constructed a large comprehensive reaction set or 'mechanism' for fluorinated hydrocarbon chemistry involving C_1 and C_2 stable and radical hydrocarbon species, including partially oxidized fluorinated hydrocarbons. The mechanism should be considered only a framework for future model development, rather than a finished product. Future refinements will require experimental validation by high-temperature flow reactor, premixed flame, and diffusion flame measurements, as well as measurements of important, yet currently uncertain rate constants.

2. THERMOCHEMISTRY

2.1. Overview

Existing thermochemical data were compiled and evaluated. Where little or no data existed for potential species of interest (most of the radicals), we estimated that thermochemistry using both empirical methods, such as group additivity (Benson, 1976) and also through application of *ab initio* molecular orbital calculations (Melius, 1990, Curtiss *et al.*, 1991; Frisch *et al.*, 1992). In all cases (experimental, empirical, and *ab initio*), significant effort was made to utilize thermochemical data for each species that was consistent with data for all other species.

There are a number of general sources of relevant compiled and evaluated thermochemical data. These include *The Chemical Thermodynamics of Organic Compounds* (Stull *et al.*, 1969), *JANAF Thermochemical Tables* (Stull and Prophet, 1971; Chase *et al.*, 1985), *Thermochemical Data of Organic Compounds* (Pedley *et al.*, 1986), *TRC Thermodynamic Tables* (Rodgers, 1989), *Physical and Thermodynamic Properties of Pure Chemicals* (Daubert and Danner, 1985), *NIST Structures and Properties Database and Estimation Program* (Stein *et al.*, 1991), and *Thermodynamic Properties of Individual Substances* (Gurvich *et al.*, 1991). There are two compilations/evaluations of fluorinated hydrocarbons in the *Journal of Physical and Chemical Reference Data: 'Ideal Gas Thermodynamic Properties of Six Fluoroethanes'* (Chen *et al.*, 1975) and *'Ideal Gas Thermodynamic Properties of Halomethanes'* (Kudchadker and Kudchadker, 1978). There are two compilations/evaluations of fluorinated hydrocarbons in the *Russian Chemical Reviews: 'Thermochemistry of Halogenomethanes'* (Kolesov, 1978) and *'Thermochemistry of Haloethanes'* (Kolesov and Papina, 1983). There are several individual sources of more recent data for thermochemistry that are relevant. These include *'Thermochemistry of Fluorocarbon Radicals'* (Rodgers, 1978), *'Hydrocarbon Bond Dissociation Energies'* (McMillen and Golden, 1982), *'A Kinetic Study of the Reactions of OH Radicals with Fluoroethanes. Estimates of C-H Bond Strengths in Fluoroalkanes'* (Martin and Paraskevopoulos, 1983) and *'Halomethylenes: Effects of Halogen Substitution on Absolute Heats of Formation'* (Lias *et al.*, 1985). There are numerous other references with thermodynamic data for fluorinated hydrocarbons that we have compiled as part of this work. These are included in the reference section and some of them will be cited and, possibly, be discussed in more detail in the relevant sections. References for thermochemical data can be found in the References Section 6.2, see Refs 1–47, (General Thermochemistry and Kinetics), Section 6.3, see Refs 48–85, (Hydrocarbon Chemistry), Section 6.4 see Refs 86–119, (Fluorine Chemistry), Section 6.5 see refs 120–250 (Fluorocarbon Thermochemistry), and Section 6.6 see Refs 251–278, (Oxidized Fluorocarbon Thermochemistry).

It should be noted that for some of the stable species and for many of the radicals, we have relied on recent *ab initio* calculations of thermochemical data. This includes both *ab initio* calculations done as part of our work and those done previously by other workers. Tschuikow-Roux and co-workers have calculated thermochemistry for the fluoroethyl radicals (Chen *et al.*, 1990a, 1990b, 1991a, 1991b). A brief discussion of the BAC-MP4 calculations can be found in Section 2.5. Further details of these calculations can be found elsewhere (Burgess *et al.*, 1994; Zachariah *et al.*, 1995). More recent thermochemistry for other *ab initio* calculations may be found elsewhere (Berry *et al.*, 1995).

The thermochemical data that was used is given in Tables 1–3 for hydrogen/oxygen and hydrocarbon species (Table 1), H/F species and C₁ fluorocarbons (Table 2), and C₂ fluorocarbons (Table 3). These tables include enthalpies of formation, entropies at standard state, and temperature-dependent heat capacities. Comparisons between our calculated values (Zachariah *et al.*, 1995) and different literature values (experimental, estimated) for heats of formation are given in Table 4. Reported uncertainties in the literature values are also given in Table 4.

A discussion of the uncertainties in the thermochemical data is given in the text with each class of species. The literature values include those that have been calculated using *ab initio* methods. A critical evaluation of the *ab initio* values in comparison with experimentally derived values is given elsewhere (Zachariah *et al.*, 1995). In each case where the uncertainty in the data from the literature was not assigned, we have provided a value based on our evaluation of the data and typical uncertainties for that type of data.

The literature values for heats of formation consist of a number of different types of data. Many are good quality, experimentally derived values based on heats of combustion or heats of reaction data, where the other reactants and products have well-established heats of formation. The uncertainty in these data are typically less than 4 kJ mol⁻¹. Some of the data, although experimentally derived, have somewhat higher uncertainties due to side reactions or where the other reactants and products have somewhat uncertain heats of formation. Typically, these values have heats of formation with uncertainties of about 4–8 kJ mol⁻¹.

In some cases, the literature values are based, in whole or in part, on bond additivity, group additivity, or other trends in heats of formation of related species. Typically, these values have heats of formation with uncertainties of about 8–12 kJ mol⁻¹. Many of the radicals have literature values for their heats of formation that were determined using the heats of formation of the parent species and bond dissociation energies that were either indirectly measured or were reasonable estimates based on trends in other molecules. For example, Martin and Paraskevopoulos (1983) have estimated C–H bond strengths in fluoroethanes and fluoroethanes (and, consequently, heats of formations for the fluoromethyl and fluoroethyl radicals) through correlations between the rates of hydrogen atom abstraction by OH radicals, C–H vibrational frequencies, and known C–H bond strengths. We have supplemented these data with our own estimates in order to provide heats of formation for the other fluoroethyl radicals in the absence of other literature values.

The thermochemical data in Tables 1–3 include entropy and temperature dependent heat capacity data, in addition to heat of formation data. References for all of these data are given in the tables. In

the following sections, there are no comparisons or discussions of the entropy and heat capacity data, because in most cases there is only a single source of data. Furthermore, the uncertainties in these data are largely dependent upon uncertainties in low-frequency bonds and barriers-to-rotation (for molecules with hindred rotors) and it is outside the scope of this work to quantitatively evaluate these data. The reader is referred to the original sources. However, based on inspection of the experimentally derived entropies, as well as comparing these data to that calculated using *ab initio* structures, one concludes that uncertainties in entropies at standard state are typically less than $0.5 \text{ J mol}^{-1} \text{ K}^{-1}$. Where there is uncertainty in low-frequency modes or barriers-to-rotation, uncertainties in entropies increase to about 2 J mol^{-1} . These values correspond to uncertainties in equilibrium constants of about 5–30% (and thus, any rate constants calculated using equilibrium constants). In contrast, uncertainties in heats of formation are typically of the order of 8 kJ mol^{-1} . This corresponds to a significantly higher uncertainty in the rate constants, for example, a factor of 2 at 1500 K. That is, uncertainties in rate constants due to uncertainties in entropies at standard states are typically very small compared to these due to uncertainties in heats of formation.

2.2. *H/O/F and Hydrocarbon Species*

We used standard hydrogen/oxygen and hydrocarbon thermochemistry (see Table 1), most of which can be found in the JANAF tables (Stull and Prophet, 1971; Chase *et al.*, 1985) or in a Sandia compilation (Kee *et al.*, 1987), as can data for fluorine and HF (see Table 2). There is a more recent value for the heat of formation of HF (Johnson *et al.*, 1973). However, we used the JANAF value for consistency, because many thermochemical and rate data for fluorinated species are based on the JANAF recommendation. More recent data on thermochemistry for C_2H_3 and HCO have been utilized. Future mechanism refinements should include re-adjustment of any other thermochemistry (or rate constants) that are based on older values for the heats of formation of these species.

Other simple species (e.g. F_2 , FO , HOF, FOF, FOO , HOOF) were initially considered in the mechanism but were later excluded because they did not contribute to the overall chemistry. For this reason, thermochemical data for these species are not included in Table 2.

2.3. *C₁ Fluorinated Hydrocarbons*

2.3.1. *Fluoromethanes*

We chose to employ heats of formation for the fluoromethanes as recommended by Kolesov (1978)

with the entropy and heat capacity data found in a review article (Rodgers *et al.*, 1974) in the *Journal of Physical and Chemical Reference Data* (JPCRD). We have calculated heats of formation for the fluoromethanes (Zachariah *et al.*, 1995) using the BAC-MP4 method (Melius, 1990) and found the calculated values to be within about 2 kJ mol^{-1} of the recommended literature values (see Table 4).

There are a number of sources of compiled or evaluated thermochemical data for the fluoromethanes (CH_3F , CH_2F_2 , CHF_3 , and CF_4). Thermochemical data for the fluoromethanes has been reviewed by Lacher and Skinner (1968), by Stull *et al.* (1969), and by Cox and Pilcher (1970). Thermochemical data can also be found in the JANAF tables (Stull and Prophet, 1971), which has been subsequently reevaluated in JPCRD (Rodgers *et al.*, 1974), by Pedley *et al.* (1986), and by Gurvich *et al.* (1991). The most recent edition of the JANAF tables (Chase *et al.*, 1985) did not reevaluate thermochemical data for the fluoromethanes. Recommendations for the heats of formation of the fluoromethanes have also been made by Kolesov (1978). Gelles and Pitzer (1953) have tabulated entropies at standard state and heat capacities as a function of temperature for the fluoromethanes (and other halogenated methanes).

Heats of formation for CH_2F_2 and CF_4 are the best known, with uncertainties of less than 1.5 kJ mol^{-1} , and are derived from their heats of combustion. The recommended value for the heat of formation of CH_2F_2 is based on a measurement by Neugebauer and Margrave (1958) of the heat of combustion of CH_2F_2 . The heat of formation of CF_4 is based on measurements of a number of different heats of reactions involving CF_4 by Scott *et al.* (1955), Good *et al.* (1956), Neugebauer and Margrave (1956), Cox *et al.* (1965), Wood *et al.* (1967), Domalski and Armstrong (1967), and Greenberg and Hubbard (1968).

The heat of formation of CHF_3 has a slightly higher uncertainty (than for CH_2F_2 and CF_4) of about 4 kJ mol^{-1} due to side reactions (producing CF_4) in its combustion. The recommended value for the heat of formation of CHF_3 is based on a heat of combustion measurement by Neugebauer and Margrave (1958). The heat of formation of CHF_3 has also been calculated using equilibrium data with CF_3Br and CF_3I as measured by Corbett *et al.* (1963), Goy *et al.* (1967), and Coomber and Whittle (1967). The heat of formation of CHF_3 can also be calculated assuming a heat of formation for $\cdot\text{CF}_3$ and kinetic data (forward and reverse reactions) involving HCl, HBr, and HI as measured by Coomber and Whittle (1966), Amphlett and Whittle (1968), and Goy *et al.* (1967), respectively.

The heat of formation of CH_3F has been estimated (with an uncertainty of about 10 kJ mol^{-1}) employing empirical trends in heats of formation of other fluoromethanes, since there are no experimentally derived

values (other than from appearance potential measurements). Although CH_3F is unlikely to be a key species in fluorinated hydrocarbon-inhibited hydrocarbon flames, as the simplest fluorinated hydrocarbon, its heat of formation is significant as a reference point for heats of formation of other fluorinated hydrocarbons. Empirical estimates for the heat of formation of CH_3F have also been made by Zahn (1934), Allen (1959), Bernstein (1965), Rodgers (1967), and Lacher and Skinner (1968). The recommended value in the JANAF tables (Stull and Prophet, 1971) is based on appearance potential for CH_3^+ from CH_3F measured by Lossing *et al.* (1954). Dibeler and Reese (1955) and Tsuda *et al.* (1964) have also measured roughly the same appearance potential.

2.3.2. Fluoromethyl radicals

We chose to employ heats of formation for the fluoromethyl radicals as recommended by McMillen and Golden (1982). For entropies at standard state and heat capacity data, we used values for $\cdot\text{CF}_3$ from the JANAF tables. Since (to our knowledge) no experimentally derived entropy and heat capacity data exist for $\cdot\text{CH}_2\text{F}$ and $\cdot\text{CHF}_2$, we used that derived from our BAC-MP4 *ab initio* calculations. Heats of formation for the fluoromethyl radicals estimated using the BAC-MP4 method are within about 4 kJ mol^{-1} of the recommended literature values (see Table 4).

There are several sources of compiled or evaluated thermochemical data for the fluoromethyl radicals. Thermochemical data for the perfluoromethyl radical ($\cdot\text{CF}_3$) can be found in the JANAF tables (Stull and Prophet, 1971) and have been reevaluated subsequently by Rodgers (1978). The heat of formation of $\cdot\text{CF}_3$ has an uncertainty of about 5 kJ mol^{-1} . Experimentally derived heats of formation (from bond dissociation energies and heat of reactions) for all the fluoromethyl radicals ($\cdot\text{CH}_2\text{F}$, $\cdot\text{CHF}_2$, $\cdot\text{CF}_3$) can be found in evaluations by McMillen and Golden (1982) and Pickard and Rodgers (1983) with uncertainties of less than 10 kJ mol^{-1} .

The evaluated thermochemical data for $\cdot\text{CH}_2\text{F}$ and $\cdot\text{CHF}_2$ are based on a number of different experimental measurements. Okafo and Whittle (1974) have used heat of reaction data to determine the bond dissociation energy for $\text{CHF}_2\text{-Br}$, from which the heat of formation of $\cdot\text{CHF}_2$ can be calculated. Martin and Paraskevopoulos (1983) have measured the rates of reaction of OH with some fluoromethanes and fluoroethanes and developed correlations between C-H bond dissociation energies, C-H stretching frequencies, and rates of abstraction of hydrogen atoms by OH radicals from fluoroalkanes. From heats of formation of the parent fluoromethanes and estimated C-H bond dissociation energies, one can determine values for the heats of formation of $\cdot\text{CH}_2\text{F}$, $\cdot\text{CHF}_2$, and $\cdot\text{CF}_3$.

Whittle and co-workers have used heat of reaction data to determine the bond dissociation energies of $\text{CHF}_2\text{-H}$ and $\text{CHF}_2\text{-Br}$ (Okafo and Whittle, 1974), from which the heat of formation of $\cdot\text{CHF}_2$ can be calculated. Using kinetic data, bond dissociation energies for $\text{CH}_2\text{F-H}$ have been obtained by Pritchard and Perona (1969) and for $\text{CHF}_2\text{-H}$ by Kerr and Timlin (1971), from which one can calculate the heats of formation of the corresponding radicals.

The evaluated thermochemical data for $\cdot\text{CF}_3$ are based on a number of different experimental measurements. The heat of formation of $\cdot\text{CF}_3$ has been calculated assuming a heat of formation for CHF_3 and kinetic data (forward and reverse reactions) involving HCl, HBr, and HI, as measured by Coomber and Whittle (1966), Amphlett and Whittle (1968), and Goy *et al.* (1967), respectively. It can also be calculated assuming a heat of formation of CF_3I and kinetic data for its reaction with I_2 , as determined by Coomber and Whittle (1966). Pritchard and Thommarson (1964) used kinetic data from competing reactions to determine the $\text{CF}_3\text{-H}$ bond dissociation energy and, consequently, the heat of formation of $\cdot\text{CF}_3$ can be calculated assuming a heat of formation for CHF_3 . Whittle and co-workers have used heat of reaction data to determine the bond dissociation energies for $\text{CF}_3\text{-CF}_3$ (Coomber and Whittle, 1967), $\text{CF}_3\text{-Br}$ (Ferguson and Whittle, 1972), and $\text{CF}_3\text{-I}$ (Okafo and Whittle, 1975), from which the heat of formation of $\cdot\text{CF}_3$ can be calculated. Tsang (1986) has determined a value for the heat of formation of $\cdot\text{CF}_3$ based on the bond dissociation energy of $\text{CF}_3\text{-Br}$ from shock tube decomposition studies. Skorobogatov and co-workers have measured equilibrium constants for reactions of type $\text{CF}_3\text{-X} \leftrightarrow \cdot\text{CF}_3 + \text{X}$ and $\text{CF}_3\text{-X} + \text{X} \leftrightarrow \cdot\text{CF}_3 + \text{X}_2$ and determined bond dissociation energies for $\text{CF}_3\text{-Br}$ (Dymov *et al.*, 1991) and $\text{CF}_3\text{-I}$ (Skorobogatov *et al.*, 1992).

2.3.3. Fluoromethylenes and fluoromethylidyne radicals

We used heats of formation for $:\text{CF}_2$ as adopted by Rodgers (1978) and for $:\text{CHF}$ as provided by Pritchard *et al.* (1984). For entropies at standard state and heat capacity data of both species, we used values from the JANAF tables. We have calculated heats of formation for the fluoromethylenes (Zachariah *et al.*, 1995) using the BAC-MP4 method and find the calculated values to be within about 15 kJ mol^{-1} of the recommended literature values (see Table 4).

There are several sources of thermochemical data for the closed-shell fluoromethylenes ($:\text{CHF}$ and $:\text{CF}_2$). Thermochemical data for these species can be found in the JANAF tables (Stull and Prophet, 1971). Rodgers (1978) has recommended a value for the heat of formation of $:\text{CHF}$ based largely on kinetic data. Hsu *et al.* (1978) and Pritchard *et al.*

(1984) have independently made a recommendation for the heat of formation of $\cdot\text{CF}_2$ based on heat of reaction and kinetic data. Lias *et al.* (1985) have provided values for the heat of formation of both $\cdot\text{CHF}$ and $\cdot\text{CF}_2$ based on appearance and ionization potentials. Unfortunately (since $\cdot\text{CHF}$ and $\cdot\text{CF}_2$ are important species), there are significant uncertainties in their heats of formation. The values for $\cdot\text{CF}_2$ are the best ($\pm 10 \text{ kJ mol}^{-1}$) and are derived from a number of different types of measurements. The uncertainty in the heat of formation for $\cdot\text{CHF}$ is even greater ($\pm 30 \text{ kJ mol}^{-1}$) due to the lack of direct, reliable data.

The experimental data for the heat of formation of $\cdot\text{CF}_2$ comes from a number of different measurements. The heat of formation of $\cdot\text{CF}_2$ has been calculated from heat of reaction or kinetic data from the decomposition of C_2F_4 by Modica and LaGraff (1965, 1966), by Zmbov *et al.* (1968), by Schug and Wagner (1978), and by Carlson (1971). Using equilibrium data in experiments by Farber *et al.* (1969), one can also determine a value. The heat of formation of $\cdot\text{CF}_2$ has also been calculated from the decomposition of various halomethanes: from the decomposition of CHF_3 by Schug and Wagner (1978), from the decomposition of CHF_2Br by Okafo and Whittle (1974), and from the decomposition of CHF_2Cl by Dalby (1964), Gozzo and Patrick (1964), Edwards and Small (1965), and Schug and Wagner (1968). The ionization potential of $\cdot\text{CF}_2$ has been used to estimate its heat of formation by Fisher *et al.* (1965), Pottie (1965), and Zmbov *et al.* (1968). Various appearance potential measurements by Walter *et al.* (1969), Berman *et al.* (1981), and Paulino and Squares (1991) have also been used to estimate a value for the heat of formation of $\cdot\text{CF}_2$. The ionization and appearance potential measurements have been reviewed in detail by Lias *et al.* (1985) and Paulino and Squires (1991).

Thermochemical data for fluoromethylidyne ($\cdot\text{CF}$) can be found in the JANAF tables (Stull and Prophet, 1971). Gurvich *et al.* (1991) have also provided thermochemical data for $\cdot\text{CF}$. In the latter review, more recent measurements by Hildenbrand (1975) were also considered, in addition to earlier measurements by Modica (1966) and Farber *et al.* (1969). We used the more recent value from Gurvich *et al.* (1991) for the heat of formation with the entropy and heat capacity data provided in the JANAF tables. The reported uncertainties in the heat of formation are about 10 kJ mol^{-1} . BAC-MP4 calculations yield a heat of formation for $\cdot\text{CF}$ (Zachariah *et al.*, 1995) that is within about $10\text{--}20 \text{ kJ mol}^{-1}$ of the recommended literature values.

2.3.4 Carbonyl fluorides and fluoromethoxy radicals

Thermochemical data for the carbonyl fluorides ($\text{CHF}=\text{O}$, $\text{CF}_2=\text{O}$, $\cdot\text{CF}=\text{O}$) can be found in the JANAF tables. We have employed these data. The

uncertainty in the heat of formation of $\text{CF}_2=\text{O}$ is reported to be about 2 kJ mol^{-1} . The JANAF recommendation for $\text{CF}_2=\text{O}$ is based on equilibrium and heat of reaction measurements by Ruff and Li (1939) and von Wartenberg and Riteris (1949). For the other two carbonyl fluorides, where there is little or no experimental data, the estimated uncertainty in their heats of formation are probably at least 15 kJ mol^{-1} .

Gurvich *et al.* (1991) have recommended a value for the heat of formation of $\cdot\text{CF}=\text{O}$ that is similar to the JANAF recommendation (about 8 kJ mol^{-1} higher). This recommendation is based on appearance potential measurements of MacNeil and Thynee (1969) and heat of reaction measurements by Heras *et al.* (1962).

We find that heats of formation for these species from our BAC-MP4 calculations (Zachariah *et al.*, 1995) are within about 20 kJ mol^{-1} of the recommended literature value, except for $\text{CF}_2=\text{O}$, where the calculated value is about 40 kJ mol^{-1} higher. Other *ab initio* calculations (Montgomery *et al.*, 1994; Schnieder and Wallington, 1994) using different approaches also predict a heat of formation for $\text{CF}_2=\text{O}$ that is higher (by about 30 kJ mol^{-1}) than the experimental value. Because of this significant difference, both uncertainties in the experimental measurements and *ab initio* calculations warrant further examination.

The greatest uncertainties here are for $\text{CHF}=\text{O}$ ($\pm 20 \text{ kJ mol}^{-1}$) and $\cdot\text{CF}=\text{O}$ ($\pm 10 \text{ kJ mol}^{-1}$), where there are little or no direct experimental data available and, consequently, their heats of formation were estimated (Stull and Prophet, 1971) using average bond dissociation energies from other related compounds. Given that reliable experimental data exists for the unimolecular decomposition of $\text{CHF}=\text{O}$ (Saito *et al.*, 1985), uncertainty in its heat of formation may be unimportant. However, under some conditions the bimolecular reaction $\cdot\text{CF}=\text{O} + \text{H}_2\text{O} \rightarrow \text{CHF}=\text{O} + \text{OH}$ (roughly 80 kJ mol^{-1} endothermic) may contribute. Consequently, uncertainty in the heat of formation of $\text{CHF}=\text{O}$ may play some role. In contrast, the heat of formation of $\cdot\text{CF}=\text{O}$ is very important, since there are no experimental data for its unimolecular decomposition, which is a primary decomposition pathway (competing with hydrogen atom combination followed by HF elimination).

We used an experimentally derived value for the heat of formation of the perfluoromethoxy radical $\text{CF}_3\text{O}\cdot$ (Batt and Walsh, 1982) with a reported estimated uncertainty of about 6 kJ mol^{-1} . For entropy at standard state and heat capacity data, we used that derived from our BAC-MP4 calculations (Zachariah *et al.*, 1995). The calculated heat of formation of $\text{CF}_3\text{O}\cdot$ is within about 30 kJ mol^{-1} of the experimentally derived value.

A number of other species, such as the other fluoromethoxy radicals ($\text{CH}_2\text{FO}\cdot$, $\text{CHF}_2\text{O}\cdot$), fluoromethanols (e.g. CF_3OH), or fluoromethylperoxy

radicals (e.g. $\text{CF}_3\text{OO}\cdot$), were initially considered in the mechanism (using *ab initio* thermochemical data). These species were later excluded, because they did not contribute to the overall chemistry. In many cases, these species were present in steady-state concentrations and, consequently, the creation and destruction reactions could be combined into a single overall reaction. Although these species may be important in atmospheric chemistry, they are present in extremely low concentrations at high temperatures in hydrocarbon-air flames.

2.4. C_2 Fluorinated Hydrocarbons

2.4.1. Fluoroethanes

We chose to use thermochemical data from a *Journal of Physical and Reference Data* (JPCRD) review (Chen *et al.*, 1975) for the six simple fluoroethanes ($\text{CH}_3\text{-CH}_2\text{F}$, $\text{CH}_3\text{-CHF}_2$, $\text{CH}_3\text{-CF}_3$, $\text{CH}_2\text{F-CF}_3$, $\text{CHF}_2\text{-CF}_3$, $\text{CF}_3\text{-CF}_3$). Thermochemical data for the three other fluoroethanes ($\text{CH}_2\text{F-CH}_2\text{F}$, $\text{CH}_2\text{F-CHF}_2$, $\text{CHF}_2\text{-CHF}_2$) were obtained from a variety of sources. For $\text{CH}_2\text{F-CH}_2\text{F}$, we used a heat of formation calculated using the C-C bond dissociation energy as determined by Kerr and Timlin (1971) and the heat of formation for $\cdot\text{CH}_2\text{F}$ as recommended by McMillen and Golden (1982). We used the heat of formation for $\text{CH}_2\text{F-CHF}_2$ as recommended by Lacher and Skinner (1968). For $\text{CHF}_2\text{-CHF}_2$, we used a heat of formation calculated using the C-C bond dissociation energy as determined by Millward *et al.* (1971b) and the heat of formation for $\cdot\text{CHF}_2$ as recommended by McMillen and Golden (1982). Standard-state entropy and heat capacities for these other three fluoroethanes were computed based on vibrational frequencies and moments of inertia from our *ab initio* calculations.

We have calculated heats of formation for the fluoroethanes (Zachariah *et al.*, 1995) using the BAC-MP4 method (Melius, 1990) and found the calculated values to be within about 10–20 kJ mol^{-1} of the recommended experimental or empirical values in the literature (see Table 4). Three of the fluoroethanes ($\text{CH}_2\text{F-CH}_2\text{F}$, $\text{CH}_2\text{F-CHF}_2$, $\text{CHF}_2\text{-CHF}_2$) have conformational isomers. At the MP4/6-31G(d,p)//HF/6-31G(d) level, the *trans* isomers are slightly more stable (about 4–7 kJ mol^{-1}) than the *gauche* isomers, except for $\text{CH}_2\text{F-CH}_2\text{F}$ where the energies are within about 0.5 kJ mol^{-1} .

We believe some reevaluation of all of the heat of formation data is warranted. For example, the heat of formation of $\text{CH}_3\text{-CF}_3$ recommended in the JPCRD review is based on old values for $\cdot\text{CH}_3$ and $\cdot\text{CF}_3$. In addition, employing a group additivity scheme with an ionic correction should yield better values for both $\text{CH}_2\text{F-CH}_2\text{F}$ and $\text{CHF}_2\text{-CHF}_2$ (see discussion below).

There are a number of sources of compiled or evaluated data for the fluoroethanes. Thermochemical data for some of the fluoroethanes can be found in JPCRD (Chen *et al.*, 1975) and the DIPPR compilation (Daubert and Danner, 1985). Recommendations for the heats of formation of some of the fluoroethanes have been made by Kolesov and Papina (1983) and Pedley *et al.* (1986). There are no experimentally derived heats of formation for two of the fluoroethanes ($\text{CH}_3\text{-CH}_2\text{F}$, $\text{CH}_2\text{F-CF}_3$). These have been estimated using bond additivity, group additivity, or other trends in heats of formation. However, there are significant uncertainties in using these procedures, because of non-covalent or ionic contributions to the stability of these species due to the high electronegativity of fluorine. For example, $\text{CH}_3\text{-CF}_3$ is about 33 kJ mol^{-1} more stable than predicted using heats of formation of $\text{CH}_3\text{-CH}_3$ and $\text{CF}_3\text{-CF}_3$. All three of these species have heats of formation that were derived from good quality experimental measurements. The additional stabilization can be rationalized as an ionic contribution to the C-C bond strength because of large differences in net charges on the carbon atoms of the $-\text{CH}_3$ and $-\text{CF}_3$ groups due to the high electronegativity of the fluorine atoms.

There are a number of different sources of experimental data for the heats of formation of the fluoroethanes. These various sources are described in the following.

The heat of formation of ethyl fluoride ($\text{CH}_3\text{-CH}_2\text{F}$) has been estimated (Chen *et al.*, 1975) using group additivity and heat of reaction data for propyl fluoride (Lacher *et al.*, 1956). A recommendation for the heat of formation of ethyl fluoride ($\text{CH}_3\text{-CH}_2\text{F}$) has also been given by Luo and Benson (1988) based on electronegativity correlations of heats of formation of substituted alkanes. This recommendation is significantly lower (15 kJ mol^{-1}) than other recommendations. This significant difference warrants further examination. $\text{CH}_3\text{-CH}_2\text{F}$ is unlikely to be important as a species in the fluorocarbon-inhibited hydrocarbon flames. However, as a simple, single-substituted fluorinated hydrocarbon (like CH_3F), its heat of formation is important as a reference point for the heats of formation of other species. For example, another $-\text{CH}_2\text{F}$ substituted fluoroethane, $\text{CH}_2\text{F-CF}_3$, has no experimentally derived heats of formation. Any uncertainties in the heats of formation and, consequently, stability of the fluoroethanes may influence product channels for fluoromethyl combinations (e.g. $\cdot\text{CH}_3 + \cdot\text{CF}_3 \rightarrow \text{CH}_3\text{-CF}_3$ versus $\cdot\text{CH}_3 + \cdot\text{CF}_3 \rightarrow \text{CH}_2=\text{CF}_2 + \text{HF}$).

Kolesov *et al.* (1968) have measured the heat of combustion of $\text{CH}_3\text{-CHF}_2$, from which one can calculate its heat of formation. The heat of formation of $\text{CH}_3\text{-CHF}_2$ could be determined from the enthalpy of hydrogenation of $\text{CF}_2=\text{CCl}_2$ as measured by Lacher *et al.* (1956), given that a reliable value

for the heat of formation of $\text{CF}_2=\text{CCl}_2$ could be obtained.

We calculated a heat of formation for $\text{CH}_2\text{F}-\text{CH}_2\text{F}$ based on the C–C bond dissociation energy ($368.6 \text{ kJ mol}^{-1}$) as determined by Kerr and Timlin (1971) and the heat of formation for $\cdot\text{CH}_2\text{F}$ ($-32.6 \text{ kJ mol}^{-1}$) as recommended by McMillen and Golden (1982). The bond dissociation energy was determined from the critical energy (E_0) calculated using RRKM analysis of experimental kinetic data for the thermal (Chang and Setser, 1969) and chemically activated decomposition of $\text{CH}_2\text{F}-\text{CH}_2\text{F}$.

Kolesov *et al.* (1965) have determined a heat of formation for CH_3-CF_3 by measuring its heat of combustion. Kinetic data for the forward and reverse reactions for $\cdot\text{CH}_3 + \cdot\text{CF}_3 \leftrightarrow \text{CH}_3-\text{CF}_3$ can be used to obtain a heat of formation for 1,1,1-trifluoroethane. Kinetic data for this reaction have been obtained by Giles and Whittle (1965), Pritchard and Perona (1970), and Chang *et al.* (1972). These data have been reviewed by Rodgers and Ford (1973).

The heat of formation of $\text{CH}_2\text{F}-\text{CHF}_2$ has been determined (Kolesov and Papina, 1983) from the enthalpy of hydrogen of $\text{CF}_2=\text{CFCl}$ as measured by Lacher *et al.* (1956).

We have calculated a heat of formation for $\text{CHF}_2-\text{CHF}_2$ based on the C–C bond dissociation energy ($382.4 \text{ kJ mol}^{-1}$) as determined by Millward *et al.* (1971b) and the heat of formation for $\cdot\text{CHF}_2$ ($-247.7 \text{ kJ mol}^{-1}$) as recommended by McMillen and Golden (1982). The bond dissociation energy was set equal to the activation energy for thermal decomposition of $\text{CHF}_2-\text{CHF}_2$, which was determined from analysis of experimental kinetic data.

The heat of formation of CHF_2-CF_3 can be obtained from equilibrium data with $\text{CF}_3-\text{CF}_2\text{Br}$ (and group additivity) as measured by Whittle and co-workers (Coomber and Whittle, 1967; Ferguson and Whittle, 1972) and from heat of reaction data for the bromination of $\text{CF}_2=\text{CF}_2$ (and group additivity) as measured by Lacher *et al.* (1956). In addition, one can calculate a value for the heat of formation for CHF_2-CF_3 from the heat of formation of the perfluoroethyl radical ($\text{CF}_3-\text{CF}_2\cdot$) and the $\text{CF}_3\text{CF}_2-\text{H}$ bond dissociation energy. Wu and Rodgers (1976) determined the heat of formation of the perfluoroethyl radical by measuring the enthalpy of its reaction with I_2 . Values for the bond dissociation energy of $\text{CF}_3\text{CF}_2-\text{H}$ have been determined by Bassett and Whittle (1972) and Martin and Paraskevopoulos (1983).

The heat of formation of CF_3-CF_3 has been determined from equilibrium data with CF_3Br as measured by Coomber and Whittle (1967b), with CF_3-CN as measured by Walker *et al.* (1970), and with CF_4 (and NF_3 as oxidizer) as measured by Sinke (1966).

2.4.2 Fluoroethyl radicals

In the absence of reliable experimental data, we used the calculated thermochemical data for the fluoroethyl radicals as provided by Tschuikow-Roux and co-workers (Chen *et al.*, 1990a, 1990b, 1991a, 1991b) for consistency. However, we believe some reevaluation of all of the heat of formation data (both experimental and *ab initio*) is warranted. For the radical $\text{CH}_3-\text{CHF}\cdot$, we used the average of the heats of formation reported by Martin and Paraskevopoulos (1983) and Tschuikow-Roux and Salomon (1987). For the three fluoroethyl radicals, $\text{CH}_2\text{F}-\text{CHF}\cdot$, $\text{CHF}_2-\text{CF}_2\cdot$, and $\text{CF}_3-\text{CHF}\cdot$, we calculated heats of formation based on C–H bond dissociation energies determined by Martin and Paraskevopoulos (1983). We note that heats of formation for the fluoroethyl radicals from our BAC-MP4 *ab initio* calculations (Zachariah *et al.*, 1955) are within about $10\text{--}20 \text{ kJ mol}^{-1}$ of the recommended literature values (see Table 4).

There are a number of sources of heats of formation for the fluoroethyl radicals. There are experimentally derived thermochemical data (Rodgers, 1978) for three of the fluoroethyl radicals ($\text{CH}_3-\text{CF}_2\cdot$, $\text{CF}_3-\text{CH}_2\cdot$, $\text{CF}_3-\text{CF}_2\cdot$). Heats of formation for the other radicals have been estimated using heats of formation for the fluoroethanes and C–H or C–F bond dissociation energies for $\text{CH}_3-\text{CHF}\cdot$ and $\text{CF}_3-\text{CHF}\cdot$ by Martin and Paraskevopoulos (1983), for $\text{CH}_3-\text{CHF}\cdot$ by Tschuikow-Roux and Salomon (1987), and for all the other fluoroethyl radicals in this work (see Table 4). Thermochemistry for all the fluoroethyl radicals have been calculated using *ab initio* molecular orbital theory by Tschuikow-Roux and co-workers (cited above). They used the experimentally derived heats of formation of the three fluoroethyl radicals recommended by Rodgers (1978). For the others, they used their calculated energies in conjunction with isodesmic–homodesmic reactions (with known experimental reaction enthalpies) to provide values that approach the ‘true’ heats of formation.

2.4.3 Fluoroethylenes and fluorovinyl radicals

There are six fluoroethylenes ($\text{CH}_2=\text{CHF}$, $\text{CH}_2=\text{CF}_2$, $\text{CHF}=\text{CHF}[Z]$, $\text{CHF}=\text{CHF}[E]$, $\text{CHF}=\text{CF}_2$, $\text{CF}_2=\text{CF}_2$), including the configurational isomers. In order to reduce the number of species in the reaction set, we use only the *Z* isomer of $\text{CHF}=\text{CHF}$, which is only slightly more stable ($\sim 1\text{--}4 \text{ kJ mol}^{-1}$).

We used the heat of formation of $\text{CH}_2=\text{CHF}$ as recommended by Gurvich *et al.* (1991). Entropy at standard state and heat capacity data were taken from the DIPPR compilation (Daubert and Danner, 1985). These data can also be found in the TRC Thermodynamic Tables (1990). The heat of formation data are based on measurements by Kolesov and Papina (1970) of the heat of combustion of vinyl

fluoride. Pedley *et al.* (1986) have also made a recommendation based on this experimental data. A heat of formation was also determined by Williamson *et al.* (1976) based on appearance potential measurements.

We have chosen to use heats of formation for CHF=CHF[E] and CHF=CHF[Z] based on appearance ionization potential measurements by Stadelman and Vogt (1980) and entropies at standard state and heat capacities based on geometries and vibrational frequencies from our BAC-MP4 *ab initio* calculations (Zachariah *et al.*, 1995). Gurvich *et al.* (1991) have also estimated heats of formation for these species using a bond additivity method. For CH₂=CF₂, we used the heat of formation recommended by Gurvich *et al.* (1991) with entropy at standard state and heat capacity data taken from Stull *et al.* (1969). Recommendations for the heat of formation for 1,1-difluoroethylene have also been made by Lacher and Skinner (1968), Stull *et al.* (1969), Cox and Pilcher (1970), and Pedley *et al.* (1986). All of these recommendations are based on heat of combustion measurements by Neugebauer and Margrave (1956) and Kolesov *et al.* (1962).

We used thermochemical data for CHF=CF₂ as recommended by Gurvich *et al.* (1991). The heat of formation data is based on an experimental measurement by Kolesov *et al.* (1962) of the heat of combustion of trifluoroethylene. Recommended values (also based on these experiments) can be found in the evaluations of Stull *et al.* (1969), Cox and Pilcher (1970), and Pedley *et al.* (1986).

We used thermochemical data for CF₂=CF₂ from the JANAF tables (Stull and Prophet, 1971). The recommended heat of formation is based on the heat of reaction data for conversion to amorphous carbon by Neugebauer and Margrave (1956) and Kolesov *et al.* (1962). Lacher and Skinner (1968), Stull *et al.* (1969), Cox and Pilcher (1970), Kolesov and Papina (1983), Pedley *et al.* (1986), and Gurvich *et al.* (1991) have all reviewed the existing experimental data and made recommendations. These evaluations were made based on a number of different sources of experimental heat of reaction data for perfluoroethylene, including the data of Lacher *et al.* (1949), Lacher *et al.* (1950), Kirkbride and Davidson (1954), von Wartenberg and Schiefer (1955), Duus (1955), Neugebauer and Margrave (1956), Lacher *et al.* (1956), Scott *et al.* (1956), Kolesov *et al.* (1962), and Edwards and Small (1964).

We note that the heats of formation for the fluoroethylenes that we have calculated using the BAC-MP4 *ab initio* method are within about 10 kJ mol⁻¹ of the recommended experimental values (see Table 4). At the MP4/6-31G(*d,p*)/HF/6-31G(*d*) level, the CHF=CHF[Z] isomer is about 0.9 kJ mol⁻¹ more stable than the *E* isomer.

There are seven fluorovinyl radicals (CHF=CH•[Z], CHF=CH•[E], CH₂=CF•, CHF=CF•[Z],

CHF=CF•[E], CF₂=CH•, CF₂=CF•), including the configurational isomers. In order to reduce the number of species in the reaction set, we used only the *Z* isomers which are only slightly more stable (~1–2 kJ mol⁻¹).

There are not any experimentally derived thermochemical data (to our knowledge) for the fluorovinyl radicals, other than the heat of formation for CF₂=CF•. The heat of formation of the perfluorovinyl radical has been estimated by Bryant (1962) based on trends in C–F bond dissociation energies for perfluorocarbons. Gurvich *et al.* (1991) recommended a value based on a review of appearance potential measurements by Thynee and MacNeil (1970), Lifshitz and Grajower (1972), and Bibby and Carter (1966). Due to the lack of experimental data for most of the fluorovinyl radicals, we chose to use thermochemical data from our BAC-MP4 *ab initio* calculations (Zachariah *et al.*, 1995) in order to provide a consistent set. We note that our calculated value is within about 10 kJ mol⁻¹ of the experimentally derived value that was recommended by Gurvich *et al.* (1991). At the MP4/6-31G(*d,p*)/HF/6-31G(*d*) level, the CHF=CH•[Z] and CHF=CF•[Z] isomers are about 1.3 and 1.7 kJ mol⁻¹, respectively, more stable than the *E* isomers.

2.4.4. Fluoroethynes, fluoroketenes, and fluoroketyl radical

Data on the thermochemistry of the fluoroethynes (C₂HF, C₂F₂) can be found in the JANAF tables (Stull and Prophet, 1971), however, with relatively large uncertainties: ±60 kJ mol⁻¹ and ±20 kJ mol⁻¹ in the heats of formation, respectively. Fluoroketenes (CHF=C=O and CF₂=C=O) and the fluoroketyl radical (•CF=C=O) can be formed through a number of channels. These channels are analogous to those considered in pure hydrocarbon chemistry for ketene (CH₂=C=O). To assess the importance of the fluoroketene species and relevant reactions, we included these species in the mechanism. There are not any experimentally derived data for these species. Consequently, we used data from our BAC-MP4 *ab initio* calculations (Zachariah *et al.*, 1995).

A number of other partially oxidized species, such as CH₃–CFO, were excluded from the mechanism based on the assumption that they would be only present in steady-state concentrations at flame temperatures. For lower temperatures, these species may become important and, consequently, our assumption should be reevaluated. It is possible that perfluoro-oxidized species, such as CF₃–CFO, may be present at flame temperatures. For example, since both •CF₃ and •CFO are present in significant concentrations, the combination of these species (and stabilization) may be a source of CF₃–CFO. This should be examined in future refinements of this mechanism.

2.5. BAC-MP4 *Ab Initio* Predictions

For a number of species considered in the reaction set, especially the radicals, there are little or no thermochemical data. Consequently, we have estimated the data using BAC-MP4 *ab initio* calculations

(see description below). In order to quantify the uncertainties in the calculated data, we have also performed calculations on many related species where there is good quality experimental data.

Structures, energies, and thermochemical data for a large number of C₁ and C₂ hydrocarbons, oxidized

Table 1. Enthalpy of formation, entropy, heat capacities for H/O, hydrocarbons

Species	$\Delta H_f^\circ(298)$ (kJ mol ⁻¹)	$S^\circ(298)$ (J mol ⁻¹ K ⁻¹)	$C_p^\circ(T)$ (J mol ⁻¹ K ⁻¹)							Ref.*	
			300	500	800	1000	1200	1500	2000		3000
N ₂	0.0	191.5	29.07	29.63	31.39	32.76	33.70	34.80	35.98	37.02	a
H ₂	0.0	130.6	28.87	29.27	29.58	30.16	31.07	32.35	34.23	37.11	a
O ₂	0.0	205.0	29.33	31.11	33.75	34.93	35.59	36.49	37.78	39.84	a
H ₂ O	-241.8	188.7	33.46	35.33	38.58	41.31	43.87	47.10	51.14	55.77	a
H ₂ O ₂	-136.1	232.9	43.57	51.65	59.80	63.64	66.75	70.50	74.80	78.91	a
H	218.0	114.6	20.78	20.78	20.78	20.78	20.78	20.78	20.78	20.78	a
O	249.2	160.9	21.89	21.25	20.98	20.91	20.88	20.84	20.82	20.94	a
OH	39.0	183.6	29.93	29.57	29.84	30.68	31.66	32.94	34.63	36.76	a
HO ₂	10.5	229.0	34.87	39.69	45.10	47.64	49.59	52.10	55.33	59.10	a
CH ₄	-74.9	186.0	35.26	46.60	62.75	72.15	78.71	86.32	94.49	101.36	a
·CH ₃	145.7	194.0	38.62	45.33	53.85	59.07	63.19	68.06	73.45	78.30	a
·CH ₂	387.0	195.5	34.50	37.15	41.57	44.21	46.36	49.11	52.45	55.33	a
·CH ₂	424.7	188.7	33.79	36.00	41.20	44.38	46.63	49.48	52.88	55.58	a
·CH	594.1	182.9	29.09	29.49	30.82	32.56	34.38	36.61	39.18	41.44	a
C ₂ H ₆	-83.9	229.0	52.61	77.89	108.05	122.59	132.68	144.83	158.64	171.05	a
C ₂ H ₅ ·	117.2	251.6	47.37	66.73	94.48	106.71	114.07	123.66	135.76	146.83	a
C ₂ H ₄	52.5	219.2	42.82	62.52	83.90	94.17	101.38	109.70	118.54	125.81	a
C ₂ H ₃ ·	294.5	227.9	45.77	57.82	71.91	78.77	83.27	89.21	96.90	104.31	a
C ₂ H ₂	226.7	200.9	44.44	54.73	63.90	68.23	71.97	76.46	81.65	87.09	a
CH ₃ OH	-201.1	239.6	43.98	59.64	79.80	89.53	96.40	104.66	114.00	121.99	a
CH ₃ O·	16.3	228.5	37.99	52.02	69.58	77.81	83.38	90.00	97.32	103.23	a
·CH ₂ OH	-17.2	246.3	47.38	60.16	73.37	78.62	82.59	87.65	93.73	98.76	a
CH ₂ O	-115.9	218.6	35.15	43.94	55.90	62.27	66.34	70.99	75.80	79.54	a
·CHO	43.5	224.5	34.49	38.81	44.93	48.20	50.22	52.53	54.96	57.04	a
CO	-110.5	197.5	29.08	29.85	31.86	33.25	34.15	35.17	36.27	37.21	a
CO ₂	-393.5	213.7	37.28	44.56	51.54	54.36	56.20	58.29	60.43	62.19	a
CH ₂ CO	-51.9	241.8	52.01	65.54	78.63	84.70	88.88	93.89	99.49	104.15	a
·CHCO	177.6	254.1	52.93	59.53	67.25	70.43	72.56	75.24	78.39	80.77	a
HCCOH	85.5	245.6	55.30	67.62	80.10	84.94	88.59	93.24	98.81	103.38	a

* See footnotes for Table 3.

Table 2. Enthalpy of formation, entropy, heat capacities for H/F/O, C₁ fluorocarbons

Species	$\Delta H_f^\circ(298)$ (kJ mol ⁻¹)	$S^\circ(298)$ (J mol ⁻¹ K ⁻¹)	$C_p^\circ(T)$ (J mol ⁻¹ K ⁻¹)							Ref.*	
			300	500	800	1000	1200	1500	2000		3000
F ₂	0.0	202.7	31.37	34.34	36.46	37.19	37.66	38.20	38.87	39.87	a
HF	-272.5	173.7	29.12	29.20	29.55	30.14	30.98	32.25	34.01	63.21	a
F	78.9	158.7	22.77	22.10	21.46	21.25	21.14	21.03	20.93	20.84	a
CH ₃ F	-232.6	222.8	37.50	51.26	68.90	77.30	83.34	90.21	96.81	102.59	b,d
CH ₂ F ₂	-452.2	246.6	42.96	58.91	76.33	83.55	88.84	94.35	99.47	103.97	b,d
CHF ₃	-697.6	259.6	51.15	69.26	85.10	91.01	94.89	98.83	102.42	105.39	b,d
CF ₄	-933.0	261.3	61.30	80.67	94.49	98.73	101.41	103.67	105.52	106.90	b,d
·CH ₂ F	-32.6	234.4	38.71	48.67	59.29	64.20	67.92	72.02	76.06	79.71	c,e
·CHF ₂	-247.7	256.0	42.21	54.10	65.33	69.66	72.60	75.69	78.47	80.92	c,e
·CF ₃	-467.4	265.0	49.94	63.30	73.24	76.37	78.27	79.92	81.29	82.30	c,d
·CHF	163.2	223.2	34.63	39.25	45.21	47.93	50.05	52.43	55.43	61.04	f,d
·CF ₂	-186.6	240.7	39.01	46.45	52.35	54.18	55.28	56.31	57.14	58.37	g,d
·CF	240.6	212.9	30.05	32.24	34.79	35.77	36.32	36.96	37.53	38.20	p,d
CHF=O	-376.6	246.7	40.50	51.65	63.12	67.92	71.20	74.70	77.94	80.67	d
CF ₂ =O	-638.9	258.8	47.41	60.49	70.82	74.39	76.71	78.78	80.58	81.96	d
·CF=O	-171.5	248.4	38.99	45.06	50.63	52.76	54.14	55.44	56.57	57.45	d
CF ₃ O·	-655.6	292.6	64.49	82.30	94.01	99.25	101.72	103.88	105.66	106.99	h,e

* See footnotes for Table 3.

Table 3. Enthalpy of formation, entropy, heat capacities for C₂ fluorocarbons

Species	$\Delta H_f^\circ(298)$ (kJ mol ⁻¹)	$S^\circ(298)$ (J mol ⁻¹ K ⁻¹)	$C_p^\circ(T)$ (J mol ⁻¹ K ⁻¹)							Ref.	
			300	500	800	1000	1200	1500	2000		3000
CH ₃ -CH ₂ F	-263.2	265.0	59.83	87.22	116.47	129.62	139.71	150.28	159.35	164.18	i
CH ₂ F-CH ₂ F	-433.9	288.2	67.88	95.13	124.30	136.74	145.96	155.31	162.30	163.96	j,e
CH ₃ -CHF ₂	-500.8	282.5	68.72	97.11	124.65	136.47	145.39	154.49	161.85	165.39	i
CH ₂ F-CHF ₂	-664.8	303.7	75.31	107.53	133.47	143.93	151.98	159.92	169.26	177.71	k,e
CH ₃ -CF ₃	-745.6	287.4	78.81	108.32	133.82	144.08	151.47	158.99	165.10	167.67	i
CHF ₂ -CHF ₂	-877.8	321.5	85.23	115.25	141.25	150.60	156.64	163.29	169.67	173.93	j,e
CH ₂ F-CF ₃	-895.8	316.2	86.58	118.04	143.15	152.09	158.17	164.43	169.66	171.50	i
CHF ₂ -CF ₃	-1104.6	333.8	96.09	127.53	151.13	158.85	164.06	168.60	170.64	169.74	i
CF ₃ -CF ₃	-1342.6	332.1	106.79	139.13	160.34	166.68	169.89	172.97	175.77	177.09	i
CH ₂ F-CH ₂ ·	-44.6	279.8	58.13	80.27	103.74	114.31	122.42	130.91	138.24	142.37	l
CH ₃ -CHF·	-76.3	274.0	58.79	79.75	103.33	114.06	122.34	130.91	138.07	141.89	j,l
CH ₂ F-CHF·	-238.5	293.4	69.59	91.24	111.69	119.75	125.52	131.33	136.07	139.86	j,l
CHF ₂ -CH ₂ ·	-277.2	297.8	67.06	90.20	111.94	121.10	128.00	135.04	140.63	142.60	j
CH ₃ -CF ₂ ·	302.5	290.4	67.34	89.22	111.30	120.80	127.83	135.52	142.85	147.42	g,l
CH ₂ F-CF ₂ ·	-446.0	311.1	74.07	97.38	118.86	127.24	133.22	139.11	143.42	144.90	l
CHF ₂ -CHF·	-451.9	310.7	76.14	99.54	119.95	127.91	133.70	139.35	143.30	143.80	l
CF ₃ -CH ₂ ·	-517.1	302.6	77.37	101.75	121.27	128.88	134.26	139.75	145.42	149.64	g,l
CHF ₂ -CF ₂ ·	-664.8	328.4	84.32	107.31	127.04	134.10	138.83	143.26	145.92	145.88	j,l
CF ₃ -CHF·	-680.7	326.3	85.84	109.68	128.34	135.01	139.45	143.76	147.55	149.47	j,l
CF ₃ -CF ₂ ·	-891.2	340.5	92.84	118.29	136.19	141.80	145.18	148.11	150.50	151.09	g,l
CH ₂ =CHF	-140.1	262.3	50.61	71.66	91.80	100.57	107.42	114.10	118.92	121.04	p,m
CHF=CHF [Z]	-297.1	268.6	58.06	79.62	99.16	107.13	112.47	118.31	124.29	128.86	n,e
CHF=CHF [E]	-292.9	267.8	59.82	80.44	99.61	107.53	112.83	118.70	124.91	129.77	n,e
CH ₂ =CF ₂	-336.4	265.2	59.33	81.55	100.20	107.74	113.14	118.70	123.44	125.80	p,o
CHF=CF ₂	-491.0	292.7	69.45	90.32	107.48	113.93	118.67	124.16	130.07	134.34	p,o
CF ₂ =CF ₂	-658.5	299.9	80.70	100.40	115.53	120.89	123.89	126.87	129.64	131.27	d
CHF=CH· [E]	124.3	258.0	50.61	67.10	81.56	87.66	92.21	97.15	101.75	104.49	e
CHF=CH· [Z]	123.0	257.0	50.74	67.33	81.76	87.92	92.44	97.29	101.69	104.19	e
CH ₂ =CF·	109.2	256.8	50.22	66.10	80.71	86.89	91.30	96.37	101.64	105.58	e
CHF=CF· [E]	-41.0	279.3	59.30	74.51	87.79	92.80	96.05	99.66	103.21	105.68	e
CHF=CF· [Z]	-42.7	279.3	59.30	74.51	87.79	92.80	96.05	99.66	103.21	105.68	e
CF ₂ =CH·	-67.8	277.0	59.20	76.36	89.73	94.73	97.78	100.81	103.08	103.88	e
CF ₂ =CF·	-216.3	300.5	68.26	83.42	95.36	99.41	101.77	104.39	106.90	108.21	e
C ₂ HF	125.5	231.5	52.48	62.17	69.69	73.22	75.83	78.82	81.96	84.57	d
C ₂ F ₂	20.9	244.0	57.07	67.96	76.67	79.74	81.54	83.46	85.20	86.16	d
CHF=C=O	-147.2	270.5	56.75	71.49	84.93	90.34	94.31	98.24	101.99	102.12	e
CF ₂ =C=O	-290.4	288.8	68.30	81.79	92.56	96.66	99.61	102.48	104.72	106.77	e
·CF=C=O	69.0	276.2	56.80	65.85	73.77	76.59	79.38	82.17	84.96	87.75	e

a Kee *et al.* (1987); b Kolesov (1978); c McMillen and Golden (1982); d Stull and Prophet (1971); e Zachariah *et al.* (1995); f Pritchard *et al.* (1984); g Rodgers (1978); h Batt and Walsh (1982); i Chen *et al.* (1975); j this work, see text; k Lacher and Skinner (1968); l Chen *et al.* (1990, 1991); m Daubert and Danner (1985); n Stadelman and Vogt (1980); o Stull *et al.* (1969); p Gurvich *et al.* (1991).

hydrocarbons, hydrofluorocarbons, and oxidized hydrofluorocarbons, including radical species, were calculated using the BAC-MP4 procedure as outlined by Melius (1986). This procedure involves *ab initio* molecular orbital calculations using the Gaussian series of programs (Frisch *et al.*, 1992), followed by application of a bond additivity correction (BAC) procedure to the *ab initio* calculated energies. The BAC procedure enables energies to be calculated at accuracies that are necessary for chemical applications, without the need to resort to large basis sets or configuration interaction terms. This is a particularly important issue when the goal is the generation of a sufficiently complete data set necessary for development of a detailed chemical mechanism.

Equilibrium geometries, vibrational frequencies,

and zero point energies were calculated at the Hartree-Fock level using a 6-31G(d) basis set (HF/6-31G*). Using these geometries, single point energies were calculated with 4th order Moller-Plesset theory using a 6-31G(d,p) basis set (MP4/6-31G**), to which the BAC procedure was applied. In the BAC method, errors in the electronic energy of a molecule are bond-wise additive and depend on bonding partner, distance, and next-nearest neighbours. The energy per bond is corrected by calibration at a given level of theory against molecules of known energy.

Table 4 lists calculated heats of formation for most of the species in the reaction set, as well as literature values (where available). We note that we have calculated thermochemical data for a number

Table 4. C₁ and C₂ Fluorinated hydrocarbon heats of formation: calculated values (BAC-MP4), literature values, and uncertainties

Species	BAC	Lit.	Uncert.	Ref.	Lit.	Ref.
CH ₄	-74.8	-74.9	0.4	a		
CH ₃ F	-233.8	-232.6	8.4	b	-247.3	y
CH ₂ F ₂	-451.1	-452.2	1.8	b	-460.7	y
CHF ₃	-699.5	-697.6	4.2	b	-697.9	y
CF ₄	-934.1	-933.0	0.4	b	-934.3	y
•CH ₃	146.0	145.7	1.3	a		
•CH ₂ F	-31.4	-32.6	8.4	c	-32.0	aa
•CHF ₂	-247.3	-247.7	8.4	c	-252.0	aa
•CF ₃	-471.9	-467.4	8.4	c	-472.0	aa
:CH ₂	429.8	424.7	4.2	d		
:CHF	131.7	163.2	12.6	e	105.0	aa
:CF ₂	-203.3	-186.6	6.3	f	-180.0	aa
•CH	613.7	594.1	0.4	g		
•CF	236.3	240.6	10.0	aa	255.2	g
CH ₂ =O	-108.5	-108.6	6.3	h		
CHF=O	-382.3	-376.6	15.0	g		
CF ₂ =O	-598.4	-638.9	1.7	g	-640.0	aa
•CH=O	38.9	37.2	8.4	a		
•CF=O	-182.9	-175.7	15.0	g	-179.0	aa
CH ₃ OH	-204.8	-201.2	0.4	a		
CF ₃ OH	-919.4	-893.3	12.6	i		
CH ₃ OF	-92.0	-72.4	12.6	i		
CF ₃ OF	-750.1	-764.8	12.6	a		
CH ₃ O•	27.6	16.7	2.9	j		
CF ₃ O•	-628.3	-655.6	6.3	i		
CH ₃ OOH	-124.6	-131.0	8.4	h		
CF ₃ OOH	-807.5	-803.3	15.0	m		
CH ₃ OO•	25.3	28.0	12.6	a		
CF ₃ OO•	-627.5	-602.5	12.6	i		
HC(O)OH	-387.3	-378.6	0.4	h		
FC(O)OH	-614.9					
HC(O)O•	-124.9	-150.6	8.4	k		
FC(O)O•	-336.9					
C ₂ H ₆	-86.9	-84.1	0.4	a		
CH ₃ -CH ₂ F	-272.4	-263.2	1.6	l		
CH ₂ F-CH ₂ F	-446.0	-433.9	11.8	m		
CH ₃ -CHF ₂	-505.3	-500.8	6.3	l	-497.0	q
CH ₂ F-CHF ₂	-671.5	-664.8	4.2	n	-691.0	q
CH ₃ -CF ₃	-755.4	-745.6	1.6	l	-747.3	q
CHF ₂ -CHF ₂	-883.3	-877.8	17.6	m		
CH ₂ F-CF ₃	-913.3	-895.8	4.2	l		
CHF ₂ -CF ₃	-1124.1	-1104.6	4.6	l		
CF ₃ -CF ₃	-1357.0	-1342.7	6.3	l	-1344.0	q
C ₂ H ₅ •	120.6	118.5		a		
CH ₂ F-CH ₂ •	-56.2	-47.7	1.9	m	-44.6	z
CH ₃ -CHF•	-75.6	-76.3	5.9	m	-72.4	z
CH ₂ F-CHF•	-247.3	-238.5	12.5	m	-235.5	z
CHF ₂ -CH ₂ •	-280.9	-285.8	15.0	m	-277.2	z
CH ₃ -CF ₂ •	-300.2	-302.5	8.4	o		
CH ₂ F-CF ₂ •	-460.1	-449.8	15.0	m	-446.0	z
CHF ₂ -CHF•	-459.8	-456.1	15.0	m	-451.9	z
CF ₃ -CH ₂ •	-526.6	-517.1	4.2	o		
CHF ₂ -CF ₂ •	-671.1	-664.8	18.7	m	-660.2	z
CF ₃ -CHF•	-703.0	-680.7	9.6	p	-688.3	z
CF ₃ -CF ₂ •	-907.6	-891.2	4.2	o	-896.0	aa
C ₂ H ₄	51.5	52.4	0.8	a		
CH ₂ =CHF	-139.2	-140.1	2.5	aa	-138.9	
CHF=CHF [Z]	-301.3	-297.1	10.0	r	-306.5	aa
CHF=CHF [E]	-302.2	-292.9	10.0	r	-303.6	aa
CH ₂ =CF ₂	-340.1	-336.4	4.0	aa	-345.2	s
CHF=CF ₂	-485.6	-491.0	9.0	aa	-495.8	s
CF ₂ =CF ₂	-653.7	-658.5	2.9	g	-659.5	aa
C ₂ H ₃ •	297.1	286.2	4.2	a		
CHF=CH• [Z]	123.1					
CHF=CH• [E]	124.1					
CH ₂ =CF•	109.1					
CHF=CF• [Z]	-41.1					
CHF=CF• [E]	-42.5					

Table 4.—Continued

Species	BAC	Lit.	Uncert.	Ref.	Lit.	Ref.
CF ₂ =CH•	-67.7					
CF ₂ =CF•	-216.4	-227.0	20.0	aa	-192.1	t
C ₂ H ₂	226.8	226.7	0.8	a		
C ₂ HF	117.8	125.5	22.0	g		
C ₂ F ₂	31.8	20.9	21.0	g		
•C ₂ H	550.5	564.8	4.2	c		
•C ₂ F	453.9	460.2	22.0	m		
CH ₂ =C=O	-40.6	-47.7	2.5	u		
CHF=C=O	-147.2					
CF ₂ =C=O	-290.4					
•CH=C=O	187.3	177.4	8.4	v		
•CF=C=O	69.0					
CH ₃ -CHO	-161.1	-166.2	0.4	h		
CF ₃ -CHO	-774.3					
CH ₃ -CO•	-7.5	-10.2	1.7	a		
CF ₃ -CO•	-609.9					

a Tsang and Hampson (1986); b Kolesov (1978); c McMillen and Golden (1982); d Kee *et al.* (1987); e Pritchard *et al.* (1984); f Rodgers (1978); g Stull and Prophet (1971); h Baulch *et al.* (1984); i Batt and Walsh (1982); j Batt *et al.* (1974); k Benson (1976); l Chen *et al.* (1975). m This work, see text; n Lacher and Skinner (1968); o Rodgers (1978); p Martin and Paraskevopoulos (1983); q Kolesov and Papina (1970); r Stadelmann and Vogt (1980); s Stull *et al.* (1969); t Bryant (1962); u Nuttall *et al.* (1971); v Lias *et al.* (1988); w Kerr and Timlin (1971); x Tschuikow-Roux and Salomon (1987); y Rodgers *et al.* (1974); z Chen *et al.* (1990, 1991); aa Gurvich *et al.* (1991).

$H_f(298)$ Calculated heat of formation at 298 K

Lit. Literature value for $H_f(298)$

Uncert. Reported uncertainty in literature value

Ref. Literature reference

of related species that are not included in the reaction set. These data are also included in Table 4 for purposes of comparison. Of the approximately 110 species, where we have calculated heats of formation, about 70 species have literature values. We note that the literature values consist of a number of different types of data, including estimated and calculated values, in addition to those that are derived from experimental measurements.

The average difference between the BAC-MP4 and the literature values is about 9.5 kJ mol⁻¹, while the standard deviation is about 7.5 kJ mol⁻¹. From these data, we conclude that for the fluorinated hydrocarbon system, that heats of formation calculated using the BAC-MP4 method provide values that are accurate to less than 10 kJ mol⁻¹ or comparable to the majority of the experimentally derived values. We believe that the precision of the *ab initio* values for any homologous series to be significantly better than that which is typically obtainable from experimental measurements. This becomes evident when calculated bond dissociation energies are compared to those derived from experimental measurements. A more detailed discussion and comparison can be found elsewhere (Zachariah *et al.*, 1995).

Of all the species, CF₂=O has the largest difference between calculated and experimental values. Although the quoted uncertainty for this molecule is small, there is reason to believe that the experimental data may have had side reactions complicating its determination. In addition, other recent calculations

(Schnieder and Wallington, 1994; Montgomery *et al.*, 1994) using other *ab initio* methods predict a heat of formation for CF₂=O that is consistent with our BAC-MP4 calculated value. There are a number of other oxyfluoro species that have significant differences between calculated and literature values. However, the heats of formation of these species were derived based on heats of reaction involving CF₂=O. Consequently, if the 'true' value for CF₂=O was closer to the calculated value, then the experimentally derived values for these other species would also be closer to their respective calculated values.

There are a number of other species with significant differences between calculated and literature values. The uncertainties in many of the literature values are high because they are only indirectly tied to experimental measurements. For example, the heat of formation of the HCOO• radical is an estimate based on group additivity. The heats of formation of two fluoroethyl radicals (CF₃-CHF• and CH₂F- CF₂•) were determined from estimated from C-H bond dissociation energies based on correlations between rates of hydrogen atom abstractions, C-H bond frequencies, and known C-H bond strengths.

To reiterate, from analysis of the data presented in Table 4, we can conclude that for the fluorinated hydrocarbon system, that heats of formation calculated using the BAC-MP4 method provide values that are accurate to less than 10 kJ mol⁻¹ or comparable in accuracy to the majority of the experimentally

derived values. Furthermore, from trends in bond dissociation energies, we believe that the precision of the *ab initio* values for any homologous series to be significantly better than that which is typically obtainable from experimental measurements.

3. REACTION KINETICS

3.1. Overview

The reaction set or 'mechanism' is too large to be described in detail here and, consequently, only an overview of important classes of reactions will be presented. Utilizing the species identified as potentially important, a grid of possible reactions was constructed. Existing chemical rate data involving these fluorinated species was then compiled and evaluated. Where rate data were available, but only over limited temperature ranges or at different pressure (for unimolecular or chemically activated steps), RRKM (Robinson and Holbrook, 1972) and QRRK (Dean and Westmoreland, 1987) analyses were used to estimate the temperature dependencies (at 1 atm) of the rates and to predict relative rates where multiple product channels were possible. Where no rate data were available for potential reactions, the rate constants were estimated by analogy to other hydrocarbon or substituted hydrocarbon reactions. The prefactors were adjusted for reaction path degeneracy and the activation energies were adjusted empirically based on relative heats of reaction or relative bond energies (i.e. Evans-Polanyi relationships).

Initially, upper limits were used for estimated rate constants. If as a result of simulations under a variety of conditions (using different agents, flame geometries, etc.), it was observed that a specific reaction with an upper limit rate constant did not significantly contribute to the destruction or creation of any of the species in the 'mechanism', then that estimate continued to be used. However, if a specific reaction contributed to the chemistry and its rate constant was an upper-limit estimate, then its value was reevaluated and possibly refined. For important contributing reactions where no good analogy was available, where significant uncertainty existed in the barrier (generally reactions with tight transition states and modest-to-large barriers), or where multiple, energetically similar product channels were possible, we calculated the geometries and energies of the transition states (Zachariah *et al.*, 1995) using the BAC-MP4 *ab initio* method. RRKM analysis was then used to obtain the temperature (and pressure) dependence of the rate constant. A brief description of the RRKM/Master Equation approach and BAC-MP4 transition state calculations used in this work are given in Sections 3.5 and 3.6, respectively.

A listing of the rate constants in the reaction set or

mechanism used in the simulations is given in Table 5. In addition, other reactions were also considered but were observed not to contribute under the conditions tested. Many of the relevant rate constants can be found in the 'NIST Chemical Kinetics Database' (Mallard *et al.*, 1992). All references for kinetic data can be found in the relevant sections of the References: Section 6.2 (General Thermochemistry and Kinetics), Section 6.7 see references 279–337 (Fluorocarbon Kinetics (Decompositions)), Section 6.8 see references 338–403 (Fluorocarbon Kinetics (Abstractions)), Section 6.9 see references 404–446 (Fluorocarbon Kinetics (Oxidations)), Section 6.10 see references 447–486 (Oxidized Fluorocarbon Kinetics), and Section 6.11 see references 487–573 (Fluorocarbon Kinetics (other)).

A qualitative discussion of the uncertainties in the rate expressions is provided with each class of reaction. For rate expressions traceable to experimental measurements, quantitative evaluation of the uncertainties can be found in the original sources.

A schematic of the possible reaction pathways for the fluorinated hydrocarbon mechanism is given in Fig. 1. This schematic provides no indication of the relative contributions of each of the possible reaction pathways since this is highly dependent upon conditions. Rather, this schematic gives an indication of the connectivity between all of the species and how the different types of reaction (e.g. thermal decompositions, chemically activated decompositions, abstractions, etc.) provide this connectivity between different types of species. For example, the linkages between each fluoromethane and the corresponding fluoromethylene are due to thermal decomposition and are indicated with bold solid arrows. Other thermal decompositions involving HF elimination (e.g. fluoroethanes \rightarrow fluoroethylenes, $\text{CHF}=\text{O} \rightarrow \text{CO}$) are also represented by bold solid arrows. Thermal decompositions involving hydrogen and fluorine atom elimination are represented by plain dotted arrows. Hydrogen atom addition/elimination reactions are represented by reversible plain dotted arrows (e.g. $\text{CH}_3\text{-CHF}\cdot \leftrightarrow \text{CH}_2=\text{CHF} + \text{H}$). Similarly, chemically activated decompositions, such as fluoromethyls \rightarrow ['hot' fluoromethanes] \rightarrow fluoromethylenes, are represented by bold dashed arrows (for reactions involving hydrogen atoms) and plain dashed arrows (for reactions involving oxygen atoms and OH radicals). Abstraction type reactions (e.g. fluoromethanes \rightarrow fluoromethyls) are represented by plain solid arrows. A few of the potential reaction pathways are not shown in Fig. 1 for purposes of maintaining clarity in the schematic representation.

For any given condition (e.g. temperature, concentration) and any given fluorocarbon, only a subset of the reactions pathways will be relevant. For each reaction pathway that is possible, each will have a different relative importance. A discussion of each of the different reaction types for each species type can be found in the following sections.

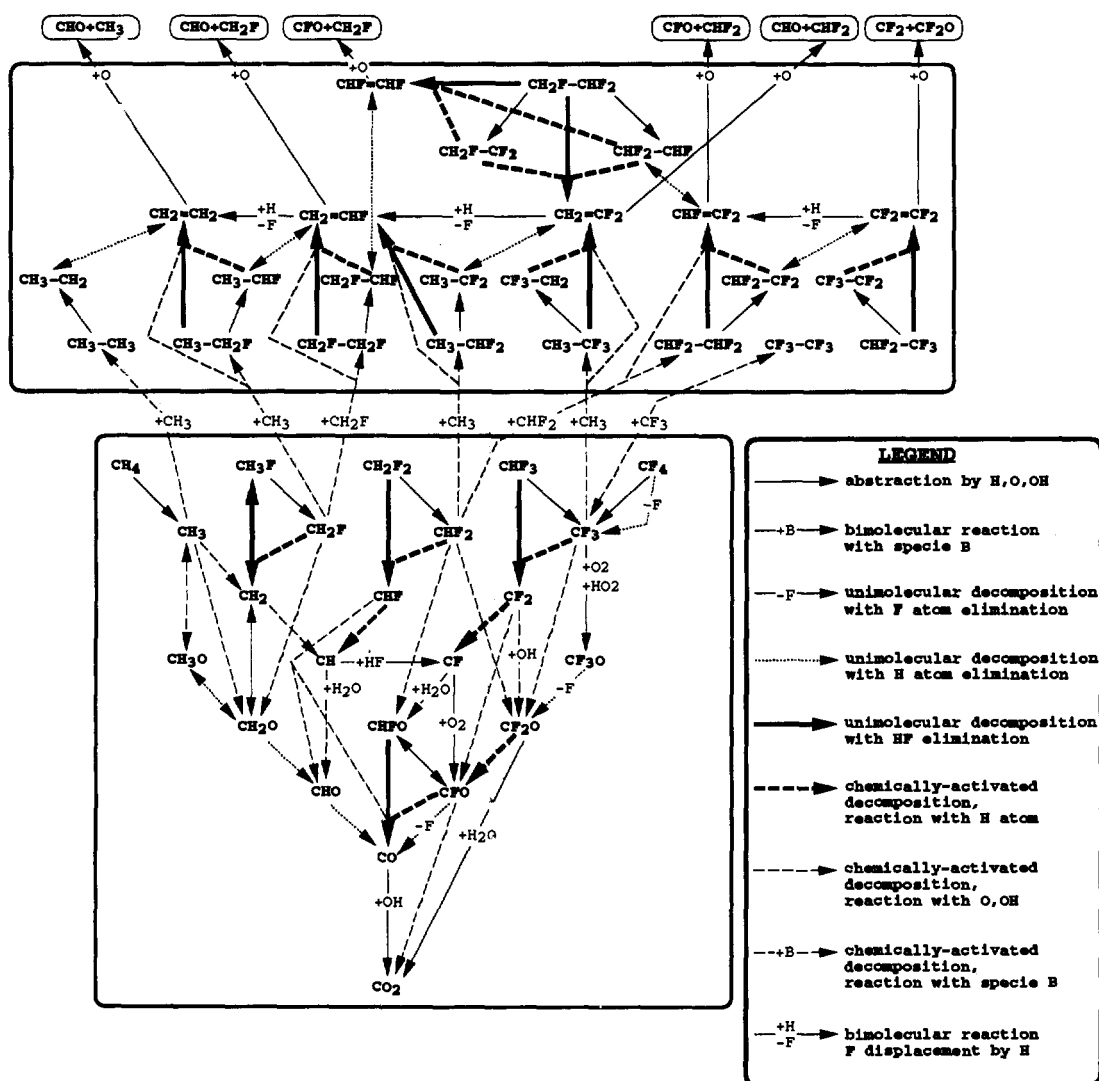


Fig. 1. Fluorinated hydrocarbon reaction pathways.

3.2. Hydrocarbon and H/O/F Chemistry

The C/H/O subset is derived from the Miller-Bowman mechanism (Miller and Bowman, 1989) and consists of about 30 species and 140 reactions (see reactions labeled 'HO' and 'HC' in Table 5). Any other hydrocarbon mechanism could be used instead. For example, the GRIMECH set (Bowman *et al.*, 1995) is a recent hydrocarbon mechanism that accurately reproduces flame speeds for methane mixtures.

The H/O/F subset consists of three species (F, HF) and eight reactions (reactions labeled 'HF' in Table 5) that are relatively well known. This is the chemistry of fluorine atoms with hydrogen- and oxygen-containing species, such as H₂, OH, and H₂O. There are three reactions of this type that were determined to participate in the chemistry under a

variety of conditions. These reactions are the combination of hydrogen and fluorine to form HF (or the reverse decomposition) and the hydrogen atom transfer reactions by fluorine atoms from H₂ and H₂O.

The HF decomposition reaction has been measured only at temperatures above about 4000 K (Jacobs *et al.*, 1965; Blauer, 1968; Blauer *et al.*, 1971). Although this reaction in the decomposition direction is unimportant at typical flame temperatures, the reverse H + F = HF combination must be considered. Extrapolating the recommended value (Baulch *et al.*, 1981) for decomposition to 1000 K may result in an uncertainty of as much as a factor of ten, especially when considering non-simple Arrhenius dependence to the rate and different third-body efficiencies. However, since many other reactions (F + H₂, H₂O, RH) contribute to fluorine atom

destruction, the uncertainty in the absolute rate of the forward or reverse reaction is most likely unimportant.

The hydrogen abstraction reactions from H₂ and H₂O by fluorine atoms have been measured only near room temperature (Wurzberg and Houston, 1980; Stevens *et al.*, 1989; Walther and Wagner, 1983). These values were extended to higher temperatures by fitting the reported values to extended Arrhenius expressions ($AT^b e^{-E/RT}$). For the H₂ reaction, an expression with $T^{0.5}$ dependence was chosen consistent with the value recommended by Cohen and Westberg (1983). For the H₂O reaction, an expression with $T^{1.5}$ dependence was chosen by analogy to other reactions.

There are a number of other reactions which were included in the mechanism, but were never observed to contribute significantly to the chemistry. These reactions include the combination of fluorine atoms to form F₂ and the hydrogen abstractions by fluorine atoms from OH, HO₂, and H₂O₂. The oxyfluoro species FO•, HOF, FOO•, and F₂O were also initially considered in the mechanism. However, given the very low concentration of fluorine atoms at high temperatures in the hydrocarbon–air flame, these species are present in extremely low concentrations and do not contribute to the overall chemistry. The rate constants used for reactions involving these species are not given in Table 5.

3.3. C₁ Fluorinated Hydrocarbon Chemistry

3.3.1. Overview

The C₁ subset of the reaction set (approximately 150 reactions) consists of the chemistry of 14 species containing one carbon (and hydrogen/fluorine/oxygen) with H, O, OH, H₂O, and other flame species. The C₁/H/F/O species used in this reaction set are the fluoromethanes (CH₃F, CH₂F₂, CHF₃, CF₄), the fluoromethyl radicals (•CH₂F, •CHF₂, •CF₃), the fluoromethylenes (:CHF, :CF₂), and fluoromethylidyne radical (•CF). The oxidized C₁ fluorocarbon species contained in this reaction set are the perfluoromethoxy radical (CF₃O•) and the carbonyl fluorides (CHF=O, CF₂=O, •CF=O). Other oxidized C₁ fluorocarbon species were initially considered in the development of the mechanism, but later were excluded, such as the other fluoromethoxy radicals (CH₂FO•, CHF₂O•), the fluorohydroxymethyl radicals (•CHFOH, •CF₂OH), the perfluoromethylperoxy radical (CF₃OO•), and perfluoromethanol (CF₃OH). Although these species (and others) may be important in atmospheric chemistry, our initial simulations suggest that they are present in extremely low concentrations at high temperatures in hydrocarbon–air flames and do not contribute to the overall chemistry.

Both thermally and chemically activated decompositions were considered (e.g. CH₂F₂ → :CHF + HF and •CHF₂ + H → :CHF + HF). Fluoromethane decompositions via abstraction of hydrogen atoms by H, O, and OH radicals are important pathways. Fluoromethane metathesis reactions with methyl, ethyl, vinyl, and fluoromethyl radicals must also be considered. The reaction set also includes reactions of fluoromethyls with O₂, O, and OH to form carbonyl fluorides (e.g. CF₂=O) and other products, and reactions of the fluoromethylenes (e.g. :CF₂) with hydrogen to form •CF and O₂, O, or OH to form carbonyl fluorides. The carbonyl fluorides (i.e. CHF=O, CF₂=O, and •CF=O) can be destroyed via unimolecular decomposition, by reactions with hydrogen atoms (both abstractions and addition/eliminations), and through reactions with OH radicals (abstractions). Destruction of CF₂=O through complex formation with H₂O and subsequent decompositions are also considered.

3.3.2. Fluoromethanes: decompositions

Rate expressions for thermally and chemically activated decompositions of the fluoromethanes are labeled 'MD' in Table 5.

The fluoromethanes are primarily destroyed in hydrocarbon flames via hydrogen atom abstraction by hydrogen and OH and through unimolecular decomposition. Destruction via hydrogen atom abstraction by oxygen atoms is a minor channel. The greatest uncertainties for the destruction of fluoromethanes are the unimolecular decompositions. Although there are reliable experimental data for these reactions, their strong temperature and pressure dependencies result in a level of uncertainty to these reactions at flame temperatures. Further mechanism refinements should provide better rate expressions for these reactions.

Both thermally and chemically activated decompositions of the fluoromethanes were considered (e.g. CHF₃ → :CF₂ + HF and •CHF₂ + H → :CF₂ + HF). There have been a number of measurements of the unimolecular decomposition of fluoromethanes (with HF elimination). We employed rate expressions for HF elimination from CH₃F and CHF₃ that fit the extended Arrhenius form ($AT^b e^{-E/RT}$) to the experimental data of Schug and Wagner (1973) and Hidaka *et al.* (1991), respectively. These experimental data were obtained at different temperatures and pressures than are relevant to atmospheric flames. The experimental data were interpolated or extrapolated and fit using temperature dependencies (T^b) that were consistent with the experimental data and RRKM analysis. For HF elimination from CH₂F₂, we employed a rate expression from our RRKM analysis using BAC-MP4 transition state energies and geometries, although there is experimental data by Politanskii and Shevchuk (1968). For H₂ elimina-

tion (minor channel) from CH_3F and CH_2F_2 , we used rate expressions from our RRKM analysis using BAC-MP4 *ab initio* transition states (Zachariah *et al.*, 1955). Fluorine atom eliminations from the fluoromethanes are negligible decomposition channels, except for CF_4 , where it is the only possible pathway. For this reaction, we used a rate expression from our RRKM/Master Equation analysis that is referenced to the room temperature measurement of the reverse reaction ($\cdot\text{CF}_3 + \text{F}$) by Plumb and Ryan (1986).

There have been no measurements (to our knowledge) for reactions involving chemically activated or 'hot' fluoromethanes other than room temperature measurements of the rate constant for $\text{CF}_3 + \text{H} \rightarrow$ products (e.g. Ryan and Plumb, 1984; Tsai and McFadden, 1989). In order to estimate values for these various reactions, as well as for the stabilized fluoromethane channels, we used RRKM analysis with experimental barriers (where they existed) or our BAC-MP4 *ab initio* transition state barriers (Zachariah *et al.*, 1995) for insertion of $\cdot\text{CHF}$ and $\cdot\text{CF}_2$ into HF and H_2 and the energetics of the reaction pathways. Although the chemically activated fluoromethane reactions are primary pathways for destruction of fluoromethyl radicals and there are no experimental rate measurements, the uncertainties in the rates are relatively small, since these are barrierless combinations.

There have been a number of measurements of the unimolecular decomposition of fluoromethanes (with HF elimination): at least two for CH_3F (Politsanskii and Shevchuk, 1968; Schug and Wagner, 1973), at least one for CH_2F_2 (Politsanskii and Shevchuk, 1968), and several for CHF_3 (Tschuikow-Roux, 1965; Tschuikow-Roux and Marte, 1965; Modica and LaGraff, 1966; Politsanskii and Shevchuk, 1968; Biordi *et al.*, 1978; Schug *et al.*, 1979; Hidaka *et al.*, 1991). In addition, there have been a number of measurements of the unimolecular decomposition of other halomethanes (eliminating HF, HCl, or HBr) such as CHF_2Cl (Norton, 1957; Edwards and Small, 1964, 1965; Gozzo and Patrick, 1964, 1966; Barnes *et al.*, 1971; Kushina *et al.*, 1972; Schug *et al.*, 1979; Zhitnev *et al.*, 1991), CHF_2Br (Cox and Simmons, 1971), CHFCl_2 (Kushina *et al.*, 1972), and CHCl_3 (Shilov and Sabirova, 1960; Schug *et al.*, 1979). All of these halomethane decomposition reactions have a small-to-moderate barrier in the reverse direction (i.e. carbene insertion into HF, HCl, or HBr) of 10–40 kJ mol^{-1} . Consequently, all of the halomethane decomposition measurements are important for evaluating the fluoromethane values (both experimental and calculated) for consistency. Furthermore, the barriers-to-insertion for $\cdot\text{CHF}$ and $\cdot\text{CF}_2$ in these reactions can be used as reference reactions for reactions of $\cdot\text{CHF}$ and $\cdot\text{CF}_2$ with many other important molecules where there is no or little information available (i.e. the reactions of $\cdot\text{CHF}$ and

$\cdot\text{CF}_2$ with H_2 , H_2O , CH_4 , C_2H_6 , fluoromethanes, fluoromethyls, etc.).

3.3.3. Fluoromethanes: abstraction of hydrogen by hydrogen atoms

Rate expressions for abstraction of hydrogen from the fluoromethanes are labeled 'MA' in Table 5.

We used rate expressions that were fits to extended Arrhenius form ($AT^b e^{-E/RT}$) to the experimental data of Westenberg and deHaas (1975) and Ridley *et al.* (1972) for abstraction of hydrogen from CH_3F and CH_2F_2 , respectively. For abstraction of hydrogen from CHF_3 , we used a fit to data for the reverse reaction from work by Ayscough and Polanyi (1956) and Berces *et al.* (1972). A temperature dependence of $T^{3.0}$ was used by analogy to that recommended for methane (Tsang and Hampson, 1986). The experimental data for these reactions were all obtained at intermediate temperatures (600–900 K) and, consequently, the uncertainties in extrapolation of these data to flame decomposition temperatures are most likely acceptable. However, modeling results suggest that flame speeds in CHF_3 doped flames are relatively sensitive to the rate of hydrogen abstraction from CHF_3 . Consequently, future refinements of this mechanism should provide the best possible rate expression for this reaction that is consistent with all available experimental data.

There have been many measurements of abstraction of hydrogen from the fluoromethanes by hydrogen atoms. There have been at least four measurements for CH_3F (Parsamyan *et al.*, 1967; Hart *et al.*, 1974; Westenberg and deHaas, 1975; Aders *et al.*, 1975), at least two measurements for CH_2F_2 (Parsamyan and Nalbanddyan, 1968; Ridley *et al.*, 1972), and a number of measurements or estimates for CHF_3 (Ayscough and Polyanyi, 1956; Pritchard *et al.*, 1956; Skinner and Ringrose, 1965; Amphlett and Whittle, 1967; Arthur and Bell, 1978; Fagarash and Moin, 1968; Kibby and Weston, 1968; Berces *et al.*, 1972; Kondratiev, 1972; Arthur *et al.*, 1975; Arthur and Bell, 1978; Richter *et al.*, 1994). We should note that many of the measurements or estimates for the CHF_3 reactions are actually values for the reverse rate or $\cdot\text{CF}_3 + \text{H}_2 \rightarrow \text{CHF}_3 + \text{H}$. Two of the citations (Kondratiev, 1972; Arthur and Bell, 1978) are evaluations of the experimental data. We have also calculated the structure and energy of each transition state for these reactions using the BAC-MP4 *ab initio* method. The calculated energy barriers compare well with the experimental values (Zachariah *et al.*, 1955).

For the $\text{CH}_3\text{F} + \text{H}$ reaction, all of the workers cited above incorrectly identified the reaction as abstraction of fluorine rather than hydrogen. These workers only measured the disappearance of the reactants and simply assigned the product channel by analogy to the $\text{CH}_3\text{Br} + \text{H}$ reaction, where it is

known that the halogen atom (Br) is abstracted. However, the C–F bond is much stronger than both the C–Br and C–H bonds. Consequently, for CH₃F, abstraction of hydrogen is more favourable than abstraction of fluorine. Our *ab initio* transition state calculations (Zachariah *et al.*, 1995) also support this conclusion, where abstraction of hydrogen from the fluoromethanes by hydrogen atoms were calculated to have barriers-to-reaction of 49.4, 40.6, and 53.6 kJ mol⁻¹ for CH₃F, CH₂F₂, and CHF₃, respectively. In contrast, the calculated barriers for abstraction of fluorine were 131.4, 142.7, 168.6, and 171.1 kJ mol⁻¹ for the CH₃F, CH₂F₂, CHF₃, and CF₄, respectively. This is a significant difference and clearly supports assignment of abstraction of hydrogen as the dominant channel.

Richter *et al.* (1994) have measured the rate of abstraction of hydrogen from CHF₃ by hydrogen atoms in H₂/O₂ premixed flames and report an activation energy of about 73 kJ mol⁻¹. This barrier would appear to be inconsistent with and significantly higher than values of 40–50 kJ mol⁻¹ that are typical for abstraction of hydrogen by hydrogen atoms from hydrocarbons (e.g. CH₄, C₂H₆) and other fluoromethanes (see references above).

3.3.4. Fluoromethanes: abstraction of hydrogen by oxygen atoms and OH radicals

Rate expressions for abstraction of hydrogen from the fluoromethanes are labeled 'MA' in Table 5.

In this work, for abstraction of hydrogen from the fluoromethanes by oxygen atoms, we fit experimental data for CH₃F (Parsamyan *et al.*, 1967), CH₂F₂ (Parsamyan and Nalbandyan, 1968), and CHF₃ (Jourdain *et al.*, 1978) to extended Arrhenius form ($AT^b e^{-E/RT}$) using a temperature dependence ($T^{1.5}$) by analogy to methane (Tsang and Hampson, 1986). For abstraction of hydrogen from the fluoromethanes by OH radicals, we used rate expressions as recommended by Cohen and Benson (1987a, 1987b) that have temperature dependencies based on transition state theory. These recommendations are based on experimental measurements at relatively low temperatures (about 300–500 K). Since these reactions are primary decomposition pathways for the fluoromethanes, it would be valuable to have experimental measurements of these rates at higher temperatures (closer to flame conditions).

There have been many measurements for abstraction of hydrogen from the fluoromethanes by hydrogen atoms, but only a few for abstraction of hydrogen by oxygen atoms or OH radicals. Parsamyan and co-workers have measured the rate of reaction for CH₃F + O (Parsamyan *et al.*, 1967) and for CH₂F₂ + O (Parsamyan and Nalbandyan, 1968). Jourdain *et al.* (1978) and Miyoshi *et al.* (1993) have measured the rate of reaction for CHF₃ + O. We have not used the more recent value by Miyoshi *et*

al. (1993), because it appears that these data may be complicated by the CHF₃ → :CF₂ + HF decomposition reaction at the highest temperatures. This should be further examined. Richter *et al.* (1994) have measured the rate of hydrogen atom abstraction from CHF₃ by oxygen in H₂/O₂ premixed flames and report an activation energy of about 13 kJ mol⁻¹. This barrier would appear to be inconsistent with and significantly lower than typical values of 35–40 kJ mol⁻¹ for hydrogen atom abstraction by oxygen from hydrocarbons (e.g. CH₄, C₂H₆) and other fluoromethanes (see references above).

As indicated above, Cohen and Benson (1987a, 1987b) used transition-state theory calculations to analyze and predict rate coefficients for reaction of OH radicals in a series of halogen-substituted methanes and ethanes. Much of their analysis is based on the experimental data of Jeong and Kaufmann (1982a, 1982b), but it is also consistent with other measurements for fluoromethanes (Howard and Evenson, 1976a; Clyne and Holt, 1979; Nip *et al.*, 1979; Talukdar *et al.*, 1991).

3.3.5. Fluoromethanes: abstraction of hydrogen by fluorine atoms and fluorine by hydrogen atoms

Rate expressions for abstraction of hydrogen by fluorine atoms are labelled 'CF' in Table 5. Rate expressions for abstraction of fluorine by hydrogen atoms are labeled 'MA' in Table 5.

There have been a number of measurements of abstraction of hydrogen from methane (CH₄) by fluorine atoms near room temperature (Wagner *et al.*, 1971; Pollock and Jones, 1973; Williams and Rowland, 1973; Manning *et al.*, 1975; Smith *et al.*, 1977; Clyne and Hodgson, 1983; Pagsberg *et al.*, 1988). In our work, we used a fit to extended Arrhenius form ($AT^b e^{-E/RT}$) to the rate constant recommended by Atkinson *et al.* (1992) using a temperature dependence ($T^{0.5}$) in order to extend the rate expression to flame temperatures. Although there is some uncertainty here in extrapolating the rate constant to flame temperatures, it is most likely unimportant. This is because this reaction occurs on almost every collision (that is, the rate cannot change by much). Furthermore, there are many other reactions (e.g. F + H₂, F + H₂O, and F + other hydrocarbons) that contribute to fluorine atom destruction.

For completeness in the reaction set (although it is unlikely that they will contribute), we have also included abstraction of hydrogen from the fluoromethanes by fluorine atoms. There have been a number of measurements for these reactions near room temperature for CH₃F (Pollock and Jones, 1973; Smith *et al.*, 1977; Manocha *et al.*, 1983), for CH₂F₂ (Pollock and Jones, 1973; Smith *et al.*, 1977; Manocha *et al.*, 1983; Clyne and Hodgson, 1985; Nielsen *et al.*, 1992), and for CHF₃ (Pollock and Jones, 1973; Goldberg and Schneider, 1976; Smith *et*

al., 1977; Clyne and Hodgson, 1983; Maricq and Szente, 1992). For these reactions, rate expressions were used where the rate constant prefactor relative to that recommended by Atkinson *et al.* (1992) for $\text{CH}_4 + \text{F}$ was adjusted to account for reaction path degeneracy (i.e. fewer number of hydrogen atoms) and the activation energy was adjusted such that the rate was consistent with the measurements at room temperature. Use of extended Arrhenius form in these cases is not justified, because of the lack of temperature-dependent experimental measurements.

For abstraction of fluorine from CH_3F , CH_2F_2 , and CHF_3 by hydrogen atoms, we employed rate expressions derived from our BAC-MP4 *ab initio* transition state calculations (Zachariah *et al.*, 1995). These pathways are negligible channels for fluoromethane destruction and were included simply for completeness in development of the reaction set. However, for reaction of hydrogen atoms with CF_4 , the only possible pathway is abstraction of fluorine. For this reaction, we used the experimentally derived rate expression of Kochubei and Moin (1969, 1971). This reaction is an important pathway for CF_4 destruction, competing with the only other possible channel—unimolecular decomposition of CF_4 to $\cdot\text{CF}_3$ and F .

3.3.6. Fluoromethanes: metathetical reactions

Rate expressions for metathetical reactions of the fluoromethanes are labeled 'MA' in Table 5.

There have been a number of measurements of metathetical reactions of methyl/fluoromethyl radicals with methane/fluoromethanes. These will not be reviewed here. In our work, we used the recommendations of Kerr and Parsonage (1976), which are consistent with the majority of the experimental data. The values recommended by Kerr and Parsonage are largely based on the pioneering work in this area by Pritchard and co-workers (e.g. Pritchard *et al.*, 1965), Whittle and co-workers (e.g. Chamberlain and Whittle, 1972), and Arthur and co-workers (e.g. Arthur and Bell, 1978).

Although there have been no experimental measurements of metathetical reactions of vinyl radicals (C_2H_3) with the fluoromethanes, one can estimate their rates by analogy to the methyl radical (CH_3) reactions. We used rate expressions for these reactions, where the activation energy was reduced by 10% (relative to the corresponding methyl radical reaction) in order to compensate for the roughly 6 kJ mol^{-1} increase in the exothermicity of the reaction.

The experimental measurements (cited above) for abstraction of hydrogen by methyl and fluoromethyl radicals were all made at relatively low temperatures (about 300–600 K). Extrapolation of these measurements to flame decomposition temperatures may in-

troduce significant uncertainty in the rates, especially since these reactions should have considerable non-simple Arrhenius temperature dependencies. In further refinements of this mechanism, these data should be critically evaluated. Experimental measurements at near flame temperatures would also be extremely valuable.

3.3.7. Fluoromethyl radical chemistry

Rate expressions for reactions involving the fluoromethyl radicals are labeled 'NN' in Table 5.

Fluoromethyl radicals are destroyed by three general pathways whose relative importances are sensitive to conditions. (1) They can combine with hydrogen atoms forming chemically activated fluoromethanes that eliminate HF (creating methylene/fluoromethylenes). (2) They can react with oxygen-containing species (i.e. O_2 , O , OH), resulting in the formation of fluoromethoxy radicals and carbonyl fluoride species. (3) They can combine with methyl or fluoromethyl radicals, forming chemically activated fluoroethanes that may be either stabilized or eliminate HF (creating ethylene/fluoroethylenes). This latter class of reactions is included with the fluoroethane (C_2) chemistry.

The fluoromethyl radicals are primarily formed by hydrogen atom abstractions from the fluoromethanes. However, there are several other channels that can contribute to their formation and are classified as C_2 chemistry. For example, the reactions $\text{CH}_2=\text{CHF} + \text{O} \rightarrow \cdot\text{CH}_2\text{F} + \text{HCO}$ and $\text{CHF}_2-\text{CF}_2\cdot + \text{H} \rightarrow \cdot\text{CHF}_2 + \cdot\text{CHF}_2$ contribute to the formation of fluoromethyl radicals. Similarly, there are a number of other decomposition channels that can be classified as C_3 chemistry, such as $\cdot\text{CH}_2\text{F} + \text{C}_2\text{H}_4 \rightarrow \cdot\text{CH}_2-\text{CH}_2-\text{CH}_2\text{F}$.

There are four potential reaction product channels following association of fluoromethyl radicals with O_2 by analogy to hydrocarbon and chlorinated hydrocarbon chemistry. (1) Stabilization of the fluoromethylperoxy radicals (e.g. $\text{CHF}_2\text{OO}\cdot$ product) or return to reactants (e.g. $\cdot\text{CHF}_2 + \text{O}_2$). (2) Internal abstraction of a hydrogen atom followed by O–O bond cleavage (e.g. $\text{CF}_2=\text{O} + \text{OH}$ products). (3) Internal abstraction of a fluorine atom followed by O–O bond cleavage (e.g. $\text{CHF}=\text{O} + \text{OF}$ products). (4) Direct dissociation of the O–O bond (e.g. $\text{CHF}_2\text{O}\cdot + \text{O}$ products). The first channel (stabilization) should be negligible at flame temperatures (i.e. the adduct returns to reactants), but may need to be considered at lower temperatures and for ignition delays. The second channel (hydrogen abstraction) should be a secondary pathway at flame temperatures, but clearly should be reevaluated at lower temperatures. The third channel (fluorine abstraction) can clearly be disregarded, because of the strong C–F bond. This is in contrast to the analogous reactions that are assumed to occur in chlorinated hydrocarbon

chemistry (e.g. Ho *et al.*, 1992). Consequently, eliminating the first three potential product pathways, we must only explicitly consider the fourth channel (direct O–O bond dissociation) to form fluoromethoxy radicals and oxygen atoms (e.g. $\text{CHF}_2\text{O}\cdot + \text{O}$ products).

There have been a number of rate measurements for the reaction of $\cdot\text{CF}_3$ with O_2 near room temperature (Vedenev *et al.*, 1978; Ryan and Plumb, 1982; Caralp *et al.*, 1986; Cooper *et al.*, 1980; Orlando and Smith, 1988), but none (to our knowledge) for reaction of the other fluoromethyl radicals with O_2 . At low temperatures, the only possible product pathway is formation of the fluoromethylperoxy radical. These types of radical species are known to play a role in atmospheric chemistry. At high temperatures in a flame, these species will be present in significantly smaller concentrations and there are other possible product pathways for the fluoromethyl + O_2 reactions. For $\cdot\text{CF}_3 + \text{O}_2 \rightarrow \text{CF}_3\text{O}\cdot + \text{O}$, we estimated a rate expression using RRKM analysis employing the reasonable assumption that there is no barrier in the reverse direction. For the reactions $\cdot\text{CH}_2\text{F} + \text{O}_2 \rightarrow \text{CH}_2\text{FO}\cdot + \text{O}$ and $\cdot\text{CHF}_2 + \text{O}_2 \rightarrow \text{CHF}_2\text{O}\cdot + \text{O}$, we assumed the fluoromethoxy radical intermediate would be present in steady-state concentrations and that it would rapidly eliminate HF after being formed. Based on these assumptions then, we simply used the $\cdot\text{CF}_3$ rate expression after adjusting for reaction enthalpies. For lower temperature conditions (than flames), these assumptions and the relevant reaction pathways and rate expressions should be reevaluated.

For reaction of the perfluoromethyl radical ($\cdot\text{CF}_3$) with oxygen atoms (eliminating fluorine), we used a rate constant corresponding to the room temperature value measured by McFadden and co-workers (Tsai *et al.*, 1989). For reaction of the other fluoromethyl radicals with oxygen atoms (eliminating hydrogen), we used rate constants scaled between those for $\cdot\text{CH}_3$ and $\cdot\text{CF}_3$. For reaction of the fluoromethyl radicals with OH radicals, we used rate constants identical to those for $\cdot\text{CH}_3$.

Fluoromethyl radicals are primarily destroyed in hydrocarbon flames through reactions with hydrogen, OH, and $\cdot\text{CH}_3$ radicals. Reactions with oxygen atoms are minor channels. The greatest uncertainty here is likely the reactions with $\cdot\text{CH}_3$ radicals (HF elimination vs stabilization), which are very temperature and pressure dependent. Further refinements of this mechanism should provide better rate expressions for these reactions, benchmarking them to experimental data that exists (see brief discussion in Section 2.4.1).

Reaction of fluoromethyl radicals with HO_2 may be important for correctly describing ignition delays. There are two possible product channels: $\cdot\text{CHF}_2 + \text{HO}_2 \rightarrow \text{CH}_2\text{F}_2 + \text{O}_2$ (disproportionation and chain termination) vs $\cdot\text{CHF}_2 + \text{HO}_2 \rightarrow \text{CHF}_2\text{O}\cdot + \text{OH}$ (combination/elimination and chain propagation).

We estimated rate expressions by analogy to the corresponding hydrocarbon reactions. We assumed that the fluoromethoxy radicals, once formed, immediately eliminate a hydrogen atom, since the C–H bond strengths are only 25–30 kJ mol^{-1} . This eliminates the need for explicitly including these species in the mechanism. For the $\text{CF}_3\text{O}\cdot$ product, a fast subsequent fluorine atom elimination step (which is explicitly included in the reaction mechanism) does not happen immediately, since the C–F bond dissociation energy is about 110 kJ mol^{-1} . If these reactions (for $\text{CH}_2\text{FO}\cdot$ and $\text{CHF}_2\text{O}\cdot$) are shown to be important for ignition delays, then the rates and branching ratios should be reevaluated.

3.3.8. Fluoromethylene destruction

Rate expressions for reactions involving the fluoromethylenes are labeled 'NN' in Table 5.

Estimates for the rates of reactions of the fluoromethylenes ($\cdot\text{CHF}$ and $\cdot\text{CF}_2$) with many species are somewhat uncertain, because reactions involving these species are significantly slower than the analogous reactions for singlet methylene ($^1\text{CH}_2$). Reactions of $^1\text{CH}_2$ are given in Table 5 (Reactions HC29–34). There also appear to be conflicting experimental data on the reactivities of the fluoromethylenes. This will not be discussed here. The fluoromethylenes can be destroyed in a number of different ways.

(1) The fluoromethylenes can be destroyed by reaction with hydrogen atoms, where we used rate expressions consistent with the room temperature values measured by McFadden and co-workers (Tsai and McFadden, 1989, 1990a). These reactions are $\cdot\text{CHF} + \text{H} \rightarrow \cdot\text{CH} + \text{HF}$ and $\cdot\text{CF}_2 + \text{H} \rightarrow \cdot\text{CF} + \text{HF}$. For the reaction $\cdot\text{CF}_2 + \text{H}$ (which is slightly slower), this necessitates employing a small activation barrier (5 kJ mol^{-1}) for the reaction.

(2) The fluoromethylenes can be destroyed by reaction with oxygen atoms, where we used rate expressions consistent with values measured at room temperature by Tsai and McFadden (1990a, 1990b). These reactions are $\cdot\text{CHF} + \text{O} \rightarrow \text{CO} + \text{HF}$ and $\cdot\text{CF}_2 + \text{O} \rightarrow \cdot\text{CF} + \text{O} + \text{F}$. A small activation barrier (4 kJ mol^{-1}) for the $\cdot\text{CF}_2$ reaction was used.

(3) The fluoromethylenes can be destroyed by reaction with OH radicals, where we used rate expressions consistent with a rate constant for reaction with CF_2 : (at 1090–1375 K) estimated by Biordi *et al.* (1978) in their flame measurements. Again a small barrier (14 kJ mol^{-1}) was used for $\cdot\text{CF}_2$ and no barrier for $\cdot\text{CHF}$. There are at least two possible product channels for reaction of OH with each species: hydrogen atom elimination(s) and HF elimination. HF elimination is likely the secondary channel, because of both the barrier-to-elimination and a

constrained transition state (lower A factor). We assigned an estimated branching ratio of $k_{\text{H}}/k_{\text{HF}} = 5$ by analogy to other reactions.

(4) The fluoromethylenes can be destroyed by reaction with HO_2 radicals. The reaction of $\cdot\text{CF}_2$ with HO_2 is major reaction pathway during ignition. We assigned rate constants referenced to the corresponding hydrocarbon reactions using $k_{\text{OH}}/k_{\text{HO}_2} = 2$ by analogy to reactions of OH and HO_2 with CH_3 . There are two possible product channels: 'abstraction' (e.g. $\text{CF}_2\cdot + \text{HO}_2 \rightarrow \cdot\text{CHF}_2 + \text{O}_2$) vs combination/dissociation (e.g. $\text{CF}_2\cdot + \text{HO}_2 \rightarrow \text{CF}_2=\text{O} + \text{OH}$). Again, we assigned an estimated branching ratio of $k_{\text{OH}}/k_{\text{O}_2} = 5$ by analogy to $\text{CH}_3 + \text{HO}_2$.

(5) The fluoromethylenes can be destroyed by reaction with O_2 , where we used the rate expression for $\cdot\text{CF}_2$ measured by Keating and Matula (1977). This rate expression is also consistent with the measurements by Modica and LaGraff (1965) and Bauer *et al.* (1969). For $\cdot\text{CHF}$, we used an equivalent rate expression (after adjusting for reaction enthalpy) with a significantly reduced, but still modest (24 kJ mol^{-1}) barrier. Since the $\cdot\text{CHF}$ reaction barrier has no experimental basis, if it is identified as a reaction that significantly contributes to the destruction of $\cdot\text{CHF}$, then this reaction should be reevaluated. An *ab initio* transition state calculation would be extremely useful in resolving this uncertainty.

(6) The fluoromethylenes can be destroyed via insertion into H_2O (a major flame species). We estimated barriers to reaction of 25 and 100 kJ mol^{-1} for $\cdot\text{CHF}$ and $\cdot\text{CF}_2$, respectively, from our BAC-MP4 *ab initio* transition state calculations.

(7) The fluoromethylenes can also be destroyed via reaction with hydrocarbons (see brief discussion in Section 2.4.1).

The fluoromethylenes ($\cdot\text{CHF}$ and $\cdot\text{CF}_2$) are largely destroyed in hydrocarbon flames via reaction with hydrogen atoms. Reactions with oxygen and OH radicals are minor channels. There are good quality experimental data for all of the reactions, which proceed with small barriers. An open question here is the probable addition of the fluoromethylenes to ethylene. This class of reactions has been ignored in this mechanism in order to minimize the number of species in the reaction set, because these reactions would lead to the formation of C_3 fluorinated hydrocarbons.

3.3.9 Fluoromethylidyne radical destruction

Rate expressions for reactions involving the fluoromethylidyne radical are labeled 'NN' in Table 5.

The rates of reactions of fluoromethylidyne ($\cdot\text{CF}$) with many species are somewhat uncertain given they are significantly slower than the analogous reactions for methylidyne ($\cdot\text{CH}$). There also appear to be

conflicting experimental data on its reactivity. This will not be discussed here. For the reactions of $\cdot\text{CF}$ with O_2 , hydrogen and oxygen, we used rate expressions with reasonable prefactors and barriers that are consistent with the room temperature rate measurements of McFadden and co-workers (Tsai *et al.*, 1989; Tsai and McFadden, 1990b) and Peeters *et al.* (1992). We note that to date we have (mis)assigned the products of the reaction $\cdot\text{CF} + \text{H} \rightarrow \text{C} + \text{HF}$ (about 25 kJ mol^{-1} exothermic) as $\text{CH} + \text{F}$ (about 20 kJ mol^{-1} endothermic). This was done to eliminate carbon, C_2H , C_4H_2 , and other fuel-rich species in order to minimize the number of species in the reaction set. If a hydrocarbon sub-mechanism is used that includes these species, the correct product channel should be used. For $\cdot\text{CF} + \text{OH} \rightarrow \text{CO} + \text{HF}$, we assumed that there was no barrier to reaction. For $\cdot\text{CF} + \text{H}_2\text{O} \rightarrow \text{products}$, we estimated an activation energy of 70 kJ mol^{-1} by analogy to other radical + H_2O reactions.

$\cdot\text{CF}$ can also be formed via $\text{CH} + \text{HF} \rightarrow \cdot\text{CF} + \text{H}_2$ (roughly 70 kJ mol^{-1} exothermic). We assumed that this reaction proceeds with no barrier, because of the high reactivity of CH. However, there may be a small barrier due to the strength of the HF bond. This reaction can be a major destruction pathway for CH in fluorine-inhibited hydrocarbon flames. Consequently, further refinements of this mechanism should provide a better estimate for this rate expression. A transition state structure and energy from *ab initio* calculations would be useful. An experimental measurement of this rate would be ideal. For reaction of $\cdot\text{CF}$ with other molecules, we assumed upper limits that should be reevaluated if those reactions are observed to contribute to $\cdot\text{CF}$ destruction.

In the reaction set, fluoromethylidyne ($\cdot\text{CF}$) is largely destroyed via reaction with O_2 and OH. Reaction with hydrogen atoms and H_2O are minor channels. Given that there is no experimental measurements for reaction of $\cdot\text{CF}$ with H_2O , limited (and inconsistent) data for reaction with O_2 , and both of these reactions are likely to have modest barriers, these reactions provide a significant uncertainty to this reaction set. Further refinements of this mechanism should address these issues for $\cdot\text{CF}$, as well as for $\cdot\text{CHF}$ and $\cdot\text{CF}_2$.

3.3.10 Carbonyl fluoride chemistry

Rate expressions for reactions involving the carbonyl fluorides are labeled 'PP' in Table 5.

An important set of species to fluorocarbon chemistry are the carbonyl fluorides ($\text{CHF}=\text{O}$, CF_2O , $\cdot\text{CF}=\text{O}$). $\text{CHF}=\text{O}$ can be destroyed via unimolecular decomposition and hydrogen atom abstraction by hydrogen, oxygen, and OH radicals. For the unimolecular decomposition (eliminating HF), we have fit the experimental data of Saito *et al.* (1985) using an

extended Arrhenius expression ($AT^b e^{-E/RT}$) using the value for E_0 (threshold energy) that they recommended based on their analysis. For the abstractions, we have substituted accepted rate expressions for the analogous $\text{CH}_2=\text{O}$ reactions. However, there is some significant uncertainty for abstraction by hydrogen atoms. The C–H bond dissociation energy in $\text{CHF}=\text{O}$ is about 45–50 kJ mol^{-1} stronger than in $\text{CH}_2=\text{O}$. Consequently, as an ‘abstraction’ the barrier should be somewhat higher. On the other hand, hydrogen atom addition followed by H_2 elimination could be more facile than the pure abstraction.

$\text{CF}_2=\text{O}$ can be destroyed via unimolecular decomposition (fluorine atom elimination), by reactions with hydrogen atoms, through reactions with OH radicals, and through reactions, potentially, with H_2O . The unimolecular decomposition is likely a negligible channel due to the strong C–F bond. There are a number of possible reactions with hydrogen atoms: (1) direct abstraction of a fluorine atom; (2) addition to the oxygen followed by 1,2-elimination of HF; and (3) addition to the carbon followed by 1,1 elimination of HF. Biordi *et al.* (1974) have estimated a rate constant for the net reaction of H with $\text{CF}_2=\text{O}$ at 1800 K based on their molecular beam sampling measurements in low-pressure flames. More recently, Richter *et al.* (1994) have estimated a rate expression on measurements at several different temperatures. We have also used BAC-MP4 *ab initio* transition state calculations (Zachariah *et al.*, 1995) followed by RRKM analysis to provide rate expressions for each of the possible channels. Our calculations are in excellent agreement with the experimental values and indicate that the addition/1,2 elimination channel dominates (92 kJ mol^{-1} barrier), the addition/1,1 elimination channel is about a factor of ten slower (101 kJ mol^{-1} barrier), and the direct abstraction channel is negligible (188 kJ mol^{-1} barrier). Modeling results suggest that changes in flame speeds upon addition of fluorinated hydrocarbons are slightly sensitive to the rate of destruction of $\text{CF}_2=\text{O}$.

$\text{CF}_2=\text{O}$ may also be destroyed via addition of OH to the carbon atom followed by 1,2-elimination of HF (Bozzelli *et al.*, 1994). However, this is a likely minor channel for destruction, because we estimate a barrier of about 105 kJ mol^{-1} for the elimination step from our BAC-MP4 *ab initio* transition state calculations (Zachariah *et al.*, 1995).

Due to the low reactivity of $\text{CF}_2=\text{O}$ and the large amounts of H_2O in hydrogen flames, $\text{CF}_2\text{O} + \text{H}_2\text{O}$ reactions must be considered. We have calculated (Zachariah *et al.*, 1995) rate expressions for $\text{CF}_2=\text{O} + \text{H}_2\text{O}$ complex formation followed by HF elimination. Flame modeling results suggest that reaction with water is a secondary destruction pathway to the hydrogen atom addition/1,2 elimination pathway. Nevertheless, it still needs to be considered.

$\cdot\text{CF}=\text{O}$ can be destroyed via unimolecular decomposition and reactions with hydrogen, oxygen, OH, and $\cdot\text{CH}_3$ radicals. Flame modeling results suggest that unimolecular decomposition and reaction with hydrogen atoms are the primary decomposition pathways. For reaction with hydrogen atoms, we used a rate constant identical to that for the analogous HCO reaction. For unimolecular decomposition, we determined a rate expression based on the reasonable assumption that combination reaction (reverse direction) is barrierless. There is significant uncertainty in the heat of formation of $\cdot\text{CF}=\text{O}$ and, consequently, there is significant uncertainty in this rate. Future refinements of this mechanism should address this issue. Flame modeling results suggest that the degree of inhibition is relatively sensitive to the rate of unimolecular decomposition of $\cdot\text{CF}=\text{O}$.

3.4. C_2 Fluorinated Hydrocarbon Chemistry

3.4.1. Overview

The C_2 subset of the reaction set (approximately 450 reactions) consists of the chemistry of 34 species containing two carbons (and hydrogen/fluorine/oxygen) with H, O, OH, H_2O , and other flame species. The $\text{C}_2/\text{H}/\text{F}/\text{O}$ species used in this reaction set are the nine fluoroethanes (e.g. $\text{CH}_2\text{F}-\text{CF}_3$), the 11 fluoroethyl radicals (e.g. $\text{CH}_2\text{F}-\text{CF}_2\cdot$), the five fluoroethylenes (e.g. $\text{CHF}=\text{CF}_2$), the five fluorovinyl radicals (e.g. $\text{CF}_2=\text{CH}\cdot$), the fluoroethynes (C_2HF , C_2F_2), and the fluoroketenes and fluoroketyl radical ($\text{CHF}=\text{CO}$, $\text{CF}_2=\text{CO}$, $\cdot\text{CF}=\text{CO}$). As indicated earlier, only the [Z] forms of $\text{CHF}=\text{CHF}$, $\text{CHF}=\text{CH}\cdot$, and $\text{CHF}=\text{CF}\cdot$ were considered to minimize the number of species in the reaction set.

The reaction set will not be described here in detail. Briefly, the fluoroethane destruction pathways (like fluoromethanes) consist of thermally and chemically activated decompositions and hydrogen atom abstraction reactions. Fluoroethyl radicals can react with hydrogen atoms creating fluoroethylenes via chemically activated fluoroethanes and HF elimination. Fluoroethyl radicals can also react with oxygen-containing species (O_2 , O, OH), resulting in the formation of oxidized fragments (e.g. $\text{CF}_3-\text{CF}_2\cdot + \text{O} \rightarrow \cdot\text{CF}_3 + \text{CF}_2=\text{O}$). Fluoroethylenes (produced from thermally and chemically activated fluoroethane decompositions) are predominantly destroyed via reaction with oxygen radicals, resulting in the formation of oxidized fragments (e.g. $\text{CH}_2=\text{CF}_2 + \text{O} \rightarrow \cdot\text{CH}=\text{O} + \cdot\text{CHF}_2$). Fluoroethylenes are also destroyed to a lesser degree through hydrogen atom abstraction by radicals such as OH, resulting in the formation of fluorovinyl radicals (e.g. $\text{CH}_2=\text{CF}_2 + \text{OH} \rightarrow \text{CF}_2=\text{CH}\cdot + \text{H}_2\text{O}$). Fluorovinyl radicals (like fluoromethyl and fluoroethyl radicals) are destroyed via reactions with

hydrogen radicals, as well as with oxygen-containing species.

3.4.2. Fluoroethanes: thermally and chemically activated decompositions

Rate expressions for thermally and chemically activated decompositions of fluoroethanes are labeled 'ED' in Table 5.

Both thermally and chemically activated decompositions of the fluoroethanes were considered, as well as stabilization of 'hot' fluoroethanes (e.g. $\text{CH}_3\text{-CF}_3 \rightarrow \text{CH}_2=\text{CF}_2 + \text{HF}$, $\cdot\text{CH}_3 + \cdot\text{CF}_3 \rightarrow \text{CH}_2=\text{CF}_2 + \text{HF}$, and $\cdot\text{CH}_3 + \cdot\text{CF}_3 \rightarrow \text{CH}_3\text{-CF}_3$). Many measurements (mainly in shock tubes) of the unimolecular decomposition of fluoroethanes have been made. The kinetics of decomposition of most of the fluoroethanes (HF elimination) have been measured in a comprehensive series of work by Tschuikow-Roux and co-workers (Tschuikow-Roux *et al.*, 1970, 1971; Tschuikow-Roux and Quiring, 1971; Millward *et al.*, 1971a, 1971b; Millward and Tschuikow-Roux, 1972; Sekhar and Tschuikow-Roux, 1974). Kinetic data for HF elimination from some of the fluoroethanes have also been obtained by Kerr and Timlin (1971) and Trotman-Dickenson and co-workers (Day and Trotman-Dickenson, 1969; Cadman *et al.*, 1970; Kochubei *et al.*, 1980; and Mitin *et al.*, 1988). We selected experimental values from these sources and used them without modification. The validity of employing these high-pressure limit values should be reevaluated for those fluoroethanes which have only a few fluorine substitutions, especially when using the reaction set at low pressure (and high temperatures).

There have been a number of measurements for reactions involving chemically activated or 'hot' fluoroethanes produced by combination of fluoromethyl radicals by Kim *et al.* (1973), by Trotman-Dickenson and co-workers (Kirk *et al.*, 1968; Phillips and Trotman-Dickenson, 1968; Cadman *et al.*, 1976), and by Pritchard and co-workers (Pritchard *et al.*, 1964; Bryant and Pritchard, 1967; Bryant *et al.*, 1967; Pritchard and Thommarson, 1967; Perona *et al.*, 1968; Pritchard and Bryant, 1968; Pritchard and Perona, 1970; Follmer and Pritchard, 1974). Some of this work includes measurements of branching ratios between product channels (i.e. HF elimination vs stabilization). There are no measurements (to our knowledge) for decomposition of hot fluoroethanes following combination of fluoroethyl radicals and hydrogen atoms. We used rate expressions for all of the hot fluoroethanes for the various product channels from our RRKM analysis (Tsang, 1994) in order to provide a consistent set (see brief discussion in Section 3.5). Further refinements of this mechanism should include using all of the existing experimental data as reference values for the RRKM calculations.

3.4.3. Fluoroethanes: fluoromethyl disproportionations and fluoromethylene insertions

Rate expressions for fluoromethyl disproportionation and fluoromethylene insertion reactions are labeled 'EC' in Table 5.

Pritchard and co-workers have made a comprehensive set of measurements of reactions involving disproportionations between (fluoro)methyl radicals (Pritchard and Follmer, 1973; Nilsson and Pritchard, 1982; Pritchard *et al.*, 1984, 1985, 1987, 1990, 1991, 1992). These studies suggest a branching ratio for disproportionation vs combination (HF elimination or stabilization) of about 10–20% at 350–500 K. We employed these data in combination with estimated barriers from our BAC-MP4 *ab initio* transition state calculations and determined rate expressions consistent with the available experimental data. We estimated that the activation energies or barriers-to-disproportionation are about 3–9 kJ mol⁻¹ for reactions involving $\cdot\text{CHF}_2$ (i.e. $\cdot\text{CF}_2$ product) and 14–19 kJ mol⁻¹ for reactions involving $\cdot\text{CH}_2\text{F}$ (i.e. $\cdot\text{CHF}$ product).

We also considered that $\cdot\text{CHF}$ and $\cdot\text{CF}_2$ may insert into C–H bonds in methane and fluoromethanes. We used rate expressions based on estimated barriers for insertion from our BAC-MP4 *ab initio* calculations of 63 and 130 kJ mol⁻¹ for $\cdot\text{CHF}$ and $\cdot\text{CF}_2$, respectively. These barriers are rather significant when compared to $\cdot\text{CH}_2$, which inserts into C–H bonds with little barrier. Our BAC-MP4 *ab initio* calculations suggest these barriers result from ionic repulsion between the electropositive hydrogen atom on the (fluoro)methane and the highly electropositive carbon atom on the fluoromethylene. For example, the hydrogen atom on CH_4 has a Mulliken charge of +0.17 and the carbon atom of $\cdot\text{CF}_2$ has a Mulliken charge of +0.54. However, there is some experimental evidence to suggest that the barriers are significantly smaller (DiFelice and Ritter, 1994a, 1994b). This apparent conflict for these important species should be addressed in future mechanism refinements.

3.4.4. Fluoroethanes: abstractions

Rate expressions for hydrogen abstractions from the fluoroethanes are labeled 'EA' in Table 5.

There have been a number of measurements of hydrogen abstractions for fluoroethanes by OH radicals. Cohen and co-workers (Cohen and Benson, 1987b; Cohen and Westberg, 1991) have used transition-state theory calculations to analyze and predict rate coefficients for a series of halogen-substituted methanes and ethanes. Much of their analysis is based on the experimental data of Clyne and Holt (1979) and Jeong *et al.* (1984). Other experimental data included in their analysis were from the measurements by Howard and Evenson (1976b), Handwerk and Zellner (1978), Nip *et al.* (1979), and Martin

and Paraskevopoulos (1983). In our work we used the values recommended by Cohen and Benson (1987a, 1987b). For the three asymmetric fluoroethanes ($\text{CH}_3\text{-CH}_2\text{F}$, $\text{CH}_3\text{-CHF}_2$, $\text{CH}_2\text{F-CHF}_2$), where there are different functional hydrogen substitutions, we estimated the branching ratios based on relative bond strengths.

There have recently been a number of precise measurements for these abstraction reactions for a number of the fluoroethanes by Huie and co-workers (Liu *et al.*, 1990; Zhang *et al.*, 1992c), by Ravishankara and co-workers (Talukdar *et al.*, 1991; Gierczak *et al.*, 1991), and by Nielsen (1991). Based on some of the more recent measurements that are newer recommendations by Cohen and Westberg (1991) for some of these reactions. The biggest changes are for reactions involving $\text{CH}_3\text{-CHF}_2$ and $\text{CHF}_2\text{-CF}_3$. However, the changes in the rate expressions are only significant at temperatures well below flame temperatures (due to T^b dependence).

Although there have been a number of measurements of hydrogen abstractions from many of the fluoroethanes by OH radicals, there have been no measurements (to our knowledge) for hydrogen abstractions by hydrogen and oxygen atoms from any of the fluoroethanes. Consequently, in this work we utilized an empirical correlation that we determined for other hydrogen abstraction reactions. For hydrogen abstraction by hydrogen and oxygen atoms, we used activation energies that were factors of 2.5 and 2.7 times, respectively, that for the analogous abstractions by OH radicals. These factors were based on the fact that the reactions with hydrogen and oxygen atoms are about 62 kJ mol^{-1} and 70 kJ mol^{-1} less exothermic, respectively, than the corresponding reactions with OH.

The fluoroethanes are largely destroyed via unimolecular decomposition and abstraction by OH radicals. Good quality experimental data are available (cited above). Future refinements of this mechanism need only to reevaluate this work and, possibly, redetermine the branching ratios for the three asymmetric fluoroethanes. However, it would be valuable to have experimental measurements of these rates at flame temperatures, because hydrogen abstractions by OH are primary decomposition pathways and the recommended values are based on experimental measurements at relatively low temperatures (300–500 K).

3.4.5. Fluoroethyl radical destruction

Rate expressions for reactions involving the fluoroethyl radicals are labeled 'GG' in Table 5.

Fluoroethyl radicals can be destroyed via reaction with flame species such as O_2 , H, O, OH, and $\cdot\text{CH}_3$. For reactions with O_2 , O, and OH, we used rate expressions by analogy to those accepted for the corresponding ethyl radical reactions (Bozzelli and Dean, 1990; Baulch *et al.*, 1992; Tsang and Hampson, 1986).

For reactions of O_2 with the three fluoroethyl radicals without a beta hydrogen ($\text{CF}_3\text{-CH}_2\cdot$, $\text{CF}_3\text{-CHF}\cdot$, $\text{CF}_3\text{-CF}_2\cdot$), we assigned the products as $\cdot\text{CF}_3 + \text{CXY=O} + \text{O}$ (i.e. C–C bond cleavage of $\text{CF}_3\text{-CXY-O}\cdot$ intermediates). These products and rate expressions were chosen by analogy to the $\cdot\text{CF}_3 + \text{O}_2$ reaction (adjusting for reaction enthalpy). Future refinements of this mechanism should consider formation of fluoroacetaldehyde species (and corresponding chemistry) following decomposition of the fluoroethoxy intermediates (e.g. $\text{CF}_3\text{-CH}_2\text{-O}\cdot \rightarrow \text{CF}_3\text{-CHO} (+\text{H}) \rightarrow \text{products}$).

For reactions of oxygen with the fluoroethyl radicals, two product channels must be considered. A third channel, abstraction of hydrogen, can be ignored by analogy to $\text{C}_2\text{H}_5 + \text{O}$. It is likely that hydrogen atom elimination (e.g. $\text{CH}_3\text{-CHF}\cdot + \text{O} \rightarrow \text{CH}_3\text{-CFO} + \text{H}$) is the dominant pathway over C–C bond cleavage (e.g. $\text{CH}_3\text{-CHF}\cdot + \text{O} \rightarrow \text{CH}_3\cdot + \text{CHF=O}$). We assigned rate constants for the hydrogen atom elimination reactions relative to that for C_2H_5 using the geometric mean rule and scaling relative to the rate constants for $\text{CH}_3 + \text{O}$ and $\text{CF}_3 + \text{O}$. In order to eliminate the fluoroacetaldehyde and (fluoro)acetylfluoride species from the reaction set (formed via the hydrogen atom elimination pathway), we assumed that these species are destroyed very quickly (that is, they are present only in steady-state concentrations) and result in the eventual formation of (fluoro)ketene species. For example, a likely reaction pathway could be $\text{CH}_2\text{F-CFO} + \text{H} \rightarrow \cdot\text{CHF-CFO} + \text{H}_2$ followed by $\cdot\text{CHF-CFO} + \text{H} \rightarrow [\text{CH}_2\text{F-CFO}]^* \rightarrow \text{CHF=CO} + \text{HF}$.

For reactions of OH with the fluoroethyl radicals, there are also two product channels that must be considered: combination/HF elimination (e.g. $\text{CH}_3\text{-CHF} + \text{OH} \rightarrow \text{CH}_3\text{-CHO} + \text{HF}$) vs hydrogen abstraction (e.g. $\text{CH}_3\text{-CHF} + \text{OH} \rightarrow \text{CH}_2=\text{CHF} + \text{H}_2\text{O}$). We have ignored several other possible channels. HF elimination involving breaking a C–H bond (e.g. $\text{CH}_3\text{-CHF} + \text{OH} \rightarrow \text{CH}_2=\text{CH(OH)} + \text{HF}$) will have a higher barrier than breaking a O–H bond (e.g. $\text{CH}_3\text{-CHF} + \text{OH} \rightarrow \text{CH}_3\text{-CHO} + \text{HF}$). Product channels involving breaking a C–C bond (e.g. $\text{CH}_3\text{-CHF} + \text{OH} \rightarrow \cdot\text{CH}_3 + \cdot\text{OCH}_2\text{F}$) were also ignored. In contrast to that for oxygen atoms, abstraction of beta hydrogen atoms from ethyl radicals by OH radicals is generally assumed to occur. We assigned rate constants for the two possible channels employing the corresponding rate constants for the analogous reactions with oxygen atoms. A small barrier (about 12 kJ mol^{-1}) was estimated for the abstraction channel. As the fluoroethyl + O reactions, we assumed that the fluoroacetaldehyde and (fluoro)acetylfluoride species are quickly destroyed, resulting in the formation of (fluoro)ketene species.

Fluoroethyl radicals may also react with hydrogen atoms and form 'hot' fluoroethanes. For these

reactions we used rate expressions from our RRKM calculations (as mentioned previously). Fluoroethyl radicals may combine with $\cdot\text{CH}_3$ to form hot fluoro-propanes (which are likely to be stabilized except at the highest temperature). Fluoroethyl radicals may also disproportionate with $\cdot\text{CH}_3$ to form CH_4 and fluoroethylenes. The first channel (combination) was simply ignored in order to exclude C_3 fluorinated species from the reaction set. The rate constants for the second channel (disproportionation) were set identical to that accepted for the reaction $\cdot\text{C}_2\text{H}_5 + \cdot\text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_4$ (Tsang and Hampson, 1986).

3.4.6. Fluoroethylenes: decompositions and reactions with hydrogen

Rate expressions for thermally and chemically activated decompositions of the fluoroethylenes are labeled 'JD' in Table 5. Rate expressions for reactions of hydrogen atoms with the fluoroethylenes are labeled 'JA' in Table 5.

In this work, we used experimental rate expressions (Simmie and Tschuikow-Roux, 1970; Simmie *et al.*, 1970) for the rate of pyrolysis (eliminating HF) of two of the fluoroethylenes ($\text{CH}_2=\text{CHF}$ and $\text{CH}_2=\text{CF}_2$). For the other fluoroethylenes, we used these rate expressions as reference points and adjusted the activation energy based on the reaction enthalpy. For thermal decomposition or pyrolysis of perfluoroethylene ($\text{CF}_2=\text{CF}_2 \rightarrow \cdot\text{CF}_2 + \cdot\text{CF}_2$), we used rate expressions from our RRKM analysis of the experimental data of Schug and Wagner (1978). These data are also consistent with the experimental rate expression of Modica and LaGraff (1966). For the other thermally and chemically activated fluoroethylene decomposition channels (e.g. $\cdot\text{CHF} + \cdot\text{CHF} \rightarrow \text{CHF}=\text{CHF}$ or $\text{C}_2\text{HF} + \text{HF}$), we used rate expressions from our RRKM calculations (based on the reverse reactions or combinations).

Fluoroethylenes can also be destroyed via reaction with hydrogen atoms. This includes hydrogen atom addition followed by stabilization of the fluoroethyl radical produced (e.g. $\text{CH}_2=\text{CF}_2 + \text{H} \rightarrow \text{CH}_3-\text{CF}_2\cdot$ or $\text{CHF}_2-\text{CH}_2\cdot$), as well as hydrogen atom addition followed by fluorine atom elimination (e.g. $\text{CH}_2=\text{CF}_2 + \text{H} \rightarrow \text{CH}_2=\text{CHF} + \text{F}$). There are some experimental data for these reactions (e.g. Teng and Jones, 1972, 1973); however, there appears to be some conflict between them. Consequently, in this mechanism, we simply employed an accepted rate expression for the hydrogen atom addition/stabilization for the analogous ethylene reaction. That is, we used rate expressions for the reactions of fluoroethylenes with hydrogen atoms by analogy to the recommendations of Tsang and Hampson (1986) for the two pathways $\text{C}_2\text{H}_4 + \text{H} \rightarrow \text{C}_2\text{H}_5$ and $\text{C}_2\text{H}_4 + \text{H} \rightarrow \text{C}_2\text{H}_3 + \text{H}_2$. For the other possible pathway for reaction of hydrogen atoms with the fluoroethylenes (hydrogen atom addition and fluorine atom

elimination or displacement), we assumed barrierless addition of fluorine atoms.

There are some significant uncertainties here for the hydrogen atom addition reactions. First, it is likely the barrier-to-addition will be influenced by the degree of fluorine substitution on the alpha carbon. Second, the efficiency of stabilization of the chemically activated or 'hot' fluoroethyl radical will be strongly influenced by the degree of fluorine substitution. Further refinements of this mechanism should address these issues. For example, reasonable estimates for the relative barriers-to-addition could be obtained from BAC-MP4 *ab initio* transition state calculations and the relative stabilization efficiencies could be estimated reasonably well using RRKM analysis.

The fluoroethylenes should also react relatively quickly with methyl and fluoromethyl radicals and with methylene and the fluoromethylenes. However, we have not included these reactions in the reaction set, because they lead to the formation of C_3 fluorinated hydrocarbons (essentially polymerization reactions). Future refinements of this mechanism should investigate the potential influence of these type of reactions on the overall chemistry.

3.4.7. Fluoroethylenes: reactions with oxygen and OH

Rate expressions for reactions of O and OH with the fluoroethylenes are labeled 'JO' in Table 5.

The fluoroethylenes are primarily destroyed via reaction with oxygen atoms (e.g. $\text{CH}_2=\text{CF}_2 + \text{O} \rightarrow \cdot\text{CHF}_2 + \text{HCO}$). For these reactions, we used rate expressions that were fits to extended Arrhenius form ($AT^b e^{-E/RT}$) to the recommendations of Cvetanovic (1987) in order to extrapolate the low-temperature measurements (300–500 K) to flame temperatures. A temperature dependence of $T^{1.0}$ was used by analogy to other reactions involving oxygen atoms. The recommended values by Cvetanovic are largely based on work in this area by Herron and Huie (1973), Jones and Moss (1974), Atkinson and Pitts (1977), and Gutman and co-workers (Park *et al.*, 1984). It should be noted that for perfluoroethylene, the only possible channel is $\text{CF}_2=\text{CF}_2 + \text{O} \rightarrow \text{CF}_2=\text{O} + \cdot\text{CF}_2$ (i.e. no hydrogen migration possible). It should also be noted that for $\text{CH}_2=\text{CHF}$ there are two possible channels ('addition' of the oxygen atom to one side or the other). We have used an estimated additional 4 kJ mol^{-1} for 'addition' of the oxygen atom to the fluorinated carbon. This is consistent with an upper limit measurement at room temperature for this reaction by Gutman and co-workers (Slagle *et al.*, 1974).

For reaction of oxygen with the fluoroethylenes, it is generally understood that the dominant pathway is where the products are the fluoromethyl and (fluoro)formyl radical (e.g. $\text{CH}_2=\text{CHF} + \text{O} \rightarrow \text{HCO} + \cdot\text{CH}_2\text{F}$) following dissociation of the chemically activated fluoroethylene oxide formed by

oxygen atom attack on the double bond. That is, the oxygen atom first 'adds' to the carbon with the last number of electronegative substituents (in this case F). A hydrogen atom on this carbon then 'migrates' to the other carbon. However, there is some evidence (Gilbert *et al.*, 1976) to suggest that the assumed methyl + formyl products (e.g. $\cdot\text{CHF}_2 + \text{HCO}$) may not be the only product channel (e.g. $\text{CHF}=\text{CHF} + \text{O} \rightarrow \text{CHF}=\text{C}=\text{O} + \text{HF}$ or $\text{CHF}=\text{CHF} + \text{O} \rightarrow \text{CHF}=\text{O} + \cdot\text{CHF}$). The numerous other possible channels are generally considered to be minor pathways: (1) stabilized fluoroethylene oxides, (2) stabilized fluoroacetaldehydes, (3) fluoroacetyl radicals + H, (4) fluorovinoxy radicals (e.g. $\cdot\text{CHF}-\text{CFO}$) + H, (5) (fluoro)formaldehydes + (fluoro)methylenes, (6) fluoroketenes + H_2 , and (7) fluorovinyl radicals + OH. The latter class of reactions, hydrogen abstraction, is a separate reaction from the first four (which are additions) and may become important at the highest temperatures. Given that the reaction of oxygen with the fluoroethylenes is a primary decomposition pathway for the fluoroethylenes and that the rate expressions are based on experimental measurements at low temperatures (300–500 K), it would be very valuable to have measurements of these reactions and product channels at near flame temperatures. *Ab initio* transition state calculations could shed some light on the relative importance of each potential reaction pathway.

Fluoroethylenes can also be destroyed via reaction with OH radicals. We have only considered hydrogen atom abstraction (and not addition/elimination). For abstraction of hydrogen atoms from the fluoroethylenes by OH radicals, we used rate expressions that were fits (with an estimated $T^{2.0}$ dependence) to the values recommended by Baulch *et al.* (1992) for $\text{C}_2\text{H}_4 + \text{OH} \rightarrow \text{C}_2\text{H}_3 + \text{H}_2\text{O}$, which is based on a measurement by Tully (1988). Clearly the C–H bond strength will be significantly influenced by fluorine substitution. This issue should be addressed in future refinements of this mechanisms.

Fluoroethylenes may also be destroyed by OH addition/elimination reactions. This could result in the formation of fluoroethanols (e.g. $\text{CHF}=\text{CH}(\text{OH})$) or possibly fluorovinoxy radicals (e.g. $\cdot\text{CHF}-\text{CFO}$). There are a number of uncertainties here and, consequently, these reaction pathways were not pursued. First, these pathways result in the production of a number of new species in the reaction set, whose thermochemistry is unknown. Second, decomposition pathways for these new species must be considered. Third, the effect of fluorine substitution on the barrier to OH addition is not known (but probably could be estimated reasonably well using RRKM analysis). Fourth, the relative rates for at least three competing reactions must be known; that is, (1) stabilization of the fluorohydroxyethyl radicals (e.g. $\cdot\text{CF}_2-\text{CF}_2-\text{OH}$) vs reversion to reactants, (2) hydrogen atom elimination, and (3) HF elimination. Future refinements of this mechanism should investi-

gate the potential importance of the OH addition/elimination reactions for the fluoroethylenes. It may be that only the perfluorocompounds may need to be considered (by analogy to the sole importance of the perfluoromethoxy radical).

3.4.8. Fluorovinyl radical destruction

Rate expressions for reactions involving the fluorovinyl radicals are labeled 'JO' in Table 5.

Westmoreland (1992) has calculated the temperature (and pressure) dependencies of the rate for the chemically activated reaction $\text{C}_2\text{H}_3 + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HCO}$. We used these values for the analogous fluorovinyl radical reactions. In this work, we used the values recommended by Warnatz (1984) and Tsang and Hampson (1986) for the $\text{C}_2\text{H}_3 + \text{O} \rightarrow \text{products}$ and $\text{C}_2\text{H}_3 + \text{OH} \rightarrow \text{products}$ reactions, respectively, for the analogous fluorovinyl radical reactions. The values recommended by Warnatz for the first reaction are based on measurements by Heinemann *et al.* (1988).

3.4.9. Fluoroethyne, fluoroketone, and fluoroketyl radical chemistry

Rate expressions for reactions involving these species are labeled 'KK' in Table 5.

For reactions involving the fluoroethynes (C_2HF , C_2F_2), the fluoroketenes ($\text{CHF}=\text{C}=\text{O}$, $\text{CF}_2=\text{C}=\text{O}$), and the fluoroketyl radical ($\cdot\text{CF}=\text{C}=\text{O}$), we used rate expressions by analogy to the corresponding hydrocarbons (C_2H_2 , CH_2CO , $\cdot\text{HCCO}$). For reaction of hydrogen atoms with the two fluoroethynes (C_2HF , C_2F_2), we used rate expressions derived from the recommendation of Warnatz (1984) for $\text{C}_2\text{H}_2 + \text{H} \rightarrow \text{C}_2\text{H}_3$, which is based on measurements by Payne and Stief (1976). For these hydrogen atom addition reactions, we employed third-body stabilization efficiencies and low-pressure limits identical to that for acetylene. Future refinements of this mechanism should provide better estimates for these reactions.

3.5. RRKM Analysis

Rate constants for chemical activation processes were determined through solution of the steady-state master equation in the context of a step ladder model and transition states that satisfy the high-pressure rate expressions. Extension to multichannel decomposition is straightforward in the sense of simply adding another term to the expression involving the decomposition channels. The step-size down parameters are taken to be $T/3 \text{ cm}^{-1}$ and lead to values near 500 cm^{-1} under conditions relevant to combustion. These numbers are consistent with fall-off data. The general procedure for RRKM (Robinson and Holbrook, 1972) is in contrast to the treatment of weak collisions generally described as the QRRK

procedure (Dean and Westmoreland, 1987). This procedure is of some validity for describing single-channel unimolecular decompositions, since Troe (1977) has derived a relationship between the collision efficiency and the step-sizes down. However, for chemically activated processes, which are really the simplest type of multichannel decompositions, this collisional efficiency is no longer related to the step-sizes. As such, it is thus an arbitrary fit parameter. Without experimental data, it is not clear how to assign this parameter. The situation is even worse when there are multiple decomposition channels. Strictly speaking, one would need to define a collision efficiency for every channel. Here again, there is at present no basis for assigning these values.

The assignment of the high-pressure rate expression is a key element in each estimation. Our procedure is to utilize experimental data where it exists. In the absence of reliable experimental data, the high-pressure rate expression is derived by analogy; for example, using the geometric mean rule. For combination reactions involving radicals, this approach is consistent with Benson's geometric approach (Benson, 1976) leading to the restricted rotor transition states that are used in this work. Thus, the combination rate expressions (Tsang, 1994) for the (fluoro)methyl radicals are based on $k(\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6)$ and $k(\text{CF}_3 + \text{CF}_3 \rightarrow \text{C}_2\text{F}_6)$. For the reactions of hydrogen atoms with (fluoro)methyl radicals, the combination rate expressions are based on $k(\text{CH}_3 + \text{H} \rightarrow \text{CH}_4)$ and $k(\text{CF}_3 + \text{H} \rightarrow \text{CHF}_3)$.

3.6. BAC-MP4 *Ab Initio* Predictions

For a number of reactions considered in the mechanism, there are no or little experimental rate data. Consequently, we have estimated that data using BAC-MP4 *ab initio* calculations of the transition state geometries and energies and RRKM/master equation analysis. A short description of the BAC-MP4 *ab initio* calculations is given in Section 2.5. The transition state for a reaction was obtained by searching for a geometry with one negative eigenvalue. This corresponds to a saddle point on the potential energy surface. This is then followed by a steepest-descent reaction path analysis to ensure that the calculated transition state corresponds to the appropriate reactants and products. BAC corrections are then assigned in the same manner as with the equilibrium structures. In order to quantify the uncertainties in the calculated data, we have also performed calculations on a number of related reactions where there is good quality experimental data.

We have calculated transition states for a number of sets of reactions, including the following:

- (1) HF elimination from the fluoromethanes (e.g. $\text{CH}_3\text{F} \rightarrow \cdot\text{CH}_2 + \text{HF}$);
- (2) H_2 elimination from the fluoromethanes (e.g. $\text{CH}_3\text{F} \rightarrow \cdot\text{CHF} + \text{H}_2$);
- (3) hydrogen atom abstraction by hydrogen from the fluoromethanes (e.g. $\text{CH}_3\text{F} + \text{H} \rightarrow \cdot\text{CH}_2\text{F} + \text{H}_2$);
- (4) fluorine atom abstraction by hydrogen from the fluoromethanes (e.g. $\text{CH}_3\text{F} + \text{H} \rightarrow \cdot\text{CH}_3 + \text{HF}$);
- (5) reactions of H_2O with the fluoromethylenes (e.g. $\cdot\text{CHF} + \text{H}_2\text{O} \rightarrow [\text{CH}_2\text{FOH}]^* \rightarrow \text{CH}_2\text{O} + \text{HF}$);
- (6) reactions of H_2O with carbonyl difluoride (e.g. $\text{CF}_2=\text{O} + \text{H}_2\text{O} \rightarrow \text{FC}(\text{O})\text{OH} + \text{HF}$);
- (7) fluorine atom abstraction by hydrogen from carbonyl difluoride (i.e. $\text{CF}_2=\text{O} + \text{H} \rightarrow \cdot\text{CF}=\text{O} + \text{HF}$);
- (8) hydrogen atom addition to carbonyl difluoride (e.g. $\text{CF}_2=\text{O} + \text{H} \rightarrow [\cdot\text{CF}_2\text{OH}]^* \rightarrow \cdot\text{CF}=\text{O} + \text{HF}$);
- (9) OH addition to carbonyl difluoride (i.e. $\text{CF}_2=\text{O} + \text{OH} \rightarrow \cdot[\text{OCF}_2(\text{OH})]^* \rightarrow \text{FC}(\text{O})\text{O}\cdot + \text{HF}$).

The *ab initio* geometries and energies of the transition states were then used as inputs to RRKM/master equation analysis in order to calculate rate expressions. The calculated rate expressions agree well with those derived from experimental measurements (where they exist). Further discussion of the *ab initio* transition state calculations can be found elsewhere (Zachariah *et al.*, 1995).

There is one reaction that is very important to the chemistry of fluorinated hydrocarbon destruction and where the calculated rate expression can be compared with good quality experimental measurements. The rate of reaction of hydrogen atoms with $\text{CF}_2=\text{O}$ has been estimated based on measurements in flames of the rate of disappearance of carbonyl difluoride. Biordi *et al.* (1974) estimated a rate constant at 1800 K for this reaction in CF_3Br inhibited methane/oxygen/argon premixed flames. More recently, Richter *et al.* (1994) have determined rate coefficients at 1175–1490 K for this reaction in CF_3H inhibited hydrogen/oxygen/argon premixed flames.

The reaction of hydrogen atoms with $\text{CF}_2=\text{O}$ has three distinct pathways, one is a direct abstraction and the other two are addition/elimination reactions.

First, hydrogen atoms can abstract fluorine (i.e. $\text{CF}_2=\text{O} + \text{H} \rightarrow \cdot\text{CF}=\text{O} + \text{HF}$). Our BAC-MP4 transition state calculations suggest a barrier of about 150 kJ mol^{-1} for this reaction. This compares well with calculated barriers of about $130\text{--}170 \text{ kJ mol}^{-1}$ for fluorine atom abstraction from the fluoromethanes. These calculated barriers are consistent with that measured by Kochubei and Moin (1971) for fluorine abstraction by hydrogen from CF_4 . They reported an activation energy of about 190 kJ mol^{-1} at 1200–1600 K. This would suggest a barrier of about 160 kJ mol^{-1} assuming a T^2 dependence to the rate.

The second pathway consists of hydrogen atom addition to the carbon atom on the carbonyl difluoride followed by 1,1-elimination of HF from the chemically activated fluoromethoxy intermediate

(i.e. $\text{CF}_2=\text{O} + \text{H} \rightarrow [\text{CHF}_2\text{O}]^* \rightarrow \cdot\text{CF}=\text{O} + \text{HF}$). The third pathway is also an addition/elimination reaction, but consists of hydrogen atom addition in this case to the oxygen atom on the carbonyl difluoride followed by 1,2-elimination of HF from the hot hydroxyfluoromethyl intermediate ($\text{CF}_2=\text{O} + \text{H} \rightarrow [\cdot\text{CF}_2\text{OH}]^* \rightarrow \cdot\text{CF}=\text{O} + \text{HF}$).

Our *ab initio* transition state calculations suggest barriers of about 50 kJ mol^{-1} and 65 kJ mol^{-1} for addition to the carbon and oxygen sides of the carbonyl difluoride, respectively. It is slightly more energetically favorable for the hydrogen atom to add to the carbon side. However, the subsequent 1,1 HF elimination step in this case in order to form the $\cdot\text{CF}=\text{O}$ product involves a transition state that is an additional 80 kJ mol^{-1} higher (a total of 130 kJ mol^{-1}). The overall energetics of this pathway is significantly less favorable than the 1,2 HF elimination step that follows hydrogen atom addition to the oxygen side. This involves a transition state that is only an additional 15 kJ mol^{-1} higher (a total of 80 kJ mol^{-1}). We have derived rate expressions based on RRKM/master equation calculations using the geometries and energies of the *ab initio* transition states. These calculated rate expressions (Zachariah *et al.*, 1995) agree extremely well with the experimental rate constants reported by Biordi *et al.* (1974) and Richter *et al.* (1994).

Further discussion of the *ab initio* transition state calculations can be found elsewhere (Zachariah *et al.*, 1995).

4. FUTURE MECHANISM REFINEMENT

4.1. Overview

The purpose of this section is to highlight uncertainties in the reaction set that may impact its ability to adequately predict the chemistry of fluorinated hydrocarbon destruction and the behavior of fluorinated hydrocarbon-inhibited hydrocarbon flames. We will mention known significant uncertainties, both those that may influence and those that are unlikely to influence the overall chemistry. For example, the heats of formation of many of the species must be estimated using empirical methods, such as group additivity. However, much of the chemistry of the destruction of fluorinated hydrocarbon species in hydrocarbon flames is irreversible. That is, it is the rates of mainly highly exothermic steps that are important and not thermodynamic considerations (free energies) or endothermic steps. For example, although there is significant uncertainty in the heat of formation of $\cdot\text{CHF}$, this should have little impact on the chemistry in hydrocarbon flames, since $\cdot\text{CHF}$ is overwhelmingly destroyed through reactions with radicals such as H and OH, and not through unimolecular decompositions. In general, the uncertainties in the reaction set will only be highlighted here.

The reaction set presented here should be considered as a framework for the development of a model that accurately describes the decomposition of fluorinated hydrocarbons and their impact on hydrocarbon flame inhibition chemistry. It should not be considered a finished product, since to date there has been very little comparison of its predictions with experimental measurements. Future refinement and validation of the mechanism will require input from measurements of flame speed, flame temperature, concentration profiles, and temperature profiles in fluorinated hydrocarbon-inhibited flames.

In the reaction set or mechanism presented here, there are a number of species with uncertain thermochemistry and a number of reactions with uncertain rate expressions. These can be divided (arbitrarily) into several classes. (1) In most cases, the uncertainties are derived from the lack of direct or even indirect experimental data for these species and reactions. (2) In some cases, certain classes of species and reactions were not included in the reaction set, because of lack of experimental data and uncertainty in the chemistry. (3) In the other cases, experimental data exist, but because of the magnitude of the reaction set, we have not yet verified that the rate expressions employed in the reaction set are fully consistent with the experimental data available.

For example, the JANAF recommended heat of formation for CHF=O is simply the average of the heats of formation of the analogous $\text{CH}_2=\text{O}$ and $\text{CF}_2=\text{O}$. Consequently, there is significant uncertainty introduced from this procedure (bond dissociation energies are strongly dependent upon α -substitution), irrespective of the uncertainties in the heats of formation of the reference compounds. For example, using the heats of formation of CH_4 (-75 kJ mol^{-1}) and CH_2F_2 (-453 kJ mol^{-1}), one would estimate using this procedure a heat of formation for CH_3F of -264 kJ mol^{-1} . This is 26 kJ mol^{-1} lower than the accepted literature value (-238 kJ mol^{-1}).

An analogous example for estimated rate constants is for the hydrogen abstraction $\text{CHF}=\text{O} + \text{H} \rightarrow \cdot\text{CF}=\text{O} + \text{H}_2$. In this case, we have simply used an accepted rate expression for the analogous reaction $\text{CH}_2=\text{O} + \text{H} \rightarrow \text{HCO} + \text{H}_2$. Given that the C-H bond dissociation energy in CHF=O is about $45\text{--}55 \text{ kJ mol}^{-1}$ stronger than in $\text{CH}_2=\text{O}$, it is likely that the barrier to abstraction for the CHF=O reaction is somewhat higher than the barrier for the $\text{CH}_2=\text{O}$ reaction. Although we have estimated that the barrier is about 10 kJ mol^{-1} higher (based upon trends in other halogen-substituted hydrocarbons), we have not (to date) employed this estimate because of some uncertainties. For example, it is likely that this reaction is not an 'abstraction', but rather an addition to the oxygen (e.g. $\text{CH}_2=\text{O} + \text{H} \rightarrow \cdot\text{CH}_2\text{OH}$) followed by a 1,2-elimination of H_2 , because hydrogen atom abstractions by hydrogen should have a barrier closer to 40 kJ mol^{-1} (like $\text{CH}_4 + \text{H} \rightarrow \cdot\text{CH}_3 + \text{H}_2$). Consequently, the effec-

tive 'barrier' may not be significantly influenced by the C–H bond strength.

Another important example of uncertainties in rate constants can be found for hydrogen atom addition/stabilization to the fluoroethylenes (e.g. $\text{CH}_2=\text{CF}_2 + \text{H} \rightarrow \text{CH}_3-\text{CF}_2\cdot$ and $\text{CHF}_2-\text{CH}_2\cdot$). We have simply employed an accepted rate expression for the hydrogen atom addition/stabilization for the analogous $\text{C}_2\text{H}_4 + \text{H} \rightarrow \cdot\text{C}_2\text{H}_5$ reaction. However, there are some significant uncertainties here. First, it is likely the barrier to addition will be influenced by the degree of fluorine substitution on the α carbon. For example, the barrier to addition for the above reaction involving $\text{CH}_2=\text{CF}_2$ may be of the order of 8 kJ mol^{-1} vs 30 kJ mol^{-1} for addition to the unsubstituted vs substituted carbon, respectively. Secondly, the efficiency with which the 'hot' fluoroethyl radical is stabilized will be strongly influenced by the degree of fluorine substitution (e.g. $\text{CHF}_2-\text{CF}_2\cdot$ vs $\text{CH}_3-\text{CHF}\cdot$). The relative barriers to addition and relative stabilization efficiencies could be calculated satisfactorily using *ab initio* and RRKM methods, respectively. However, to date we have not done these calculations.

4.2. Thermochemistry

There are a number of other species in this reaction set that have significant uncertainties in their heats of formation, because of the lack of direct experimental data.

The heat of formation of CH_3F has been estimated based on trends in the heats of formation of the other fluoromethanes. Although CH_3F is unlikely to be a key species in fluorinated hydrocarbon-inhibited hydrocarbon flames, as the simplest fluorinated hydrocarbon, its heat of formation is significant as a reference point for heats of formation of other fluorinated hydrocarbons. An experimentally derived heat of formation for CH_3F would be very valuable.

The value recommended in the JANAF tables for the heat of formation of $\cdot\text{CHF}$ is based on the average of the heats of formation of $\cdot\text{CH}_2$ and $\cdot\text{CF}_2$. Other values are based on estimates of bond dissociation energies or the absence of $\cdot\text{CHF}$ as a product in certain reactions (Staemmler, 1974, Hsu *et al.*, 1978, Pritchard *et al.*, 1984). Consequently, there are significant uncertainties introduced from these procedures (i.e. bond dissociation energies are strongly dependent upon α -substitution). Most reactions that create or destroy $\cdot\text{CHF}$ are highly irreversible reactions (e.g. $\cdot\text{CHF} + \text{H} \rightarrow \text{CH} + \text{HF}$) and, consequently, are unaffected by the energetics of the reactions. However, disproportionation reactions involving $\cdot\text{CHF}$ may proceed with small barriers and have modest heats of reaction (e.g. $\cdot\text{CH}_3 + \cdot\text{CH}_2\text{F} \rightarrow \text{CH}_4 + \cdot\text{CHF}$). For these reactions, the uncertainty in the heat of formation of $\cdot\text{CHF}$ may be important.

The literature value for the heat of formation of $\text{CF}_2=\text{O}$ is reported with a relatively low uncertainty. However, our BAC-MP4 *ab initio* calculations predict a value that is about 40 kJ mol^{-1} higher than the experimental number. Other *ab initio* calculations (Montgomery *et al.*, 1994; Schneider and Wallington, 1994) using different approaches also predict a heat of formation for $\text{CF}_2=\text{O}$ that is higher (by about 30 kJ mol^{-1}) than the experimental value. There is reason to believe that there have been side reactions or wall reactions that complicated the measurements. Furthermore, the heats of formation of all the oxygenated C_1 fluorocarbons (e.g. $\text{CF}_3\text{O}\cdot$, $\cdot\text{CF}=\text{O}$, etc.) are referenced to $\text{CF}_2=\text{O}$. Because of these issues, both uncertainties in the experimental measurements and *ab initio* calculations warrant further examination. A new, reliable experimental measurement would be ideal.

The JANAF recommended heat of formation for $\text{CHF}=\text{O}$ is based on the average of the heats of formation of the analogous $\text{CH}_2=\text{O}$ and $\text{CF}_2=\text{O}$. Although this procedure introduces significant uncertainty, it may not be important, since there are relatively good experimentally derived rate expressions for the thermal decomposition of formyl fluoride ($\text{CHF}=\text{O} \rightarrow \text{CO} + \text{HF}$).

The value recommended in the JANAF tables for the heat of formation of $\cdot\text{CF}=\text{O}$ is based on estimates of the C–F bond dissociation energy in $\text{CF}_2=\text{O}$. In contrast to that for $\text{CHF}=\text{O}$, the heat of formation of $\cdot\text{CF}=\text{O}$ is important, since there are no experimental data for the unimolecular decomposition $\cdot\text{CF}=\text{O} \rightarrow \text{CO} + \text{F}$, which is a primary destruction pathway for $\cdot\text{CF}=\text{O}$ (competing with hydrogen atom combination followed by HF elimination). Therefore, it would be very useful to obtain a better value (smaller uncertainty) for the heat of formation of $\cdot\text{CF}=\text{O}$ that is based on some type of experimental measurement.

There are no experimentally derived heats of formation for many of the fluoroethanes ($\text{CH}_3-\text{CH}_2\text{F}$, $\text{CHF}_2-\text{CHF}_2$, $\text{CH}_2\text{F}-\text{CF}_3$). These have been estimated using bond additivity, group additivity, or other empirical trends in heats of formation. However, there are significant uncertainties in using these procedures, because of non-covalent or ionic contributions to the stability of these species due to the high electronegativity of fluorine. Furthermore, the stability of the fluoroethanes will influence product channels for fluoromethyl combination reaction (e.g. $\cdot\text{CH}_3 + \cdot\text{CF}_3 \rightarrow \text{CH}_3-\text{CF}_3$ vs. $\cdot\text{CH}_3 + \cdot\text{CF}_3 \rightarrow \text{CH}_2=\text{CF}_2 + \text{HF}$).

There are experimentally derived heats of formation (i.e. heat of reaction data) for only three of the fluoroethyl radicals ($\text{CH}_3-\text{CF}_2\cdot$, $\text{CF}_3-\text{CH}_2\cdot$, $\text{CF}_3-\text{CF}_2\cdot$). Values for the eight other fluoroethyl radicals have been estimated using heat of formation of the parent fluoroethanes (which in some cases are also estimates) and C–H and C–F bond dissociation energies (largely estimates). The stability of the

fluoroethyl radicals can be of importance for the destruction of fluoroethylenes (e.g. $\text{CH}_2=\text{CF}_2 + \text{H} \leftrightarrow \text{CH}_3-\text{CF}_2\cdot$ and $\text{CH}_3-\text{CF}_2\cdot + \text{H} \rightarrow \text{CH}_2=\text{CHF} + \text{HF}$).

There are no experimentally derived heats of formation for the fluoroketenes ($\text{CHF}=\text{C}=\text{O}$, $\text{CF}_2=\text{C}=\text{O}$) and the fluoroketyl radical ($\cdot\text{CF}=\text{C}=\text{O}$). In order to include these potential important species in the mechanism, it was necessary to use thermochemical data from our *ab initio* calculations. There are a number of reversible reactions involving these species that are important under stoichiometric to fuel-rich conditions. Consequently, the uncertainties in the heats of formation of these species may contribute to uncertainties in flame speeds, flame temperatures, and flame products. These uncertainties should be better quantified in future mechanism refinements.

4.3. Kinetics

A brief discussion of the major uncertainties in the rate expressions used in this mechanism can be found in each individual section.

5. REACTION SET

5.1. Description of Listing

The reaction set listing (Table 5) is divided into sets of similar reaction types (e.g. fluoromethanes: thermally and chemically activated decompositions, fluoromethanes: atom abstraction and metathesis, fluoromethyls: oxidation, etc.). For each reaction, the reaction number and reaction are given and followed by the Arrhenius parameters. The listing is essentially a CHEMKIN II reaction input file (Kee *et al.*, 1989).

The reactions are numbered according to the following scheme.

HO-xx	Hydrogen/Oxygen Chemistry
HC-xx	Hydrocarbon Chemistry
HF-xx	Hydrogen/Oxygen/Fluorine Chemistry
MD-xx	Fluoromethanes: Thermal and Activated Decompositions
MA-xx	Fluoromethanes: Abstractions
NN-xx	Fluoromethyl, Fluoromethylene, Fluoromethylidene Chemistry
PP-xx	Carbonyl Fluorides and Fluoromethoxy Chemistry
ED-xx	Fluoromethanes: Thermal and Activated Decompositions
EC-xx	Hot Fluoroethanes and Fluoroethyls: Fluoromethylene Reactions
EA-xx	Fluoroethanes: Abstractions by X (H, O, OH)
ER-xx	Fluoroethanes: Abstractions by R (C_xH_y)
GG-xx	Fluoroethyl Chemistry
JD-xx	Fluoroethylenes: Thermal and Activated Decompositions

JA-xx Fluoroethylenes: Additions and Abstractions

JO-xx Fluoroethylenes and Fluorovinyls: Oxidations

KK-xx Fluoroethyne and Fluoroketene Chemistry

CF-xx H Atom Abstraction by Fluorine

The symbol '=' in the reaction indicates a reversible reaction and the symbol '>' indicates an irreversible reaction. For reference purposes, the heat of reaction (in kcal/mol) is also given for a number of reactions (but not all). In addition, a notation and references are given to provide traceability on each rate expression. A detailed legend for the notation given for each is at the end of Table 5. For example in the listing, $\text{CH}_3\text{F} + \text{H} = \text{CH}_2\text{F} + \text{H}_2$ (reaction MA-13) has Arrhenius parameters $A = 2.70\text{E}03$, $b = 3.00$, $E/R = 2667$, where the rate expression is $k = A * T^b * \exp(-E/RT)$. The units are $A_1 = \text{mol/s}$, $A_2 = \text{mol/cm}^3/\text{s}$, $A_3 = \text{mol/cm}^6/\text{s}$ (for first-, second-, and third-order reactions, respectively), $T = \text{K}$, $E = \text{kJ/mol}$, and $R = 8.314 \text{ J/mol/K}$ of 1.987 cal/mol/K . Please note $1 \text{ cal} = 4.184 \text{ J}$ (for conversion from SI units). For this reaction example, the notation and references 'xf', '75WES/DEH', and 'nist' indicate that the rate expression is our fit to the experimental data of Westenberg and deHaas (1975).

A number of the unimolecular reactions have rate expressions with third-body efficiencies and/or low pressure fall-off parameters. For example, $\text{H} + \text{O}_2 \rightarrow \text{HO}_2 + \text{M}$ (reaction HO-13) has explicit third-body efficiencies for $\text{M} = \text{H}_2\text{O}$, CO_2 , CO , and N_2 . An example of a rate expression with low-pressure fall-off parameters is the reaction $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6 + \text{M}$ (reaction HC-16), where 'LOW' and 'TROW' are low-pressure and Troe fall-off parameters. The reader is referred to Kee *et al.* (1989) for more details on third-body efficiencies and fall-off parameters.

For reference purposes, at the end of Table 5, the experimental rate expression ($A = 1.80\text{E}13$, $b = 0.00$, $E/R = 4803$) and the temperature range ($T = 600\text{--}900 \text{ K}$) from this work (75WES/DEH) are also given. In some cases, where rate expressions were estimated relative to a reference reaction, the A-factor or activation energy were adjusted. For example in the listing, the reaction $\text{CH}_3\text{F} + \text{C}_2\text{H}_3 = \text{CH}_2\text{F} + \text{C}_2\text{H}_4$ (reaction MA-20) has the notations 'r CH₃' and 'E*0.9'. These indicate that an activation energy was used that was 90% of the activation energy for the analogous abstraction by CH_3 , a reaction that is slightly more exothermic.

In order to reduce (slightly) the number of species in the reaction set, the isomers $\text{CHF}=\text{CHF}[E]$, $\text{CHF}=\text{CH}\cdot[E]$, and $\text{CHF}=\text{CF}\cdot[E]$ were excluded (retaining the Z isomers). The differences in energies and chemistries are sufficiently small that this is justified. We note that a number of the fluoroethanes and fluoroethyl radicals have both *trans* and *gauche* forms. In this work, we used thermochemistry for the most stable conformational isomers.

Table 5. Reaction set listing

HO	H ₂ /O ₂ system: combination, decomposition	A	b	E/R	Note	ref1	ref2	Hr
1	H + H + M = H ₂	1.00E + 18	-1.00	0	+ M		MBA139	
2	H ₂ /O/ H ₂ O/0/ CO ₂ /0/ = H ₂	9.20E + 16	-0.60	0	+ H ₂		MBA140	
3	H + H + H ₂ O = H ₂	6.00E + 19	-1.25	0	+ H ₂ O		MBA141	
4	H + H + CO ₂ = H ₂	5.49E + 20	-2.00	0	+ CO ₂		MBA142	
5	O + O + M = O ₂	1.89E + 13	0.00	-900	+ M	86TSA/HAM	MBA145	
6	H + OH + M = H ₂ O	1.60E + 22	-2.00	0	+ M		MBA143	
7	H + O + M = OH	6.20E + 16	-0.60	0	+ M		MBA144	
	H ₂ /O ₂ system: atom transfers							
8	O + OH = O ₂	4.00E + 14	-0.50	0	+ H	81HOW/SMI	MBA132	
9	O + H ₂ = OH	5.06E + 04	2.67	3166	+ H	88SUT/MIC	MBA133	
10	OH + OH = O	6.00E + 08	1.30	0	+ H ₂ O		MBA138	
11	H ₂ + O ₂ = OH	1.70E + 13	0.00	24046	+ OH	71JAC/HOU	MBA130	
12	OH + H ₂ = H ₂ O	1.17E + 09	1.30	1825	+ H	79COH/WES	MBA131	
	H ₂ /O ₂ system: peroxy and peroxide							
13	H + O ₂ + M = HO ₂	3.61E + 17	-0.72	0	+ M		MBA134	
14	H ₂ O/18.6/ CO ₂ /4.2/ H ₂ /2.9/ CO/2.1/ N ₂ /1.3/ + HO ₂ = H ₂	1.25E + 13	0.00	0	+ O ₂		MBA146	
15	O + HO ₂ = O ₂	1.40E + 13	0.00	540	+ OH		MBA137	
16	OH + HO ₂ = H ₂ O	7.50E + 12	0.00	0	+ O ₂		MBA135	
17	H ₂ O ₂ + M = OH	1.30E + 17	0.00	22899	+ OH + M		MBA148	
18	H + HO ₂ = OH	1.40E + 14	0.00	540	+ OH		MBA136	
19	HO ₂ + HO ₂ = H ₂ O ₂	2.00E + 12	0.00	0	+ O ₂	84WAR	MBA147	
20	H ₂ O ₂ + H = HO ₂	1.60E + 12	0.00	1912	+ H ₂		MBA149	
21	H ₂ O ₂ + OH = H ₂ O	1.00E + 13	0.00	906	+ HO ₂		MBA150	
	HC C ₁ hydrocarbons: methane							
1	CH ₄ + H = CH ₃	2.20E + 04	3.00	4404	+ H ₂	73CLA/DOV	MBA004	
2	CH ₄ + O = CH ₃	1.02E + 09	1.50	4330	+ OH	86SUT/MIC	MBA005	
3	CH ₄ + OH = CH ₃	1.60E + 06	2.10	1238	+ H ₂ O	83BAU/CRA	MBA005	
4	CH ₄ + O ₂ = CH ₃	7.90E + 13	0.00	28183	+ HO ₂	72SKI/LIF	MBA003	
5	CH ₄ + HO ₂ = CH ₃	1.80E + 11	0.00	9411	+ H ₂ O ₂	72SKI/LIF	MBA006	
6	C ₁ hydrocarbons: methyl CH ₃ + H (+M) = CH ₄	6.00E + 16	-1.00	0	(+M)	84WAR 89STE/SMI	MBA002	
	LOW/8.00E26 -3.0 0/ SR1/0.45 797 979/ H ₂ /2.0/ CO/2.0/ CO ₂ /3.0/ H ₂ O/5.0/							
7	CH ₃ + H = CH ₂	9.00E + 13	0.00	7599	+ H ₂		MBA013	
8	CH ₃ + O = CH ₂ O	8.00E + 13	0.00	0	+ H		MBA009	
9	CH ₃ + OH = CH ₂	7.50E + 06	2.00	2516	+ H ₂ O		MBA012	

Table 5 (continued)

HC	A	b	E/R	Note	ref1	ref2	Hr
10 CH ₃	2.24E + 40	-8.20	5875		87DEA/WES		
11 CH ₃	2.64E + 19	-1.80	4060		87DEA/WES		
12 CH ₃	5.74E + 12	-0.23	7011		87DEA/WES		
13 CH ₃	8.90E + 19	-1.80	4060		87DEA/WES		
14 CH ₃	2.05E + 18	-1.57	14710		86TSA/HAM	MBA008	
15 CH ₃	2.00E + 13	0.00	0		86TSA/HAM	MBA007	
16 CH ₃	9.03E + 16	-1.20	329		88WAG/WAR	MBA001	
					88WAG/SAR		
					88WAG/SAR		
LOW/3.18E411 -7.0 2762/							
TROE/0.6401 6927 132/							
H ₂ /2.0/ CO/2.0/ CO ₂ /3.0/ H ₂ O/5.0/							
C ₁ hydrocarbons: methylene (triplet)							
17 CH ₂	2.50E + 13	0.00	0			MBA026	
18 CH ₂	5.00E + 13	0.00	0			MBA043	
19 CH ₂	1.10E + 11	0.00	503			MBA042	
20 CH ₂	3.00E + 13	0.00	0			MBA044	
21 CH ₂	1.60E + 12	0.00	503			MBA045	
22 CH ₂	5.00E + 13	0.00	4529			MBA046	
23 CH ₂	6.90E + 11	0.00	252			MBA047	
24 CH ₂	1.90E + 10	0.00	-503			MBA048	
25 CH ₂	8.60E + 10	0.00	-252			MBA049	
26 CH ₂	4.30E + 10	0.00	-252			MBA050	
27 CH ₂	3.00E + 13	0.00	0			MBA072	
28 CH ₂	4.00E + 13	0.00	0			MBA114	
C ₁ hydrocarbons: methylene (singlet)							
29 CH ₂ SING	1.00E + 13	0.00	0			MBA106	
H/0.0/							
30 CH ₂ SING	2.00E + 14	0.00	0			MBA111	
31 CH ₂ SING	3.00E + 13	0.00	0			MBA109	
32 CH ₂ SING	7.00E + 13	0.00	0			MBA110	
33 CH ₂ SING	4.00E + 13	0.00	0			MBA107	
34 CH ₂ SING	1.20E + 14	0.00	0			MBA108	
C ₁ hydrocarbons: methylidyne							
35 CH ₂	1.00E + 18	-1.56	0			MBA024	
36 CH ₂	1.13E + 07	2.00	1510			MBA025	
37 CH	3.30E + 13	0.00	0		82BER/FLE	MBA027	
38 CH	5.70E + 13	0.00	0		81MES/FIL	MBA028	
39 CH	3.00E + 13	0.00	0			MBA029	
40 CH	3.40E + 12	0.00	347		82BER/FLE	MBA030	
41 CH	1.17E + 15	-0.75	0			MBA032	
42 CH	9.46E + 13	0.00	-259		88ZAB/FLE	MBA033	

43	CH	+ CH ₂	= C ₂ H ₂	+ H	4.00E + 13	0.00	0	MBA035	
44	CH	+ CH ₃	= C ₂ H ₃	+ H	3.00E + 13	0.00	0	MBA036	
45	CH	+ CH ₄	= C ₂ H ₄	+ H	6.00E + 13	0.00	0	MBA037	
46	C ₂ H ₃	+ CH	= CH ₂	+ C ₂ H ₂	5.00E + 13	0.00	0	MBA086	
47	HCCO	+ CH	= C ₂ H ₂	+ CO	5.00E + 13	0.00	0	MBA104	
<i>Oxidized C₁ hydrocarbons: methanol</i>									
48	CH ₃ OH	+ H	= CH ₃ O	+ H ₂	8.00E + 12	0.00	3067	90NOR	
49	CH ₃ OH	+ OH	= CH ₃ O	+ H ₂ O	1.50E + 13	0.00	2999	75BOW	
50	CH ₃ OH	+ CH ₃	= CH ₃ O	+ CH ₄	1.45E + 01	3.10	3490	90NOR	
51	CH ₃ OH	+ O ₂	= CH ₂ OH	+ HO ₂	2.05E + 13	0.00	22505	90NOR	
52	CH ₃ OH	+ H	= CH ₂ OH	+ H ₂	3.20E + 13	0.00	3067	90NOR	
53	CH ₃ OH	+ O	= CH ₂ OH	+ OH	3.88E + 05	2.50	1550	90NOR	
54	CH ₃ OH	+ OH	= CH ₂ OH	+ H ₂ O	1.50E + 13	0.00	2999	75BOW	
55	CH ₃ OH	+ HO ₂	= CH ₂ OH	+ H ₂ O ₂	3.98E + 13	0.00	9763	90NOR	
56	CH ₃ OH	+ CH ₃	= CH ₂ OH	+ CH ₄	3.19E + 01	3.17	3609	90NOR	
<i>Oxidized C₁ hydrocarbons: methoxy, hydroxymethyl</i>									
57	CH ₃ O	+ M	= CH ₂ O	+ H + M	1.00E + 14	0.00	12582	MBA014	
58	CH ₃ O	+ O ₂	= CH ₂ O	+ HO ₂	6.30E + 10	0.00	1309	MBA022	
59	CH ₃ O	+ H	= CH ₂ O	+ H ₂	2.00E + 13	0.00	0	MBA016	
60	CH ₃ O	+ O	= CH ₂ O	+ OH	1.00E + 13	0.00	0	MBA020	
61	CH ₃ O	+ OH	= CH ₂ O	+ H ₂ O	1.00E + 13	0.00	0	MBA018	
62	CH ₂ OH	+ M	= CH ₂ O	+ H + M	1.00E + 14	0.00	12582	MBA015	
63	CH ₂ OH	+ O ₂	= CH ₂ O	+ HO ₂	1.48E + 13	0.00	755	MBA023	
64	CH ₂ OH	+ H	= CH ₂ O	+ H ₂	2.00E + 13	0.00	0	MBA017	
65	CH ₂ OH	+ O	= CH ₂ O	+ OH	1.00E + 13	0.00	0	MBA021	
66	CH ₂ OH	+ OH	= CH ₂ O	+ H ₂ O	1.00E + 13	0.00	0	MBA019	
<i>Oxidized C₁ hydrocarbons: formaldehyde and formyl</i>									
67	CH ₂ O	+ M	= HCO	+ H + M	3.31E + 16	0.00	40765	80DEA/JOH	
68	CH ₂ O	+ H	= HCO	+ H ₂	2.19E + 08	1.77	1510	86TSA/HAM	
69	CH ₂ O	+ O	= HCO	+ OH	1.80E + 13	0.00	1550	80KLE/SKO	
70	CH ₂ O	+ OH	= HCO	+ H ₂ O	3.43E + 09	1.18	-225	86TSA/HAM	
71	HCO	+ M	= CO	+ H + M	2.50E + 14	0.00	8456	84WAR	
<i>CO/1.9/ H₂/1.9/ CH₄/2.8/ CO₂/3.0/ H₂O/5.0/</i>									
72	HCO	+ H	= CO	+ H ₂	1.19E + 13	0.25	0	MBA057	
73	HCO	+ O	= CO	+ OH	3.00E + 13	0.00	0	MBA058	
74	HCO	+ O	= CO ₂	+ H	3.00E + 13	0.00	0	MBA059	
75	HCO	+ OH	= CO	+ H ₂ O	1.00E + 14	0.00	0	MBA055	
76	HCO	+ O ₂	= CO	+ HO ₂	3.30E + 13	-0.40	0	MBA060	
<i>Oxidized C₁ hydrocarbons: carbon monoxide</i>									
77	CO	+ O + M	= CO ₂	+ M	6.17E + 14	0.00	1510	86TSA/HAM	
78	CO	+ OH	= CO ₂	+ H	1.51E + 07	1.30	-381	MBA062	
79	CO	+ O ₂	= CO ₂	+ O	1.60E + 13	0.00	20634	MBA063	
80	CO	+ HO ₂	= CO ₂	+ OH	5.80E + 13	0.00	11542	MBA064	

Table 5 (continued)

HC	A	b	E/R	Note	ref1	ref2	Hr
<i>C₂ hydrocarbons: ethane</i>							
81 C ₂ H ₆	+ H ₂	3.50	2622		73CAL/DOV	MBA066	
82 C ₂ H ₆	+ OH	2.00	2574		84WAR	MBA067	
83 C ₂ H ₆	+ H ₂ O	1.05	911		83TUL/RAV	MBA068	
84 C ₂ H ₆	+ CH ₃	4.00	4177		73CLA/DOV	MBA065	
<i>C₂ hydrocarbons: ethyl</i>							
85 C ₂ H ₅	+ CH ₃	0.00	0			MBA074	
86 C ₂ H ₅	+ CH ₃	0.00	0		86TSA/HAM		
87 C ₂ H ₅	+ C ₂ H ₄ + HO ₂	-2.77	995		90BOZ/DEA		
<i>C₂ hydrocarbons: ethylene</i>							
88 C ₂ H ₄	+ H ₂ + M	0.00	28083		83KIE/KAP	MBA128	
89 C ₂ H ₄	+ H + M	0.00	41449			MBA129	
90 C ₂ H ₄ + H	(+M)	1.50	498		86TSA/HAM		
91 C ₂ H ₄	LOW/6.37E27 -2.8 -54/ H ₂ O/5.0/ CO/2.0/ CO ₂ /3.0/	0.00	4278		73PEE/MAH	MBA073	
92 C ₂ H ₄	+ H	1.20	375		84WAR	MBA069	
93 C ₂ H ₄	+ OH	2.00	1434	rf.		MBA070	
<i>C₂ hydrocarbons: vinyl</i>							
94 C ₂ H ₃	+ H ₂	0.00	0		92BAU/COB		
95 C ₂ H ₃	+ OH	0.00	0			MBA083	
96 C ₂ H ₃	+ CH ₂	0.00	0			MBA084	
97 C ₂ H ₃	+ O ₂	-8.22	3538	a/s	92WES		
98 C ₂ H ₃	+ O ₂	-4.55	2758	direct	92WES		
99 C ₂ H ₃	+ O	0.00	0		84WAR	MBA081	
<i>C₂ hydrocarbons: acetylene</i>							
100 C ₂ H ₂ + H	(+M)	0.00	1213		76PAY/STI	MBA079	
LOW/2.67E27 -3.5 2410/ H ₂ O/5.0/ CO/2.0/ CO ₂ /3.0/							
101 C ₂ H ₂	+ OH	2.30	6794			MBA088	
102 C ₂ H ₂	+ OH	4.50	-503			MBA089	
103 C ₂ H ₂	+ OH	4.00	-1007			MBA090	
104 C ₂ H ₂	+ O	2.00	956			MBA076	
105 C ₂ H ₂	+ O	2.00	956			MBA077	
106 C ₂ H ₂	+ O ₂	1.50	15148			MBA126	
<i>Oxidized C₂ hydrocarbons: ketene, HCCOH</i>							
107 HCCOH	+ H	0.00	0		79MIC/NAV	MBA091	
108 CH ₂ CO	+ H	0.00	1725			MBA094	
109 CH ₂ CO	+ H	0.00	4026		83WAS/HAT	MBA095	

						A	b	E/R	Note	ref1	ref2	Hr
110	CH ₂ CO	+ O	= CO ₂	+ CH ₂	1.75E + 12	0.00		679			MBA093	
111	CH ₂ CO	+ O	= HCCO	+ OH	1.00E + 13	0.00		4026			MBA096	
112	CH ₂ CO	+ OH	= HCCO	+ H ₂ O	7.50E + 12	0.00		1007			MBA097	
113	CH ₂ CO	(+M)	= CH ₂ + CO	(+M)	3.00E + 14	0.00		35772			MBA098	
LOW/3.60E15 0.0 59270/												
114	<i>Oxidized C₂ hydrocarbons: ketyl</i>											
115	HCCO	+ H	+ CH ₂ SING	+ CO	1.00E + 14	0.00		0			MBA101	
116	HCCO	+ O	+ H	+ 2CO	1.00E + 14	0.00		0			MBA102	
117	HCCO	+ O ₂	+ 2CO	+ OH	1.60E + 12	0.00		430		92BAU/COB	MBA103	
118	HCCO	+ HCCO	+ C ₂ H ₂	+ 2CO	1.00E + 13	0.00		0			MBA105	
119	HCCO	+ CH ₂	+ C ₂ H ₃	+ CO	3.00E + 13	0.00		0			MBA115	
HF H/F/O chemistry												
1	HF	+ M	= H	+ F	3.12E + 13	0.00		49985	xh	81BAU/DUX	ref2	135
2	H ₂	+ F	= H	+ HF	2.56E + 12	0.50		327	xf	89STE/BRU	nist	-32
3	OH	+ F	= O	+ HF	2.00E + 13	0.00		0	r	H + HNO ₃	nist	-34
4	HO ₂	+ F	= O ₂	+ HF	2.89E + 12	0.50		0	xf	83WAL/WAG	nist	-86
5	H ₂ O	+ F	= OH	+ HF	1.30E + 09	1.50		0	xf	83WAL/WAG	nist	-17
6	H ₂ O ₂	+ F	= HO ₂	+ HF	1.73E + 12	0.50		0	xf	83WAL/WAG	nist	-49
MD Fluoromethanes: thermal decomposition												
1	CH ₂ SING	+ HF	= CH ₃ F		1.91E + 23	-3.62		896	xg	73SCH/WAG	nist	-89
2	CHF	+ H ₂	= CH ₃ F		2.25E + 17	-2.85		6543	ak		nist	-83
3	CH ₂ F	+ H	= CH ₃ F		3.03E + 21	-3.38		1741	ak		nist	-97
4	CHF	+ HF	= CH ₂ F ₂		3.64E + 24	-4.26		2043	ak		nist	-72
5	CF ₂	+ H ₂	= CH ₂ F ₂		1.70E + 06	-0.71		20584	ak		nist	-62
6	CHF ₂	+ H	= CH ₂ F ₂		2.75E + 06	-0.32		3870	ak		nist	-99
7	CHF ₃	+ M	= CF ₂	+ HF	2.39E + 30	-4.00		34751	xg	91HID/NAK	nist	61
8	CF ₃	+ F	= CF ₄		1.60E + 39	-7.90		4504	xk	86PLU/RVA	nist	-130
Fluoromethanes: activated decomposition												
9	CH ₂ F	+ H	= CH ₂ SING	+ HF	8.19E + 15	-0.63		254	ak		nist	-9
10	CH ₂ F	+ H	= CHF	+ H ₂	5.21E + 08	1.16		503	ak		nist	-15
11	CH ₂ SING	+ HF	= CHF	+ H ₂	2.08E + 07	1.27		4192	ak		nist	-6
12	CH ₃	+ F	= CH ₂ SING	+ HF	1.62E + 16	-0.88		-494	k		nist	-18
13	CH ₃	+ F	= CH ₂ F	+ H	1.36E + 12	-0.39		-133	k		nist	-9
14	CHF ₂	+ H	= CHF	+ HF	1.49E + 14	-0.11		51	ak		nist	-27
15	CHF ₂	+ H	= CF ₂	+ H ₂	5.50E + 03	2.42		-211	ak		nist	-37
16	CHF	+ HF	= CF ₂	+ H ₂	5.77E + 06	1.35		9009	ak		nist	-10
17	CHF	+ F	= CHF	+ HF	5.00E + 13	0.00		0	ak		nist	-46
18	CF ₃	+ H	= CF ₂	+ HF	5.50E + 13	0.00		0	xk	89TSA/MCF	nist	-46
19	CHF ₂	+ F	= CF ₂	+ HF	3.00E + 13	0.00		0	k		nist	-69

Table 5 (continued)

MA	Fluoromethanes: H atom abstraction by H, O, OH, HO ₂	A	b	E/R	Note	ref1	ref2	Hr	
1	CH ₃ F	+ H	2.70E + 03	2667	xf	75WES/DEH	nist	-6	
2	CH ₂ F ₂	= CH ₂ F	1.65E + 03	2818	xf	72RID/DAV	nist	-4	
3	CF ₃	= CHF ₂	3.00	2667	xf	72BER/MAR	nist	-5	
4	CH ₃ F	+ H ₂	6.30E + 01	3523	xf	67PAR/AZA	nist	-4	
5	CH ₂ F ₂	+ O	6.50E + 07	3070	xf	68PAR/NAL	nist	-2	
6	CHF ₃	+ O	2.25E + 07	4655	xf	78JOU/LEB	nist	7	
7	CH ₃ F	+ OH	1.00E + 08	1480	xt	82JEO/KAU	91COH/WES	-20	
8	CH ₂ F ₂	+ OH	2.60E + 08	1278	xt	82JEO/KAU	91COH/WES	-19	
9	CHF ₃	+ OH	2.80E + 07	2160	xt	82JEO/KAU	87COH/BEN	-10	
10	CH ₂ F	+ H ₂ O ₂	5.77E + 06	-302	rCH ₃	E*1.0	nist	-11	
11	CHF ₂	+ H ₂ O ₂	1.20E + 10	-302	rCH ₃	E*1.0	nist	-13	
12	CF ₃	+ H ₂ O ₂	1.20E + 10	-302	rCH ₃	E*1.0	nist	-21	
<i>Fluoromethanes: F atom abstraction by H</i>									
13	CH ₃ F	+ H	2.75E + 14	15803	a		nist	-28	
14	CH ₂ F ₂	= CH ₃	5.50E + 13	17162	a		nist	-17	
15	CHF ₃	= CHF ₂	8.00E + 13	20282	a		nist	-5	
16	CF ₄	= CF ₃	1.10E + 15	22446	x	71KOC/MOI		-5	
<i>Fluoromethanes: H atom abstraction by CH₃, C₂H₃</i>									
17	CH ₃ F	+ CH ₃	1.50E + 11	5737	x	65PRI/BRY		-6	
18	CH ₂ F ₂	= CH ₂ F	8.70E + 10	5133	x	65PRI/BRY		-5	
19	CF ₃	= CHF ₂	8.34E + 11	5496	x	78ART/BEL		-4	
20	CH ₃ F	+ C ₂ H ₃	1.50E + 11	5184	rCH ₃	E*0.9	nist	-10	
21	CH ₂ F ₂	= CH ₂ F	9.00E + 10	4630	rCH ₃	E*0.9	nist	-9	
22	CF ₃	+ C ₂ H ₄	8.00E + 11	6039	rCH ₃	E*1.1	nist	0	
<i>Fluoromethanes: H atom abstraction by fluoromethyls</i>									
23	CH ₃ F	+ CF ₃	1.35E + 12	5637	x	67GIL/QUI		-10	
24	CH ₂ F ₂	= CH ₂ F	9.00E + 10	7046	rCH ₃	E*1.4	nist	1	
25	CH ₂ F ₂	= CHF ₂	7.20E + 11	5637	x	67GIL/QUI		-8	
<i>Fluoromethanes: H atom abstraction from CH₂O, CH₃OH, HCO by fluoromethyls</i>									
26	CH ₂ O	+ CH ₃ F	5.54E + 03	4177	rCH ₃	E*1.4	nist	-9	
27	CH ₃ O	= HCO	5.54E + 03	3926	rCH ₃	E*1.3	nist	-10	
28	CH ₂ O	= HCO	5.54E + 03	2315	rCH ₃	E*0.79	nist	-19	
29	HCO	+ CH ₃ F	9.00E + 13	0	rCH ₃		nist	-83	
30	HCO	+ CHF ₂	9.00E + 13	0	rCH ₃		nist	-84	
31	HCO	+ CF ₃	9.00E + 13	0	rCH ₃		nist	-93	
32	HCO	+ CH ₃ F	2.70E + 13	0	rul		nist	-82	
33	HCO	+ CHF ₂	2.70E + 13	0	rul		nist	-51	
34	HCO	= CF ₂ CO	2.70E + 13	0	rul		nist	-31	

NN	Fluoromethyls: oxidation	A	b	E/R	Note	ref1	ref2	Hr	
1	CH ₂ F + O ₂	2.26E + 09	1.14	14343	rCF ₃	dH	nist	28	
2	CHF ₂ + O ₂	2.26E + 09	1.14	8304	rCF ₃	dH	nist	21	
3	CF ₃ + O ₂	2.26E + 09	1.14	10820	k		nist	-91	
4	CH ₂ F + O	5.70E + 13	0.00	0	rCH ₃	CF ₃	nist	-103	
5	CHF ₂ + O	3.70E + 13	0.00	0	rCH ₃	CF ₃	nist	-81	
6	CF ₃ + O	1.87E + 13	0.00	0	x	89TSA/BEL	nist	-95	
7	CH ₂ F + OH	2.50E + 13	0.00	0	rCH ₃		nist	-105	
8	CHF ₂ + OH	2.50E + 13	0.00	0	rCH ₃		nist	-115	
9	CF ₃ + OH	2.00E + 13	0.00	0	rCH ₃		nist	-49	
10	CH ₂ F + HO ₂	3.00E + 12	0.00	0	rCH ₃		nist	-50	
11	CHF ₂ + HO ₂	3.00E + 12	0.00	0	rCH ₃		nist	-59	
12	CF ₃ + HO ₂	2.00E + 12	0.00	0	rCH ₃		nist	-24	
13	CH ₂ F + HO ₂	1.50E + 13	0.00	0	rCH ₃		nist	-37	
14	CHF ₂ + HO ₂	1.50E + 13	0.00	0	rCH ₃		nist	-32	
15	CF ₃ + HO ₂	1.00E + 13	0.00	0	rCH ₃		nist		
<i>Fluoromethylenes: oxidation</i>									
16	CHF + H ₂ O	5.00E + 12	0.00	3271	a		nist	29	
17	CF ₂ + H ₂ O	5.00E + 12	0.00	12582	a		nist	52	
18	CHF + O ₂	2.00E + 13	0.00	8304	rCF ₂	E-10	nist	-60	
19	CF ₂ + O ₂	2.01E + 13	0.00	13337	x	77KEA/MAT		-51	
20	CHF + O	8.43E + 13	0.00	0	x	90TSA/MCF		-181	
21	CF ₂ + O	7.00E + 13	0.00	503	xf	90TSA/MCF		-38	
22	CHF + OH	4.00E + 12	0.00	0	rCF ₂ /5		nist	-95	
23	CF ₂ + OH	4.00E + 12	0.00	1761	rCF ₂ /5		nist	-78	
24	CHF + OH	2.00E + 13	0.00	1761	rCF ₂		nist	-68	
25	CF ₂ + OH	2.00E + 13	0.00	1761	xf	78BIO/LAZ			
26	CHF + HO ₂	1.00E + 13	0.00	0	rOH/2		nist		
27	CF ₂ + HO ₂	1.00E + 13	0.00	1761	rOH/2		nist		
28	CHF + HO ₂	2.00E + 12	0.00	0	r/5		nist		
29	CF ₂ + HO ₂	2.00E + 12	0.00	1761	r/5		nist		
<i>Fluoromethylenes: destruction</i>									
30	CHF + H	2.95E + 14	0.00	0	x	90TSA/MCF		-5	
31	CF ₂ + H	2.00E + 14	0.00	629	xf	89TSA/MCF		-12	
32	CH ₂ O + CHF	1.00E + 13	0.00	7549	rCH ₄		nist	1	
33	CH ₂ O + CHF	1.00E + 13	0.00	7549	rCH ₄		nist	-81	
34	CH ₂ O + CF ₂	1.00E + 13	0.00	20634	rCH ₄		nist	23	
35	CH ₂ O + CF ₂	1.00E + 13	0.00	20634	rCH ₄		nist	-28	
36	HCO + CHF	2.00E + 13	0.00	7549	rCH ₄		nist	-74	
37	HCO + CF ₂	2.00E + 13	0.00	20634	rCH ₄		nist	-52	
<i>Fluoromethylidyne: oxidation</i>									
38	CF + O ₂	2.00E + 13	0.00	906	xf		nist	-43	
39	CF + H ₂ O	2.00E + 13	0.00	8556	rCl	92PEE/VAN		-42	

Table 5 (continued)

	A	b	E/R	Note	ref1	ref2	Hr
40 CF	4.00E + 13	0.00	503	+ F	90TSA/MCF	nist	-128
41 CF	3.00E + 13	0.00	503	+ HF		nist	-162
42 CF	1.00E + 13	0.00	0	+ OH		nist	-95
<i>Fluoromethylidyne: destruction</i>							
43 CH	3.00E + 13	0.00	0	+ H ₂		nist	-17
44 CF	4.00E + 13	0.00	377	+ F	89TSA/MCF	nist	
				+ HF			
				+ H			
				+ CH ₃			
45 CF	3.00E + 13	0.00	0	+ C ₂ H ₃		nist	-20
46 CF	3.00E + 13	0.00	0	+ CH ₂ CF		nist	-9
47 CF	3.00E + 13	0.00	0	+ C ₂ HF		nist	-73
48 CF	3.00E + 13	0.00	0	+ CH ₂ SING		nist	-82
49 CF	3.00E + 13	0.00	0	+ H		nist	-24
50 CF	5.00E + 12	0.00	5033	+ CH ₂ CHF		nist	-27
51 CF	1.00E + 13	0.00	0	+ C ₂ H ₄		nist	-123
	6.00E + 13	0.00	0	+ CH ₂ F		nist	
				+ CF ₂		nist	
use these products (correct) if C is in mechanism							
PP Fluoromethoxy: destruction	A	b	E/R	Note	ref1	ref2	Hr
1 CF ₃ O	9.03E + 26	-3.42	10921	+ F		nist	17
2 CF ₃ O	1.00E + 14	0.00	0	+ HF		nist	-118
3 CF ₃ O	1.00E + 13	0.00	2516	+ HF + H		nist	
4 CF ₃ O	1.00E + 13	0.00	2516	+ HF + OH		nist	
5 CF ₃ O	8.00E + 12	0.00	1158	+ HF + CH ₃	92CHE/ZHU	nist	
6 CF ₃ O	1.20E + 13	0.00	1158	+ HF + C ₂ H ₅		nist	
7 CF ₃ O	1.00E + 13	0.00	2516	+ HF + C ₂ H ₅		nist	
8 CF ₃ O	1.00E + 13	0.00	2516	+ CH ₂ CF		nist	
9 CF ₃ O	5.00E + 12	0.00	2516	+ HF + HCO		nist	
10 CF ₃ O	5.00E + 12	0.00	2516	+ HF + CO		nist	
<i>Carbonyl fluorides: CHF=O, CF₂=O</i>							
11 CF ₂ O	1.00E + 12	0.00	0	+ F		nist	-131
12 CHF ₂ O	2.48E + 25	-3.00	21641	+ HF	85SAI/KUR	nist	-2
13 CF ₂ O	7.40E - 03	3.84	12632	+ 2HF	th/FC(O)OH	nist	-13
14 CF ₂ O	5.50E + 08	1.42	9512	+ HF	Oodd	nist	-3
15 CF ₂ O	1.20E + 10	0.83	11223	+ HF	Cadd	nist	-3
16 CF ₂ O	2.40E + 07	1.88	18067	+ HF	abstract	nist	-3
17 CF ₂ O	2.70E + 03	2.38	10569	+ HF + F	Oodd th/FCO ₂	nist	-3
18 CHF ₂ O	1.10E + 08	1.77	1510	+ H ₂	A/2	nist	-4
19 CHF ₂ O	9.00E + 12	0.00	1550	+ OH		nist	-2
20 CHF ₂ O	1.72E + 09	1.18	-225	+ H ₂ O		nist	-18
21 CF ₂ O	1.00E + 11	0.00	1963	+ HO ₂		nist	-13
22 CHF ₂ O	2.00E + 12	0.00	4529	+ CH ₃	E*0.56	nist	-4
23 CHF ₂ O	2.00E + 12	0.00	4529	+ CH ₂ F		nist	2

							A	b	E/R	Note	ref1	ref2	Hr
24	CHF ₂ O	+ CHF ₂	= CF ₂ O	+ CH ₂ F ₂	2.00E + 12	0.00			4529	r		mist	1
25	CHF ₃ O	+ CF ₃	= CF ₃ O	+ CHF ₃	2.00E + 12	0.00			4529	r		mist	-8
26	CHF ₂ O	+ C ₂ H ₃	= CF ₂ O	+ C ₂ H ₄	2.00E + 12	0.00			2516	r	E	mist	-8
<i>Carbonyl fluorides: CF=O</i>													
27	CO	+ F + M	= CF ₂ O	+ F + O	1.03E + 19	-1.40			-245	k		mist	33
28	CF ₂ O	+ O ₂	= CO ₂	+ HF	2.00E + 13	0.00			12079	ul		mist	25
29	CF ₃ O	+ H	= CO	+ HF	1.20E + 14	0.00			0	r	HCO	mist	-102
30	CF ₂ O	+ O	= CO ₂	+ F	3.00E + 13	0.00			0	r	HCO	mist	-94
31	CF ₂ O	+ OH	= CO ₂	+ HF	3.00E + 13	0.00			0	r	HCO	mist	-128
32	CF ₂ O	+ HO ₂	= CO ₂	+ F + OH	3.00E + 13	0.00			0	r	HCO	mist	-28
33	CF ₂ O	+ CH ₃	= CH ₂ CO	+ HF	2.70E + 13	0.00			0	ul		mist	-85
34	CF ₂ O	+ CH ₃ F	= CHF ₂ O	+ HF	2.70E + 13	0.00			0	ul		mist	-52
35	CF ₂ O	+ CHF ₂	= CF ₂ CO	+ HF	2.70E + 13	0.00			0	ul		mist	-35
<i>ED Fluoroethanes: thermal decomposition</i>													
1	CH ₃ -CH ₂ F		= C ₂ H ₄	+ HF	2.63E + 13	0.00			30146	x	70CAD/DAY		11
2	CH ₃ -CHF ₂		= CH ₂ :CHF	+ HF	7.94E + 13	0.00			31152	x	70TSC/QUI		22
3	CH ₃ -CF ₃		= CH ₂ :CF ₂	+ HF	1.00E + 14	0.00			34575	x	71TSL/QUI		
4	CH ₂ F-CH ₂ F		= CH ₂ :CHF	+ HF	2.50E + 13	0.00			31656	x	71KER/TIM		5
5	CH ₂ F-CHF ₂		= CHF:CHF-Z	+ HF	1.26E + 14	0.00			34776	x	74SEK/TSC		8
6	CH ₂ F-CHF ₂		= CH ₂ :CF ₂	+ HF	1.00E + 13	0.00			32914	x	72MIL/TSC		37
7	CH ₂ F-CF ₃		= CHF:CF ₂	+ HF	2.63E + 13	0.00			35581	x	71MIL/HAR		32
8	CHF ₂ -CHF ₂		= CHF:CF ₂	+ HF	2.00E + 13	0.00			34927	x	71MIL/HAR		41
9	CHF ₂ -CF ₃		= CF ₂ :CF ₂	+ HF	4.00E + 13	0.00			36034	x	71TSC/MIL		
<i>Fluoroethanes: activated decomposition, ethyl + H (HF elimination)</i>													
10	CH ₂ F-CH ₂	+ H	= C ₂ H ₄	+ HF	1.44E + 20	-2.12			871	k		mist	
11	CH ₃ -CHF	+ H	= C ₂ H ₄	+ HF	2.27E + 20	-2.21			981	k		mist	
12	CH ₂ F-CHF	+ H	= CH ₂ :CHF	+ HF	2.06E + 23	-3.23			1147	k		mist	
13	CHF ₂ -CH ₂	+ H	= CF ₂ :CHF	+ HF	5.24E + 16	-0.93			443	k		mist	
14	CH ₃ -CF ₂	+ H	= CH ₂ :CHF	+ HF	2.09E + 16	-0.85			427	k		mist	
15	CHF ₂ -CHF	+ H	= CHF:CHF-Z	+ HF	1.86E + 20	-2.29			881	k		mist	
16	CHF ₂ -CHF	+ H	= CH ₂ :CF ₂	+ HF	9.95E + 19	-2.34			896	k		mist	
17	CH ₂ F-CF ₂	+ H	= CHF:CHF-Z	+ HF	6.32E + 19	-2.21			820	k		mist	
18	CH ₂ F-CF ₂	+ H	= CH ₂ :CF ₂	+ HF	3.36E + 19	-2.26			835	k		mist	
19	CF ₃ -CH ₂	+ H	= CH ₂ :CF ₂	+ HF	1.12E + 21	-2.27			1127	k		mist	
20	CHF ₂ -CF ₂	+ H	= CHF:CF ₂	+ HF	1.81E + 22	-2.92			1545	k		mist	
21	CF ₃ -CF ₂	+ H	= CF ₂ :CF ₂	+ HF	1.41E + 21	-2.40			1827	k		mist	
<i>Fluoroethanes: activated decomposition, ethyl + H (methyl formation)</i>													
22	CH ₂ F-CH ₂	+ H	= CH ₃	+ CH ₂ F	3.80E + 11	0.64			319	k		mist	
23	CH ₃ -CHF	+ H	= CH ₃	+ CH ₂ F	3.47E + 10	0.90			689	k		mist	
24	CH ₂ F-CHF	+ H	= CH ₂ F	+ CH ₂ F	1.79E + 14	-0.11			664	k		mist	
25	CHF ₂ -CH ₂	+ H	= CH ₂ :CHF	+ CHF ₂	2.02E + 06	2.16			227	k		mist	
26	CH ₃ -CF ₂	+ H	= CH ₃	+ CHF ₂	1.62E + 05	2.50			689	k		mist	
27	CHF ₂ -CHF	+ H	= CH ₂ F	+ CHF ₂	6.36E + 12	0.32			735	k		mist	

Table 5 (continued)

ED		A	b	E/R	Note	ref1	ref2	Hr
28	CH ₂ F-CF ₂	3.64E + 12	0.33	594	k		nist	
29	CF ₃ -CH ₂	2.48E + 11	0.82	1444	k		nist	
30	CHF ₂ -CF ₂	3.25E + 15	-0.52	1510	k		nist	
31	CF ₃ -CF ₂	4.37E + 16	-0.75	2194	k		nist	
<i>Fluoroethanes: activated decomposition, ethyl + H (stabilization)</i>								
32	CH ₂ F-CH ₂	1.19E + 35	-8.51	4097	k		nist	
33	CH ₃ -CHF	9.57E + 38	-9.24	3704	k		nist	
34	CH ₂ F-CHF	1.56E + 45	10.80	4061	k		nist	
35	CHF ₂ -CH ₂	2.96E + 37	-9.05	3603	k		nist	
36	CH ₃ -CF ₂	3.11E + 40	-9.59	3619	k		nist	
37	CHF ₂ -CHF	1.20E + 45	-10.60	3785	k		nist	
38	CH ₂ F-CF ₂	2.74E + 43	-10.50	3860	k		nist	
39	CF ₃ -CH ₂	7.27E + 42	-9.86	3704	k		nist	
40	CHF ₂ -CF ₂	3.77E + 46	-10.80	4519	k		nist	
41	CF ₃ -CF ₂	1.12E + 47	-10.80	2063	k		nist	
<i>Fluoroethanes: activated decomposition, ethyl + H (H atom elimination)</i>								
42	CH ₂ F-CH ₂	1.87E + 01	3.10	69	k		nist	
43	CHF ₂ -CH ₂	1.59E - 03	4.35	79	k		nist	
44	CH ₂ F-CF ₂	6.40E - 01	3.53	921	k		nist	
<i>Fluoroethanes: activated decomposition, methyl + methyl (HF elimination)</i>								
45	CH ₃	2.35E + 19	-1.86	941	k		nist	
46	CH ₂ F	7.56E + 21	-2.79	1303	k		nist	
47	CH ₃	1.90E + 15	-0.59	319	k		nist	
48	CH ₂ F	3.88E + 20	-2.35	1453	k		nist	
49	CH ₂ F	2.23E + 20	-2.41	1465	k		nist	
50	CH ₃	5.53E + 19	-1.94	1228	k		nist	
51	CHF ₂	2.20E + 19	-1.95	2063	k		nist	
52	CHF ₂	7.00E + 16	-1.17	2179	k		nist	
<i>Fluoroethanes: activated decomposition, methyl + methyl (stabilization)</i>								
53	CH ₃	1.57E + 31	-6.27	2235	k		nist	
54	CH ₂ F	2.37E + 24	-3.79	1152	k		nist	
55	CH ₃	1.93E + 35	-7.69	2899	k		nist	
56	CH ₂ F	9.61E + 38	-8.36	3493	k		nist	
57	CH ₃	2.26E + 33	-6.64	2526	k		nist	
58	CHF ₂	1.78E + 24	-3.50	1691	k		nist	
59	CHF ₂	2.61E + 26	-4.16	2063	k		nist	
60	CF ₃	1.63E + 36	-7.26	3548	xvk		nist	

EC	Fluoroethanes: methyl + methyl disproportionation (carbene formation)	A	b	E/R	Note	ref1	ref2	Hr	
1	CH ₃ F + CH ₂ F = CH ₄ + CHF	3.00E + 13	0.00	1711	ra CF ₂		nist		
2	CH ₂ F + CH ₃ F = CH ₃ F + CHF	3.00E + 13	0.00	2416	r CF ₂		nist		
3	CHF ₂ + CH ₂ F = CH ₂ F ₂ + CHF	3.00E + 13	0.00	2315	r CF ₂		nist		
4	CF ₃ + CH ₂ F = CHF ₃ + CHF	3.00E + 13	0.00	403	xf	67BRY/PRI	nist		
5	CH ₃ F + CHF ₂ = CH ₄ + CF ₂	3.00E + 13	0.00	1107	xf	74FOL/PRI	nist		
6	CH ₂ F + CHF ₂ = CH ₃ F + CF ₂	3.00E + 13	0.00	805	xf	84PRI/NIL	nist		
7	CHF ₂ + CHF ₂ = CH ₂ F ₂ + CF ₂	3.00E + 13	0.00	1007	xf	69PRI/FOL	nist		
8	CF ₃ + CHF ₂ = CHF ₃ + CF ₂	3.00E + 13	0.00				nist		
<i>Fluoroethanes: carbene insertion into fluoromethanes</i>									
9	CH ₃ F + CH ₂ SING = C ₂ H ₄ + HF	3.00E + 13	0.00	0	r		nist	-101	
10	CH ₂ F ₂ + CH ₃ SING = CH ₂ :CHF + HF	2.00E + 13	0.00	0	r		nist	-91	
11	CHF ₃ + CH ₂ SING = CH ₂ :CF ₂ + HF	1.00E + 13	0.00	0	r		nist	-77	
12	CF ₄ + CH ₃ SING = CHF:CF ₂ + HF	4.00E + 13	0.00	15601	a		nist	-62	
13	CH ₄ + CHF = C ₂ H ₄ + HF	4.00E + 13	0.00	7549	a		nist	-66	
14	CH ₃ F + CHF = CH ₂ :CHF + HF	3.00E + 13	0.00	7549	r CH ₄		nist	-74	
15	CH ₂ F ₂ + CHF = CH ₂ :CF ₂ + HF	1.00E + 13	0.00	7549	r CH ₄		nist	-70	
16	CH ₂ F ₂ + CHF = CHF:CHF-Z + HF	1.00E + 13	0.00	7549	r CH ₄		nist	-63	
17	CHF ₃ + CHF = CHF:CF ₂ + HF	1.00E + 13	0.00	7549	r CH ₄		nist	-47	
18	CF ₄ + CHF = CF ₂ :CF ₂ + HF	4.00E + 13	0.00	15601	a		nist	-30	
19	CH ₄ + CF ₂ = CH ₂ :CHF + HF	4.00E + 13	0.00	20634	a		nist	-36	
20	CH ₃ F + CF ₂ = CH ₂ :CF ₂ + HF	1.50E + 13	0.00	20634	r CH ₄		nist	-49	
21	CH ₃ F + CF ₂ = CHF:CHF-Z + HF	1.50E + 13	0.00	20634	r CH ₄		nist	-42	
22	CH ₂ F ₂ + CF ₂ = CHF:CF ₂ + HF	2.00E + 13	0.00	20634	r CH ₄		nist	-37	
23	CHF ₃ + CF ₂ = CF ₂ :CF ₂ + HF	1.00E + 13	0.00	20634	r CH ₄		nist	-11	
24	CF ₄ + CF ₂ = CF ₃ :CF ₃ + HF	4.00E + 13	0.00	25667	r CH ₄ + 10		nist	-56	
<i>Fluoroethyls: carbene insertion into fluoromethyls</i>									
25	CH ₂ F + CH ₂ = CH ₂ :CHF + H	4.00E + 13	0.00	0	r CH ₃		nist	-66	
26	CH ₂ F + CH ₂ = C ₂ H ₄ + F	4.00E + 13	0.00	0	r		nist	-54	
27	CHF ₂ + CH ₂ = CH ₂ :CF ₂ + H	4.00E + 13	0.00	0	r		nist	-63	
28	CHF ₂ + CH ₂ = CH ₂ :CHF + F	4.00E + 13	0.00	0	r		nist	-47	
29	CF ₃ + CH ₂ = CH ₂ :CF ₂ + F	4.00E + 13	0.00	0	r		nist	-41	
30	CH ₂ F + CH ₂ SING = CH ₂ :CHF + H	4.00E + 12	0.00	0	r		nist	-75	
31	CH ₂ F + CH ₂ SING = C ₂ H ₄ + F	2.00E + 12	0.00	0	r		nist	-63	
32	CHF ₂ + CH ₂ SING = CH ₂ :CF ₂ + H	2.00E + 12	0.00	0	r		nist	-72	
33	CHF ₂ + CH ₂ SING = CH ₂ :CHF + F	2.00E + 12	0.00	0	r		nist	-55	
34	CF ₃ + CH ₂ SING = CH ₂ :CF ₂ + F	6.00E + 12	0.00	0	r		nist	-50	
35	CH ₃ F + CHF = CHF:CHF-Z + H	6.00E + 12	0.00	0	r		nist	-46	
36	CH ₂ F + CHF = CH ₂ :CHF + H	4.00E + 12	0.00	0	r		nist	-46	
37	CH ₂ F + CHF = CH ₂ :CHF + F	2.00E + 12	0.00	0	r		nist	-37	
38	CHF ₂ + CHF = CHF:CF ₂ + H	2.00E + 12	0.00	0	r		nist	-42	
39	CHF ₂ + CHF = CHF:CHF-Z + F	4.00E + 12	0.00	0	r		nist	-27	
40	CF ₃ + CHF = CHF:CF ₂ + F	6.00E + 12	0.00	0	r		nist	-20	

Table 5 (continued)

EC	A	b	E/R	Note	ref1	ref2	Hr
41	CH ₃	6.00E + 12	1761	r		nist	-21
42	CH ₂ F	4.00E + 12	1761	r		nist	-20
43	CH ₂ F ₂	2.00E + 12	1761	r		nist	-12
44	CHF ₂	2.00E + 12	1761	r		nist	-6
44	CHF ₂	4.00E + 12	1761	r		nist	-1
EA Fluoroethanes: H atom abstraction by H, O, OH							
1	CH ₃ -CH ₂ F	5.50E + 08	4580	r OH	10AE + 8	nist	2
2	CH ₃ -CH ₂ F	2.90E + 08	3070	r OH	5AE + 5	nist	3
3	CH ₃ -CH ₂ F	5.50E + 07	550	rx	92COH/WES	nist	-13
4	CH ₃ -CH ₂ F	3.30E + 08	4580	r OH	10AE + 8	nist	
5	CH ₃ -CH ₂ F	1.60E + 08	3070	r OH	5AE + 5	nist	
6	CH ₃ -CH ₂ F	3.30E + 07	550	rx	91COH/WES	nist	
7	CH ₃ -CHF ₂	1.50E + 08	4831	r OH	10AE + 8	nist	
8	CH ₃ -CHF ₂	7.50E + 08	3322	r OH	A*5E + 5	nist	
9	CH ₃ -CHF ₂	1.54E + 07	570	rx	91COH/WES	nist	
10	CH ₃ -CHF ₂	4.40E + 07	4680	r OH	A*10E + 8	nist	
11	CH ₃ -CHF ₂	2.20E + 07	3171	r OH	A*5E + 5	nist	
12	CH ₃ -CHF ₂	4.40E + 06	670	rx	91COH/WES	nist	
13	CH ₃ -CF ₃	4.00E + 10	6392	r OH	A*10E + 8	nist	3
14	CH ₃ -CF ₃	2.00E + 10	4882	r OH	A*5E + 5	nist	4
15	CH ₃ -CF ₃	4.08E + 09	2350	xt	79CLY/HOL	nist	-12
16	CH ₂ F-CH ₂ F	6.00E + 08	4831	r OH	A*10E + 8	87COH/BEN	-11
17	CH ₂ F-CH ₂ F	3.00E + 08	3322	r OH	A*5E + 5	nist	-10
18	CH ₂ F-CH ₂ F	6.16E + 07	810	xt	83MAR/PAR	91COH/WES	-26
19	CH ₂ F-CH ₂ F	2.00E + 08	4932	r OH	A*10E + 8	nist	
20	CH ₂ F-CH ₂ F	1.00E + 08	3422	r OH	A*5E + 5	nist	
21	CH ₂ F-CH ₂ F	2.05E + 07	906	rx	87COH/BEN	nist	
22	CH ₂ F-CH ₂ F	1.00E + 08	5536	r OH	A*10E + 8	nist	
23	CH ₂ F-CH ₂ F	5.00E + 07	4026	r OH	A*5E + 5	nist	
24	CH ₂ F-CH ₂ F	1.06E + 07	1510	tx	87COH/BEN	nist	
25	CH ₂ F-CF ₃	2.00E + 08	5284	r OH	A*10E + 8	nist	-2
26	CH ₂ F-CF ₃	1.00E + 08	3775	r OH	A*5E + 5	nist	-1
27	CH ₂ F-CF ₃	2.10E + 07	1270	xt	79CLY/HOL	87COH/BEN	-17
28	CHF ₂ -CHF ₂	1.60E + 07	5335	r OH	A*10E + 8	nist	
29	CHF ₂ -CHF ₂	8.00E + 07	3825	r OH	A*5E + 5	nist	
30	CHF ₂ -CHF ₂	1.60E + 07	1330	xt	79CLY/HOL	87COH/BEN	
31	CHF ₂ -CF ₃	7.00E + 07	5133	r OH	A*10E + 8	nist	0
32	CHF ₂ -CF ₃	1.40E + 07	3624	r OH	A*5E + 5	nist	1
33	CHF ₂ -CF ₃	1.40E + 07	1130	xt	79CLY/HOL	87COH/BEN	-15
34	CF ₃ -CF ₃	1.00E + 15	15098	r CF ₄		nist	

Table 5 (continued)

ER	A	E/R	Note	ref1	ref2	Hr
31	$\text{CH}_2\text{F}-\text{CF}_3$ + CH_2F	5033	r CH_3		nist	2
32	$\text{CHF}_2-\text{CHF}_2$ + CH_2F	5536	r CH_3		nist	10
33	CHF_2-CF_3 + CH_2F	5033	r CH_3		nist	4
34	$\text{CH}_3-\text{CH}_2\text{F}$ + CHF_2	6543	r CH_3		nist	
35	$\text{CH}_3-\text{CH}_2\text{F}$ + CHF_2	5033	r CH_3		nist	
36	CH_3-CHF_2 + CHF_2	6039	r CH_3		nist	
37	CH_3-CHF_2 + CHF_2	5033	r CH_3		nist	
38	CH_3-CF_3 + CHF_2	6039	r CH_3		nist	
39	$\text{CH}_2\text{F}-\text{CH}_2\text{F}$ + CHF_2	5033	r CH_3		nist	
40	$\text{CH}_2\text{F}-\text{CHF}_2$ + CHF_2	5033	r CH_3		nist	
41	$\text{CH}_2\text{F}-\text{CHF}_2$ + CHF_2	5033	r CH_3		nist	
42	$\text{CH}_2\text{F}-\text{CF}_3$ + CHF_2	5033	r CH_3		nist	
43	$\text{CHF}_2-\text{CHF}_2$ + CHF_2	5033	r CH_3		nist	
44	CHF_2-CF_3 + CHF_2	5003	r CH_3		nist	
45	$\text{CH}_3-\text{CH}_2\text{F}$ + CF_3	4127	x	71QUI/WHI		
46	$\text{CH}_3-\text{CH}_2\text{F}$ + CF_3	4127	x	71QUI/WHI		
47	CH_3-CHF_2 + CF_3	3573	x	66OKS/PRA		
48	CH_3-CHF_2 + CF_3	3573	x	66OKS/PRA		
49	CH_3-CF_3 + CF_3	6794	x	67GIL/QUI		
50	$\text{CH}_2\text{F}-\text{CH}_2\text{F}$ + CF_3	3825	r		nist	
51	$\text{CH}_2\text{F}-\text{CHF}_2$ + CF_3	3624	r		nist	
52	$\text{CH}_2\text{F}-\text{CHF}_2$ + CF_3	4026	r		nist	
53	$\text{CH}_2\text{F}-\text{CF}_3$ + CF_3	3221	r		nist	
54	$\text{CHF}_2-\text{CHF}_2$ + CF_3	5989	x	67GIL/QUI		
55	CHF_2-CF_3 + CF_3	5083	x	67GIL/QUI		
GG Fluoroethyls: association with O_2						
1	CH_3-CHF + O_2	995	r C_2H_5		nist	
2	CH_3-CF_2 + O_2	995	r C_2H_5		nist	
3	$\text{CH}_2\text{F}-\text{CH}_2$ + O_2	995	r C_2H_5		nist	
4	$\text{CH}_2\text{F}-\text{CHF}$ + O_2	995	r C_2H_5		nist	
5	$\text{CH}_2\text{F}-\text{CF}_2$ + O_2	995	r C_2H_5		nist	
6	CHF_2-CH_2 + O_2	995	r C_2H_5		nist	
7	CHF_2-CHF + O_2	995	r C_2H_5		nist	
8	CHF_2-CF_2 + O_2	995	r C_2H_5		nist	
9	CF_3-CH_2 + O_2	22144	r CF_3		nist	
10	CF_3-CHF + O_2	11575	r CF_3		nist	
11	CF_3-CF_2 + O_2	11575	r CF_3		nist	
Fluoroethyls: association with O						
12	$\text{CH}_2\text{F}-\text{CH}_2$ + O	0	r $\text{CH}_3/\text{C}_2\text{H}_5$		nist	
13	CHF_2-CH_2 + O	0	r		nist	

14	CF ₃ -CH ₂	+ O	= CF ₂ CO + HF + H	6.60E + 13	0.00	0	r	nist
15	CH ₃ -CHF	+ O	= CH ₂ CO + HF + H	4.40E + 13	0.00	0	r	nist
16	CH ₂ F-CHF	+ O	= CHF ₂ CO + HF + H	4.40E + 13	0.00	0	r	nist
17	CHF ₂ -CHF	+ O	= CF ₂ CO + HF + H	4.40E + 13	0.00	0	r	nist
18	CF ₃ -CHF	+ O	= CF ₃ + CF ₂ O + H	4.40E + 13	0.00	0	r	nist
19	CH ₃ -CF ₂	+ O	= CH ₂ CO + HF + F	2.20E + 13	0.00	0	r	nist
20	CH ₂ F-CF ₂	+ O	= CHF ₂ CO + HF + F	2.20E + 13	0.00	0	r	nist
21	CHF ₂ -CF ₂	+ O	= CF ₂ CO + HF + F	2.20E + 13	0.00	0	r	nist
22	CF ₃ -CF ₂	+ O	= CF ₃ + CF ₂ O + F	2.20E + 13	0.00	0	r	nist
23	CH ₂ F-CH ₂	+ O	= CH ₂ O + CH ₂ F	3.30E + 13	0.00	0	r	nist
24	CHF ₂ -CH ₂	+ O	= CH ₂ O + CHF ₂	3.30E + 13	0.00	0	r/2	nist
25	CF ₃ -CH ₂	+ O	= CH ₂ O + CF ₃	3.30E + 13	0.00	0	r/2	nist
26	CH ₃ -CHF	+ O	= CHF ₂ O + CH ₃	2.20E + 13	0.00	0	r/2	nist
27	CH ₂ F-CHF	+ O	= CHF ₂ O + CH ₂ F	2.20E + 13	0.00	0	r/2	nist
28	CHF ₂ -CHF	+ O	= CHF ₂ O + CHF ₂	2.20E + 13	0.00	0	r/2	nist
29	CF ₃ -CHF	+ O	= CHF ₂ O + CF ₃	2.20E + 13	0.00	0	r/2	nist
30	CH ₃ -CF ₂	+ O	= CF ₂ O + CH ₃	1.10E + 13	0.00	0	r/2	nist
31	CH ₂ F-CF ₂	+ O	= CF ₂ O + CH ₂ F	1.10E + 13	0.00	0	r/2	nist
32	CHF ₂ -CF ₂	+ O	= CF ₂ O + CHF ₂	1.10E + 13	0.00	0	r/2	nist
33	CF ₃ -CF ₂	+ O	= CF ₂ O + CF ₃	1.10E + 13	0.00	0	r/2	nist
34	CH ₂ F-CH ₂	+ OH	= CH ₂ CO + HF + H ₂	6.60E + 13	0.00	0	r/5	nist
35	CHF ₂ -CH ₂	+ OH	= CHF ₂ CO + HF + H ₂	6.60E + 13	0.00	0	r/5	nist
36	CF ₃ -CH ₂	+ OH	= CF ₂ CO + HF + H ₂	6.60E + 13	0.00	0	r/5	nist
37	CH ₃ -CHF	+ OH	= CH ₂ CO + H ₂ + HF	4.40E + 13	0.00	0	r/5	nist
38	CH ₂ F-CHF	+ OH	= CH ₂ CO + HF + HF	4.40E + 13	0.00	0	r/5	nist
39	CHF ₂ -CHF	+ OH	= CHF ₂ CO + HF + HF	4.40E + 13	0.00	0	r/5	nist
40	CF ₃ -CHF	+ OH	= CF ₂ CO + HF + HF	4.40E + 13	0.00	0	r/5	nist
41	CH ₃ -CF ₂	+ OH	= CH ₂ CO + HF + HF	2.20E + 13	0.00	0	r/5	nist
42	CH ₂ F-CF ₂	+ OH	= CHF ₂ CO + HF + HF	2.20E + 13	0.00	0	r/5	nist
43	CHF ₂ -CF ₂	+ OH	= CF ₂ CO + HF + HF	2.20E + 13	0.00	0	r/5	nist
44	CF ₃ -CF ₂	+ OH	= CF ₃ + CF ₂ O + HF	2.20E + 13	0.00	0	r/5	nist
45	CH ₂ F-CH ₂	+ OH	= CH ₂ :CHF + H ₂ O	6.60E + 13	0.00	1510	r E + 3	nist
46	CHF ₂ -CH ₂	+ OH	= CH ₂ :CF ₂ + H ₂ O	6.60E + 13	0.00	1510	r E + 3	nist
47	CH ₃ -CHF	+ OH	= CH ₂ :CHF + H ₂ O	4.40E + 13	0.00	1510	r E + 3	nist
48	CH ₂ F-CHF	+ OH	= CHF:CHF-Z + H ₂ O	4.40E + 13	0.00	1510	r E + 3	nist
49	CHF ₂ -CHF	+ OH	= CHF:CF ₂ + H ₂ O	4.40E + 13	0.00	1510	r E + 3	nist
50	CH ₃ -CF ₂	+ OH	= CH ₂ :CF ₂ + H ₂ O	2.20E + 13	0.00	1510	r E + 3	nist
51	CH ₂ F-CF ₂	+ OH	= CHF:CF ₂ + H ₂ O	2.20E + 13	0.00	1510	r E + 3	nist
52	CHF ₂ -CF ₂	+ OH	= CH ₂ :CF ₂ + H ₂ O	2.20E + 13	0.00	1510	r E + 3	nist
<i>Fluoroethyls: association with HO₂</i>								
53	CH ₃ -CHF	+ HO ₂	= CH ₃ + CHF ₂ O + OH	3.00E + 13	0.00	0	r C ₂ H ₅	nist
54	CH ₃ -CF ₂	+ HO ₂	= CH ₃ + CF ₂ O + OH	3.00E + 13	0.00	0	r C ₂ H ₅	nist
55	CH ₂ F-CH ₂	+ HO ₂	= CH ₂ F + CH ₂ O + OH	3.00E + 13	0.00	0	r C ₂ H ₅	nist
56	CH ₂ F-CHF	+ HO ₂	= CH ₂ F + CHF ₂ O + OH	3.00E + 13	0.00	0	r C ₂ H ₅	nist
57	CH ₂ F-CF ₂	+ HO ₂	= CH ₂ F + CF ₂ O + OH	3.00E + 13	0.00	0	r C ₂ H ₅	nist
58	CHF ₂ -CH ₂	+ HO ₂	= CHF ₂ + CH ₂ O + OH	3.00E + 13	0.00	0	r C ₂ H ₅	nist

Table 5 (continued)

GG	A	b	E/R	Note	ref1	ref2	Hr
59	CHF ₂ -CHF + HO ₂	0.00	0	= CHF ₂ + CHF ₂ O + OH		nist	r C ₂ H ₅
60	CHF ₂ -CF ₂ + HO ₂	0.00	0	= CHF ₂ + CF ₂ O + OH		nist	r C ₂ H ₅
61	CF ₃ -CH ₂ + HO ₂	0.00	0	= CF ₃ + CH ₂ O + OH		nist	r C ₂ H ₅
62	CF ₃ -CHF + HO ₂	0.00	0	= CF ₃ + CHF ₂ O + OH		nist	r C ₂ H ₅
63	CF ₃ -CF ₂ + HO ₂	0.00	0	= CF ₃ + CF ₂ O + OH		nist	r C ₂ H ₅
64	CH ₃ -CHF + HO ₂	0.00	0	= CH ₃ :CHF + H ₂ O ₂	2A/3	nist	r C ₂ H ₅
65	CH ₃ -CF ₂ + HO ₂	0.00	0	= CH ₂ :CF ₂ + H ₂ O ₂	2A/3	nist	r C ₂ H ₅
66	CH ₂ F-CH ₂ + HO ₂	0.00	0	= CH ₂ :CHF + H ₂ O ₂	2A/3	nist	r C ₂ H ₅
67	CH ₂ F-CHF + HO ₂	0.00	0	= CHF:CHF-Z + H ₂ O ₂	2A/3	nist	r C ₂ H ₅
68	CH ₂ F-CF ₂ + HO ₂	0.00	0	= CHF:CF ₂ + H ₂ O ₂	1A/3	nist	r C ₂ H ₅
69	CHF ₂ -CH ₂ + HO ₂	0.00	0	= CH ₂ :CF ₂ + H ₂ O ₂	1A/3	nist	r C ₂ H ₅
70	CHF ₂ -CHF + HO ₂	0.00	0	= CHF:CF ₂ + H ₂ O ₂	1A/3	nist	r C ₂ H ₅
71	CHF ₂ -CF ₂ + HO ₂	0.00	0	= CF ₂ :CF ₂ + H ₂ O ₂	1A/3	nist	r C ₂ H ₅
72	CH ₃ -CHF + HO ₂	0.00	0	= CH ₃ -CH ₃ F + O ₂		nist	r C ₂ H ₅
73	CH ₃ -CF ₂ + HO ₂	0.00	0	= CH ₃ -CHF ₂ + O ₂		nist	r C ₂ H ₅
74	CH ₂ F-CH ₂ + HO ₂	0.00	0	= CH ₃ -CH ₂ F + O ₂		nist	r C ₂ H ₅
75	CH ₂ F-CHF + HO ₂	0.00	0	= CH ₂ F-CH ₂ F + O ₂		nist	r C ₂ H ₅
76	CH ₂ F-CF ₂ + HO ₂	0.00	0	= CH ₂ F-CHF ₂ + O ₂		nist	r C ₂ H ₅
77	CHF ₂ -CH ₂ + HO ₂	0.00	0	= CH ₃ -CHF ₂ + O ₂		nist	r C ₂ H ₅
78	CHF ₂ -CHF + HO ₂	0.00	0	= CHF ₂ F-CHF ₂ + O ₂		nist	r C ₂ H ₅
79	CHF ₂ -CF ₂ + HO ₂	0.00	0	= CHF ₂ -CHF ₂ + O ₂		nist	r C ₂ H ₅
80	CF ₃ -CH ₂ + HO ₂	0.00	0	= CH ₃ -CF ₃ + O ₂		nist	r C ₂ H ₅
81	CF ₃ -CHF + HO ₂	0.00	0	= CH ₂ F-CF ₃ + O ₂		nist	r C ₂ H ₅
82	CF ₃ -CF ₂ + HO ₂	0.00	0	= CHF ₂ -CF ₃ + O ₂		nist	r C ₂ H ₅
<i>Fluoroethylenes: disproportionation with CH₃</i>							
83	CH ₃ F-CH ₂ + CH ₃	-0.50	0	= CH ₂ :CHF + CH ₄	2A/3	nist	r C ₂ H ₅
84	CHF ₂ -CH ₂ + CH ₃	-0.50	0	= CH ₂ :CF ₂ + CH ₄	1A/3	nist	r C ₂ H ₅
85	CH ₃ -CHF + CH ₃	-0.50	0	= CH ₂ :CHF + CH ₄		nist	r C ₂ H ₅
86	CH ₂ F-CHF + CH ₃	-0.50	0	= CHF:CHF-Z + CH ₄	2A/3	nist	r C ₂ H ₅
87	CHF ₂ -CHF + CH ₃	-0.50	0	= CHF:CF ₂ + CH ₄	1A/3	nist	r C ₂ H ₅
88	CH ₃ -CF ₂ + CH ₃	-0.50	0	= CH ₂ :CF ₂ + CH ₄		nist	e C ₂ H ₅
89	CH ₂ F-CF ₂ + CH ₃	-0.50	0	= CHF:CF ₂ + CH ₄	2A/3	nist	r C ₂ H ₅
90	CHF ₂ -CF ₂ + CH ₃	-0.50	0	= CF ₂ :CF ₂ + CH ₄	1A/3	nist	r C ₂ H ₅
<i>Fluoroethylenes: thermal decompositions</i>							
1	CH ₂ :CHF	0.00	35632	+ HF			x
2	CH ₂ :CF ₂	0.00	43281	+ HF			x
3	CHF:CHF-Z	0.00	39255	+ HF			r + dH
4	CHF:CF ₂	0.00	50327	+ HF			r + dH
JD	A	b	E/R	Note	ref1	ref2	Hr
	1.00E + 14	0.00	35632	x	70SIM/QUI	nist	37
	2.50E + 14	0.00	43281	x	70SIM/TSC	nist	37
	2.50E + 14	0.00	39255	r + dH		nist	
	2.50E + 14	0.00	50327	r + dH		nist	

JA	Fluoroethylenes: H atom addition (stabilization)	A	b	E/R	Note	ref1	ref2	Hr
1	CH ₂ :CHF + H (+M)	4.20E + 08	1.50	498	r C ₂ H ₄		nist	
2	CH ₂ :CHF + H (+M)	4.20E + 08	1.50	498	r C ₂ H ₄		nist	
3	CH ₂ :CF ₂ + H (+M)	4.20E + 08	1.50	498	r C ₂ H ₄		nist	
4	CH ₂ :CF ₂ + H (+M)	4.20E + 08	1.50	498	r C ₂ H ₄		nist	
5	LOW/3.19E27 -2.8 -5.4/ H ₂ /2.0/ CO(2.0/ CO ₂ /3.0 H ₂ O-5.0/ CH ₂ :CHF-Z + H (+M) = CH ₂ F-CHF (+M)	8.40E + 08	1.50	498	r C ₂ H ₄		nist	
6	H ₂ /2.0/ CO(2.0/ CO ₂ /3.0 H ₂ O/5.0/ CH ₂ :CHF ₂ + H (+M) = CHF ₂ -CHF (+M)	4.20E + 08	1.50	498	r C ₂ H ₄		nist	
7	CH ₂ :CF ₂ + H (+M) = CH ₂ F-CF ₂ (+M)	4.20E + 08	1.50	498	r C ₂ H ₄		nist	
8	LOW/3.19E27 -2.8 -5.4/ H ₂ /2.0/ CO(2.0/ CO ₂ /3.0 H ₂ O/5.0/				r C ₂ H ₄		nist	
Fluoroethylenes: activated decomposition, methylene combination (HF elimination)								
5	CH ₂ SING + CHF = C ₂ H ₂ + HF 1.70E + 20 -2.12	1.70E + 20	-2.12	1198	r		nist	
6	CH ₂ SING + CF ₂ = C ₂ HF + HF 1.70E + 20 -2.12	1.70E + 20	-2.12	1198	r		nist	
7	CHF + CHF = C ₂ HF + HF 1.70E + 20 -2.12	1.70E + 20	-2.12	1198	r		nist	
8	CHF + CF ₂ = C ₂ F ₂ + HF 8.51E + 19 -2.12	8.51E + 19	-2.12	1198	k		nist	
Fluoroethylenes: activated decomposition, methylene combination (stabilization)								
9	CH ₂ SING + CHF = CH ₂ :CHF 3.10E + 24 -3.80	3.10E + 24	-3.80	1424	r		nist	
10	CH ₂ SING + CF ₂ = CH ₂ :CF ₂ 3.10E + 24 -3.80	3.10E + 24	-3.80	1424	r		nist	
11	CHF + CHF = CHF:CHF-Z 1.55E + 24 -3.80	1.55E + 24	-3.80	1424	r		nist	
12	CHF + CF ₂ = CHF:CF ₂ 3.10E + 24 -3.80	3.10E + 24	-3.80	1424	k		nist	
13	CF ₂ :CF ₂ + M = CF ₂ + M 3.96E + 50 -9.06	3.96E + 50	-9.06	42929	xk	78SCH/WAG	nist	
Fluoroethylenes: activated decomposition, methylene combination (H atom elimination)								
14	CH ₂ SING + CHF = CH ₂ :CF + H 1.64E + 07 1.56	1.64E + 07	1.56	2899	r		nist	
15	CH ₂ SING + CHF = CHF:CH-Z + H 3.28E + 07 1.56	3.28E + 07	1.56	2899	r		nist	
16	CH ₂ SING + CF ₂ = CF ₂ :CH + H 3.28E + 07 1.56	3.28E + 07	1.56	2899	r		nist	
17	CHF + CHF = CHF:CF-Z + H 3.28E + 07 1.56	3.28E + 07	1.56	2899	r		nist	
18	CHF + CF ₂ = CF ₂ :CF + H 1.64E + 07 1.56	1.64E + 07	1.56	2899	k		nist	
Fluoroethylenes: activated decomposition, vinyl + H (HF elimination)								
19	CH ₂ :CF + H = C ₂ H ₂ + HF 5.98E + 20 976	5.98E + 20	-2.31	976	r		nist	
20	CHF:CH-Z + H = C ₂ H ₂ + HF 5.98E + 20 976	5.98E + 20	-2.31	976	r		nist	
21	CF ₂ :CH + H = C ₂ HF + HF 5.98E + 20 976	5.98E + 20	-2.31	976	r		nist	
22	CHF:CF-Z + H = C ₂ HF + HF 5.98E + 20 976	5.98E + 20	-2.31	976	r		nist	
23	CF ₂ :CF + H = C ₂ F ₂ + HF 5.98E + 20 976	5.98E + 20	-2.31	976	k		nist	
Fluoroethylenes: activated decomposition, vinyl + H (stabilization)								
24	CH ₂ :CF + H = CH ₂ :CHF 2.40E + 34 2536	2.40E + 34	-7.11	2536	r		nist	
25	CHF:CH-Z + H = CH ₂ :CHF 2.40E + 34 2536	2.40E + 34	-7.11	2536	r		nist	
26	CF ₂ :CH + H = CH ₂ :CF ₂ 2.40E + 34 2536	2.40E + 34	-7.11	2536	r		nist	
27	CHF:CF-Z + H = CHF:CHF-Z 2.40E + 34 2536	2.40E + 34	-7.11	2536	r		nist	
28	CF ₂ :CF + H = CHF:CF ₂ 2.40E + 34 2536	2.40E + 34	-7.11	2536	k		nist	

Table 5 (continued)

JA	A	b	E/R	Note	ref1	ref2	Hr
8	CF ₂ :CF ₂ LOW/6.37E27 H ₂ /2.0/ CO/2.0/ CO ₂ /3.0/ H ₂ O/5.0/	1.50	498	(+M) = CHF ₂ -CF ₂		nist nist nist	
<i>Fluoroethylenes: H atom addition (F atom displacement)</i>							
9	C ₃ H ₄ + F	0.00	0	= CH ₂ :CHF + H		nist	
10	CH ₂ :CHF + F	0.00	0	= CH ₂ :CF ₂ + H		nist	
11	CH ₂ :CHF + F	0.00	0	= CHF:CHF-Z + H		nist	
12	CHF:CHF-Z + F	0.00	0	= CHF:CF ₂ + H		nist	
13	CHF:CF ₂ + F	0.00	0	= CF ₂ :CF ₂ + H		nist	
<i>Fluoroethylenes: H atom abstraction by H</i>							
14	CH ₂ :CHF + H	2.53	6161	= CHF:CH-Z + H ₂		nist	
15	CH ₂ :CHF + H	2.53	6161	= CH ₂ :CF + H ₂		nist	
16	CH ₂ :CF ₂ + H	2.53	6161	= CF ₂ :CH + H ₂		nist	
17	CHF:CHF-Z + H	2.53	6161	= CHF:CF-Z + H ₂		nist	
18	CHF:CF ₂ + H	2.53	6161	= CF ₂ :CF + H ₂		nist	
<i>Fluoroethylenes: oxidation by O</i>							
1	CH ₂ :CHF + O	1.00	659	= CH ₂ F + HCO		nist	
2	CHF:CHF-Z + O	1.00	800	= CH ₂ F + CF ₂ O	87CVE	nist	
3	CH ₂ :CF ₂ + O	1.00	750	= CHF ₂ + HCO	87CVE	nist	
4	CHF:CF ₂ + O	1.00	579	= CHF ₂ + CF ₂ O	87CVE	nist	
5	CF ₂ :CF ₂ + O	1.00	0	= CF ₂ + CF ₂ :O	87CVE	nist	
6	CH ₂ :CHF + O	1.00	1158	= CH ₃ + CF ₂ O	74SLA/GUT	nist	
<i>Fluoroethylenes: H atom abstraction by OH</i>							
7	CH ₂ :CHF + OH	2.00	1434	= CHF:CH-Z + H ₂ O	88TUL	nist	-6
8	CH ₂ :CHF + OH	2.00	1434	= CH ₂ :CF + H ₂ O	88TUL	nist	-10
9	CHF:CHF-Z + OH	2.00	1434	= CHF:CF-Z + H ₂ O	88TUL	nist	-5
10	CH ₂ :CF ₂ + OH	2.00	1434	= CF ₂ :CH + H ₂ O	88TUL	nist	
11	CHF:CF ₂ + OH	2.00	1434	= CH ₂ :CF + H ₂ O	88TUL	nist	1
<i>Fluoroethyls: oxidation by O₂</i>							
12	CH ₂ :CF + O ₂	-4.55	2758	= CH ₂ O + CF ₂ O	direct	nist	
13	CHF:CH-Z + O ₂	-4.55	2758	= CHF ₂ O + HCO	direct	nist	
14	CHF:CF-Z + O ₂	-4.55	2758	= CHF ₂ O + CF ₂ O	direct	nist	
15	CF ₂ :CH + O ₂	-4.55	2758	= CF ₂ :O + HCO	direct	nist	
16	CF ₂ :CF + O ₂	-4.55	2758	= CF ₂ :O + CF ₂ O	direct	nist	
17	CH ₂ :CF + O ₂	-8.22	3538	= CH ₂ O + CF ₂ O	a/s	nist	
18	CHF:CH-Z + O ₂	-8.22	3538	= CHF ₂ O + HCO	a/s	nist	
19	CHF:CF-Z + O ₂	-8.22	3538	= CHF ₂ O + CF ₂ O	a/s	nist	
20	CF ₂ :CH + O ₂	-8.22	3538	= CF ₂ :O + HCO	a/s	nist	
21	CF ₂ :CF + O ₂	-8.22	3538	= CF ₂ :O + CF ₂ O	a/s	nist	

					A	b	E/R	Note	ref1	ref2	Hr
<i>Fluoroalkynes: oxidation by O</i>											
22	CH ₂ CF	+ O	= CH ₂ CO	+ F	3.00E + 13	0.00	0	r C ₂ H ₃		nist	
23	CHF:CF-Z	+ O	= CHF ₂ CO	+ F	3.00E + 13	0.00	0	r C ₂ H ₃		nist	
24	CF ₂ CF	+ O	= CF ₂ CO	+ F	3.00E + 13	0.00	0	r C ₂ H ₃		nist	
25	CHF:CH-Z	+ O	= CHF ₂ CO	+ H	3.00E + 13	0.00	0	r C ₂ H ₃		nist	
26	CF ₂ :CH	+ O	= CF ₂ CO	+ H	3.00E + 13	0.00	0	r C ₂ H ₃		nist	
<i>Fluoroalkynes: oxidation by OH</i>											
27	CH ₂ :CF	+ OH	= CH ₂ CO	+ HF	3.00E + 13	0.00	0	r C ₂ H ₃		nist	
28	CHF:CH-Z	+ OH	= CH ₂ CO	+ HF	3.00E + 13	0.00	0	r C ₂ H ₃		nist	
29	CHF:CF-Z	+ OH	= CHF ₂ CO	+ HF	2.00E + 13	0.00	0	r C ₂ H ₃		nist	
30	CF ₂ :CF	+ OH	= CF ₂ CO	+ HF	1.00E + 13	0.00	0	r C ₂ H ₃		nist	
31	CH ₂ :CF	+ OH	= CH ₃	+ CF ₂ O	3.00E + 13	0.00	0	r C ₂ H ₃		nist	
32	CHF:CH-Z	+ OH	= CH ₂ F	+ HCO	3.00E + 13	0.00	0	r C ₂ H ₃		nist	
33	CHF:CF-Z	+ OH	= CH ₂ F	+ CF ₂ O	4.00E + 13	0.00	0	r C ₂ H ₃		nist	
34	CF ₂ :CF	+ OH	= CHF ₂	+ CF ₂ O	5.00E + 13	0.00	0	r C ₂ H ₃		nist	
<i>KK Fluoroethynes: H atom addition/stabilization</i>											
1	C ₂ HF	+ H (+M)	= CH ₂ :CF	(+M)	2.80E + 12	0.00	1213	r C ₂ H ₂		nist	
2	C ₂ HF	+ H (+M)	= CHF:CH-Z	(+M)	1.40E + 12	0.00	1213	r C ₂ H ₂		nist	
3	LOW/0.67E27	-3.5 2410/									
	H ₂ /2/ CO/2/	CO ₂ /3/ H ₂ O/5/									
4	C ₂ F ₂	+ H (+M)	= CHF:CF-Z	(+M)	2.80E + 12	0.00	1213	r C ₂ H ₄		nist	
<i>Fluoroethynes: oxidation</i>											
5	C ₂ HF	+ O	= FCCO-E	+ H	1.00E + 07	2.00	956	r C ₂ H ₂ × 2	MB A077	nist	
6	C ₂ F ₂	+ O	= FCCO-E	+ F	1.00E + 07	2.00	956	r C ₂ H ₂ × 2	MB A077	nist	
7	C ₂ HF	+ OH	= CHF ₂ CO	+ H	2.18E - 04	4.50	-503	r C ₂ H ₂ × 2	MB A089	nist	
8	C ₂ HF	+ OH	= CH ₂ F	+ CO	2.50E - 04	4.00	-1007	r C ₂ H ₂ /2	MB A090	nist	
9	C ₂ HF	+ OH	= HCCO	+ HF	2.50E - 04	4.00	-1007	r C ₂ H ₂ /2	MB A090	nist	
10	C ₂ F ₂	+ OH	= CF ₂ CO	+ H	2.18E - 04	4.50	-503	r C ₂ H ₂	MB A089	nist	
11	C ₂ F ₂	+ OH	= FCCO-E	+ HF	2.50E - 04	4.00	-1007	r C ₂ H ₂	MB A090	nist	
<i>Fluoroalkenes, fluoroalkynes</i>											
12	CHF ₂ CO	+ H	= CH ₂ F	+ CO	1.13E + 13	0.00	1725	r CH ₂ CO	MB A094	nist	
13	CF ₂ CO	+ H	= CHF ₂	+ CO	1.13E + 13	0.00	1725	r CH ₂ CO	MB A094	nist	
14	CHF ₂ CO	+ H	= FCCO-E	+ H ₂	5.00E + 13	0.00	4026	r CH ₂ CO	MB A095	nist	
15	CHF ₂ CO	+ O	= CHF:O	+ CO	1.00E + 13	0.00	4026	ul		nist	
16	CF ₂ CO	+ O	= CF ₂ :O	+ CO	1.00E + 13	0.00	4026	ul		nist	
17	CHF ₂ CO	+ OH	= FCCO-E	+ H ₂ O	7.50E + 12	0.00	1007	r CH ₂ CO	MB A097	nist	
18	FCCO-E	+ H	= CHF	+ CO	1.00E + 14	0.00	0	r HCCO	MB A101	nist	
19	FCCO-E	+ O	= CF:O	+ CO	1.00E + 14	0.00	0	r HCCO	MB A102	nist	
<i>CF F atom reactions</i>											
1	CH ₄	+ F	= CH ₃	+ HF	5.90E + 12	0.50	226	xf	92ATK/BAU	nist	-31
2	CH ₃ F	+ F	= CH ₂ F	+ HF	1.35E + 14	0.00	604	xf	83MAN/SET	nist	-37

Table 5 (continued)

CF		A	b	E/R	Note	ref1	ref2	Hr
3	CH ₂ F ₂	9.00E + 13	0.00	931	xf	85CLY/HOD	nist	-36
4	CHF ₃	4.50E + 13	0.00	1862	xf	83CLY/HOD	nist	-27
5	CH ₃ OH	2.62E + 09	1.44	-103	x	91GLA/KOS		
6	CH ₃ OH	4.62E + 07	1.97	-151	x	91GLA/KOS		
7	CH ₂ O	6.00E + 13	0.00	1007	r CHFO		nist	-45
8	CHF ₂ O	2.65E + 13	0.00	906	x	90FRA/ZHA	nist	-35
9	CH ₃ O	3.00E + 13	0.00	0	ul		nist	-114
10	HCO	1.00E + 13	0.00	0	ul		nist	-120
11	C ₂ H ₆	8.00E + 12	0.00	151	x	60FET/KNO		
12	CH ₃ -CH ₂ F	9.00E + 13	0.00	403	r C ₂ H ₆		nist	
13	CH ₃ -CHF ₂	1.00E + 14	0.00	403	r C ₂ H ₆		nist	
14	CH ₃ -CF ₃	1.00E + 14	0.00	2013	r C ₂ H ₆		nist	
15	CH ₃ -CH ₂ F	6.00E + 13	0.00	101	r C ₂ H ₆		nist	
16	CH ₂ F-CH ₂ F	1.30E + 14	0.00	403	r C ₂ H ₆		nist	
17	CH ₂ F-CHF ₂	1.30E + 14	0.00	403	r C ₂ H ₆		nist	
18	CH ₂ F-CF ₃	6.00E + 13	0.00	604	r C ₂ H ₆		nist	
19	CH ₃ -CHF ₂	3.00E + 13	0.00	403	r C ₂ H ₆		nist	
20	CH ₂ F-CHF ₂	3.00E + 13	0.00	604	r C ₂ H ₆		nist	
21	CHF ₂ -CHF ₂	6.00E + 13	0.00	604	r C ₂ H ₆		nist	
22	CHF ₂ -CF ₂	4.00E + 13	0.00	705	r C ₂ H ₆		nist	-33
23	CH ₂ H ₄	1.00E + 14	0.00	1007	r CH ₄		nist	-34
24	CH ₃ CF ₂	3.00E + 13	0.00	0	r H		nist	-18
25	C ₂ H ₃	2.00E + 13	0.00	0	r H		nist	
Ref Reference reactions (H,F,O)								
1	HF	3.12E + 13	0.00	49985	x	81BAU/DUX	3000-5000K?	
2	H ₂	7.23E + 13	0.00	470	x	89STE/BRU	221-376K	
3	HO ₂	5.00E + 13	0.00	400	x	83WAL/WAG	300K	
4	H ₂ O	2.53E + 13	0.00	400	x	83WAL/WAG	243-369K	
5	H ₂ O ₂	3.00E + 13	0.00	400	x	83WAL/WAG	300K	
<i>Reference reactions (fluoromethane: decomposition)</i>								
6	CH ₃ F	1.00E + 14	0.00	42778	x	79SCH/WAG	1150-1570K	
7	CH ₃ F	1.00E + 16	0.00	33971	x	79SCH/WAG	1150-1570K	
8	CH ₂ F ₂	8.90E + 12	0.00	35380	x	68POL/SHE	1060-1320K	
9	CHF ₃	1.30E + 16	0.00	29391	x	91HID/NAK	1500-2500K	
10	CF ₃	7.80E + 12	0.00	400	x	86PLU/PYA	295K	
11	CF ₃	5.48E + 13	0.00	400	x	89TSA/MCF	298K	
<i>Reference reactions (fluoromethane: abstraction, metathesis)</i>								
12	CH ₃ F	1.80E + 13	0.00	4731	x	75WES/DEH	605-871K	
13	CH ₂ F ₂	1.32E + 13	0.00	4731	x	72RID/DAV	873-953K	

14	CHF ₃	+ H	= CF ₃	+ H ₂	3.32E + 13	0.00	5536	xrev	78ART/BEL	350-600K	-2
15	CF ₃	+ H ₂	= CHF ₃	+ H	8.90E + 11	0.00	4781	x	78ART/BEL	350-600K	-4
16	CH ₃ F	+ O	= CH ₂ F	+ OH	7.83E + 12	0.00	4882	x	67PAR/AZA	858-933K	-2
17	CH ₂ F ₂	+ O	= CHF ₂	+ OH	2.65E + 12	0.00	4429	x	68PAR/NAL	873-953K	-18
18	CHF ₃	+ O	= CF ₃	+ OH	5.00E + 12	0.00	5385	x	78JOU/LEB	390-620K	-13
19	CH ₄	+ F	= CH ₃	+ HF	1.80E + 14	0.00	403	xv	92ATK/BAU	250-450K	-4
20	CH ₃ F	+ F	= CH ₂ F	+ HF	0.34 CH ₄ + F			x	83MAN/SET	300K	-102
21	CH ₂ F ₂	+ F	= CHF ₂	+ HF	3.40E + 12			x	85CLY/HOD	298K	-94
22	CHF ₃	+ F	= CF ₃	+ HF	9.00E + 10			x	83CLY/HOD	298K	-128
23	CH ₃ F	+ OH	= CH ₂ F	+ H ₂ O	4.90E + 12	0.00	1887	x	82JEO/KAU	292-480K	
24	CH ₂ F ₂	+ OH	= CHF ₂	+ H ₂ O	2.65E + 12	0.00	1772	x	82JEO/KAU	250-492K	
25	CHF ₃	+ OH	= CF ₃	+ H ₂ O	1.80E + 12	0.00	2914	x	82JEO/KAU	387-380K	
26	CH ₃	+ H ₂ O ₂	= CH ₄	+ HO ₂	1.21E + 10	0.00	-300	xv	86TSA/HAM		
27	CH ₂ O	+ CH ₃	= HCO	+ CH ₄	5.54E + 03	2.81	2950	xv	86TSA/HAM		
28	CH ₃ OH	+ CH ₃	= CH ₃ O	+ CH ₄	1.44E + 01	3.10	3490	xv	86TSA/HAM		
29	CH ₃ OH	+ CH ₃	= CH ₂ OH	+ CH ₄	3.20E + 01	3.20	3608	xv	87TSA		
30	HCO	+ CH ₃	= CO	+ CH ₄	1.20E + 14	0.00	0	xv	86TSA/HAM		
<i>Reference reactions (fluoromethyl oxidation)</i>											
31	CH ₃	+ O	= CH ₂ O	+ H	8.43E + 13	0.00	0	xv	92BAU/COB		
32	CH ₃	+ OH	= Products	+ H	3.61E + 13	0.00	0	xv	92BAU/COB		
33	CH ₃	+ HO ₂	= CH ₃ O	+ OH	1.81E + 13	0.00	0	v	92BAU/COB		
34	CH ₃	+ HO ₂	= CH ₄	+ O ₂	3.61E + 12	0.00	0	v	86TSA/HAM		
35	CF ₃	+ O	= CF ₂ O	+ F	1.87E + 13			x	89TSA/BEL	293K	
<i>Reference reactions (fluoromethylene, fluoromethylidyne oxidation, destruction)</i>											
36	CF ₂	+ F ₂	= CF ₃	+ F	5.00E + 10	0.00		x	82SEE/ROT	550K	
37	CF ₂	+ F ₂	= CF ₃	+ F	1.20E + 09			xul	86PLU/RYA	295K	
38	CF ₂	+ O	= Products	+ F	1.21E + 13			x	90TSA/MCF	293K	
39	CF ₂	+ OH	= CF ₂ O	+ H	5.00E + 12			x	78BIO/LAZ	1090-1375K	
38	CH	+ O ₂	= Products	+ H	3.30E + 13	0.00	0	xv	92BAU/COB		
39	CH	+ H ₂ O	= Products	+ H	5.70E + 12	0.00	-382	xv	92BAU/COB		
40	CF	+ H	= Products	+ H	1.15E + 13			x	89TSA/MCF	298K	
41	CF	+ O	= Products	+ O	7.23E + 12			x	90TSA/MCF	293K	
42	CF	+ O ₂	= Products	+ O ₂	9.64E + 11			x	92PEE/VAN	294K	
<i>Reference reactions (carbonyl fluorides)</i>											
43	CHF ₃ O	+ M	= CO	+ HF	2.48E + 25	-3.00	2164I	xg	85SAI/KUR	nist	
44	CHF ₃ O	+ H	= CF ₂ O	+ H ₂	1.10E + 08	1.77	1510	r	A/2	nist	
45	CHF ₃ O	+ O	= CF ₂ O	+ OH	9.00E + 12	0.00	1550	r		nist	
46	CHF ₃ O	+ OH	= CF ₂ O	+ H ₂ O	1.72E + 09	1.18	-225	r		nist	
47	CF ₂ O	+ H ₂ O ₂	= CHF ₂ O	+ HO ₂	1.00E + 11	0.00	1963	r	E*0.56	nist	
48	CHF ₃ O	+ CH ₃	= CF ₂ O	+ CH ₄	2.00E + 12	0.00	4529	rul		nist	
49	CF ₂ O	+ H	= CO	+ HF	1.20E + 14	0.00	0	r		nist	
50	CF ₂ O	+ O	= CO ₂	+ F	3.00E + 13	0.00	0	r		nist	
51	CF ₂ O	+ OH	= CO ₂	+ HF	3.00E + 13	0.00	0	r		nist	
52	CF ₂ O	+ HO ₂	= CO ₂	+ F + OH	3.00E + 13	0.00	0	r		nist	

Table 5 (continued)

Ref	A	b	E _J R	Note	ref1	ref2	Hr
53	CH ₃ F		0	r		mist	-101
54	CH ₂ F	4.00E + 13	0	r CH ₃		mist	-66
		4.00E + 13					
	Reference reactions (fluoroethanes: H atom abstractions by H, O, OH)						
55	CH ₃ -CH ₂ F	5.50E + 07	550	FXI	91COH/WES	mist	-13
56	CH ₃ -CH ₂ F	3.30E + 07	550	FXI	91COH/WES	mist	
57	CH ₃ -CHF ₂	1.54E + 07	570	FXI	91COH/WES	mist	
58	CH ₃ -CHF ₂	4.40E + 06	670	FXI	91COH/WES	mist	
59	CH ₂ F-CHF ₂	2.05E + 07	906	FXI	87COH/BEN	mist	
60	CH ₂ F-CHF ₂	1.06E + 07	1510	FXI	87CIH/BEN	mist	
	Reference reactions (fluoroethanes: H atom abstraction by CH ₃ , C ₂ H ₅ , C ₂ H ₅ , HCO)						
61	CH ₃ -CH ₂ F	2.00E + 11	6744	r		mist	1
62	CH ₃ -CHF	5.50E + 03	2969	r C ₂ H ₅		mist	
	Reference reactions (fluoroethanes, fluoroethyls: association with O ₂ , O, HO ₂)						
63	CH ₃ -CHF	9.00E + 09	503	r C ₂ H ₅		mist	
64	CH ₃ -CHF	2.56E + 19	995	r C ₂ H ₅		mist	
65	CH ₂ F-CH ₂	6.60E + 13	0	r C ₂ H ₅	3A/3	mist	
66	CH ₃ -CHF	3.00E + 11	0	r C ₂ H ₅	2A/3	mist	
	Reference reactions (fluoroethylenes: H atom addition/stabilization, F atom displacement, H atom abstraction)						
67	CH ₂ :CF ₂	4.20E + 08	498	r C ₂ H ₄		mist	
	LOW/3.19E27			r C ₂ H ₄		mist	
				ref		mist	
68	CH ₂ :CHF	3.30E + 05	6161	r C ₂ H ₄		mist	
	Reference reactions (fluoroethylenes: oxidation by O)						
69	CH ₂ :CHF	5.30E + 09	659	xf	87CVE	mist	
70	CHF:CHF-Z	7.00E + 09	800	xf	87CVE	mist	
71	CH ₂ :CF ₂	4.30E + 09	750	xf	87CVE	mist	
72	CHF:CF ₂	6.00E + 09	579	xf	87CVE	mist	
73	CF ₂ :CF ₂	1.90E + 09	0	xf	87CVE	mist	
	Reference reactions (fluoroethylenes: H atom abstraction by OH)						
74	CH ₂ :CHF	2.00E + 06	1434	xf	88TUL	mist	-6
	Reference reactions (fluoroethyls)						
75	CH ₂ :CF	4.48E + 26	2758	r C ₂ H ₃	direct	mist	
76	CH ₂ :CF	1.05E + 38	3538	r C ₂ H ₃	a/s	mist	
77	CH ₂ :CF	3.00E + 13	0	r C ₂ H ₃		mist	
78	CH ₂ :CF	3.00E + 13	0	r C ₂ H ₃		mist	

<i>Reference reactions (fluoroethynes)</i>									
79	C ₂ HF	+ H (+M)	= CHF;CH-Z	(+M)	1.40E + 12	0.00	1213	r C ₂ H ₂	nist
	LOW/0.67E27	-3.5 2410/							
	H ₂ /2/	CO/2/							
80	C ₂ HF	+ O	= FCCO-E	+ H	1.00E + 07	2.00	956	r C ₂ H ₂ × 2	MB A077
81	C ₂ HF	+ OH	= CHFCO	+ H	2.18E - 04	4.50	-503	r C ₂ H ₂ × 2	MB A089
82	C ₂ HF	+ OH	= CH ₂ F	+ CO	2.50E - 04	4.00	-1007	r C ₂ H ₂ /2	MB A090
<i>Reference reactions (fluoroethenes, fluoroalkynes)</i>									
83	CHFCO	+ H	= CH ₂ F	+ CO	1.13E + 13	0.00	1725	r CH ₂ CO	MB A094
84	CHFCO	+ H	= FCCO-E	+ H ₂	5.00E + 13	0.00	4026	r CH ₂ CO	MB A095
85	CHFCO	+ OH	= FCCO-E	+ H ₂ O	7.50E + 12	0.00	1007	r CH ₂ CO	MB A097
86	FCCO-E	+ H	= CHF	+ CO	1.00E + 14	0.00	0	r HCCO	MB A101
87	FCCO-E	+ O	= CF ₂ O	+ CO	1.00E + 14	0.00	0	r HCCO	MB A102
<i>Reference reactions (F atom reactions)</i>									
88	CH ₂ O	+ F	= HCO	+ HF	6.00E + 13	0.00	1007	r CHFO	nist
89	C ₂ H ₃	+ F	= C ₂ H ₂	+ HF	2.00E + 13	0.00	0	r C ₂ H ₃	nist
90	CHF;CF-Z	+ F	= CHF	+ CF ₂	1.00E + 13	0.00	0	r C ₂ H ₃	nist
91	CF ₂ ;CF ₂	+ F	= CF ₃	+ CF ₂	3.00E + 13	0.00	0	r C ₂ H ₃	nist

k $AT^b e^{-E/RT}$; prefactor (mol cm³/s⁻¹); **b** temperature dependence (dimensionless); **E/R** activation energy (K); **Hr** heat of reaction (kcal mol).
x experimental data; **xh** experimental data measured at high temperatures; **xf** experimental data fit with reasonable temperature dependence (T^b); **xg** experimental data fit with temperature dependence; **xt** experimental data fit with TST temperature dependence; **xk** RRM benchmarked to experimental data; **xv** evaluated recommendation based on experimental data; **xrev** based on experimental data for reverse reaction. **r** relative to reference reaction (e.g. r CH₃—referenced to analogous reaction for CH₃); **ru** relative to reference reaction, upper limit estimate; **ul** upper limit estimate. **k** RRM; **a** calculated with *ab initio* transition state partition functions; **ak** RRM with *ab initio* thermodynamics. Notation for this table is overleaf.

Table 5 (continued)

Notation	Reference	Notation	Reference
65PRI/BRY	Pritchard <i>et al.</i> , 1965	81BAU/DUX	Baulch <i>et al.</i> , 1981
65TSC	Tschuikow-Roux, 1965	81HOW/SMI	Howard and Smith, 1981
67PAR/AZA	Parsamyan <i>et al.</i> , 1970	81MES/FIL	Messing <i>et al.</i> , 1981
68PAR/NAL	Parsamyan and Nalbanddyan, 1968	81VEY/LES	Veyret and Lesclaus, 1981
70CAD/DAY	Cadman <i>et al.</i> , 1970	82BER/FLE	Berman <i>et al.</i> , 1982
70SIM/QUI	Simmie <i>et al.</i> , 1970	83BAU/CRA	Baulch <i>et al.</i> , 1983
70TSC/QUI	Tschuikow-Roux <i>et al.</i> , 1970	83KIE/KAP	Kiefer <i>et al.</i> , 1983
71BRA/BEL	Brabbs <i>et al.</i> , 1971	83TUL/RAV	Tully <i>et al.</i> , 1983
71JAC/HOU	Jachimowski and Houghton, 1971	83WAL/WAG	Walther and Wagner, 1983
71KER/TIM	Kerr and Timlin, 1971	83WAS/HAT	Washida <i>et al.</i> , 1983
71KOC/MOI	Kochubei and Moïn, 1971	84RYA/PLU	Ryan and Plumb, 1984
71MIL/HAR	Millward <i>et al.</i> , 1971	84TEM/WAG	Temps and Wagner, 1984
71TSC/MIL	Tschuikow-Roux <i>et al.</i> , 1971	84WAR	Warnatz, 1984
71TSC/QUI	Tschuikow-Roux <i>et al.</i> , 1971	85SAI/KUR	Saito <i>et al.</i> , 1985
71WAG/WAR	Wagner <i>et al.</i> , 1971	86PLU/RYA	Plumb and Ryan, 1986
72BER/MAR	Berces <i>et al.</i> , 1972	86SUT/MIC	Sutherland <i>et al.</i> , 1986
72KER/PAR	Kerr and Parsonage, 1972	86TSA/HAM	Tsang and Hampton, 1986
72MIL/TSC	Millward and Tschuikow-Roux, 1972	87COH/BEN	Cohen and Benson, 1987
72RID/DAV	Ridley <i>et al.</i> , 1972	87CVE	Cvetanovic, 1987
72SKI/LIF	Skinner <i>et al.</i> , 1972	87DEA/WES	Dean and Westmoreland, 1987
73CLA/DOV	Clark and Dove, 1973	88SUT/MIC	Sutherland <i>et al.</i> , 1988
73PEE/MAH	Peeters and Mahnen, 1973	88WAG/WAR	Wagner and Wardlaw, 1988
73SCH/WAG	Schug and Wagner, 1973	88ZAB/FLE	Zabarnick <i>et al.</i> , 1988
74SEK/TSC	Sekhar and Tschuikow-Roux, 1974	89STE/BRU	Stevens <i>et al.</i> , 1989
74SLA/GUT	Slagle <i>et al.</i> , 1974	89STE/SMI	Stewart <i>et al.</i> , 1989
75BOW	Bowman, 1975	89TSA/BEL	Tsai <i>et al.</i> , 1989
75WES/DEH	Westenberg and de Haas, 1975	90TSA/MCF	Tsai and McFadden, 1989
76PAY/STI	Payne and Stief, 1976	90BOZ/DEA	Bozzeili and Dean, 1990
77ATR/BAL	Atri <i>et al.</i> , 1977	90NOR	Norton, 1990
77KEA/MAT	Keating and Matula, 1977	90TSA/MCF	Tsai and McFadden, 1990
78ART/BEL	Arthur and Bell, 1978	91COH/WES	Cohen and Westberg, 1991
78BIO/LAZ	Biordi <i>et al.</i> , 1978	91HID/NAK	Hidaka <i>et al.</i> , 1991
78JOU/LEB	Jourdain <i>et al.</i> , 1978	92BAU/COB	Baulch <i>et al.</i> , 1992
79COH/WES	Cohen and Westberg, 1979	92MAR/SZE	Mariq and Szenté, 1992
79MIC/NAV	Michael <i>et al.</i> , 1979	92WES	Westmoreland, 1992
79SCH/WAG	Schug <i>et al.</i> , 1979	RRKM	this work, RRRM calculations
80BUT/FLE	Butler <i>et al.</i> , 1980	ORRK	this work, ORRK calculations
80DEA/JOH	Dean <i>et al.</i> , 1980	BAC	this work, BAC-MP4 and RRRM calculations
80KLE/SKO	Klemm <i>et al.</i> , 1980	ref	this work, by analogy to other reactions

The hydrogen/oxygen and hydrocarbon reaction subsets of the mechanism are derived from the Miller–Bowman mechanism (Miller and Bowman, 1989) and consists of about 30 species and 140 reactions. Any other hydrocarbon mechanism could be used instead. For example, the GRIMECH set (Bowman *et al.*, 1995) is a recent hydrocarbon mechanism that accurately reproduces flame speeds for methane mixtures.

In this work, some modifications to the Miller–Bowman mechanism were made. All nitrogen-containing species and reactions were removed. A number of the rich species (e.g. C₂H, C₄H₂) were eliminated from the mechanism in order to keep the number of species in the mechanism to a manageable level. A number of species (e.g. CH₃OH) were also added to the mechanism. In addition to these additions and deletions, a number of rate constants for a number of reactions (e.g. CH₃ + OH) were adjusted to provide correct fall-off and product channel ratios. In this section of the reaction set, the notation for the reference is slightly different. For example, for CH₄ + H = CH₃ + H₂ (reaction HC-1), the notation '73CLA/DOV MBA004' means that this rate expression was determined by Clark and Dove (1973) and was reaction #4 in Table A of the Miller–Bowman mechanism (Miller and Bowman, 1989). Where only the Miller–Bowman reference is given, either the expression is directly attributable to that work or the origins/traceability of the expression are not clear.

Acknowledgements—The authors wish to acknowledge support of the project 'Agent Screening for Halong 1301 Aviation Replacement' by the U.S. Naval Air Systems Command, the U.S. Army Aviation and Troop Command, the Federal Aviation Administration Technical Center, and the U.S. Air Force. This program at NIST (Grosshandler *et al.*, 1994) was under the direction of Mr. Michael Bennett at the Wright Patterson AFB Flight Dynamics Laboratory, Vehicle Subsystems Division, Survivability Enhancement Branch. The authors also wish to express their gratitude to Dr. Carl F. Melius of Sandia National Laboratories for use of the BAC (Bond Additivity Corrections) code.

6. REFERENCES

6.1. Overview

A list of references is given below that was compiled and reviewed as part of this work. The list of references is divided into a number of different sections:

- (6.2) General Thermochemistry and Kinetics
- (6.3) Hydrocarbon Chemistry
- (6.4) Fluorine Chemistry
- (6.5) Fluorocarbon Thermochemistry
- (6.6) Oxidized Fluorocarbon Thermochemistry

- (6.7) Fluorocarbon Kinetics (Decompositions)
- (6.8) Fluorocarbon Kinetics (Abstractions)
- (6.9) Fluorocarbon Kinetics (Oxidations)
- (6.10) Oxidized Fluorocarbon Kinetics
- (6.11) Fluorocarbon Kinetics (Other)
- (6.12) Flame Inhibition (Halogens) and
- (6.13) Flame Inhibition (non-Halogens).

The references for 'Hydrocarbon Kinetics' are not meant to be comprehensive, but rather a documentation of those rate constants used in this work. The references for 'Flame Inhibition' are also not meant to be comprehensive, but rather representative of flame inhibition chemistry as related to this work. In the other reference sections, all relevant references are included, both those references for which thermochemical or kinetic data were utilized in the reaction set, as well as other related sources of relevant data.

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