

5. FLAME INHIBITION CHEMISTRY AND THE SEARCH FOR ADDITIONAL FIRE FIGHTING CHEMICALS

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Replacements for the current commercial halons should possess a diverse set of properties which are rarely found together in the same molecule. Thus, the ideal candidate for the replacement of halon 1301 would be a nontoxic gas which is reactive in flames and in the troposphere, yet at the same time, inert in the stratosphere and in its storage environment. The present generation of replacements, as typified by the core candidates listed in Section 1, were selected on the basis of a compromise, whereby fire suppression efficiency was sacrificed to ensure acceptable environmental properties. The research reported in this section was directed at developing the capability to predict the fire suppression effectiveness, propensity to generate corrosive combustion products, and environmental impact of a molecule on the basis of its structure. This is essential to the development of a rational approach to the search for new and more effective fire fighting chemicals.

The immediate objective of the research described in Section 5.1 was to provide a chemical basis for understanding the relative fire suppression efficiencies of the core candidates. In this pursuit, a kinetic mechanism, accounting for the interactions of substituted fluoromethanes and fluoroethanes in hydrocarbon flames, was developed and incorporated into a computer model. The expectation is that fire scientists will some day be able to use this model to predict the performance of replacement candidates, thereby reducing the time and expense involved in laboratory screening.

The fire suppression efficiencies of the core candidates are poor compared to halon 1301. This implies that much higher concentrations will be required to put out a fire. The levels of corrosive by-products, particularly HCl and HF, generated in the extinction process are likely to be considerably higher, as well. The empirical study summarized in Section 5.2 was undertaken to identify the factors which determine the potential of an agent to form acid gases in a combustion environment so that the worst offenders can be eliminated from further consideration.

Additional research was conducted to expand the scope of agent screening beyond the core candidates. This effort is described in Section 5.3. Structure/activity relationships (SARs) for ozone depletion and global warming were tested and developed. These were used, in conjunction with experimental measurements of fire suppression efficiency and considerations of the commercial availability and suitability for total flooding, to identify the most promising candidates from an exhaustive list of possibilities.

5.1 Kinetics of Fluorine-Inhibited Hydrocarbon Flames

5.1.1 Project Objectives. The major objective of this subtask 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 the objective of this subtask, 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. Unfortunately, neither such a mechanism nor a review of the relevant chemistry existed prior to this study. Consequently, a significant effort was required in order to "simply" construct such a comprehensive mechanism prior to its utilization in any simulations.

The focus of this task was restricted to the chemistry involving only fluoromethanes and fluoroethanes. This includes both those candidate agents specifically being considered as replacements (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 for all of the other possible fluoromethanes (CH_3F , CHF_3 , CF_4) and fluoroethanes ($\text{CH}_3\text{-CH}_2\text{F}$, $\text{CH}_3\text{-CHF}_2$, $\text{CH}_3\text{-CF}_3$, $\text{CH}_2\text{F-CH}_2\text{F}$, $\text{CH}_2\text{F-CHF}_2$, $\text{CHF}_2\text{-CHF}_2$). The two chlorine-substituted agents (CHF_2Cl , $\text{CF}_3\text{-CHF}_2\text{Cl}$) and the larger fluorinated hydrocarbon agents (C_3F_8 , $\text{C}_3\text{F}_7\text{H}$, C_4F_{10} , cyclo- C_4H_8) were not specifically considered. Including these additional candidate agents would 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 as developed as part of this subtask.

The complete set of fluoromethanes and fluoroethanes were studied for two basic reasons. 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 describe the decomposition of the four specific agents (and resultant chemistry) adequately, it is necessary to describe the chemistry of all of the many 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) $\bullet\text{CF}_3$ radicals. These $\bullet\text{CF}_3$ radicals will then react with methyl radicals, $\bullet\text{CH}_3$, 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, $\text{CH}_3\text{-CF}_3$. In order to predict the products in the flame correctly, the magnitude and rate of heat release in the flame, and ultimately the effectiveness of the added agent, it is also necessary to describe correctly the decomposition of these two additional stable fluorinated hydrocarbon species ($\text{CH}_3\text{-CF}_3$, $\text{CH}_2=\text{CF}_2$). When the decomposition channels for these two molecules are considered and for all of the other reaction channels for $\bullet\text{CF}_3$, as well as for all of the relevant chemistry for the other three specific candidate agents, very quickly most of the possible fluoromethanes and fluoroethanes must be considered.

Second, given that as part of the overall project there was, unfortunately, no directly related experimental task to these simulations, it was imperative to provide a level of self-consistency to this 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 benchmarking of the simulations with experimental measurements.

5.1.2 Background. There has been a significant amount of work over many years investigating the effectiveness of halogenated fire suppressants (Ellis, 1948; Simmons and Wolfhard, 1955; Rosser

et al., 1958; Friedman and Levy, 1963; Fenimore and Jones, 1963; Halpern, 1966; McHale *et al.*, 1971; Day *et al.*, 1971; Creitz, 1972; Biordi *et al.*, 1973; Larsen, 1974; Brown, 1975; Gann, 1975; Larsen, 1975; Skinner, 1975; Biordi *et al.*, 1976; Biordi *et al.*, 1978; Fristrom and Van Tiggelen, 1979; Dixon-Lewis, 1979; Westbrook, 1980; Safieh *et al.*, 1982; Westbrook, 1983; Vandooren *et al.*, 1988; Masri, 1992; Morris *et al.*, 1992), as well as other types of fire suppressants (Jorissen and Meuwissen, 1924; Jorissen *et al.*, 1932; Lask and Wagner, 1962; Ibiricu and Gaydon, 1964; Fristrom, 1967; McHale, 1969; Creitz, 1970; Cotton and Jenkins, 1971; Hastie, 1973; Jensen and Jones, 1978; Jensen and Jones, 1982). We will not review this body of work, but refer the reader to those relevant sources. However, in the following sections we will provide a brief overview of the most relevant work relating to the agents being considered as part of this project. For the most part, this means the chemistry of CF_3Br flame suppression. We will also describe the general and specific physical and chemical processes that are most important in influencing flame suppression and other effects (*e.g.*, ignition, promotion, by-products) in hydrocarbon flames. This will include those factors specifically related to the candidate agents.

The chemistry of CF_3Br and its role in flame suppression has been reviewed in detail by others. A number of these works are referenced in the prior section. A large part of our work is based on the pioneering work in this area by Biordi and coworkers (Biordi *et al.*, 1978) and Westbrook (1983). In earlier experiments on a range of candidates, CF_3Br was identified as being very effective for extinguishing flames. However, its mechanism was not understood. Biordi and coworkers constructed the first flame-sampling molecular beam mass spectrometer in order to understand how CF_3Br inhibited combustion in hydrocarbon flames. In this work, they measured both stable and radical species in methane flames that were doped with CF_3Br . Many of the relevant elementary reactions describing 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 . This mechanism was then used to model the inhibition of CF_3Br in hydrocarbon flames. As a result of this work and other work, it is generally agreed that flame suppression by bromine-containing compounds is a result of catalytic destruction of H atoms by Br atoms in the flame. 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 through a number of reactions regenerate Br atoms. It was also determined in these studies that $\bullet\text{CF}_3$, formed by decomposition of CF_3Br , also removes H 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 in inhibiting hydrocarbon flames. Most of these effects are intimately related. For example, a 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 temperature decrease and so on. One can separate suppression effects into two general categories: physical and chemical (although there is overlap). We prefer a definition where chemical effects are directly related to the characteristics of the specific molecule, such as H or F or Cl substitution, and physical effects are not. For example, heat capacity to a first approximation is largely a function of the number of atoms in the molecule and their connectivity, but not the identity of the molecule. Consequently, heat capacity can be considered an effect of more of a physical nature than a chemical one.

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 our task (largely dealing with the chemistry of these agents). Physical effects were addressed by other tasks in the overall project that consisted of measurements of PVT properties, discharge dynamics, dispersion mechanics, as well as measurements of extinction effectiveness for a number of more realistic geometries than can be

considered in this modeling task. We will not discuss these in any detail here and refer the reader to the sections dealing with other tasks. 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 we could not directly address in our 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 (which of course speeds flame chemistry). On the other hand, the agents are large molecules with many atoms. Consequently, their high heat capacities may result in a decrease in temperature in the flame prior to complete combustion (which of course slows flame chemistry). The competition between these two factors will be strongly dependent upon conditions; most important of which will probably be the mechanics of mixing of the fuel and oxidizer (including diffusion processes).

Another set of competing effects involves the fluorinated radicals produced by decomposition of the agents. 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 (preheat) of the flame. Consequently, these radicals may be involved in termination steps, such as $\bullet\text{CHF}_2 + \text{HO}_2\bullet \rightarrow \text{CH}_2\text{F}_2 + \text{O}_2$, slowing radical chain reactions and inhibiting the flame. These radicals will also simply compete with hydrocarbon radicals for important H, O, and OH radicals. On the other hand, these radicals can also react with stable molecules in the colder air stream, such as O_2 , generating more radicals, such as O atoms, and thereby initiating chemistry or promoting combustion of the fuel.

These and other chemical effects (and the relative importance of each) are being considered as part of this work.

5.1.3 Reaction Engineering Approach

5.1.3.1 Species Thermochemistry. We have 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. Existing thermochemical data was compiled and evaluated. Where little or no data existed for potential species of interest (most of the radicals), we have estimated that thermochemistry using both empirical methods, such as group additivity (Benson, 1976), and also through application of *ab initio* molecular orbital calculations (Frisch *et al.*, 1992; Curtiss *et al.*, 1991; Melius, 1990). Where heat capacity data existed, but only over a limited temperature range, these data were fit to two splined polynomials which extrapolated to the theoretical high temperature limit and were well-behaved at intermediate temperatures (*e.g.*, Figure 1). In all cases (experimental, empirical, and *ab initio*), significant effort was made to utilize thermochemical data for each which was consistent (correct relative values) with data for all other species. Figure 1 shows a typical fit to heat capacity data for one of the fluoroethanes. This figure is a (black & white) "screen dump" of the (color) display window of the interactive, graphics program "NIST FITCP," which was developed as part of this subtask.

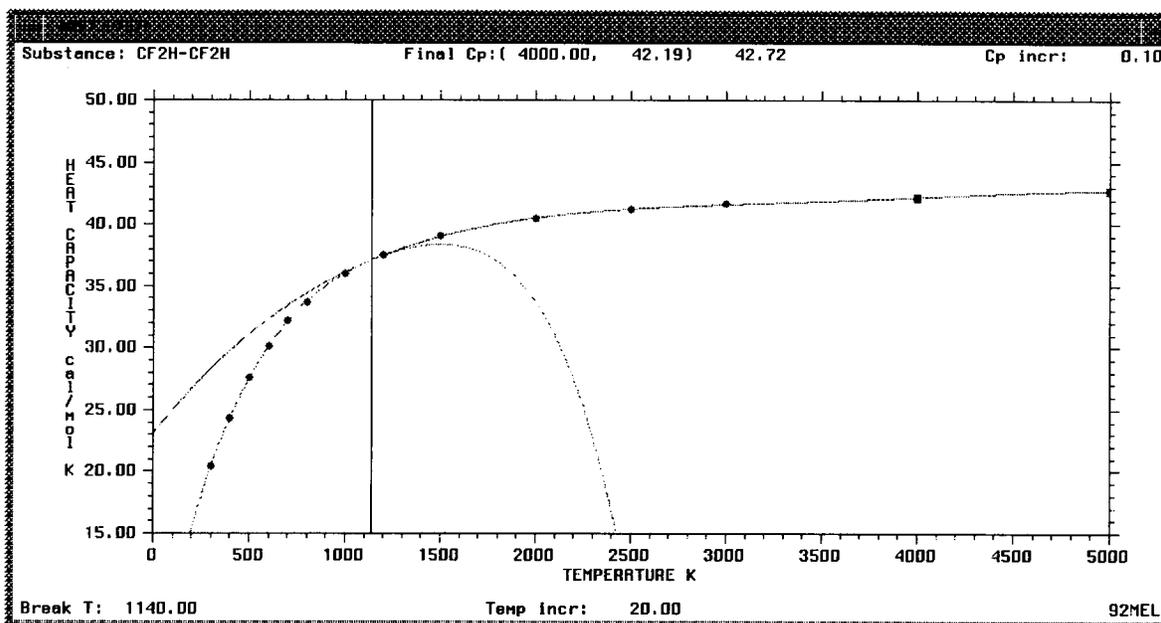


Figure 1. NIST FITCP. Typical fit to heat capacity data for a fluoroethane. This is a (black & white) "screen dump" of the (color) display window of the interactive, graphics program "NIST FITCP" developed as part of this subtask.

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), *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). 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 a few 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), and "Halomethylenes: Effects of Halogen Substitution on Absolute Heats of Formation" (Lias *et al.*, 1985). There are a numerous other references with thermodynamic data for fluorinated hydrocarbons that we have compiled as part of this work and will be discussed in more detail in a later publication. It should be noted that for most of the radicals, we have relied upon recent *ab initio* calculations of thermochemical data. This includes both *ab initio* calculations done as part of this subtask of the project and those done previously by other workers. Tschuikow-Roux and coworkers have calculated thermochemistry for the fluoroethyl radicals (Chen *et al.*, 1990a, 1990b; Chen *et al.*, 1991a, 1991b). Melius has calculated thermochemistry for many stable and radical fluorinated species (Melius, 1993). Nyden (1993) has used *ab initio* calculations to obtain thermochemical data for a number of the fluoroethanes and fluoroethyl radicals. Details of our *ab initio* calculations will be given in a subsequent section.

A listing of the thermochemistry that was used for fluorinated hydrocarbon species is given in Table 1, consisting of enthalpies of formation and entropies (at standard state) and temperature-dependent heat capacities. Standard thermochemistry for hydrocarbon, hydrogen/oxygen, and hydrogen/fluorine/oxygen species was used and is not included in this table.

5.1.3.1.1 Hydrocarbon and H/O/F Thermochemistry. We have used standard hydrogen/oxygen and hydrocarbon thermochemistry, most of which can be found in the JANAF tables (Stull and Prophet, 1971). More recent thermochemistry for C_2H_3 and HCO has been utilized. Further refinement of this mechanism should include re-adjustment of any other thermochemistry or rate constants that are based upon the older values for the heat of formation of these two species.

Thermochemistry for F, F_2 , and HF can be found in the JANAF tables as can data for $FO\bullet$, $FOO\bullet$, FOF, and HOF. (The latter species were eventually excluded from the reaction set as the simulations showed that their concentrations were negligible at high temperatures under hydrocarbon flame conditions). The thermochemical data for F, F_2 , and HF are very well established. Although there is a more recent value for the heat of formation of HF, the values contained in the JANAF table were used for consistency. This is because there are many thermochemical and rate data for fluorinated species that are based on the current JANAF recommendation for HF. Further refinement of this mechanism should include evaluation of this new value for HF and re-adjustment of any other thermodynamic or kinetic data that are based on HF thermochemistry.

5.1.3.1.2 C_1 Fluorinated Hydrocarbon Thermochemistry. Thermochemical data for the fluoromethanes: CH_3F , CH_2F_2 , CHF_3 , and CF_4 can be found in the JANAF tables (Stull and Prophet, 1971). The thermodynamic properties of these fluoromethanes have also been re-examined subsequently (Rodgers *et al.*, 1974). As part of this subtask of the project, we have also calculated this data using the BAC-MP4 *ab initio* method (Melius, 1990). Details of our *ab initio* calculations

will be given in a subsequent section. Melius (1993) has also calculated this thermochemical data for the fluoromethanes. It is necessary to have *ab initio* calculated values for these molecules with well known thermochemical data in order to adequately benchmark *ab initio* calculations for those molecules with unknown or uncertain thermochemistry. Entropy and heat capacity data for the fluoromethanes are derived from spectroscopic data and are known to a very good level of certainty (less than 0.5 J/mol/K for entropies). Heats of formation for CH_2F_2 and CF_4 are the best known, with levels of uncertainty of less than 1.5 kJ/mol. The values for CH_2F_2 and CF_4 are derived from their heats of combustion (which are dependent on the heat of formation of HF). These data also correlate well with heats of formation for other fluorine-containing molecules. Heats of formation of CH_3F and CHF_3 have somewhat higher uncertainties of less than 10 kJ/mol. The heat of formation of CH_3F is derived from appearance potential measurements (high level of uncertainty) and also from bond additivity correlations with heats of formation for CH_4 and the other fluoromethanes. The heat of formation of CHF_3 is obtained from heat of combustion data for CHF_3 , equilibrium data with other compounds, and some kinetic data. The data derived from heat of combustion appear to be complicated by competing reactions. Heats of formation for the fluoromethanes calculated using BAC-MP4 are within 1-3 kJ/mol of the experimentally derived values (except for CF_4 , the reference compound). A better BAC correction should be possible using correlations with all experimental data for fluoromethanes and fluoroethanes rather than just one compound (CF_4).

Thermochemical data for the perfluoromethyl radical ($\bullet\text{CF}_3$) can be found in the JANAF tables. More recent experimentally derived values for the heat of formation of $\bullet\text{CF}_3$ can be found elsewhere (Rodgers, 1978; McMillen and Golden, 1982; Tsang, 1986). These suggest a value that is about 4 kJ/mol higher than the JANAF recommendation. All of these heat of formation data are derived from kinetic experiments for the forward and reverse rates of several reaction. The JANAF recommendation is also based in part of correlations with heats of formation (and bond strengths) for other fluorine-containing compounds. The entropy and heat capacity data for $\bullet\text{CF}_3$ in the JANAF table are derived from spectroscopic measurements with an uncertainty of about 5 J/mol/K in the entropy. The other fluoromethyl radicals ($\bullet\text{CH}_2\text{F}$, $\bullet\text{CHF}_2$) are not in the JANAF tables. However, reliable, experimentally derived values for these two compounds can be found in other evaluated sources (McMillen and Golden, 1982; Pickard and Rodgers, 1983).

As part of this subtask of the project, we have also calculated thermochemical data for the fluoromethyl radicals using the BAC-MP4 *ab initio* method. These data have also been calculated by Melius (1993). We have used the entropies and heat capacities for $\bullet\text{CH}_2\text{F}$ and $\bullet\text{CHF}_2$ from the *ab initio* calculations in the kinetic simulations part of this subtask, since there does not exist (to our knowledge) experimental values for these two radical species. Heats of formation for $\bullet\text{CH}_2\text{F}$, $\bullet\text{CHF}_2$, and $\bullet\text{CF}_3$ calculated by this method are within 1-2 kJ/mol of the experimentally derived values. Although there are the experimentally derived values for $\bullet\text{CH}_2\text{F}$ and $\bullet\text{CHF}_2$, we have used the *ab initio* values in order to be consistent with other *ab initio* calculations. Undoubtedly, these data should be critically evaluated in further refinements of the mechanism. This may consist of using *ab initio* calculations benchmarked appropriately to experimental values.

Thermochemical data for the fluoromethylenes, $:\text{CHF}$ and $:\text{CF}_2$, can be found in the JANAF tables. Unfortunately (since $:\text{CHF}$ and $:\text{CF}_2$ are very important species), there are significant uncertainties in their heats of formation. The values for $:\text{CF}_2$ are the best and are derived from appearance potential, ionization potentials, kinetic data, and heats of reactions with heats of formation for related molecules. The best value based on ionization potential data is $-186(\pm 10)$ kJ/mol. The kinetic data appear to provide the most consistent values. The JANAF recommendation is $-182(\pm 6)$ kJ/mol (with a range of -172 to 190 kJ/mol). More recently Rodgers (1978) has recommended a

value based largely upon kinetic data of $-187(\pm 4)$ kJ/mol. Subsequently, Lias and coworkers (Lias *et al.*, 1985) have recommended a significantly lower value of $-205(\pm 13)$ kJ/mol. This recommendation was based solely on appearance potential and ionization data. Depending on what data were used, values ranged from -172 to -213 kJ/mol could be obtained. Given the large uncertainty in values derived from appearance and ionization potentials and given that it is essential to use a heat of formation for :CF_2 that is consistent with kinetic data, we believe that the JANAF recommendation or possibly the more recent value of Rodgers should be used. To date we have employed the JANAF recommendation until all of the experimental and *ab initio* data have been critically evaluated.

The uncertainty in the heat of formation for :CHF is even greater due to the lack of direct, reliable data (heat of reaction, kinetic, or otherwise). The recommended JANAF value of $126(\pm 29)$ kJ/mol is based very roughly on bond energies from other molecules. More recently, Lin and coworkers (Hsu *et al.*, 1978) and Pritchard and coworkers (Pritchard *et al.*, 1984) have independently recommended $163(\pm 8)$ kJ/mol based upon heat of reaction and kinetic data. However, Lias and coworkers again considered the kinetic and heat of reaction data to be unreliable and have used proton affinity values to make a recommendation of $108(\pm 13)$ kJ/mol, which is much lower than all other recommendations. Again, since it is necessary to use a value that is consistent with kinetic data for neutral thermal species (not ionic species), we believe that either the JANAF value or the Lin and Pritchard value should be used. To date we have employed the JANAF recommendation until all of the experimental and *ab initio* data have been critically evaluated.

As part of this subtask of the project, we have also calculated thermochemical data for :CHF and :CF_2 using the BAC-MP4 *ab initio* method. These data have also been calculated by Melius (1993). The calculated value for :CF_2 is about 10-15 kJ/mol lower than the best experimentally derived values. For :CHF , the BAC-MP4 *ab initio* value is about 25 kJ/mol higher than the JANAF value and 10 kJ/mol lower than the value determined by Lin and coworkers (Hsu *et al.*, 1978) and Pritchard and coworkers (Pritchard *et al.*, 1984). We have also calculated heats of formation for :CHF and :CF_2 using G2 *ab initio* theory (Curtiss *et al.*, 1991) and obtain better agreement with the experimentally-derived values (within 5-10 kJ/mol of the JANAF recommendations).

Thermochemical data for most of the other possible C_1 fluorinated hydrocarbons can be found in the JANAF tables. These include $\bullet\text{CF}$, $\text{CHF}=\text{O}$, $\text{CF}_2=\text{O}$, and $\bullet\text{CF}=\text{O}$. The biggest uncertainties here are for $\text{CHF}=\text{O}$ and $\bullet\text{CF}=\text{O}$ where no direct experimental data are available and, consequently, their heats of formation were calculated using average bond dissociation energies from other related compounds. We have calculated thermochemistry for these carbonyl fluorides using the BAC-MP4 *ab initio* method, as well using the G2 *ab initio* method. For $\bullet\text{CF}=\text{O}$ and $\text{CHF}=\text{O}$, the *ab initio* values are about 10 kJ/mol and 20 kJ/mol lower than their respective JANAF recommendations. For $\text{CF}_2=\text{O}$, the *ab initio* values are about 20-40 kJ/mol higher than the JANAF recommendation. Given the importance of these species and the uncertain thermochemistry, further refinement of this mechanism will require these values be re-examined. To date, we have used the JANAF values for consistency. There is an experimentally derived value for the heat of formation of $\text{CF}_3\text{O}\bullet$ (Batt and Walsh, 1982). However, we have used our BAC-MP4 *ab initio* value for the sake of consistency because we have relied solely on *ab initio* values for the other fluoromethoxy radicals and for a number of reactions involving $\text{CF}_3\text{O}\bullet$. Undoubtedly, all of these data should be re-evaluated in order to provide the best values.

5.1.3.1.3 C_2 Fluorinated Hydrocarbon Thermochemistry. The thermochemical data for C_2 fluorinated hydrocarbons that were used in this work are given in Table 1.

Thermodynamic properties for most of the fluoroethanes are derived from experimental data. This work is compiled and evaluated in the *Journal of Physical and Chemical Reference Data* (Chen *et al.*, 1975). These data and data for other fluoroethanes can be also found in the DIPPR compilation (Daubert and Danner, 1985).

There are experimentally derived thermochemical data (Rodgers, 1978) for a few of the fluoroethyl radicals ($\text{CH}_3\text{-CH}_2\bullet$, $\text{CF}_3\text{-CH}_2\bullet$, $\text{CF}_3\text{-CF}_2\bullet$). Thermochemistry for all of the fluoroethyl radicals have been calculated through the application of *ab initio* molecular orbital theory by Tschuikow-Roux and coworkers (Chen *et al.*, 1990a, 1990b; Chen *et al.*, 1991a, 1991b). Thermochemistry for a number of the fluoroethyl radicals have also been calculated using the BAC-MP4 and the G2 *ab initio* methods. We have used experimentally derived data, calculated some values using group additivity, and also calculated some of the values using the BAC-MP4 *ab initio* method. To date, we have chosen to use those values for the complete set calculated by Tschuikow-Roux and coworkers for consistency. In their work, the experimental heat of formation data for the three fluoroethyl radicals were employed. For the other fluoroethyl radicals, they determined heat of formations by benchmarking their *ab initio* values to experimental data using a series of isodesmic reactions. Future refinement of this mechanism will need to consider all of the *ab initio* calculations with the relevant experimental data using bond additivity and group additivity methods, as well as using isodesmic reactions. This would yield the best, consistent thermochemistry for all of the fluoroethyl radicals which are, whole or in part, experimentally derived.

Thermochemistry for $\text{CF}_2=\text{CF}_2$ can be found in the JANAF tables and data for $\text{CH}_2=\text{CHF}$ and $\text{CH}_2=\text{CF}_2$ in DIPPR (Daubert and Danner, 1985). For the three other fluoroethylenes ($\text{CHF}=\text{CHF}(E)$, $\text{CHF}=\text{CHF}(Z)$, $\text{CHF}=\text{CF}_2$), we have used thermochemistry from our *ab initio* calculations. Melius (1993) has also calculated this data. Again, as in the case of the fluoroethyl radicals, future refinement of this mechanism would involve benchmarking the *ab initio* calculations with the experimental data to provide a consistent set. There are not experimentally derived thermochemical data (to our knowledge) for the fluorovinyl radicals. Consequently, we have used values that we have calculated as part of this subtask the BAC-MP4 *ab initio* method.

The thermochemistry of the fluoroacetylenes (C_2HF , C_2F_2) can be found in the JANAF tables. We have used these values. However, there are relatively large uncertainties in these data: ± 60 kJ/mol and ± 20 kJ/mol in the heats of formation of C_2HF and C_2F_2 , respectively. Further refinement of this mechanism should critically evaluate the sensitivity of the simulations to these data. Fluoroketenes and the fluoroketyl radical can be formed through a number of channels (analogous to simple hydrocarbon chemistry). To assess the importance of these species and relevant reactions, we have included these species in the mechanism. There are not experimentally derived data for these species. Consequently, we have had to rely upon values which we have calculated as part of this task using the BAC-MP4 *ab initio* method.

5.1.3.1.4 *Ab Initio* Thermochemistry. As part of this subtask, we have calculated thermochemistry for many fluorinated species through the application of *ab initio* molecular orbital theory. In this work, the GAUSSIAN series of programs was used (Frisch *et al.*, 1992). In the BAC-MP4 *ab initio* method (Melius, 1990), the geometries are optimized at the Hartree-Fock level, the relative energies are then calculated at the MP4 level, and finally the absolute energies are calculated by applying a Bond Additivity Correction (BAC). The BAC is based on the type of bond (*e.g.*, C-H, C-F), its bond length, the identity of all next nearest neighbors, and the bond length between the nearest neighbor and the next nearest neighbor. Both calculated and experimental derived (where available) heats of formation for these compounds are summarized in Table 2 and Table 3. A discussion of the

comparison between experimental heats of formation for these fluorinated hydrocarbons and the *ab initio* values is presented elsewhere in sections dealing with each class of compounds. It is necessary to have *ab initio* calculated values for molecules with well known thermochemical data in order to adequately benchmark *ab initio* calculations for those molecules with unknown or uncertain thermochemistry.

Thermochemical data for all of the species that we have calculated are given in Appendix A in a "JANAF style" tabular format. Values for moments of inertia, vibrational frequencies, bond distances, bond angles, heat of formation at 0 K, heat of formation at standard state, and entropy at standard state are given for each species. Heat capacity, free energy of formation, and other thermochemical quantities as a function of temperature are also given for each species. Many of the species included in Appendix A were initially considered in the chemical mechanism, but subsequently eliminated to keep the reaction set to a manageable level, because the simulations indicated they did not significantly contribute to the overall chemistry. Consequently, many of the species are not found in Table 1, which contains only those species employed in the final chemical kinetic mechanism used in the premixed flame simulations. The importance of some of the species, such as perfluoromethanol (CF_3OH) or the fluoroacetaldehydes (*e.g.*, $\text{CHF}_2\text{-CHO}$), should be reexamined in future refinements of this chemical mechanism. For example, they would undoubtedly play larger roles at lower temperatures.

We have calculated thermochemical data using the BAC-MP4 *ab initio* method for all of the possible C_1 fluorinated hydrocarbons. This work includes the fluoromethanes (CH_3F , CH_2F_2 , CHF_3 , CF_4), fluoromethyls ($\bullet\text{CH}_2\text{F}$, $\bullet\text{CHF}_2$, $\bullet\text{CF}_3$), fluoromethylenes (:CHF , :CF_2), and fluoromethylidyne ($\bullet\text{CF}$). We have also calculated thermochemistry for most of the possible oxidized C_1 fluorinated hydrocarbons. This includes all of the carbonyl fluorides ($\text{CF}_2=\text{O}$, CHFO , $\bullet\text{CFO}$), one of the fluoromethanols (CF_3OH), all of the fluoromethoxy radicals ($\text{CH}_2\text{FO}\bullet$, $\text{CHF}_2\text{O}\bullet$, $\text{CF}_3\text{O}\bullet$), one of the hydroxyfluoromethyl radicals ($\bullet\text{CF}_2\text{OH}$), one of the fluoromethylperoxy radicals ($\text{CF}_3\text{OO}\bullet$), one of the fluoromethylperoxides (CF_3OOH), and fluoroformic acid (FCO_2H). We note that there are energetically different, configurational isomers for the hydroxyfluoromethyl radicals and we calculated values for each. Melius (1993) has also calculated thermochemistry for some of the species and for a number of related species including the other fluoromethanols (CH_2FOH , CHF_2OH) and the other fluoromethylperoxy radicals ($\text{CH}_2\text{FOO}\bullet$, $\text{CHF}_2\text{OO}\bullet$), including the energetically different, configurational isomers when possible.

Thermochemical data for some of the fluoroethanes ($\text{CH}_3\text{-CH}_2\text{F}$, $\text{CH}_3\text{-CHF}_2$, $\text{CH}_3\text{-CF}_3$, $\text{CHF}_2\text{-CHF}_2$, $\text{CHF}_2\text{-CF}_3$), some of the fluoroethyl radicals ($\text{CHF}_2\text{-CH}_2\bullet$, $\text{CH}_3\text{-CF}_2\bullet$, $\text{CF}_3\text{-CH}_2\bullet$, $\text{CHF}_2\text{-CF}_2\bullet$, $\text{CF}_3\text{-CF}_2\bullet$), all of the fluoroethylenes ($\text{CH}_2=\text{CHF}$, $\text{CHF}=\text{CHF}$, $\text{CH}_2=\text{CF}_2$, $\text{CHF}=\text{CF}_2$, $\text{CF}_2=\text{CF}_2$), and all of the fluorovinyl radicals ($\text{CH}_2=\text{CF}\bullet$, $\text{CHF}=\text{CH}\bullet$, $\text{CHF}=\text{CF}\bullet$, $\text{CF}_2=\text{CH}\bullet$, $\text{CF}_2=\text{CF}\bullet$), have been calculated by Melius (1993) using the BAC-MP4 *ab initio* method. We note that $\text{CHF}=\text{CHF}$ and two of the fluorovinyl radicals each have two energetically different, configurational isomers (*Z* and *E*). In addition, Melius (1993) has calculated thermochemistry for oxidized C_2 fluorinated hydrocarbon species, including the fluoroacetaldehydes ($\text{CH}_2\text{F-CHO}$, $\text{CHF}_2\text{-CHO}$, CF_3HO) and the fluoroacetyl radicals ($\text{CH}_2\text{F-CO}\bullet$, $\text{CHF}_2\text{-CO}\bullet$, $\text{CF}_3\text{-CO}\bullet$); In addition to these calculations, there have been *ab initio* calculations for the fluoroethanes and fluoroethyl radicals by other workers using other methods. As indicated previously, Tschuikow-Roux and coworkers have calculated thermochemistry for all of the fluoroethyl radicals in a series of papers (Chen *et al.*, 1990a, 1990b; Chen *et al.*, 1991a, 1991b). In addition, Nyden (1993) has used G2 *ab initio* calculations (Curtiss *et al.*, 1991) to obtain thermochemistry for a number of the fluoroethanes and fluoroethyl radicals.

As part of this task, we have replicated the calculations of Melius using the BAC-MP4 method for a number of these molecules. We have also calculated thermochemical data for a number of other related species, which were necessary to have either to include directly in the chemical mechanism or to benchmark (in combination with experimental data) other *ab initio* calculations. These include some of the other fluoroethanes ($\text{CH}_2\text{F}-\text{CH}_2\text{F}$, $\text{CH}_2\text{F}-\text{CHF}_2$, $\text{CH}_2\text{F}-\text{CF}_3$), the two fluoroacetylenes (C_2HF , C_2F_2 , $\bullet\text{C}_2\text{F}$), the two fluoroketenes/ethenones ($\text{CHF}=\text{C}=\text{O}$, $\text{CF}_2=\text{C}=\text{O}$), and the fluoro-ketyl radical ($\bullet\text{CF}=\text{C}=\text{O}$).

Using both the experimentally derived and the *ab initio* calculated thermochemistry values presented in Tables 2 and 3, group additivity values (for heats of formation) for the fluoroethanes were determined which were consistent with the majority of the data. These values are relatively useful, since employing the group additivity method of Benson (1976), one can obtain relatively good thermochemistry in the absence of experimental or calculated data. For a complicated system such as being considered in this project (fluorinated-hydrocarbons), this is an extremely valuable tool. In determining group additivity values consistent with the majority of the data, the best correlations were obtained when a correction for repulsive interactions between fluorines on adjacent carbons was included. It was observed that the *ab initio* values often differed from the experimentally derived values in a consistent fashion. In general, with increasing number of C-F bonds in the molecules, the difference between the *ab initio* and the experimentally derived heats of formation also increased. This *ab initio* values were, in general, lower than the experimentally derived values in the range of 5-15 kJ/mol (depending on the *ab initio* method) per C-F bond. This trend was used to benchmark the *ab initio* values when determining group additivity values consistent with all the data. Group values were also determined for chloroethanes for reference. All of these data are shown in Figure 2.

5.1.3.2 Reaction Kinetics. 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 pressures (for unimolecular or chemically activated steps), RRKM (Robinson and Holbrook, 1972) and QRRK (Dean and Westmoreland, 1987) methods were used to estimate the temperature dependencies (at 1 atmosphere pressure) 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 rate constant prefactors were adjusted for reaction path degeneracy and the rate constant 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 simulation 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. If however, a specific reaction contributed to the chemistry and its rate constant was an upper-limit estimate, then its value was re-examined 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, *ab initio* methods were used to calculate the geometries and energies of the transition states. RRKM methods were then applied to obtain the temperature (and pressure) dependence of the rate constant. The procedure used for iterative development of the mechanism is schematically shown in Figure 3.

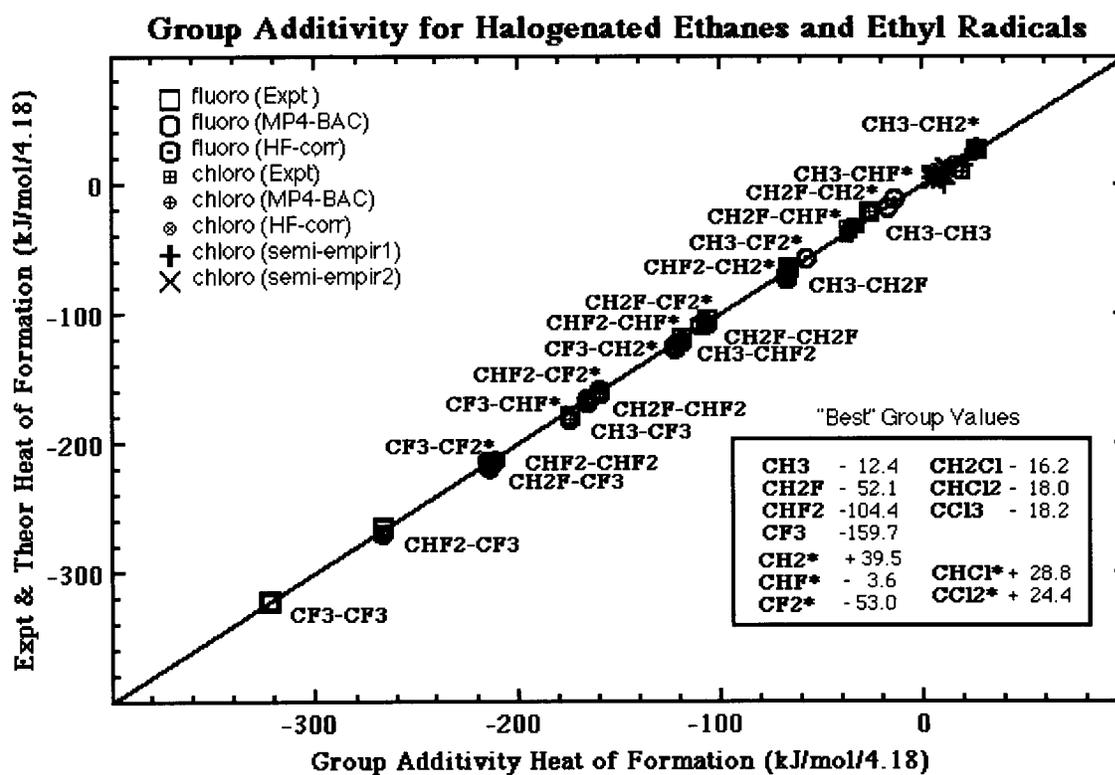


Figure 2. Empirically-Determined Halocarbon Thermochemistry. Group values were determined for predicting heats of formation of fluorinated and chlorinated ethanes consistent with the majority of experimental and *ab initio* data.

Reaction Mechanism Development & Validation

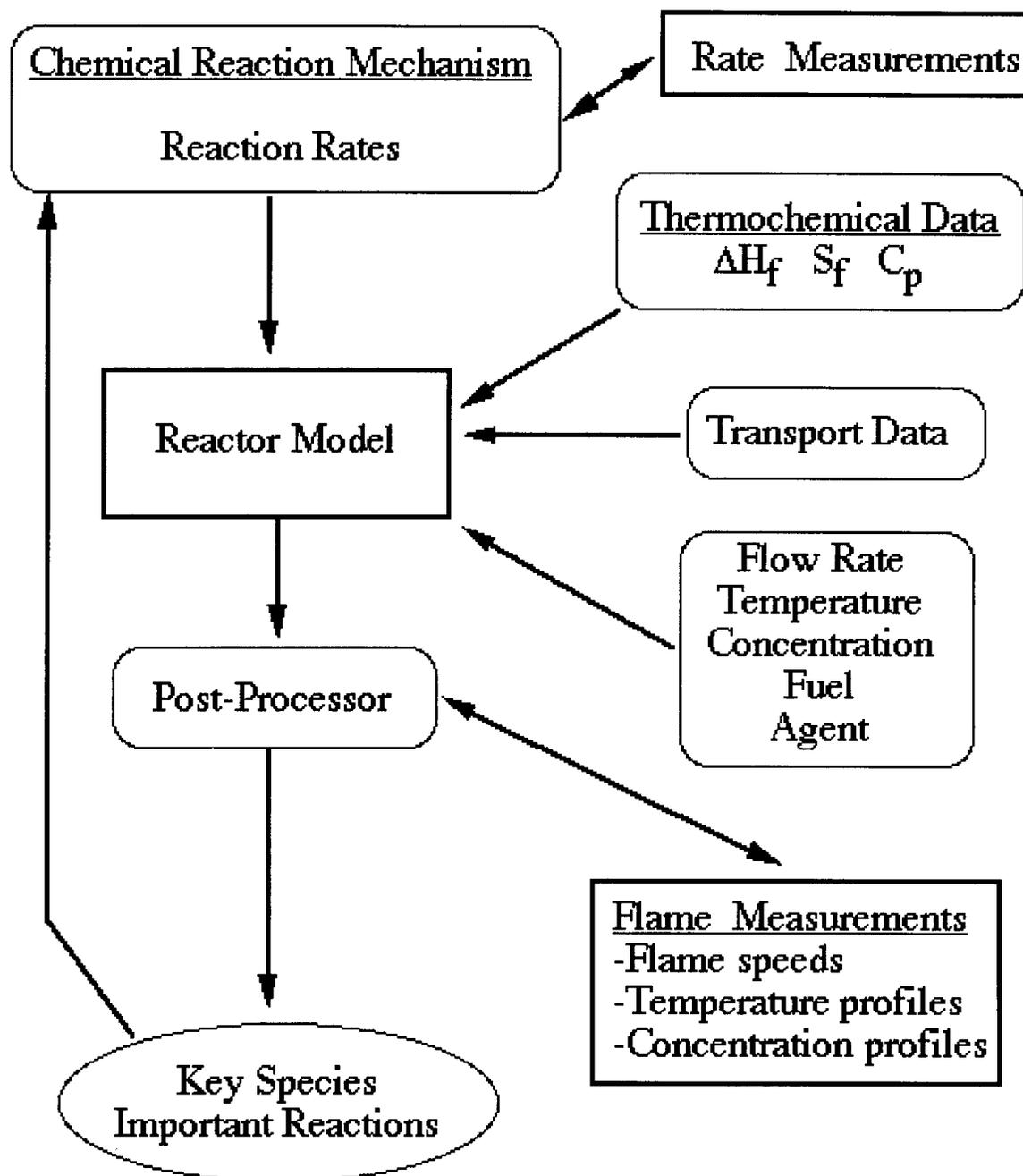


Figure 3. Reaction Mechanism Development and Validation.

Table 1. Fluorinated Hydrocarbons: Enthalpy of Formation, Entropy, Heat Capacities

Fluorocarbon	$\Delta H_f^\circ(298)$	$S^\circ(298)$	$C_p^\circ(T)$						ref
			300	500	800	1000	1200	1500	
CH ₃ F	-234.3	222.8	37.50	51.26	68.90	77.30	83.34	90.21	a
CH ₂ F ₂	-450.6	246.6	42.96	58.91	76.33	83.55	88.84	94.35	a
CHF ₃	-697.0	259.6	51.15	69.26	85.10	91.01	94.89	98.83	a
CF ₄	-933.2	261.3	61.30	80.67	94.49	98.73	101.41	103.67	a
•CH ₂ F	-31.5	234.4	38.71	48.67	59.29	64.20	67.92	72.02	b
•CHF ₂	-247.3	256.0	42.21	54.10	65.33	69.66	72.60	75.69	b
•CF ₃	-470.3	265.0	49.94	63.30	73.24	76.37	78.27	79.92	a
:CHF	125.5	223.2	34.63	39.25	45.21	47.93	50.05	52.43	a
:CF ₂	-182.0	240.7	39.01	46.45	52.35	54.18	55.28	56.31	a
•CF	255.2	212.9	30.05	32.24	34.79	35.77	36.32	36.96	a
CF ₃ O•	-628.3	275.2	56.44	73.91	86.83	90.89	93.40	95.56	b
CHF=O	-376.6	246.7	40.50	51.65	63.12	67.92	71.20	74.70	a
CF ₂ =O	-638.9	258.8	47.41	60.49	70.82	74.39	76.71	78.78	a
•CF=O	-171.5	248.4	38.99	45.06	50.63	52.76	54.14	55.44	a
CHF=C=O	-147.2	270.5	56.75	71.49	84.93	90.34	94.31	98.24	c
CF ₂ =C=O	-290.4	288.8	68.30	81.79	92.56	96.66	99.61	102.48	c
•CF=C=O(E)	69.0	276.2	56.8	65.85	73.77	76.59	94.38	98.22	c
CH ₃ -CHF ₂	-493.7	282.5	68.72	97.11	124.65	136.47	145.39	154.49	d
CH ₂ F-CHF ₂	-643.5	311.7	75.31	107.53	133.47	143.93	151.98	159.92	e
CH ₃ -CF ₃	-745.6	287.4	78.81	108.32	133.82	144.08	151.47	158.99	d
CHF ₂ -CHF ₂	-890.1	314.8	85.23	115.25	141.25	150.60	156.64	163.29	b
CH ₂ F-CF ₃	-895.8	316.2	86.58	118.04	143.15	152.09	158.17	164.43	d
CHF ₂ -CF ₃	-1104.6	333.8	96.09	127.53	151.13	158.85	164.06	168.60	d
CF ₃ -CF ₃	-1343.9	332.1	106.79	139.13	160.34	166.68	169.89	172.97	a
CH ₃ -CHF•	-72.4	274.0	58.79	79.75	103.33	114.06	122.34	130.91	e
CH ₂ F-CHF•	-235.5	293.4	69.59	91.24	111.69	119.75	125.52	131.33	f
CHF ₂ -CH ₂ •	-277.2	297.8	67.06	90.20	111.94	121.10	128.00	135.04	e
CH ₃ -CF ₂ •	-302.5	290.4	67.34	89.22	111.30	120.80	127.83	135.52	e
CH ₂ F-CF ₂ •	-446.0	311.1	74.07	97.38	118.86	127.24	133.22	139.11	f
CHF ₂ -CHF•	-451.9	310.7	76.14	99.54	119.95	127.91	133.70	139.35	f
CF ₃ -CH ₂ •	-517.1	302.6	77.37	101.75	121.27	128.88	134.26	139.75	e
CHF ₂ -CF ₂ •	-660.2	328.4	84.32	107.31	127.04	134.10	138.83	143.26	f
CF ₃ -CHF•	-688.3	326.3	85.84	109.68	128.34	135.01	139.45	143.76	f
CF ₃ -CF ₂ •	-891.2	340.5	92.84	118.29	136.19	141.80	145.18	148.11	f
CH ₂ =CHF	-138.9	262.3	50.61	71.66	91.80	100.57	107.42	114.10	d
CHF=CHF(Z)	-301.2	268.6	58.06	79.62	99.16	107.13	112.47	118.31	b

Table 1. Fluorinated Hydrocarbons: Enthalpy of Formation, Entropy, Heat Capacities

Fluorocarbon	$\Delta H_f^\circ(298)$	$S^\circ(298)$	$C_p^\circ(T)$						ref
			300	500	800	1000	1200	1500	
CHF=CHF(<i>E</i>)	-302.2	267.8	59.82	80.44	99.61	107.53	112.83	118.70	b
CH ₂ =CF ₂	-336.8	265.2	59.33	81.55	100.20	107.74	113.14	118.70	d
CHF=CF ₂	-495.8	292.7	69.45	90.32	107.48	113.93	118.67	124.16	b
CF ₂ =CF ₂	-658.5	299.9	80.70	100.40	115.53	120.89	123.89	126.87	a
CHF=CH•(<i>E</i>)	124.3	258.0	50.61	67.10	81.56	87.66	92.21	97.15	c
CHF=CH•(<i>Z</i>)	123.0	257.0	50.74	67.33	81.76	87.92	92.44	97.29	c
CH ₂ =CF•	109.2	256.8	50.22	66.10	80.71	86.89	91.30	96.37	c
CHF=CF•(<i>E</i>)	-41.0	279.3	59.30	74.51	87.79	92.80	96.05	99.66	c
CHF=CF•(<i>Z</i>)	-42.7	279.3	59.30	74.51	87.79	92.80	96.05	99.66	c
CF ₂ =CH•	-67.8	277.0	59.20	76.36	89.73	94.73	97.78	100.81	c
CF ₂ =CF•	-216.3	300.5	68.26	83.42	95.36	99.41	101.77	104.39	c
C ₂ HF	125.5	231.5	52.48	62.17	69.69	73.22	75.83	78.82	a
C ₂ F ₂	20.9	244.0	57.07	67.96	76.67	79.74	81.54	83.46	a

NOTATION $\Delta H_f^\circ(298)$: enthalpy of formation (kJ/mol) at standard state (1 atmosphere; 298.15 K) $S^\circ(298)$: entropy (kJ/mol) at standard state (1 atmosphere; 298.15 K) $C_p^\circ(T)$: heat capacity (J/mol/K) at constant pressure at standard state (1 atmosphere; T = 300, 500, 800, 1000, 1200, and 1500 K)**REFERENCES**

- a. Stull and Prophet, 1971
- b. Melius, 1993
- c. this work
- d. Daubert and Danner, 1985
- e. Chen *et al.*, 1990a; Chen *et al.*, 1990b
- f. Chen *et al.*, 1991a; Chen *et al.*, 1991b

Table 2. BAC-MP4 Thermochemical Computations (C₁): Enthalpy of Formation (kJ/mol)

FLUOROCARBON	BAC-MP4	ref	G2	ref	expt	ref
CH ₃ F	-233.9	a,b	-246.4	c	-234.3	d
CH ₂ F ₂	-451.0	a,b	-456.6	c	-450.6	d
CHF ₃	-699.6	a,b	-716.6	c	-697.1	d
CF ₄	-934.3	a,b	-962.7	c	-933.0	d
•CH ₂ F	-31.4	a,b			-32.6	e
•CHF ₂	-247.3	a,b	-252.9	c	-247.7	e
•CF ₃	-471.5	a,b	-483.0	c	-470.3	d
:CHF	152.7	b	131.8	a	125.5	d
:CF ₂	-203.3	a,b	-190.0	a	-182.0	d
•CF	236.4	b			255.2	d
CHF=O	-395.0	a,b			-376.6	d
CF ₂ =O	-598.3	a,b	-620.1	a	-638.9	d
•CF=O	-182.8	a,b			-171.5	d
CH ₂ FO•	-194.6	b				
CHF ₂ O•	-405.8	b				
CF ₃ O•	-628.4	a,b			-655.6	f
CF ₃ OH	-219.8	a,b				
CH ₂ FOH(E)	-412.1	b				
CHF ₂ OH(E)	-684.5	b				
•CF ₂ OH(E)	-456.5	a,b	-455.2			
•CF ₂ OH(G)	-463.2	a,b				
CF ₃ OOH	-807.5	a				
CH ₂ FOO•	-172.8	b				
CHF ₂ OO•	-401.2	b				
CF ₃ OO•	-627.6	a,b				
CF(O)OH	-615.0	a				

Enthalpy of Formation (kJ/mol) at standard state (1 atmosphere; 298.15 K)

BAC-MP4: calculated (BAC-MP4 *ab initio* method: Melius, 1990)

G2: calculated (G2 *ab initio* method: Curtiss *et al.*, 1991)

expt: experimentally derived

REFERENCES

- a: this work
 b: Melius, 1993
 c: Nyden, 1993
 d: Stull and Prophet, 1971
 e: McMillen and Golden, 1982
 f: Batt and Walsh, 1982

Table 3. BAC-MP4 Thermochemical Computations (C_2): Enthalpy of Formation (kJ/mol)

FLUOROCARBON	BAC-MP4	ref	TSC	ref	G2	ref	expt	ref
CH ₃ -CH ₂ F	-272.4	a,b			-284.1	c	-263.2	f
CH ₂ F-CH ₂ F	-446.9	b			-489.9	c	-431.0	f
CH ₃ -CHF ₂	-505.4	b			-518.5	c	-493.7	f
CH ₂ F-CHF ₂	-671.5	a					-643.5	g
CH ₃ -CF ₃	-755.2	b			-777.0	c	-745.6	f
CHF ₂ -CHF ₂	-890.4	a,b						
CH ₂ F-CF ₃	-913.4	b					-895.8	f
CHF ₂ -CF ₃	-1124.2	b					-1104.6	f
CF ₃ -CF ₃							-1343.9	d
CH ₂ F-CH ₂ •	-56.2	a	-44.8	i		c		
CH ₃ -CHF•			-72.4	i	-79.1	c		
CH ₂ F-CHF•			-235.6	j	-255.8	c		
CHF ₂ -CH ₂ •	-280.7	b	-277.4	i	-294.2	c		
CH ₃ -CF ₂ •	-300.0	b	-302.5	i	-309.7	c	-302.5	h
CH ₂ F-CF ₂ •			-446.0	j				
CHF ₂ -CHF•			-451.9	j				
CF ₃ -CH ₂ •	-527.2	b	-517.1	i			-517.1	h
CHF ₂ -CF ₂ •	-673.2	b	-660.2	j				
CF ₃ -CHF•			-688.3	j				
CF ₃ -CF ₂ •	-907.5	b	-891.2	j			-891.2	h
CH ₂ =CHF	-139.3	a,b					-138.9	f
CHF=CHF(Z)	-301.2	a,b						
CHF=CHF(E)	-302.1	a,b						
CH ₂ =CF ₂	-340.2	a,b					-336.8	f
CHF=CF ₂	-485.8	a,b						
CF ₂ =CF ₂	-653.5	a,b					-658.6	d
CHF=CH•(Z)	124.3	a,b						
CHF=CH•(E)	123.0	b						
CH ₂ =CF•	109.2	a,b						
CHF=CF•(Z)	-41.0	b						

Table 3. BAC-MP4 Thermochemical Computations (C₂): Enthalpy of Formation (kJ/mol)

FLUOROCARBON	BAC-MP4	ref	TSC	ref	G2	ref	expt	ref
CHF=CF•(E)	- 42.7	b						
CF ₂ =CH•	- 67.8	a,b						
CF ₂ =CF•	-216.3	a,b						
C ₂ HF	118.0	a					125.5	d
C ₂ F ₂	31.8	a					20.9	d
•C ₂ F	454.0	a						
CHF=C=O	-147.3	a						
CF ₂ =C=O	-290.4	a						
•CF=C=O(E)	69.0	a						
CH ₂ F-CHO(Z)	-322.6	b						
CH ₂ F-CHO(E)	-328.9	b						
CHF ₂ -CHO(E)	-525.1	b						
CHF ₂ -CHO(Z)	-538.9	b						
CF ₃ -CHO	-774.5	b						
CH ₂ F-CO•(Z)	-169.9	b						
CH ₂ F-CO•(E)	-172.8	b						
CHF ₂ -CO•(Z)	-377.4	b						
CF ₃ -CO•(Z)	-610.0	b						
CF ₃ -CO•(E)	-611.3	b						

Enthalpy of Formation (kJ/mol) at standard state (1 atmosphere; 298.15 K)

BAC-MP4: calculated (BAC-MP4 *ab initio* method: Melius, 1990)

TSC: calculated (*ab initio* method of references i,j)

G2: calculated (G2 *ab initio* method: Curtiss *et al.*, 1991)

expt: experimentally derived

REFERENCES

a: this work

b: Melius, 1993

c: Nyden, 1993

d: Stull and Prophet, 1971

e: McMillen and Golden, 1982

f: Daubert and Danner, 1985

g: Pedley, 1986

h: Rodgers, 1978

i: Chen *et al.*, 1990a; Chen *et al.*, 1990b

j: Chen *et al.*, 1991a; Chen *et al.*, 1991b

A listing of the rate constants in the reaction set or mechanism used in the simulations is given in Appendix B. In addition, other reactions were also considered, but were observed not to contribute under the conditions tested. The hydrocarbon and hydrogen/oxygen reaction subsets of the mechanism were derived from the Miller-Bowman mechanism (Miller and Bowman, 1989). Some modifications to this accepted mechanism were made. Many of the relevant rate constants can be found in the "NIST Chemical Kinetics Database" (Mallard *et al.*, 1993).

5.1.3.1.1 Hydrocarbon/H/O/F Kinetics. 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. Some modifications to this accepted mechanism were made. All N-containing species (except N_2) and reactions were removed. A number of the rich species (*e.g.*, C_2H , C_4H_2) were eliminated from the mechanism in order to keep the number of species in the mechanism to a manageable level. Eliminating these species is valid, since the agent is (in general) added to the air (fuel lean). A number of species (*e.g.*, CH_3OH) were also added to the mechanism. In addition to these addition and deletions, a number of rate constants for a number of reactions (*e.g.*, CH_3+OH) were adjusted to provide correct falloff and product-channel ratios.

Most of the reactions involving F and HF with hydrogen- and oxygen-containing species have been measured and the uncertainties in these values are relatively low. There are three reactions of this type which were determined to participate in the chemistry under a variety of conditions. These reactions are the combination of H and F to form HF (and the reverse decomposition) and the hydrogen abstractions by F atoms from H_2 and H_2O . The rate expressions used for these contributing reactions are given in Appendix B.

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 ($F + H_2$, H_2O , RH) contribute to F atom destruction, the uncertainty in the absolute rate of the forward or reverse reaction is most likely unimportant.

The hydrogen abstraction reactions of F atoms with H_2 and H_2O 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. For the H_2 reaction, an expression with $T^{0.5}$ dependence was chosen consistent with the recommended value (Cohen and Westberg, 1983). For the H_2O 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 to the chemistry. These reactions include the combination of F atoms to form F_2 and the hydrogen abstractions by F atoms from OH, HO_2 , and H_2O_2 . The oxy-fluoro-species $FO\bullet$, HOF , $FOO\bullet$, and F_2O were also initially considered in the mechanism. However, given the very low concentration of F 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 will be detailed later in another publication.

5.1.3.2.2 C_1 Fluorinated Hydrocarbon Kinetics. The C_1 reaction subset of the mechanism consists of about 15 species (fluorocarbons) and 200 reactions (including reactions with H, O, OH, etc.). Both thermally and chemically activated decompositions are considered (*e.g.*, $CH_2F_2 \rightarrow :CHF$

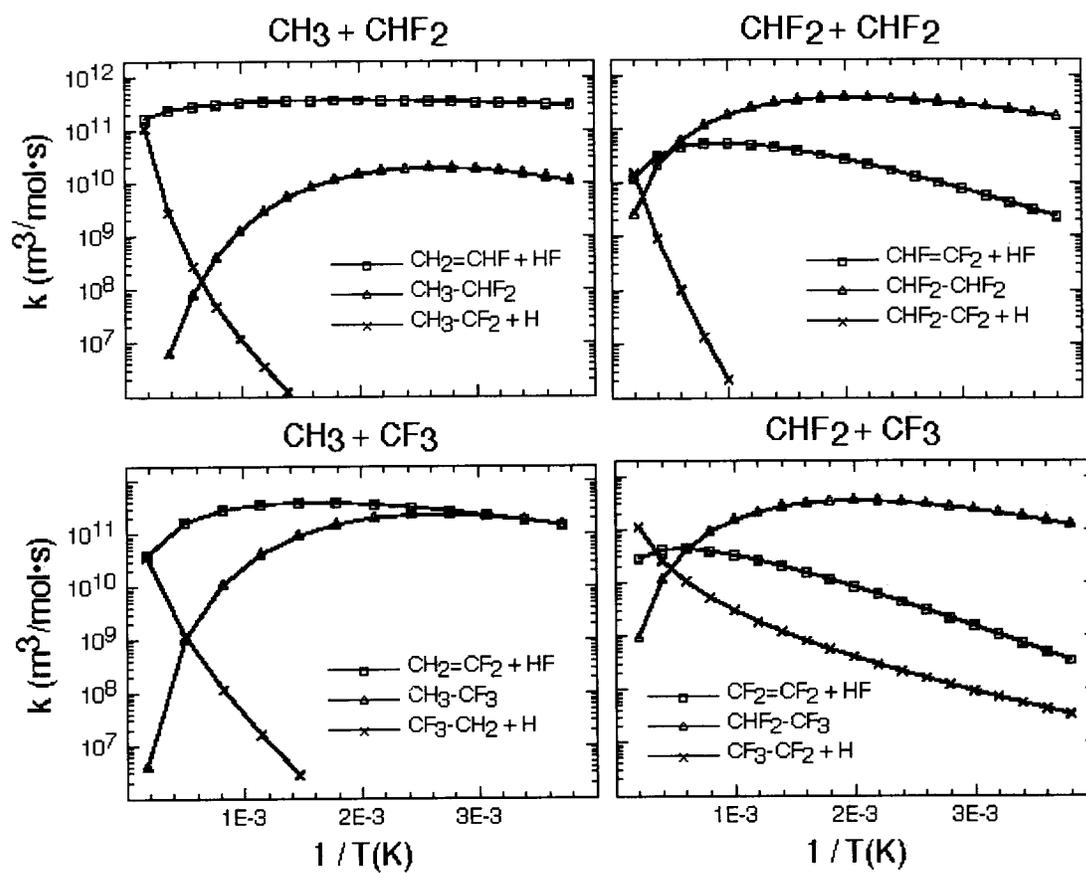


Figure 4. RRKM Predictions of Product Channels for Fluoromethyl Combinations.

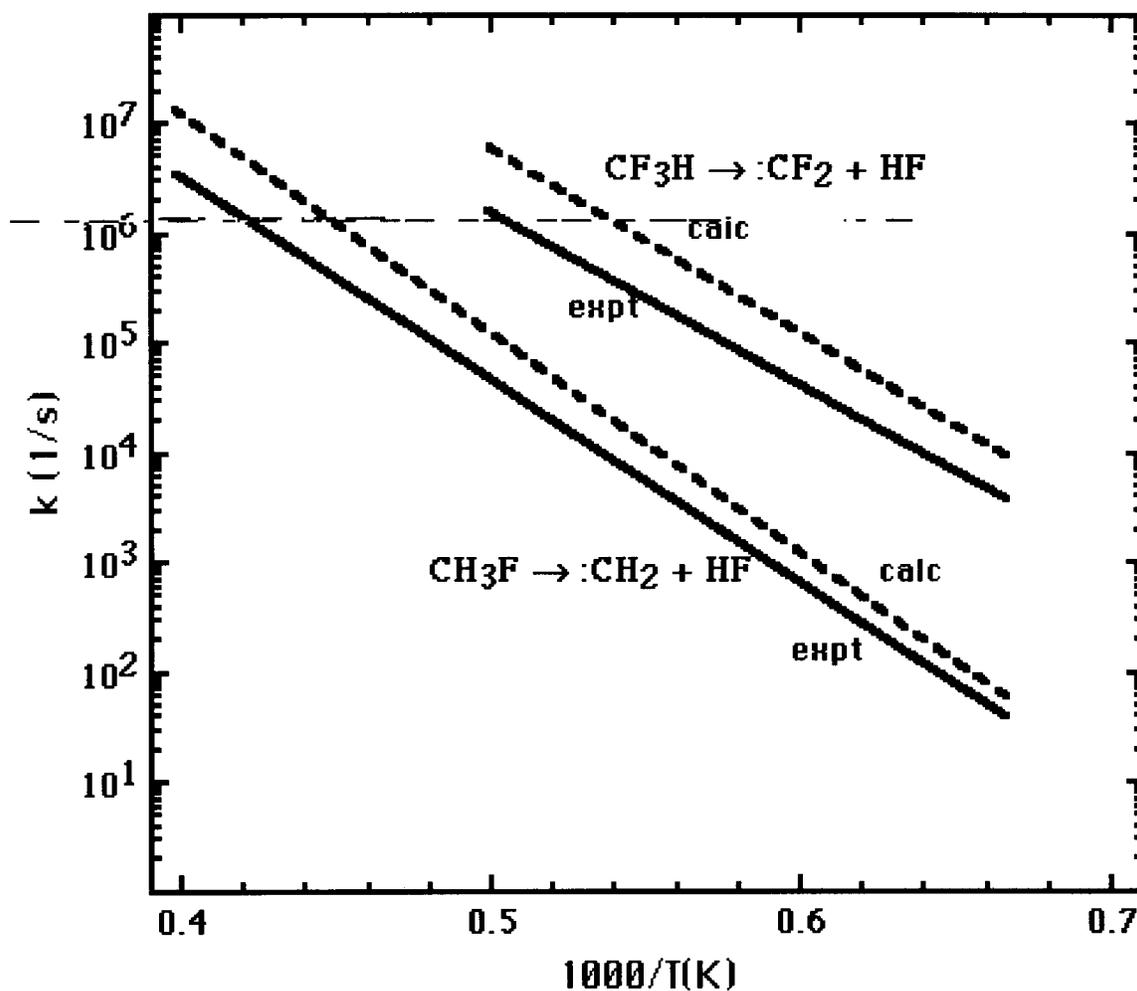


Figure 5. Comparison between Experimental and Calculated Rate Constants. *Ab initio* and RRKM methods for calculating rate constants must be validated by comparison to known, experimentally-derived values.

+ HF and $\bullet\text{CHF}_2 + \text{H} \rightarrow \text{:CHF} + \text{HF}$). Fluoromethane decompositions via abstraction of H atoms by H, O, and OH radicals are also considered.

There have been a number of measurements of the unimolecular decomposition of fluoromethanes (with HF elimination): at least two for CH_3F (Politanskii and Shevchuk, 1967; Schug and Wagner, 1973), at least one for CH_2F_2 (Politanskii and Shevchuk, 1968), and several for CHF_3 (Tschuikow-Roux, 1965; Tschuikow-Roux and Marte, 1965; Modica and LaGraff, 1966; Politanskii and Shevchuk, 1968; Biordi *et al.*, 1978; Schug *et al.*, 1979; Hidaka *et al.*, 1991). In addition, there have been quite a few measurements of the unimolecular decomposition of other halomethanes (eliminating HF, HCl, or HBr) such as CHF_2Cl (Norton, 1957; Edwards and Small, 1964; Gozzo and Patrick, 1964; Edwards and Small, 1965; Gozzo and Patrick, 1966; Barnes *et al.*, 1971; Kushina *et al.*, 1972; Schug *et al.*, 1979; Zhitnev *et al.*, 1990; 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. Consequently, all of the halomethane measurements are important from the point of evaluating the fluoromethane values (both experimental and calculated) for consistency. Furthermore, the barriers-to-insertion of :CHF and :CF_2 in these reactions can be used to benchmark reactions of :CHF and :CF_2 with many other important molecules where there is no or little information available (*i.e.*, the reactions of :CHF and :CF_2 with H_2 , H_2O , CH_4 , C_2H_6 , fluoromethanes, fluoromethyls, etc.).

In this work, we have employed rate expressions for HF elimination from CH_3F and CHF_3 that are fits to extended Arrhenius form to the experimental data of Schug and Wagner (1973) for CH_3F and to the experimental data of Hidaka *et al.* (1991) for CHF_3 . These data were obtained, in general, at different temperatures and pressures than are relevant to the atmospheric flame conditions considered here. The experimental data were interpolated or extrapolated and fit using temperature dependencies (T^b) that were consistent with the experimental data and our RRKM calculations (using our BAC-MP4 barriers) for these systems. For HF elimination from CH_2F_2 , we have employed a rate expression from our RRKM/BAC-MP4 calculations, although there is reasonable experimental data by Politanskii and Shevchuk (1968) that could be used. For the H_2 elimination channels for CH_3F and CH_2F_2 decompositions, we have used rate expressions from our RRKM calculations using our BAC-MP4 *ab initio* barriers. The H_2 elimination pathways are minor channels and were included for completeness. F atom eliminations from the fluoromethanes are negligible decomposition channels, except for CF_4 , where it is the only possible pathway. For this reaction, we have used a rate expression that is a fit to extended Arrhenius form to the room temperature value of Plumb and Ryan (1986a, 1986b) using a reasonable temperature dependence ($T^{-1.0}$). Further refinement of this mechanism should include critical evaluation of all of the experimental data (for the HF elimination channels) and the *ab initio* barriers. RRKM methods should be used to obtain rate expressions that are consistent with both rate and (especially) thermochemical data. Although there is some uncertainties in the rate expressions for pyrolysis of the fluoromethanes due to extrapolation of measurements from other temperatures and pressures, these uncertainties are most likely acceptable since the primary decomposition pathways in atmospheric flames are by H atom abstraction by H and OH radicals and not by pyrolysis.

There have been no measurements to our knowledge for reactions involving chemically activated or "hot" fluoromethanes other than the room temperature measurements of the rate of reaction for $\text{CF}_3 + \text{H} \rightarrow \text{Products}$ by Ryan and Plumb (1984) and Tsai and McFadden (1989). This class of reactions is simply the radical combination of fluoromethyls and H atoms to form two product channels, HF or H_2 elimination, when the hot fluoromethane is not stabilized or returned to reactants.

We have used RRKM methods with the BAC-MP4 *ab initio* barriers to insertion for :CHF and :CF₂ into HF and H₂ and the energetics of the reactions pathways to estimate values for these various reactions, as well as for the stabilized fluoromethane channels. The barriers to insertion for :CHF and :CF₂ into HF are derived from the experimental measurements for the unimolecular decomposition of the fluoromethanes. An example of a similar set of RRKM calculations for fluoroethane decompositions (both thermal and chemically activated decompositions) is shown in Figure 4. These RRKM calculations were done for all of the fluoromethanes and fluoroethanes (only four for the fluoroethanes are shown in Figure 4).

We have also used the BAC-MP4 *ab initio* method (Melius, 1990) to provide estimates of the energy and structure of the transition state for some of these reactions, which agree well with the experimental values for the HF reactions. For insertion into H₂, where there are no experimental data, *ab initio* calculations were used to estimate the energy and structure of each transition state. Comparisons between experimental and *ab initio* calculated values for a few of these reactions are shown in Figure 5. Although there are no experimental measurements at flame temperatures for chemically activated fluoromethane decompositions and these are primary pathways for destruction of fluoromethyl radicals, the corresponding uncertainties in the rate expressions are small since these combinations are barrierless and occur nearly on every collision.

There have been a quite a number of measurements for H atom abstractions from fluoromethanes by H radicals, but only a few for H atom abstraction by O or OH radicals. For H atom abstraction by H radicals, there have been at least 3 measurements for CH₃F (Hart *et al.*, 1974; Westenberg and deHaas, 1975; Aders *et al.*, 1975), at least one measurement for CH₂F₂ (Ridley *et al.*, 1972), and quite a few for CHF₃ (Ayscough and Polanyi, 1956; Pritchard *et al.*, 1956; Skinner and Ringrose, 1965; Amphlett and Whittle, 1967; Arthur and Bell, 1968; Fagarash and Moin, 1968, Kibby and Weston, 1968; Berces *et al.*, 1972; Kondratiev, 1972; Arthur *et al.*, 1975; Arthur and Bell, 1978). We should note that many of the measurements for the CHF₃ reactions are actually measurements of the reverse rate or CF₃ + H₂ → CHF₃ + 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 H atom abstraction reactions from the fluoromethanes using the BAC-MP4 *ab initio* method. The energy barriers are included in Table 4 and compare well with the experimental values.

For the CH₃F + H reaction, all of the workers cited above incorrectly identified the reaction as abstraction of F atoms instead of H atoms. These workers only measured the disappearance of the reactants and simply assigned the product channel by analogy to the CH₃Br + H reaction, where it is known that the halogen atom (Br) is abstracted. However, the C-F bond is much stronger than the C-Br bond or even the C-H bond. Consequently in CH₃F, the H atom instead of the F atom, is abstracted. Our *ab initio* calculations (see Table 4) also support this argument where abstractions of H atoms from the fluoromethanes by H radicals were calculated to have energy barriers of 49.4, 40.6, 53.6 kJ/mol for the CH₃F, CH₂F₂, CHF₃ series, respectively. These same calculations yield barriers-to-abstraction of F atoms of 131.4, 142.7, 168.6, 171.1 kJ/mol for the CH₃F, CH₂F₂, CHF₃, CF₄ series, respectively. This is a significant difference and clearly supports assignment of H atom abstraction as the dominant channel.

In this work, we have used our fits to extended Arrhenius form to the experimental data of Westenberg and deHaas (1975), Ridley *et al.* (1972), and Arthur and Bell (1978) for H atom abstraction from CH₃F, CH₂F₂, and CHF₃, respectively. A temperature dependence of T^{3.0} was used in analogy to the recommended value (Tsang and Hampson, 1986) for H atom abstraction from methane (CH₄). The experimental data were all obtained at modest temperatures (600-900 K). The uncertainties in extrapolation of this data to flame decomposition temperatures is most likely

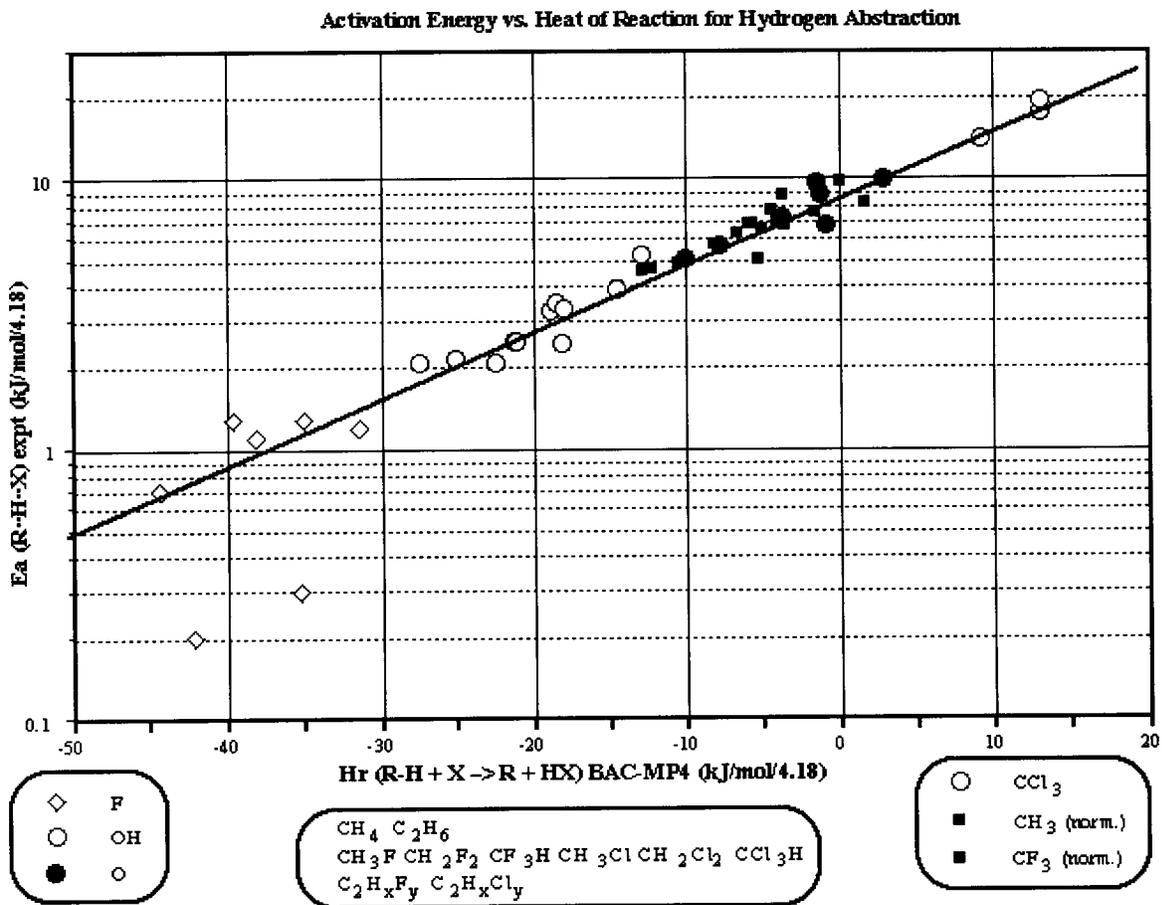
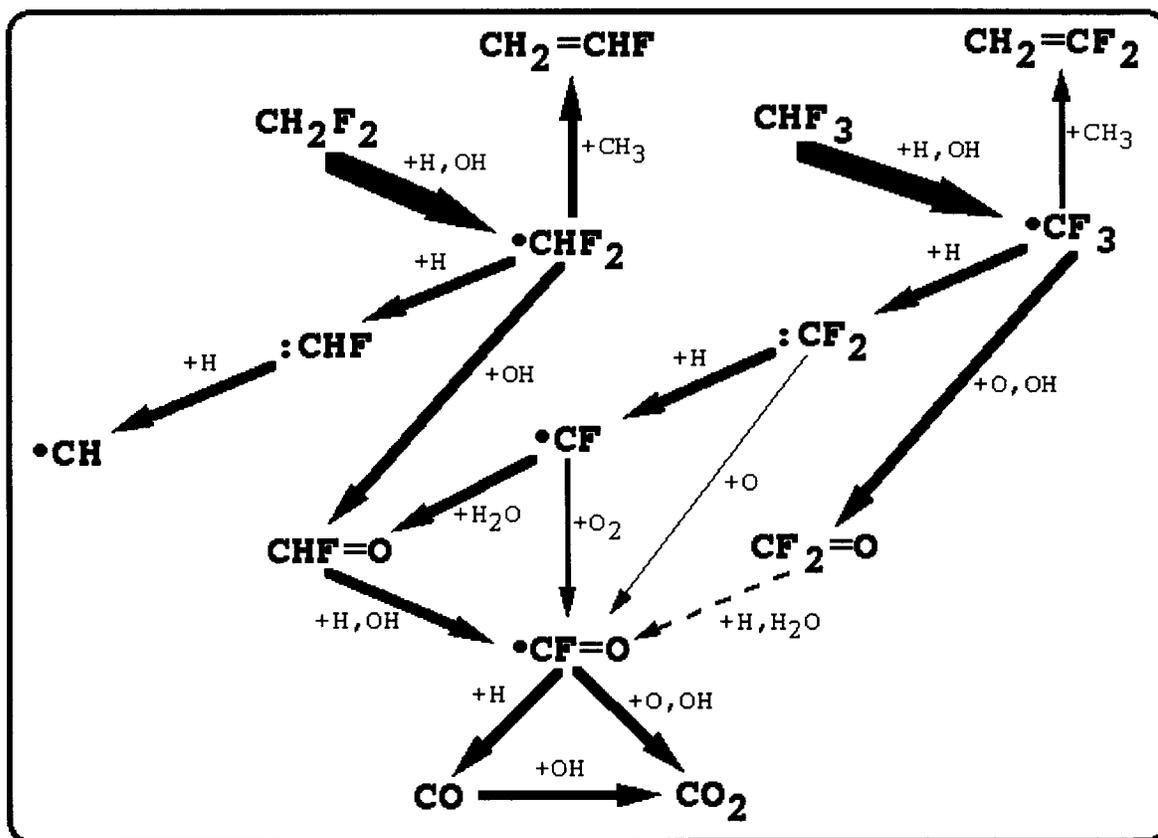


Figure 6. Empirically-Determined Activation Energies. In the absence of experimental data, the rate constant for a reaction can be estimated relatively well using its heat of reaction and known rate constants for other similar reactions.

Figure 7. Typical Reaction Pathways for CH_2F_2 and CHF_3 .

acceptable. We note that based on our limited evaluation, the trends in the rate expressions for this homologous series appear to be consistent with changes in the number of H atoms and the C-H bond strengths or heats of reaction (*e.g.*, Figure 6).

For the F atom abstraction reactions from CH_3F , CH_2F_2 , and CHF_3 by H radicals, we have employed rate expressions derived from our BAC-MP4 *ab initio* calculations. The F atom abstraction pathways are negligible channels and these reactions were included simply for completeness in development of this reaction set. However, for reaction of H atoms with CF_4 , the only possible pathway is F atom abstraction. For this reaction, we have used the experimentally derived rate expression of Kochubei and Moin (1969, 1971).

There have only been a few measurements of H atom abstractions from fluoromethanes by O radicals. Parsamyan and coworkers have measured the rate of reaction for CH_3F (Parsamyan *et al.*, 1967) and for CH_2F_2 (Parsamyan and Nalbandyan, 1968). Jourdain *et al.* (1978) and Miyoshi *et al.* (1993) have measured the rate of reaction for CHF_3 . In our work, we have used our fits to extended Arrhenius form to the experimental data using a temperature dependence of $T^{1.5}$ in analogy to the recommended value (Tsang and Hampson, 1986) for H atom abstraction from methane (CH_4). We note that we have not used the more recent value for $\text{CHF}_3 + \text{O}$ by Miyoshi *et al.* (1993), because it appears that this data may be complicated by the $\text{CHF}_3 \rightarrow \text{:CF}_2 + \text{HF}$ decomposition reaction at the highest temperatures. This should be examined in more detail, since our conclusion was based on a limited evaluation of the data.

There have been a few measurements of H atom abstractions from fluoromethanes by OH radicals. Cohen and Benson (1987a, 1987b) 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 Jeong and Kaufman (1982), but is also consistent with other measurements for fluoromethanes (Howard and Evenson, 1976; Clyne and Holt, 1979; Nip *et al.*, 1979; Talukdar *et al.*, 1991). In our work, we have used the recommendations of Cohen and Benson (1987a, 1987b). Since these recommendations are based on experimental measurements are relatively low temperatures (about 300-500 K) and these reactions are primary decomposition pathways for the fluoromethanes and significantly higher temperatures, it would be valuable to have experimental measurements of these rates near flame temperatures. We note that based on our limited evaluation, the trends in the rate expressions for this homologous series appear to be consistent with changes in the number of H atoms and the C-H bond strengths or heats of reaction (*e.g.*, Figure 6).

There have been quite a few measurements of H atom abstraction from methane (CH_4) by F atoms at or 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 have used a fit to extended Arrhenius form to the recommended rate constant of Atkinson *et al.* (1992) using a reasonable temperature dependence ($T^{0.5}$) in order to extend the rate expression to flame temperatures. Although there is some uncertainty in extrapolating the rate constant to flame temperatures, this uncertainty is most likely unimportant since this reaction occurs on almost every collision and there are many other reactions (*e.g.*, $\text{F} + \text{H}_2$, $\text{F} + \text{H}_2\text{O}$, and $\text{F} + \text{other hydrocarbons}$) that contribute to F atom destruction. For completeness in the reaction set (although it is unlikely that they will contribute), we have also included the reactions for H atom abstractions from the fluoromethanes by F atoms. There have also been a number of measurements for these reactions at or near room temperature for CH_3F (Pollock and Jones, 1973; Smith *et al.*, 1977; Manocha *et al.*, 1983), for CH_2F_2 (Pollock and Jones, 1973; Smith *et al.*, 1977; Manocha *et al.*, 1983; Clyne and Hodgson, 1985; Nielsen *et al.*, 1992), and for CHF_3 (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 for $\text{CH}_4 + \text{F}$ (Atkinson *et al.*, 1992) was adjusted to account for reaction path degeneracy (*i.e.*, fewer number of H 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.

There have been quite a few measurements of metathetical reactions of methyl/fluoromethyl radicals with methane/fluoromethanes. These will not be reviewed here. In our work, we have used the recommendations of Kerr and Parsonage (1976) which are consistent with the majority of the experimental data and empirical relationships for barriers to reactions (such as shown in Figure 6). The recommended values are largely based on the pioneering work in this area by Pritchard and coworkers (*e.g.*, Pritchard *et al.*, 1965), Whittle and coworkers (*e.g.*, Chamberlain and Whittle, 1972), and Arthur and coworkers (*e.g.*, Arthur and Bell, 1978). We note that based on our limited evaluation, the trends in the rate expressions for this homologous series appear to be consistent with changes in the number of H atoms and the C-H bond strengths or heats of reaction (*e.g.*, Figure 6).

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 have used rate expressions for these reactions where the activation energy was reduced by 10% (due to the roughly 6 kJ/mol decrease in the heat of reaction) consistent with the empirical relationship demonstrated in Figure 6.

Given the abundance of H and OH radicals in hydrocarbon flames and the somewhat higher barrier for H atom abstraction by methyl/fluoromethyl and vinyl radicals, these are secondary reaction pathways. However, under pyrolytic conditions they may contribute (especially the C_2H_3 reactions which have the lowest barriers) and, consequently, for completeness should be retained in the reaction set. The experimental measurements for H atom abstractions by the methyl/fluoromethyl radicals were all made at relatively low temperatures (about 300-600 K). Extrapolation of these measurements to flame decomposition temperatures may introduce significant uncertainty in the rates especially since these reactions should have considerable non-simple Arrhenius temperature dependencies. In further refinement of this mechanism, these data should be critically evaluated. Experimental measurements at significantly higher temperatures would also be extremely valuable.

Fluoromethyl radicals are destroyed by three general pathways whose relative importance are sensitive to conditions. 1) Fluoromethyl radicals can combine with H atoms forming chemically activated fluoromethanes which may either be stabilized or eliminate HF or H_2 (creating methylene/fluoromethylenes). This class of reactions was discussed with the fluoromethane chemistry. 2) Fluoromethyl radicals can react with oxygen-containing species (*i.e.*, O_2 , O, OH) resulting in the formation of fluoromethoxy radicals and carbonyl fluoride species (as well as elimination by-products). 3) Fluoromethyl radicals can also combine with methyl (CH_3) or fluoromethyl radicals forming chemically activated fluoroethanes which may either be stabilized or eliminate HF (creating ethylene/fluoroethylenes). This class of reactions will be discussed with the fluoroethane chemistry.

There have been a number of measurements of the reaction of CF_3 with O_2 at or near room temperature (Vedenev *et al.* 1978; Ryan and Plumb, 1982; Caralp *et al.*, 1986; Cooper *et al.*, 1988; 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 type 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. By analogy to the $\text{CH}_3 + \text{O}_2$ reaction, fluoromethoxy radicals (and O atom by-product) can be formed upon dissociation of the O-O bond. The fluoromethylperoxy radical complex may also rearrange and undergo an internal abstraction reaction (of H atoms) creating fluoroformaldehyde species ($\text{CHF}=\text{O}$ or $\text{CF}_2=\text{O}$) and OH. In contrast to that assumed for the analogous chloromethyl

radical + O₂ → (chloro)formaldehyde + ClO reactions (Ho *et al.*, 1992), abstraction of F atoms is not possible because of the much stronger C-F bond. In our work we have assumed that at flame temperatures, the primary product channel is dissociation of the complex to fluoromethoxy radicals and O atoms. This assumption should be examined in more detail in further refinements of this mechanism. There are not any measurements (to our knowledge) for these reactions. For the flame chemistry, this is a minor channel. However, at lower temperatures and/or under ignition conditions, this class of reactions should be pathways which contribute to the chemistry.

The other various existing data and our many estimations, calculations, and evaluations for other reactions involving C₁ fluorocarbon species will not be discussed in further detail here. In many homologous series of reactions, missing rate constants (*i.e.*, no experimental data) were estimated by analogy to other reactions. For example, an empirical relationship between the activation energy and the heat of reaction for H atom abstraction reactions was determined. This is shown in Figure 6. As a result, in the absence of experimental data, the rate constant for a reaction can be estimated relatively well using its heat of reaction and known rate constants for other similar reactions.

Typical reaction pathways for the decomposition of two potential agents, CH₂F₂ and CHF₃, are shown in Figure 7. Briefly, fluoromethane decompositions via abstraction of H atoms by O and OH radicals are also considered with abstractions by OH and H the major decomposition pathways. The fluoromethyls produced via these reactions are destroyed by several pathways whose relative importance are sensitive to conditions. These pathways include reactions with H radicals, CH₃ radicals, and oxygen-containing species (O₂, O, OH). The products of the latter reactions consist of carbonyl fluorides (*i.e.*, CF₂=O, CHF=O, •CF=O) and HF or other elimination products (*e.g.*, •CHF₂ + OH → CHF=O + HF). In the simulations, it was observed almost exclusively that any reaction channel with an HF product was the dominant channel. The fluoromethylenes (:CHF, :CF₂) were largely created by combination of fluoromethyls and H radicals via chemically activated fluoromethanes (and HF elimination). The fluoromethylenes were predominantly destroyed similarly by combination with H radicals via chemically activated fluoromethylenes (and HF elimination creating •CH and •CF). •CF radicals created here were largely consumed by reactions with H₂O and O₂ resulting in CHF=O and •CF=O formation.

5.1.3.2.3 C₂ Fluorinated Hydrocarbon Kinetics. The C₂ reaction subset consisted of about 40 species and 400 reactions. This reaction set will not be described here in detail. Briefly, the fluoroethane destruction pathways (like fluoromethanes) consist of thermally and chemically activated decompositions and H atom abstraction reactions. Fluoroethyl radicals can react with H radicals (like fluoromethyls) creating fluoroethylenes (via chemically activated fluoroethanes and HF elimination). Fluoroethyl radicals can also react with oxygen-containing species (O₂, O, OH) resulting in the formation of oxidized fragments (*e.g.*, CF₃-CF₂• + O → •CF₃ + CF₂=O). Fluoroethylenes (produced from thermally and chemically activated fluoroethane decompositions) are predominantly destroyed via reaction with O radicals resulting in the formation of oxidized fragments (*e.g.*, CH₂=CF₂ + O → •CH=O + •CHF₂). Fluoroethylenes are also destroyed to a lesser degree through H atom abstraction by radicals such as OH, resulting in formation of fluorovinyl radicals (*e.g.*, CH₂=CF₂ + OH → CF₂=CH• + H₂O). Fluorovinyl radicals (like fluoromethyl and fluoroethyl radicals) are destroyed via reactions with H radicals, as well as with oxygen-containing species. However, it was observed that the fluorovinyl radicals established a dynamic equilibrium with the parent fluoroethylenes, irrespective of the specific creation and destruction pathways.

The kinetics of decomposition of most of the fluoroethanes (HF elimination) has been measured in a comprehensive series of work by Tschuikow-Roux and coworkers (Tschuikow-Roux *et al.*, 1970; Tschuikow-Roux and Quiring, 1971; Tschuikow-Roux *et al.*, 1971; Millward *et al.*, 1971; Millward

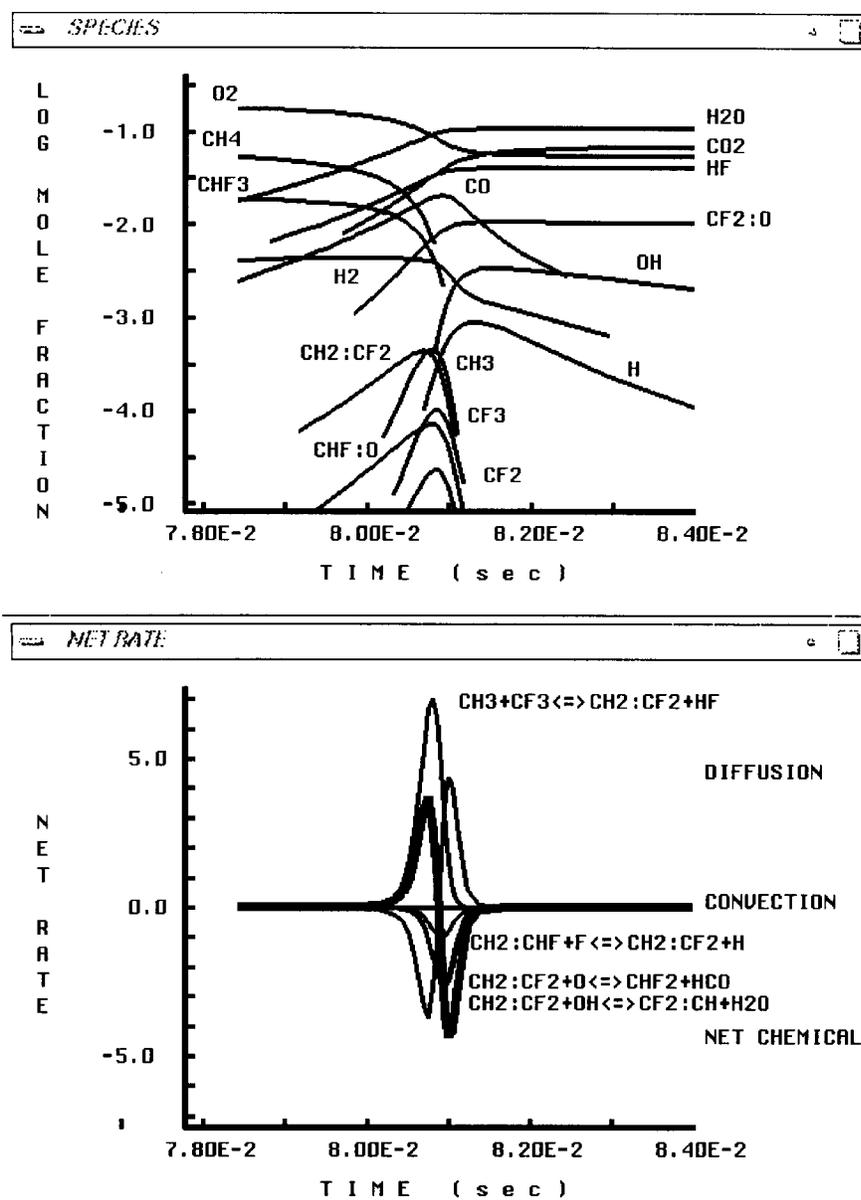


Figure 8. Typical concentration profiles of an agent (1.9% CHF₃) and its decomposition intermediates and products in a lean ($\phi=0.65$), premixed methane/air flame.

and Tschuikow-Roux, 1972; Sekhar and Tschuikow-Roux, 1974). Data for HF elimination from the other fluoroethanes have been obtained by Kerr and Timlin (1971) and Trotman-Dickenson and coworkers (Cadman *et al.*, 1970). Fluoroethane decomposition kinetics have also been measured by a few other workers (Kochubei *et al.*, 1980; Mitin *et al.*, 1988). In our work, we have used the rate expressions for these reactions as reported. However, the measurements by Tschuikow-Roux and coworkers were at significantly higher pressures (3-5 atm.). Consequently, our rates should be considered as upper limits to the rates in flames at atmospheric conditions. Future refinement of this mechanism should use RRK methods benchmarked to the experimental data to provide better values for the temperature (and pressure) dependencies of these unimolecular decomposition reactions.

There have been quite a few measurements of H atom abstractions from fluoroethanes by OH radicals. Cohen and Benson (1987a, 1987b) 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 was from the measurements by Howard and Evenson (1976), Handwerk and Zellner (1978), Nip *et al.* (1979), and Martin and Paraskevopoulos (1983). In our work to date, we have used the recommendations of 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 H substitutions, we have estimated the relative branching ratios. Recently there have been a number of good measurements for these reactions for a number of the fluoroethanes by Huie and coworkers (Liu *et al.*, 1990; Zhang *et al.*, 1992), by Ravishankara and coworkers (Talukdar *et al.*, 1991; Gierczak *et al.*, 1991), and by Nielsen (1991). Based on some of the more recent measurements there 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 (because T^b dependence). Since these recommendations are based on experimental measurements are relatively low temperatures (about 300-500 K) and these reactions are primary decomposition pathways for the fluoroethanes at significantly higher temperatures, it would be valuable to have experimental measurements of these rates near flame temperatures. We note that based on our limited evaluation, the trends in the rate expressions for this homologous series appear to be consistent with changes in the number of H atoms and the C-H bond strengths or heats of reaction (*e.g.*, Figure 6).

There have been no measurements (to our knowledge) for abstraction of H atoms from the fluoroethanes by H and O radicals. We have estimated the rates for these reactions by analogy to those for H atom abstraction from the fluoroethanes by OH radicals. Each prefactor and activation energy was scaled relative its OH reaction by the same amount as in series of H atom abstraction from the unsubstituted-ethane (C_2H_6) by H, O, and OH radicals.

There have been quite a few measurements of the reactions of O atoms with fluoroethylenes. These will not be reviewed here. In our work, we have used our fits to extended Arrhenius form to the recommendations of Cvetanovic (1987) in order to extrapolate the low temperature values (300-500 K) to flame temperatures. A temperature dependence of $T^{1.0}$ was used in analogy to other reactions. 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 coworkers (Park *et al.*, 1984). Typical creation and destruction paths for $\text{CH}_2=\text{CHF}$ are shown in Figure 8.

For this class of reactions, it is generally understood that the dominant pathway is where the products are the fluoromethyl and (fluoro)formyl radical (*e.g.* $\text{CH}_2=\text{CHF} + \text{O} \rightarrow \text{HCO} + \bullet\text{CH}_2\text{F}$) following dissociation of the chemically activated fluoroethylene oxide formed by O atom attack on the double bond; that is, the O atom "adds" to the side with the least number of electronegative substitutions (*i.e.*, F) and the H atom "migrates" to the other side. The numerous other possible

channels are generally considered to be minor pathways: fluorine-substitute analogs of 1) stabilized ethylene oxide, 2) stabilized acetaldehyde, 3) formaldehyde + methylene, 4) acetyl radical + H, 5) ketene + H₂, and 6) vinyl radical + OH. The latter, abstraction of H atom, is a separate reaction from the first four (addition/elimination). For completeness in the reaction set, we have included the latter abstraction reaction using rate expressions based on analogy to the value estimated by Fontijn and coworkers (Mahmud *et al.*, 1987) for the unsubstituted ethylene reaction. It should be noted that for pefluoroethylene, the only possible channel is $\text{CF}_2=\text{CF}_2 + \text{O} \rightarrow \text{CF}_2=\text{O} + \text{:CF}_2$ (*i.e.*, no H migration possible). It should also be noted that for $\text{CH}_2=\text{CHF}$ there are two possible channels ("addition" of the O atom to one side or the other). We have used an estimated additional 4 kJ/mol for "addition" of the O atom to the fluorinated carbon. This is consistent with a upper limit measurement at room temperature for this reaction by Gutman and coworkers (Slagle *et al.*, 1974). Given that this is a primary decomposition pathway for the fluoroethylenes and that the rate expression we are using 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.

Most of the rate expressions used in our work for reactions involving fluoroethyl radicals, fluoroethylenes, fluorovinyl radicals, and fluoroacetylenes were estimated by analogy to the reactions for the unsubstituted hydrocarbon species. The rate constant prefactors were adjusted to account for reaction path degeneracy (*i.e.*, number of H atoms). To date, we have not adjusted the activation energies. Clearly, for H atom abstraction reactions, the barriers should change with C-H bond strengths and for unimolecular and chemically activated reactions, the rates should be very sensitive to changes in stabilization with different number of F atom substitutions. Future modifications of this mechanism should address this issue.

In our work, we have used rate expressions for the fluorovinyl radicals by analogy to that for $\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2$ measured by Bozzelli and Dean (1990). We have used the recommendation of Baulch *et al.* (1992) for $\text{C}_2\text{H}_5 + \text{O} \rightarrow \text{CH}_2\text{O} + \text{CH}_3$ to estimate the analogous reactions for fluorovinyl radicals. In our work, we have used rate expressions for the reactions of fluoroethylenes with H 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 abstraction of H atoms from the fluoroethylenes by OH radicals, we have used our fit (with an estimated $T^{2.0}$ dependence) to the recommendation of 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). 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 have used these values for the analogous fluorovinyl radical reactions. In our work, we have used the recommendations of 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 recommendation for the first reaction by Warnatz is based on measurements by Heinemann *et al.* (1988). For reaction of H atoms with the two fluoroacetylenes (C_2HF , C_2F_2), we have 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).

5.1.3.3 Reactor Models. This large set of rate constants or "mechanism" was used to model the fluorinated hydrocarbon chemistry under a variety of conditions including different fuels, equivalence ratios, different agents, agent concentrations, and for a variety of reactor geometries. Since it is not yet possible to model a turbulent, chemically reacting flow, we relied upon employing a number of geometries in order to provide a good picture of realistic conditions. Simple plug flow conditions (1-D/time, no diffusion) were used to test a wide variety of conditions and to "debug" the mechanism since these types of calculations can be performed relatively quickly. The plug flow

Table 4. BAC-MP4 Transition State Calculations: Activation Energy for Reaction (kJ/mol)

TRANSITION STATE				ΔH_f°	E_a
CH ₃ F		→ :CH ₂	+ HF	120.8	368.6
		→ :CHF	+ H ₂	*182.4	418.8
CH ₂ F ₂		→ :CHF	+ HF	-121.8	327.2
		→ :CF ₂	+ H ₂	-51.9	406.7
		→ :CH ₂	+ F ₂	*346.4	792.0
CHF ₃		→ :CF ₂	+ HF	-388.3	313.8
		→ :CHF	+ F ₂	*52.3	754.4
CF ₃ OH		→ CF ₂ =O	+ HF	-741.8	180.3
CH ₂ FO•		→ •CH=O	+ HF	-109.6	87.4
CH ₂ FO•		→ CF ₂ =O	+ F	-19.2	177.8
CHF ₂ O•		→ •CF=O	+ HF	-94.6	311.3
CHF ₂ O•		→ CF ₂ =O	+ H	-328.9	77.0
•CF ₂ OH(E)		→ •CF=O	+ HF	-300.0	156.5
		→ CF ₂ =O	+ H	-315.2	141.3
		→ CHF ₂ O•		-301.9	154.6
CH ₃ -CH ₂ F		→ CH ₂ =CH ₂	+ HF	-4.6	270.3
CHF ₂ -CHF ₂		→ CH ₂ F ₂	+ :CF ₂	-375.5	514.9
CH ₄	+ :CF ₂	→ CH ₃ -CHF ₂		39.7	317.9
CH ₃ F	+ H	→ •CH ₂ F	+ H ₂	28.9	50.2
		→ •CH ₃	+ HF	110.9	131.4
CH ₂ F ₂	+ H	→ •CHF ₂	+ H ₂	-189.1	40.6
		→ •CH ₂ F	+ HF	-87.0	142.7
CHF ₃	+ H	→ •CF ₃	+ H ₂	-431.0	53.6
		→ •CHF ₂	+ HF	-317.6	168.6
CF ₄	+ H	→ •CF ₃	+ HF	-545.2	171.1
CF ₂ =O	+ H	→ •CF=O	+ HF	-229.7	150.6
		→ •CF ₂ OH		-315.1	65.3
			(G2)	-368.2	33.9
		→ CHF ₂ O•		-302.1	78.2

Table 4. BAC-MP4 Transition State Calculations: Activation Energy for Reaction (kJ/mol)

TRANSITION STATE				ΔH_f°	E_a
CF ₂ =O	+ H ₂ O	→ FC(O)OH	+ HF	-718.8	121.3
			(G2)	-710.4	151.5
CH ₃ -CHF•		→ CH ₂ =CH•	+ HF	216.7	289.1
CH ₂ F-CH ₂ •		→ CH ₂ =CHF	+ H	98.3	154.4

BAC-MP4 *ab initio* calculations (Melius, 1990)

G2 *ab initio* calculations (Curtis *et al.*, 1991)

ΔH_f° : enthalpy of formation (kJ/mol) at standard state (1 atmosphere; 298.15 K)

E_a : activation energy (kJ/mol) at 298.15 K

*: spin contaminated

calculations provide essentially the limit of maximum concentration gradients since diffusion or the interaction between reactant-like and product-like molecules is neglected. A limited set of freely propagating, premixed flame calculations (1-D/time and distance, axial diffusion) were done to provide more realistic concentration and temperature gradients in the model. This was the primary method of calculating the effects of agents on flame speed and extinction.

In addition, a limited set of continually stirred tank reactor (CSTR), burner-stabilized premixed flame, and opposed-flow diffusion flame (OFDF) calculations was also done. The CSTR calculations can be considered as providing an upper limit to the importance of diffusion since reactants, intermediates, and products chemically interact or are completely mixed. This is a case of essentially minimal concentration gradients and may provide some analogies to turbulent reacting flows. The burner-stabilized, premixed flame more closely mimics a number of realistic burning geometries such as a flame near a fuel line leak or possibly a pool fire where the surfaces in these cases can provide a large heat sink to the flame. The opposed-flow diffusion flame geometry provides a somewhat realistic model of flame conditions which exist where a burning fuel jet or rapidly heated expanding fuel vapor comes in contact with the surrounding air. Unfortunately, these calculations which provide the most realistic picture of diffusion-dominated conditions, are also the most time-consuming computationally. Consequently, only a limited number of these have been done. It is expected that more calculations will be performed when a greater degree of certainty has been developed in the reaction mechanism or when experimental measurements in the OFDF geometry become available.

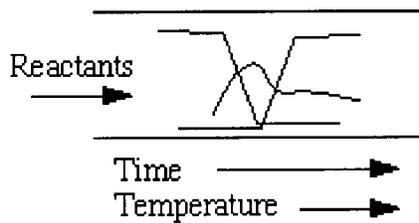
Schematic representations of these reactor geometries are shown in Figure 9.

5.1.4 Fluorinated Hydrocarbon Chemistry and Flame Suppression

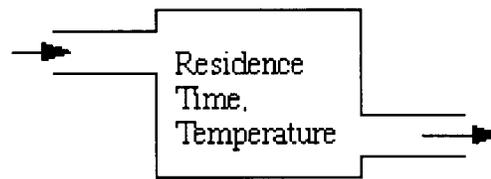
5.1.4.1 Reaction Path Analysis. The fluoromethanes decomposed primarily through H atom abstraction by OH radicals in the premixed flame with H atom abstraction by H radicals the major secondary pathway (on the order of 10-20%). H atom abstraction by O radicals and unimolecular decomposition eliminating HF are the next important minor decomposition channels (generally contributing less than 10%). These minor pathways only begin to contribute as secondary channels at the highest temperatures in the premixed flame and the unimolecular decomposition channel at high

REACTOR MODELS

No Transport

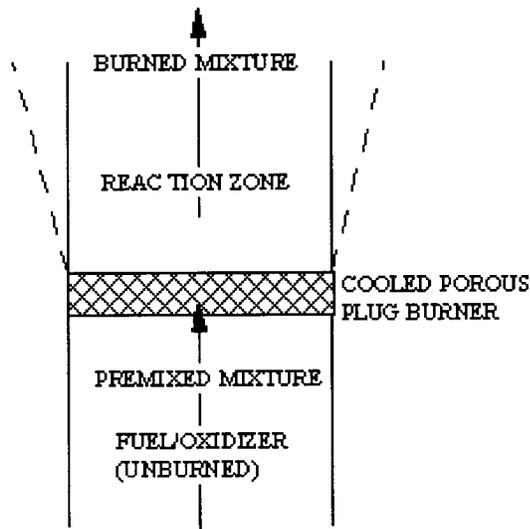


Plug Flow Reactor (PFR)

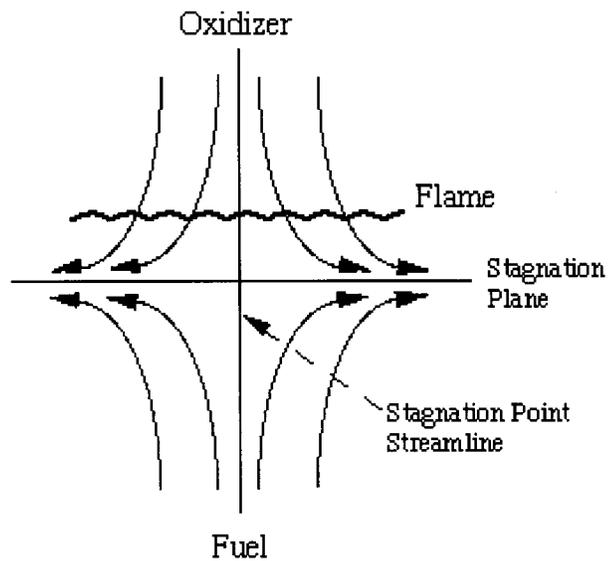


Perfectly Stirred Reactor (PSR)

1-D Transport



Premixed Flame



Counter Flow Diffusion Flame

Figure 9. Reactor Models.

temperatures/short residence times under plug flow conditions. It is likely that the unimolecular decomposition channel also plays a role in a diffusion flame due to the lack of fuel (and consequently H and OH radicals) in the preheat, oxygen side of the flame. Abstraction by methyl, fluoromethyl, and vinyl radicals are negligible in the premixed flame although they may be minor channels in plug flow or diffusion flames. Abstraction of F atoms by H radicals is negligible for CH_3F , CH_2F_2 , and CHF_3 , since the H atom abstraction channel has a significant lower barrier (30-50 kJ/mol) than the F atom abstraction channel (120-160 kJ/mol). However, in the case of CF_4 , F atom abstraction by H radicals is the only possible abstraction channel. Similarly, since there is no HF elimination channel, the only possible unimolecular decomposition pathway for CF_4 is elimination of F atoms.

There are two possible channels for production of fluoromethanes. The first involves the insertion of methylene ($:\text{CH}_2$) into HF (reverse reaction of the unimolecular decomposition) and the second is disproportionation between fluoromethyl radicals to form fluoromethanes and $:\text{CF}_2$. Although latter channel has significant experimental basis (Pritchard *et al.*,), there is some uncertainty with regard to this reaction, because there is also evidence to suggest that the reverse reaction or insertion of $:\text{CF}_2$ (a closed shell species) should have a modest barrier. Channels of the first type can contribute small amounts to "recycling" of F mass in the system. For example, CH_2F_2 can decompose via H atom abstraction reactions to form $\bullet\text{CHF}_2$, which can react with H radicals to create $:\text{CHF}$ and HF (by elimination from chemically activated CH_2F_2). The $:\text{CHF}$ formed via this pathway can then insert into HF (which is present in large concentrations in the system) and consequently reform CH_2F_2 . However, in the cases we have tested, this channel contributes generally less than 10% to the net rate of reaction for CH_2F_2 . On the other hand, this channel may be significant in predicting by-products of incomplete combustion. For example, CH_3F and the intermediates and products of its decomposition will always be formed in hydrocarbon flames irrespective of fluorocarbon starting material simply because the HF (always present in the fluorinated hydrocarbon-doped flame) will react with singlet methylene ($^1:\text{CH}_2$) (always present in hydrocarbon flames). The latter channel involving the disproportionation between fluoromethyl radicals to form fluoromethanes and $:\text{CF}_2$ should be investigated further.

There are three general channels for the destruction of the fluoromethyl radicals: (1) reaction with H radicals creating (fluoro)methylenes and HF - via chemically activated fluoromethanes; (2) reaction with O and OH radicals creating elimination products (*i.e.*, H, HF) and (fluoro)formaldehydes (CH_2O , $\text{CHF}=\text{O}$, $\text{CF}_2=\text{O}$) - via both thermal and chemically activated fluoromethoxy radicals; and (3) reaction with CH_3 radicals creating (fluoro)ethylenes and HF - via chemically activated fluoroethanes.

The relative importance of these three general channels depends upon fuel, agent, flame geometry, and other conditions. For example, under more realistic conditions in a diffusion flame where the agent is added to the air stream, the importance of the CH_3 combination route should be substantially diminished (as should the H combination to some degree), because of the lack of fuel (mixed) in the air. On the other hand the OH combination route should significantly increase in importance due to its high dispersion in the flame due to the abundance of H_2O in the flame. Similarly, the O atom reaction route should decrease in importance. Furthermore, other otherwise minor oxidative routes such as $\bullet\text{CH}_2\text{F} + \text{O}_2$ and $\bullet\text{CH}_2\text{F} + \text{HO}_2$ may begin to contribute in the preheat, oxygen rich side of the flame. For ignition delays under plug flow conditions these oxidative routes should be very important as contributors (like analogous reactions for pure hydrocarbons systems).

At high agent concentrations, autocombination of fluoromethyl radicals are contributing reactions. For $\text{CF}_3 + \text{CF}_3$, there is no HF elimination channel possible and, consequently, $\text{CF}_3\text{-CF}_3$ is the sole product (at the highest temperatures this rate falls-off slightly). For $\bullet\text{CHF}_2 + \bullet\text{CHF}_2$, the elimination channel is diminished somewhat in importance, since the $\text{CHF}_2\text{-CHF}_2$ with four heavy F

atoms can effectively stabilize the heat of reaction and compete as a product channel. This trend can be seen in Figure 4 (RRKM calculations).

The fluoromethyl radicals are primarily formed by H atom abstractions from the fluoromethanes. However, there are several other channels which can contribute to their formation and should be discussed in detail with reactions classified as C₂ chemistry. For example, the reactions $\text{CH}_2=\text{CHF} + \text{O} \rightarrow \bullet\text{CH}_2\text{F} + \text{HCO}$ or $\text{CHF}_2\text{-CF}_2\bullet + \text{H} \rightarrow \bullet\text{CHF}_2 + \bullet\text{CHF}_2$ contribute to the formation of fluoromethyl radicals. Similarly, there are a number of other decomposition channels which can be classified as C₂ or C₃ chemistry such as $\bullet\text{CH}_2\text{F} + \text{C}_2\text{H}_4 \rightarrow \bullet\text{CH}_2\text{-CH}_2\text{-CH}_2\text{F}$. These should be investigated further.

5.1.4.2 Freely Propagating, Premixed Flame Simulations. Adiabatic, freely propagating, premixed flame calculations (Kee *et al.*, 1985) were performed utilizing the reaction mechanism outlined above. Typically, fuel lean CH₄/air mixtures were simulated in order to be most sensitive to flame speed changes and (in a practical sense) since agents are added to the air supply. It would be more realistic to simulate agent effects in a diffusion flame. We have performed a few opposed flow diffusion flame calculations; however, those results are preliminary.

A summary of the effects on adiabatic flame temperature and speed are shown in Figure 10 and Figure 11 for addition of a variety of "agents" to a CH₄/air flame (equivalence ratio of 0.65). In addition to potential fluorinated hydrocarbon agents (CF₄, CHF₃, CH₂F₂, CF₃-CF₃, CF₃-CF₂H, CF₃-CFH₂), other species were added to investigate the effect of heat capacity and heat release on changes in flame speed and temperature. These reference "agents" include N₂, H₂O, CO₂, HF, and CH₄. In order to correct for differences in heat capacities for the different "agents", the amount of added "agent" was normalized to an equivalent amount of N₂, adjusting for relative heat capacities at 1500 K. For example, addition of 1% CF₄ (with C_p = 105 J/mol/K) would be roughly equivalent to addition of 3% N₂ (with C_p = 35 J/mol/K). Using heat capacities at other temperatures (1000-2000 K) had little impact on the relative normalized mole fractions.

In Figure 10, it can be seen that the effect of the various agents on flame temperature can be bracketed by addition of inert molecules (N₂, H₂O, CO₂, HF), where there is a decrease in flame temperature, and by addition of more fuel (CH₄), where there is a large increase in flame temperature. The decrease in flame temperature upon addition of the inerts is due to dilution and increased heat capacity of the mixture. The increase in flame temperature upon addition of more fuel is due to increased heat release as the fuel lean mixture becomes more rich. Addition of agents which are more fuel-like results in larger increases in flame temperature. All of the fluorinated hydrocarbons are fuels since they all eventually decompose, burn, and form CO₂, H₂O, and HF (liberating heat). At one extreme is CF₄, very little of which decomposes in the flame, and consequently, there is only a small increase in flame temperature relative to addition of inerts. On the other extreme is CH₂F₂, which completely burns forming highly exothermic products CO₂ and HF. In Figure 11, a range of effects on flame speed for the various added agents can be observed. For the inert molecules and the nearly inert fluorinated hydrocarbons (CF₄, CF₃-CF₃), a decrease in flame speed is observed consistent with dilution of the mixture. On the other extreme, for CH₄ (the fuel) and CH₂F₂ (a slightly poorer fuel), an increase in flame speed is observed. Of the various agents considered, only CHF₃ was seen to have any chemical effect in flame suppression. Figure 10 and Figure 11 show that although there is an increase in flame temperature upon CHF₃ addition, there is also a decrease in flame speed relative to inert molecule addition. Inspection of reaction pathways for CHF₃ and other agents (see Figure 7) reveals that a significant amount of decomposed CHF₃ results in the formation of a relatively unreactive perfluorocompound, carbonyl fluoride (CF₂=O). Decomposition of CF₂=O occurs only very slowly via reaction with either H radicals (H addition + HF elimination) or

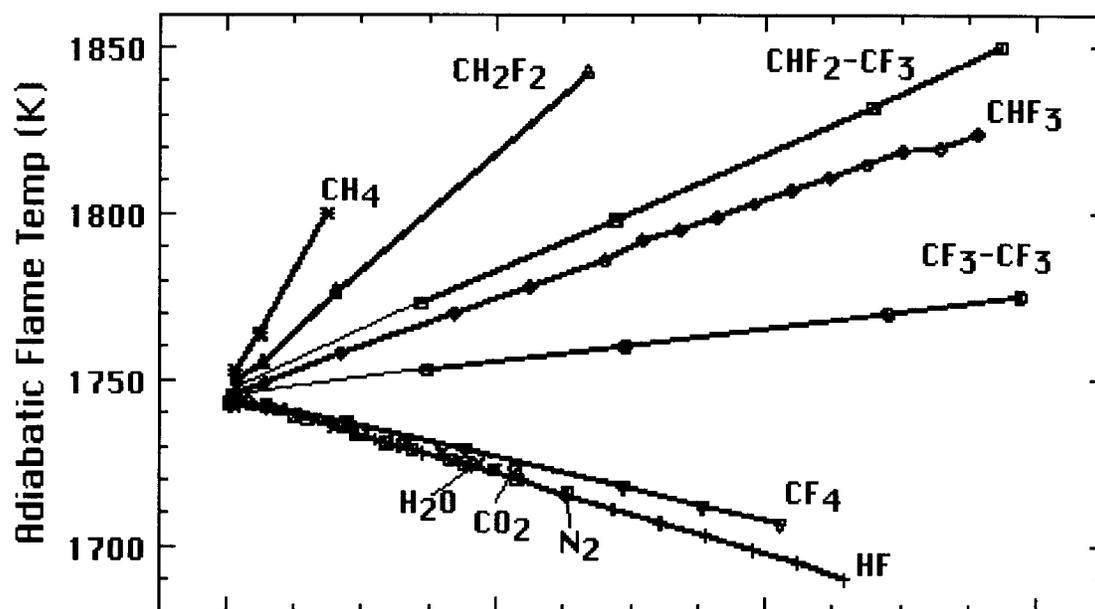


Figure 10. Effect of Agents on Flame Temperature.

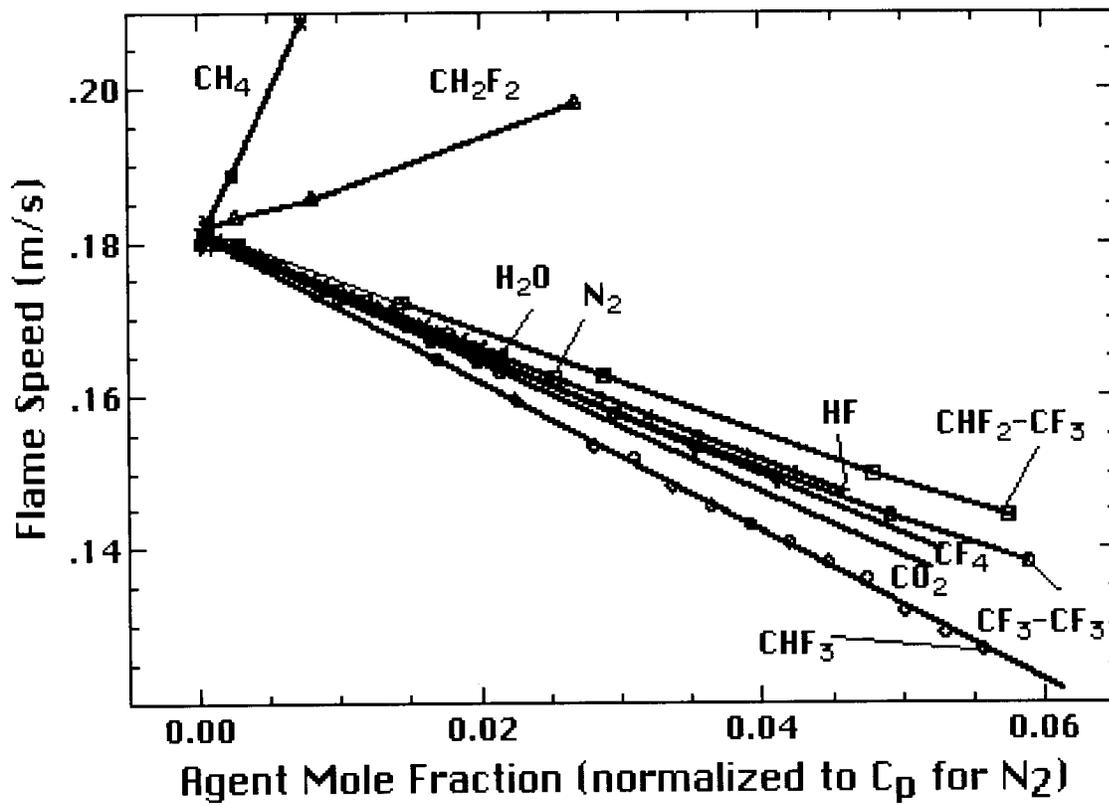


Figure 11. Effect of Agents on Flame Speed.

with H_2O (through a hot fluoroformic intermediate). For all other agents, this $\text{CF}_2=\text{O}$ bottleneck is avoided.

5.1.5 Discussion. These simulations are consistent with qualitative trends observed in experimental measurements of agent effectiveness in the work by others in other parts of the overall project at NIST. However, in order to quantitatively predict agent effectiveness, experimental validation of the mechanism will be necessary.

As indicated in the last section, the premixed flame simulations demonstrate that differences in the relative influence of candidate agents on hydrocarbon flames can be explained largely by simple differences in their relative heat capacities and relative amounts of heat release due to agent combustion. That is, flame extinction upon addition of each of the potential agents is only due to simple dilution of the flame by increased heat capacity of the mixture (consequently, reduced flame temperatures). This result is not surprising and was the expected behavior in the absence of any simulations or experimental measurements of agent effectiveness.

The majority of the candidate agents are perfluorocarbons, which are essentially inert relative to the fuel, and therefore by definition, cannot (chemically) inhibit flames. These inert "agents" can extinguish flames by dilution; however, so can equivalent amounts of completely inert molecules, such as N_2 or CO_2 , as well as sufficient excess oxygen (O_2) in premixed flames.

In contrast to completely inert molecules, the nearly inert perfluorocarbons will eventually decompose (at least partially) under flame conditions (at the highest temperatures and long times), resulting in exothermic products CO_2 and HF (liberating heat) and increasing flame temperatures. However, since the perfluorocarbons decompose much slower than the hydrocarbon fuels, their decomposition intermediates and products cannot participate in the hydrocarbon combustion chemistry. Consequently, these "agents" cannot directly influence flame chemistry, but can only increase flame temperatures; that is, relative to inert molecules these agents can only indirectly promote combustion (through heat release) and cannot suppress flame processes.

This expected behavior was observed in the simulations (i.e., Figures 10 and 11). For example, addition of $\text{CF}_3\text{-CF}_3$ increases both flame temperature and speed relative to addition of inert molecules. Inspection of concentration profiles and reaction pathways in the premixed flame simulations for the perfluorocarbons CF_4 and $\text{CF}_3\text{-CF}_3$ reveal that the small fraction of these compounds that decompose, do so in the post-flame zone (subsequent to the important combustion chemistry). The larger the perfluorocarbon, the more readily it decomposes; that is, a larger fraction of it decomposes for a given set of conditions. Consequently, more heat is released and more enhancement of the flame is expected. This trend can be seen in Figures 10 and 11, where both flame temperature and speed are increased relative to inert molecules, going from CF_4 to the larger and less stable $\text{CF}_3\text{-CF}_3$. It should be noted that in accordance with this behavior, one of the perfluorocarbons, cyclo- C_4F_8 , is expected to have a larger enhancement than the corresponding alkane, because it is likely to decompose more rapidly (to two molecules of $\text{CF}_2=\text{CF}_2$) and have more combustible intermediates (thereby liberating more heat, increasing flame temperature and speed). In our work, we did not simulate the effect of agents with three or more carbons atoms, because of the additional complexity of the chemistry that must be considered. Consequently, we have no simulations to quantitatively support the above predicted qualitative behavior of the large molecules.

The influence of addition of the hydrofluorocarbon agents to hydrocarbon flames can best be described in reference to the related perfluorocarbons. The perfluorocarbons are relatively inert molecules, because they are relatively slow to decompose even under flame conditions. Hydrogen atom substitution of these molecules will significantly increase their reactivity and enable them to decompose prior to or during combustion (as opposed to in post-flame zones). However, for the

same reason, hydrogen atom substitution should significantly increase their fuel characteristics. That is, the hydrofluorocarbons will contribute excess heat when they decompose and their products react further to form exothermic products CO_2 and HF . Of course, these agents will also contribute hydrogen atoms (fuel) to the chemistry. These hydrofluorocarbon agents may also decompose sufficiently "early" that the radicals they produce may enhance ignition chemistry (promotion). However, the fluorinated radicals, which are less combustible than the corresponding hydrocarbon radicals, may also compete for important radicals in the flame, thereby slowing flame propagation (inhibition). In order for the hydrofluorocarbons to inhibit flames, these competitive reactions must be sufficient to counteract both the enhancement of flame chemistry due the hydrogen atom-substitution and the heat release due to combustion of the added agent. The simulations indicate that this radical scavenging effect is never dominant.

The influence of addition of the hydrochlorofluorocarbon agents to hydrocarbon flames can best be described in reference to their hydrofluorocarbon analogues (*e.g.*, $\text{CF}_3\text{-CHFCl}$ versus $\text{CF}_3\text{-CHF}_2$). The primary decomposition pathway for the hydrofluorocarbons is through H atom abstraction by H or OH radicals in the flame. In general, HF elimination is a minor contributing pathway except under pyrolytic conditions where it may be dominant. However, for the hydrochlorofluorocarbons, decomposition by HCl elimination is an energetically feasible pathway. Consequently, these molecules may have a different chemical effect on the flame, if HCl (or other Cl-substituted molecules) influence the chemistry. One of the primary reasons for the effectiveness of CF_3Br is that HBr that is formed is recycled to Br atoms (which scavenge H atoms in the flame) through the energetically favorable reaction $\text{HBr} + \text{OH} \rightarrow \text{Br} + \text{H}_2\text{O}$ ($\Delta H_{\text{rxn}} = -130 \text{ kJ/mol}$). On the other hand F atoms do not catalytically destroy H atoms because HF, once formed, is never consumed. This is because the reaction $\text{HF} + \text{OH} \rightarrow \text{F} + \text{H}_2\text{O}$ ($\Delta H_{\text{rxn}} = +75 \text{ kJ/mol}$) is essentially energetically prohibited. However, the analogous reaction $\text{HCl} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O}$ ($\Delta H_{\text{rxn}} = -65 \text{ kJ/mol}$) is energetically favorable. Therefore, Cl atoms may catalytically destroy H atoms in the flame (like Br atoms) and consequently, the hydrochlorofluorocarbon agents may be more effective than their hydrofluorocarbon analogues. The one exception to this may be CHF_2Cl . In this case, HCl elimination yields $:\text{CF}_2$ (relatively reactive), while for $\text{CF}_3\text{-CHFCl}$, HCl elimination should yield $\text{CF}_2=\text{CF}_2$ (relatively unreactive). The $:\text{CF}_2$ species may be formed sufficiently "early" in the flame that it may enhance ignition chemistry (potential source of radicals). If this is the case, CHF_2Cl could promote, rather than inhibit the flame. In our work, we did not simulate the effect of agents with chlorine atoms (simultaneous with fluorine atoms), because of the additional complexity of the chemistry that must be considered. Consequently, we have no simulations to quantitatively support this predicted qualitative behavior for the hydrochlorofluorocarbon agents.

We did not perform any substantial number of simulations with other fuels. However, as discussed above, the differences in the relative influence of candidate agents on hydrocarbon flames can be explained largely by simple differences in their relative heat capacities and relative amounts of heat release due to agent combustion. That is, flame extinction upon addition of each of the potential agents is only due to simple dilution of the flame by increased heat capacity of the mixture and consequently, reduced flame temperatures. Therefore, a fuel with a higher adiabatic flame temperature should require more added agent in proportion with its higher energy content to slow the flame speed by a given amount (or completely extinguish the flame). We did not perform a sufficient number of simulations to quantitatively support this predicted qualitative behavior between fuels.

5.1.6 Recommendations. Of all the potential agents considered, only trifluoromethane (CHF_3) was observed in the simulations to inhibit hydrocarbon flames to any degree. All of the other potential agents either had no influence (inert molecules), were promoters (H atom substituted), or were fuels themselves (such as CH_2F_2). Consequently, we would recommend CHF_3 (although it was not one of

the 12 candidate agents). However, there may be other properties that would preclude its use such as toxicity or corrosiveness.

Of all of the specific candidate agents, we would recommend perfluoroethane ($\text{CF}_3\text{-CF}_3$), since our simulations indicate that it will extinguish flames through dilution on a par with N_2 based on their relative heat capacities. $\text{CF}_3\text{-CF}_3$ may be preferable to N_2 because it is denser than air or because of other properties. Based on our simulations, the single H atom-substituted hydrofluorocarbons should always be less effective than their perfluorocarbon analogues (*e.g.*, $\text{CF}_3\text{-CF}_2\text{H}$ versus $\text{CF}_3\text{-CF}_3$) because their fuel-like characteristics (heat release) will always dominate any radical scavenging.

Based on the effectiveness of CHF_3 in the simulations and knowledge of its mechanism for inhibition, there are other potential agents which should be considered. Any molecule that decomposes readily to yield perfluoromethyl radicals ($\bullet\text{CF}_3$) could provide some degree of chemical inhibition of flame processes. That is, any molecule $\text{CF}_3\text{-X}$ which has a weak bond (C-X) between the CF_3 group and any other group (denoted by X). $\text{CF}_3\text{-Br}$ is the best example (although undesirable because of its ODP). $\text{CF}_3\text{-I}$ is another simple example. We would also recommend perfluoroacetone ($\text{CF}_3\text{-C(O)-CF}_3$) and hexafluoroazomethane ($\text{CF}_3\text{-N=N-CF}_3$). These potential agents are known to be good sources of perfluoromethyl radicals ($\bullet\text{CF}_3$) and may decompose sufficiently "early" in the flame that the $\bullet\text{CF}_3$ radicals generated could participate in ignition chemistry. The $\bullet\text{CF}_3$ radicals can be a sink for terminating radical production through the reaction $\bullet\text{CF}_3 + \text{HO}_2 \rightarrow \text{CHF}_3 + \text{O}_2$, which is a contributing reaction (but not the dominant one) in the effectiveness of CF_3Br flame inhibition. The $\bullet\text{CF}_3$ radicals will also simply compete for all radicals in the flame. These molecules are amenable to simulations, since their decomposition products ($\bullet\text{CF}_3$, CO, and N_2) are already contained in the mechanism which has been developed. These agents should also be readily available for use in experimental determinations of their potential effectiveness. However, there may be other properties that would preclude their use such as toxicity, corrosiveness, or instability.

5.2 Acid Gas Formation in Halogenated Hydrocarbon-Inhibited Flames

5.2.1 Objective and Background. The objective of this part of the research project was to obtain an understanding of the chemical and physical process of acid gas formation in inhibited flames in order to predict the amount of acid gas formed in suppressed dry bay and engine nacelle fires. This is a continuing project, and this section of the report describes results of preliminary work to date.

The halogen acid or hydrogen halide HX (where X represents the halogen) is a thermodynamically stable product in mixtures containing hydrogen and halogen atoms. Since the halogenated hydrocarbon molecules of the present inhibitors can decompose in flames through thermal decomposition or radical attack, formation of the stable halogen acid is likely. The proposed alternatives to halon 1301 (CF_3Br), primarily fluorinated and chlorinated hydrocarbons, are required in much higher concentrations than 1301 (Section 4). Consequently, they have the potential to have correspondingly higher concentrations of decomposition by-products. The acid gases hydrogen fluoride (HF) and hydrogen chloride (HCl) are believed to be the most corrosive of these products.

In order to understand the formation rates of acid gases in dry bay and engine nacelle fires it is necessary to examine the thermodynamics and chemical kinetics relevant to the formation of the acid gases as well as the effects of the flow field and mixing on the chemistry. An engine nacelle fire may be similar to a steady turbulent spray diffusion flame, whereas a dry bay fire may resemble a rapidly advancing turbulent premixed flame. Because suppression of the dry bay fires is rapid, occurring in a time of under 100 ms, it is also necessary to consider transient effects on the acid gas formation process.

Formation of acid gases in inhibited hydrocarbon flames has been studied for many years. The research can be categorized as either global measurements of HF produced in suppressed fires, or detailed flame structure measurements. Burdon *et al.*, (1955) ignited mixtures of fuel, air, and CH_3Br in flasks, analyzed the products and found copious amounts of HBr. Numerous premixed low pressure flame studies (*e.g.* Wilson, 1965; Biordi *et al.*, 1973; Safieh *et al.*, 1982; and Vandooren *et al.*, 1988) used mass spectroscopy to measure the profiles of hydrogen halides and other products in hydrogen, carbon monoxide, and hydrocarbon flames inhibited by CH_3Br , CF_3Br , and CF_3H . These studies indicated conversion efficiencies of the halogens in the inhibitor into halogen acids on the order of unity. Acid gas formation in hydrocarbon-air pool fires suppressed by CF_3Br has been studied by Sheinson *et al.* (1981, 1982). These studies, in test volumes of 1.7 and 650 m^3 , stressed the difficulties in probe sampling for acid gases. The latter study described an *in situ* IR absorption method for measuring HBr and HF. To overcome these limitations and also provide time-resolved acid gas concentration data, Smith *et al.* (1993) developed a new HX sampling technique and obtained HX and inhibitor concentrations as functions of time for discharge of CF_3Br into a 56 m^3 space. In a series of experiments with a variety of fuels and halogenated inhibitors, Yamashika (1973) showed that the extinction time for a compartment fire sprayed with inhibitor is dependent upon the discharge rate and room volume. He then showed (Yamashika, 1974) that the amounts of hydrogen halides and carbonyl halides are also dependent upon the discharge rate. Using a simple model of acid gas formation based on the steady-state rates, he developed a model of transient acid gas formation to explain his results.

In more recent studies, Ferreira *et al.* (1992a,b) injected CF_3Br , C_3HF_7 , and C_4F_{10} into an enclosure fire and measured the HF produced using ion-selective electrodes. Di Nenno *et al.* (1993) introduced halon alternatives into compartment fires and measured the HF, HCl, and COF_2 produced using Fourier transform infrared spectroscopy. These studies again confirmed the importance of injection rate and fuel consumption rate on the amount of acid gas produced. Filipczak (1993) introduced CF_2ClBr and CF_3Br into a methane flame and measured the O_2 , CO_2 , H_2O , HF, HCl, HBr, and unreacted inhibitor using a mass spectrometer. Hoke and Herud (1993) are currently developing a fast-response ion-selective electrode for measuring HF and HCl produced in extinguished fires in crew compartments of combat vehicles.

Previous research related to understanding acid gas formation in inhibited flames can be seen to include both detailed flame structure measurements and global measurements of HF produced in suppressed fires. The inhibited low-pressure premixed flame studies provide detailed data on the concentration profiles of major species as a function of position in the flame for inhibition by CH_3Br , CF_3Br , and CF_3H . These results provide the basis for obtaining a good understanding of the underlying chemical kinetics of the formation of acid gases. The second category of experiments is global measurements of the amount of acid gas formed in suppressed diffusion flames. These studies provide important information on the magnitude of the acid gases produced and allow a comparison of the relative amount of acid gases formed by new halon alternatives. In addition, some progress has been made (Yamashika, 1974; Smith *et al.*, 1993) in developing engineering models of acid gas formation in suppressed flames. There remains a need to develop a fundamental basis for interpreting the data on acid gas formation in flames suppressed by halon alternatives, and to understand the chemical kinetic rates of acid gas formation in flames inhibited by these alternative agents. In particular, there exists a need to understand the relationship between fuel and inhibitor type, flame characteristics, and the concentrations of by-products formed.

5.2.2 Experimental Approach. The formation of toxic and corrosive by-products in flames suppressed by halogenated hydrocarbons may be controlled by transport rates of the inhibitor into the

flame, chemical kinetic rates, and equilibrium thermodynamics. These phenomena in turn will be affected by the fuel type, local stoichiometry, inhibitor type and concentration, and the characteristics of the flow field (mixing rates, strain, and stabilization mechanisms). The approach in this research is to study the influence of key parameters (including the fuel type, inhibitor type and concentration, rate of inhibitor injection, and flame type) through systematic experiments on laboratory-scale flames. Inhibitor will be added to the fuel or air stream of co- and counter-flow diffusion flames and premixed flames under steady-state and transient conditions. Inhibitor type, concentration, and injection rates will be varied as will fuel type. The diffusion flames will be operated under both laminar and turbulent conditions to vary the mixing rates, and premixed flames will be studied over a range of fuel-air equivalence ratios. This is an ongoing project. At this point, the measurements of steady-state acid gas formation rates in inhibited co-flow propane-air diffusion flames have been completed. The apparatus used to obtain these data, the results, and their interpretation are presented below.

The experiments were performed with a propane-air co-flow diffusion flame. Two burner types were used. The first was modelled after the cup burner described by Booth *et al.* (1973) and Bajpai (1974). The experimental arrangement is shown in Figure 12. The burner consists of a 28 mm diameter pyrex cup positioned concentrically in a 120 mm diameter 450 mm tall chimney at about 150 mm from the base. In these experiments with propane, the cup burner was modified for use with a gaseous fuel (liquid fuels will be tested in future experiments). The cup was filled with 1 mm diameter glass beads and covered with a stainless steel screen. The second burner consisted of a 25 cm long pyrex tube with a 0.50 mm diameter opening positioned concentrically and at the same height as the cup burner, with the same chimney. The cold flow Reynolds number based on the exit velocity in the tube was 10,500. This second burner, referred to here as the jet burner, was designed to provide turbulent mixing of the inhibitor in the air stream with the fuel.

The air used was shop compressed air (filtered and dried) which was passed through an 0.01 micron filter to remove aerosols and particulates, a carbon filter to remove organic vapors, and a desiccant bed to remove water vapor. The fuel gas was propane (Matheson, CP grade) at flow rate of 0.114 l/min at 21 °C. Gas flows were measured with rotameters (Matheson 1050 series) which were calibrated with bubble and dry (American Meter Co. DTM-200A and DTM-325) flow meters. Inhibitor gases were of different purities from various suppliers.

Before measuring HF in the product gases, the concentration of inhibitor in the air stream necessary to extinguish the flame was determined. The inhibitor was then added to the co-flowing air stream at a concentration of either 50 or 90% of the extinguishing concentration, and the product gases were sampled for acid gas. In one series of experiments with the cup burner, the inhibitor was added to the gaseous propane stream at 70% of the concentration which was found to extinguish the flame.

A wet chemistry technique was used to measure the HF and HCl concentrations in the exhaust gases from the co-flow diffusion flames. A glass funnel was placed over the chimney and the exhaust gases passed through the 4.0 cm diameter neck. A quartz probe, centered in the neck, extracted a measured fraction of the product gases (approximately 0.5%), and directed the gases through polyethylene sample lines to polyethylene impingers filled with water which trapped the acid gases. The sample flow was continued for a total collection time of sixty seconds. The quartz probe and sample lines were washed with water which was returned to the impinger. The sample was tested for F⁻ and Cl⁻ using ion-selective electrodes (Orion models 96-09 and 96-17B). It should be noted that since COF₂ is known to hydrolyze rapidly in the presence of water, this technique for acid gas measurement includes F⁻ from both HF and COF₂. To reduce the effects of sampling losses reported by other investigators, a quartz probe and polyethylene sample lines were used, the distance from the

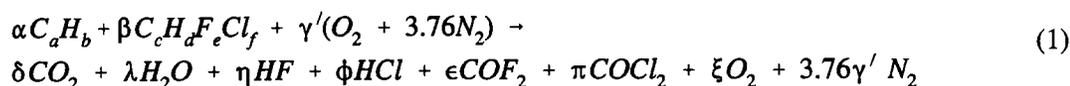
chimney top to the bubbler was kept small (~ 10 cm) and the sample lines were washed with the bubbler fluid immediately after the sample was collected.

5.2.3 Model for Acid Gas Formation. A model for the amount of acid gas formed in an inhibited diffusion flame can be developed in a manner analogous to the determination of the local equivalence ratio and structure for diffusion flames. In the classic Burke-Schumann analysis (Burke and Schumann, 1928), the chemical reaction is assumed to occur at a sheet. This location serves as a sink for the fuel and oxidizer which are assumed to diffuse there in stoichiometric proportions based on complete reaction to the most stable products (i.e., HF formation is assumed to be controlled by equilibrium thermodynamics rather than chemical kinetics). This model will be referred to as the stoichiometric model.

In the case of a flame inhibited by halogenated hydrocarbons, a thermodynamic analysis shows that in equilibrium, the inhibitor readily breaks down to CO_2 , HX, and H_2O . Consequently, the inhibitor is assumed to be consumed like a fuel and form the most stable products. The assumptions used in the stoichiometric model are:

1. there is complete reaction of the inhibitor molecule with fuel and air to the most stable products;
2. the inhibitor in the air stream which by-passes the flame sheet does not decompose through interaction with the post-combustion product gases;
3. there is no loss of acid gases to the chimney walls; and
4. the product gases are perfectly mixed.

An equation for the reaction of an arbitrary hydrocarbon with air and arbitrary halogenated hydrocarbon inhibitor is:



In this equation α is specified as is β when inhibitor is present only in the fuel stream. For inhibitor present in the air stream, β is determined by the concentration of inhibitor in the air stream and the ratio of the diffusion rates for oxygen and inhibitor.

$$\beta = \frac{\alpha(a+b/4)}{1/(\rho r) - [c+1/4(d-e-f)]} \quad (2)$$

Where ρ is the ratio of the binary diffusion coefficient of the inhibitor in nitrogen to that of oxygen with nitrogen and r is the ratio of the concentration of inhibitor to oxygen in the air stream. An atom balance for all species provides all of the unknown coefficients, and an estimate of amount of acid gas formed per mole of fuel $(\eta + \phi)/\alpha$ is then readily found.

5.2.4 Results and Discussion. The acid gases produced were measured at inhibitor concentrations of 50 and 90% of the concentration of inhibitor found to extinguish the flame when the inhibitor was added to the co-flowing air stream in the cup burner and jet burner, and at 70% of the extinction concentration for inhibitor added to the propane fuel stream for the cup burner. Table 5 lists the extinction concentrations for each agent for inhibitor added to the air stream of both burners, and for

inhibitor added to the fuel stream of the cup burner. As the table indicates, the jet burner flame typically requires about 50% less inhibitor in the air stream to extinguish the flame than the cup burner, even for identical fuel and air flows, although there are notable exceptions: CF_3Br , which required about one fifth as much inhibitor in the jet burner than in the cup burner, and C_2HF_5 and the $\text{CH}_2\text{F}_2/\text{C}_2\text{H}_2\text{F}_4$ mixture which had nearly the same extinction concentrations. In addition to providing the necessary extinction conditions for specification of inhibitor flows at 50 and 90% of extinction, these results also demonstrate the sensitivity of the extinction conditions to the burner geometry.

The measured HF for these diffusion flames is shown in Figures 13 and 14. These figures present the HF produced (moles/min) for each inhibitor for the five burner/inhibitor combinations. The total flow was about 1 mole/min. For each inhibitor, the measured HF is plotted for the cup burner and for the turbulent jet burner with inhibitor present in the air stream at 50 and 90% the extinction value, and for inhibitor added to the fuel stream in the cup burner at 70% of the value necessary to cause extinction. The figure indicates that the amount of HF varies with both the flame type and the inhibitor type by about a factor of five for each. Note that the fuel and air flows are held constant in these data. Hydrogen chloride was also measured in these experiments and the results are qualitatively the same as for HF. For clarity of presentation, however, only the HF results are presented.

In order to provide insight into the controlling parameters in inhibited diffusion flames, the data of Figures 13 and 14 are presented in an alternative form in Figures 15 to 26. In these figures, the amount of HF produced is plotted as a function of the inhibitor concentration in air. The symbols represent the experimental data, while the lines marked F and H represent estimates of the fluxes of fluorine and hydrogen into the reaction zone based on the stoichiometric model described above.

Figure 15 shows the measured and estimated HF production rates in a propane-air diffusion flame for C_2F_6 in the cup and jet burners. The squares are the experimental data for the cup (c) and jet (j) burners at 50 and 90% of extinction, and with inhibition addition to the fuel stream (f) of the cup burner of 70% of the extinction concentration. The estimated uncertainty on the HF are $\pm 10\%$ of the value for each data point. The curve labeled F in Figure 15 is the maximum fluoride atom mass flux into the reaction sheet of the diffusion flame calculated using the stoichiometric model described above. The curve labeled F' in Figure 15 is the fluoride mass flux when the diffusion rate of the inhibitor relative to oxygen is modified to account for preferential diffusion of oxygen relative to the inhibitor using the molecular weight correction factor

$$\sqrt{W_i + W_{N_2} / W_{N_2} W_i} / \sqrt{W_{O_2} + W_{N_2} / W_{O_2} W_{N_2}} .$$

In this equation, W_{N_2} , W_{O_2} , and W_i are the molecular weights of nitrogen, oxygen, and inhibitor.

The predicted fluorine and hydrogen fluxes are based on actual experimental flows which vary slightly from run to run. The slight variations in flows cause the slight discontinuities in the F and H curves as in Figure 16.

Qualitatively, the curves F and F' are seen to increase with increasing inhibitor concentration in air, and the mass flux of inhibitor into the reaction zone is lower when a lower rate of diffusion is used for the inhibitor. The curves labeled H and H' (coincident for C_2F_6) show the estimated hydrogen atom flux into the reaction zone as a function of inhibitor concentration in the air stream. Since this inhibitor does not contain hydrogen, all of the hydrogen is from the propane, and

Table 5. Extinction concentrations in percent for halon alternatives added to a co-flow propane-air cup burner and jet burner flame

Inhibitor	Extinction Concentration in air (%)	
	cup	jet
CF ₃ Br	4.3 (± 0.1)	0.8 (± 0.02)
C ₃ H ₂ F ₆	7.2 (± 0.2)	4.0 (± 0.1)
CH ₂ F ₂ /C ₂ H ₂ F ₄	15.2 (± 0.5)	15.5 (± 0.5)
C ₄ F ₁₀	5.0 (± 0.2)	3.2 (± 0.1)
C ₂ HClF ₄	8.6 (± 0.3)	4.2 (± 0.1)
C ₂ H ₂ F ₄	11.1 (± 0.3)	9.5 (± 0.3)
C ₂ HF ₅	10.2 (± 0.3)	6.2 (± 0.2)
CHClF ₂	13.8 (± 0.4)	6.7 (± 0.2)
C ₃ HF ₇	7.6 (± 0.2)	4.2 (± 0.1)
C ₂ F ₆	9.4 (± 0.3)	3.8 (± 0.1)
C ₃ F ₈	7.5 (± 0.2)	3.8 (± 0.1)
C ₄ F ₈	7.6 (± 0.2)	5.1 (± 0.2)

increasing inhibitor in the air stream does not increase the hydrogen flux into the flame. One would expect that the HF production rate would not be greater than the estimated flux of F or H into the reaction zone. For this inhibitor, the flame appears to be hydrogen limited above about 5% C₂F₆ in the air stream; however, when there is not enough hydrogen, the most stable product is COF₂, which is known to rapidly hydrolyze in the presence of water, and would also appear as F⁻ in the bubbler. Consequently, the hydrogen limit may or may not exist (depending upon whether the kinetics are fast enough to form COF₂ in the hydrogen-limited case).

Also shown in the figure are the experimentally measured HF production rates for the jet and cup burners (labeled c and j respectively) at 50 and 90% of the extinction concentration of C₂F₆. As indicated, the measured quantities of HF are lower than both the fluorine and hydrogen limits, and the measured values are closer to the estimated limits when the effects of preferential diffusion are included as described above. The results for the inhibitor addition to the fuel stream in the cup burner (labeled f) are plotted at an inhibitor concentration of zero so that they can be included in the figure.

When viewed in this manner, the behavior of the alternative inhibitors falls into three categories. In the first category are those inhibitors (C₂F₆, C₃F₈, C₄F₁₀, C₃F₈, C₂HF₅, and C₃HF₇; Figures 15 to 20) where, at the highest inhibitor concentration tested (cup burner at 90% of extinction), the estimated hydrogen flux into the reaction zone is lower than the fluorine flux, and is not a strong function of the inhibitor concentration. For these inhibitors, the HF produced does not increase significantly when the inhibitor concentration in the air stream increases above that necessary for a hydrogen/fluorine ratio in the reaction zone of about unity (the region of where the lines marked F and H or F' and H' cross in Figures 15 to 26). The second category includes those inhibitors

($C_2H_2F_4$, C_2HClF_4 , $C_3H_2F_6$, and $CH_2F_2/C_2H_2F_4$; Figures 21 to 24) for which the estimated H and F fluxes are about equal. For these inhibitors, the amount of HF produced increases with increasing inhibitor concentration in the air, but the highest concentration tested corresponds roughly to a unity F/H ratio in the reaction zone. The last category consists of CF_3Br and $CHClF_2$ (Figures 25 and 26) for which the estimated hydrogen flux is much higher than fluorine flux, and there is estimated always to be more hydrogen than fluorine in the reaction zone. For these inhibitors, the HF produced is always increasing with higher agent concentration in the air stream.

Although the stoichiometric model is very simple and is only expected to provide an upper limit on the amount of HF formed, it is instructive to investigate the possible reasons that the measured HF production rates might be lower than the estimates. Lower HF may be measured in the experiments due to experimental difficulties, for example: loss of HF to the chimney walls, loss in the sampling system, HF undetected by the ion-selective electrodes, or imperfect mixing in the product gases. Based on exploratory parametric tests, these loss mechanisms are considered to be of secondary importance. The predicted values of the HF production do not include chemical kinetic limitations and the estimates of transport rates into the reaction zone are only approximate. Additional experiments will be performed to allow examination of these important parameters.

5.2.5 Future Work. In order to eliminate the error associated with the estimates of the inhibitor transport rate into the reaction zone, experiments will be performed with inhibitor added to the reactant stream in a premixed burner. Adding known concentrations of inhibitor to a premixed flame and measuring the HF production rates will eliminate the need to estimate transport rates of inhibitor into the flame and allow a better assessment of kinetic limitations to HF formation. The premixed flame will also be used to perform measurements of the burning rate reduction with addition of inhibitor. These measurements will be used to validate chemical kinetic mechanisms of the reaction of hydrocarbons, halogens, and air. Measurements of the final product species in inhibited flames will provide insight into the kinetic mechanisms and can be used for comparison with kinetic modeling results. Finally, detailed flame structure measurements in inhibited counterflow diffusion flames will allow comparison with the results of detailed numerical calculations of the flame structure to provide a sound fundamental basis for estimates of HF production rates in suppressed dry bay and engine nacelle fires. The approach to be used in developing a model for HF production in these fires is similar to that of Yamashika (Yamashika, 1974). The experimentally determined steady-state production rates for HF will be used to predict the time-dependent production rate of HF. The important parameters then become the value of the extinction concentration for a given fire and the time it takes the concentration to reach this concentration. Since chemical kinetic limitations appear to affect HF formation rates, detailed flame structure measurements together with numerical modelling of the kinetics are necessary to provide the background for development of a global model of HF formation.

Although results on acid gas production in JP8 cup burner flames have not yet been obtained, it is possible to use the propane results and the model described above to obtain estimates of the amount of acid gas (HF and HCl) that would be formed in a turbulent JP8 flame suppressed by the proposed alternative agents, and use this estimate as a basis for ranking the agents with respect to acid gas formation. The quantity of HX (sum of HF and HCl) formed is estimated from the steady state production rates predicted by the stoichiometric model for JP8 fuel with suppressant present at 50% of the extinction value. Kinetic limitations are estimated from those indicated by the propane results. Table 6 provides the rank ordering of the agents and gives the fraction of acid gas the agent forms in

Table 6. Relative ranking of alternative inhibitors with respect to steady state hydrogen halide production rates

Inhibitor	Relative Steady State Acid Gas Production
CF ₃ Br	0.05 (± 0.01)
C ₂ HClF ₄	0.16 (± 0.03)
C ₂ F ₆	0.21 (± 0.03)
C ₄ F ₁₀	0.27 (± 0.04)
CHClF ₂	0.31 (± 0.05)
C ₄ F ₈	0.32 (± 0.05)
C ₃ F ₈	0.34 (± 0.05)
C ₃ HF ₇	0.35 (± 0.05)
C ₂ HF ₅	0.41 (± 0.06)
C ₃ H ₂ F ₆	0.43 (± 0.06)
C ₂ H ₂ F ₄	0.74 (± 0.10)
CH ₂ F ₂ /C ₂ H ₂ F ₄	1.0 (± 0.10)

steady state compared to the agent which has the highest acid gas formation rate (CH₂F₂/C₂HF₅). The agent CF₃Br is listed for comparison. In practice, the amount of acid gas formed in a suppressed fire will be dependent upon the time it takes the agent to reach the extinction concentration. For example, the rank ordering in the list below (which is based on steady-state results) can be greatly affected by the injection system used and the mixing characteristics of the particular agent once it is released.

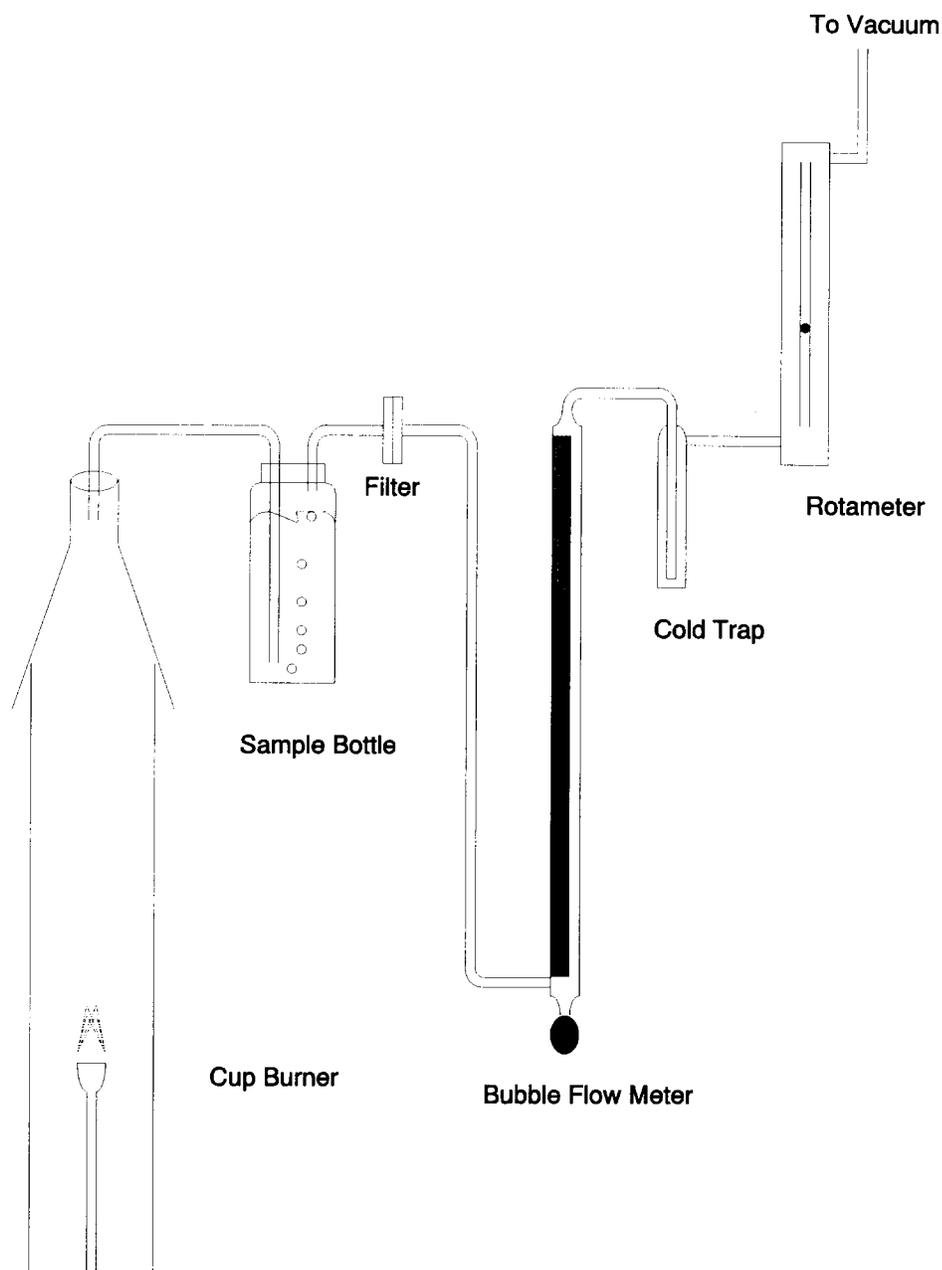


Figure 12. Experimental apparatus for co-flow diffusion flame studies of acid gas formation in inhibited propane-air flames.

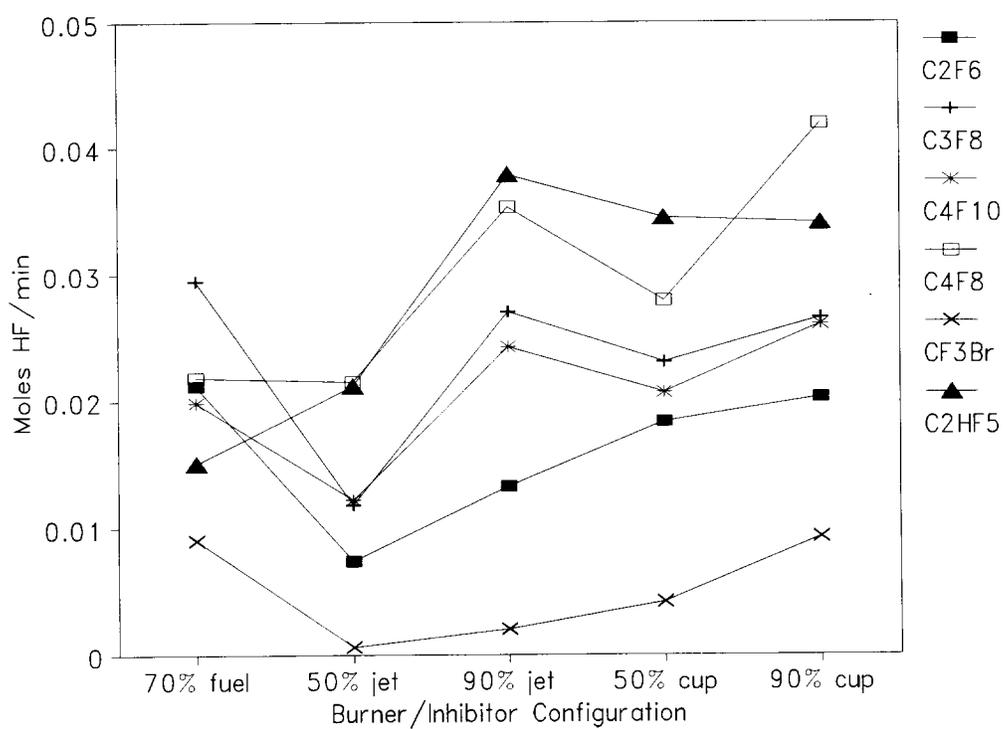


Figure 13. Measured HF production rates in co-flow propane-air diffusion flames. Data are shown for cup and jet burners at 50 and 90% of the extinction concentration for agent added to the air stream, and at 70% in the fuel stream in the cup burner.

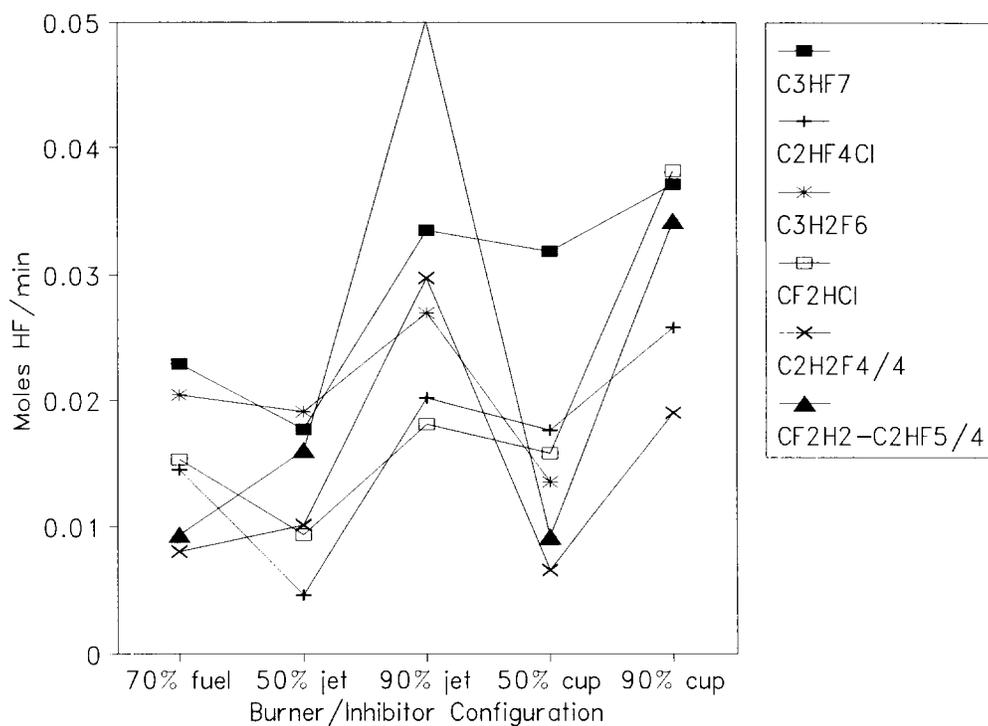


Figure 14. Measured HF production rates in cup and jet burners. Note that the curves for $\text{CF}_2\text{H}_2/\text{C}_2\text{HF}_5$ and $\text{C}_2\text{H}_2\text{F}_4$ are reduced by a factor of 4.

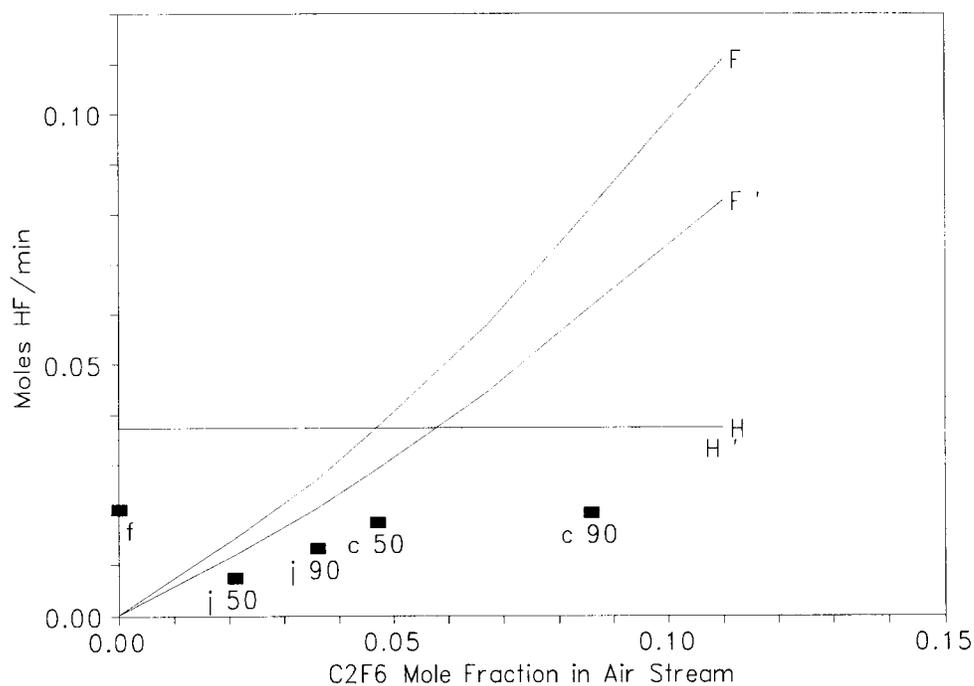


Figure 15. HF produced vs. C₂F₆ mole fraction for cup (c) and jet (j) burners at 50 and 90% of extinction, and with inhibitor addition to the fuel stream (f) of cup burner at 70% of extinction.

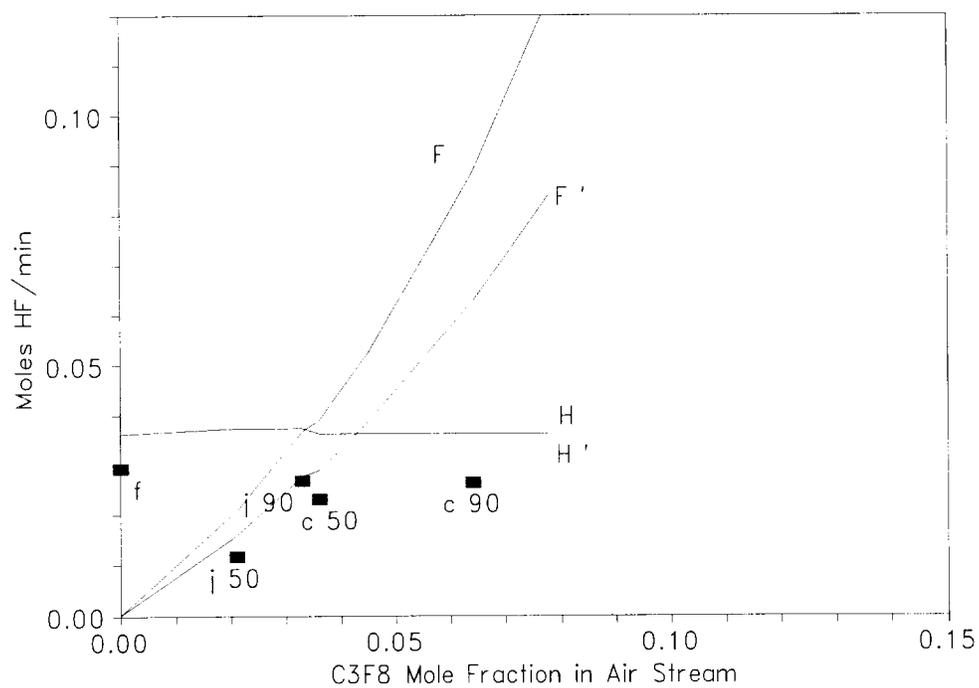


Figure 16. HF produced as a function of C_3F_8 mole fraction in air stream. Label definitions as in Figure 15. Discontinuities in curves are due to slight variations in flows from run to run.

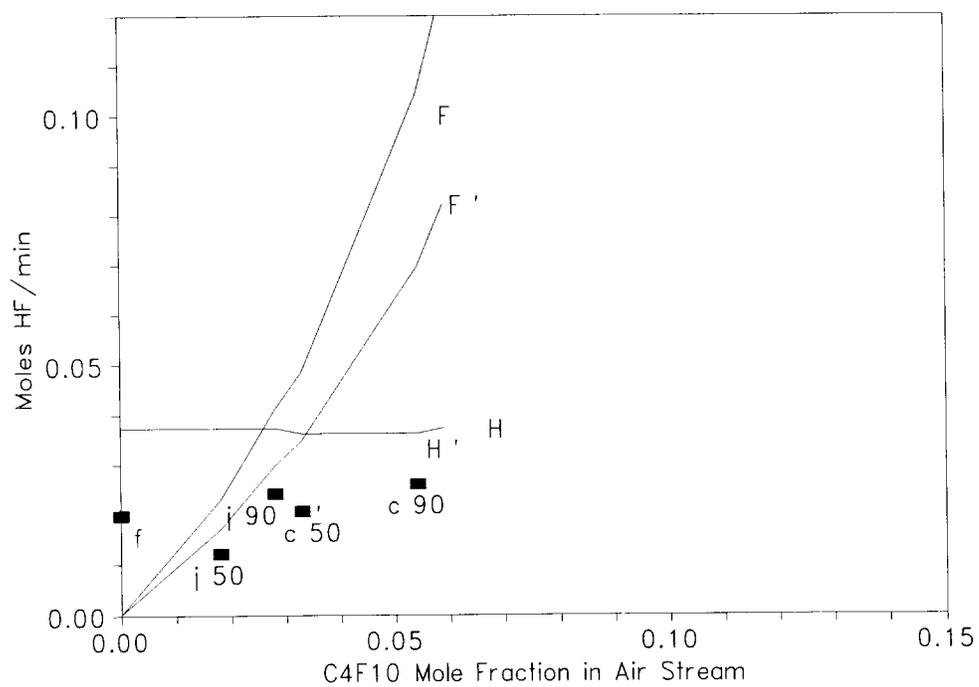


Figure 17. Moles of HF produced as a function of the C₄F₁₀ mole fraction in the air stream. Label definitions as in Figure 15.

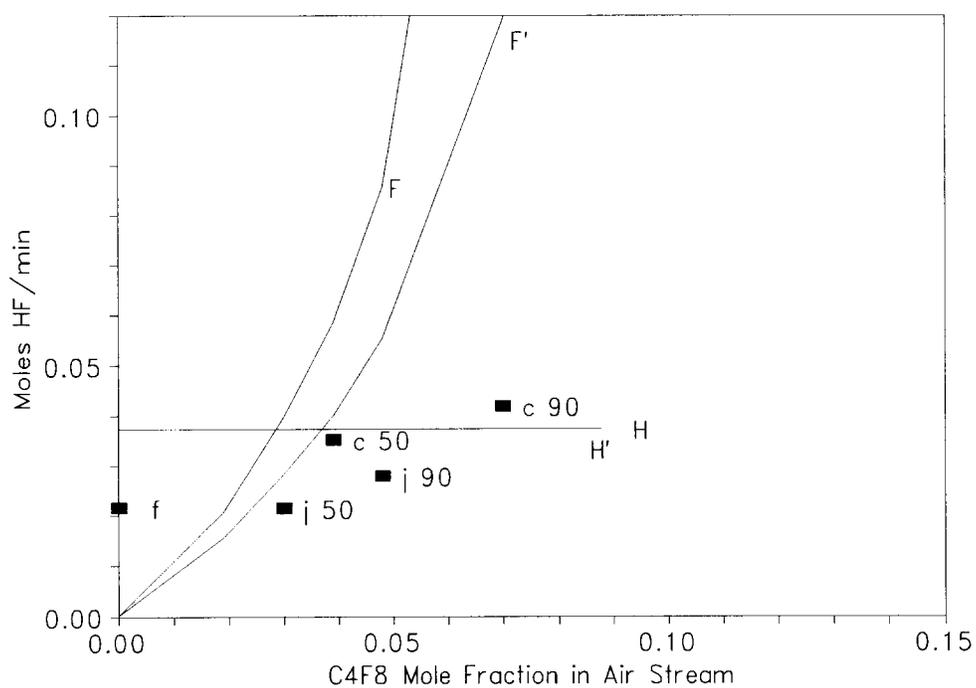


Figure 18. Moles of HF produced as a function of the C₄F₈ mole fraction in the air stream. Label definitions as in Figure 15.

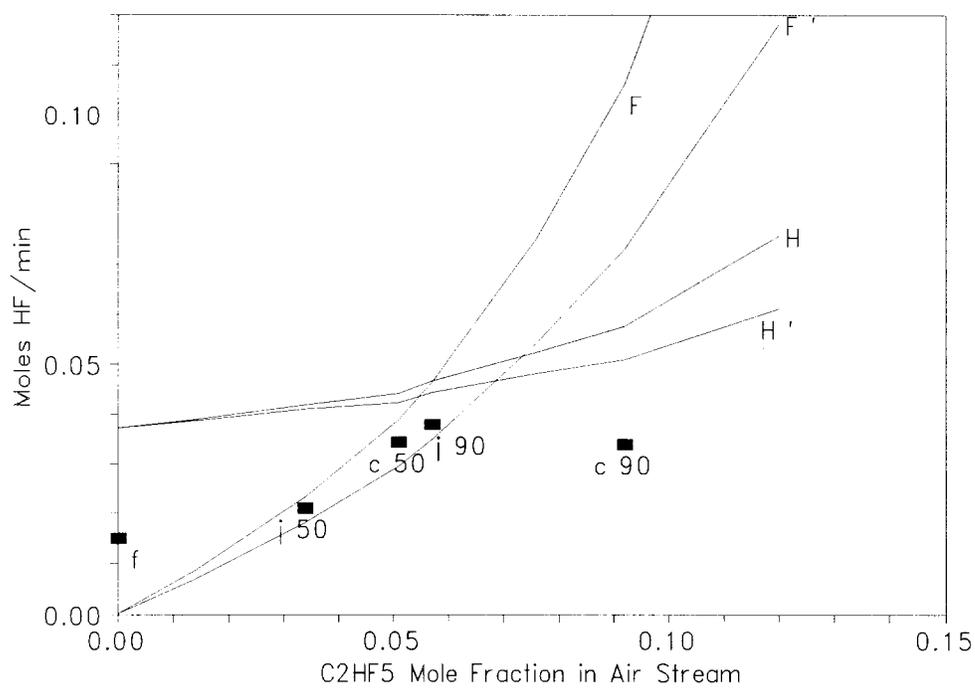


Figure 19. Moles of HF produced as a function of the C₂HF₅ mole fraction in the air stream. Label definitions as in Figure 15.

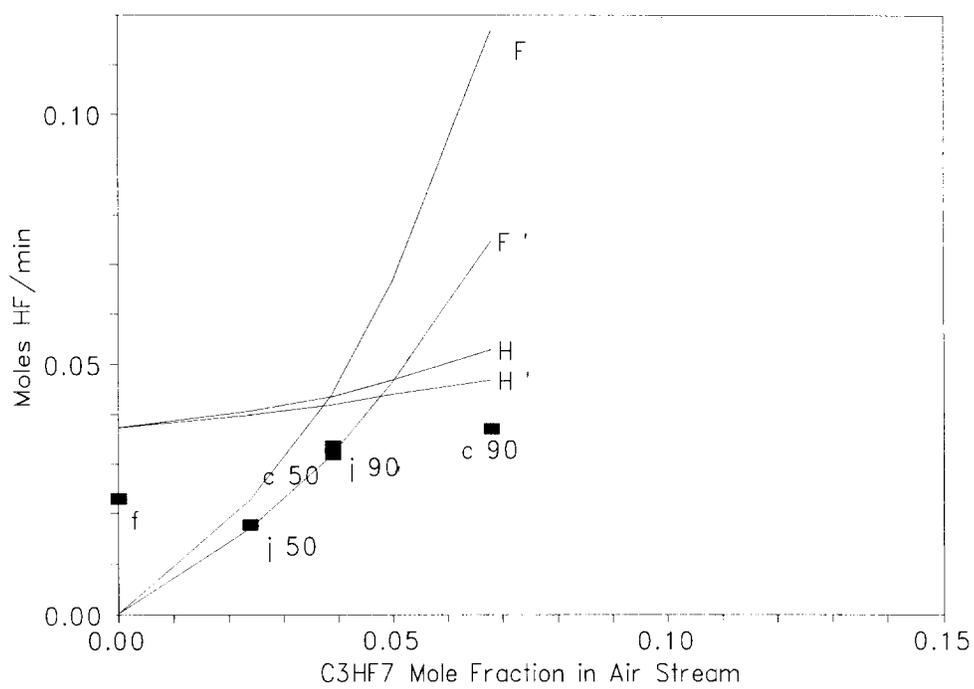


Figure 20. Moles of HF produced as a function of the C_3HF_7 mole fraction in the air stream. Label definitions as in Figure 15.

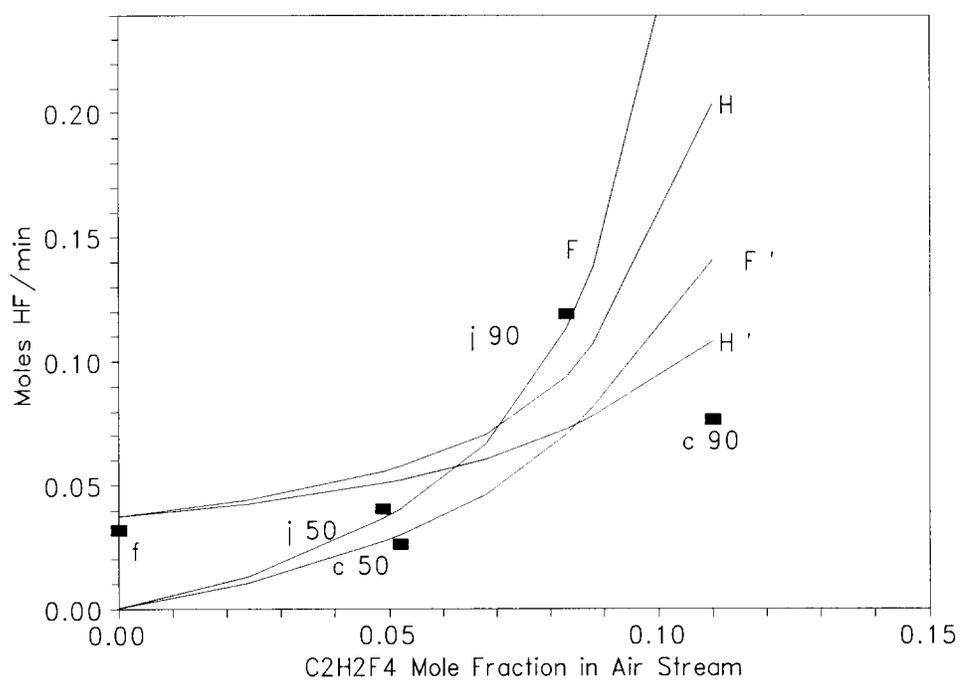


Figure 21. Moles of HF produced as a function of the C₂H₂F₄ mole fraction in the air stream. Label definitions as in Figure 15.

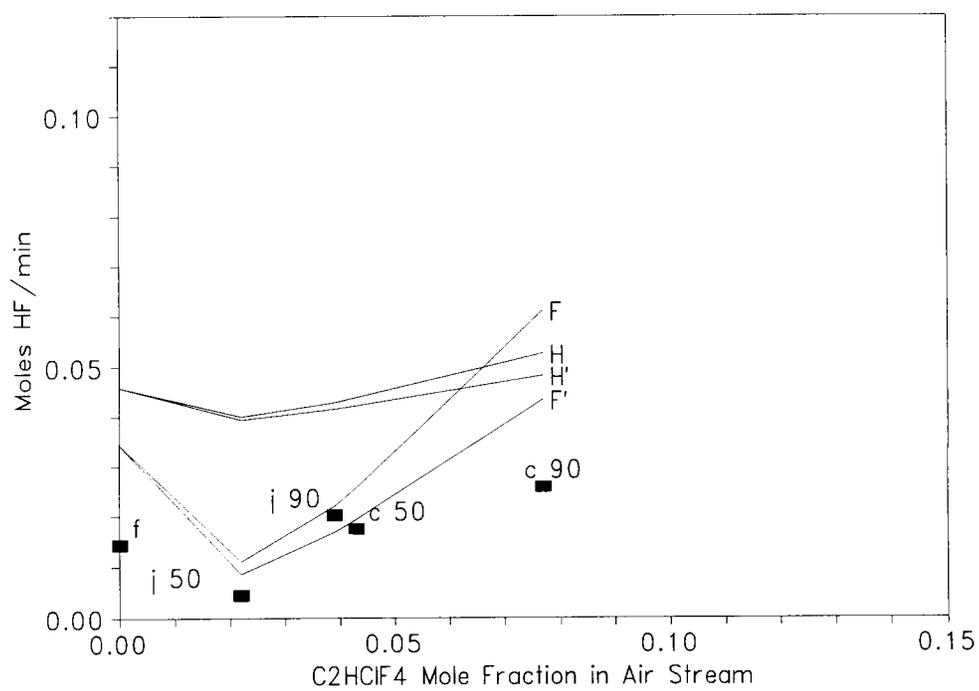


Figure 22. Moles of HF produced as a function of the C_2HClF_4 mole fraction in the air stream. Label definitions as in Figure 15.

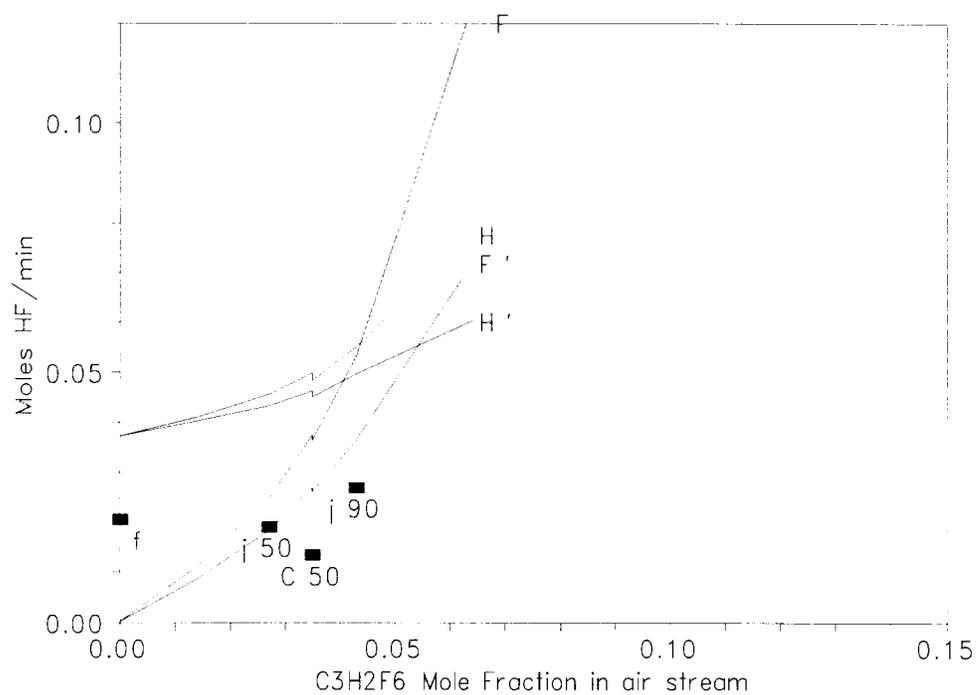


Figure 23. Moles of HF produced as a function of the C₃H₂F₆ mole fraction in the air stream. Label definitions as in Figure 15.

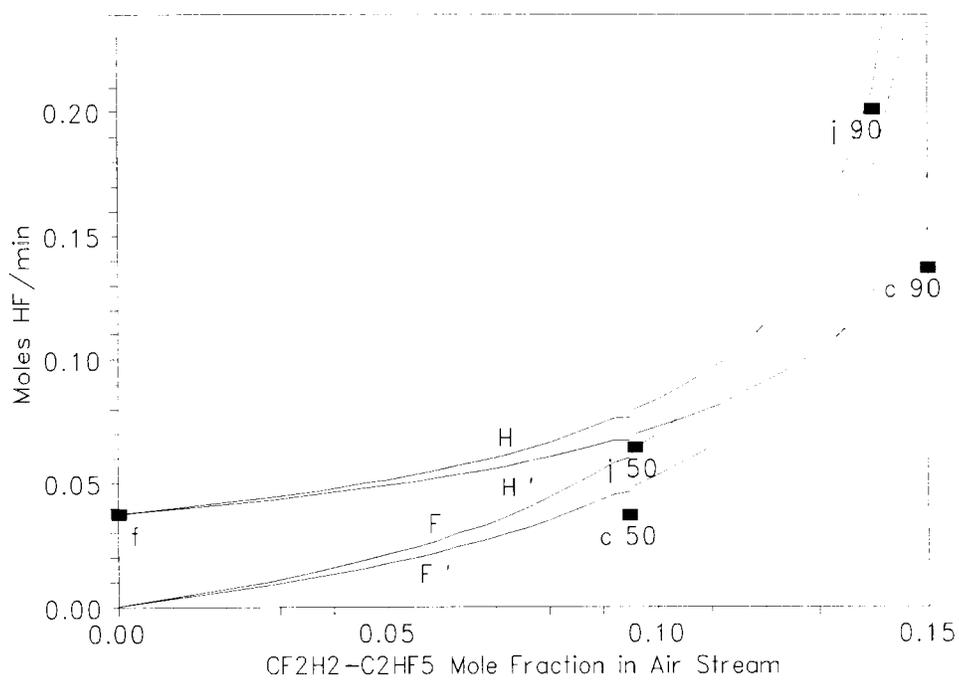


Figure 24. Moles of HF produced as a function of the CF₂H₂/C₂HF₅ mole fraction in the air stream. Label definitions as in Figure 15.

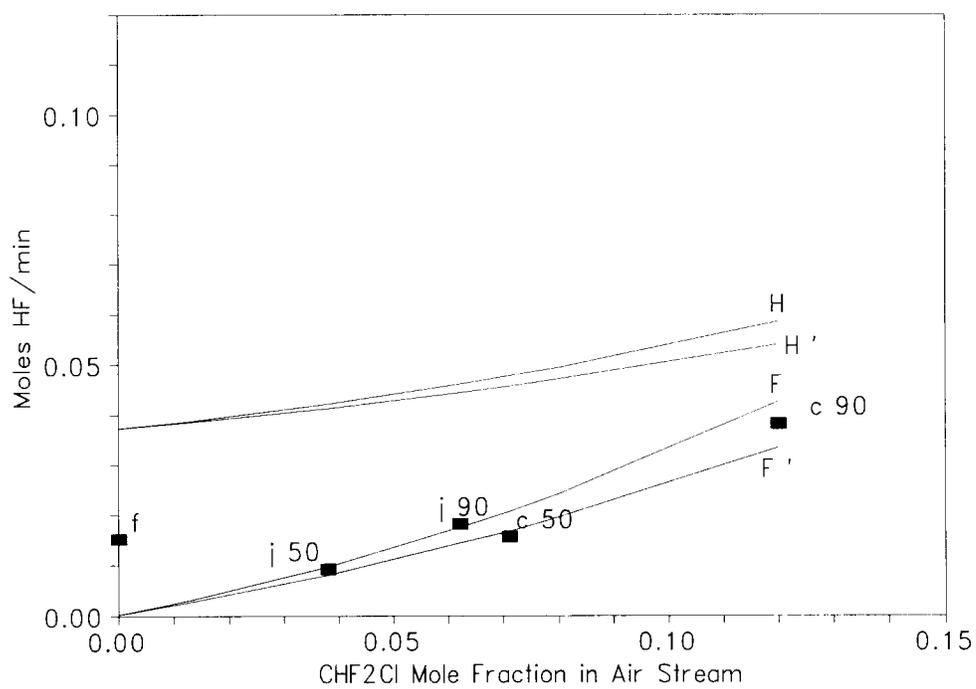


Figure 25. Moles of HF produced as a function of the CHF₂Cl mole fraction in the air stream. Label definitions as in Figure 15.

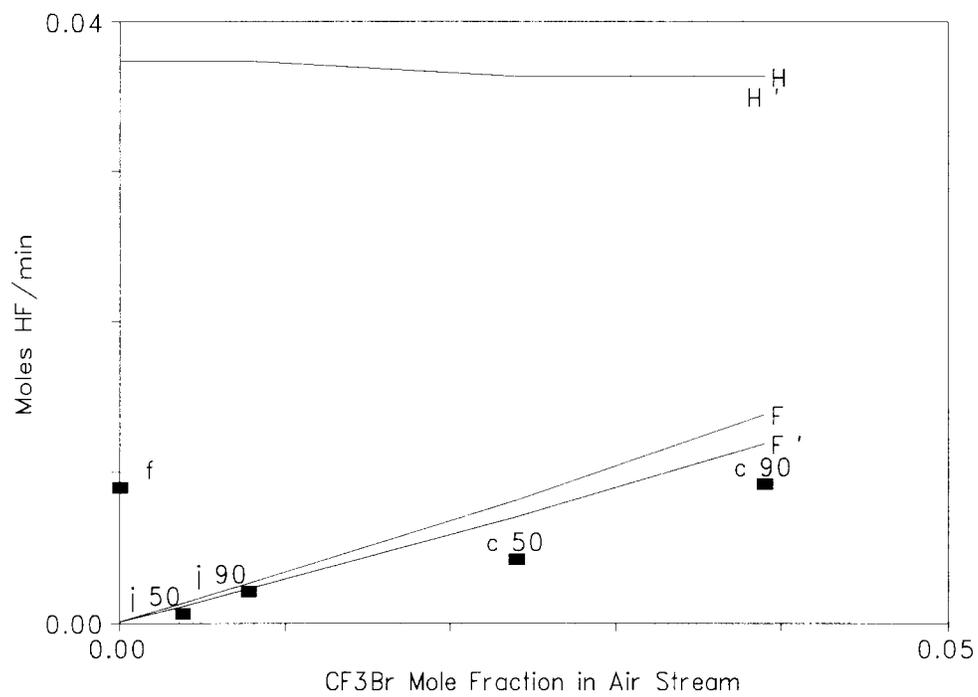


Figure 26. Moles of HF produced as a function of the CF₃Br mole fraction in the air stream. Label definitions as in Figure 15.

5.3 Alternative Low ODP Chemicals with High Fire Suppression Effectiveness

The major objectives of this research were to broaden the scope of alternative agent screening beyond the core candidates listed in Section 1 and to develop and test structure/activity relationships for environmental impact. The motivation for this pursuit was supplied by the following considerations which could be expected to affect the outcome of the alternative agents program:

1. the original list of compounds might not include a viable candidate;
2. guidelines for environmental impact might change without warning; and
3. a new class of environmentally safe fire extinguishants might be identified.

5.3.1 Background. The mechanism by which halons extinguish fires is thought to involve both chemical and physical processes (Sheinson *et al.*, 1989 and Pitts *et al.*, 1990). Simulations using detailed kinetic models (Westbrook, 1983) indicate that hydrogen halides (HX), which form when halons are introduced into flames, promote radical recombination via $\text{HX} + \text{H}(\text{OH}) \rightarrow \text{H}_2(\text{H}_2\text{O}) + \text{X}$. This inhibits the combustion process by reducing the concentration of radicals in the reaction zone. At some point, the rate of recombination exceeds the rate of propagation and the flame is extinguished. Physical suppression results from the removal of thermal energy from the flame by the vibrational excitation of the agent. This mechanism is universal in the sense that all molecules absorb heat, however, it is much less efficient than chemical suppression for the low molecular weight compounds which are most suitable for total flooding applications. Those halocarbons which contain Br or I are chemically active and are considerably more effective (per unit mass) than the corresponding F and Cl-containing compounds which act predominantly as physical suppressants (see Table 7 in Section 4).

The current commercial halons pose a serious threat to the ozone layer. The determining factor is whether they are sufficiently stable to make it into the stratosphere where over 90% of the column height of atmospheric ozone is located (Finlayson-Pitts and Pitts, 1986). Once they enter the stratosphere, halon molecules are photolyzed by short wavelength UV radiation. The halogen atoms released in this process are capable of catalyzing the destruction of ozone through the following mechanism:



where X is Cl, Br or I.

The precise definition of ozone depletion potential (ODP) (Wuebbles, 1983) is

$$ODP(RX) = \frac{\Delta O_3(RX)}{\Delta O_3(CFCl_3)}, \quad (5)$$

where ΔO_3 is the amount of ozone destroyed by emission of compound RX over its entire atmospheric lifetime. This quantity is computed by modeling molecular transport, typically as a function of both latitude and altitude, through the troposphere and into the stratosphere. Chemical and photolytic processes, which can remove the compound from the atmosphere, are accounted for by kinetic

mechanisms which are parameterized on the basis of measured rate constants. The computed ODP depends on the following critical factors:

1. the fraction of molecules which reach the stratosphere, which in turn, depends on how long the molecule survives before it is oxidized or otherwise destroyed in the troposphere;
2. the number of Cl, Br and I atoms in the molecule; and
3. their relative efficiencies in catalyzing the destruction of O₃ according to the mechanism summarized in Equation (1).

The catalytic efficiency of Br is approximately 40 times greater than that of Cl (Pyle *et al.*, 1991). The conversion of halogen oxides into free halogen atoms via



is responsible for a large part of this enhancement. The kinetic constants for the analogous reactions of IO with ClO and BrO have not been measured. There is an indication, however, that low levels of I may greatly enhance the ozone destruction efficiencies of both Cl and Br (Huie, 1993), which are far more prevalent than I in the stratosphere.

The ozone depletion potential of fluorocarbons is essentially zero because, unlike the other halogens, atomic F is quickly converted to the hydrogen halide, HF, which is chemically and photolytically inert. On the other hand, any organic molecule which contains F will absorb infrared radiation in the atmospheric window region between 800 and 1400 cm⁻¹ and will, therefore, have a nonzero global warming potential (GWP). Differences in the GWPs of these compounds are determined primarily by how long they survive in the troposphere.

On the basis of this analysis it is apparent that the most effective suppressants will contain the ozone depleting halogens Br or I. These compounds will almost certainly contain F, as well, since the substitution of F for H atoms is usually necessary to reduce flammability and increase volatility. On this basis, it is clear that low values of both ODP and GWP will be realized only in compounds which have short tropospheric lifetimes (τ_1). Thus, in the process of identifying replacement agents, their propensity to engage in one or more of the following processes which can remove these chemicals from the troposphere was a major concern:

1. reaction with OH radicals;
2. photolysis by long wavelength (> 290 nm) UV-VIS radiation; and
3. hydrolysis and/or solvation in H₂O.

5.3.2 Methods. An exploratory list of 103 potential halon alternatives representing 10 distinct chemical families was cited in NIST TN 1279 (Pitts *et al.*, 1990). This document served as the point of departure and was augmented as new possibilities arose during the course of this investigation.

A short list was constructed from the most promising exploratory compounds. These candidates were selected on the basis of fire suppression effectiveness, suitability for total flooding applications in aircraft dry bays and engine nacelles, commercial availability and ODP. Other properties, including GWP and acute toxicity were also taken into consideration.

The results of cup burner and other fire suppression measurement techniques were available for many of the exploratory compounds (Purdue Research Foundation, 1950; Sheinson, *et al.* 1989; Zallen, 1992). Additional cup burner measurements (see Table 7 of Section 4) were conducted on representative compounds from chemical families which were rated highly with respect to the other

Table 7. ODP, GWP and τ_1 of Selected HCFCs

Formula	HCFC	τ_1	ODP	GWP
CHCl ₂ CF ₃	123	1.6	0.016	0.19
CH ₃ CCl ₃	NA	6.3	0.11	0.024
CHClFCF ₃	124	6.6	0.019	0.10
CH ₃ CCl ₂ F	141b	7.8	0.080	0.092
CHClF ₂	22	15.3	0.051	0.36
CH ₃ CClF ₂	142b	19.1	0.056	0.37

Values taken from Fischer *et al.*, 1989.

selection criteria but for which there were no data relating to their effectiveness as flame suppressants. Compounds requiring suppression concentrations significantly higher than the core candidates were eliminated from further consideration.

Volatility is a critical factor in agent dispersal. Compounds having boiling points above ambient temperature (25 °C), with the possible exception of powders, are not suitable for total flooding applications and were not considered any further.

This investigation was primarily directed at finding near-term solutions to the urgent problem created by the production phaseout of halon 1301. The time and expense involved in developing the capability to produce a new agent was considered prohibitive. Consequently, any compound appearing on the exploratory list which could not be purchased from a commercial vendor was eliminated from further consideration. It will be beneficial to remove this limitation in future investigations directed at identifying second-generation halon replacement candidates.

The hypothesis that τ_1 is a reasonable predictor of both ODP (Herron, 1990) and GWP (Herron, 1990) is confirmed by the data listed in Table 7 and plotted in Figures 27 and 28. Qualitative assessments of τ_1 , and consequently of environmental impact, can be made on the basis of SARs pertaining to the specific chemical family under consideration. Thus, for example, saturated halocarbons (SH) can react with OH if they have a labile C-H bond. The presence of certain functional groups, such as an ether (HE) or carbonyl (HK) oxygen, increase the absorption cross-section for UV-VIS radiation and can activate C-H bonds for abstraction of H by OH (Zhang *et al.*, 1992a). Similarly, OH radicals are known to attack π bonds in unsaturated halocarbons (UH). Many inorganic compounds, including the silicon, germanium (SG), sulfur (S) and phosphorous (P) halides have a tendency to hydrolyze, while metallic compounds (M) are frequently water soluble. The presence of a heavy halogen, particularly I (HI), shifts the absorption spectrum of the compound to the red and thereby increases the likelihood that these compounds will photolyze in the troposphere. This is especially true if there are multiple halogens bonded to the same carbon.

More reliable assessments of τ_1 can be made on the basis of laboratory measurements. At NIST, rate constants for reaction with OH (k_{OH}) have been measured by flash photolysis resonance fluorescence (Kurylo and Braun, 1976). In this technique, a small fraction of the OH radicals generated by photolysis of H₂O are excited by exposure to a high intensity lamp. The time dependent concentrations are monitored by detecting the emissions of resonant radiation from OH at 308 nm with a photomultiplier. A discharge flow technique coupled with electron paramagnetic resonance detection of OH has also been used to measure the OH rate constants for many halogen-containing compounds (Orkin and Khamaganov, 1993a). In either case, the rate constants for the pseudo first-order reaction (*i.e.* [RX] \gg [OH]) are given by

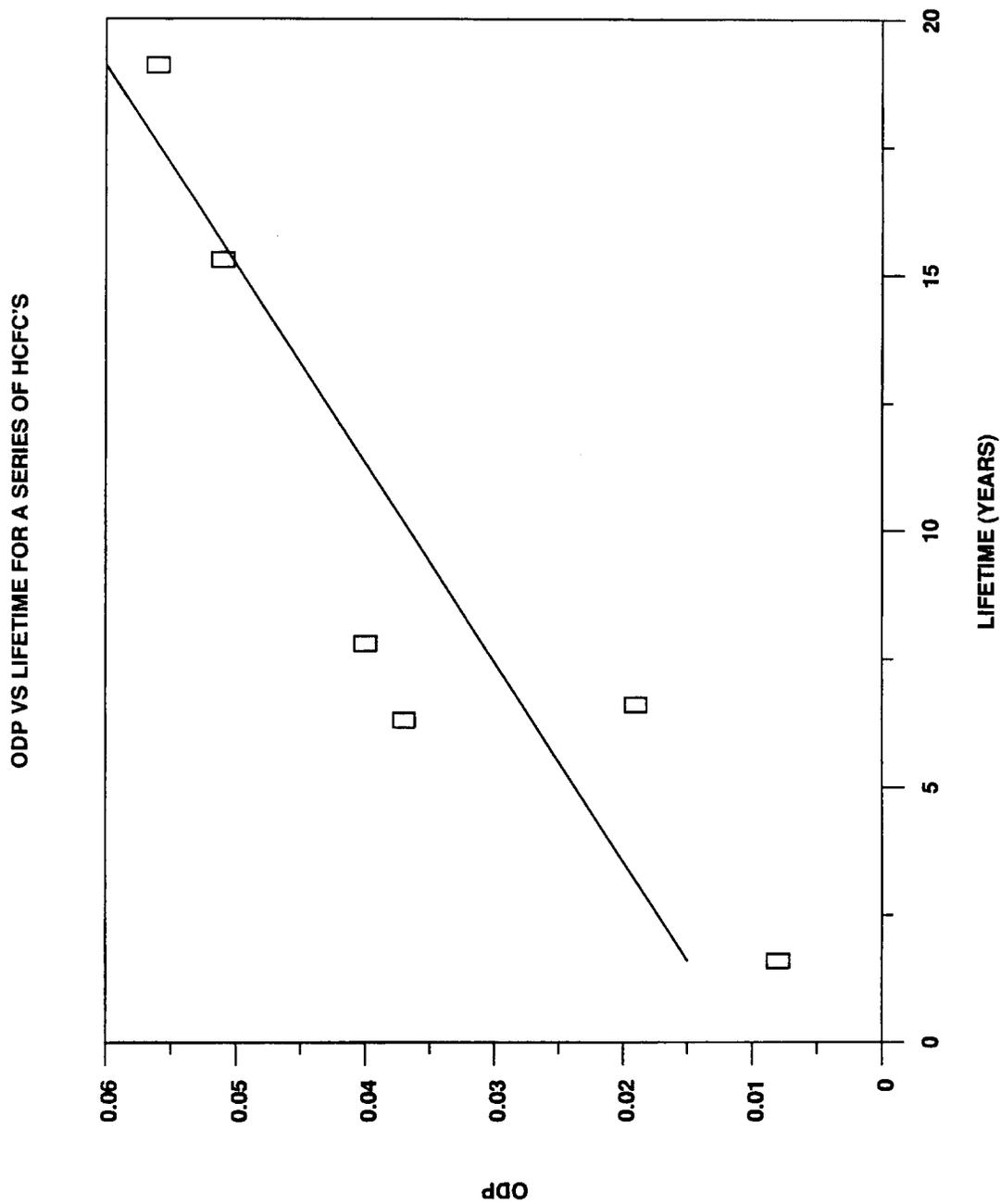


Figure 27. ODP, normalized by dividing the computed value by the number of Cl atoms in the molecule, plotted as a function of tropospheric lifetime.

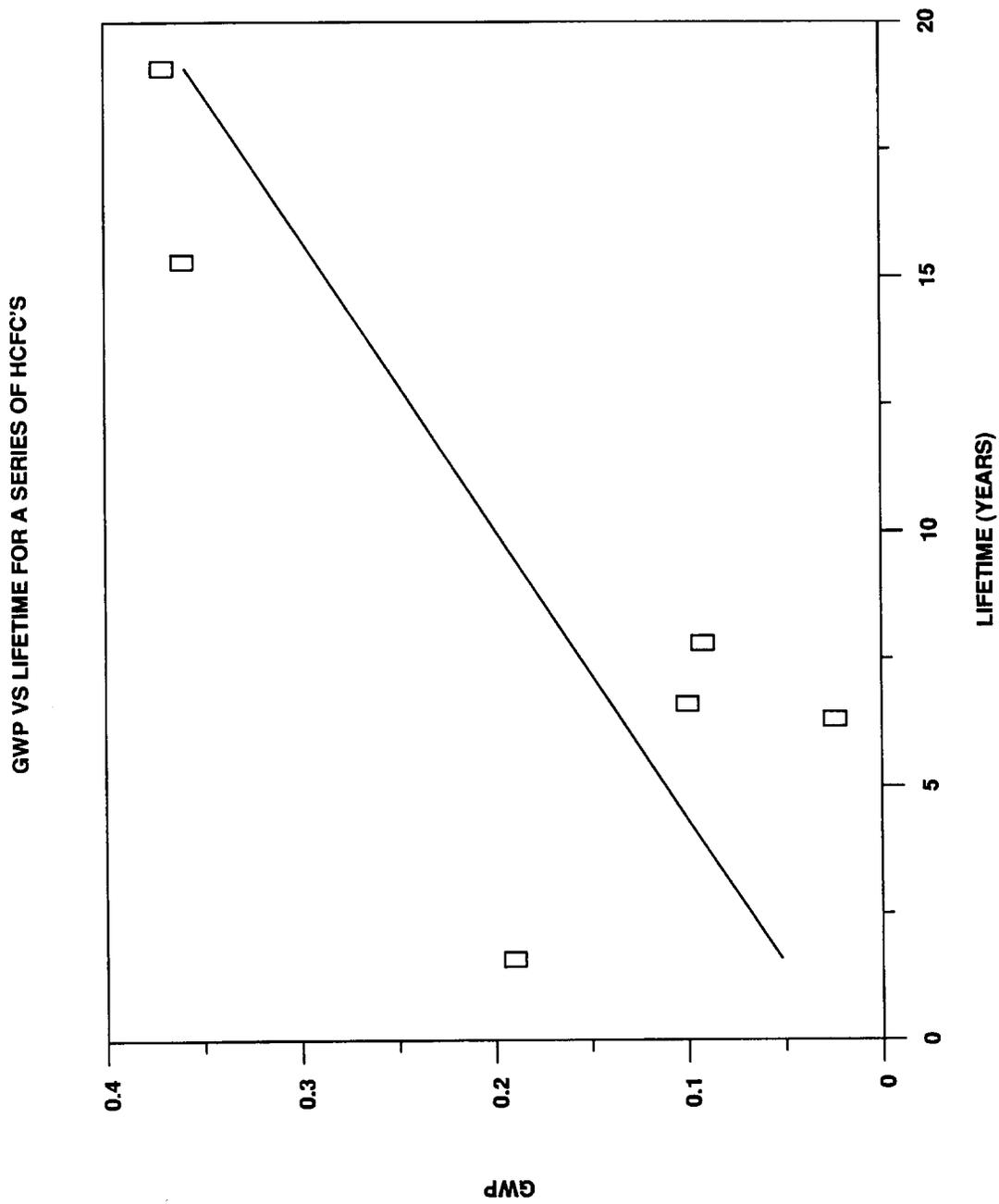


Figure 28. GWP plotted as a function of tropospheric lifetime.

$$k_{OH} = -\frac{1}{[RX]} \frac{d\ln[OH]}{dt}, \quad (7)$$

where RX denotes the compound under investigation and square brackets are used to indicate concentrations. According to Arrhenius theory, the temperature dependence of the rate constant is given in Equation (8).

$$k = A \exp\left(\frac{-E_a}{RT}\right), \quad (8)$$

where R is the gas constant and T is the temperature in Kelvins. The kinetic constants, A and E_a , are the bimolecular collision frequency and activation energy (energy barrier for the reaction), respectively.

In lieu of performing simulations with an atmospheric model, tropospheric lifetimes were estimated from

$$\tau_l = 7.0 \frac{k_{MC}(277)}{k_s(277)}, \quad (9)$$

where $k_{MC}(277)$ and $k_s(277)$ are the rate constants for the reactions of methyl chloroform (CH_3CCl_3) and the alternative agent with OH at 277 K and 7.0 is the lifetime (in years) of CH_3CCl_3 (Zhang *et al.*, 1992b). Methyl chloroform is used as a standard because it has an intermediate τ_l , which is useful for modeling the atmospheric transport of a wide range of compounds, and it is known to have only anthropogenic sources. Kinetic constants for some representative compounds are listed in Table 8.

Experimental measurements of OH reactivity are very expensive. Painstaking efforts have to be taken to ensure sample purity because trace amounts of a reactive contaminant will invalidate the results. In the present investigation, measured rate constants were supplemented with values obtained from correlations between τ_l and C-H bond dissociation energies (BDEs). The basis of these correlations is the hypothesis that the rate determining step in the reaction between OH and saturated halocarbons is the abstraction of a H to form H_2O . This process requires breaking a C-H bond in the halocarbon. The natural logarithm of τ_l (Fischer *et al.*, 1989) is plotted as a function of the smallest C-H BDE (McMillan and Golden, 1982) in the molecule for a series of HFCs in Figure 29. The linearity of this plot confirms the validity of this hypothesis.

Experimental determinations of BDEs are difficult to make and are subject to large errors, however, recent advances in the theory and application of molecular quantum mechanics have made the calculation of chemically accurate BDEs in small halocarbons almost routine (Curtiss *et al.*, 1991). The C-H and C-X BDEs were computed for some small molecules using a variety of *ab initio* methods including: local (LDA) and nonlocal density functional approximations (NLDA); Hartree-Fock (HF) and HF corrected to fourth order in the Moller-Plesset perturbation expansion of the energy (MP4); and the Gaussian-G1 (G1) and -G2 (G2) procedures. The results of these calculations are listed in Tables 9 and 10. The rms error from the experimental BDEs (McMillan and Golden, 1982) for the fluoro- and chloromethanes corresponding to the most accurate calculations (G2) are less than 5 kJ/mole and 10 kJ/mole, respectively.

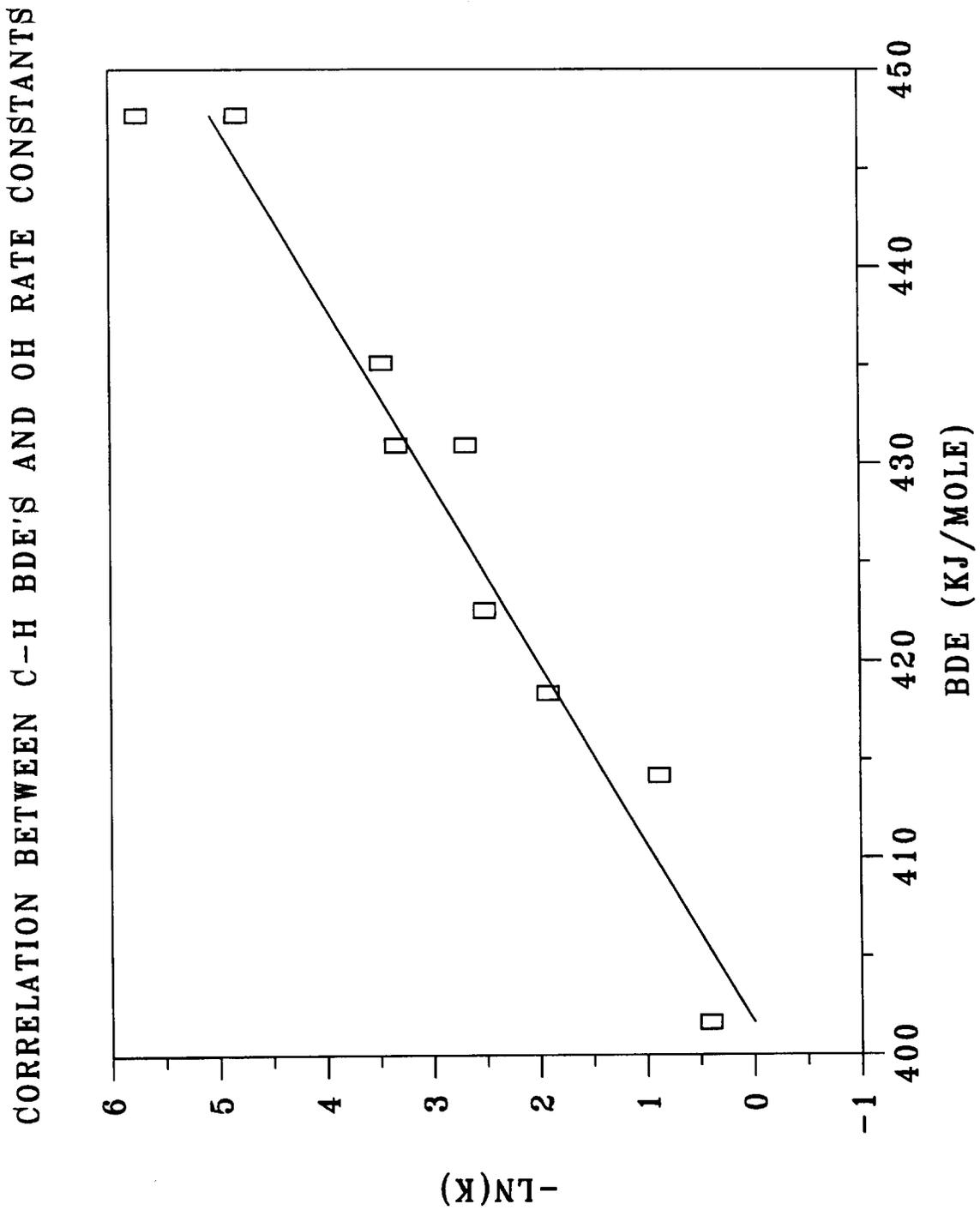


Figure 29. Tropospheric lifetime plotted as a function of C-H BDE.

Table 8. OH Kinetic Constants and τ_1 's of Selected Compounds

Compound	A ($\times 10^{12}$) ^a	E _a /R (K)	τ_1 (years) ^b
Substituted Methanes			
CH ₄	7.0	2061	12.8
CHF ₃	0.49	2115	192
CHF ₂ Cl	0.81	1516	14.0
CHF ₂ Br	0.93	1326	6.8
Substituted Ethanes ^c			
CH ₃ CH ₃	7.8	1020	0.27
CH ₂ FCF ₃	1.03	1588	14.3
CH ₂ BrCF ₃	0.85	1113	3.4
CHClBrCF ₃	1.28	995	1.6
Substituted Ethenes			
CH ₂ =CH ₂	2.03	-411	0.0047
CH ₂ =CHBr	1.8	-405	0.0068
CF ₂ =CCl ₂	1.5	-480	0.0062

a. In units of cm³ molecule⁻¹ s⁻¹.

b. From Equation 9.

c. Orkin and Khamaganov, 1993a and 1993b.

Table 9. C-H and C-F BDEs in the Fluoromethanes, kJ/mol

Bond	LDA ^a	NLDA ^a	HF ^b	MP4 ^b	G1 ^b	G2 ^b	Exp. ^c
CH ₃ -H	494	464	362	458	434	435	440
CH ₂ F-H	464	447	353	440	422	424	424
CHF ₂ -H	458	496	354	441	422	424	432
CF ₃ -H	482	461	462	462	443	445	447
CH ₃ -F	570	478	273	447	462	463	460
CH ₂ F-F	599	502	322	488	503	505	500
CHF ₂ -F	621	565	359	520	535	537	534
CF ₃ -F	629	510	374	533	548	551	546

aBiosym Technologies, Inc., 1992.

bFrisch, M.J., *et al*, 1992.

cMcMillan and Golden., 1982.

Table 10. C-H and C-Cl BDEs in the Chloromethanes, kJ/mol

Bond	LDA ^a	NLDA ^a	HF ^b	MP4 ^b	G1 ^b	G2 ^b	Exp. ^c
CH ₃ -H	494	464	362	458	434	435	440
CH ₂ Cl-H CH ₂ Cl-H	4654	4444	3513	4184	4164	4164	4224
CHCl ₂ -H	431	419	338	401	401	401	414
CCl ₃ -H	415	401	322	385	390	390	401
CH ₃ -Cl	376	351	226	340	349	347	354
CH ₂ Cl-Cl	334	320	200	318	337	334	335
CHCl ₂ -Cl	304	286	165	291	321	315	325
CCl ₃ -Cl	272	247	128	265	301	297	306

^aBiosym Technologies, Inc., 1992.^bFrisch, M.J. *et al.*, 1992.^cMcMillan and Golden, 1982.Table 11. Photolytic Rate Constants and τ_1 's of Selected Compounds^a

Compound	k_p	τ_1 (years) ^b
CF ₂ ClBr	2.2×10^{-9}	14
CF ₂ Br ₂	2.3×10^{-8}	1.3
CF ₃ I	6.4×10^{-6}	0.0047

^aHerron, 1990 and references therein.^bFrom Equation 11.

Rate constants for photolysis were obtained from

$$k_p = \int f \sigma d\lambda, \quad (10)$$

where the integral is over the wavelength range of atmospherically accessible solar radiation, f is the solar flux of photons, and σ is the measured UV-VIS absorption cross-section. Values for representative compounds are listed in Table 11. In this approximation, the quantum yield for photodissociation is assumed to be unity. Tropospheric lifetimes were estimated from

$$\tau_l = \frac{3 \times 10^{-8}}{k_p}, \quad (11)$$

where the factor in the numerator converts from seconds to years.

5.3.2.2 Exploratory List. The plan of work for this task was based on a strategic organization of the candidates into four working categories. The first of these, hereafter referred to as Category I, comprise the 41 halocarbons identified in NIST TN 1279 which contain at least one Cl, Br or I atom. These compounds are listed in Table 12. Unfortunately, all Category I compounds have some potential for ozone depletion and global warming. The expectation was, however, that the environmental impact of some of these compounds would be acceptable due to their reactivity with OH radicals, or their tendencies to undergo photolysis in the troposphere.

The Category II candidates, which are listed in Table 13, are the complementary set of halocarbons which contain F as the only halogen. As a group, fluorocarbons are much less effective as fire suppressants than are the analogous compounds containing Br or I (see Table 7 of Section 4). All of the compounds in this category are considered to have zero ODP; however, GWP was an important consideration.

Category III consists of the halogen-containing inorganic compounds identified in NIST TN 1279 (Table 14). Many of these compounds, for example CrO_2Cl_2 and SnCl_4 , are highly toxic and are, therefore, not viable halon replacement candidates. The justification for their further consideration was that some are extremely effective flame inhibitors. The expectation was that new and important principles would be learned in the process of evaluating and comparing their effectiveness as fire suppressants and that these insights could be immediately applied to further the primary objectives of this project.

The non-halogenated inorganic compounds identified in NIST TN 1279 were placed in Category IV. They are listed in Table 15. All have zero ODP and minimal GWP.

5.3.3 Results. The selection process was carried out in two steps. First, compounds were eliminated from the exploratory list on the basis of boiling point (BP), commercial availability (CA), and other readily available data. Core candidates (indicated by the presence of an asterisk) were evaluated elsewhere in this report (see Section 10.2) and were not explicitly included in this process.

Table 12. Category I Compounds

Compound Formula	Chemical Family	Basis for Elimination or Further Consideration
CBr_2F_2	SH	ODP ^a
$\text{C}_2\text{Br}_2\text{F}_4$	SH	BP ^b
CHClF_2^*	SH	see Section 10.2
$\text{C}_2\text{H}_3\text{Cl}_3$	SH	BP
$\text{C}_2\text{HCl}_2\text{F}_3$	SH	BP
$\text{C}_2\text{HClF}_4^*$	SH	see Section 10.2
$\text{C}_2\text{H}_3\text{Cl}_2\text{F}$	SH	BP
$\text{C}_2\text{H}_3\text{ClF}_2$	SH	FSN ^c
CHBrF_2	SH	ODP
CHBrClF	SH	BP
$\text{C}_2\text{HBrClF}_3$	SH	BP
$\text{C}_2\text{HBrClF}_3$	SH	BP
C_2HBrF_4	SH	CA ^d
$\text{C}_2\text{H}_2\text{BrF}_3$	SH	BP
$\text{C}_2\text{HBr}_2\text{F}_3$	SH	BP
$\text{C}_2\text{H}_2\text{Br}_2\text{F}_2$	SH	BP
$\text{C}_2\text{H}_2\text{Br}_2\text{F}_2$	SH	BP
C_3HBrF_6	SH	BP
$\text{C}_3\text{H}_2\text{Br}_2\text{F}_4$	SH	BP
$\text{C}_3\text{H}_2\text{Br}_2\text{F}_4$	SH	BP
$\text{C}_3\text{H}_2\text{BrF}_5$	SH	BP
$\text{CF}_3\text{COCH}_2\text{Br}$	HK	BP
$\text{BrCF}_2\text{COOCF}_3$	HK	BP
$\text{CF}_3\text{COOCH}_2\text{Br}$	HK	BP
$\text{BrCF}_2\text{CF}=\text{CF}_2$	UH	BP
$\text{CF}_3\text{CF}=\text{CFBr}$	UH	BP
$\text{CF}_3\text{BrC}=\text{CHCF}_3$	UH	BP
$\text{CHF}_2\text{OCF}_2\text{CHFCI}$	HE	BP
$\text{CF}_3\text{CHClOCHF}_2$	HE	BP
$\text{CF}_2\text{BrOCF}_2\text{Br}$	HE	CA
$\text{CF}_2\text{BrOCF}_3$	HE	CA
$\text{CBrF}_2\text{OCF}_2\text{CHFCI}$	HE	BP

Table 12. Category I Compounds

Compound Formula	Chemical Family	Basis for Elimination or Further Consideration
BrC ₄ F ₇ O	HE	BP
CF ₃ I	HI	short list
CF ₂ ClI	HI	CA
CF ₂ BrCF ₂ I	HI	BP
CF ₂ ICF ₂ I	HI	BP
CH ₃ I	HI	BP
CH ₃ CH ₂ I	HI	BP
CH ₃ CH ₂ CH ₂ I	HI	BP
CF ₃ CF ₂ CF ₂ I	HI	BP

- a. ozone depletion potential
- b. boiling point
- c. fire suppression number (see the definition given in Section 4.5.5.3)
- d. commercial availability
- * core candidate

Table 13. Category II Compounds

Compound	Family	Basis for Elimination or Further Consideration
CF ₄	SH	FSN
C ₂ F ₆ *	SH	see Section 10.2
C ₃ F ₈ *	SH	see Section 10.2
C ₄ F ₁₀ *	SH	see Section 10.2
C ₄ F ₈ *	SH	see Section 10.2
CHF ₃	SH	FSN
C ₂ HF ₅ *	SH	see Section 10.2
C ₂ H ₂ F ₄ *	SH	see Section 10.2
CF ₃ COCF ₃	HK	FSN
CF ₃ COOCOCF ₃	HK	BP
(iC ₃ F ₇) ₂ CO	HK	BP
CF ₃ COOCH ₃	HK	BP
C ₃ F ₆	UH	short list
C ₄ F ₈	UH	FSN
CF ₃ C ₆ H ₅	UH	BP
CF ₃ CH=CF ₂	UH	short list
CF ₂ CH=CHCF ₃	UH	FSN
CF ₃ CH=CH ₂	UH	FSN
(C ₄ F ₉)CH=CH(C ₄ F ₉)	UH	BP
(CF ₃) ₂ C=C(CF ₃) ₂	UH	BP
CHF ₂ OCHF ₂	HE	FSN
CHF ₂ OCF ₃	HE	FSN
C ₄ F ₉ C ₄ F ₇ O	HE	BP
C ₄ F ₈ O	HE	BP
CF ₃ SCF ₃	HE	CA
(CF ₃) ₃ N	HE	CA

Table 14. Category III Compounds

Compound	Chemical Family	Basis for Elimination or Further Consideration
SF ₆	S	FSN
SF ₅ Cl	S	FSN
SF ₅ Br	S	CA
PF ₃	P	hazardous
PCl ₃	P	BP
PF ₂ Br	P	CA
POF ₃	P	hazardous
POCl ₃	P	BP
POF ₂ Br	P	BP
SiCl ₄	SG	BP
SiCl ₃ F	SG	CA
SiF ₄	SG	short list
SiBrF ₃	SG	CA
SiBr ₃ F	SG	BP
Si(CH ₃) ₃ Cl	SG	BP
SiCH ₃ Cl ₃	SG	BP
Si(CH ₃) ₃ CH ₂ Cl	SG	BP
GeCl ₄	SG	BP
CrO ₂ Cl ₂	M	BP
SnCl ₄	M	BP
TiCl ₄	M	BP

The major reason for the elimination of each exploratory compound is noted next to its chemical formula in Tables 12-15. Although values for ODP and relative fire suppression efficiency, as indicated by fire suppression number (FSN) (Section 4.5.5.3), could not be found for every compound on the exploratory list, a reasonable assessment could usually be made on the basis of measured values obtained for other members from the same chemical family. Those candidates which were considered to merit further study, as well as, a few additional possibilities which arose during the course of this investigation, were included in a short list of compounds. These compounds were evaluated in the second step of the search process.

Table 15. Category IV Compounds

Compound	Chemical Family	Basis for Elimination or Further Consideration
Si(CH ₃) ₄	SG	BP
Ge(CH ₃) ₄	SG	CA
NaHCO ₃	M	see Section 10.2
NaC ₂ H ₃ CO ₂	M	BP
KHCO ₃	M	BP
K ₂ C ₂ O ₄ •H ₂ O	M	BP
KC ₂ H ₃ CO ₂	M	BP
K ₂ C ₅ H ₇ O ₂ •½H ₂ O	M	BP
Cr(C ₅ H ₇ O ₂) ₃	M	BP
Pb(C ₂ H ₅) ₄	M	BP
Fe(CO) ₅	M	BP
N ₂	I	FSN
CO ₂	I	FSN
Ar	I	FSN

5.3.3.1 Development of the Short List. The fire suppression characteristics of the chlorocarbons are comparable to their fluorocarbon analogs (see Table 7 of Section 4). Two of these compounds, CF₂=CClF and CHFCl₂, appeared to offer promising atmospheric properties, as well. The ozone destruction efficiency of Cl is significantly less than that of Br. Thus, for example, the ODP of CHF₂Cl is only 0.055, whereas the ODP of CHF₂Br is 1.4 (Pyle *et al.*, 1991). The presence of a π bond ensures that the τ_1 of CF₂=CClF will be short (see Table 8) which suggests that both the ODP and GWP will be low. The computed BDE for the C-H bond in CHFCl₂ is 398 kJ/mole which is 17 kJ/mole less than the C-H BDE in CHF₂Cl. On the basis of the correlation in Figure 29, this effect should correspond to an order of magnitude reduction in τ_1 . Consequently, the ODP of CHFCl₂ should be significantly lower than 0.055 even though it contains twice as many ozone depleting halogens as CHF₂Cl.

The brominated methanes, particularly CF₂Br₂ and CBr₄, were of further interest. The presence of multiple Br atoms ensures a low FSN and imparts a significant cross-section for the absorption of long wavelength UV-VIS radiation which, in turn, increases the likelihood that these compounds will be photolyzed in the troposphere (see Table 13). The possibility that one of the brominated ethanes might be viable was raised by recent results obtained for CF₃CHBrCl (Orkin and Khamaganov, 1992b). The best estimate ODP for this compound is 0.14 (Pyle *et al.*, 1991) which is almost at the upper limit of acceptability. The brominated ethenes, CF₂=CFBr and CF₂=CHBr, are reactive with OH and were also expected to have acceptable ODPs.

Table 16. The Short List of Candidates

Family	Chemical Formula	Basis for Elimination or Further Consideration
Category I		
Chlorinated Methanes	CHFC1 ₂	FSN (2.9)
Chlorinated Ethenes	CF ₂ =CClF	FSN (2.8)
Brominated Methanes	CHF ₂ Br, CF ₂ Br ₂ , CBr ₃	ODP (1.4, 1.25) BP (107 °C)
Brominated Ethanes	CH ₂ BrCF ₃	BP (26 °C)
Brominated Ethenes	CF ₂ =CBr, CF ₂ =CHBr	FSN (2.3, 1.9)
Iodocarbons	CF ₃ I	recommended
Category II		
Fluorinated Ethenes	CF ₂ =CFCF ₃	FSN (2.5)
Category III		
Silicon Compounds	SiF ₄	FSN (3.3)
Nitrogen Compounds	NF ₃	FSN (oxidizer)

The iodocarbons are effective suppressants (Nimitz and Lankford, 1993) and they are known to be light sensitive, which suggests that they will be photolyzed in the troposphere. The iodine analog of halon 1301, CF₃I, was considered particularly attractive because it also has a low boiling point (-22.5 °C) which makes it suitable for total flooding applications.

All of the compounds in Category II have zero ODP; however, the high GWP of the saturated fluorocarbons on the exploratory list might play an important role in determining whether they can be used as fire extinguishants. Many of these compounds are core candidates and were already undergoing thorough testing. Thus, in an effort to avoid a duplication of effort, the decision was made to focus on the unsaturated fluorocarbons. Particular attention was placed on compounds, such as CF₂=CHCF₃ and CF₂=CFCF₃, where the C-F bond might be weakened by resonance stabilization in the radical. The rationale was the hypothesis that the exceptionally strong C-F bonds, which characterize most of the fluorocarbons, might have an adverse effect on their effectiveness as flame suppressants.

Similar reasoning was used to justify the further consideration of two inorganic halides, SiF₄ and NF₃. The former compound readily hydrolyzes to HF and silanol in the atmosphere, whereas the N-F bonds in the latter molecule are exceptionally weak.

5.3.3.2 Recommendations. The short list is presented in Table 18 along with the primary reason for the elimination of each candidate. The FSNs of the chlorinated methanes and ethenes, the fluorinated ethenes, and SiF₄ were noticeably worse than the corresponding values obtained for the leading candidates from the core list. The brominated ethenes were a little better, but not enough to warrant the recommendation of a Br-containing compound. NF₃ was disqualified because it behaved

as an oxidizer resulting in a visible increase in the intensity of the cup burner flame. Two of the compounds on the short list, CHF_2Br and CF_2Br_2 , were eliminated because their ODPs were unacceptably high, as were the boiling points of CFBr_3 and CH_2BrCF_3 . The boiling point of the former compound was mistakenly reported as 10.7°C in some of the relevant literature (Zallen, 1992). The actual boiling point of CFBr_3 is 107°C . On the basis of the reasoning presented in this section, it was determined that CF_3I is the only candidate which merits further consideration with respect to the near term applications of the sponsor.

The concentration of CF_3I required to extinguish the cup burner flame was $3.2 \pm 0.3\%$ by volume. This is almost identical to the value obtained for halon 1301 (3.1%). The UV-VIS cross-section for CF_3I is displayed in Figure 30. The short τ_1 of this molecule is attributable to the tail of this curve which extends to wavelengths beyond 290 nm where there is an appreciable solar flux at ground-level.

Detonation and deflagration suppression tests (see Section 4.5) have indicated that CF_3I is the most effective agent tested (including halon 1301) at mole fractions less than about 3%. Its effectiveness in suppressing detonation, however, diminished at higher concentrations, eventually becoming one of the least effective agents at concentrations exceeding 6%. The C-I bond in CF_3I is very weak. The results obtained from photofragmentation translational spectroscopy indicate that the corresponding BDE is about 223 kJ/mole (Felder, 1992). This suggests that reactivity, particularly when in the presence of metals which can function as heterogeneous catalysts, may present a significant problem. Indeed, the results of coupon corrosion tests have indicated the possibility of aggressive interactions between CF_3I and both AM355 and CD172 (see Section 7.2).

Atmospheric modeling of CF_3I was performed by the Atmospheric and Geophysical Sciences Division at Lawrence Livermore National Laboratory. This effort was intended to be a first attempt at a solution to a difficult problem. Computed values for the ODP of CF_3I , particularly for releases at altitude, should be considered as preliminary estimates due to the presence of a number of serious data gaps in the stratospheric chemistry of iodine. These include (Miziolek, 1993):

1. the absence of rate constants and branching ratios for the critical reactions of IO with BrO and ClO;
2. no measurements of the rate of photolysis of IO; and
3. no studies of the temperature dependencies of the reactions of IO with HO_2 and O.

The calculations performed at LLNL were based on the extended IOx chemistry which uses bromine analog rate constants for the reactions of IO with ClO, OH and NO_3 , as well as, for the reaction of HI with O. The values obtained for the ODP and tropospheric lifetime corresponding to a ground-level release were 0.011 and 1.15 days, respectively. These findings are consistent with the previous estimates made by Susan Solomon. The LLNL group also performed a simulated high altitude release of CF_3I at 19.5 km (over latitudes extending from 23.5 to 58.2 degrees N). They calculated an ODP of 13.7 and a lifetime of 9.05 hours. Please note that the ODP value for the release of CF_3I at altitude is very close to the ground level ODP of CF_3Br (~ 16). This is an artifact of the extended IOx chemistry used in the LLNL model which assumes that the stratospheric chemistry of I is essentially identical to that of Br.

5.3.4 Conclusions. CF_3I is a viable candidate for the replacement of halon 1301. This is the first iodine-containing compound to be seriously considered. Other members of this family may have applications as fire extinguishants, and as refrigerants and foam blowing agents, as well. Every effort should be made to resolve the uncertainties in the stratospheric chemistry of iodine so that there is a clear path to examine all of the potential uses of these compounds.

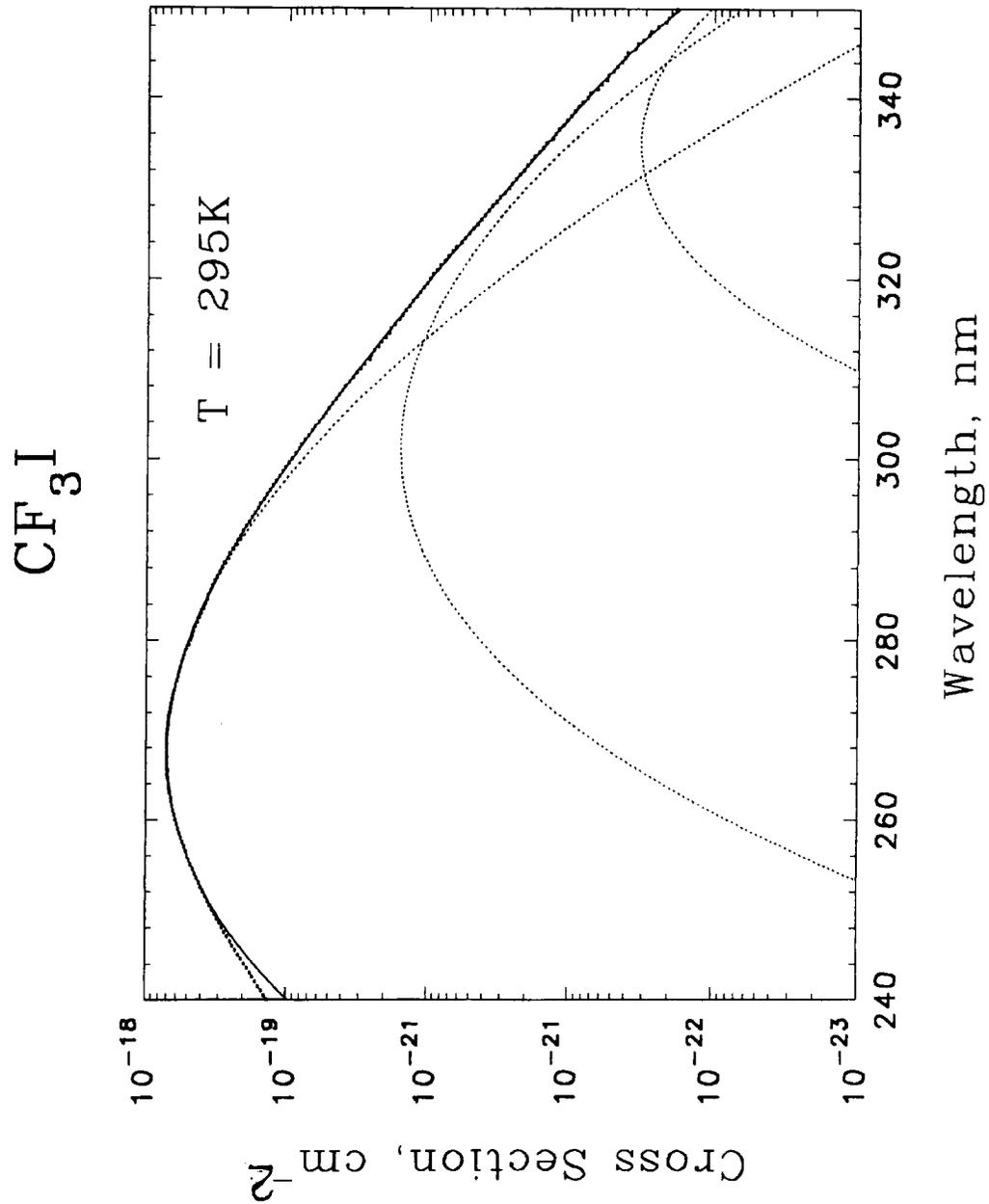


Figure 30. Absorption Cross-Section for CF_3I . The smooth curve was obtained by fitting the discrete absorption data to 3 Gaussians (dotted lines).

The research reported in this section is the first step in a rationale approach to the search for new and more effective fire fighting chemicals. Additional research, directed at developing the capability to predict key properties on the basis of molecular structure, is ongoing and will determine the prospects for identifying a new generation of zero ODP, low GWP fire suppressants.

5.4 References

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Appendix A. Tabulation of *Ab Initio* Thermochemical Data for Fluorinated Hydrocarbons.

Thermochemical data calculated using the BAC-MP4 *ab initio* method for fluorinated hydrocarbons (and a few other reference species) are presented in a "JANAF style" tabular format. Values for principal moments of inertia (I_a , I_b , I_c in kg m^2), fundamental vibrational frequencies (ν_i in cm^{-1}), equilibrium bond distances (R_e in 10^{-10} m), equilibrium bond angles (θ_e in degrees), heat of formation at 0 K (ΔH_f^0 : 0 K, 1 atmosphere in kJ mol^{-1}), heat of formation at standard state (ΔH_f^0 : 298.15 K, 1 atmosphere in kJ mol^{-1}), and entropy at standard state (S^0 : 298.15 K, 1 atmosphere in $\text{J K}^{-1} \text{mol}^{-1}$) are given for each species. Heat capacity (C_p^0 in $\text{J K}^{-1} \text{mol}^{-1}$), free energy of formation (ΔG_f^0 in kJ mol^{-1}), equilibrium constant for formation ($\text{Log } K_f$, dimensionless), and other ideal gas phase thermal functions (as a function of temperature) are also given for each species.

HF

$\Delta H_f^\circ(0 \text{ K})$	= -273.22 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	= -273.29 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	= 173.37 J K ⁻¹ mol ⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 1.32 1.32

Vibrational Frequencies (cm⁻¹)
 3890.2

Bond Distances (10⁻¹⁰ m) Bond Angles (°) Dihedral Angles (°)
 F1-H1 0.911

Enthalpy Reference Temperature = T_r = 298.15 K
 Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _P ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	29.10	153.38	-4.31	-273.22	-274.30	95.52
200	29.10	161.75	-2.86	-273.22	-274.68	71.74
250	29.10	168.25	-1.40	-273.26	-275.06	57.47
300	29.10	173.55	0.05	-273.30	-275.39	47.95
350	29.10	178.04	1.51	-273.34	-275.77	41.15
400	29.10	181.92	2.96	-273.42	-276.10	36.05
450	29.10	185.35	4.42	-273.51	-276.44	32.09
500	29.12	188.42	5.87	-273.63	-276.73	28.91
600	29.17	193.73	8.79	-273.88	-277.36	24.14
700	29.28	198.23	11.71	-274.18	-277.90	20.74
800	29.47	202.16	14.65	-274.47	-278.40	18.18
900	29.74	205.64	17.61	-274.81	-278.86	16.18
1000	30.07	208.79	20.60	-275.10	-279.32	14.59
1100	30.45	211.68	23.62	-275.39	-279.70	13.28
1200	30.84	214.34	26.69	-275.68	-280.08	12.19
1300	31.24	216.83	29.79	-275.93	-280.45	11.27
1400	31.63	219.16	32.94	-276.19	-280.79	10.48
1500	32.01	221.35	36.12	-276.44	-281.12	9.79
1600	32.38	223.43	39.34	-276.65	-281.42	9.19
1700	32.71	225.40	42.59	-276.86	-281.71	8.66
1800	33.03	227.28	45.88	-277.02	-281.96	8.18
1900	33.33	229.07	49.20	-277.23	-282.25	7.76
2000	33.60	230.79	52.54	-277.40	-282.50	7.38
2100	33.85	232.44	55.91	-277.52	-282.75	7.03
2200	34.08	234.02	59.31	-277.69	-283.01	6.72
2300	34.29	235.54	62.73	-277.82	-283.26	6.43
2400	34.48	237.00	66.17	-277.94	-283.47	6.17
2500	34.66	238.41	69.63	-278.07	-283.72	5.93
2600	34.83	239.78	73.10	-278.15	-283.93	5.70
2700	34.98	241.09	76.59	-278.28	-284.14	5.50
2800	35.12	242.37	80.10	-278.36	-284.39	5.30
2900	35.25	243.60	83.62	-278.45	-284.60	5.13
3000	35.37	244.80	87.15	-278.53	-284.80	4.96

F₂

$\Delta H_f^\circ(0 \text{ K})$ = 1.21 kJ mol⁻¹
 $\Delta H_f^\circ(298.15 \text{ K})$ = 1.13 kJ mol⁻¹
 $S^\circ(298.15 \text{ K})$ = 201.42 J K⁻¹ mol⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 28.53 28.53

Vibrational Frequencies (cm⁻¹)
 1111.7

Bond Distances (10⁻¹⁰ m) **Bond Angles** (°) **Dihedral Angles** (°)
 F1-F2 1.345

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	29.12	181.18	-4.37	1.21	1.34	-0.47
200	29.28	189.58	-2.92	1.17	1.38	-0.36
250	29.67	196.15	-1.44	1.17	1.42	-0.30
300	30.25	201.61	0.05	1.13	1.51	-0.26
350	30.94	206.32	1.59	1.09	1.55	-0.23
400	31.63	210.50	3.15	1.05	1.63	-0.21
450	32.28	214.26	4.75	0.96	1.72	-0.20
500	32.87	217.69	6.38	0.92	1.80	-0.19
600	33.85	223.78	9.72	0.84	1.97	-0.17
700	34.58	229.05	13.14	0.75	2.13	-0.16
800	35.12	233.71	16.62	0.71	2.34	-0.15
900	35.53	237.87	20.16	0.63	2.55	-0.15
1000	35.85	241.63	23.73	0.59	2.80	-0.15
1100	36.09	245.06	27.33	0.54	3.01	-0.14
1200	36.29	248.21	30.94	0.50	3.22	-0.14
1300	36.44	251.12	34.58	0.46	3.47	-0.14
1400	36.57	253.82	38.23	0.46	3.68	-0.14
1500	36.67	256.35	41.89	0.42	3.93	-0.14
1600	36.76	258.72	45.57	0.42	4.14	-0.14
1700	36.83	260.95	49.25	0.38	4.39	-0.14
1800	36.89	263.06	52.93	0.38	4.64	-0.13
1900	36.94	265.05	56.62	0.38	4.85	-0.13
2000	36.99	266.95	60.32	0.33	5.10	-0.13
2100	37.02	268.76	64.02	0.33	5.36	-0.13
2200	37.06	270.48	67.72	0.33	5.56	-0.13
2300	37.09	272.13	71.43	0.29	5.82	-0.13
2400	37.12	273.70	75.14	0.29	6.07	-0.13
2500	37.14	275.22	78.86	0.29	6.32	-0.13
2600	37.16	276.68	82.57	0.29	6.53	-0.13
2700	37.17	278.08	86.29	0.29	6.78	-0.13
2800	37.19	279.43	90.01	0.25	7.03	-0.13
2900	37.21	280.74	93.73	0.25	7.28	-0.13
3000	37.22	282.00	97.45	0.25	7.49	-0.13

CH₃F

$\Delta H_f^\circ(0 \text{ K})$	= -225.48 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	= -233.83 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	= 231.46 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
5.25	31.84	31.84

Vibrational Frequencies (cm ⁻¹)				
1059.4	1171.3	1171.4	1474.7	1476.1
1476.1	2886.7	2958.1	2958.6	

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-H1	1.082				
C1-F1	1.365	H1-C1-F1	109.13		
C1-H2	1.082	H1-C1-H2	109.84	F1-C1-H2	119.54
C1-H3	1.082	H1-C1-H3	109.84	F1-C1-H3	-119.54

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	Log K _f
150	33.32	207.76	-5.15	-229.33	-221.79	77.24
200	33.82	217.40	-3.47	-230.79	-219.07	57.22
250	35.22	225.07	-1.75	-232.34	-216.02	45.13
300	37.59	231.69	0.07	-233.89	-212.63	37.02
350	40.67	237.71	2.03	-235.39	-208.99	31.19
400	44.14	243.37	4.14	-236.81	-205.14	26.79
450	47.73	248.77	6.44	-238.20	-201.12	23.34
500	51.27	253.99	8.92	-239.41	-196.94	20.57
600	57.91	263.93	14.38	-241.58	-188.28	16.39
700	63.81	273.31	20.47	-243.34	-179.24	13.38
800	68.99	282.18	27.12	-244.76	-170.00	11.10
900	73.49	290.57	34.25	-245.85	-160.58	9.32
1000	77.41	298.52	41.80	-246.65	-151.00	7.89
1100	80.81	306.06	49.71	-247.27	-141.38	6.71
1200	83.75	313.22	57.94	-247.69	-131.67	5.73
1300	86.30	320.03	66.45	-247.94	-121.92	4.90
1400	88.52	326.51	75.19	-248.07	-112.17	4.18
1500	90.44	332.68	84.14	-248.07	-102.38	3.57
1600	92.12	338.57	93.27	-248.03	-92.63	3.02
1700	93.59	344.20	102.56	-247.86	-82.89	2.55
1800	94.88	349.59	111.98	-247.69	-73.14	2.12
1900	96.01	354.75	121.53	-247.40	-63.47	1.74
2000	97.02	359.70	131.19	-247.11	-53.81	1.41
2100	97.91	364.46	140.93	-246.77	-44.22	1.10
2200	98.70	369.03	150.76	-246.40	-34.64	0.82
2300	99.40	373.43	160.67	-245.98	-25.15	0.57
2400	100.04	377.68	170.64	-245.56	-15.65	0.34
2500	100.60	381.77	180.67	-245.10	-6.23	0.13
2600	101.11	385.73	190.76	-244.60	3.18	-0.06
2700	101.58	389.55	200.89	-244.09	12.51	-0.24
2800	102.00	393.25	211.07	-243.59	21.84	-0.41
2900	102.38	396.84	221.29	-243.05	31.17	-0.56
3000	102.73	400.32	231.55	-242.50	40.46	-0.70

CH₂F₂

$\Delta H_f^\circ(0 \text{ K})$	= -443.25 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	= -451.06 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	= 252.16 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
16.51	77.17	88.30

Vibrational Frequencies (cm ⁻¹)				
509.7	1105.4	1122.6	1164.4	1258.4
1463.6	1529.2	2941.9	3006.3	

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-H1	1.078				
C1-F1	1.338	H1-C1-F1	108.93		
C1-F2	1.338	H1-C1-F2	108.91	F1-C1-F2	118.26
C1-H2	1.078	H1-C1-H2	112.48	F1-C1-H2	-120.89

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	34.84	226.11	-5.69	-447.06	-436.85	152.12
200	36.88	236.40	-3.90	-448.40	-433.25	113.15
250	39.63	244.91	-1.99	-449.78	-429.36	89.70
300	43.09	252.43	0.08	-451.12	-425.18	74.02
350	47.01	259.36	2.33	-452.37	-420.74	62.79
400	51.07	265.90	4.78	-453.55	-416.18	54.35
450	55.07	272.15	7.43	-454.63	-411.45	47.76
500	58.86	278.15	10.28	-455.64	-406.64	42.48
600	65.63	289.50	16.52	-457.27	-396.73	34.54
700	71.32	300.06	23.38	-458.57	-386.52	28.84
800	76.08	309.90	30.75	-459.57	-376.18	24.56
900	80.09	319.10	38.57	-460.28	-365.68	21.22
1000	83.48	327.72	46.75	-460.78	-355.10	18.55
1100	86.35	335.81	55.25	-461.16	-344.47	16.36
1200	88.81	343.43	64.01	-461.33	-333.80	14.53
1300	90.90	350.63	72.99	-461.41	-323.09	12.98
1400	92.70	357.43	82.18	-461.37	-312.42	11.66
1500	94.26	363.88	91.53	-461.29	-301.71	10.51
1600	95.60	370.01	101.02	-461.08	-291.00	9.50
1700	96.77	375.84	110.64	-460.87	-280.37	8.61
1800	97.80	381.40	120.37	-460.57	-269.70	7.83
1900	98.69	386.71	130.20	-460.24	-259.12	7.12
2000	99.48	391.79	140.11	-459.86	-248.57	6.49
2100	100.18	396.66	150.09	-459.49	-238.07	5.92
2200	100.80	401.34	160.14	-459.07	-227.61	5.40
2300	101.36	405.84	170.25	-458.61	-217.19	4.93
2400	101.85	410.16	180.41	-458.15	-206.82	4.50
2500	102.29	414.32	190.61	-457.65	-196.52	4.11
2600	102.69	418.35	200.87	-457.14	-186.23	3.74
2700	103.05	422.23	211.15	-456.64	-175.98	3.40
2800	103.38	425.98	221.48	-456.10	-165.77	3.09
2900	103.68	429.61	231.83	-455.55	-155.56	2.80
3000	103.95	433.14	242.21	-455.01	-145.35	2.53

CHF₃

$\Delta H_f^\circ(0\text{ K})$	= -692.49 kJ mol ⁻¹
$\Delta H_f^\circ(298.15\text{ K})$	= -699.45 kJ mol ⁻¹
$S^\circ(298.15\text{ K})$	= 268.72 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
78.94	79.02	144.03

Vibrational Frequencies (cm ⁻¹)				
491.7	492.1	680.7	1126.9	1185.7
1186.0	1413.4	1413.6	3036.6	

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-H1	1.074	H1-C1-F1	110.44	F1-C1-F2	120.03
C1-F1	1.316	H1-C1-F2	110.44	F1-C1-F3	-120.03
C1-F2	1.316	H1-C1-F3	110.44		
C1-F3	1.316				

Enthalpy Reference Temperature = T_r = 298.15 K
 Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	37.19	239.03	-6.52	-696.22	-682.54	237.67
200	41.66	250.32	-4.55	-697.39	-677.85	177.02
250	46.48	260.13	-2.35	-698.48	-672.83	140.57
300	51.40	269.04	0.10	-699.48	-667.64	116.24
350	56.25	277.33	2.79	-700.36	-662.29	98.83
400	60.86	285.14	5.72	-701.15	-656.80	85.76
450	65.11	292.56	8.87	-701.87	-651.24	75.59
500	68.96	299.62	12.22	-702.45	-645.59	67.44
600	75.48	312.80	19.46	-703.33	-634.17	55.21
700	80.63	324.84	27.27	-703.96	-622.62	46.46
800	84.73	335.88	35.55	-704.38	-610.95	39.89
900	88.01	346.05	44.19	-704.59	-599.23	34.78
1000	90.70	355.47	53.13	-704.67	-587.52	30.69
1100	92.90	364.23	62.31	-704.63	-575.72	27.34
1200	94.74	372.39	71.70	-704.50	-563.96	24.55
1300	96.28	380.03	81.25	-704.33	-552.20	22.19
1400	97.58	387.22	90.94	-704.08	-540.45	20.16
1500	98.69	393.99	100.76	-703.75	-528.69	18.41
1600	99.64	400.39	110.68	-703.41	-516.98	16.88
1700	100.46	406.45	120.68	-703.04	-505.30	15.53
1800	101.17	412.22	130.77	-702.62	-493.67	14.32
1900	101.79	417.71	140.91	-702.20	-482.04	13.25
2000	102.33	422.94	151.12	-701.74	-470.49	12.29
2100	102.81	427.94	161.38	-701.24	-458.98	11.42
2200	103.23	432.74	171.68	-700.74	-447.56	10.63
2300	103.61	437.33	182.02	-700.23	-436.14	9.90
2400	103.94	441.75	192.40	-699.69	-424.80	9.25
2500	104.24	446.00	202.81	-699.15	-413.50	8.64
2600	104.51	450.09	213.25	-698.60	-402.25	8.08
2700	104.75	454.04	223.71	-698.06	-391.04	7.56
2800	104.97	457.86	234.20	-697.47	-379.82	7.09
2900	105.17	461.55	244.71	-696.89	-368.65	6.64
3000	105.35	465.11	255.23	-696.30	-357.48	6.22

CF₄

$\Delta H_f^\circ(0 \text{ K})$	= -928.60 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	= -934.37 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	= 273.27 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
142.60	142.61	142.61

Vibrational Frequencies (cm ⁻¹)				
422.0	422.0	609.8	609.8	609.8
895.5	1314.2	1314.2	1314.2	

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-F1	1.302				
C1-F2	1.302	F1-C1-F2	109.47		
C1-F3	1.302	F1-C1-F3	109.47	F2-C1-F3	120.00
C1-F4	1.302	F1-C1-F4	109.47	F2-C1-F4	-120.00

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	40.79	238.66	-7.64	-932.20	-913.07	317.94
200	48.23	251.41	-5.42	-933.12	-906.55	236.76
250	55.45	262.96	-2.82	-933.83	-899.85	188.00
300	61.97	273.66	0.11	-934.37	-893.03	155.48
350	67.73	283.65	3.36	-934.79	-886.13	132.24
400	72.75	293.03	6.87	-935.08	-879.18	114.80
450	77.09	301.85	10.62	-935.25	-872.20	101.24
500	80.83	310.18	14.57	-935.33	-865.21	90.38
600	86.78	325.47	22.97	-935.38	-851.19	74.10
700	91.16	339.19	31.88	-935.21	-837.22	62.47
800	94.40	351.59	41.17	-934.87	-823.24	53.75
900	96.85	362.85	50.73	-934.50	-809.27	46.97
1000	98.72	373.16	60.51	-934.08	-795.34	41.54
1100	100.17	382.64	70.46	-933.58	-781.45	37.11
1200	101.32	391.40	80.54	-933.07	-767.60	33.41
1300	102.25	399.56	90.72	-932.57	-753.75	30.28
1400	103.00	407.16	100.98	-932.03	-739.94	27.61
1500	103.62	414.29	111.32	-931.48	-726.18	25.29
1600	104.13	420.99	121.70	-930.90	-712.45	23.26
1700	104.56	427.32	132.14	-930.35	-698.77	21.47
1800	104.93	433.30	142.61	-929.77	-685.13	19.88
1900	105.24	438.99	153.12	-929.18	-671.57	18.46
2000	105.51	444.39	163.66	-928.60	-658.06	17.19
2100	105.74	449.55	174.22	-927.97	-644.59	16.03
2200	105.94	454.47	184.80	-927.38	-631.20	14.99
2300	106.12	459.18	195.41	-926.76	-617.85	14.03
2400	106.28	463.70	206.03	-926.17	-604.55	13.16
2500	106.42	468.04	216.66	-925.54	-591.28	12.35
2600	106.54	472.22	227.31	-924.92	-578.10	11.61
2700	106.65	476.24	237.97	-924.29	-564.92	10.93
2800	106.75	480.12	248.64	-923.62	-551.79	10.29
2900	106.84	483.87	259.32	-922.99	-538.69	9.70
3000	106.92	487.49	270.01	-922.36	-525.59	9.15

•CH₂F

$\Delta H_f^\circ(0 \text{ K})$	=	-27.57 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	=	-31.44 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	=	234.32 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
3.15	26.82	29.53

Vibrational Frequencies (cm ⁻¹)				
771.2	1134.2	1143.5	1443.5	2962.3
3087.6				

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-F1	1.331				
C1-H1	1.073	F1-C1-H1	113.95		
C1-H2	1.073	F1-C1-H2	113.95	H1-C1-H2	144.84

Enthalpy Reference Temperature = T_r = 298.15 K
 Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	33.58	210.04	-5.28	-29.25	-30.29	10.55
200	34.60	219.82	-3.58	-29.96	-30.54	7.98
250	36.40	227.72	-1.80	-30.71	-30.63	6.40
300	38.74	234.56	0.07	-31.46	-30.59	5.32
350	41.31	240.72	2.07	-32.22	-30.42	4.54
400	43.90	246.41	4.20	-32.89	-30.12	3.93
450	46.37	251.72	6.46	-33.56	-29.75	3.45
500	48.68	256.73	8.84	-34.18	-29.33	3.06
600	52.76	265.97	13.92	-35.27	-28.28	2.46
700	56.25	274.38	19.37	-36.19	-27.07	2.02
800	59.25	282.09	25.15	-37.03	-25.69	1.68
900	61.88	289.22	31.21	-37.70	-24.23	1.41
1000	64.17	295.86	37.51	-38.28	-22.64	1.18
1100	66.18	302.08	44.03	-38.79	-21.00	1.00
1200	67.94	307.91	50.74	-39.20	-19.33	0.84
1300	69.47	313.41	57.61	-39.54	-17.57	0.71
1400	70.81	318.61	64.63	-39.83	-15.82	0.59
1500	71.99	323.54	71.77	-40.12	-14.02	0.49
1600	73.02	328.21	79.02	-40.33	-12.22	0.40
1700	73.93	332.67	86.37	-40.50	-10.42	0.32
1800	74.73	336.92	93.81	-40.67	-8.62	0.25
1900	75.44	340.98	101.31	-40.79	-6.86	0.19
2000	76.07	344.87	108.89	-40.92	-5.10	0.13
2100	76.63	348.59	116.52	-41.05	-3.35	0.08
2200	77.12	352.17	124.21	-41.09	-1.63	0.04
2300	77.57	355.61	131.95	-41.17	0.08	0.00
2400	77.97	358.92	139.72	-41.21	1.76	-0.04
2500	78.33	362.10	147.54	-41.25	3.39	-0.07
2600	78.66	365.18	155.39	-41.30	5.02	-0.10
2700	78.95	368.16	163.27	-41.34	6.65	-0.13
2800	79.22	371.03	171.18	-41.34	8.28	-0.15
2900	79.46	373.82	179.11	-41.34	9.87	-0.18
3000	79.68	376.52	187.07	-41.34	11.51	-0.20

•CHF₂

$\Delta H_f^\circ(0 \text{ K})$	= -243.76 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	= -247.27 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	= 255.94 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
12.20	74.78	85.62

Vibrational Frequencies (cm ⁻¹)				
521.4	1041.3	1150.0	1180.8	1343.1
3005.3				

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-H1	1.076	H1-C1-F1	113.77	F1-C1-F2	128.66
C1-F1	1.314	H1-C1-F2	113.77		
C1-F2	1.314				

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	34.75	230.08	-5.64	-245.35	-244.01	84.97
200	36.72	240.33	-3.86	-246.02	-243.51	63.59
250	39.27	248.79	-1.96	-246.65	-242.80	50.73
300	42.25	256.21	0.08	-247.27	-242.00	42.13
350	45.43	262.96	2.27	-247.90	-241.08	35.98
400	48.55	269.23	4.62	-248.45	-240.12	31.35
450	51.48	275.12	7.12	-248.95	-239.07	27.75
500	54.15	280.68	9.77	-249.41	-237.94	24.86
600	58.70	290.98	15.41	-250.20	-235.64	20.51
700	62.33	300.31	21.47	-250.83	-233.17	17.40
800	65.25	308.83	27.86	-251.33	-230.62	15.06
900	67.63	316.65	34.51	-251.75	-227.99	13.23
1000	69.60	323.89	41.37	-252.13	-225.27	11.77
1100	71.24	330.60	48.41	-252.42	-222.51	10.57
1200	72.63	336.86	55.61	-252.63	-219.74	9.56
1300	73.80	342.72	62.93	-252.84	-216.94	8.72
1400	74.80	348.23	70.36	-253.01	-214.10	7.99
1500	75.65	353.41	77.89	-253.17	-211.25	7.36
1600	76.39	358.32	85.49	-253.30	-208.36	6.80
1700	77.03	362.97	93.16	-253.38	-205.52	6.31
1800	77.59	367.39	100.89	-253.47	-202.67	5.88
1900	78.08	371.60	108.68	-253.55	-199.87	5.49
2000	78.51	375.62	116.51	-253.59	-197.07	5.15
2100	78.89	379.46	124.38	-253.63	-194.30	4.83
2200	79.22	383.14	132.29	-253.68	-191.54	4.55
2300	79.53	386.66	140.22	-253.72	-188.82	4.29
2400	79.79	390.05	148.19	-253.76	-186.10	4.05
2500	80.03	393.32	156.18	-253.76	-183.43	3.83
2600	80.24	396.46	164.19	-253.76	-180.79	3.63
2700	80.44	399.49	172.23	-253.76	-178.11	3.45
2800	80.62	402.42	180.28	-253.76	-175.48	3.27
2900	80.78	405.25	188.35	-253.76	-172.84	3.11
3000	80.92	407.99	196.43	-253.72	-170.21	2.96

•CF₃

$\Delta H_f^\circ(0 \text{ K})$	= -469.24 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	= -471.90 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	= 264.64 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
75.31	75.31	145.53

Vibrational Frequencies (cm ⁻¹)				
490.6	490.6	676.5	1086.2	1285.9
1285.9				

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-F1	1.301	X1-C1-F1	107.60	F1-C1-F2	120.00
C1-F2	1.301	X1-C1-F2	107.60	F1-C1-F3	-120.00
C1-F3	1.301	X1-C1-F3	107.60		

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	37.22	235.13	-6.47	-470.74	-464.76	161.84
200	41.58	246.43	-4.51	-471.20	-462.71	120.84
250	46.02	256.19	-2.31	-471.62	-460.57	96.23
300	50.22	264.95	0.09	-471.91	-458.36	79.80
350	54.09	272.99	2.70	-472.16	-456.10	68.07
400	57.57	280.45	5.49	-472.33	-453.80	59.26
450	60.64	287.41	8.45	-472.50	-451.50	52.41
500	63.32	293.94	11.55	-472.62	-449.19	46.92
600	67.62	305.88	18.11	-472.75	-444.51	38.70
700	70.80	316.56	25.04	-472.79	-439.82	32.82
800	73.16	326.17	32.24	-472.83	-435.14	28.41
900	74.94	334.90	39.65	-472.79	-430.41	24.98
1000	76.31	342.87	47.22	-472.75	-425.68	22.23
1100	77.37	350.19	54.91	-472.71	-420.91	19.99
1200	78.22	356.96	62.68	-472.71	-416.14	18.11
1300	78.89	363.25	70.54	-472.67	-411.37	16.53
1400	79.44	369.12	78.46	-472.62	-406.56	15.17
1500	79.89	374.61	86.42	-472.58	-401.79	13.99
1600	80.26	379.78	94.43	-472.58	-397.02	12.96
1700	80.58	384.66	102.47	-472.54	-392.25	12.05
1800	80.84	389.27	110.55	-472.50	-387.52	11.24
1900	81.07	393.65	118.64	-472.50	-382.79	10.52
2000	81.27	397.81	126.76	-472.46	-378.11	9.87
2100	81.43	401.78	134.90	-472.42	-373.42	9.29
2200	81.58	405.57	143.05	-472.42	-368.78	8.76
2300	81.71	409.20	151.21	-472.37	-364.18	8.27
2400	81.83	412.68	159.39	-472.33	-359.61	7.83
2500	81.93	416.02	167.57	-472.29	-355.05	7.42
2600	82.01	419.24	175.77	-472.25	-350.54	7.04
2700	82.10	422.34	183.98	-472.21	-346.02	6.69
2800	82.17	425.32	192.19	-472.16	-341.50	6.37
2900	82.24	428.21	200.41	-472.12	-336.98	6.07
3000	82.30	431.00	208.64	-472.08	-332.46	5.79

:CHF (singlet)

$\Delta H_f^\circ(0 \text{ K})$ = 152.59 kJ mol⁻¹
 $\Delta H_f^\circ(298.15 \text{ K})$ = 152.77 kJ mol⁻¹
 $S^\circ(298.15 \text{ K})$ = 222.83 J K⁻¹ mol⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 1.72 22.40 24.12

Vibrational Frequencies (cm⁻¹)
 1189.2 1404.2 2732.5

Bond Distances (10⁻¹⁰ m) **Bond Angles** (°) **Dihedral Angles** (°)
 Cl-F1 1.295 F1-C1-H1 102.80
 Cl-H1 1.104

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	33.27	199.73	-4.99	153.09	145.35	-50.61
200	33.41	209.32	-3.33	153.09	142.72	-37.28
250	33.84	216.81	-1.64	152.97	140.16	-29.28
300	34.62	223.04	0.06	152.76	137.57	-23.95
350	35.66	228.46	1.82	152.51	135.02	-20.15
400	36.85	233.30	3.63	152.21	132.55	-17.31
450	38.09	237.71	5.51	151.92	130.08	-15.10
500	39.33	241.78	7.44	151.59	127.65	-13.33
600	41.66	249.17	11.49	150.92	122.88	-10.70
700	43.72	255.74	15.77	150.25	118.24	-8.82
800	45.53	261.70	20.23	149.58	113.72	-7.42
900	47.08	267.16	24.86	148.95	109.29	-6.34
1000	48.41	272.19	29.64	148.32	104.93	-5.48
1100	49.56	276.86	34.53	147.70	100.71	-4.78
1200	50.54	281.21	39.54	147.11	96.48	-4.20
1300	51.38	285.29	44.64	146.52	92.38	-3.71
1400	52.10	289.13	49.81	145.94	88.28	-3.29
1500	52.72	292.74	55.06	145.35	84.27	-2.93
1600	53.26	296.16	60.35	144.77	80.25	-2.62
1700	53.73	299.41	65.71	144.18	76.27	-2.34
1800	54.14	302.49	71.10	143.59	72.34	-2.10
1900	54.50	305.43	76.53	143.05	68.41	-1.88
2000	54.81	308.23	82.00	142.47	64.48	-1.68
2100	55.09	310.91	87.49	141.92	60.50	-1.51
2200	55.33	313.48	93.01	141.34	56.57	-1.34
2300	55.56	315.94	98.56	140.79	52.63	-1.20
2400	55.75	318.31	104.12	140.21	48.70	-1.06
2500	55.93	320.59	109.71	139.66	44.77	-0.94
2600	56.08	322.79	115.31	139.08	40.84	-0.82
2700	56.22	324.91	120.93	138.53	36.90	-0.71
2800	56.35	326.95	126.55	137.99	32.97	-0.62
2900	56.47	328.93	132.19	137.40	29.08	-0.52
3000	56.58	330.85	137.85	136.86	25.23	-0.44

:CF₂ (singlet)

$\Delta H_f^\circ(0 \text{ K}) = -203.84 \text{ kJ mol}^{-1}$
 $\Delta H_f^\circ(298.15 \text{ K}) = -203.33 \text{ kJ mol}^{-1}$
 $S^\circ(298.15 \text{ K}) = 240.43 \text{ J K}^{-1} \text{ mol}^{-1}$

Moments of Inertia (10^{-47} kg m^2)
 9.35 64.95 74.30

Vibrational Frequencies (cm^{-1})
 651.0 1155.5 1240.8

Bond Distances (10^{-10} m)	Bond Angles ($^\circ$)	Dihedral Angles ($^\circ$)
C1-F1 1.283		
C1-F2 1.283	F1-C1-F2 104.47	

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$
 Standard State Pressure = $p_o = 1 \text{ atmosphere}$

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	33.91	215.80	-5.35	-203.30	-208.07	72.45
200	35.20	225.72	-3.63	-203.26	-209.66	54.76
250	36.96	233.76	-1.82	-203.30	-211.29	44.15
300	38.94	240.67	0.07	-203.34	-212.92	37.07
350	40.97	246.82	2.07	-203.43	-214.51	32.02
400	42.90	252.42	4.17	-203.51	-216.15	28.22
450	44.66	257.58	6.36	-203.59	-217.74	25.27
500	46.23	262.37	8.63	-203.68	-219.33	22.91
600	48.79	271.04	13.39	-203.93	-222.46	19.37
700	50.71	278.70	18.37	-204.18	-225.56	16.83
800	52.14	285.57	23.51	-204.43	-228.61	14.93
900	53.22	291.78	28.78	-204.76	-231.58	13.44
1000	54.04	297.43	34.15	-205.14	-234.51	12.25
1100	54.69	302.62	39.58	-205.52	-237.40	11.27
1200	55.20	307.39	45.08	-205.94	-240.20	10.46
1300	55.61	311.83	50.62	-206.40	-242.96	9.76
1400	55.94	315.97	56.20	-206.86	-245.68	9.17
1500	56.22	319.83	61.81	-207.36	-248.40	8.65
1600	56.45	323.47	67.44	-207.86	-251.04	8.20
1700	56.64	326.90	73.10	-208.36	-253.72	7.79
1800	56.80	330.14	78.77	-208.87	-256.35	7.44
1900	56.94	333.21	84.46	-209.41	-258.95	7.12
2000	57.06	336.14	90.16	-209.95	-261.58	6.83
2100	57.16	338.92	95.87	-210.50	-264.18	6.57
2200	57.25	341.59	101.59	-211.04	-266.81	6.33
2300	57.33	344.13	107.32	-211.58	-269.45	6.12
2400	57.40	346.57	113.06	-212.13	-272.04	5.92
2500	57.46	348.92	118.80	-212.67	-274.68	5.74
2600	57.52	351.18	124.55	-213.22	-277.32	5.57
2700	57.56	353.35	130.30	-213.76	-279.95	5.42
2800	57.61	355.44	136.06	-214.30	-282.55	5.27
2900	57.65	357.46	141.82	-214.85	-285.10	5.14
3000	57.68	359.42	147.59	-215.39	-287.65	5.01

CHF=O

$\Delta H_f^\circ(0 \text{ K})$ = -378.57 kJ mol⁻¹
 $\Delta H_f^\circ(298.15 \text{ K})$ = -382.28 kJ mol⁻¹
 $S^\circ(298.15 \text{ K})$ = 246.15 J K⁻¹ mol⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 8.84 68.99 77.83

Vibrational Frequencies (cm⁻¹)
 659.1 1050.8 1115.1 1374.1 1876.5
 2996.9

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)
C1-O1	1.164			
C1-F1	1.314	O1-C1-F1	123.03	
C1-H1	1.081	O1-C1-H1	126.96	

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	33.92	221.26	-5.42	-380.20	-377.40	131.41
200	35.38	231.20	-3.69	-380.91	-376.35	98.29
250	37.57	239.32	-1.87	-381.62	-375.14	78.38
300	40.21	246.40	0.08	-382.29	-373.80	65.08
350	43.03	252.81	2.15	-382.96	-372.38	55.57
400	45.86	258.74	4.38	-383.59	-370.83	48.42
450	48.57	264.29	6.74	-384.13	-369.24	42.86
500	51.12	269.55	9.23	-384.68	-367.56	38.40
600	55.64	279.28	14.58	-385.60	-364.09	31.69
700	59.43	288.15	20.33	-386.35	-360.45	26.90
800	62.61	296.30	26.44	-386.98	-356.69	23.29
900	65.26	303.83	32.84	-387.52	-352.88	20.48
1000	67.49	310.83	39.48	-387.98	-348.95	18.23
1100	69.37	317.35	46.33	-388.36	-344.97	16.38
1200	70.96	323.45	53.34	-388.69	-340.95	14.84
1300	72.32	329.19	60.51	-388.94	-336.94	13.54
1400	73.47	334.59	67.80	-389.20	-332.84	12.42
1500	74.47	339.69	75.20	-389.40	-328.74	11.45
1600	75.32	344.53	82.69	-389.57	-324.64	10.60
1700	76.07	349.12	90.26	-389.74	-320.54	9.85
1800	76.72	353.49	97.90	-389.87	-316.44	9.18
1900	77.28	357.65	105.60	-389.95	-312.38	8.59
2000	77.78	361.63	113.35	-390.07	-308.32	8.05
2100	78.22	365.43	121.16	-390.16	-304.26	7.57
2200	78.61	369.08	129.00	-390.20	-300.24	7.13
2300	78.96	372.58	136.88	-390.28	-296.27	6.73
2400	79.27	375.95	144.79	-390.33	-292.29	6.36
2500	79.55	379.19	152.73	-390.37	-288.32	6.02
2600	79.80	382.32	160.69	-390.41	-284.43	5.71
2700	80.02	385.33	168.69	-390.41	-280.50	5.43
2800	80.22	388.25	176.70	-390.45	-276.60	5.16
2900	80.41	391.07	184.73	-390.45	-272.67	4.91
3000	80.58	393.79	192.78	-390.45	-268.74	4.68

CF₂=O

$\Delta H_f^\circ(0 \text{ K})$	= -595.34 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	= -598.38 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	= 258.58 J K ⁻¹ mol ⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 68.97 69.00 137.97

Vibrational Frequencies (cm⁻¹)
 563.3 610.1 779.0 976.6 1305.5
 1953.0

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)
C1-O1	1.157			
C1-F1	1.290	O1-C1-F1	125.86	
C1-F2	1.290	O1-C1-F2	125.86	

Enthalpy Reference Temperature = T_r = 298.15 K
 Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	35.51	230.72	-6.11	-596.93	-590.11	205.49
200	39.15	241.41	-4.25	-597.52	-587.77	153.50
250	43.37	250.60	-2.18	-597.98	-585.30	122.29
300	47.51	258.88	0.09	-598.40	-582.75	101.46
350	51.30	266.49	2.56	-598.73	-580.15	86.58
400	54.69	273.57	5.21	-598.98	-577.48	75.41
450	57.68	280.18	8.02	-599.23	-574.80	66.72
500	60.31	286.40	10.97	-599.40	-572.12	59.76
600	64.64	297.80	17.23	-599.65	-566.68	49.33
700	67.98	308.02	23.87	-599.82	-561.16	41.87
800	70.58	317.27	30.80	-599.94	-555.64	36.28
900	72.61	325.71	37.97	-600.07	-550.07	31.92
1000	74.22	333.45	45.31	-600.11	-544.46	28.44
1100	75.51	340.59	52.80	-600.15	-538.86	25.59
1200	76.55	347.20	60.40	-600.24	-533.25	23.21
1300	77.40	353.36	68.10	-600.28	-527.60	21.20
1400	78.11	359.13	75.88	-600.28	-521.91	19.47
1500	78.69	364.54	83.72	-600.32	-516.26	17.98
1600	79.18	369.63	91.61	-600.36	-510.62	16.67
1700	79.60	374.44	99.55	-600.36	-504.97	15.51
1800	79.95	379.00	107.53	-600.40	-499.32	14.49
1900	80.26	383.33	115.54	-600.40	-493.71	13.57
2000	80.53	387.46	123.58	-600.40	-488.11	12.75
2100	80.76	391.39	131.65	-600.40	-482.54	12.00
2200	80.96	395.15	139.73	-600.45	-477.02	11.33
2300	81.14	398.76	147.84	-600.45	-471.49	10.71
2400	81.29	402.21	155.96	-600.40	-466.01	10.14
2500	81.43	405.53	164.10	-600.40	-460.57	9.62
2600	81.55	408.73	172.24	-600.40	-455.14	9.14
2700	81.67	411.81	180.41	-600.36	-449.70	8.70
2800	81.77	414.78	188.58	-600.36	-444.26	8.29
2900	81.86	417.66	196.76	-600.32	-438.86	7.90
3000	81.94	420.43	204.95	-600.28	-433.42	7.55

•CF=O

$\Delta H_f^\circ(0 \text{ K})$	= -183.43 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	= -182.87 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	= 248.32 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
4.19	70.99	75.18

Vibrational Frequencies (cm ⁻¹)		
632.0	1081.1	1915.2

Bond Distances (10 ⁻¹⁰ m)	Bond Angles (°)	Dihedral Angles (°)
Cl-O1 1.152		
Cl-F1 1.304	O1-Cl-F1 128.26	

Enthalpy Reference Temperature = T_r = 298.15 K
 Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	34.00	223.66	-5.36	-182.88	-188.66	65.70
200	35.33	233.61	-3.63	-182.84	-190.62	49.78
250	36.97	241.66	-1.82	-182.84	-192.59	40.24
300	38.67	248.55	0.07	-182.88	-194.56	33.87
350	40.30	254.64	2.05	-182.92	-196.52	29.33
400	41.84	260.12	4.10	-182.97	-198.49	25.92
450	43.27	265.14	6.23	-183.05	-200.46	23.26
500	44.57	269.76	8.43	-183.13	-202.38	21.14
600	46.85	278.10	13.00	-183.38	-206.23	17.95
700	48.71	285.46	17.78	-183.64	-210.08	15.67
800	50.22	292.07	22.73	-183.97	-213.80	13.96
900	51.44	298.06	27.82	-184.35	-217.48	12.62
1000	52.42	303.53	33.01	-184.77	-221.12	11.55
1100	53.22	308.57	38.29	-185.23	-224.68	10.67
1200	53.88	313.23	43.65	-185.69	-228.20	9.93
1300	54.43	317.56	49.07	-186.15	-231.67	9.31
1400	54.88	321.61	54.53	-186.69	-235.10	8.77
1500	55.25	325.41	60.04	-187.19	-238.45	8.30
1600	55.57	328.99	65.58	-187.74	-241.79	7.89
1700	55.84	332.36	71.15	-188.28	-245.14	7.53
1800	56.08	335.56	76.75	-188.82	-248.45	7.21
1900	56.28	338.60	82.37	-189.37	-251.75	6.92
2000	56.45	341.49	88.00	-189.91	-255.01	6.66
2100	56.61	344.25	93.65	-190.50	-258.32	6.42
2200	56.74	346.89	99.32	-191.04	-261.58	6.21
2300	56.86	349.41	105.00	-191.63	-264.89	6.02
2400	56.96	351.83	110.70	-192.17	-268.19	5.84
2500	57.05	354.16	116.39	-192.76	-271.50	5.67
2600	57.14	356.40	122.11	-193.30	-274.76	5.52
2700	57.21	358.56	127.82	-193.89	-278.07	5.38
2800	57.28	360.64	133.54	-194.43	-281.33	5.25
2900	57.34	362.65	139.28	-195.02	-284.60	5.13
3000	57.39	364.59	145.01	-195.56	-287.82	5.01

CH₂FO•

$\Delta H_f^\circ(0 \text{ K})$	= -186.73 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	= -194.40 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	= 257.00 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
15.36	75.54	85.58

Vibrational Frequencies (cm ⁻¹)				
527.3	911.9	1047.1	1108.4	1198.1
1412.9	1439.9	2885.3	2937.7	

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-O1	1.345				
C1-F1	1.354	O1-C1-F1	112.61		
C1-H1	1.084	O1-C1-H1	108.34	F1-C1-H1	119.89
C1-H2	1.084	O1-C1-H2	108.34	F1-C1-H2	-119.89

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	34.80	230.58	-5.78	-190.54	-180.83	62.98
200	37.20	240.89	-3.98	-191.88	-177.44	46.34
250	40.56	249.53	-2.05	-193.22	-173.68	36.29
300	44.61	257.28	0.08	-194.43	-169.70	29.54
350	48.97	264.48	2.42	-195.56	-165.48	24.70
400	53.32	271.31	4.98	-196.56	-161.17	21.04
450	57.45	277.83	7.75	-197.48	-156.69	18.19
500	61.27	284.08	10.72	-198.24	-152.13	15.89
600	67.93	295.86	17.19	-199.49	-142.84	12.43
700	73.42	306.76	24.27	-200.41	-133.30	9.95
800	77.98	316.87	31.84	-201.04	-123.68	8.08
900	81.79	326.28	39.84	-201.46	-113.97	6.62
1000	85.00	335.07	48.18	-201.67	-104.22	5.44
1100	87.71	343.30	56.82	-201.75	-94.43	4.48
1200	90.03	351.03	65.71	-201.71	-84.60	3.68
1300	92.00	358.32	74.81	-201.59	-74.77	3.00
1400	93.70	365.20	84.10	-201.42	-64.98	2.42
1500	95.16	371.71	93.55	-201.12	-55.19	1.92
1600	96.42	377.90	103.13	-200.79	-45.40	1.48
1700	97.52	383.78	112.83	-200.46	-35.65	1.10
1800	98.48	389.38	122.62	-200.04	-25.94	0.75
1900	99.32	394.73	132.52	-199.62	-16.28	0.45
2000	100.06	399.84	142.49	-199.16	-6.69	0.17
2100	100.71	404.74	152.52	-198.66	2.89	-0.07
2200	101.29	409.44	162.63	-198.15	12.38	-0.29
2300	101.81	413.95	172.78	-197.61	21.84	-0.50
2400	102.27	418.30	182.99	-197.07	31.25	-0.68
2500	102.69	422.48	193.23	-196.52	40.63	-0.85
2600	103.06	426.51	203.52	-195.98	49.96	-1.00
2700	103.40	430.41	213.85	-195.39	59.25	-1.15
2800	103.70	434.18	224.20	-194.81	68.49	-1.28
2900	103.98	437.82	234.58	-194.18	77.74	-1.40
3000	104.23	441.35	245.00	-193.59	86.94	-1.51

CHF₂O•

$\Delta H_f^\circ(0 \text{ K})$	= -398.90 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	= -405.62 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	= 274.61 J K ⁻¹ mol ⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 76.21 78.48 141.68

Vibrational Frequencies (cm⁻¹)
 443.3 499.4 644.7 1014.8 1147.3
 1154.8 1355.1 1390.9 2961.3

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-O1	1.346				
C1-H1	1.080	O1-C1-H1	106.89		
C1-F1	1.327	O1-C1-F1	111.12	H1-C1-F1	120.39
C1-F2	1.327	O1-C1-F2	111.12	H1-C1-F2	-120.39

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	37.81	244.21	-6.68	-402.58	-389.53	135.65
200	42.61	255.73	-4.67	-403.76	-385.01	100.56
250	47.71	265.79	-2.42	-404.76	-380.24	79.45
300	52.85	274.94	0.10	-405.64	-375.30	65.34
350	57.84	283.47	2.87	-406.39	-370.20	55.25
400	62.51	291.50	5.88	-407.06	-365.01	47.66
450	66.77	299.11	9.11	-407.56	-359.74	41.76
500	70.58	306.35	12.55	-407.98	-354.43	37.02
600	76.96	319.80	19.94	-408.57	-343.67	29.92
700	81.95	332.06	27.89	-408.90	-332.84	24.84
800	85.89	343.27	36.29	-409.03	-322.00	21.02
900	89.04	353.57	45.04	-408.99	-311.08	18.05
1000	91.61	363.09	54.08	-408.86	-300.20	15.68
1100	93.72	371.92	63.35	-408.61	-289.28	13.74
1200	95.47	380.16	72.81	-408.32	-278.40	12.12
1300	96.93	387.86	82.43	-407.98	-267.52	10.75
1400	98.17	395.09	92.19	-407.61	-256.65	9.58
1500	99.22	401.90	102.06	-407.19	-245.81	8.56
1600	100.13	408.33	112.03	-406.73	-235.02	7.67
1700	100.90	414.43	122.08	-406.22	-224.26	6.89
1800	101.57	420.21	132.21	-405.72	-213.55	6.20
1900	102.16	425.72	142.39	-405.22	-202.88	5.58
2000	102.68	430.97	152.64	-404.68	-192.30	5.02
2100	103.12	435.99	162.93	-404.13	-181.71	4.52
2200	103.52	440.80	173.26	-403.55	-171.21	4.07
2300	103.88	445.41	183.63	-403.00	-160.75	3.65
2400	104.19	449.84	194.04	-402.42	-150.37	3.27
2500	104.47	454.10	204.47	-401.83	-140.04	2.93
2600	104.73	458.20	214.93	-401.20	-129.70	2.61
2700	104.96	462.16	225.41	-400.62	-119.45	2.31
2800	105.16	465.98	235.92	-399.99	-109.20	2.04
2900	105.35	469.67	246.45	-399.36	-98.99	1.78
3000	105.52	473.25	256.99	-398.74	-88.78	1.55

CF₃O•

$\Delta H_f^\circ(0 \text{ K})$	= -623.37 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	= -628.33 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	= 292.57 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
136.13	139.58	144.70

Vibrational Frequencies (cm ⁻¹)				
224.6	410.9	572.2	583.2	607.1
883.4	1274.8	1277.7	1309.3	

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-O1	1.353				
C1-F1	1.308	O1-C1-F1	111.34		
C1-F2	1.308	O1-C1-F2	111.33	F1-C1-F2	120.51
C1-F3	1.307	O1-C1-F3	106.73	F1-C1-F3	-119.74

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	44.59	255.71	-8.12	-626.68	-609.94	212.39
200	51.68	269.51	-5.71	-627.43	-604.25	157.81
250	58.40	281.78	-2.96	-627.98	-598.44	125.03
300	64.49	292.97	0.12	-628.35	-592.50	103.16
350	69.89	303.33	3.48	-628.56	-586.55	87.53
400	74.63	312.98	7.10	-628.69	-580.53	75.81
450	78.76	322.01	10.93	-628.69	-574.55	66.69
500	82.30	330.49	14.96	-628.65	-568.56	59.39
600	87.95	346.03	23.49	-628.35	-556.60	48.45
700	92.10	359.91	32.51	-627.89	-544.67	40.64
800	95.17	372.42	41.87	-627.35	-532.83	34.79
900	97.49	383.77	51.51	-626.76	-521.03	30.24
1000	99.25	394.14	61.35	-626.18	-509.32	26.60
1100	100.63	403.66	71.35	-625.51	-497.60	23.63
1200	101.72	412.47	81.47	-624.88	-485.93	21.15
1300	102.59	420.65	91.69	-624.25	-474.30	19.06
1400	103.29	428.28	101.98	-623.58	-462.75	17.26
1500	103.88	435.42	112.34	-622.96	-451.20	15.71
1600	104.36	442.14	122.75	-622.29	-439.74	14.35
1700	104.77	448.48	133.21	-621.66	-428.32	13.16
1800	105.11	454.48	143.71	-620.99	-416.94	12.10
1900	105.41	460.17	154.23	-620.36	-405.60	11.15
2000	105.66	465.59	164.79	-619.73	-394.34	10.30
2100	105.88	470.75	175.36	-619.06	-383.13	9.53
2200	106.07	475.67	185.96	-618.40	-372.00	8.83
2300	106.24	480.39	196.58	-617.77	-360.91	8.20
2400	106.38	484.92	207.21	-617.10	-349.87	7.61
2500	106.52	489.26	217.85	-616.43	-338.90	7.08
2600	106.63	493.44	228.51	-615.80	-327.94	6.59
2700	106.73	497.47	239.18	-615.13	-317.06	6.13
2800	106.83	501.36	249.86	-614.46	-306.19	5.71
2900	106.91	505.11	260.54	-613.79	-295.35	5.32
3000	106.99	508.73	271.24	-613.12	-284.51	4.95

•CF₂OH

$\Delta H_f^\circ(0\text{ K})$	= -451.87 kJ mol ⁻¹
$\Delta H_f^\circ(298.15\text{ K})$	= -456.47 kJ mol ⁻¹
$S^\circ(298.15\text{ K})$	= 298.07 J K ⁻¹ mol ⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 76.29 78.01 146.52

Vibrational Frequencies (cm⁻¹)
 30.9 500.4 514.0 623.0 987.3
 1215.0 1267.2 1301.6 3570.6

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-O1	1.324				
C1-F1	1.318	O1-C1-F1	114.03		
C1-F2	1.317	O1-C1-F2	114.35	F1-C1-F2	126.17
O1-H1	0.954	C1-O1-H1	111.32	F2-O1-H1	68.56

Enthalpy Reference Temperature = T_r = 298.15 K
 Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	45.43	262.55	-7.78	-454.55	-444.26	154.69
200	50.13	276.25	-5.40	-455.30	-440.70	115.10
250	55.09	287.97	-2.77	-455.97	-437.02	91.30
300	59.94	298.44	0.11	-456.47	-433.17	75.42
350	64.49	308.03	3.22	-456.89	-429.28	64.06
400	68.64	316.92	6.55	-457.23	-425.35	55.54
450	72.34	325.22	10.08	-457.44	-421.37	48.91
500	75.59	333.01	13.78	-457.60	-417.35	43.60
600	80.90	347.28	21.61	-457.73	-409.32	35.63
700	84.95	360.08	29.92	-457.73	-401.29	29.94
800	88.11	371.63	38.58	-457.56	-393.25	25.67
900	90.63	382.16	47.52	-457.35	-385.18	22.36
1000	92.70	391.82	56.69	-457.10	-377.15	19.70
1100	94.43	400.74	66.05	-456.77	-369.11	17.53
1200	95.90	409.02	75.57	-456.43	-361.12	15.72
1300	97.15	416.75	85.22	-456.06	-353.13	14.19
1400	98.23	423.99	94.99	-455.64	-345.14	12.88
1500	99.17	430.80	104.86	-455.22	-337.23	11.74
1600	99.99	437.22	114.82	-454.76	-329.32	10.75
1700	100.71	443.31	124.85	-454.30	-321.46	9.88
1800	101.34	449.08	134.96	-453.84	-313.63	9.10
1900	101.90	454.58	145.12	-453.34	-305.85	8.41
2000	102.40	459.82	155.34	-452.83	-298.11	7.79
2100	102.84	464.83	165.60	-452.29	-290.45	7.22
2200	103.24	469.62	175.90	-451.79	-282.84	6.71
2300	103.59	474.21	186.25	-451.24	-275.27	6.25
2400	103.91	478.63	196.62	-450.66	-267.73	5.83
2500	104.20	482.88	207.03	-450.11	-260.29	5.44
2600	104.46	486.97	217.46	-449.53	-252.84	5.08
2700	104.69	490.92	227.92	-448.94	-245.43	4.75
2800	104.91	494.73	238.40	-448.36	-238.07	4.44
2900	105.10	498.41	248.90	-447.77	-230.75	4.16
3000	105.28	501.98	259.42	-447.14	-223.43	3.89

CH₂FOH hocf trans

$\Delta H_f^\circ(0 \text{ K})$ = -400.07 kJ mol⁻¹
 $\Delta H_f^\circ(298.15 \text{ K})$ = -412.09 kJ mol⁻¹
 $S^\circ(298.15 \text{ K})$ = 252.25 J K⁻¹ mol⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 17.26 77.89 89.86

Vibrational Frequencies (cm⁻¹)
 -115.0 507.5 1024.4 1125.5 1150.2
 1237.7 1250.2 1482.3 1536.4 2875.1
 2917.0 3671.3

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-O1	1.377	O1-C1-F1	106.83	F1-C1-H1	117.94
C1-F1	1.344	O1-C1-H1	111.76	F1-C1-H2	-117.94
C1-H1	1.084	O1-C1-H2	111.76	F1-O1-H3	180.00
C1-H2	1.084	C1-O1-H3	110.14		
O1-H3	0.947				

Enthalpy Reference Temperature = T_r = 298.15 K
 Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	34.89	225.93	-5.75	-406.06	-387.40	134.90
200	37.10	236.25	-3.96	-408.11	-380.91	99.48
250	40.23	244.84	-2.03	-410.16	-373.88	78.11
300	44.23	252.52	0.08	-412.17	-366.43	63.80
350	48.78	259.68	2.41	-414.05	-358.69	53.53
400	53.50	266.50	4.96	-415.76	-350.70	45.80
450	58.14	273.07	7.75	-417.35	-342.50	39.75
500	62.53	279.43	10.77	-418.82	-334.13	34.90
600	70.37	291.54	17.43	-421.33	-316.98	27.59
700	77.01	302.90	24.81	-423.38	-299.45	22.34
800	82.63	313.56	32.80	-425.09	-281.58	18.39
900	87.43	323.58	41.30	-426.43	-263.55	15.30
1000	91.55	333.01	50.26	-427.56	-245.39	12.82
1100	95.11	341.90	59.60	-428.44	-227.07	10.78
1200	98.20	350.32	69.27	-429.15	-208.66	9.08
1300	100.88	358.28	79.22	-429.70	-190.20	7.64
1400	103.22	365.85	89.43	-430.16	-171.67	6.41
1500	105.26	373.04	99.86	-430.45	-153.13	5.33
1600	107.05	379.89	110.47	-430.70	-134.60	4.39
1700	108.62	386.43	121.26	-430.87	-116.06	3.57
1800	110.01	392.68	132.19	-430.95	-97.53	2.83
1900	111.24	398.66	143.26	-430.99	-78.99	2.17
2000	112.33	404.40	154.44	-430.95	-60.50	1.58
2100	113.30	409.90	165.72	-430.91	-42.01	1.04
2200	114.16	415.19	177.09	-430.78	-23.56	0.56
2300	114.94	420.28	188.55	-430.66	-5.15	0.12
2400	115.64	425.19	200.08	-430.53	13.22	-0.29
2500	116.26	429.92	211.67	-430.32	31.55	-0.66
2600	116.83	434.50	223.33	-430.12	49.87	-1.00
2700	117.34	438.91	235.04	-429.86	68.16	-1.32
2800	117.81	443.19	246.80	-429.61	86.44	-1.61
2900	118.24	447.33	258.60	-429.36	104.73	-1.89
3000	118.62	451.34	270.44	-429.07	123.01	-2.14

CH₂FOH hocf cis

$\Delta H_f^\circ(0 \text{ K})$ = -408.78 kJ mol⁻¹
 $\Delta H_f^\circ(298.15 \text{ K})$ = -420.73 kJ mol⁻¹
 $S^\circ(298.15 \text{ K})$ = 252.71 J K⁻¹ mol⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 18.72 76.24 89.66

Vibrational Frequencies (cm⁻¹)
 -375.3 490.1 997.9 1120.0 1150.6
 1239.3 1257.0 1460.0 1542.4 2913.8
 2963.3 3672.2

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-O1	1.376				
C1-F1	1.360	O1-C1-F1	109.55		
C1-H1	1.081	O1-C1-H1	110.31	F1-C1-H1	118.65
C1-H2	1.081	O1-C1-H2	110.31	F1-C1-H2	-118.65
O1-H3	0.948	C1-O1-H3	108.83	F1-O1-H3	0.00

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	35.07	226.22	-5.79	-414.72	-396.14	137.94
200	37.34	236.61	-3.98	-416.81	-389.66	101.76
250	40.51	245.26	-2.04	-418.82	-382.63	79.94
300	44.53	252.99	0.08	-420.78	-375.22	65.33
350	49.08	260.19	2.42	-422.67	-367.52	54.85
400	53.80	267.05	4.99	-424.38	-359.53	46.95
450	58.41	273.66	7.80	-425.97	-351.37	40.78
500	62.77	280.04	10.83	-427.40	-343.00	35.83
600	70.55	292.19	17.51	-429.91	-325.93	28.37
700	77.12	303.57	24.90	-431.96	-308.44	23.02
800	82.68	314.25	32.90	-433.63	-290.70	18.98
900	87.43	324.27	41.41	-435.01	-272.71	15.83
1000	91.52	333.69	50.36	-436.10	-254.60	13.30
1100	95.06	342.59	59.69	-436.98	-236.35	11.22
1200	98.12	350.99	69.36	-437.73	-218.03	9.49
1300	100.80	358.95	79.31	-438.27	-199.62	8.02
1400	103.13	366.51	89.50	-438.73	-181.21	6.76
1500	105.17	373.70	99.92	-439.07	-162.72	5.67
1600	106.96	380.54	110.53	-439.28	-144.22	4.71
1700	108.53	387.08	121.31	-439.45	-125.77	3.86
1800	109.92	393.32	132.23	-439.57	-107.28	3.11
1900	111.15	399.30	143.29	-439.61	-88.83	2.44
2000	112.24	405.03	154.46	-439.57	-70.37	1.84
2100	113.22	410.53	165.73	-439.53	-51.97	1.29
2200	114.09	415.81	177.10	-439.45	-33.60	0.80
2300	114.87	420.91	188.54	-439.32	-15.23	0.35
2400	115.57	425.81	200.07	-439.15	3.10	-0.07
2500	116.20	430.54	211.66	-438.99	21.34	-0.45
2600	116.77	435.11	223.30	-438.78	39.62	-0.80
2700	117.29	439.53	235.01	-438.57	57.86	-1.12
2800	117.76	443.80	246.76	-438.32	76.07	-1.42
2900	118.19	447.94	258.56	-438.06	94.27	-1.70
3000	118.58	451.95	270.40	-437.77	112.47	-1.96

CH₂FOH hocf gauche

$\Delta H_f^\circ(0 \text{ K}) = -419.24 \text{ kJ mol}^{-1}$
 $\Delta H_f^\circ(298.15 \text{ K}) = -430.32 \text{ kJ mol}^{-1}$
 $S^\circ(298.15 \text{ K}) = 257.60 \text{ J K}^{-1} \text{ mol}^{-1}$

Moments of Inertia (10^{-47} kg m^2)
 18.02 78.78 89.64

Vibrational Frequencies (cm^{-1})
 351.4 528.7 1019.3 1068.8 1132.5
 1244.4 1362.7 1446.2 1522.1 2903.0
 2990.6 3657.1

Bond Distances (10^{-10} m)		Bond Angles ($^\circ$)		Dihedral Angles ($^\circ$)	
C1-O1	1.364				
C1-F1	1.361	O1-C1-F1	110.75		
C1-H1	1.077	O1-C1-H1	107.47	F1-C1-H1	118.27
C1-H2	1.083	O1-C1-H2	112.40	F1-C1-H2	-119.38
O1-H3	0.948	C1-O1-H3	109.90	F1-O1-H3	63.74

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$
 Standard State Pressure = $p_o = 1 \text{ atmosphere}$

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH_f°	ΔG_f°	
150	38.24	227.38	-6.56	-425.09	-406.68	141.61
200	42.16	239.00	-4.55	-426.94	-400.28	104.54
250	46.56	248.97	-2.34	-428.73	-393.46	82.20
300	51.52	257.92	0.10	-430.37	-386.27	67.26
350	56.76	266.25	2.79	-431.87	-378.86	56.54
400	61.97	274.16	5.74	-433.21	-371.20	48.47
450	66.89	281.72	8.95	-434.38	-363.42	42.18
500	71.41	288.98	12.39	-435.43	-355.51	37.14
600	79.18	302.68	19.92	-437.06	-339.41	29.55
700	85.49	315.34	28.17	-438.27	-323.00	24.10
800	90.69	327.08	36.99	-439.11	-306.48	20.01
900	95.05	338.01	46.31	-439.70	-289.78	16.82
1000	98.76	348.21	56.03	-440.03	-273.05	14.26
1100	101.96	357.77	66.10	-440.16	-256.23	12.17
1200	104.73	366.75	76.47	-440.20	-239.41	10.42
1300	107.13	375.23	87.10	-440.07	-222.59	8.94
1400	109.24	383.24	97.96	-439.86	-205.73	7.68
1500	111.08	390.84	109.01	-439.57	-188.95	6.58
1600	112.69	398.06	120.23	-439.19	-172.13	5.62
1700	114.12	404.93	131.60	-438.73	-155.39	4.77
1800	115.38	411.49	143.11	-438.27	-138.70	4.02
1900	116.49	417.83	154.73	-437.73	-122.17	3.36
2000	117.48	423.99	166.46	-437.19	-105.86	2.76
2100	118.37	429.89	178.28	-436.56	-89.66	2.23
2200	119.16	435.56	190.18	-435.93	-73.51	1.75
2300	119.87	441.01	202.15	-435.30	-57.45	1.31
2400	120.51	446.27	214.20	-434.63	-41.51	0.90
2500	121.08	451.34	226.30	-433.92	-25.56	0.53
2600	121.60	456.23	238.45	-433.21	-9.75	0.20
2700	122.07	460.96	250.66	-432.50	6.02	-0.12
2800	122.50	465.53	262.90	-431.75	21.76	-0.41
2900	122.89	469.96	275.19	-430.99	37.45	-0.67
3000	123.25	474.26	287.51	-430.24	53.09	-0.92

CHF₂OH hcoh trans

$\Delta H_f^\circ(0 \text{ K})$ = -674.25 kJ mol⁻¹
 $\Delta H_f^\circ(298.15 \text{ K})$ = -684.31 kJ mol⁻¹
 $S^\circ(298.15 \text{ K})$ = 275.29 J K⁻¹ mol⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 80.43 81.32 144.72

Vibrational Frequencies (cm⁻¹)
 300.8 498.6 532.3 640.5 1025.3
 1118.6 1192.0 1309.9 1384.2 1437.7
 3040.2 3630.2

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-O1	1.340				
O1-H1	0.951	C1-O1-H1	109.83		
C1-H2	1.073	O1-C1-H2	109.50	H1-C1-H2	180.00
C1-F1	1.337	O1-C1-F1	110.98	H2-C1-F1	121.21
C1-F2	1.337	O1-C1-F2	110.98	H2-C1-F2	-121.21

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	41.48	240.87	-7.52	-679.98	-658.19	229.18
200	47.87	253.81	-5.29	-681.62	-650.70	169.94
250	54.35	265.22	-2.75	-683.08	-642.83	134.31
300	60.68	275.67	0.11	-684.34	-634.71	110.50
350	66.65	285.45	3.28	-685.42	-626.34	93.47
400	72.12	294.67	6.74	-686.34	-617.89	80.68
450	77.00	303.43	10.46	-687.14	-609.27	70.72
500	81.30	311.74	14.42	-687.72	-600.61	62.74
600	88.39	327.18	22.93	-688.69	-583.08	50.76
700	93.90	341.21	32.08	-689.27	-565.43	42.19
800	98.30	354.03	41.73	-689.61	-547.69	35.76
900	101.92	365.81	51.78	-689.73	-529.86	30.75
1000	104.95	376.70	62.17	-689.73	-512.00	26.74
1100	107.53	386.82	72.83	-689.61	-494.13	23.46
1200	109.75	396.27	83.73	-689.40	-476.26	20.73
1300	111.67	405.13	94.84	-689.10	-458.44	18.42
1400	113.34	413.47	106.12	-688.73	-440.58	16.44
1500	114.80	421.53	117.56	-688.31	-423.09	14.73
1600	116.08	429.17	129.14	-687.85	-405.64	13.24
1700	117.20	436.43	140.83	-687.35	-388.28	11.93
1800	118.20	443.35	152.62	-686.80	-370.95	10.76
1900	119.08	449.94	164.51	-686.22	-353.76	9.72
2000	119.86	456.24	176.49	-685.59	-336.64	8.79
2100	120.56	462.28	188.53	-684.96	-319.57	7.95
2200	121.19	468.07	200.64	-684.34	-302.63	7.18
2300	121.75	473.63	212.80	-683.62	-285.73	6.49
2400	122.25	478.98	225.02	-682.95	-268.91	5.85
2500	122.70	484.12	237.28	-682.24	-252.17	5.27
2600	123.11	489.09	249.59	-681.53	-235.52	4.73
2700	123.49	493.88	261.93	-680.78	-218.91	4.23
2800	123.83	498.52	274.31	-680.03	-202.34	3.77
2900	124.14	503.00	286.73	-679.27	-185.81	3.35
3000	124.42	507.35	299.16	-678.48	-169.33	2.95

CHF₂OH hcoh gauche

$\Delta H_f^\circ(0 \text{ K}) = -662.24 \text{ kJ mol}^{-1}$
 $\Delta H_f^\circ(298.15 \text{ K}) = -671.82 \text{ kJ mol}^{-1}$
 $S^\circ(298.15 \text{ K}) = 279.18 \text{ J K}^{-1} \text{ mol}^{-1}$

Moments of Inertia (10^{-47} kg m^2)
 79.20 81.24 146.47

Vibrational Frequencies (cm^{-1})
 199.0 485.7 489.9 679.7 1066.7
 1096.2 1199.5 1264.6 1403.9 1457.5
 2971.2 3666.2

Bond Distances (10^{-10} m)		Bond Angles ($^\circ$)		Dihedral Angles ($^\circ$)	
C1-O1	1.348	C1-O1-H1	110.08	H1-C1-H2	68.50
O1-H1	0.949	O1-C1-H2	113.85	H2-C1-F1	121.02
C1-H2	1.079	O1-C1-F1	107.51	H2-C1-F2	-121.31
C1-F1	1.321	O1-C1-F2	110.36		
C1-F2	1.339				

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$
 Standard State Pressure = $p_o = 1 \text{ atmosphere}$

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH_f°	ΔG_f°	
150	44.53	244.12	-7.75	-667.72	-646.39	225.08
200	49.88	257.57	-5.40	-669.23	-639.06	166.90
250	54.93	269.15	-2.77	-670.61	-631.37	131.91
300	59.97	279.55	0.11	-671.87	-623.37	108.53
350	64.99	289.12	3.26	-672.95	-615.17	91.81
400	69.82	298.09	6.65	-673.96	-606.85	79.24
450	74.35	306.57	10.28	-674.80	-598.40	69.46
500	78.49	314.60	14.13	-675.55	-589.86	61.62
600	85.61	329.55	22.40	-676.72	-572.58	49.84
700	91.37	343.62	31.30	-677.56	-555.38	41.44
800	96.08	356.56	40.72	-678.10	-538.23	35.14
900	99.99	368.51	50.56	-678.48	-521.03	30.24
1000	103.27	379.59	60.76	-678.64	-503.84	26.32
1100	106.08	389.92	71.25	-678.73	-486.64	23.11
1200	108.48	399.58	82.00	-678.64	-469.49	20.44
1300	110.56	408.65	92.98	-678.48	-452.37	18.18
1400	112.36	417.20	104.14	-678.23	-435.30	16.24
1500	113.93	425.27	115.47	-677.93	-418.27	14.57
1600	115.30	432.92	126.95	-677.56	-401.33	13.10
1700	116.51	440.19	138.55	-677.14	-384.43	11.81
1800	117.57	447.10	150.27	-676.68	-367.61	10.67
1900	118.51	453.70	162.08	-676.18	-350.83	9.64
2000	119.35	460.01	173.98	-675.63	-334.18	8.73
2100	120.09	466.05	185.97	-675.05	-317.57	7.90
2200	120.75	471.83	198.02	-674.46	-301.04	7.15
2300	121.35	477.39	210.13	-673.83	-284.55	6.46
2400	121.88	482.75	222.30	-673.16	-268.19	5.84
2500	122.37	487.90	234.52	-672.49	-251.88	5.26
2600	122.80	492.86	246.78	-671.82	-235.64	4.73
2700	123.20	497.66	259.09	-671.11	-219.45	4.25
2800	123.55	502.29	271.43	-670.40	-203.30	3.79
2900	123.88	506.78	283.80	-669.69	-187.19	3.37
3000	124.18	511.12	296.21	-668.94	-171.13	2.98

CF₃OH

$\Delta H_f^\circ(0 \text{ K})$	= -910.77 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	= -919.44 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	= 290.10 J K ⁻¹ mol ⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)

143.10 144.11 145.53

Vibrational Frequencies (cm⁻¹)

233.3 427.8 440.7 583.1 607.5
 617.1 888.9 1123.5 1234.9 1323.7
 1414.0 3654.0

Bond Distances (10⁻¹⁰ m)

C1-O1 1.331
 C1-F1 1.320
 C1-F2 1.320
 C1-F3 1.304
 O1-H1 0.950

Bond Angles (°)

O1-C1-F1 111.91
 O1-C1-F2 111.91
 O1-C1-F3 108.83
 C1-O1-H1 110.26

Dihedral Angles (°)

F1-C1-F2 119.76
 F1-C1-F3 -120.12
 F1-O1-H1 -59.80

Enthalpy Reference Temperature = T_r = 298.15 K**Standard State Pressure = p_o = 1 atmosphere**

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	46.20	250.71	-8.70	-916.21	-890.48	310.08
200	54.91	265.20	-6.17	-917.55	-881.69	230.27
250	63.14	278.35	-3.22	-918.64	-872.62	182.32
300	70.58	290.53	0.13	-919.48	-863.37	150.32
350	77.21	301.92	3.83	-920.10	-854.00	127.45
400	83.05	312.62	7.84	-920.52	-844.54	110.28
450	88.13	322.70	12.12	-920.81	-835.04	96.93
500	92.53	332.22	16.64	-921.02	-825.55	86.24
600	99.61	349.75	26.26	-921.07	-806.47	70.20
700	104.93	365.52	36.51	-920.86	-787.39	58.75
800	109.01	379.81	47.21	-920.44	-768.35	50.17
900	112.22	392.84	58.27	-919.89	-749.35	43.49
1000	114.81	404.81	69.63	-919.27	-730.40	38.15
1100	116.95	415.85	81.22	-918.56	-711.49	33.78
1200	118.74	426.11	93.01	-917.76	-692.66	30.15
1300	120.26	435.68	104.96	-916.88	-673.88	27.07
1400	121.55	444.63	117.06	-916.00	-655.13	24.44
1500	122.67	453.06	129.27	-915.08	-636.47	22.16
1600	123.65	461.01	141.59	-914.12	-617.85	20.17
1700	124.49	468.53	153.99	-913.16	-599.36	18.41
1800	125.24	475.67	166.48	-912.11	-580.91	16.86
1900	125.89	482.46	179.04	-911.11	-562.50	15.46
2000	126.47	488.93	191.66	-910.02	-544.21	14.21
2100	126.98	495.11	204.33	-908.97	-526.01	13.08
2200	127.44	501.03	217.05	-907.84	-507.85	12.06
2300	127.85	506.70	229.81	-906.76	-489.82	11.12
2400	128.22	512.16	242.62	-905.63	-471.83	10.27
2500	128.56	517.40	255.46	-904.50	-453.92	9.48
2600	128.86	522.44	268.33	-903.33	-436.06	8.76
2700	129.13	527.31	281.23	-902.20	-418.27	8.09
2800	129.38	532.01	294.16	-901.02	-400.53	7.47
2900	129.60	536.56	307.11	-899.81	-382.84	6.90
3000	129.81	540.95	320.08	-898.64	-365.18	6.36

CF₃OO•

$\Delta H_f^\circ(0\text{ K})$	= -620.53 kJ mol ⁻¹
$\Delta H_f^\circ(298.15\text{ K})$	= -627.46 kJ mol ⁻¹
$S^\circ(298.15\text{ K})$	= 314.37 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
144.76	249.01	251.97

Vibrational Frequencies (cm ⁻¹)				
122.1	278.9	420.0	442.3	571.0
593.0	686.4	878.3	1124.2	1251.0
1287.7	1340.3			

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-O1	1.372	C1-O1-O2	110.50	O2-C1-F1	180.00
O1-O2	1.314	O1-C1-F1	106.06	O2-C1-F2	60.61
C1-F1	1.300	O1-C1-F2	111.13	O2-C1-F3	-60.61
C1-F2	1.304	O1-C1-F3	111.13		
C1-F3	1.304				

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	53.17	269.64	-9.87	-625.42	-596.93	207.86
200	62.72	286.11	-6.98	-626.39	-587.27	153.37
250	71.63	301.09	-3.63	-627.06	-577.43	120.64
300	79.61	314.87	0.15	-627.47	-567.52	98.81
350	86.58	327.67	4.30	-627.64	-557.52	83.20
400	92.55	339.62	8.77	-627.64	-547.56	71.50
450	97.59	350.82	13.52	-627.47	-537.56	62.40
500	101.82	361.32	18.51	-627.22	-527.60	55.12
600	108.32	380.49	29.04	-626.47	-507.77	44.20
700	112.89	397.54	40.12	-625.55	-488.06	36.42
800	116.17	412.84	51.60	-624.50	-468.48	30.59
900	118.57	426.67	63.35	-623.46	-449.03	26.06
1000	120.37	439.26	75.32	-622.41	-429.65	22.44
1100	121.75	450.80	87.45	-621.37	-410.37	19.49
1200	122.83	461.44	99.70	-620.32	-391.12	17.03
1300	123.68	471.30	112.03	-619.32	-372.00	14.95
1400	124.37	480.49	124.45	-618.31	-352.92	13.17
1500	124.93	489.16	136.93	-617.31	-334.05	11.63
1600	125.39	497.43	149.46	-616.35	-315.43	10.30
1700	125.78	505.23	162.03	-615.38	-296.90	9.12
1800	126.10	512.61	174.64	-614.42	-278.49	8.08
1900	126.38	519.62	187.27	-613.50	-260.20	7.15
2000	126.62	526.28	199.93	-612.54	-241.96	6.32
2100	126.83	532.63	212.61	-611.62	-223.84	5.57
2200	127.01	538.69	225.31	-610.70	-205.85	4.89
2300	127.16	544.50	238.03	-609.78	-187.90	4.27
2400	127.30	550.07	250.76	-608.86	-170.08	3.70
2500	127.42	555.42	263.50	-607.89	-152.34	3.18
2600	127.53	560.56	276.26	-606.97	-134.64	2.70
2700	127.62	565.51	289.02	-606.09	-117.03	2.26
2800	127.71	570.30	301.79	-605.17	-99.45	1.86
2900	127.79	574.91	314.57	-604.25	-81.96	1.48
3000	127.86	579.37	327.36	-603.33	-64.48	1.12

CF₃OOH

$\Delta H_f^\circ(0\text{ K})$	= -797.30 kJ mol ⁻¹
$\Delta H_f^\circ(298.15\text{ K})$	= -807.48 kJ mol ⁻¹
$S^\circ(298.15\text{ K})$	= 314.50 J K ⁻¹ mol ⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 146.17 260.61 262.43

Vibrational Frequencies (cm⁻¹)
 138.6 256.6 289.0 429.1 437.1
 571.9 604.2 673.8 879.1 1067.5
 1262.5 1293.6 1318.6 1438.0 3629.8

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-O1	1.351				
O1-O2	1.388	C1-O1-O2	108.42		
C1-F1	1.305	O1-C1-F1	106.36	O2-C1-F1	179.75
C1-F2	1.306	O1-C1-F2	112.36	O2-C1-F2	60.07
C1-F3	1.314	O1-C1-F3	111.48	O2-C1-F3	-61.40
O2-H1	0.952	O1-O2-H1	102.23	C1-O2-H1	104.50

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	57.60	265.92	-10.77	-804.16	-766.89	267.04
200	68.35	283.91	-7.62	-805.63	-754.25	196.98
250	78.04	300.13	-3.96	-806.72	-741.24	154.87
300	86.75	315.03	0.16	-807.51	-728.06	126.76
350	94.56	328.95	4.69	-808.01	-714.79	106.67
400	101.50	342.05	9.59	-808.31	-701.49	91.60
450	107.57	354.36	14.81	-808.43	-688.18	79.88
500	112.81	365.97	20.32	-808.39	-674.84	70.50
600	121.14	387.31	32.02	-807.89	-648.19	56.43
700	127.21	406.46	44.45	-807.09	-621.66	46.39
800	131.70	423.75	57.40	-806.05	-595.26	38.86
900	135.08	439.46	70.75	-804.88	-568.94	33.02
1000	137.70	453.83	84.40	-803.62	-542.79	28.35
1100	139.79	467.06	98.29	-802.32	-516.68	24.53
1200	141.48	479.29	112.36	-800.98	-490.70	21.36
1300	142.88	490.67	126.59	-799.60	-464.84	18.68
1400	144.05	501.31	140.95	-798.22	-439.07	16.38
1500	145.05	511.28	155.42	-796.80	-413.38	14.39
1600	145.90	520.67	169.98	-795.42	-387.77	12.66
1700	146.64	529.54	184.62	-794.00	-362.29	11.13
1800	147.28	537.93	199.33	-792.53	-336.90	9.78
1900	147.85	545.91	214.10	-791.11	-311.62	8.57
2000	148.34	553.51	228.92	-789.69	-286.44	7.48
2100	148.78	560.76	243.78	-788.22	-261.33	6.50
2200	149.17	567.69	258.69	-786.76	-236.35	5.61
2300	149.51	574.33	273.63	-785.29	-211.46	4.80
2400	149.82	580.81	288.61	-783.83	-186.94	4.07
2500	150.10	587.06	303.62	-782.37	-162.55	3.40
2600	150.36	593.07	318.65	-780.90	-138.24	2.78
2700	150.58	598.86	333.70	-779.40	-114.01	2.21
2800	150.79	604.46	348.78	-777.93	-89.87	1.68
2900	150.98	609.87	363.88	-776.42	-65.81	1.19
3000	151.15	615.10	378.99	-774.96	-41.80	0.73

CH₃-CH₂F

$\Delta H_f^\circ(0\text{ K})$	= -256.98 kJ mol ⁻¹
$\Delta H_f^\circ(298.15\text{ K})$	= -272.35 kJ mol ⁻¹
$S^\circ(298.15\text{ K})$	= 265.04 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
22.84	88.06	100.54

Vibrational Frequencies (cm ⁻¹)				
243.8	392.5	783.4	866.8	1043.2
1106.9	1168.9	1269.4	1381.2	1417.4
1452.5	1468.9	1502.8	2868.8	2895.9
2924.5	2929.2	2947.8		

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.512	C1-C2-H1	110.47	H1-C2-H2	119.95
C2-H1	1.084	C1-C2-H2	110.48	H1-C2-H3	239.98
C2-H2	1.084	C1-C2-H3	110.34	H1-C1-H4	59.17
C2-H3	1.086	C2-C1-H4	111.55	H1-C1-H5	180.93
C1-H4	1.083	C2-C1-H5	111.56	H1-C1-F1	300.06
C1-H5	1.083	C2-C1-F1	109.54		
C1-F1	1.373				

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	42.22	231.14	-7.39	-264.85	-244.05	84.98
200	47.14	244.05	-5.17	-267.44	-236.77	61.83
250	52.92	255.19	-2.69	-269.99	-228.86	47.81
300	59.58	265.41	0.11	-272.42	-220.45	38.38
350	66.68	275.10	3.25	-274.72	-211.67	31.59
400	73.79	284.45	6.75	-276.77	-202.55	26.45
450	80.60	293.52	10.61	-278.65	-193.22	22.43
500	86.99	302.33	14.79	-280.33	-183.68	19.19
600	98.41	319.20	24.09	-283.13	-164.10	14.29
700	108.16	335.10	34.44	-285.27	-144.10	10.75
800	116.55	350.09	45.71	-286.86	-123.76	8.08
900	123.78	364.24	57.77	-287.98	-103.26	5.99
1000	130.03	377.61	70.50	-288.70	-82.59	4.31
1100	135.44	390.25	83.81	-289.11	-61.80	2.93
1200	140.12	402.24	97.62	-289.24	-40.96	1.78
1300	144.18	413.62	111.87	-289.16	-20.13	0.81
1400	147.70	424.43	126.49	-288.86	0.71	-0.03
1500	150.75	434.83	141.44	-288.44	21.38	-0.74
1600	153.42	444.84	156.68	-287.90	41.84	-1.37
1700	155.75	454.40	172.16	-287.23	62.22	-1.91
1800	157.80	463.55	187.87	-286.52	82.51	-2.39
1900	159.59	472.30	203.76	-285.68	102.68	-2.82
2000	161.19	480.70	219.81	-284.80	122.72	-3.20
2100	162.60	488.77	236.02	-283.88	142.63	-3.55
2200	163.85	496.53	252.36	-282.92	162.42	-3.86
2300	164.98	504.00	268.82	-281.92	182.09	-4.14
2400	165.98	511.19	285.38	-280.83	201.67	-4.39
2500	166.88	518.13	302.04	-279.74	221.08	-4.62
2600	167.69	524.84	318.78	-278.65	240.41	-4.83
2700	168.43	531.32	335.60	-277.52	259.66	-5.02
2800	169.09	537.60	352.49	-276.35	278.86	-5.20
2900	169.70	543.67	369.44	-275.18	297.98	-5.37
3000	170.25	549.56	386.45	-273.97	317.06	-5.52

CH₃-CH₂Cl

$\Delta H_f^\circ(0 \text{ K})$	= -98.58 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	= -113.66 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	= 276.16 J K ⁻¹ mol ⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 26.35 153.85 169.86

Vibrational Frequencies (cm⁻¹)

248.4	319.4	641.6	761.9	944.9
1055.8	1062.6	1247.5	1305.9	1398.2
1455.6	1463.7	1468.7	2869.1	2925.6
2938.8	2945.4	2990.0		

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.517	C1-C2-H1	111.05	H1-C2-H2	120.85
C2-H1	1.083	C1-C2-H2	111.05	H1-C2-H3	240.43
C2-H2	1.083	C1-C2-H3	109.22	H1-C1-H4	58.34
C2-H3	1.086	C2-C1-H4	111.79	H1-C1-H5	180.81
C1-H4	1.079	C2-C1-H5	111.80	H1-C1-C11	299.58
C1-H5	1.079	C2-C1-C11	111.49		
C1-C11	1.799				

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	Log K _f
150	43.87	240.51	-7.80	-106.40	-85.65	29.82
200	49.58	253.94	-5.48	-108.95	-78.37	20.47
250	56.04	265.72	-2.85	-111.42	-70.50	14.73
300	63.15	276.55	0.12	-113.76	-62.13	10.82
350	70.51	286.83	3.44	-115.90	-53.43	7.97
400	77.71	296.70	7.14	-117.86	-44.43	5.80
450	84.49	306.23	11.18	-119.58	-35.19	4.09
500	90.76	315.45	15.56	-121.13	-25.77	2.69
600	101.79	332.98	25.20	-123.68	-6.53	0.57
700	111.11	349.37	35.87	-125.56	13.14	-0.98
800	119.06	364.72	47.40	-126.94	33.10	-2.16
900	125.92	379.14	59.68	-127.86	53.22	-3.09
1000	131.85	392.72	72.60	-128.45	73.47	-3.84
1100	137.00	405.53	86.08	-128.70	93.81	-4.45
1200	141.46	417.64	100.04	-128.74	114.18	-4.97
1300	145.33	429.12	114.41	-128.53	134.60	-5.41
1400	148.70	440.01	129.14	-128.16	154.98	-5.78
1500	151.63	450.37	144.19	-127.65	175.35	-6.11
1600	154.19	460.24	159.51	-127.07	195.64	-6.39
1700	156.44	469.79	175.06	-126.36	215.69	-6.63
1800	158.41	478.96	190.83	-125.56	235.52	-6.83
1900	160.15	487.74	206.78	-124.68	255.27	-7.02
2000	161.69	496.16	222.89	-123.76	274.89	-7.18
2100	163.05	504.24	239.15	-122.80	294.39	-7.32
2200	164.26	512.01	255.53	-121.80	313.76	-7.45
2300	165.35	519.49	272.03	-120.75	333.00	-7.56
2400	166.32	526.69	288.63	-119.66	352.13	-7.66
2500	167.20	533.65	305.32	-118.53	371.12	-7.75
2600	167.99	540.36	322.09	-117.40	390.03	-7.84
2700	168.70	546.85	338.94	-116.23	408.82	-7.91
2800	169.35	553.13	355.86	-115.06	427.56	-7.98
2900	169.93	559.21	372.83	-113.85	446.27	-8.04
3000	170.47	565.11	389.87	-112.63	464.93	-8.09

CH₂F-CH₂•

$\Delta H_f^\circ(0 \text{ K})$	=	-46.02 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	=	-56.22 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	=	275.18 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
20.06	82.42	96.41

Vibrational Frequencies (cm ⁻¹)				
158.7	382.9	439.8	831.2	956.3
1060.3	1100.4	1227.7	1388.3	1426.0
1486.1	2855.7	2906.9	2973.9	3070.7

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.489	C2-C1-F1	110.04		
C1-F1	1.371	C2-C1-H1	111.36	F1-C1-H1	240.16
C1-H1	1.084	C1-C2-H2	119.68	F1-C2-H2	163.95
C2-H2	1.074	C1-C2-H3	119.22	F1-C2-H3	-32.85
C2-H3	1.074	C2-C1-H4	111.93	F1-C1-H4	119.10
C1-H4	1.087				

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	45.71	238.96	-7.95	-51.42	-40.04	13.94
200	50.91	252.83	-5.53	-53.09	-36.02	9.41
250	56.40	264.77	-2.85	-54.73	-31.59	6.60
300	62.27	275.57	0.11	-56.27	-26.86	4.68
350	68.26	285.62	3.38	-57.70	-21.88	3.27
400	74.12	295.11	6.94	-58.99	-16.74	2.19
450	79.64	304.17	10.79	-60.17	-11.42	1.33
500	84.77	312.83	14.90	-61.17	-6.02	0.63
600	93.85	329.11	23.84	-62.84	5.10	-0.45
700	101.57	344.17	33.62	-64.14	16.53	-1.23
800	108.19	358.18	44.12	-65.02	28.12	-1.83
900	113.90	371.26	55.23	-65.61	39.83	-2.31
1000	118.85	383.52	66.87	-65.94	51.63	-2.70
1100	123.14	395.05	78.98	-66.02	63.47	-3.01
1200	126.86	405.93	91.48	-65.94	75.35	-3.28
1300	130.09	416.22	104.33	-65.73	87.28	-3.51
1400	132.90	425.96	117.49	-65.35	99.16	-3.70
1500	135.35	435.22	130.90	-64.89	111.00	-3.87
1600	137.49	444.02	144.54	-64.35	122.84	-4.01
1700	139.36	452.42	158.39	-63.72	134.60	-4.14
1800	141.00	460.43	172.41	-63.05	146.27	-4.24
1900	142.45	468.09	186.59	-62.30	157.90	-4.34
2000	143.73	475.43	200.89	-61.55	169.41	-4.42
2100	144.87	482.47	215.33	-60.71	180.83	-4.50
2200	145.88	489.24	229.86	-59.83	192.17	-4.56
2300	146.79	495.74	244.50	-58.95	203.43	-4.62
2400	147.60	502.00	259.22	-58.03	214.56	-4.67
2500	148.33	508.05	274.02	-57.11	225.60	-4.71
2600	148.99	513.88	288.88	-56.15	236.61	-4.75
2700	149.58	519.51	303.81	-55.15	247.53	-4.79
2800	150.12	524.96	318.80	-54.18	258.36	-4.82
2900	150.61	530.24	333.84	-53.14	269.20	-4.85
3000	151.06	535.35	348.92	-52.13	280.04	-4.88

CH₂=CHF

$\Delta H_f^\circ(0 \text{ K})$	= -131.00 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	= -139.21 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	= 252.27 J K ⁻¹ mol ⁻¹

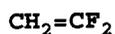
Moments of Inertia (10⁻⁴⁷ kg m²)
 12.50 77.57 90.08

Vibrational Frequencies (cm⁻¹)
 467.3 714.3 915.5 922.0 976.7
 1148.6 1300.9 1393.4 1690.0 3003.1
 3060.3 3086.1

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)
C1-C2	1.309			
C1-F1	1.329	C2-C1-F1	122.38	
C1-H1	1.072	C2-C1-H1	125.70	
C2-H2	1.073	C1-C2-H2	119.75	
C2-H3	1.074	C1-C2-H3	121.50	

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	35.88	223.78	-6.26	-134.89	-129.45	45.08
200	39.66	234.58	-4.38	-136.36	-127.49	33.29
250	44.65	243.95	-2.28	-137.86	-125.10	26.14
300	50.26	252.58	0.09	-139.24	-122.47	21.32
350	55.98	260.76	2.75	-140.54	-119.62	17.85
400	61.47	268.60	5.69	-141.75	-116.61	15.22
450	66.57	276.14	8.89	-142.80	-113.43	13.17
500	71.23	283.39	12.34	-143.76	-110.16	11.51
600	79.31	297.12	19.88	-145.44	-103.34	9.00
700	86.01	309.87	28.15	-146.73	-96.27	7.18
800	91.65	321.73	37.05	-147.78	-88.99	5.81
900	96.47	332.81	46.45	-148.57	-81.55	4.73
1000	100.60	343.19	56.32	-149.20	-74.01	3.87
1100	104.17	352.95	66.56	-149.66	-66.36	3.15
1200	107.26	362.15	77.13	-150.00	-58.66	2.55
1300	109.93	370.84	88.00	-150.21	-50.88	2.05
1400	112.25	379.08	99.11	-150.33	-43.14	1.61
1500	114.27	386.89	110.44	-150.37	-35.31	1.23
1600	116.04	394.33	121.96	-150.37	-27.57	0.90
1700	117.58	401.41	133.64	-150.33	-19.79	0.61
1800	118.94	408.17	145.47	-150.21	-12.09	0.35
1900	120.14	414.63	157.42	-150.04	-4.39	0.12
2000	121.20	420.82	169.49	-149.83	3.18	-0.08
2100	122.14	426.76	181.66	-149.62	10.75	-0.27
2200	122.98	432.46	193.91	-149.37	18.24	-0.43
2300	123.73	437.95	206.25	-149.08	25.65	-0.58
2400	124.41	443.23	218.66	-148.74	32.97	-0.72
2500	125.01	448.32	231.13	-148.45	40.25	-0.84
2600	125.56	453.23	243.66	-148.07	47.49	-0.95
2700	126.05	457.98	256.24	-147.74	54.68	-1.06
2800	126.50	462.57	268.87	-147.36	61.84	-1.15
2900	126.90	467.02	281.54	-146.94	68.99	-1.24
3000	127.28	471.33	294.25	-146.52	76.19	-1.33



$$\begin{aligned}\Delta H_f^\circ(0 \text{ K}) &= -332.84 \text{ kJ mol}^{-1} \\ \Delta H_f^\circ(298.15 \text{ K}) &= -340.11 \text{ kJ mol}^{-1} \\ S^\circ(298.15 \text{ K}) &= 270.73 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Moments of Inertia (10^{-47} kg m^2)
74.36 78.66 153.02

Vibrational Frequencies (cm^{-1})
423.0 528.3 629.6 712.8 864.8
918.6 951.6 1332.4 1386.2 1747.8
3026.7 3113.8

Bond Distances (10^{-10} m)	Bond Angles ($^\circ$)	Dihedral Angles ($^\circ$)
C1-C2 1.305		
C1-F1 1.303	C2-C1-F1 125.19	
C1-F2 1.303	C2-C1-F2 125.27	
C2-H1 1.070	C1-C2-H1 119.93	
C2-H2 1.071	C1-C2-H2 119.82	

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$
Standard State Pressure = $p_o = 1 \text{ atmosphere}$

T/K	C_p° - J K ⁻¹ mol ⁻¹ -	S°	$H^\circ - H^\circ(T_r)$	ΔH_f° kJ mol ⁻¹	ΔG_f° kJ mol ⁻¹	Log K_f
150	38.53	238.25	-7.18	-336.64	-327.98	114.21
200	44.95	250.18	-5.10	-337.94	-324.93	84.86
250	52.09	260.98	-2.67	-339.11	-321.58	67.19
300	59.09	271.10	0.11	-340.16	-318.03	55.37
350	65.58	280.70	3.23	-341.04	-314.30	46.91
400	71.40	289.85	6.66	-341.83	-310.49	40.54
450	76.58	298.57	10.36	-342.50	-306.56	35.58
500	81.17	306.88	14.31	-343.09	-302.59	31.61
600	88.83	322.38	22.82	-344.01	-294.47	25.64
700	94.94	336.55	32.02	-344.68	-286.23	21.36
800	99.93	349.56	41.77	-345.18	-277.82	18.14
900	104.06	361.58	51.97	-345.51	-269.37	15.63
1000	107.54	372.73	62.56	-345.72	-260.83	13.62
1100	110.49	383.12	73.47	-345.85	-252.21	11.98
1200	113.00	392.84	84.64	-345.89	-243.59	10.60
1300	115.15	401.97	96.05	-345.85	-234.93	9.44
1400	117.00	410.58	107.66	-345.77	-226.27	8.44
1500	118.60	418.71	119.44	-345.64	-217.61	7.58
1600	119.99	426.40	131.38	-345.47	-208.99	6.82
1700	121.20	433.72	143.44	-345.26	-200.37	6.16
1800	122.26	440.68	155.61	-345.01	-191.84	5.57
1900	123.19	447.31	167.88	-344.76	-183.30	5.04
2000	124.01	453.65	180.25	-344.47	-174.89	4.57
2100	124.74	459.72	192.69	-344.13	-166.48	4.14
2200	125.38	465.54	205.19	-343.80	-158.20	3.76
2300	125.96	471.12	217.76	-343.46	-149.95	3.41
2400	126.48	476.49	230.38	-343.09	-141.80	3.09
2500	126.94	481.67	243.05	-342.71	-133.72	2.79
2600	127.36	486.65	255.77	-342.33	-125.65	2.52
2700	127.73	491.47	268.52	-341.92	-117.65	2.28
2800	128.08	496.12	281.31	-341.50	-109.70	2.05
2900	128.39	500.62	294.14	-341.08	-101.75	1.83
3000	128.67	504.98	306.99	-340.62	-93.76	1.63

CHF=CHF fccf cis

$\Delta H_f^\circ(0 \text{ K})$ = -294.43 kJ mol⁻¹
 $\Delta H_f^\circ(298.15 \text{ K})$ = -301.29 kJ mol⁻¹
 $S^\circ(298.15 \text{ K})$ = 274.29 J K⁻¹ mol⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 38.51 139.95 178.47

Vibrational Frequencies (cm⁻¹)
 225.8 491.8 747.9 803.9 905.7
 1004.3 1110.8 1254.7 1380.3 1759.7
 3070.6 3094.3

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.307				
C1-F1	1.324	C2-C1-F1	122.58		
C1-H1	1.070	C2-C1-H1	123.07		
C2-H2	1.070	C1-C2-H2	123.07		
C2-F2	1.324	C1-C2-F2	122.58	F1-C2-F2	0.00

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	41.39	241.12	-7.29	-297.94	-289.70	100.88
200	46.30	253.68	-5.10	-299.11	-286.81	74.91
250	52.07	264.62	-2.65	-300.29	-283.63	59.26
300	58.19	274.65	0.11	-301.33	-280.29	48.80
350	64.22	284.08	3.17	-302.29	-276.73	41.30
400	69.88	293.03	6.52	-303.13	-273.09	35.66
450	75.04	301.56	10.15	-303.88	-269.32	31.26
500	79.67	309.71	14.02	-304.55	-265.47	27.73
600	87.53	324.96	22.39	-305.60	-257.65	22.43
700	93.84	338.94	31.47	-306.39	-249.62	18.63
800	99.00	351.82	41.12	-306.98	-241.46	15.77
900	103.28	363.74	51.24	-307.40	-233.22	13.53
1000	106.87	374.81	61.76	-307.69	-224.89	11.75
1100	109.91	385.14	72.60	-307.90	-216.48	10.28
1200	112.49	394.81	83.72	-307.98	-208.07	9.06
1300	114.70	403.91	95.09	-307.98	-199.62	8.02
1400	116.60	412.48	106.65	-307.94	-191.13	7.13
1500	118.25	420.58	118.39	-307.86	-182.67	6.36
1600	119.67	428.26	130.29	-307.73	-174.22	5.69
1700	120.91	435.55	142.33	-307.52	-165.81	5.09
1800	122.00	442.50	154.47	-307.31	-157.40	4.57
1900	122.96	449.12	166.72	-307.11	-149.12	4.10
2000	123.80	455.45	179.06	-306.81	-140.83	3.68
2100	124.54	461.51	191.48	-306.52	-132.63	3.30
2200	125.20	467.32	203.97	-306.23	-124.52	2.96
2300	125.79	472.90	216.51	-305.89	-116.48	2.64
2400	126.32	478.26	229.12	-305.56	-108.49	2.36
2500	126.80	483.43	241.78	-305.18	-100.54	2.10
2600	127.22	488.41	254.48	-304.80	-92.68	1.86
2700	127.61	493.22	267.22	-304.39	-84.85	1.64
2800	127.96	497.87	280.00	-303.97	-77.07	1.44
2900	128.28	502.36	292.81	-303.55	-69.29	1.25
3000	128.57	506.72	305.65	-303.13	-61.50	1.07

CHF=CHF fccf trans

$\Delta H_f^\circ(0 \text{ K})$ = -295.64 kJ mol⁻¹
 $\Delta H_f^\circ(298.15 \text{ K})$ = -302.24 kJ mol⁻¹
 $S^\circ(298.15 \text{ K})$ = 273.56 J K⁻¹ mol⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 14.20 204.16 218.35

Vibrational Frequencies (cm⁻¹)
 308.1 337.6 538.5 846.3 928.0
 1128.5 1144.3 1269.3 1269.3 1747.6
 3062.2 3071.4

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.306				
C1-F1	1.329	C2-C1-F1	120.24		
C1-H1	1.070	C2-C1-H1	125.28		
C2-H2	1.070	C1-C2-H2	125.28		
C2-F2	1.329	C1-C2-F2	120.25	F1-C2-F2	180.00

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	42.76	239.06	-7.58	-299.16	-290.66	101.21
200	48.41	252.14	-5.30	-300.29	-287.65	75.13
250	54.12	263.55	-2.74	-301.33	-284.43	59.42
300	59.93	273.93	0.11	-302.29	-281.00	48.92
350	65.63	283.60	3.25	-303.17	-277.44	41.40
400	71.01	292.72	6.67	-303.93	-273.76	35.75
450	75.96	301.37	10.34	-304.64	-269.99	31.34
500	80.45	309.61	14.25	-305.26	-266.14	27.80
600	88.10	324.98	22.70	-306.23	-258.28	22.49
700	94.30	339.04	31.83	-306.98	-250.29	18.68
800	99.39	351.98	41.52	-307.52	-242.13	15.81
900	103.61	363.93	51.68	-307.94	-233.93	13.58
1000	107.16	375.04	62.22	-308.19	-225.60	11.78
1100	110.16	385.40	73.09	-308.36	-217.23	10.32
1200	112.72	395.10	84.24	-308.40	-208.82	9.09
1300	114.91	404.21	95.62	-308.40	-200.41	8.05
1400	116.79	412.79	107.21	-308.36	-191.96	7.16
1500	118.42	420.91	118.97	-308.24	-183.51	6.39
1600	119.83	428.60	130.88	-308.07	-175.10	5.72
1700	121.06	435.90	142.93	-307.90	-166.73	5.12
1800	122.13	442.85	155.09	-307.65	-158.36	4.60
1900	123.08	449.48	167.35	-307.40	-150.08	4.13
2000	123.91	455.81	179.70	-307.15	-141.88	3.71
2100	124.65	461.88	192.13	-306.81	-133.72	3.33
2200	125.30	467.69	204.63	-306.52	-125.65	2.98
2300	125.88	473.27	217.19	-306.19	-117.61	2.67
2400	126.41	478.64	229.80	-305.81	-109.66	2.39
2500	126.88	483.81	242.47	-305.43	-101.80	2.13
2600	127.30	488.80	255.18	-305.06	-93.97	1.89
2700	127.68	493.61	267.93	-304.64	-86.15	1.67
2800	128.02	498.26	280.71	-304.22	-78.41	1.46
2900	128.34	502.76	293.53	-303.80	-70.67	1.27
3000	128.62	507.11	306.38	-303.38	-62.93	1.10

CHF=CF₂

$\Delta H_f^\circ(0 \text{ K}) = -480.24 \text{ kJ mol}^{-1}$
 $\Delta H_f^\circ(298.15 \text{ K}) = -485.56 \text{ kJ mol}^{-1}$
 $S^\circ(298.15 \text{ K}) = 292.39 \text{ J K}^{-1} \text{ mol}^{-1}$

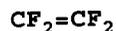
Moments of Inertia (10^{-47} kg m^2)
 76.88 212.39 289.27

Vibrational Frequencies (cm^{-1})
 223.0 306.8 468.9 585.8 605.0
 815.9 921.9 1144.8 1265.0 1368.2
 1824.4 3105.2

Bond Distances (10^{-10} m)		Bond Angles ($^\circ$)		Dihedral Angles ($^\circ$)	
C1-C2	1.304				
C1-F1	1.298	C2-C1-F1	125.42		
C1-F2	1.303	C2-C1-F2	122.87		
C2-H1	1.068	C1-C2-H1	123.39		
C2-F3	1.327	C1-C2-F3	120.55		

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$
Standard State Pressure = $p_o = 1 \text{ atmosphere}$

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	47.30	253.10	-8.66	-483.50	-471.66	164.24
200	55.00	267.77	-6.10	-484.34	-467.60	122.12
250	62.34	280.84	-3.16	-485.01	-463.42	96.82
300	69.13	292.82	0.13	-485.60	-459.07	79.93
350	75.30	303.94	3.74	-486.06	-454.68	67.85
400	80.82	314.36	7.65	-486.43	-450.20	58.79
450	85.72	324.17	11.81	-486.72	-445.72	51.73
500	90.05	333.44	16.21	-486.98	-441.16	46.09
600	97.23	350.51	25.59	-487.27	-432.04	37.61
700	102.85	365.94	35.60	-487.44	-422.88	31.55
800	107.31	379.98	46.12	-487.48	-413.67	27.01
900	110.90	392.83	57.04	-487.44	-404.38	23.47
1000	113.83	404.67	68.27	-487.31	-395.10	20.64
1100	116.24	415.63	79.78	-487.14	-385.81	18.32
1200	118.26	425.84	91.51	-486.93	-376.48	16.39
1300	119.95	435.37	103.42	-486.72	-367.15	14.75
1400	121.39	444.32	115.50	-486.43	-357.82	13.35
1500	122.61	452.73	127.70	-486.18	-348.53	12.14
1600	123.66	460.68	140.01	-485.85	-339.24	11.07
1700	124.56	468.21	152.42	-485.55	-330.03	10.14
1800	125.35	475.35	164.92	-485.22	-320.83	9.31
1900	126.03	482.15	177.49	-484.84	-311.71	8.57
2000	126.63	488.62	190.12	-484.51	-302.67	7.90
2100	127.16	494.82	202.81	-484.13	-293.67	7.30
2200	127.63	500.75	215.55	-483.71	-284.76	6.76
2300	128.05	506.43	228.34	-483.34	-275.93	6.27
2400	128.42	511.88	241.16	-482.92	-267.15	5.81
2500	128.75	517.13	254.02	-482.50	-258.45	5.40
2600	129.05	522.19	266.91	-482.08	-249.83	5.02
2700	129.32	527.07	279.83	-481.62	-241.21	4.67
2800	129.56	531.77	292.77	-481.16	-232.67	4.34
2900	129.78	536.32	305.74	-480.70	-224.10	4.04
3000	129.98	540.73	318.73	-480.24	-215.52	3.75



$\Delta H_f^\circ(0 \text{ K})$	= -650.28 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	= -653.67 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	= 311.22 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
148.83	252.80	401.64

Vibrational Frequencies (cm ⁻¹)				
198.9	199.9	382.0	431.3	530.1
540.3	563.3	777.2	1163.6	1341.2
1355.2	1915.3			

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.300	C2-C1-F1	123.44		
C1-F1	1.301	C2-C1-F2	123.45		
C1-F2	1.302	C1-C2-F3	123.45		
C2-F3	1.301	C1-C2-F4	123.43		
C2-F4	1.301				

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$
 Standard State Pressure = $p_o = 1 \text{ atmosphere}$

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	54.99	265.02	-10.18	-653.08	-637.64	222.03
200	64.99	282.25	-7.17	-653.46	-632.41	165.17
250	73.43	297.68	-3.70	-653.62	-627.18	131.04
300	80.51	311.72	0.15	-653.67	-621.95	108.28
350	86.53	324.59	4.33	-653.62	-616.72	92.03
400	91.74	336.49	8.79	-653.54	-611.49	79.85
450	96.26	347.56	13.49	-653.42	-606.30	70.37
500	100.21	357.92	18.41	-653.25	-601.12	62.79
600	106.65	376.78	28.76	-652.83	-590.78	51.43
700	111.57	393.61	39.69	-652.37	-580.53	43.32
800	115.36	408.77	51.04	-651.87	-570.28	37.23
900	118.29	422.53	62.73	-651.41	-560.07	32.50
1000	120.60	435.12	74.68	-650.90	-549.90	28.72
1100	122.43	446.70	86.83	-650.40	-539.74	25.63
1200	123.90	457.42	99.15	-649.90	-529.57	23.05
1300	125.10	467.39	111.60	-649.44	-519.44	20.87
1400	126.08	476.70	124.16	-648.98	-509.32	19.00
1500	126.90	485.42	136.81	-648.52	-499.23	17.38
1600	127.58	493.63	149.54	-648.06	-489.19	15.97
1700	128.16	501.39	162.33	-647.60	-479.19	14.72
1800	128.65	508.73	175.17	-647.14	-469.24	13.62
1900	129.08	515.69	188.05	-646.68	-459.36	12.63
2000	129.44	522.32	200.98	-646.22	-449.57	11.74
2100	129.76	528.65	213.94	-645.76	-439.86	10.94
2200	130.04	534.69	226.93	-645.30	-430.20	10.21
2300	130.28	540.48	239.95	-644.84	-420.66	9.55
2400	130.50	546.02	252.99	-644.38	-411.16	8.95
2500	130.69	551.36	266.05	-643.88	-401.71	8.39
2600	130.86	556.48	279.13	-643.42	-392.38	7.88
2700	131.01	561.43	292.22	-642.91	-383.05	7.41
2800	131.15	566.20	305.33	-642.41	-373.76	6.97
2900	131.28	570.80	318.45	-641.91	-364.47	6.56
3000	131.39	575.25	331.58	-641.41	-355.18	6.18

CHF=CH• fcch trans

$\Delta H_f^\circ(0 \text{ K})$ = 126.86 kJ mol⁻¹
 $\Delta H_f^\circ(298.15 \text{ K})$ = 123.11 kJ mol⁻¹
 $S^\circ(298.15 \text{ K})$ = 257.01 J K⁻¹ mol⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 9.65 75.95 85.60

Vibrational Frequencies (cm⁻¹)
 481.1 643.7 756.2 809.8 1080.2
 1246.5 1474.5 3017.9 3103.5

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.322				
C1-H1	1.074	C2-C1-H1	125.44		
C1-F1	1.330	C2-C1-F1	121.98	H1-C1-F1	180.00
C2-H2	1.068	C1-C2-H2	132.85	F1-C2-H2	180.00

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	36.24	227.94	-6.38	125.19	121.71	-42.38
200	40.54	238.94	-4.47	124.43	120.62	-31.51
250	45.61	248.53	-2.31	123.72	119.70	-25.01
300	50.76	257.32	0.09	123.09	118.95	-20.71
350	55.60	265.52	2.75	122.51	118.24	-17.64
400	59.99	273.23	5.64	122.01	117.61	-15.36
450	63.89	280.52	8.74	121.55	117.03	-13.58
500	67.35	287.42	12.02	121.17	116.52	-12.17
600	73.15	300.20	19.05	120.46	115.60	-10.06
700	77.83	311.78	26.59	119.87	114.81	-8.57
800	81.73	322.41	34.56	119.37	114.14	-7.45
900	85.05	332.24	42.89	118.95	113.51	-6.59
1000	87.91	341.36	51.51	118.62	112.97	-5.90
1100	90.38	349.86	60.41	118.28	112.47	-5.34
1200	92.51	357.82	69.53	118.03	112.05	-4.88
1300	94.36	365.29	78.86	117.78	111.67	-4.49
1400	95.94	372.34	88.35	117.61	111.34	-4.15
1500	97.30	379.00	97.99	117.44	111.00	-3.87
1600	98.46	385.31	107.75	117.28	110.67	-3.61
1700	99.45	391.31	117.63	117.15	110.33	-3.39
1800	100.29	397.01	127.61	117.07	109.96	-3.19
1900	101.00	402.45	137.66	116.94	109.58	-3.01
2000	101.60	407.64	147.78	116.86	109.12	-2.85
2100	102.11	412.61	157.96	116.78	108.66	-2.70
2200	102.53	417.36	168.19	116.69	108.11	-2.57
2300	102.89	421.92	178.46	116.61	107.57	-2.44
2400	103.20	426.30	188.77	116.48	106.94	-2.33
2500	103.45	430.52	199.10	116.40	106.27	-2.22
2600	103.66	434.58	209.46	116.32	105.56	-2.12
2700	103.84	438.49	219.85	116.23	104.85	-2.03
2800	103.99	442.27	230.25	116.11	104.10	-1.94
2900	104.11	445.92	240.67	115.98	103.39	-1.86
3000	104.22	449.45	251.10	115.90	102.72	-1.79

CHF=CH• fccch cis

$\Delta H_f^\circ(0 \text{ K})$ = 127.78 kJ mol⁻¹
 $\Delta H_f^\circ(298.15 \text{ K})$ = 124.11 kJ mol⁻¹
 $S^\circ(298.15 \text{ K})$ = 257.95 J K⁻¹ mol⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 12.29 71.42 83.71

Vibrational Frequencies (cm⁻¹)
 437.4 629.4 825.3 853.1 1053.2
 1252.8 1452.6 3062.1 3100.3

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.321				
C1-H1	1.071	C2-C1-H1	125.39		
C1-F1	1.336	C2-C1-F1	121.96	H1-C1-F1	180.00
C2-H2	1.068	C1-C2-H2	135.69	F1-C2-H2	0.00

Enthalpy Reference Temperature = T_r = 298.15 K
 Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	36.63	228.77	-6.40	126.15	122.55	-42.67
200	40.76	239.86	-4.47	125.44	121.42	-31.71
250	45.62	249.49	-2.31	124.73	120.50	-25.17
300	50.62	258.26	0.09	124.10	119.62	-20.83
350	55.39	266.43	2.74	123.51	118.91	-17.74
400	59.76	274.12	5.62	122.97	118.24	-15.44
450	63.66	281.39	8.71	122.51	117.61	-13.65
500	67.13	288.27	11.97	122.13	117.03	-12.23
600	72.94	301.02	18.98	121.38	116.02	-10.10
700	77.62	312.58	26.51	120.79	115.19	-8.59
800	81.51	323.16	34.46	120.29	114.43	-7.47
900	84.82	332.95	42.76	119.83	113.72	-6.60
1000	87.66	342.05	51.38	119.45	113.14	-5.91
1100	90.14	350.53	60.25	119.12	112.55	-5.35
1200	92.28	358.46	69.35	118.83	112.09	-4.88
1300	94.14	365.92	78.65	118.57	111.63	-4.49
1400	95.76	372.96	88.12	118.37	111.21	-4.15
1500	97.15	379.61	97.74	118.20	110.83	-3.86
1600	98.35	385.92	107.50	118.03	110.46	-3.61
1700	99.39	391.90	117.36	117.91	110.04	-3.38
1800	100.27	397.61	127.32	117.78	109.62	-3.18
1900	101.02	403.04	137.37	117.65	109.16	-3.00
2000	101.67	408.24	147.49	117.57	108.66	-2.84
2100	102.22	413.20	157.68	117.49	108.11	-2.69
2200	102.68	417.97	167.91	117.40	107.53	-2.55
2300	103.07	422.54	178.19	117.32	106.86	-2.43
2400	103.40	426.93	188.51	117.24	106.19	-2.31
2500	103.68	431.15	198.87	117.15	105.44	-2.20
2600	103.91	435.22	209.25	117.07	104.68	-2.10
2700	104.11	439.14	219.66	117.03	103.89	-2.01
2800	104.27	442.93	230.08	116.94	103.09	-1.92
2900	104.41	446.59	240.52	116.86	102.30	-1.84
3000	104.52	450.12	250.98	116.73	101.55	-1.77

CH₂=CF•

$\Delta H_f^\circ(0 \text{ K})$	=	112.80 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	=	109.10 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	=	256.78 J K ⁻¹ mol ⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 7.56 81.01 88.57

Vibrational Frequencies (cm⁻¹)
 427.0 613.9 796.9 905.2 1092.7
 1366.6 1536.6 2975.1 3076.3

Bond Distances (10 ⁻¹⁰ m)	Bond Angles (°)	Dihedral Angles (°)
C1-C2 1.324		
C1-H1 1.076	C2-C1-H1 120.95	
C1-H2 1.072	C2-C1-H2 119.84	
C2-F1 1.306	C1-C2-F1 128.27	

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	36.77	227.59	-6.39	111.13	107.74	-37.51
200	40.85	238.73	-4.46	110.42	106.65	-27.86
250	45.51	248.35	-2.30	109.75	105.77	-22.10
300	50.25	257.09	0.09	109.08	104.98	-18.28
350	54.78	265.18	2.72	108.45	104.31	-15.56
400	58.97	272.78	5.56	107.91	103.68	-13.54
450	62.75	279.94	8.61	107.40	103.14	-11.97
500	66.15	286.73	11.83	106.94	102.68	-10.72
600	71.94	299.30	18.74	106.15	101.80	-8.86
700	76.67	310.73	26.17	105.44	101.13	-7.55
800	80.62	321.20	34.03	104.85	100.54	-6.57
900	83.96	330.86	42.26	104.31	100.12	-5.81
1000	86.84	339.82	50.80	103.85	99.75	-5.21
1100	89.32	348.18	59.60	103.47	99.50	-4.72
1200	91.47	356.01	68.63	103.09	99.33	-4.32
1300	93.35	363.36	77.87	102.80	99.20	-3.99
1400	94.99	370.29	87.27	102.51	99.12	-3.70
1500	96.42	376.84	96.83	102.26	99.08	-3.45
1600	97.70	383.08	106.53	102.05	98.99	-3.23
1700	98.82	389.04	116.34	101.88	98.87	-3.04
1800	99.81	394.72	126.26	101.71	98.74	-2.87
1900	100.69	400.14	136.28	101.55	98.58	-2.71
2000	101.47	405.33	146.37	101.42	98.32	-2.57
2100	102.17	410.29	156.54	101.34	98.07	-2.44
2200	102.79	415.06	166.77	101.25	97.78	-2.32
2300	103.34	419.64	177.07	101.17	97.40	-2.21
2400	103.82	424.05	187.41	101.13	96.99	-2.11
2500	104.25	428.30	197.81	101.09	96.52	-2.02
2600	104.63	432.39	208.24	101.09	96.02	-1.93
2700	104.96	436.35	218.71	101.04	95.48	-1.85
2800	105.25	440.17	229.20	101.04	94.93	-1.77
2900	105.50	443.86	239.73	101.04	94.39	-1.70
3000	105.73	447.44	250.29	101.04	93.89	-1.63

CHF=CF• fccf cis

$\Delta H_f^\circ(0 \text{ K}) = -38.79 \text{ kJ mol}^{-1}$
 $\Delta H_f^\circ(298.15 \text{ K}) = -41.10 \text{ kJ mol}^{-1}$
 $S^\circ(298.15 \text{ K}) = 281.12 \text{ J K}^{-1} \text{ mol}^{-1}$

Moments of Inertia (10^{-47} kg m^2)
 32.42 146.49 178.91

Vibrational Frequencies (cm^{-1})
 204.1 401.4 718.9 727.9 945.6
 1120.4 1325.5 1579.2 3097.9

Bond Distances (10^{-10} m)		Bond Angles ($^\circ$)		Dihedral Angles ($^\circ$)	
C1-C2	1.324	C2-C1-H1	123.49	H1-C1-F1	180.00
C1-H1	1.068	C2-C1-F1	121.44	F1-C2-F2	0.00
C1-F1	1.330	C1-C2-F2	128.59		
C2-F2	1.300				

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$
Standard State Pressure = $p_o = 1 \text{ atmosphere}$

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	42.88	247.25	-7.41	-40.00	-40.96	14.27
200	47.64	260.26	-5.15	-40.42	-41.25	10.77
250	52.62	271.44	-2.65	-40.79	-41.46	8.66
300	57.55	281.47	0.10	-41.13	-41.63	7.25
350	62.21	290.70	3.10	-41.42	-41.71	6.23
400	66.48	299.29	6.32	-41.67	-41.80	5.46
450	70.31	307.34	9.74	-41.88	-41.88	4.86
500	73.71	314.92	13.34	-42.09	-41.88	4.38
600	79.37	328.86	21.00	-42.38	-41.88	3.65
700	83.81	341.42	29.17	-42.63	-41.80	3.12
800	87.35	352.83	37.73	-42.89	-41.67	2.72
900	90.22	363.27	46.61	-43.05	-41.42	2.40
1000	92.58	372.88	55.75	-43.22	-41.17	2.15
1100	94.55	381.77	65.11	-43.39	-40.84	1.94
1200	96.21	390.05	74.64	-43.56	-40.42	1.76
1300	97.62	397.77	84.33	-43.72	-40.00	1.61
1400	98.83	405.02	94.15	-43.89	-39.54	1.48
1500	99.87	411.85	104.09	-44.02	-39.08	1.36
1600	100.78	418.30	114.11	-44.14	-38.58	1.26
1700	101.57	424.40	124.23	-44.27	-38.07	1.17
1800	102.27	430.19	134.42	-44.39	-37.61	1.09
1900	102.90	435.70	144.67	-44.52	-37.20	1.02
2000	103.46	440.96	154.98	-44.64	-36.78	0.96
2100	103.96	445.98	165.35	-44.73	-36.40	0.91
2200	104.42	450.79	175.76	-44.81	-36.07	0.86
2300	104.83	455.42	186.21	-44.85	-35.86	0.81
2400	105.20	459.89	196.71	-44.94	-35.69	0.78
2500	105.54	464.19	207.24	-44.98	-35.61	0.74
2600	105.85	468.34	217.80	-45.02	-35.56	0.71
2700	106.14	472.34	228.40	-45.02	-35.52	0.69
2800	106.39	476.20	239.02	-45.02	-35.52	0.66
2900	106.63	479.94	249.66	-45.02	-35.48	0.64
3000	106.84	483.56	260.32	-45.02	-35.44	0.62

CHF=CF• fccf trans

$\Delta H_f^\circ(0 \text{ K})$ = -40.46 kJ mol⁻¹
 $\Delta H_f^\circ(298.15 \text{ K})$ = -42.52 kJ mol⁻¹
 $S^\circ(298.15 \text{ K})$ = 279.28 J K⁻¹ mol⁻¹

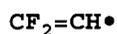
Moments of Inertia (10⁻⁴⁷ kg m²)
 10.31 207.95 218.26

Vibrational Frequencies (cm⁻¹)
 295.9 297.9 518.3 684.6 1049.1
 1163.1 1259.9 1568.4 3051.6

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.327	C2-C1-H1	124.86	H1-C1-F1	180.00
C1-H1	1.072	C2-C1-F1	120.07	F1-C2-F2	180.00
C1-F1	1.327	C1-C2-F2	125.81		
C2-F2	1.304				

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	44.03	244.16	-7.69	-41.71	-42.22	14.69
200	49.58	257.62	-5.35	-42.01	-42.34	11.06
250	54.62	269.25	-2.74	-42.30	-42.43	8.87
300	59.32	279.65	0.11	-42.51	-42.51	7.40
350	63.69	289.14	3.18	-42.76	-42.51	6.35
400	67.70	297.93	6.47	-42.93	-42.55	5.55
450	71.32	306.12	9.95	-43.10	-42.51	4.94
500	74.55	313.81	13.60	-43.26	-42.51	4.44
600	79.97	327.91	21.33	-43.47	-42.38	3.69
700	84.26	340.57	29.55	-43.68	-42.26	3.15
800	87.68	352.05	38.15	-43.85	-42.01	2.74
900	90.46	362.54	47.07	-44.02	-41.76	2.42
1000	92.75	372.19	56.23	-44.18	-41.42	2.16
1100	94.65	381.12	65.60	-44.35	-41.05	1.95
1200	96.25	389.42	75.14	-44.48	-40.63	1.77
1300	97.60	397.17	84.84	-44.64	-40.12	1.61
1400	98.75	404.44	94.65	-44.77	-39.66	1.48
1500	99.73	411.28	104.58	-44.94	-39.12	1.36
1600	100.58	417.74	114.60	-45.10	-38.62	1.26
1700	101.32	423.86	124.69	-45.23	-38.12	1.17
1800	101.96	429.66	134.85	-45.40	-37.66	1.09
1900	102.53	435.18	145.08	-45.52	-37.20	1.02
2000	103.02	440.45	155.35	-45.69	-36.82	0.96
2100	103.46	445.47	165.67	-45.81	-36.44	0.91
2200	103.85	450.29	176.04	-45.94	-36.11	0.86
2300	104.20	454.91	186.44	-46.07	-35.86	0.81
2400	104.51	459.34	196.87	-46.19	-35.65	0.78
2500	104.79	463.60	207.34	-46.28	-35.44	0.74
2600	105.04	467.71	217.83	-46.40	-35.31	0.71
2700	105.27	471.67	228.34	-46.48	-35.19	0.68
2800	105.48	475.49	238.88	-46.61	-35.06	0.65
2900	105.67	479.19	249.43	-46.69	-34.94	0.63
3000	105.85	482.77	260.01	-46.78	-34.81	0.61



$\Delta H_f^\circ(0 \text{ K})$	=	-64.94 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	=	-67.66 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	=	276.92 J K ⁻¹ mol ⁻¹

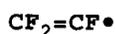
Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
70.89	76.08	146.97

Vibrational Frequencies (cm ⁻¹)				
416.4	519.1	528.2	624.3	818.7
903.8	1278.3	1585.6	3128.7	

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.311				
C1-F1	1.309	C2-C1-F1	125.05		
C1-F2	1.304	C2-C1-F2	124.78	F1-C1-F2	180.00
C2-H1	1.066	C1-C2-H1	133.92	F1-C2-H1	0.00

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$
 Standard State Pressure = $p_o = 1 \text{ atmosphere}$

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K_f
	C_p°	S°	$H^\circ-H^\circ(T_r)$	ΔH_f°	ΔG_f°	
150	39.61	243.63	-7.33	-66.48	-66.90	23.30
200	46.39	255.96	-5.19	-66.99	-66.99	17.49
250	53.12	267.05	-2.70	-67.40	-66.99	13.99
300	59.19	277.29	0.11	-67.66	-66.90	11.65
350	64.48	286.81	3.20	-67.86	-66.82	9.97
400	69.04	295.70	6.54	-67.99	-66.73	8.71
450	72.97	304.04	10.08	-68.12	-66.57	7.73
500	76.37	311.91	13.82	-68.16	-66.48	6.94
600	81.94	326.39	21.72	-68.24	-66.23	5.77
700	86.26	339.37	30.12	-68.24	-65.98	4.92
800	89.70	351.13	38.90	-68.24	-65.69	4.29
900	92.46	361.84	47.99	-68.24	-65.35	3.79
1000	94.70	371.70	57.32	-68.24	-64.98	3.39
1100	96.50	380.80	66.86	-68.20	-64.56	3.07
1200	97.96	389.25	76.56	-68.20	-64.10	2.79
1300	99.14	397.13	86.41	-68.20	-63.64	2.56
1400	100.08	404.50	96.36	-68.24	-63.18	2.36
1500	100.84	411.43	106.40	-68.24	-62.68	2.18
1600	101.46	417.94	116.52	-68.32	-62.17	2.03
1700	101.95	424.11	126.70	-68.37	-61.67	1.90
1800	102.35	429.94	136.92	-68.45	-61.21	1.78
1900	102.68	435.47	147.18	-68.58	-60.79	1.67
2000	102.94	440.75	157.48	-68.70	-60.42	1.58
2100	103.15	445.77	167.80	-68.83	-60.08	1.49
2200	103.32	450.57	178.15	-68.95	-59.75	1.42
2300	103.46	455.16	188.51	-69.12	-59.50	1.35
2400	103.58	459.57	198.88	-69.33	-59.29	1.29
2500	103.67	463.79	209.27	-69.50	-59.12	1.24
2600	103.75	467.86	219.66	-69.71	-58.99	1.19
2700	103.81	471.77	230.07	-69.91	-58.87	1.14
2800	103.86	475.55	240.48	-70.12	-58.79	1.10
2900	103.91	479.19	250.89	-70.37	-58.62	1.06
3000	103.94	482.71	261.31	-70.58	-58.45	1.02



$\Delta H_f^\circ(0 \text{ K})$	= -215.73 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	= -216.36 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	= 300.48 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
72.80	217.89	290.68

Vibrational Frequencies (cm ⁻¹)				
204.0	279.2	414.0	459.3	588.3
864.4	1203.3	1318.0	1663.5	

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.319				
C1-F1	1.304	C2-C1-F1	124.76		
C1-F2	1.303	C2-C1-F2	122.90	F1-C1-F2	180.00
C2-F3	1.302	C1-C2-F3	126.52	F1-C2-F3	0.00

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$
 Standard State Pressure = $p_o = 1 \text{ atmosphere}$

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K_f
	C_p°	S°	$H^\circ - H^\circ(T_r)$	ΔH_f°	ΔG_f°	
150	49.70	260.20	-8.84	-216.65	-214.14	74.56
200	57.00	275.54	-6.17	-216.61	-213.30	55.71
250	63.09	288.94	-3.16	-216.52	-212.55	44.40
300	68.28	300.90	0.13	-216.35	-211.79	36.88
350	72.81	311.77	3.66	-216.19	-211.12	31.50
400	76.81	321.75	7.40	-215.98	-210.46	27.48
450	80.32	330.99	11.33	-215.81	-209.79	24.35
500	83.41	339.60	15.42	-215.60	-209.16	21.85
600	88.47	355.24	24.02	-215.27	-207.99	18.10
700	92.33	369.15	33.07	-214.93	-206.82	15.43
800	95.29	381.64	42.45	-214.64	-205.64	13.43
900	97.58	392.97	52.09	-214.39	-204.47	11.87
1000	99.37	403.30	61.94	-214.18	-203.30	10.62
1100	100.81	412.80	71.95	-214.01	-202.05	9.59
1200	101.98	421.58	82.09	-213.89	-200.83	8.74
1300	102.95	429.73	92.33	-213.76	-199.53	8.02
1400	103.76	437.35	102.66	-213.68	-198.24	7.40
1500	104.45	444.47	113.06	-213.64	-196.94	6.86
1600	105.04	451.18	123.53	-213.59	-195.64	6.39
1700	105.55	457.57	134.06	-213.55	-194.47	5.97
1800	106.00	463.61	144.63	-213.51	-193.30	5.61
1900	106.39	469.36	155.24	-213.47	-192.17	5.28
2000	106.74	474.82	165.89	-213.43	-191.13	4.99
2100	107.04	480.03	176.57	-213.43	-190.12	4.73
2200	107.29	485.02	187.28	-213.38	-189.16	4.49
2300	107.52	489.80	198.02	-213.34	-188.28	4.28
2400	107.72	494.38	208.77	-213.26	-187.44	4.08
2500	107.88	498.77	219.55	-213.22	-186.65	3.90
2600	108.02	503.01	230.34	-213.17	-185.90	3.73
2700	108.13	507.09	241.14	-213.13	-185.18	3.58
2800	108.22	511.02	251.95	-213.05	-184.47	3.44
2900	108.30	514.82	262.78	-213.01	-183.76	3.31
3000	108.35	518.49	273.60	-212.92	-183.05	3.19

C₂HF

$\Delta H_f^\circ(0 \text{ K})$	=	117.86 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	=	117.80 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	=	227.71 J K ⁻¹ mol ⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 84.53 84.53

Vibrational Frequencies (cm⁻¹)
 441.6 441.6 685.4 685.4 1042.9
 2262.5 3293.0

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)
C1-C2	1.177			
C1-H1	1.055	C2-C1-H1	180.00	
C2-F1	1.269	C1-C2-F1	180.00	

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	34.59	199.26	-6.26	117.82	110.42	-38.45
200	39.94	209.94	-4.40	117.78	107.95	-28.19
250	45.02	219.41	-2.27	117.78	105.44	-22.03
300	49.38	228.02	0.09	117.82	102.93	-17.92
350	52.98	235.91	2.65	117.86	100.37	-14.98
400	55.94	243.18	5.38	117.91	97.82	-12.77
450	58.42	249.92	8.24	117.95	95.27	-11.06
500	60.51	256.18	11.21	117.99	92.72	-9.68
600	63.94	267.53	17.44	117.95	87.57	-7.62
700	66.70	277.60	23.98	117.82	82.47	-6.15
800	69.03	286.67	30.77	117.61	77.45	-5.06
900	71.04	294.91	37.78	117.32	72.47	-4.21
1000	72.78	302.49	44.97	117.03	67.57	-3.53
1100	74.30	309.50	52.33	116.69	62.72	-2.98
1200	75.64	316.03	59.82	116.32	57.95	-2.52
1300	76.81	322.13	67.45	115.90	53.26	-2.14
1400	77.83	327.86	75.18	115.52	48.58	-1.81
1500	78.72	333.26	83.01	115.10	43.93	-1.53
1600	79.51	338.36	90.92	114.68	39.33	-1.28
1700	80.20	343.21	98.91	114.31	34.69	-1.07
1800	80.81	347.81	106.96	113.89	30.08	-0.87
1900	81.35	352.19	115.06	113.47	25.44	-0.70
2000	81.83	356.38	123.23	113.09	20.75	-0.54
2100	82.26	360.38	131.43	112.68	16.07	-0.40
2200	82.65	364.22	139.68	112.30	11.30	-0.27
2300	82.99	367.90	147.96	111.92	6.53	-0.15
2400	83.30	371.43	156.27	111.55	1.72	-0.04
2500	83.58	374.84	164.62	111.17	-3.14	0.07
2600	83.83	378.12	172.99	110.79	-8.03	0.16
2700	84.05	381.29	181.38	110.42	-12.89	0.25
2800	84.26	384.35	189.80	110.08	-17.78	0.33
2900	84.45	387.31	198.23	109.75	-22.68	0.41
3000	84.62	390.18	206.69	109.41	-27.49	0.48

C₂F₂

$\Delta H_f^\circ(0\text{ K})$	=	29.96 kJ mol ⁻¹
$\Delta H_f^\circ(298.15\text{ K})$	=	31.82 kJ mol ⁻¹
$S^\circ(298.15\text{ K})$	=	245.88 J K ⁻¹ mol ⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 231.40 231.40

Vibrational Frequencies (cm⁻¹)
 291.1 291.1 407.1 407.1 771.4
 1321.2 2502.4

Bond Distances (10 ⁻¹⁰ m)	Bond Angles (°)	Dihedral Angles (°)
C1-C2 1.166		
C1-F1 1.275	C2-C1-F1 180.00	
C2-F2 1.275	C1-C2-F2 180.00	

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	43.72	210.49	-7.76	30.42	26.69	-9.30
200	50.36	224.02	-5.40	30.84	25.40	-6.63
250	55.28	235.81	-2.75	31.34	23.93	-5.00
300	59.05	246.24	0.11	31.84	22.38	-3.89
350	62.05	255.58	3.14	32.30	20.71	-3.09
400	64.51	264.03	6.31	32.72	18.95	-2.48
450	66.59	271.75	9.59	33.10	17.20	-1.99
500	68.37	278.86	12.96	33.39	15.36	-1.60
600	71.31	291.60	19.95	33.85	11.63	-1.01
700	73.66	302.78	27.20	34.14	7.87	-0.59
800	75.58	312.74	34.67	34.31	4.10	-0.27
900	77.16	321.74	42.30	34.35	0.33	-0.02
1000	78.48	329.93	50.09	34.31	-3.35	0.18
1100	79.58	337.47	57.99	34.18	-7.03	0.33
1200	80.51	344.44	66.00	34.02	-10.63	0.46
1300	81.30	350.91	74.09	33.81	-14.23	0.57
1400	81.96	356.96	82.26	33.56	-17.78	0.66
1500	82.53	362.64	90.48	33.26	-21.30	0.74
1600	83.01	367.97	98.76	32.97	-24.81	0.81
1700	83.43	373.02	107.08	32.64	-28.37	0.87
1800	83.80	377.80	115.44	32.34	-31.88	0.93
1900	84.12	382.34	123.84	32.01	-35.44	0.97
2000	84.39	386.66	132.26	31.67	-39.04	1.02
2100	84.63	390.79	140.72	31.34	-42.63	1.06
2200	84.85	394.73	149.19	31.00	-46.32	1.10
2300	85.04	398.51	157.69	30.67	-50.04	1.14
2400	85.21	402.13	166.20	30.33	-53.76	1.17
2500	85.36	405.61	174.73	30.00	-57.53	1.20
2600	85.50	408.96	183.27	29.66	-61.34	1.23
2700	85.62	412.19	191.83	29.33	-65.19	1.26
2800	85.73	415.30	200.39	29.00	-68.99	1.29
2900	85.83	418.32	208.97	28.70	-72.80	1.31
3000	85.93	421.23	217.56	28.37	-76.57	1.33

•C₂F

$\Delta H_f^\circ(0 \text{ K})$	=	448.94 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	=	453.86 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	=	218.02 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
75.82	75.82	

Vibrational Frequencies (cm ⁻¹)		
217.8	1003.0	2071.7

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)	Dihedral Angles (°)
C1-C2	1.196		
C1-F1	1.272	C2-C1-F1	179.35

Enthalpy Reference Temperature = T_r = 298.15 K
 Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	39.16	190.07	-6.05	451.91	437.65	-152.39
200	40.38	201.51	-4.07	452.71	432.75	-113.01
250	41.44	210.64	-2.02	453.38	427.60	-89.34
300	42.49	218.28	0.08	453.88	422.37	-73.54
350	43.53	224.91	2.23	454.26	417.06	-62.24
400	44.53	230.79	4.43	454.51	411.66	-53.75
450	45.49	236.09	6.68	454.68	406.27	-47.15
500	46.40	240.93	8.98	454.76	400.83	-41.87
600	48.08	249.54	13.70	454.68	389.99	-33.95
700	49.53	257.06	18.59	454.34	379.15	-28.29
800	50.77	263.76	23.61	453.80	368.48	-24.06
900	51.81	269.80	28.74	453.13	357.86	-20.77
1000	52.68	275.31	33.96	452.33	347.40	-18.15
1100	53.40	280.36	39.27	451.45	337.02	-16.00
1200	54.00	285.04	44.63	450.45	326.81	-14.22
1300	54.50	289.38	50.06	449.40	316.69	-12.72
1400	54.93	293.43	55.53	448.32	306.65	-11.44
1500	55.29	297.24	61.04	447.14	296.69	-10.33
1600	55.60	300.81	66.59	445.97	286.81	-9.36
1700	55.86	304.19	72.16	444.76	276.98	-8.51
1800	56.08	307.39	77.76	443.55	267.19	-7.75
1900	56.28	310.43	83.38	442.29	257.40	-7.08
2000	56.45	313.32	89.01	440.99	247.65	-6.47
2100	56.60	316.08	94.67	439.74	237.94	-5.92
2200	56.73	318.72	100.34	438.44	228.20	-5.42
2300	56.85	321.24	106.01	437.14	218.49	-4.96
2400	56.95	323.66	111.70	435.85	208.74	-4.54
2500	57.04	325.99	117.40	434.55	199.03	-4.16
2600	57.13	328.23	123.11	433.25	189.33	-3.80
2700	57.20	330.39	128.83	431.96	179.66	-3.48
2800	57.27	332.46	134.55	430.62	170.00	-3.17
2900	57.33	334.48	140.28	429.32	160.41	-2.89
3000	57.38	336.42	146.02	428.02	150.88	-2.63

CHF=C=O

$\Delta H_f^\circ(0 \text{ K})$ = -144.68 kJ mol⁻¹
 $\Delta H_f^\circ(298.15 \text{ K})$ = -147.19 kJ mol⁻¹
 $S^\circ(298.15 \text{ K})$ = 270.51 J K⁻¹ mol⁻¹

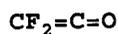
Moments of Inertia (10⁻⁴⁷ kg m²)
 14.45 180.24 194.69

Vibrational Frequencies (cm⁻¹)
 252.4 479.7 615.2 681.3 1027.8
 1207.3 1425.2 2107.9 3073.7

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)
C1-C2	1.308			
C1-F1	1.339	C2-C1-F1	120.10	
C1-H1	1.067	C2-C1-H1	122.43	
C2-O1	1.147	C1-C2-O1	180.00	

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	41.64	237.24	-7.30	-146.06	-145.35	50.61
200	46.89	249.94	-5.09	-146.48	-145.06	37.88
250	52.00	260.95	-2.62	-146.86	-144.68	30.23
300	56.74	270.86	0.10	-147.19	-144.26	25.12
350	61.06	279.93	3.05	-147.49	-143.80	21.46
400	64.95	288.34	6.20	-147.74	-143.30	18.71
450	68.45	296.20	9.54	-147.99	-142.76	16.57
500	71.58	303.58	13.04	-148.20	-142.21	14.86
600	76.94	317.12	20.48	-148.53	-141.08	12.28
700	81.30	329.32	28.40	-148.87	-139.83	10.43
800	84.89	340.41	36.71	-149.20	-138.53	9.04
900	87.88	350.59	45.35	-149.49	-137.15	7.96
1000	90.40	359.99	54.27	-149.75	-135.69	7.09
1100	92.51	368.70	63.42	-150.04	-134.18	6.37
1200	94.30	376.83	72.76	-150.29	-132.59	5.77
1300	95.83	384.44	82.27	-150.54	-130.96	5.26
1400	97.13	391.59	91.92	-150.79	-129.33	4.83
1500	98.25	398.33	101.69	-151.04	-127.65	4.45
1600	99.22	404.71	111.57	-151.25	-125.98	4.11
1700	100.06	410.75	121.53	-151.50	-124.31	3.82
1800	100.79	416.49	131.57	-151.71	-122.67	3.56
1900	101.44	421.96	141.69	-151.92	-121.04	3.33
2000	102.00	427.17	151.86	-152.13	-119.45	3.12
2100	102.50	432.16	162.08	-152.34	-117.95	2.93
2200	102.94	436.94	172.36	-152.51	-116.44	2.76
2300	103.33	441.52	182.67	-152.72	-114.98	2.61
2400	103.68	445.93	193.02	-152.88	-113.60	2.47
2500	104.00	450.17	203.41	-153.05	-112.21	2.34
2600	104.28	454.25	213.82	-153.18	-110.92	2.23
2700	104.54	458.19	224.26	-153.34	-109.62	2.12
2800	104.77	462.00	234.73	-153.47	-108.32	2.02
2900	104.98	465.68	245.22	-153.64	-107.03	1.93
3000	105.17	469.24	255.72	-153.76	-105.69	1.84



$\Delta H_f^\circ(0 \text{ K})$	= -289.91 kJ mol ⁻¹
$\Delta H_f^\circ(298.15 \text{ K})$	= -290.43 kJ mol ⁻¹
$S^\circ(298.15 \text{ K})$	= 288.81 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
76.39	209.01	285.39

Vibrational Frequencies (cm ⁻¹)				
206.6	273.3	378.2	442.2	672.8
793.3	1314.7	1450.3	2208.3	

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.300				
C1-F1	1.312	C2-C1-F1	122.97		
C1-F2	1.312	C2-C1-F2	122.97		
C2-O1	1.151	C1-C2-O1	180.00		

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$
 Standard State Pressure = $p_o = 1 \text{ atmosphere}$

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K_f
	C_p°	S°	$H^\circ - H^\circ(T_r)$	ΔH_f°	ΔG_f°	
150	50.22	248.43	-8.86	-290.79	-286.35	99.71
200	57.28	263.88	-6.16	-290.75	-284.89	74.40
250	63.05	277.30	-3.15	-290.62	-283.47	59.22
300	67.84	289.23	0.13	-290.41	-282.09	49.12
350	71.94	300.01	3.62	-290.20	-280.79	41.90
400	75.49	309.85	7.31	-290.03	-279.49	36.50
450	78.62	318.93	11.16	-289.83	-278.24	32.29
500	81.39	327.36	15.17	-289.66	-276.98	28.94
600	86.04	342.62	23.55	-289.32	-274.55	23.90
700	89.73	356.17	32.34	-289.07	-272.17	20.31
800	92.67	368.36	41.47	-288.91	-269.74	17.61
900	95.03	379.41	50.86	-288.78	-267.36	15.52
1000	96.93	389.52	60.46	-288.70	-264.89	13.84
1100	98.47	398.84	70.23	-288.65	-262.42	12.46
1200	99.73	407.46	80.14	-288.65	-259.91	11.31
1300	100.77	415.48	90.17	-288.70	-257.40	10.34
1400	101.64	422.99	100.29	-288.74	-254.85	9.51
1500	102.37	430.02	110.49	-288.82	-252.30	8.79
1600	102.98	436.65	120.76	-288.91	-249.78	8.15
1700	103.51	442.91	131.08	-289.03	-247.23	7.60
1800	103.96	448.84	141.46	-289.11	-244.72	7.10
1900	104.35	454.47	151.88	-289.24	-242.25	6.66
2000	104.69	459.83	162.33	-289.37	-239.83	6.26
2100	104.98	464.95	172.81	-289.49	-237.44	5.91
2200	105.24	469.84	183.32	-289.62	-235.10	5.58
2300	105.47	474.52	193.86	-289.74	-232.84	5.29
2400	105.67	479.01	204.42	-289.87	-230.62	5.02
2500	105.85	483.33	214.99	-289.99	-228.40	4.77
2600	106.01	487.49	225.58	-290.12	-226.27	4.55
2700	106.16	491.49	236.20	-290.20	-224.14	4.34
2800	106.29	495.35	246.82	-290.33	-222.00	4.14
2900	106.40	499.08	257.45	-290.45	-219.87	3.96
3000	106.51	502.70	268.10	-290.54	-217.69	3.79

•CF=C=O

$\Delta H_f^\circ(0\text{ K})$	=	66.65 kJ mol ⁻¹
$\Delta H_f^\circ(298.15\text{ K})$	=	69.03 kJ mol ⁻¹
$S^\circ(298.15\text{ K})$	=	276.17 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
5.47	195.70	201.18

Vibrational Frequencies (cm ⁻¹)				
250.8	279.2	496.8	764.5	1332.9
1712.2				

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.398				
C1-F1	1.296	C2-C1-F1	125.03		
C2-O1	1.163	X1-C2-O1	128.40	C1-C2-O1	180.00

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	45.16	241.23	-7.63	67.70	59.54	-20.74
200	49.89	254.90	-5.25	68.16	56.74	-14.82
250	53.68	266.45	-2.66	68.62	53.81	-11.24
300	56.84	276.52	0.10	69.04	50.75	-8.84
350	59.56	285.50	3.02	69.45	47.66	-7.11
400	61.96	293.61	6.05	69.83	44.43	-5.80
450	64.10	301.03	9.21	70.12	41.21	-4.78
500	66.02	307.89	12.46	70.42	37.95	-3.96
600	69.23	320.22	19.23	70.84	31.34	-2.73
700	71.75	331.09	26.28	71.09	24.69	-1.84
800	73.72	340.80	33.56	71.21	18.03	-1.18
900	75.27	349.58	41.02	71.17	11.42	-0.66
1000	76.49	357.58	48.61	71.04	4.90	-0.25
1100	77.46	364.91	56.30	70.84	-1.63	0.08
1200	78.24	371.69	64.09	70.54	-8.08	0.35
1300	78.89	377.98	71.95	70.17	-14.52	0.58
1400	79.41	383.84	79.86	69.75	-20.88	0.78
1500	79.85	389.34	87.83	69.29	-27.20	0.95
1600	80.22	394.50	95.83	68.78	-33.51	1.09
1700	80.53	399.38	103.87	68.24	-39.79	1.22
1800	80.79	403.99	111.93	67.66	-46.11	1.34
1900	81.02	408.36	120.03	67.07	-52.38	1.44
2000	81.22	412.52	128.14	66.44	-58.70	1.53
2100	81.39	416.49	136.27	65.81	-65.06	1.62
2200	81.53	420.28	144.41	65.19	-71.42	1.70
2300	81.67	423.91	152.58	64.56	-77.82	1.77
2400	81.78	427.38	160.75	63.89	-84.22	1.83
2500	81.89	430.72	168.93	63.26	-90.67	1.89
2600	81.98	433.94	177.13	62.59	-97.11	1.95
2700	82.06	437.03	185.33	61.92	-103.60	2.00
2800	82.14	440.02	193.54	61.30	-110.04	2.05
2900	82.20	442.90	201.75	60.63	-116.44	2.10
3000	82.26	445.69	209.98	59.96	-122.80	2.14

CH₂F-CHO fcco trans

$\Delta H_f^\circ(0\text{ K})$	= -319.20 kJ mol ⁻¹
$\Delta H_f^\circ(298.15\text{ K})$	= -328.72 kJ mol ⁻¹
$S^\circ(298.15\text{ K})$	= 286.63 J K ⁻¹ mol ⁻¹

Moments of Inertia (10 ⁻⁴⁷ kg m ²)		
20.71	190.45	205.95

Vibrational Frequencies (cm ⁻¹)				
84.2	315.4	514.9	721.1	1019.8
1078.4	1105.5	1222.5	1328.4	1391.8
1461.2	1821.7	2857.6	2910.4	2959.4

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.511	C1-C2-O1	122.12	C1-C2-H1	180.00
C2-O1	1.186	O1-C2-H1	122.54	O1-C1-F1	180.00
C2-H1	1.093	C2-C1-F1	109.29	F1-C1-H2	119.87
C1-F1	1.364	C2-C1-H2	109.91	F1-C1-H3	-119.87
C1-H2	1.082	C2-C1-H3	109.91		
C1-H3	1.082				

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	48.26	248.84	-8.27	-324.22	-308.74	107.51
200	53.38	263.40	-5.74	-325.81	-303.38	79.23
250	58.64	275.86	-2.95	-327.31	-297.65	62.19
300	64.14	287.03	0.12	-328.78	-291.62	50.77
350	69.75	297.33	3.46	-330.12	-285.39	42.59
400	75.28	307.00	7.10	-331.33	-278.95	36.42
450	80.60	316.17	11.00	-332.46	-272.34	31.61
500	85.60	324.92	15.17	-333.46	-265.64	27.75
600	94.55	341.33	24.20	-335.14	-251.96	21.94
700	102.19	356.50	34.07	-336.44	-238.03	17.76
800	108.68	370.58	44.64	-337.44	-223.89	14.62
900	114.22	383.75	55.81	-338.15	-209.66	12.17
1000	118.94	396.35	67.48	-338.65	-195.56	10.21
1100	122.98	408.18	79.60	-338.95	-181.46	8.62
1200	126.43	419.32	92.09	-339.11	-167.36	7.28
1300	129.40	429.84	104.89	-339.11	-153.26	6.16
1400	131.95	439.79	117.97	-339.03	-139.20	5.19
1500	134.16	449.22	131.29	-338.90	-125.14	4.36
1600	136.07	458.18	144.80	-338.65	-111.17	3.63
1700	137.73	466.70	158.50	-338.36	-97.28	2.99
1800	139.18	474.83	172.36	-338.03	-83.43	2.42
1900	140.46	482.60	186.35	-337.65	-69.71	1.92
2000	141.59	490.03	200.46	-337.23	-56.02	1.46
2100	142.58	497.16	214.67	-336.77	-42.47	1.06
2200	143.46	503.99	228.98	-336.31	-29.04	0.69
2300	144.25	510.56	243.37	-335.77	-15.65	0.36
2400	144.95	516.88	257.83	-335.26	-2.38	0.05
2500	145.58	522.97	272.36	-334.68	10.79	-0.23
2600	146.15	528.85	286.95	-334.13	23.85	-0.48
2700	146.67	534.53	301.60	-333.55	36.90	-0.71
2800	147.13	540.02	316.29	-332.92	49.87	-0.93
2900	147.55	545.33	331.03	-332.34	62.80	-1.13
3000	147.93	550.47	345.80	-331.67	75.77	-1.32

CH₂F-CHO fcco gauche

$\Delta H_f^\circ(0\text{ K})$	= -312.67 kJ mol ⁻¹
$\Delta H_f^\circ(298.15\text{ K})$	= -322.75 kJ mol ⁻¹
$S^\circ(298.15\text{ K})$	= 281.30 J K ⁻¹ mol ⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 41.73 135.31 171.87

Vibrational Frequencies (cm⁻¹)

164.6	251.0	722.4	726.2	845.9
1111.1	1124.2	1239.4	1380.4	1405.7
1464.4	1835.0	2815.4	2881.6	2918.0

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.507	C1-C2-O1	124.47	C1-C2-H1	180.03
C2-O1	1.183	O1-C2-H1	121.76	O1-C1-F1	0.10
C2-H1	1.096	C2-C1-F1	111.18	F1-C1-H2	120.95
C1-F1	1.351	C2-C1-H2	109.23	F1-C1-H3	-120.96
C1-H2	1.085	C2-C1-H3	109.21		
C1-H3	1.085				

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	46.37	245.13	-7.96	-317.94	-301.92	105.13
200	50.97	259.05	-5.53	-319.62	-296.35	77.39
250	56.38	270.93	-2.85	-321.25	-290.37	60.66
300	62.45	281.68	0.12	-322.80	-284.05	49.46
350	68.80	291.71	3.39	-324.22	-277.52	41.41
400	75.10	301.24	6.99	-325.47	-270.79	35.36
450	81.15	310.35	10.89	-326.60	-263.88	30.63
500	86.83	319.18	15.08	-327.57	-256.90	26.84
600	96.93	335.93	24.27	-329.11	-242.71	21.13
700	105.41	351.53	34.39	-330.16	-228.28	17.03
800	112.46	366.07	45.28	-330.83	-213.68	13.95
900	118.31	379.67	56.82	-331.16	-198.99	11.55
1000	123.16	392.39	68.90	-331.25	-184.22	9.62
1100	127.19	404.32	81.42	-331.16	-169.41	8.05
1200	130.55	415.53	94.31	-330.91	-154.60	6.73
1300	133.37	426.10	107.51	-330.54	-139.79	5.62
1400	135.73	436.07	120.98	-330.08	-125.02	4.66
1500	137.74	445.50	134.66	-329.53	-110.25	3.84
1600	139.44	454.45	148.53	-328.99	-95.52	3.12
1700	140.90	462.95	162.56	-328.36	-80.88	2.48
1800	142.16	471.04	176.72	-327.69	-66.27	1.92
1900	143.26	478.75	191.00	-327.02	-51.76	1.42
2000	144.20	486.13	205.38	-326.35	-37.32	0.97
2100	145.03	493.18	219.86	-325.60	-22.97	0.57
2200	145.76	499.95	234.41	-324.89	-8.74	0.21
2300	146.41	506.44	249.03	-324.18	5.44	-0.12
2400	146.98	512.68	263.71	-323.42	19.54	-0.42
2500	147.49	518.69	278.44	-322.67	33.51	-0.70
2600	147.95	524.49	293.22	-321.88	47.45	-0.95
2700	148.35	530.08	308.05	-321.12	61.34	-1.19
2800	148.72	535.48	322.91	-320.33	75.14	-1.40
2900	149.06	540.70	337.81	-319.57	88.99	-1.60
3000	149.36	545.76	352.74	-318.78	102.80	-1.79

CHF₂-CHO hcco cis

$\Delta H_f^\circ(0\text{ K}) = -530.70\text{ kJ mol}^{-1}$
 $\Delta H_f^\circ(298.15\text{ K}) = -538.95\text{ kJ mol}^{-1}$
 $S^\circ(298.15\text{ K}) = 304.75\text{ J K}^{-1}\text{ mol}^{-1}$

Moments of Inertia (10^{-47} kg m^2)
 87.24 211.96 272.48

Vibrational Frequencies (cm^{-1})
 76.3 315.5 368.5 416.3 592.2
 977.7 1081.8 1127.5 1131.2 1312.2
 1368.9 1395.3 1841.3 2875.1 3003.1

Bond Distances (10^{-10} m)		Bond Angles ($^\circ$)		Dihedral Angles ($^\circ$)	
C1-C2	1.516	C1-C2-O1	122.03	C1-C2-H1	180.00
C2-O1	1.183	O1-C2-H1	123.13	O1-C1-H2	0.00
C2-H1	1.091	C2-C1-H2	112.55	H2-C1-F1	121.72
C1-H2	1.077	C2-C1-F1	108.25	H2-C1-F2	-121.72
C1-F1	1.339	C2-C1-F2	108.25		
C1-F2	1.339				

Enthalpy Reference Temperature = $T_r = 298.15\text{ K}$
Standard State Pressure = $p_o = 1\text{ atmosphere}$

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	53.07	261.96	-9.38	-535.51	-516.60	179.89
200	60.40	278.25	-6.55	-536.81	-510.11	133.22
250	67.02	292.44	-3.37	-537.94	-503.38	105.17
300	73.30	305.21	0.13	-538.98	-496.39	86.43
350	79.34	316.95	3.95	-539.90	-489.28	73.02
400	85.08	327.93	8.07	-540.74	-482.04	62.94
450	90.42	338.26	12.46	-541.45	-474.67	55.10
500	95.34	348.04	17.11	-542.08	-467.27	48.81
600	103.90	366.20	27.10	-543.08	-452.25	39.37
700	110.95	382.76	37.87	-543.79	-437.06	32.61
800	116.78	397.97	49.28	-544.21	-421.79	27.54
900	121.62	412.01	61.22	-544.51	-406.43	23.59
1000	125.66	425.19	73.60	-544.59	-391.12	20.43
1100	129.06	437.62	86.36	-544.59	-376.02	17.85
1200	131.94	449.25	99.42	-544.46	-360.87	15.71
1300	134.38	460.18	112.75	-544.30	-345.81	13.89
1400	136.47	470.47	126.31	-544.00	-330.75	12.34
1500	138.26	480.20	140.05	-543.71	-315.77	11.00
1600	139.80	489.41	153.96	-543.33	-300.83	9.82
1700	141.14	498.14	168.02	-542.92	-285.98	8.79
1800	142.30	506.46	182.20	-542.50	-271.21	7.87
1900	143.32	514.39	196.48	-542.00	-256.56	7.05
2000	144.21	521.95	210.87	-541.54	-241.96	6.32
2100	145.00	529.20	225.33	-540.99	-227.48	5.66
2200	145.70	536.14	239.87	-540.45	-213.13	5.06
2300	146.32	542.80	254.48	-539.90	-198.82	4.52
2400	146.88	549.21	269.14	-539.32	-184.68	4.02
2500	147.38	555.38	283.86	-538.73	-170.58	3.56
2600	147.82	561.32	298.62	-538.15	-156.57	3.15
2700	148.23	567.06	313.43	-537.52	-142.63	2.76
2800	148.59	572.60	328.27	-536.89	-128.74	2.40
2900	148.93	577.96	343.15	-536.22	-114.89	2.07
3000	149.23	583.15	358.06	-535.59	-101.09	1.76

CHF₂-CHO hcco trans

$\Delta H_f^\circ(0\text{ K})$	= -514.55 kJ mol ⁻¹
$\Delta H_f^\circ(298.15\text{ K})$	= -525.02 kJ mol ⁻¹
$S^\circ(298.15\text{ K})$	= 287.06 J K ⁻¹ mol ⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 99.38 183.42 232.28

Vibrational Frequencies (cm⁻¹)

-109.3	266.0	308.3	496.2	782.7
871.4	960.5	1151.3	1157.2	1379.3
1385.4	1413.6	1842.9	2853.1	2964.4

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.529	C1-C2-O1	121.33	C1-C2-H1	180.00
C2-O1	1.181	O1-C2-H1	122.22	O1-C1-H2	180.00
C2-H1	1.092	C2-C1-H2	112.87	H2-C1-F1	120.90
C1-H2	1.079	C2-C1-F1	108.92	H2-C1-F2	-120.90
C1-F1	1.335	C2-C1-F2	108.92		
C1-F2	1.335				

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	44.57	250.93	-7.95	-520.15	-499.57	173.96
200	50.58	264.57	-5.57	-521.87	-492.46	128.62
250	56.80	276.52	-2.88	-523.54	-484.97	101.32
300	63.27	287.44	0.12	-525.09	-477.14	83.08
350	69.76	297.69	3.44	-526.51	-469.11	70.01
400	76.02	307.42	7.09	-527.81	-460.87	60.18
450	81.89	316.71	11.04	-528.94	-452.50	52.52
500	87.28	325.62	15.27	-529.99	-443.96	46.38
600	96.66	342.39	24.48	-531.79	-426.64	37.14
700	104.34	357.89	34.54	-533.17	-409.07	30.52
800	110.65	372.25	45.30	-534.30	-391.25	25.55
900	115.86	385.59	56.64	-535.13	-373.30	21.66
1000	120.19	398.03	68.45	-535.84	-355.22	18.55
1100	123.82	409.66	80.65	-536.35	-337.02	16.00
1200	126.87	420.57	93.19	-536.77	-318.78	13.87
1300	129.45	430.83	106.01	-537.10	-300.45	12.07
1400	131.64	440.50	119.07	-537.31	-282.09	10.52
1500	133.52	449.65	132.33	-537.48	-263.72	9.18
1600	135.14	458.32	145.77	-537.60	-245.39	8.01
1700	136.54	466.56	159.35	-537.64	-227.02	6.98
1800	137.75	474.40	173.07	-537.69	-208.70	6.06
1900	138.81	481.88	186.90	-537.69	-190.46	5.24
2000	139.74	489.02	200.82	-537.64	-172.21	4.50
2100	140.56	495.86	214.84	-537.56	-154.05	3.83
2200	141.29	502.41	228.93	-537.48	-135.94	3.23
2300	141.93	508.71	243.09	-537.35	-117.86	2.68
2400	142.51	514.76	257.32	-537.23	-99.87	2.17
2500	143.02	520.59	271.59	-537.06	-81.96	1.71
2600	143.49	526.21	285.92	-536.89	-64.06	1.29
2700	143.90	531.63	300.29	-536.72	-46.19	0.89
2800	144.28	536.87	314.70	-536.51	-28.37	0.53
2900	144.62	541.94	329.14	-536.31	-10.54	0.19
3000	144.93	546.85	343.62	-536.10	7.32	-0.13

CF₃-CHO fcco cis

$\Delta H_f^\circ(0 \text{ K}) = -767.26 \text{ kJ mol}^{-1}$
 $\Delta H_f^\circ(298.15 \text{ K}) = -774.30 \text{ kJ mol}^{-1}$
 $S^\circ(298.15 \text{ K}) = 318.28 \text{ J K}^{-1} \text{ mol}^{-1}$

Moments of Inertia (10^{-47} kg m^2)
 148.91 273.72 278.81

Vibrational Frequencies (cm^{-1})
 73.1 251.9 309.1 423.1 514.7
 515.0 688.4 834.9 981.5 1225.3
 1226.0 1329.8 1382.7 1857.1 2893.7

Bond Distances (10^{-10} m)		Bond Angles ($^\circ$)		Dihedral Angles ($^\circ$)	
C1-C2	1.524	C1-C2-O1	122.16	C1-C2-H1	180.00
C2-O1	1.178	O1-C2-H1	123.85	O1-C1-F1	0.00
C2-H1	1.089	C2-C1-F1	112.37	F1-C1-F2	121.11
C1-F1	1.306	C2-C1-F2	109.29	F1-C1-F3	-121.11
C1-F2	1.321	C2-C1-F3	109.29		
C1-F3	1.321				

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$
Standard State Pressure = $p_o = 1 \text{ atmosphere}$

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	57.57	271.58	-10.32	-771.74	-748.85	260.76
200	65.83	289.25	-7.22	-772.78	-741.07	193.54
250	73.49	304.75	-3.72	-773.62	-733.08	153.16
300	80.68	318.78	0.15	-774.33	-724.92	126.21
350	87.39	331.72	4.37	-774.92	-716.68	106.95
400	93.55	343.80	8.91	-775.42	-708.35	92.50
450	99.14	355.41	13.74	-775.80	-700.11	81.26
500	104.15	366.44	18.84	-776.09	-691.87	72.27
600	112.60	386.82	29.71	-776.42	-675.38	58.80
700	119.27	405.25	41.33	-776.59	-658.94	49.17
800	124.59	422.03	53.55	-776.55	-642.54	41.95
900	128.85	437.41	66.24	-776.38	-626.14	36.34
1000	132.31	451.58	79.31	-776.13	-609.82	31.85
1100	135.14	464.70	92.70	-775.80	-593.50	28.18
1200	137.48	476.91	106.34	-775.42	-577.22	25.12
1300	139.43	488.31	120.19	-774.96	-560.99	22.54
1400	141.07	499.00	134.22	-774.54	-544.84	20.33
1500	142.45	509.07	148.41	-774.04	-528.73	18.41
1600	143.63	518.56	162.72	-773.54	-512.71	16.74
1700	144.65	527.54	177.13	-772.99	-496.77	15.26
1800	145.52	536.07	191.65	-772.45	-480.91	13.95
1900	146.28	544.18	206.24	-771.91	-465.14	12.79
2000	146.94	551.91	220.91	-771.32	-449.45	11.74
2100	147.52	559.29	235.63	-770.73	-433.92	10.79
2200	148.04	566.36	250.41	-770.11	-418.44	9.93
2300	148.49	573.13	265.24	-769.48	-403.09	9.15
2400	148.89	579.63	280.11	-768.85	-387.81	8.44
2500	149.26	585.89	295.02	-768.22	-372.67	7.79
2600	149.58	591.91	309.96	-767.60	-357.61	7.18
2700	149.87	597.72	324.94	-766.93	-342.59	6.63
2800	150.13	603.32	339.94	-766.26	-327.61	6.11
2900	150.37	608.74	354.97	-765.59	-312.71	5.63
3000	150.58	613.98	370.02	-764.92	-297.78	5.18

$\text{CH}_2\text{F-CO}\cdot$ fcco trans

$\Delta H_f^\circ(0 \text{ K})$ = -166.94 kJ mol⁻¹
 $\Delta H_f^\circ(298.15 \text{ K})$ = -172.61 kJ mol⁻¹
 $S^\circ(298.15 \text{ K})$ = 286.12 J K⁻¹ mol⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 16.81 192.13 203.68

Vibrational Frequencies (cm⁻¹)
 137.9 312.2 496.2 841.8 895.3
 1100.8 1215.2 1346.3 1450.6 1924.3
 2907.3 2963.7

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.518				
C2-O1	1.163	C1-C2-O1	126.50	O1-C1-F1	180.00
C1-F1	1.354	C2-C1-F1	110.32	F1-C1-H1	120.13
C1-H1	1.082	C2-C1-H1	108.76	F1-C1-H2	-120.13
C1-H2	1.082	C2-C1-H2	108.76		

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$
 Standard State Pressure = $p_o = 1 \text{ atmosphere}$

T/K	- J K ⁻¹ mol ⁻¹ -		kJ mol ⁻¹			Log K_f
	C_p°	S°	$H^\circ - H^\circ(T_r)$	ΔH_f°	ΔG_f°	
150	46.86	249.59	-8.03	-170.04	-162.92	56.73
200	51.81	263.63	-5.57	-170.96	-160.41	41.89
250	56.95	275.65	-2.86	-171.84	-157.69	32.95
300	62.26	286.50	0.11	-172.63	-154.85	26.96
350	67.50	296.49	3.35	-173.34	-151.88	22.67
400	72.46	305.83	6.84	-174.01	-148.82	19.44
450	77.02	314.63	10.57	-174.56	-145.73	16.91
500	81.14	322.95	14.52	-175.06	-142.55	14.89
600	88.15	338.39	23.00	-175.85	-136.02	11.84
700	93.82	352.41	32.10	-176.44	-129.37	9.65
800	98.47	365.25	41.74	-176.90	-122.59	8.00
900	102.33	377.07	51.79	-177.28	-115.73	6.72
1000	105.57	388.02	62.21	-177.53	-108.83	5.68
1100	108.32	398.22	72.92	-177.74	-101.80	4.83
1200	110.65	407.74	83.89	-177.90	-94.77	4.12
1300	112.64	416.68	95.07	-177.99	-87.70	3.52
1400	114.34	425.09	106.43	-178.07	-80.58	3.01
1500	115.81	433.03	117.96	-178.15	-73.47	2.56
1600	117.09	440.54	129.62	-178.20	-66.36	2.17
1700	118.20	447.68	141.40	-178.20	-59.29	1.82
1800	119.16	454.55	153.28	-178.20	-52.38	1.52
1900	120.01	461.18	165.25	-178.20	-45.69	1.26
2000	120.76	467.51	177.30	-178.20	-39.08	1.02
2100	121.42	473.57	189.42	-178.15	-32.55	0.81
2200	122.01	479.39	201.60	-178.11	-26.07	0.62
2300	122.53	484.97	213.84	-178.07	-19.71	0.45
2400	122.99	490.34	226.12	-178.03	-13.39	0.29
2500	123.41	495.51	238.45	-177.95	-7.15	0.15
2600	123.79	500.49	250.82	-177.86	-1.00	0.02
2700	124.13	505.31	263.22	-177.78	5.15	-0.10
2800	124.44	509.96	275.66	-177.69	11.21	-0.21
2900	124.72	514.46	288.13	-177.61	17.28	-0.31
3000	124.97	518.81	300.62	-177.53	23.39	-0.41

CH₂F-CO• fcco gauche

$\Delta H_f^\circ(0 \text{ K}) = -164.01 \text{ kJ mol}^{-1}$
 $\Delta H_f^\circ(298.15 \text{ K}) = -169.85 \text{ kJ mol}^{-1}$
 $S^\circ(298.15 \text{ K}) = 285.88 \text{ J K}^{-1} \text{ mol}^{-1}$

Moments of Inertia (10^{-47} kg m^2)
 36.25 139.26 170.32

Vibrational Frequencies (cm^{-1})
 180.3 228.0 671.5 809.3 894.7
 1081.2 1240.7 1370.1 1453.3 1943.7
 2914.0 2961.7

Bond Distances (10^{-10} m)		Bond Angles ($^\circ$)		Dihedral Angles ($^\circ$)	
C1-C2	1.513	C1-C2-O1	129.10	O1-C1-F1	0.00
C2-O1	1.160	C2-C1-F1	111.84	F1-C1-H1	120.87
C1-F1	1.356	C2-C1-H1	108.40	F1-C1-H2	-120.84
C1-H1	1.082	C2-C1-H2	108.38		
C1-H2	1.082				

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$
 Standard State Pressure = $p_o = 1 \text{ atmosphere}$

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH_f°	ΔG_f°	
150	46.47	250.10	-7.86	-167.11	-160.08	55.74
200	50.74	264.00	-5.44	-168.07	-157.61	41.16
250	55.51	275.76	-2.79	-168.99	-154.89	32.36
300	60.67	286.26	0.11	-169.87	-152.05	26.47
350	65.92	295.92	3.27	-170.67	-149.03	22.24
400	71.02	304.98	6.69	-171.42	-145.90	19.05
450	75.82	313.63	10.36	-172.05	-142.72	16.57
500	80.26	321.85	14.25	-172.59	-139.49	14.57
600	88.01	337.19	22.66	-173.43	-132.88	11.57
700	94.35	351.25	31.78	-174.01	-126.11	9.41
800	99.51	364.19	41.47	-174.43	-119.29	7.79
900	103.71	376.15	51.63	-174.68	-112.34	6.52
1000	107.16	387.26	62.18	-174.81	-105.31	5.50
1100	110.00	397.61	73.04	-174.85	-98.28	4.67
1200	112.35	407.29	84.17	-174.85	-91.17	3.97
1300	114.32	416.36	95.51	-174.81	-84.06	3.38
1400	115.98	424.89	107.04	-174.72	-76.94	2.87
1500	117.38	432.94	118.72	-174.64	-69.83	2.43
1600	118.58	440.55	130.53	-174.51	-62.72	2.05
1700	119.61	447.78	142.45	-174.39	-55.65	1.71
1800	120.49	454.64	154.47	-174.26	-48.62	1.41
1900	121.26	461.17	166.57	-174.14	-41.63	1.14
2000	121.93	467.41	178.74	-173.97	-34.69	0.91
2100	122.52	473.37	190.98	-173.85	-27.78	0.69
2200	123.04	479.08	203.27	-173.68	-21.00	0.50
2300	123.50	484.56	215.61	-173.55	-14.23	0.32
2400	123.90	489.83	227.99	-173.38	-7.53	0.16
2500	124.27	494.89	240.42	-173.22	-0.92	0.02
2600	124.60	499.77	252.87	-173.09	5.69	-0.11
2700	124.89	504.48	265.35	-172.92	12.26	-0.24
2800	125.16	509.03	277.87	-172.76	18.79	-0.35
2900	125.39	513.51	290.41	-172.59	25.06	-0.45
3000	125.61	517.87	302.97	-172.42	31.30	-0.55

CHF₂-CO• hcco cis

$\Delta H_f^\circ(0 \text{ K})$ = -372.92 kJ mol⁻¹
 $\Delta H_f^\circ(298.15 \text{ K})$ = -377.35 kJ mol⁻¹
 $S^\circ(298.15 \text{ K})$ = 310.33 J K⁻¹ mol⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 82.99 209.20 274.09

Vibrational Frequencies (cm⁻¹)
 53.8 366.7 407.3 410.6 590.0
 946.7 1133.6 1150.5 1319.5 1366.4
 1940.6 2976.4

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.539	C1-C2-O1	126.14	O1-C1-H1	0.00
C2-O1	1.158	C2-C1-H1	112.14	H1-C1-F1	121.17
C1-H1	1.078	C2-C1-F1	108.00	H1-C1-F2	-121.17
C1-F1	1.330	C2-C1-F2	108.00		
C1-F2	1.330				

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	50.83	270.46	-8.79	-375.47	-366.10	127.47
200	56.46	285.83	-6.09	-376.14	-362.84	94.76
250	61.86	299.01	-3.11	-376.77	-359.45	75.10
300	67.12	310.75	0.13	-377.35	-355.97	61.98
350	72.19	321.71	3.62	-377.90	-352.50	52.60
400	76.96	332.08	7.36	-378.36	-349.03	45.58
450	81.38	341.80	11.33	-378.78	-345.56	40.11
500	85.41	350.95	15.51	-379.15	-342.04	35.73
600	92.32	367.82	24.42	-379.78	-335.01	29.16
700	97.91	383.07	33.95	-380.24	-327.94	24.47
800	102.42	396.97	43.99	-380.62	-320.87	20.95
900	106.11	409.72	54.43	-380.91	-313.76	18.21
1000	109.14	421.48	65.20	-381.12	-306.65	16.02
1100	111.64	432.39	76.25	-381.33	-299.49	14.22
1200	113.73	442.55	87.52	-381.50	-292.34	12.72
1300	115.48	452.04	98.99	-381.62	-285.18	11.46
1400	116.97	460.96	110.62	-381.71	-278.07	10.37
1500	118.23	469.36	122.38	-381.79	-270.96	9.43
1600	119.32	477.29	134.26	-381.87	-263.88	8.61
1700	120.25	484.80	146.24	-381.96	-256.86	7.89
1800	121.06	491.93	158.31	-382.00	-249.87	7.25
1900	121.76	498.72	170.45	-382.00	-242.92	6.68
2000	122.38	505.19	182.66	-382.04	-236.06	6.17
2100	122.92	511.37	194.93	-382.04	-229.28	5.70
2200	123.40	517.29	207.25	-382.04	-222.59	5.28
2300	123.83	522.97	219.61	-382.04	-215.98	4.90
2400	124.20	528.43	232.01	-382.04	-209.41	4.56
2500	124.54	533.67	244.45	-382.00	-202.92	4.24
2600	124.85	538.72	256.92	-381.96	-196.48	3.95
2700	125.12	543.60	269.42	-381.92	-190.12	3.68
2800	125.37	548.30	281.95	-381.87	-183.76	3.43
2900	125.59	552.85	294.50	-381.79	-177.40	3.20
3000	125.80	557.25	307.06	-381.75	-171.04	2.98

CF₃-CO• fcco cis

$\Delta H_f^\circ(0 \text{ K})$ = -606.51 kJ mol⁻¹
 $\Delta H_f^\circ(298.15 \text{ K})$ = -609.88 kJ mol⁻¹
 $S^\circ(298.15 \text{ K})$ = 323.59 J K⁻¹ mol⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 144.25 275.19 275.38

Vibrational Frequencies (cm⁻¹)
 58.1 234.3 388.6 411.9 523.5
 531.4 667.3 795.4 1203.3 1240.3
 1269.0 1959.9

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.541	C1-C2-O1	126.31	O1-C1-F1	0.00
C2-O1	1.155	C2-C1-F1	112.19	F1-C1-F2	120.64
C1-F1	1.310	C2-C1-F2	108.91	F1-C1-F3	-120.64
C1-F2	1.313	C2-C1-F3	108.91		
C1-F3	1.313				

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	53.57	277.64	-9.77	-608.94	-595.22	207.26
200	62.06	294.65	-6.86	-609.40	-590.61	154.25
250	69.84	310.08	-3.54	-609.69	-586.09	122.45
300	76.67	324.08	0.14	-609.86	-581.58	101.26
350	82.65	336.94	4.14	-609.99	-577.10	86.12
400	87.87	348.83	8.41	-609.99	-572.66	74.78
450	92.42	359.91	12.93	-609.94	-568.23	65.96
500	96.37	370.28	17.66	-609.90	-563.84	58.90
600	102.82	389.17	27.64	-609.69	-555.13	48.33
700	107.71	406.03	38.19	-609.44	-546.56	40.78
800	111.45	421.21	49.16	-609.19	-538.02	35.13
900	114.35	434.99	60.46	-608.94	-529.53	30.73
1000	116.63	447.60	72.02	-608.69	-521.08	27.22
1100	118.43	459.19	83.78	-608.52	-512.67	24.34
1200	119.88	469.92	95.70	-608.31	-504.26	21.95
1300	121.06	479.90	107.75	-608.14	-495.89	19.92
1400	122.03	489.21	119.91	-608.02	-487.56	18.19
1500	122.83	497.94	132.15	-607.89	-479.28	16.69
1600	123.50	506.16	144.47	-607.81	-470.99	15.38
1700	124.08	513.92	156.85	-607.68	-462.79	14.22
1800	124.56	521.26	169.28	-607.60	-454.68	13.19
1900	124.98	528.23	181.77	-607.52	-446.60	12.28
2000	125.34	534.86	194.28	-607.43	-438.61	11.45
2100	125.65	541.19	206.83	-607.35	-430.70	10.71
2200	125.93	547.23	219.41	-607.27	-422.84	10.04
2300	126.16	553.02	232.02	-607.18	-415.09	9.43
2400	126.38	558.57	244.65	-607.06	-407.40	8.87
2500	126.57	563.90	257.29	-606.97	-399.78	8.35
2600	126.73	569.03	269.96	-606.89	-392.25	7.88
2700	126.89	573.97	282.64	-606.81	-384.76	7.44
2800	127.02	578.74	295.34	-606.68	-377.27	7.04
2900	127.14	583.35	308.05	-606.60	-369.82	6.66
3000	127.26	587.80	320.77	-606.47	-362.33	6.31

CF₃-CO• fcco trans

$\Delta H_f^\circ(0 \text{ K})$ = -606.43 kJ mol⁻¹
 $\Delta H_f^\circ(298.15 \text{ K})$ = -611.24 kJ mol⁻¹
 $S^\circ(298.15 \text{ K})$ = 306.16 J K⁻¹ mol⁻¹

Moments of Inertia (10⁻⁴⁷ kg m²)
 142.55 273.76 275.81

Vibrational Frequencies (cm⁻¹)
 -78.5 225.9 320.7 417.8 518.9
 527.3 664.5 792.6 1199.3 1240.1
 1270.4 1953.8

Bond Distances (10 ⁻¹⁰ m)		Bond Angles (°)		Dihedral Angles (°)	
C1-C2	1.546				
C2-O1	1.155	C1-C2-O1	124.97		
C1-F1	1.311	C2-C1-F1	110.39	O1-C1-F1	180.00
C1-F2	1.312	C2-C1-F2	109.83	F1-C1-F2	119.86
C1-F3	1.312	C2-C1-F3	109.83	F1-C1-F3	-119.86

Enthalpy Reference Temperature = T_r = 298.15 K
Standard State Pressure = p_o = 1 atmosphere

T/K	- J K ⁻¹ mol ⁻¹ -		----- kJ mol ⁻¹ -----			Log K _f
	C _p ^o	S ^o	H ^o -H ^o (T _r)	ΔH _f ^o	ΔG _f ^o	
150	49.12	264.78	-9.13	-609.65	-594.00	206.84
200	58.05	280.15	-6.44	-610.36	-588.69	153.74
250	65.93	293.97	-3.34	-610.86	-583.25	121.86
300	72.78	306.61	0.13	-611.24	-577.73	100.59
350	78.74	318.29	3.92	-611.53	-572.16	85.39
400	83.94	329.15	8.00	-611.78	-566.56	73.98
450	88.46	339.31	12.31	-611.95	-560.95	65.11
500	92.40	348.83	16.83	-612.08	-555.34	58.01
600	98.80	366.27	26.41	-612.29	-544.00	47.36
700	103.67	381.89	36.54	-612.45	-532.67	39.75
800	107.39	395.98	47.10	-612.62	-521.24	34.03
900	110.28	408.81	57.99	-612.79	-509.82	29.59
1000	112.54	420.55	69.14	-612.96	-498.27	26.03
1100	114.34	431.36	80.48	-613.17	-486.72	23.11
1200	115.78	441.37	91.99	-613.42	-475.09	20.68
1300	116.95	450.69	103.63	-613.67	-463.42	18.62
1400	117.91	459.39	115.37	-613.92	-451.70	16.85
1500	118.71	467.55	127.21	-614.21	-439.99	15.32
1600	119.38	475.24	139.11	-614.50	-428.27	13.98
1700	119.95	482.49	151.08	-614.84	-416.52	12.80
1800	120.43	489.36	163.10	-615.13	-404.80	11.75
1900	120.84	495.88	175.16	-615.47	-393.13	10.81
2000	121.20	502.09	187.27	-615.80	-381.46	9.96
2100	121.51	508.01	199.40	-616.14	-369.82	9.20
2200	121.78	513.67	211.57	-616.47	-358.23	8.51
2300	122.02	519.09	223.76	-616.81	-346.69	7.87
2400	122.24	524.29	235.97	-617.10	-335.18	7.29
2500	122.42	529.28	248.20	-617.43	-323.72	6.76
2600	122.59	534.09	260.45	-617.77	-312.25	6.27
2700	122.74	538.72	272.72	-618.06	-300.83	5.82
2800	122.88	543.18	285.00	-618.40	-289.41	5.40
2900	123.00	547.50	297.30	-618.69	-277.98	5.01
3000	123.11	551.67	309.60	-619.02	-266.48	4.64

Appendix B. Fluorinated Hydrocarbon Reaction Rate Constants

REACTION	A	b	E	note/reference	H
H₂/O₂ System: Combination, Decomposition					
H + H +M = H ₂ + M H ₂ /0/ H ₂ O/0/ CO ₂ /0/	1.00E18	-1.00	0.	!MBA139	
H + H +H ₂ = 2H ₂	9.20E16	-0.60	0.	!MBA140	
H + H +H ₂ O = H ₂ + H ₂ O	6.00E19	-1.25	0.	!MBA141	
H + H +CO ₂ = H ₂ + CO ₂	5.49E20	-2.00	0.	!MBA142	
O + O +M = O ₂ + M	1.89E13	0.00	-1788.	!MBA145	86TSA/HAM
H + OH +M = H ₂ O + M H ₂ O/5/	1.60E22	-2.00	0.	!MBA143	
H + O +M = OH + M H ₂ O/5/	6.20E16	-0.60	0.	!MBA144	
H₂/O₂ System: Atom Transfers					
O + OH = O ₂ + H	4.00E14	-0.50	0.	!MBA132	81HOW/SMI
O + H ₂ = OH + H	5.06E04	2.67	6290.	!MBA133	88SUT/MIC
2OH = O + H ₂ O	6.00E08	1.30	0.	!MBA138	
H ₂ + O ₂ = 2OH	1.70E13	0.00	47780.	!MBA130	71JAC/HOU
OH + H ₂ = H ₂ O + H	1.17E09	1.30	3626.	!MBA131	79COH/WES
H₂/O₂ System: Peroxyl and Peroxide					
H + O ₂ + M = HO ₂ + M H ₂ O/18.6/ CO ₂ /4.2/ H ₂ /2.9/ CO/2.1/ N ₂ /1.3/	3.61E17	-0.72	0.	!MBA134	
H + HO ₂ = H ₂ + O ₂	1.25E13	0.00	0.	!MBA146	
O + HO ₂ = O ₂ + OH	1.40E13	0.00	1073.	!MBA137	
OH + HO ₂ = H ₂ O + O ₂	7.50E12	0.00	0.	!MBA135	
H ₂ O ₂ + M = 2OH + M	1.30E17	0.00	45500.	!MBA148	
H + HO ₂ = 2OH	1.40E14	0.00	1073.	!MBA136	
2HO ₂ = H ₂ O ₂ + O ₂	2.00E12	0.00	0.	!MBA147	
C₁ Hydrocarbons: Methane					
CH ₄ + H = CH ₃ + H ₂	2.20E04	3.00	8750.	!MBA004	73CLA/DOV
CH ₄ + O = CH ₃ + OH	1.02E09	1.50	8604.	!MBA005	86SUT/MIC
CH ₄ + OH = CH ₃ + H ₂ O	1.60E06	2.10	2460.	!MBA005	83BAU/CRA
CH ₄ + O ₂ = CH ₃ + HO ₂	7.90E13	0.00	56000.	!MBA003	72SKI/LIF
CH ₄ + HO ₂ = CH ₃ + H ₂ O ₂	1.80E11	0.00	18700.	!MBA006	72SKI/LIF
C₁ Hydrocarbons: Methyl					
CH ₃ + H (+M) = CH ₄ (+M) LOW/8.00E26 -3.0 0./ SRI/0.45 797. 979./ H ₂ /2.0/ CO/2.0/ CO ₂ /3.0/ H ₂ O/5.0/	6.00E16	-1.00	0.	!MBA002	84WAR !(89STE/SMI2)
CH ₃ + H = CH ₂ + H ₂	9.00E13	0.00	15100.	!MBA013	
CH ₃ + O = CH ₂ O + H	8.00E13	0.00	0.	!MBA009	
CH ₃ + OH = CH ₂ + H ₂ O	7.50E06	2.00	5000.	!MBA012	
CH ₃ + OH = CH ₃ OH	2.24E40	-8.20	11673.	!87DEA/WES	
CH ₃ + OH = CH ₂ OH + H	2.64E19	-1.80	8068.	!87DEA/WES	
CH ₃ + OH = CH ₃ O + H	5.74E12	-0.23	13931.	!87DEA/WES	
CH ₃ + OH = CH ₂ SING + H ₂ O	8.90E19	-1.80	8067.	!87DEA/WES	
CH ₃ + O ₂ = CH ₃ O + O	2.05E18	-1.57	29229.	!MBA008	86TSA/HAM
CH ₃ + HO ₂ = CH ₃ O + OH	2.00E13	0.00	0.	!MBA007	86TSA/HAM
CH ₃ + CH ₃ (+M) = C ₂ H ₆ (+M) LOW/3.18E41 -7.0 2762./ TROE/0.6041 6927. 132./ H ₂ /2.0/ CO/2.0/ CO ₂ /3.0/ H ₂ O/5.0/	9.03E16	-1.20	654.	!MBA001	88WAG/WAR !(88WAG/WAR)

C₁ Hydrocarbons: Methylene (triplet)						
CH ₂ +OH = CH ₂ O+H	2.50E13	0.00	0.	!	MBA026	
CH ₂ +O = CO+2H	5.00E13	0.00	0.	!	MBA043	
CH ₂ +CO ₂ = CH ₂ O+CO	1.10E11	0.00	1000.	!	MBA042	
CH ₂ +O = CO+H ₂	3.00E13	0.00	0.	!	MBA044	
CH ₂ +O ₂ = CO ₂ +2H	1.60E12	0.00	1000.	!	MBA045	
CH ₂ +O ₂ = CH ₂ O+O	5.00E13	0.00	9000.	!	MBA046	
CH ₂ +O ₂ = CO ₂ +H ₂	6.90E11	0.00	500.	!	MBA047	
CH ₂ +O ₂ = CO+H ₂ O	1.90E10	0.00	-1000.	!	MBA048	
CH ₂ +O ₂ = CO+OH+H	8.60E10	0.00	-500.	!	MBA049	
CH ₂ +O ₂ = HCO+OH	4.30E10	0.00	-500.	!	MBA050	
CH ₂ +CH ₃ = C ₂ H ₄ +H	3.00E13	0.00	0.	!	MBA072	
2CH ₂ = C ₂ H ₂ +H ₂	4.00E13	0.00	0.	!	MBA114	
C₁ Hydrocarbons: Methylene (singlet)						
CH ₂ SING+M = CH ₂ +M H/0.0/	1.00E13	0.00	0.	!	MBA106	
CH ₂ SING+H = CH ₂ +H	2.00E14	0.00	0.	!	MBA111	
CH ₂ SING+O ₂ = CO+OH+H	3.00E13	0.00	0.	!	MBA109	
CH ₂ SING+H ₂ = CH ₃ +H	7.00E13	0.00	0.	!	MBA110	
CH ₂ SING+CH ₄ = 2CH ₃	4.00E13	0.00	0.	!	MBA107	
CH ₂ SING+C ₂ H ₆ = CH ₃ +C ₂ H ₅	1.20E14	0.00	0.	!	MBA108	
C₁ Hydrocarbons: Methylidyne						
CH ₂ +H = CH+H ₂	1.00E18	-1.56	0.	!	MBA024	
CH ₂ +OH = CH+H ₂ O	1.13E07	2.00	3000.	!	MBA025	
CH+O ₂ = HCO+O	3.30E13	0.00	0.	!	MBA027	82BER/FLE
CH+O = CO+H	5.70E13	0.00	0.	!	MBA028	83MES/FIL
CH+OH = HCO+H	3.00E13	0.00	0.	!	MBA029	
CH+CO ₂ = HCO+CO	3.40E12	0.00	690.	!	MBA030	82BER/FLE
CH+H ₂ O = CH ₂ O+H	1.17E15	-0.75	0.	!	MBA032	
CH+CH ₂ O = CH ₂ CO+H	9.46E13	0.00	-515.	!	MBA033	88ZAB/FLE
CH+CH ₂ = C ₂ H ₂ +H	4.00E13	0.00	0.	!	MBA035	
CH+CH ₃ = C ₂ H ₃ +H	3.00E13	0.00	0.	!	MBA036	
CH+CH ₄ = C ₂ H ₄ +H	6.00E13	0.00	0.	!	MBA037	80BUT/FLE
C ₂ H ₃ +CH = CH ₂ +C ₂ H ₂	5.00E13	0.00	0.	!	MBA086	
HCCO+CH = C ₂ H ₂ +CO	5.00E13	0.00	0.	!	MBA104	
REACTION	A	b	E	note/reference		H
Oxidized C₁ Hydrocarbons: Methanol						
CH ₃ OH + H = CH ₃ O + H ₂	8.00E12	0.00	6095.	!	90NOR	
CH ₃ OH + OH = CH ₃ O + H ₂ O	1.50E13	0.00	5960.	!	75BOW	
CH ₃ OH + CH ₃ = CH ₃ O + CH ₄ +16	1.45E+1	3.10	6935.	!	90NOR	
CH ₃ OH + O ₂ = CH ₂ OH+ HO ₂	2.05E13	0.00	44717.	!	90NOR	
CH ₃ OH + H = CH ₂ OH+ H ₂	3.20E13	0.00	6095.	!	90NOR	
CH ₃ OH + O = CH ₂ OH+ OH	3.88E05	2.50	3080.	!	90NOR	
CH ₃ OH + OH = CH ₂ OH+ H ₂ O	1.50E13	0.00	5960.	!	75BOW	
CH ₃ OH + HO ₂ = CH ₂ OH+ H ₂ O ₂	3.98E13	0.00	19400.	!	90NOR	
CH ₃ OH + CH ₃ = CH ₂ OH+ CH ₄	3.19E01	3.17	7172.	!	90NOR	
Oxidized C₁ Hydrocarbons: Methoxy, Hydroxymethyl						
CH ₃ O+M = CH ₂ O+H+M	1.00E14	0.00	25000.	!	MBA014	
CH ₃ O+O ₂ = CH ₂ O+HO ₂	6.30E10	0.00	2600.	!	MBA022	
CH ₃ O+H = CH ₂ O+H ₂	2.00E13	0.00	0.	!	MBA016	
CH ₃ O+O = CH ₂ O+OH	1.00E13	0.00	0.	!	MBA020	
CH ₃ O+OH = CH ₂ O+H ₂ O	1.00E13	0.00	0.	!	MBA018	
CH ₂ OH+M = CH ₂ O+H+M	1.00E14	0.00	25000.	!	MBA015	
CH ₂ OH+O ₂ = CH ₂ O+HO ₂	1.48E13	0.00	1500.	!	MBA023	
CH ₂ OH+H = CH ₂ O+H ₂	2.00E13	0.00	0.	!	MBA017	
CH ₂ OH+O = CH ₂ O+OH	1.00E13	0.00	0.	!	MBA021	
CH ₂ OH+OH = CH ₂ O+H ₂ O	1.00E13	0.00	0.	!	MBA019	

Oxidized C₁ Hydrocarbons: Formaldehyde						
CH ₂ O+M	= HCO+H+M	3.31E16	0.00	81000.	!MBA053	80DEA/JOH
CH ₂ O+H	= HCO+H ₂	2.19E08	1.77	3000.	!MBA052	86TSA/HAM
CH ₂ O+O	= HCO+OH	1.80E13	0.00	3080.	!MBA054	80KLE/SOK
CH ₂ O+OH	= HCO+H ₂ O	3.43E09	1.18	-447.	!MBA051	86TSA/HAM
Oxidized C₁ Hydrocarbons: Formyl						
HCO + M	= CO + H + M	2.50E14	0.00	16802.	!MBA056	84WAR
CO/1.9/ H ₂ /1.9/ CH ₄ /2.8/ CO ₂ /3.0/ H ₂ O/5.0/						
HCO + H	= CO + H ₂	1.19E13	0.25	0.	!MBA057	
HCO + O	= CO + OH	3.00E13	0.00	0.	!MBA058	84WAR
HCO + O	= CO ₂ + H	3.00E13	0.00	0.	!MBA059	84WAR
HCO + OH	= CO + H ₂ O	1.00E14	0.00	0.	!MBA055	84TEM/WAG
HCO + O ₂	= CO + HO ₂	3.30E13	-0.40	0.	!MBA060	81VEY/LES
Oxidized C₁ Hydrocarbons: Carbon Monoxide						
CO + O+M	= CO ₂ + M	6.17E14	0.00	3000.	!MBA061	86TSA/HAM
CO + OH	= CO ₂ + H	1.51E07	1.30	-758.	!MBA062	
CO + O ₂	= CO ₂ + O	1.60E13	0.00	41000.	!MBA063	71BRA/BEL
CO + HO ₂	= CO ₂ + OH	5.80E13	0.00	22934.	!MBA064	77ATR/BAL
REACTION		A	b	E	note/reference	
C₂ Hydrocarbons: Ethane						
C ₂ H ₆ + H	= C ₂ H ₅ + H ₂	5.40E02	3.50	5210.	!MBA066	73CAL/DOV
C ₂ H ₆ + O	= C ₂ H ₅ + OH	3.00E07	2.00	5115.	!MBA067	84WAR
C ₂ H ₆ + OH	= C ₂ H ₅ + H ₂ O	8.70E09	1.05	1810.	!MBA068	83TUL/RAV
C ₂ H ₆ + CH ₃	= C ₂ H ₅ + CH ₄	5.50E-1	4.00	8300.	!MBA065	73CLA/DOV
C₂ Hydrocarbons: Ethyl						
C ₂ H ₅ +H	= CH ₃ +CH ₃	1.00E14	0.00	0.	!MBA074	
C ₂ H ₅ + O	= CH ₂ O + CH ₃	1.60E13	0.	0.	!86TSA/HAM	
C ₂ H ₅ +O ₂	= C ₂ H ₄ +HO ₂	2.56E19	-2.77	1977.	!90BOZ/DEA	
C₂ Hydrocarbons: Ethylene						
C ₂ H ₄ +M	= C ₂ H ₂ +H ₂ +M	1.50E15	0.00	55800.	!MBA128	83KIE/KAP
C ₂ H ₄ +M	= C ₂ H ₃ +H+M	1.40E16	0.00	82360.	!MBA129	
C ₂ H ₄ +H (+M)	= C ₂ H ₅ (+M)	8.40E08	1.5	990.	!86TSA/HAM	
LOW/6.37E27 -2.8 -54./						
H ₂ /2.0/ CO/2.0/ CO ₂ /3.0/ H ₂ O/5.0/						
C ₂ H ₄ +H	= C ₂ H ₃ +H ₂	1.10E14	0.00	8500.	!MBA069	73PEE/MAH
C ₂ H ₄ +O	= CH ₃ +HCO	1.60E09	1.20	746.	!MBA070	84WAR
C ₂ H ₄ +OH	= C ₂ H ₃ +H ₂ O	4.50E06	2.00	2850.	!fit	ref
C₂ Hydrocarbons: Vinyl						
C ₂ H ₃ +H	= C ₂ H ₂ +H ₂	1.20E13	0.00	0.	!92BAU/COB	
C ₂ H ₃ +OH	= C ₂ H ₂ +H ₂ O	5.00E12	0.00	0.	!MBA083	
C ₂ H ₃ +CH ₂	= C ₂ H ₂ +CH ₃	3.00E13	0.00	0.	!MBA084	
C ₂ H ₃ +O ₂	= CH ₂ O+HCO	1.05E38	-8.22	7030.	!92WES	a/s
C ₂ H ₃ +O ₂	= CH ₂ O+HCO	4.48E26	-4.55	5480.	!92WES	direct
C ₂ H ₃ +O	= CH ₂ CO+H	3.00E13	0.00	0.	!MBA081	84WAR
C₂ Hydrocarbons: Acetylene						
C ₂ H ₂ +H (+M)	= C ₂ H ₃ (+M)	5.54E12	0.00	2410.	!MBA079	76PAY/STI
LOW/2.67E27 -3.5 2410./						
H ₂ /2.0/ CO/2.0/ CO ₂ /3.0/ H ₂ O/5.0/						
C ₂ H ₂ +OH	= HCCOH+H	5.04E05	2.30	13500.	!MBA088	
C ₂ H ₂ +OH	= CH ₂ CO+H	2.18E-4	4.50	-1000.	!MBA089	
C ₂ H ₂ +OH	= CH ₃ +CO	4.83E-4	4.00	-2000.	!MBA090	
C ₂ H ₂ +O	= CH ₂ +CO	1.02E07	2.00	1900.	!MBA076	
C ₂ H ₂ +O	= HCCO+H	1.02E07	2.00	1900.	!MBA077	
C ₂ H ₂ +O ₂	= HCCO+OH	2.00E08	1.50	30100.	!MBA126	

Oxidized C₂ Hydrocarbons: Ketene, HCCOH

HCCOH+H	=	CH ₂ CO+H	1.00E13	0.00	0.	!MBA091
CH ₂ CO+H	=	CH ₃ +CO	1.13E13	0.00	3428.	!MBA094
CH ₂ CO+H	=	HCCO+H ₂	5.00E13	0.00	8000.	!MBA095
CH ₂ CO+O	=	CO ₂ +CH ₂	1.75E12	0.00	1350.	!MBA093
CH ₂ CO+O	=	HCCO+OH	1.00E13	0.00	8000.	!MBA096
CH ₂ CO+OH	=	HCCO+H ₂ O	7.50E12	0.00	2000.	!MBA097
CH ₂ CO(+M)	=	CH ₂ +CO(+M)	3.00E14	0.00	70980.	!MBA098
LOW/3.60E15			0.0	59270./		

Oxidized C₂ Hydrocarbons: Ketyl

HCCO+H	=	CH ₂ SING+CO	1.00E14	0.00	0.	!MBA101
HCCO+O	=	H+2CO	1.00E14	0.00	0.	!MBA102
HCCO+O ₂	=	2CO+OH	1.60E12	0.00	854.	!MBA103
2HCCO	=	C ₂ H ₂ +2CO	1.00E13	0.00	0.	!MBA105
HCCO+CH ₂	=	C ₂ H ₃ +CO	3.00E13	0.00	0.	!MBA115

REACTION	A	b	E	note/reference	H
H/F/O Chemistry					
HF + M = H + F	3.12E13	0.00	99320.	!	81BAU/DUX+134
H ₂ + F = H + HF	2.56E12	0.50	650.	!fit	89STE/BRU -31
OH + F = O + HF	2.00E13	0.00	0.	!ref	H+HNO ₃ -33
HO ₂ + F = O ₂ + HF	2.89E12	0.50	0.	!fit	83WAL/WAG -86
H ₂ O + F = OH + HF	1.30E09	1.50	0.	!fit	83WAL/WAG -16
H ₂ O ₂ + F = HO ₂ + HF	1.73E12	0.50	0.	!fit	83WAL/WAG -48

Fluoromethanes: Thermal Decomposition

CH ₂ SING + HF = CH ₃ F	1.91E23	-3.62	1780.	!fit	73SCH/WAG -88
CHF + H ₂ = CH ₃ F	2.25E17	-2.85	13000.	!RRKM	BAC
CH ₂ F + H = CH ₃ F	3.03E21	-3.38	3460.	!RRKM	BAC -97
CHF + HF = CH ₂ F ₂	3.64E24	-4.26	4060.	!RRKM	BAC -71
CF ₂ + H ₂ = CH ₂ F ₂	1.70E06	-0.71	40900.	!RRKM	BAC
CHF ₂ + H = CH ₂ F ₂	2.75E06	-0.32	7690.	!RRKM	BAC -102
CHF ₃ + M = CF ₂ + HF	2.39E30	-4.00	69050.	!fit	91HID/NAK +61
CF ₃ + F = CF ₄	3.60E15	-1.00	0.	!fit	86PLU/RVA-130

Fluoromethanes: Activated Decomposition

CH ₂ F + H = CH ₂ SING + HF	8.19E15	-0.63	505.	!RRKM	BAC -8
CH ₂ F + H = CHF + H ₂	5.21E08	1.16	1000.	!RRKM	BAC
CH ₂ SING + HF = CHF + H ₂	2.08E07	1.27	8330.	!RRKM	BAC -14
CHF ₂ + H = CHF + HF	1.49E14	-0.11	101.	!RRKM	BAC
CHF ₂ + H = CF ₂ + H ₂	5.50E03	2.42	-420.	!RRKM	BAC
CHF + HF = CF ₂ + H ₂	5.77E06	1.35	17900.	!RRKM	BAC
CF ₃ + H = CF ₂ + HF	5.50E13	0.00	0.	!RRKM	89TSA/MCF -46

Fluoromethanes: H Atom Abstraction by H, O, F, OH, HO2									
CH3F	+ H	= CH2F	+ H2	2.70E03	3.00	5300.	!fit	75WES/DEH	-6
CH2F2	+ H	= CHF2	+ H2	1.65E03	3.00	5600.	!fit	72RIN/DAV	-6
CHF3	+ H	= CF3	+ H2	1.70E04	3.00	8500.	!fit	78ART/BEL	
CH3F	+ O	= CH2F	+ OH	6.50E07	1.50	7000.	!fit	67PAR/AZA	
CH2F2	+ O	= CHF2	+ OH	2.25E07	1.50	6100.	!fit	68PAR/NAL	
CHF3	+ O	= CF3	+ OH	1.00E08	1.50	9250.	!fit	78JOU/LEB	
CH4	+ F	= CH3	+ HF	5.90E12	0.50	450.	!fit	71WAG/WAR	-31
CH3F	+ F	= CH2F	+ HF	1.35E14	0.00	1200.	!fit		-37
CH2F2	+ F	= CHF2	+ HF	9.00E13	0.00	1850.	!fit		-35
CHF3	+ F	= CF3	+ HF	4.50E13	0.00	3700.	!fit		-27
CH3F	+ OH	= CH2F	+ H2O	2.60E08	1.50	2940.	!	91COH/WES	-20
CH2F2	+ OH	= CHF2	+ H2O	2.80E07	1.70	2540.	!	91COH/WES	-10
CHF3	+ OH	= CF3	+ H2O	5.77E06	1.80	4292.	!	87COH/BEN	-10
CH2F	+ H2O2	= CH3F	+ HO2	1.20E10	0.00	-600.	!ref		-11
CHF2	+ H2O2	= CH2F2	+ HO2	1.20E10	0.00	-600.	!ref		-12
CF3	+ H2O2	= CHF3	+ HO2	1.20E10	0.00	-600.	!ref		-21
REACTION				A	b	E		note/reference	H
Fluoromethanes: H Atom Abstraction by CH3, C2H3, C2H5									
CH3F	+ CH3	= CH2F	+ CH4	1.50E11	0.00	11400.	!65PRI/BRY		-6
CH2F2	+ CH3	= CHF2	+ CH4	8.70E10	0.00	10200.	!65PRI/BRY	chk	-2
CF3	+ CH4	= CHF3	+ CH3	8.34E11	0.00	10920.	!78ART/BEL		-4
CH3F	+ C2H3	= CH2F	+ C2H4	1.50E11	0.00	10300.	!ref	E*0.90	-8
CH2F2	+ C2H3	= CHF2	+ C2H4	9.00E10	0.00	9200.	!ref	E*0.90	-6
CF3	+ C2H4	= CHF3	+ C2H3	8.00E11	0.00	12000.	!ref	E*1.1	-2
CH3F	+ C2H5	= CH2F	+ C2H6	1.50E11	0.00	16300.	!ref	E*1.43	0
CH2F2	+ C2H5	= CHF2	+ C2H6	9.00E10	0.00	14600.	!ref	E*1.43	+2
CF3	+ C2H6	= CHF3	+ C2H5	7.59E11	0.00	7980.	!78ART/BEL		-10
Fluoromethanes: H Atom Abstraction by Fluoromethyls									
CH3F	+ CF3	= CH2F	+ CHF3	1.35E12	0.00	11200.	!67GIL/QUI		-10
CH2F2	+ CH2F	= CHF2	+ CH3F	9.00E10	0.00	14000.	!ref	CH3 E*1.4	+1
CH2F2	+ CF3	= CHF2	+ CHF3	7.20E11	0.00	11200.	!67GIL/QUI		-8
Fluoromethanes: F Atom Abstraction									
CH3F	+ H	= CH3	+ HF	2.75E14	0.00	31400.	!BAC		-28
CH2F2	+ H	= CH2F	+ HF	5.50E13	0.00	34100.	!BAC		-16
CHF3	+ H	= CHF2	+ HF	8.00E13	0.00	40300.	!BAC		-4
CF4	+ H	= CF3	+ HF	1.10E15	0.00	44600.	!	71KOC/MOI	-4

Fluoromethyls: H Atom Abstraction from CH2O, CH3OH, HCO									
REACTION	A	b	E	note/reference	H				
CH2O + CH2F = HCO + CH3F	5.54E03	2.81	8300.	!ref	E*1.4 - 9				
CH2O + CHF2 = HCO + CH2F2	5.54E03	2.81	7800.	!ref	E*1.3 -10				
CH2O + CF3 = HCO + CHF3	5.54E03	2.81	4600.	!ref	E*.79 -19				
CH3OH + CH2F = CH3O + CH3F	1.44E01	3.10	9800.	!ref	E*1.4 + 5				
CH3OH + CHF2 = CH3O + CH2F2	1.44E01	3.10	9000.	!ref	E*1.3 + 4				
CH3OH + CF3 = CH3O + CHF3	1.44E01	3.10	5500.	!ref	E*.79 - 4				
CH3OH + CH2F = CH2OH + CH3F	3.20E01	3.20	10000.	!ref	E*1.4 - 3				
CH3OH + CHF2 = CH2OH + CH2F2	3.20E01	3.20	9300.	!ref	E*1.3 - 5				
CH3OH + CF3 = CH2OH + CHF3	3.20E01	3.20	5700.	!ref	E*.79 -13				
HCO + CH2F = CO + CH3F	0.90E14	0.00	0.	!ref					
HCO + CHF2 = CO + CH2F2	0.90E14	0.00	0.	!ref					
HCO + CF3 = CO + CHF3	0.90E14	0.00	0.	!ref	-91				
HCO + CH2F = CH2CO + HF	2.70E13	0.00	0.	!est					
HCO + CHF2 = CHF3CO + HF	2.70E13	0.00	0.	!est					
HCO + CF3 = CF2CO + HF	2.70E13	0.00	0.	!est					
Fluoromethyls: Oxidation									
CH2F + O2 =>CHF:O + O +H	2.26E09	1.14	19500.	!ref	cf3 +dH				
CHF2 + O2 =>CF2:O + O +H	2.26E09	1.14	20500.	!ref	cf3 +dH				
CF3 + O2 = CF3O + O	2.26E09	1.14	21500.	!RRKM					
CF3O + M = CF2:O + F	9.03E26	-3.42	21700.	!RRKM					
CH2F + O = CHF:O + H	5.70E13	0.00	0.	!ref	ch3 cf3 -90				
CHF2 + O = CF2:O + H	3.70E13	0.00	0.	!ref	ch3 cf3 -103				
CF3 + O = CF2:O + F	1.90E13	0.00	0.	!	89TSA/BEL -80				
CH2F + OH = CH2O + HF	2.50E13	0.00	0.	!ref	ch3 -95				
CHF2 + OH = CHF:O + HF	2.50E13	0.00	0.	!ref	ch3 -105				
CF3 + OH = CF2:O + HF	2.00E13	0.00	0.	!ref	ch3 -114				
CH2F + HO2 = CH3F + O2	3.00E12	0.00	0.	!ref	ch3 -48				
CHF2 + HO2 = CH2F2 + O2	3.00E12	0.00	0.	!ref	ch3 -50				
CF3 + HO2 = CHF3 + O2	2.00E12	0.00	0.	!ref	ch3				
CH2F + HO2 =>CHF:O + OH+ H	1.50E13	0.00	0.	!ref					
CHF2 + HO2 =>CF2:O + OH+ H	1.50E13	0.00	0.	!ref					
CF3 + HO2 = CF3O + OH	1.00E13	0.00	0.	!ref					
CF3O + M = CF2:O + F	9.03E26	-3.42	21700.	!wt k19					
CF3O + H = CF2:O + HF	1.00E14	0.00	0.	!nistk19					
CH3 + F = CH2SING + HF	1.62E16	-0.88	-981.	!ref	-17				
CH2F + F = CHF + HF	5.00E13	0.00	0.	!ref	-46				
CHF2 + F = CF2 + HF	3.00E13	0.00	0.	!ref	-68				
CH3 + F = CH2F + H	1.36E12	-0.39	-265.	!ref	- 9				
REACTION	A	b	E	note/reference	H				

Fluoromethylenes: Oxidation									
CHF	+ O2	= CHF:O	+ O	2.00E13	0.00	16500.	!ref	cf2 E-10	-60
CF2	+ O2	= CF2:O	+ O	2.00E13	0.00	26500.	!	77KEA/MAT	-50
CHF	+ O	= CO	+ HF	9.00E13	0.00	0.	!	90TSA/MCF-181	
CF2	+ O	= CF:O	+ F	5.00E13	0.00	0.	!ref	chf	-169
CHF	+ OH	= HCO	+ HF	5.00E12	0.00	0.	!ref	cf2	-94
CF2	+ OH	= CF:O	+ HF	5.00E12	0.00	0.	!ref	cf2	-71
CHF	+ OH	= CHF:O	+ H	5.00E12	0.00	0.	!ref	cf2	-77
CF2	+ OH	= CF2:O	+ H	5.00E12	0.00	0.	!fit	78BIO/LAZ	-68
Fluoromethylenes: Destruction									
CHF	+ H2O	= CH2F	+ OH	5.00E12	0.00	29000.	!est	Hrxn	+29
CF2	+ H2O	= CHF2	+ OH	5.00E12	0.00	51000.	!est	Hrxn	+51
CHF	+ H	= CH	+ HF	2.00E14	0.00	0.	!	89TSA/MCF	
CF2	+ H	= CF	+ HF	2.00E14	0.00	0.	!	89TSA/MCF	
CF4	+CH2SING	= CHF:CF2	+ HF	4.00E13	0.00	5000.	!ref	ch4	
CH4	+ CHF	= C2H4	+ HF	4.00E13	0.00	29000.	!BAC		
CH4	+ CF2	= CH2:CHF	+ HF	4.00E13	0.00	80000.	!BAC		
CHF	+ H2O	= CH2F	+ OH	5.00E12	0.00	29000.	!est dh		+29
CF2	+ H2O	= CHF2	+ OH	5.00E12	0.00	51000.	!est dh		+51
CH2O	+ CHF	= HCO	+ CH2F	1.00E13	0.00	29000.	!ref	CH4	
CH2O	+ CHF	= CH2CO	+ HF	1.00E13	0.00	29000.	!ref	CH4	
CH2O	+ CF2	= HCO	+ CHF2	1.00E13	0.00	80000.	!ref	CH4	+22
CH2O	+ CF2	= CHF:CO	+ HF	1.00E13	0.00	80000.	!ref	CH4	
HCO	+ CHF	= CO	+ CH2F	2.00E13	0.00	29000.	!ref	CH4	
HCO	+ CF2	= CO	+ CHF2	2.00E13	0.00	80000.	!ref	CH4	
Fluoromethylenes: Insertion into Fluoromethanes									
CH3F	+CH2SING	= C2H4	+ HF	4.00E13	0.00	0.	!ref		
CH2F2	+CH2SING	= CH2:CHF	+ HF	4.00E13	0.00	0.	!ref		
CHF3	+CH2SING	= CH2:CF2	+ HF	4.00E13	0.00	0.	!ref		
CF4	+CH2SING	= CHF:CF2	+ HF	4.00E13	0.00	5000.	!ref		
CH4	+ CHF	= C2H4	+ HF	4.00E13	0.00	29000.	!BAC		
CH3F	+ CHF	= CH2:CHF	+ HF	4.00E13	0.00	29000.	!ref	CH4	
CH2F2	+ CHF	= CH2:CF2	+ HF	2.00E13	0.00	29000.	!ref	CH4	
CH2F2	+ CHF	= CHF:CHF-Z	+HF	1.00E13	0.00	29000.	!ref	CH4	
CH2F2	+ CHF	= CHF:CHF-E	+HF	1.00E13	0.00	29000.	!ref	CH4	
CHF3	+ CHF	= CHF:CF2	+ HF	4.00E13	0.00	29000.	!ref	CH4	
CF4	+ CHF	= CF2:CF2	+ HF	4.00E13	0.00	29000.	!ref	CH4	
CH4	+ CF2	= CH2:CHF	+ HF	4.00E13	0.00	80000.	!BAC		
CH3F	+ CF2	= CH2:CF2	+ HF	2.00E13	0.00	80000.	!ref	CH4	
CH3F	+ CF2	= CHF:CHF-Z	+HF	1.00E13	0.00	80000.	!ref	CH4	
CH3F	+ CF2	= CHF:CHF-E	+HF	1.00E13	0.00	80000.	!ref	CH4	
CH2F2	+ CF2	= CHF:CF2	+ HF	4.00E13	0.00	80000.	!ref	CH4	
CHF3	+ CF2	= CF2:CF2	+ HF	4.00E13	0.00	80000.	!ref	CH4	
CF4	+ CF2	= CF3-CF3		4.00E13	0.00	80000.	!ref	CH4	

Fluoromethylenes: Insertion into Fluoromethyls										
CH2F	+	CH2	=	CH2:CHF	+	H	4.00E13	0.00	0.	!ref CH3
CH2F	+	CH2	=	C2H4	+	F	4.00E13	0.00	0.	!ref CH3
CHF2	+	CH2	=	CH2:CF2	+	H	4.00E13	0.00	0.	!ref CH3
CHF2	+	CH2	=	CH2:CHF	+	F	4.00E13	0.00	0.	!ref CH3
CF3	+	CH2	=	CH2:CF2	+	F	4.00E13	0.00	0.	!ref CH3
CH2F	+	CH2SING	=	CH2:CHF	+	H	4.00E12	0.00	0.	!ref CH3
CH2F	+	CH2SING	=	C2H4	+	F	2.00E12	0.00	0.	!ref CH3
CHF2	+	CH2SING	=	CH2:CF2	+	H	2.00E12	0.00	0.	!ref CH3
CHF2	+	CH2SING	=	CH2:CHF	+	F	4.00E12	0.00	0.	!ref CH3
CF3	+	CH2SING	=	CH2:CF2	+	F	6.00E12	0.00	0.	!ref CH3
CH3	+	CHF	=	CH2:CHF	+	H	1.00E12	0.00	2000.	!est -46
CH2F	+	CHF	=	CHF:CHF-Z	+	H	1.00E12	0.00	2000.	!est -46
CH2F	+	CHF	=	CHF:CHF-E	+	H	1.00E12	0.00	2000.	!est -46
CH2F	+	CHF	=	CH2:CHF	+	F	1.00E12	0.00	2000.	!est -37
CHF2	+	CHF	=	CHF:CF2	+	H	1.00E12	0.00	2000.	!est -42
CHF2	+	CHF	=	CHF:CHF-Z	+	F	1.00E12	0.00	2000.	!est -27
CHF2	+	CHF	=	CHF:CHF-E	+	F	1.00E12	0.00	2000.	!est -27
CF3	+	CHF	=	CHF:CF2	+	F	1.00E12	0.00	5000.	!est -20
CH3	+	CF2	=	CH2:CF2	+	H	1.10E11	0.00	5200.	!ref -21
CH2F	+	CF2	=	CHF:CF2	+	H	1.10E11	0.00	5200.	!ref -20
CH2F	+	CF2	=	CH2:CF2	+	F	1.10E11	0.00	5200.	!ref -12
CHF2	+	CF2	=	CF2:CF2	+	H	1.10E11	0.00	5200.	!ref -6
CHF2	+	CF2	=	CHF:CF2	+	F	1.10E11	0.00	5200.	!ref -1
Fluoromethylidyne: Oxidation										
CF	+	O2	=	CF:O	+	O	3.00E13	0.00	0.	!ref ch
CF	+	H2O	=>	CHF:O	+	H	3.00E13	0.00	0.	!ref ch
CF	+	O	=>	CO	+	F	7.00E12	0.00	0.	!fit
CF	+	OH	=>	CO	+	HF	3.00E13	0.00	0.	!est
CF	+	HO2	=>	CF:O	+	OH	1.00E13	0.00	0.	!est
Fluoromethylidyne: Destruction										
CH	+	HF	=	CF	+	H2	3.00E13	0.00	0.	!ref ch -17
CF	+	CH3	=>	CH2:CF	+	H	3.00E13	0.00	0.	!est
CF	+	C2H5	=>	CH2:CF	+	CH3	3.00E13	0.00	0.	!est
CF	+	C2H3	=>	C2HF	+	CH2	3.00E13	0.00	0.	!est
CF	+	CH2	=>	C2HF	+	H	3.00E13	0.00	0.	!est
CF	+	CH2SING	=>	C2HF	+	H	3.00E12	0.00	0.	!est
CF	+	CH4	=>	CH2:CHF	+	H	1.00E13	0.00	0.	!est
CF	+	C2H4	=>	C2H2	+	CH2F	1.00E13	0.00	0.	!est
CF	+	CH2O	=>	CHF	+	HCO	1.00E13	0.00	8000.	!est + 7
CF	+	HCO	=>	CHF	+	CO	1.00E13	0.00	0.	!est
CF	+	F	=	CF2			6.00E13	0.00	0.	!fit

Carbonyl Fluorides: CHF=O, CF2=O

CHF:O	+ M	= CO	+ HF	2.48E25	-3.00	43000.	!fit	85SAI/KUR	
CF2:O	+ H2O	=>CO2	+2HF	3.92E00	3.08	27600.	!BAC		
CF2:O	+ H	= CF:O	+ HF	2.91E13	-0.03	32910.	!QRRK	BAC Oadd	
CF2:O	+ H	= CF:O	+ HF	1.02E02	2.89	32980.	!QRRK	BAC Cadd	
CHF:O	+ H	= HCO	+ HF	2.91E13	-0.03	32910.	!ref	cf2o Oadd	
CHF:O	+ H	= HCO	+ HF	1.02E02	2.89	32980.	!ref	cf2o Cadd	
CHF:O	+ H	= CF:O	+ H2	1.10E08	1.77	3000.	!ref/2		- 4
CHF:O	+ O	= CF:O	+ OH	9.00E12	0.00	3080.	!ref	ch2o	-2
CHF:O	+ OH	= CF:O	+ H2O	1.72E09	1.18	-447.	!ref	ch2o	-18
CF:O	+ H2O2	= CHF:O	+ HO2	1.00E11	0.00	3900.	!ref	E*0.56	-13
CHF:O	+ CH3	= CF:O	+ CH4	2.00E12	0.00	9000.	!ref	uplim	- 5
CHF:O	+ CH2F	= CF:O	+ CH3F	2.00E12	0.00	9000.	!ref	uplim	+ 1
CHF:O	+ CHF2	= CF:O	+ CH2F2	2.00E12	0.00	9000.	!ref		0
CHF:O	+ CF3	= CF:O	+ CHF3	2.00E12	0.00	9000.	!ref		- 8
CHF:O	+ C2H3	= CF:O	+ C2H4	2.00E12	0.00	5000.	!ref	E*0.9	
CHF:O	+ C2H5	= CF:O	+ C2H6	2.00E12	0.00	13000.	!ref	E*1.43	

Carbonyl Fluorides: CF=O

CF:O	+ M	= CO	+ F	1.89E18	-0.865	39000.	!RRKM		+32
CF:O	+ H	= CO	+ HF	1.20E14	0.00	0.	!ref	hco	
CF:O	+ O	= CO2	+ F	3.00E13	0.00	0.	!ref	hco	
CF:O	+ OH	= CO2	+ HF	3.00E13	0.00	0.	!ref	hco	
CF:O	+ HO2	=>CO2	+ F+OH	3.00E13	0.00	0.	!ref		
CF:O	+ CH3	= CO	+ CH3F	1.00E13	0.00	0.	!est		
CF:O	+ CH3	= CH2CO	+ HF	2.70E13	0.00	0.	!est		
CF:O	+ F	= CF2:O		1.00E12	0.00	0.	!wtsang1		-131
CF:O	+ O2	=>CO2	+ F + O	2.00E13	0.00	24000.	!nist k20		+24
CF:O	+ CH2F	= CO	+ CH2F2	1.00E13	0.00	0.	!est, k19		
CF:O	+ CHF2	= CO	+ CHF3	1.00E13	0.00	0.	!est, k19		
CF:O	+ CF3	= CO	+ CF4	1.00E13	0.00	0.	!est, k19		
CF:O	+ CH2F	= CHF:O	+ HF	2.70E13	0.00	0.	!est, k19		
CF:O	+ CHF2	= CF2:O	+ HF	2.70E13	0.00	0.	!est, k19		
CF:O	+ CF:O	= CO	+ CF2:O	2.23E13	0.00	318.	!92MAR/SZE2		

Fluoroethanes: Thermal Decomposition

CH3-CH2F	= C2H4	+ HF	2.00E13	0.00	58800.	!	70CAD/DAY	+11
CH3-CHF2	= CH2:CHF	+ HF	7.94E13	0.00	61900.	!	70TSC/QUI	+22
CH3-CF3	= CH2:CF2	+ HF	1.00E14	0.00	69000.	!	71TSC/QUI	
CH2F-CH2F	= CH2:CHF	+ HF	2.50E13	0.00	61800.	!	71KER/TIM	+ 5
CH2F-CHF2	= CHF:CHF-Z	+ HF	1.20E14	0.00	69600.	!	74SEK/TSC	
CH2F-CHF2	= CHF:CHF-E	+ HF	3.00E13	0.00	65800.	!	74SEK/TSC	
CH2F-CHF2	= CH2:CF2	+ HF	1.00E13	0.00	65800.	!	74SEK/TSC	+ 8
CH2F-CF3	= CHF:CF2	+ HF	2.50E13	0.00	63200.	!	72MIL/TSC	+37
CHF2-CHF2	= CHF:CF2	+ HF	2.00E13	0.00	70000.	!	71MIL/HAR	+32
CHF2-CF3	= CF2:CF2	+ HF	4.00E13	0.00	72000.	!	71TSC/MIL	+41

Fluoroethanes: Activated Decomposition, Ethyl + H (HF elimination)							
CH2F-CH2 + H = C2H4 + HF	1.44E20	-2.12	1730.	!RRKM			
CH3-CHF + H = C2H4 + HF	2.27E20	-2.21	1950.	!RRKM			
CH2F-CHF + H = CH2:CHF + HF	2.06E23	-3.23	2280.	!RRKM			
CHF2-CH2 + H = CH2:CHF + HF	5.24E16	-0.933	880.	!RRKM			
CH3-CF2 + H = CH2:CHF + HF	2.09E16	-0.854	848.	!RRKM			
CHF2-CHF + H = CHF:CHF-Z+ HF	1.86E20	-2.29	1750.	!RRKM			
CHF2-CHF + H = CHF:CHF-E+ HF	1.07E19	-1.84	1520.	!RRKM			
CHF2-CHF + H = CH2:CF2 + HF	9.95E19	-2.34	1780.	!RRKM			
CH2F-CF2 + H = CHF:CHF-Z+ HF	6.32E19	-2.21	1630.	!RRKM			
CH2F-CF2 + H = CHF:CHF-E+ HF	3.95E18	-1.77	1390.	!RRKM			
CH2F-CF2 + H = CH2:CF2 + HF	3.36E19	-2.26	1660.	!RRKM			
CF3-CH2 + H = CH2:CF2 + HF	1.12E21	-2.27	2240.	!RRKM			
CHF2-CF2 + H = CHF:CF2 + HF	1.81E22	-2.92	3070.	!RRKM			
CF3-CF2 + H = CF2:CF2 + HF	1.41E21	-2.40	3630.	!RRKM			
Fluoroethanes: Activated Decomposition, Ethyl + H (methyl formation)							
CH2F-CH2 + H = CH3 + CH2F	3.80E11	0.635	633.	!RRKM			
CH3-CHF + H = CH3 + CH2F	3.47E10	0.90	1370.	!RRKM			
CH2F-CHF + H = CH2F + CH2F	1.79E14	-0.105	1320.	!RRKM			
CHF2-CH2 + H = CH3 + CHF2	2.02E06	2.16	451.	!RRKM			
CH3-CF2 + H = CH3 + CHF2	1.62E05	2.50	1370.	!RRKM			
CHF2-CHF + H = CH2F + CHF2	6.36E12	0.318	1460.	!RRKM			
CH2F-CF2 + H = CH2F + CHF2	3.64E12	0.329	1180.	!RRKM			
CF3-CH2 + H = CH3 + CF3	2.48E11	0.816	2870.	!RRKM			
CHF2-CF2 + H = CHF2 + CHF2	3.25E15	-0.524	3000.	!RRKM			
CF3-CF2 + H = CHF2 + CF3	4.37E16	-0.746	4360.	!RRKM			
Fluoroethanes: Activated Decomposition, Ethyl + H (stabilization)							
CH2F-CH2 + H = CH3-CH2F	1.19E35	-8.51	8140.	!RRKM			
CH3-CHF + H = CH3-CH2F	9.57E38	-9.24	7360.	!RRKM			
CH2F-CHF + H = CH2F-CH2F	1.56E45	-10.80	8070.	!RRKM			
CHF2-CH2 + H = CH3-CHF2	2.96E37	-9.05	7160.	!RRKM			
CH3-CF2 + H = CH3-CHF2	3.11E40	-9.59	7190.	!RRKM			
CHF2-CHF + H = CH2F-CHF2	1.20E44	-10.60	7520.	!RRKM			
CH2F-CF2 + H = CH2F-CHF2	2.74E43	-10.50	7670.	!RRKM			
CF3-CH2 + H = CH3-CF3	7.27E42	-9.86	7360.	!RRKM			
CHF2-CF2 + H = CHF2-CHF2	3.77E46	-10.80	8980.	!RRKM			
CF3-CF2 + H = CHF2-CF3	1.12E47	-10.80	4100.	!RRKM			
Fluoroethanes: Activated Decomposition, Ethyl + H (H atom elimination)							
CH2F-CH2 + H = CH3-CHF + H	1.87E01	3.10	137.	!RRKM			
CHF2-CH2 + H = CHF2-CH2 + H	1.59E-3	4.35	157.	!RRKM			
CH2F-CF2 + H = CHF2-CHF + H	0.64E00	3.53	1830.	!RRKM			
Fluoroethanes: Activated Decomposition, Methyl + Methyl (HF elimination)							
CH3 + CH2F = C2H4 + HF	2.35E19	-1.86	1870.	!RRKM			
CH2F + CH2F = CH2:CHF + HF	7.56E21	-2.79	2590.	!RRKM			
CH3 + CHF2 = CH2:CHF + HF	1.90E15	-0.586	634.	!RRKM			
CH2F + CHF2 = CHF:CHF-Z+ HF	3.88E20	-2.35	2888.	!RRKM			
CH2F + CHF2 = CHF:CHF-E+ HF	1.09E19	-1.83	2670.	!RRKM			
CH2F + CHF2 = CH2:CF2 + HF	2.23E20	-2.41	2910.	!RRKM			
CH3 + CF3 = CH2:CF2 + HF	5.53E19	-1.94	2440.	!RRKM			
CHF2 + CHF2 = CHF:CF2 + HF	2.20E19	-1.95	4100.	!RRKM			
CHF2 + CF3 = CF2:CF2 + HF	7.00E16	-1.17	4330.	!RRKM			

Fluoroethanes: Activated Decomposition, Methyl + Methyl (stablization)									
CH3	+	CH2F	=	CH3-CH2F	1.57E31	-6.27	4440.	!RRKM	
CH2F	+	CH2F	=	CH2F-CH2F	2.37E24	-3.79	2290.	!RRKM	
CH3	+	CHF2	=	CH3-CHF2	1.93E35	-7.69	5760.	!RRKM	
CH2F	+	CHF2	=	CH2F-CHF2	9.61E38	-8.36	6940.	!RRKM	
CH3	+	CF3	=	CH3-CF3	1.78E33	-6.64	5020.	!RRKM	
CHF2	+	CHF2	=	CHF2-CHF2	2.26E24	-3.50	3360.	!RRKM	
CHF2	+	CF3	=	CHF2-CF3	2.61E26	-4.16	4100.	!RRKM	
CF3	+	CF3	=	CF3-CF3	1.63E36	-7.26	7050.	!RRKM	
Fluoroethanes: H Atom Abstraction by H, O, OH									
CH3-CH2F	+	H	=	CH2F-CH2	+ H2	5.50E08	1.60	9100.	!ref 10AE+8 +2
CH3-CH2F	+	O	=	CH2F-CH2	+ OH	2.90E08	1.60	6100.	!ref 5AE+5 +3
CH3-CH2F	+	OH	=	CH2F-CH2	+ H2O	5.50E07	1.60	1093.	!ref -13
CH3-CH2F	+	H	=	CH3-CHF	+ H2	3.30E08	1.60	9100.	!ref 10AE+8
CH3-CH2F	+	O	=	CH3-CHF	+ OH	1.60E08	1.60	6100.	!ref 5AE+5
CH3-CH2F	+	OH	=	CH3-CHF	+ H2O	3.30E07	1.60	1093.	!ref
CH3-CHF2	+	H	=	CHF2-CH2	+ H2	1.50E08	1.60	9600.	!ref 10A E+8
CH3-CHF2	+	O	=	CHF2-CH2	+ OH	7.50E08	1.60	6600.	!ref A*5 E+5
CH3-CHF2	+	OH	=	CHF2-CH2	+ H2O	1.54E07	1.60	1132.	!ref
CH3-CHF2	+	H	=	CH3-CF2	+ H2	0.44E08	1.60	9300.	!ref A*10 E+8
CH3-CHF2	+	O	=	CH3-CF2	+ OH	2.20E07	1.60	6300.	!ref A*5 E+5
CH3-CHF2	+	OH	=	CH3-CF2	+ H2O	0.44E07	1.60	1332.	!ref
CH3-CF3	+	H	=	CF3-CH2	+ H2	4.00E10	1.10	12700.	!ref A*10E+8 + 3
CH3-CF3	+	O	=	CF3-CH2	+ OH	2.00E10	1.10	9700.	!ref A*5E+5 + 4
CH3-CF3	+	OH	=	CF3-CH2	+ H2O	4.08E09	1.10	4670.	!87COH/BEN -12
CH2F-CH2F	+	H	=	CH2F-CHF	+ H2	6.00E08	1.70	9600.	!ref A*10 E+8 -11
CH2F-CH2F	+	O	=	CH2F-CHF	+ OH	3.00E08	1.70	6600.	!ref A*5 E+5 -10
CH2F-CH2F	+	OH	=	CH2F-CHF	+ H2O	6.16E07	1.70	1610.	!87COH/BEN -26
CH2F-CHF2	+	H	=	CHF2-CHF	+ H2	2.00E08	1.70	9800.	!ref A*10 E+8
CH2F-CHF2	+	O	=	CHF2-CHF	+ OH	1.00E08	1.70	6800.	!ref A*5 E+5
CH2F-CHF2	+	OH	=	CHF2-CHF	+ H2O	2.05E07	1.70	1800.	!ref
CH2F-CHF2	+	H	=	CH2F-CF2	+ H2	1.00E08	1.70	11000.	!ref A*10 E+8
CH2F-CHF2	+	O	=	CH2F-CF2	+ OH	5.00E07	1.70	8000.	!ref A*5 E+5
CH2F-CHF2	+	OH	=	CH2F-CF2	+ H2O	1.06E07	1.70	3000.	!ref
CH2F-CF3	+	H	=	CF3-CHF	+ H2	2.00E08	1.70	10500.	!ref A*10 E+8 - 2
CH2F-CF3	+	O	=	CF3-CHF	+ OH	1.00E08	1.70	7500.	!ref A*5 E+5 - 1
CH2F-CF3	+	OH	=	CF3-CHF	+ H2O	2.10E07	1.70	2524.	!87COH/BEN -17
CHF2-CHF2	+	H	=	CHF2-CF2	+ H2	1.60E07	1.70	10600.	!ref A*10 E+8
CHF2-CHF2	+	O	=	CHF2-CF2	+ OH	8.00E07	1.70	7600.	!ref A*5 E+5
CHF2-CHF2	+	OH	=	CHF2-CF2	+ H2O	1.60E07	1.70	2643.	!87COH/BEN
CHF2-CF3	+	H	=	CF3-CF2	+ H2	1.40E07	1.60	10200.	!ref A*10 E+8 + 0
CHF2-CF3	+	O	=	CF3-CF2	+ OH	7.00E07	1.60	7200.	!ref A*5 E+5 + 1
CHF2-CF3	+	OH	=	CF3-CF2	+ H2O	1.40E07	1.60	2246.	!87COH/BEN -15
!*** NOTE F ATOM ABSTRACTION ***									
CF3-CF3	+	H	=	CF3-CF2	+ HF	1.00E15	0.00	30000.	!ref CF4

Fluoroethanes: H Atom Abstraction by F

C2H6	+ F	= C2H5	+ HF	8.00E12	0.00	300.	!60FET/KNO2	-36
CH3-CH2F	+ F	= CH2F-CH2	+ HF	9.00E13	0.00	800.	!ref	
CH3-CHF2	+ F	= CHF2-CH2	+ HF	1.00E14	0.00	800.	!ref	
CH3-CF3	+ F	= CF3-CH2	+ HF	1.00E14	0.00	4000.	!ref	
CH3-CH2F	+ F	= CH3-CHF	+ HF	6.00E13	0.00	200.	!ref	
CH2F-CH2F	+ F	= CH2F-CHF	+ HF	1.30E14	0.00	800.	!ref	
CH2F-CHF2	+ F	= CHF2-CHF	+ HF	1.30E14	0.00	800.	!ref	
CH2F-CF3	+ F	= CF3-CHF	+ HF	6.00E13	0.00	1200.	!ref	
CH3-CHF2	+ F	= CH3-CF2	+ HF	3.00E13	0.00	800.	!ref	
CH2F-CHF2	+ F	= CH2F-CF2	+ HF	3.00E13	0.00	1200.	!ref	
CHF2-CHF2	+ F	= CHF2-CF2	+ HF	6.00E13	0.00	1200.	!ref	
CHF2-CF3	+ F	= CF3-CF2	+ HF	4.00E13	0.00	1400.	!ref	-33

Fluoroethanes: Association with HO2

CH3-CHF	+ H2O2	= CH3-CH2F	+ HO2	9.00E09	0.00	1000.	!ref
CH3-CF2	+ H2O2	= CH3-CHF2	+ HO2	9.00E09	0.00	1000.	!ref
CH2F-CH2	+ H2O2	= CH3-CH2F	+ HO2	9.00E09	0.00	1000.	!ref
CH2F-CHF	+ H2O2	= CH2F-CH2F	+ HO2	9.00E09	0.00	1000.	!ref
CH2F-CF2	+ H2O2	= CH2F-CHF2	+ HO2	9.00E09	0.00	1000.	!ref
CHF2-CH2	+ H2O2	= CH3-CHF2	+ HO2	9.00E09	0.00	1000.	!ref
CHF2-CHF	+ H2O2	= CH2F-CHF2	+ HO2	9.00E09	0.00	1000.	!ref
CHF2-CF2	+ H2O2	= CHF2-CHF2	+ HO2	9.00E09	0.00	1000.	!ref
CF3-CH2	+ H2O2	= CH3-CF3	+ HO2	9.00E09	0.00	1000.	!ref
CF3-CHF	+ H2O2	= CH2F-CF3	+ HO2	9.00E09	0.00	1000.	!ref
CF3-CF2	+ H2O2	= CHF2-CF3	+ HO2	9.00E09	0.00	1000.	!ref

Fluoroethanes: H Atom Abstraction by CH₃, C₂H₅, C₂H₃

CH ₃ -CH ₂ F	+	CH ₃	=	CH ₂ F-CH ₂	+	CH ₄	2.00E11	0.00	13400.	!ref		+ 1
CH ₃ -CH ₂ F	+	C ₂ H ₅	=	CH ₂ F-CH ₂	+	C ₂ H ₆	2.00E11	0.00	16000.	!ref	CH ₃ +3	+ 6
CH ₃ -CH ₂ F	+	C ₂ H ₃	=	CH ₂ F-CH ₂	+	C ₂ H ₄	2.00E11	0.00	10000.	!ref	CH ₃ -3	+ 4
CH ₃ -CH ₂ F	+	CH ₃	=	CH ₃ -CHF	+	CH ₄	1.50E11	0.00	10000.	!ref		
CH ₃ -CH ₂ F	+	C ₂ H ₅	=	CH ₃ -CHF	+	C ₂ H ₆	1.50E11	0.00	13000.	!ref	CH ₃ +3	
CH ₃ -CH ₂ F	+	C ₂ H ₃	=	CH ₃ -CHF	+	C ₂ H ₄	1.50E11	0.00	7000.	!ref	CH ₃ -3	
CH ₃ -CHF ₂	+	CH ₃	=	CHF ₂ -CH ₂	+	CH ₄	2.00E11	0.00	12000.	!ref		
CH ₃ -CHF ₂	+	C ₂ H ₅	=	CHF ₂ -CH ₂	+	C ₂ H ₆	2.00E11	0.00	15000.	!ref	CH ₃ +3	
CH ₃ -CHF ₂	+	C ₂ H ₃	=	CHF ₂ -CH ₂	+	C ₂ H ₄	2.00E11	0.00	9000.	!ref	CH ₃ -3	
CH ₃ -CHF ₂	+	CH ₃	=	CH ₃ -CF ₂	+	CH ₄	8.00E10	0.00	10000.	!ref		
CH ₃ -CHF ₂	+	C ₂ H ₃	=	CH ₃ -CF ₂	+	C ₂ H ₄	8.00E10	0.00	7000.	!ref	CH ₃ -3	
CH ₃ -CHF ₂	+	C ₂ H ₅	=	CH ₃ -CF ₂	+	C ₂ H ₆	8.00E10	0.00	13000.	!ref	CH ₃ +3	
CH ₃ -CF ₃	+	CH ₃	=	CF ₃ -CH ₂	+	CH ₄	2.00E11	0.00	12000.	!ref		+ 2
CH ₃ -CF ₃	+	C ₂ H ₃	=	CF ₃ -CH ₂	+	C ₂ H ₄	2.00E11	0.00	9000.	!ref	CH ₃ -3	+ 5
CH ₃ -CF ₃	+	C ₂ H ₅	=	CF ₃ -CH ₂	+	C ₂ H ₆	2.00E11	0.00	15000.	!ref	CH ₃ +3	+ 7
CH ₂ F-CH ₂ F	+	CH ₃	=	CH ₂ F-CHF	+	CH ₄	3.00E11	0.00	10400.	!ref		-12
CH ₂ F-CH ₂ F	+	C ₂ H ₃	=	CH ₂ F-CHF	+	C ₂ H ₄	3.00E11	0.00	7000.	!ref	CH ₃ -3	- 9
CH ₂ F-CH ₂ F	+	C ₂ H ₅	=	CH ₂ F-CHF	+	C ₂ H ₆	3.00E11	0.00	13000.	!ref	CH ₃ +3	- 7
CH ₂ F-CHF ₂	+	CH ₃	=	CHF ₂ -CHF	+	CH ₄	2.00E11	0.00	10000.	!ref		
CH ₂ F-CHF ₂	+	C ₂ H ₃	=	CHF ₂ -CHF	+	C ₂ H ₄	2.00E11	0.00	7000.	!ref	CH ₃ -3	
CH ₂ F-CHF ₂	+	C ₂ H ₅	=	CHF ₂ -CHF	+	C ₂ H ₆	2.00E11	0.00	13000.	!ref	CH ₃ +3	
CH ₂ F-CHF ₂	+	CH ₃	=	CH ₂ F-CF ₂	+	CH ₄	1.00E11	0.00	9600.	!ref		
CH ₂ F-CHF ₂	+	C ₂ H ₃	=	CH ₂ F-CF ₂	+	C ₂ H ₄	1.00E11	0.00	7000.	!ref	CH ₃ -3	
CH ₂ F-CHF ₂	+	C ₂ H ₅	=	CH ₂ F-CF ₂	+	C ₂ H ₆	1.00E11	0.00	13000.	!ref	CH ₃ +3	
CH ₂ F-CF ₃	+	CH ₃	=	CF ₃ -CHF	+	CH ₄	2.00E11	0.00	10000.	!ref		- 3
CH ₂ F-CF ₃	+	C ₂ H ₃	=	CF ₃ -CHF	+	C ₂ H ₄	2.00E11	0.00	7000.	!ref	CH ₃ -3	+ 0
CH ₂ F-CF ₃	+	C ₂ H ₅	=	CF ₃ -CHF	+	C ₂ H ₆	2.00E11	0.00	13000.	!ref	CH ₃ +3	+ 2
CHF ₂ -CHF ₂	+	CH ₃	=	CHF ₂ -CF ₂	+	CH ₄	3.00E11	0.00	10000.	!ref		
CHF ₂ -CHF ₂	+	C ₂ H ₃	=	CHF ₂ -CF ₂	+	C ₂ H ₄	3.00E11	0.00	7000.	!ref	CH ₃ -3	
CHF ₂ -CHF ₂	+	C ₂ H ₅	=	CHF ₂ -CF ₂	+	C ₂ H ₆	3.00E11	0.00	13000.	!ref	CH ₃ +3	
CHF ₂ -CF ₃	+	CH ₃	=	CF ₃ -CF ₂	+	CH ₄	5.70E10	0.00	9500.	!64PRI/THO		- 1
CHF ₂ -CF ₃	+	C ₂ H ₃	=	CF ₃ -CF ₂	+	C ₂ H ₄	6.00E10	0.00	7000.	!ref	CH ₃ -3	+ 2
CHF ₂ -CF ₃	+	C ₂ H ₅	=	CF ₃ -CF ₂	+	C ₂ H ₆	6.00E10	0.00	13000.	!ref	CH ₃ +3	+ 4

Fluoroethanes: H Atom Abstraction by Fluoromethyls											
CH3-CH2F	+	CH2F	=	CH2F-CH2	+	CH3F	2.00E11	0.00	13000.	!ref CH3	+ 6
CH3-CH2F	+	CH2F	=	CH3-CHF	+	CH3F	1.50E11	0.00	10000.	!ref CH3	
CH3-CHF2	+	CH2F	=	CHF2-CH2	+	CH3F	2.00E11	0.00	12000.	!ref CH3	
CH3-CHF2	+	CH2F	=	CH3-CF2	+	CH3F	8.00E10	0.00	10000.	!ref CH3	
CH3-CF3	+	CH2F	=	CF3-CH2	+	CH3F	2.00E11	0.00	12000.	!ref CH3	+ 7
CH2F-CH2F	+	CH2F	=	CH2F-CHF	+	CH3F	3.00E11	0.00	10000.	!ref CH3	- 7
CH2F-CHF2	+	CH2F	=	CHF2-CHF	+	CH3F	2.00E11	0.00	10000.	!ref CH3	
CH2F-CHF2	+	CH2F	=	CH2F-CF2	+	CH3F	1.00E11	0.00	10000.	!ref CH3	
CH2F-CF3	+	CH2F	=	CF3-CHF	+	CH3F	2.00E11	0.00	10000.	!ref CH3	+ 2
CHF2-CHF2	+	CH2F	=	CHF2-CF2	+	CH3F	3.00E11	0.00	11000.	!ref CH3	+10
CHF2-CF3	+	CH2F	=	CF3-CF2	+	CH3F	2.00E11	0.00	10000.	!ref CH3	+ 4
CH3-CH2F	+	CHF2	=	CH2F-CH2	+	CH2F2	2.00E11	0.00	13000.	!ref CH3	
CH3-CH2F	+	CHF2	=	CH3-CHF	+	CH2F2	1.50E11	0.00	10000.	!ref CH3	
CH3-CHF2	+	CHF2	=	CHF2-CH2	+	CH2F2	2.00E11	0.00	12000.	!ref CH3	
CH3-CHF2	+	CHF2	=	CH3-CF2	+	CH2F2	8.00E10	0.00	10000.	!ref CH3	
CH3-CF3	+	CHF2	=	CF3-CH2	+	CH2F2	2.00E11	0.00	12000.	!ref CH3	
CH2F-CH2F	+	CHF2	=	CH2F-CHF	+	CH2F2	3.00E11	0.00	10000.	!ref CH3	
CH2F-CHF2	+	CHF2	=	CHF2-CHF	+	CH2F2	2.00E11	0.00	10000.	!ref CH3	
CH2F-CHF2	+	CHF2	=	CH2F-CF2	+	CH2F2	1.00E11	0.00	10000.	!ref CH3	
CH2F-CF3	+	CHF2	=	CF3-CHF	+	CH2F2	2.00E11	0.00	10000.	!ref CH3	
CHF2-CHF2	+	CHF2	=	CHF2-CF2	+	CH2F2	3.00E11	0.00	10000.	!ref CH3	
CHF2-CF3	+	CHF2	=	CF3-CF2	+	CH2F2	2.00E11	0.00	10000.	!ref CH3	
CH3-CH2F	+	CF3	=	CH2F-CH2	+	CHF3	9.50E11	0.00	8200.	!71QUI/WHI	
CH3-CH2F	+	CF3	=	CH3-CHF	+	CHF3	9.50E11	0.00	8200.	!71QUI/WHI	
CH3-CHF2	+	CF3	=	CHF2-CH2	+	CHF3	3.10E10	0.00	7100.	!66OKS/PRA	
CH3-CHF2	+	CF3	=	CH3-CF2	+	CHF3	3.10E10	0.00	7100.	!66OKS/PRA	
CH3-CF3	+	CF3	=	CF3-CH2	+	CHF3	1.45E12	0.00	13500.	!67GIL/QUI	
CH2F-CH2F	+	CF3	=	CH2F-CHF	+	CHF3	5.00E11	0.00	7600.	!ref	
CH2F-CHF2	+	CF3	=	CHF2-CHF	+	CHF3	3.00E11	0.00	7200.	!ref	
CH2F-CHF2	+	CF3	=	CH2F-CF2	+	CHF3	2.00E11	0.00	8000.	!ref	
CH2F-CF3	+	CF3	=	CF3-CHF	+	CHF3	3.00E11	0.00	6400.	!ref	
CHF2-CHF2	+	CF3	=	CHF2-CF2	+	CHF3	5.70E11	0.00	11900.	!67GIL/QUI	
CHF2-CF3	+	CF3	=	CF3-CF2	+	CHF3	1.40E11	0.00	10100.	!67GIL/QUI	
Fluoroethanes: H Atom Abstraction by HCO											
CH3-CHF	+	CH2O	=	CH3-CH2F	+	HCO	5.50E03	2.80	5900.	!ref	
CH3-CF2	+	CH2O	=	CH3-CHF2	+	HCO	5.50E03	2.80	5900.	!ref	
CH2F-CH2	+	CH2O	=	CH3-CH2F	+	HCO	5.50E03	2.80	5900.	!ref	
CH2F-CHF	+	CH2O	=	CH2F-CH2F	+	HCO	5.50E03	2.80	5900.	!ref	
CH2F-CF2	+	CH2O	=	CH2F-CHF2	+	HCO	5.50E03	2.80	5900.	!ref	
CHF2-CH2	+	CH2O	=	CH3-CHF2	+	HCO	5.50E03	2.80	5900.	!ref	
CHF2-CHF	+	CH2O	=	CH2F-CHF2	+	HCO	5.50E03	2.80	5900.	!ref	
CHF2-CF2	+	CH2O	=	CHF2-CHF2	+	HCO	5.50E03	2.80	5900.	!ref	
CF3-CH2	+	CH2O	=	CH3-CF3	+	HCO	5.50E03	2.80	5900.	!ref	
CF3-CHF	+	CH2O	=	CH2F-CF3	+	HCO	5.50E03	2.80	5900.	!ref	
CF3-CF2	+	CH2O	=	CHF2-CF3	+	HCO	5.50E03	2.80	5900.	!ref	

Fluoroethyls: Association with O₂

CH ₃ -CHF	+ O ₂	= CH ₂ :CHF	+ HO ₂	2.56E19	-2.77	1977.	!ref
CH ₃ -CF ₂	+ O ₂	= CH ₂ :CF ₂	+ HO ₂	2.56E19	-2.77	1977.	!ref
CH ₂ F-CH ₂	+ O ₂	= CH ₂ :CHF	+ HO ₂	2.56E19	-2.77	1977.	!ref
CH ₂ F-CHF	+ O ₂	= CHF:CHF-E	+HO ₂	1.28E19	-2.77	1977.	!ref
CH ₂ F-CHF	+ O ₂	= CHF:CHF-Z	+HO ₂	1.28E19	-2.77	1977.	!ref
CH ₂ F-CF ₂	+ O ₂	= CHF:CF ₂	+ HO ₂	2.56E19	-2.77	1977.	!ref
CHF ₂ -CH ₂	+ O ₂	= CH ₂ :CF ₂	+ HO ₂	2.56E19	-2.77	1977.	!ref
CHF ₂ -CHF	+ O ₂	= CHF:CF ₂	+ HO ₂	2.56E19	-2.77	1977.	!ref
CHF ₂ -CF ₂	+ O ₂	= CF ₂ :CF ₂	+ HO ₂	2.56E19	-2.77	1977.	!ref
CF ₃ -CH ₂	+ O ₂	=>CF ₃	+ CH ₂ O + O	1.30E13	0.00	44000.	!ref CF ₃ +dH
CF ₃ -CHF	+ O ₂	=>CF ₃	+ CHF:O+ O	1.30E13	0.00	23000.	!ref CF ₃
CF ₃ -CF ₂	+ O ₂	=>CF ₃	+ CF ₂ :O+ O	1.30E13	0.00	23000.	!ref CF ₃

Fluoroethyls: Association with O

CH ₂ F-CH ₂	+ O	= CH ₂ O	+ CH ₂ F	6.60E13	0.00	0.	!ref
CHF ₂ -CH ₂	+ O	= CH ₂ O	+ CHF ₂	6.60E13	0.00	0.	!ref
CF ₃ -CH ₂	+ O	= CH ₂ O	+ CF ₃	6.60E13	0.00	0.	!ref
CH ₃ -CHF	+ O	= CHF:O	+ CH ₃	4.40E13	0.00	0.	!ref
CH ₂ F-CHF	+ O	= CHF:O	+ CH ₂ F	4.40E13	0.00	0.	!ref
CHF ₂ -CHF	+ O	= CHF:O	+ CHF ₂	4.40E13	0.00	0.	!ref
CF ₃ -CHF	+ O	= CHF:O	+ CF ₃	4.40E13	0.00	0.	!ref
CH ₃ -CF ₂	+ O	= CF ₂ :O	+ CH ₃	2.20E13	0.00	0.	!ref
CH ₂ F-CF ₂	+ O	= CF ₂ :O	+ CH ₂ F	2.20E13	0.00	0.	!ref
CHF ₂ -CF ₂	+ O	= CF ₂ :O	+ CHF ₂	2.20E13	0.00	0.	!ref
CF ₃ -CF ₂	+ O	= CF ₂ :O	+ CF ₃	2.20E13	0.00	0.	!ref

Fluoroethyls: Association with HO2

CH3-CHF	+	HO2	=>CH3+CHF:O+OH	3.00E13	0.00	0.	!ref
CH3-CF2	+	HO2	=>CH3+CF2:O+OH	3.00E13	0.00	0.	!ref
CH2F-CH2	+	HO2	=>CH2F+CH2O+ OH	3.00E13	0.	0.	!ref
CH2F-CHF	+	HO2	=>CH2F+CHF:O+OH	3.00E13	0.	0.	!ref
CH2F-CF2	+	HO2	=>CH2F+CF2:O+OH	3.00E13	0.	0.	!ref
CHF2-CH2	+	HO2	=>CHF2+CH2O+ OH	3.00E13	0.	0.	!ref
CHF2-CHF	+	HO2	=>CHF2+CHF:O+OH	3.00E13	0.	0.	!ref
CHF2-CF2	+	HO2	=>CHF2+CF2:O+OH	3.00E13	0.	0.	!ref
CF3-CH2	+	HO2	=>CF3 +CH2O+ OH	3.00E13	0.	0.	!ref
CF3-CHF	+	HO2	=>CF3 +CHF:O+OH	3.00E13	0.	0.	!ref
CF3-CF2	+	HO2	=>CF3 +CF2:O+OH	3.00E13	0.	0.	!ref

CH3-CHF	+	HO2	= CH2:CHF + H2O2	3.00E11	0.	0.	!ref
CH3-CF2	+	HO2	= CH2:CF2 + H2O2	3.00E11	0.	0.	!ref
CH2F-CH2	+	HO2	= CH2:CHF + H2O2	2.00E11	0.	0.	!ref
CH2F-CHF	+	HO2	= CHF:CHF-Z+ H2O2	2.00E11	0.	0.	!ref
CH2F-CHF	+	HO2	= CHF:CHF-E+ H2O2	2.00E11	0.	0.	!ref
CH2F-CF2	+	HO2	= CHF:CF2 + H2O2	2.00E11	0.	0.	!ref
CHF2-CH2	+	HO2	= CH2:CF2 + H2O2	1.00E11	0.	0.	!ref
CHF2-CHF	+	HO2	= CHF:CF2 + H2O2	1.00E11	0.	0.	!ref
CHF2-CF2	+	HO2	= CF2:CF2 + H2O2	1.00E11	0.	0.	!ref

CH3-CHF	+	HO2	= CH3-CH2F + O2	3.00E11	0.	0.	!ref
CH3-CF2	+	HO2	= CH3-CHF2 + O2	3.00E11	0.	0.	!ref
CH2F-CH2	+	HO2	= CH3-CH2F + O2	3.00E11	0.	0.	!ref
CH2F-CHF	+	HO2	= CH2F-CH2F+ O2	3.00E11	0.	0.	!ref
CH2F-CF2	+	HO2	= CH2F-CHF2+ O2	3.00E11	0.	0.	!ref
CHF2-CH2	+	HO2	= CH3-CHF2 + O2	3.00E11	0.	0.	!ref
CHF2-CHF	+	HO2	= CH2F-CHF2+ O2	3.00E11	0.	0.	!ref
CHF2-CF2	+	HO2	= CHF2-CHF2+ O2	3.00E11	0.	0.	!ref
CF3-CH2	+	HO2	= CH3-CF3 + O2	3.00E11	0.	0.	!ref
CF3-CHF	+	HO2	= CH2F-CF3 + O2	3.00E11	0.	0.	!ref
CF3-CF2	+	HO2	= CHF2-CF3 + O2	3.00E11	0.	0.	!ref

Fluoroethylenes: Activated Decomposition, Methylene comb'n (HF elimination)

CH2SING	+	CHF	= C2H2 + HF	17.02E19	-2.12	2380.	!ref
CH2SING	+	CF2	= C2HF + HF	17.02E19	-2.12	2380.	!ref
CHF	+	CHF	= C2HF + HF	17.02E19	-2.12	2380.	!ref
CHF	+	CF2	= C2F2 + HF	8.51E19	-2.12	2380.	!RRKM

Fluoroethylenes: Activated Decomposition, Methylene comb'n (stabilization)

CH2SING	+	CHF	= CH2:CHF	3.10E24	-3.80	2830.	!ref
CH2SING	+	CF2	= CH2:CF2	3.10E24	-3.80	2830.	!ref
CHF	+	CHF	= CHF:CHF-Z	1.55E24	-3.80	2830.	!ref
CHF	+	CHF	= CHF:CHF-E	1.55E24	-3.80	2830.	!ref
CHF	+	CF2	= CHF:CF2	3.10E24	-3.80	2830.	!RRKM

Fluoroethylenes: Activated Decomposition, Methylene comb'n (H atom elim'n)

CH2SING	+	CHF	= CH2:CF + H	1.64E07	1.56	5740.	!ref
CH2SING	+	CHF	= CHF:CH-Z + H	1.64E07	1.56	5740.	!ref
CH2SING	+	CHF	= CHF:CH-E + H	1.64E07	1.56	5740.	!ref
CH2SING	+	CF2	= CF2:CH + H	3.28E07	1.56	5740.	!ref
CHF	+	CHF	= CHF:CF-Z + H	1.64E07	1.56	5740.	!ref
CHF	+	CHF	= CHF:CF-E + H	1.64E07	1.56	5740.	!ref
CHF	+	CF2	= CF2:CF + H	1.64E07	1.56	5740.	!RRKM

Fluoroethylenes: Activated Decomposition, Vinyl + H (HF elimination)							
CH2:CF	+ H	= C2H2	+ HF	5.98E20	-2.31	1940.	!ref
CHF:CH-Z	+ H	= C2H2	+ HF	5.98E20	-2.31	1940.	!ref
CHF:CH-E	+ H	= C2H2	+ HF	5.98E20	-2.31	1940.	!ref
CF2:CH	+ H	= C2HF	+ HF	5.98E20	-2.31	1940.	!ref
CHF:CF-Z	+ H	= C2HF	+ HF	5.98E20	-2.31	1940.	!ref
CHF:CF-E	+ H	= C2HF	+ HF	5.98E20	-2.31	1940.	!ref
CF2:CF	+ H	= C2F2	+ HF	5.98E20	-2.31	1940.	!RRKM
Fluoroethylenes: Activated Decomposition, Vinyl + H (stabilization)							
CH2:CF	+ H	= CH2:CHF		2.40E34	-7.11	5040.	!ref
CHF:CH-Z	+ H	= CH2:CHF		2.40E34	-7.11	5040.	!ref
CHF:CH-E	+ H	= CH2:CHF		2.40E34	-7.11	5040.	!ref
CF2:CH	+ H	= CH2:CF2		2.40E34	-7.11	5040.	!ref
CHF:CF-Z	+ H	= CHF:CHF-Z		2.40E34	-7.11	5040.	!ref
CHF:CF-E	+ H	= CHF:CHF-E		2.40E34	-7.11	5040.	!ref
CF2:CF	+ H	= CHF:CF2		2.40E34	-7.11	5040.	!RRKM
Fluoromethylene Combination							
CHF	+ CF2	= CF2:CF	+ H	1.64E07	1.56	5740.	!ref
CF2:CF2	+ M	= CF2 + CF2	+ M	7.80E15	0.50	55690.	! 65TSC
Fluoroethylenes: Thermal Decompositions							
CH2:CHF	= C2H2	+ HF		1.00E14	0.00	70800.	!70TSC
CH2:CF2	= C2HF	+ HF		2.50E14	0.00	86000.	!70TSC
CHF:CHF-Z	= C2HF	+ HF		2.50E14	0.00	78000.	!ref +dH 37
CHF:CHF-E	= C2HF	+ HF		2.50E14	0.00	79000.	!ref +dH 38
CF2:CF2	+ M	= CF2 + CF2	+ M	7.80E15	0.50	55690.	!65TSC
CHF:CHF-Z	= CHF:CHF-E			2.63E13	0.00	60700.	!74JEF
CH2:CF2	+ CF3	= CF2:CH	+ CHF3	7.24E10	0.00	4000.	!72KER/PAR + 7
C2H4	+ F2	= CH2F-CH2	+ F	1.38E14	0.00	13600.	!88RAF
C2H4	+ F2	= CH2:CHF	+ HF	1.90E13	0.00	11040.	!88RAF
C2H4	+ F	= C2H3	+ HF	1.00E14	0.00	2000.	!ref -34
Fluoroethylenes: H Atom Addition (stabilization)							
CH2:CHF	+ H(+M)	= CH2F-CH2	(+M)	4.20E08	1.50	990.	!ref
CH2:CHF	+ H(+M)	= CH3-CHF	(+M)	4.20E08	1.50	990.	!ref
CH2:CF2	+ H(+M)	= CHF2-CH2	(+M)	4.20E08	1.50	990.	!ref
CH2:CF2	+ H(+M)	= CH3-CF2	(+M)	4.20E08	1.50	990.	!ref
	LOW/3.19E27	-2.8	-54./				!ref
	H2/2.0/ CO/2.0/ CO2/3.0/ H2O/5.0/						!ref
CHF:CHF-Z+	H(+M)	= CH2F-CHF	(+M)	8.40E08	1.50	990.	!ref
CHF:CHF-E+	H(+M)	= CH2F-CHF	(+M)	8.40E08	1.50	990.	!ref
	LOW/6.37E27	-2.8	-54./				!ref
	H2/2.0/ CO/2.0/ CO2/3.0/ H2O/5.0/						!ref
CHF:CF2	+ H(+M)	= CHF2-CHF	(+M)	4.20E08	1.50	990.	!ref
CHF:CF2	+ H(+M)	= CH2F-CF2	(+M)	4.20E08	1.50	990.	!ref
	LOW/3.19E27	-2.8	-54./				!ref
	H2/2.0/ CO/2.0/ CO2/3.0/ H2O/5.0/						!ref
CF2:CF2	+ H(+M)	= CHF2-CF2	(+M)	8.40E08	1.50	990.	!ref
	LOW/6.37E27	-2.8	-54./				!ref
	H2/2.0/ CO/2.0/ CO2/3.0/ H2O/5.0/						!ref
Fluoroethylenes: H Atom Addition (F atom displacement)							
C2H4	+ F	= CH2:CHF	+ H	2.00E13	0.00	0.	!ref
CH2:CHF	+ F	= CH2:CF2	+ H	2.00E12	0.00	0.	!ref
CH2:CHF	+ F	= CHF:CHF-Z+	H	5.00E12	0.00	0.	!ref
CH2:CHF	+ F	= CHF:CHF-E+	H	5.00E12	0.00	0.	!ref
CHF:CHF-Z	+ F	= CHF:CF2	+ H	4.00E12	0.00	0.	!ref
CHF:CHF-E	+ F	= CHF:CF2	+ H	4.00E12	0.00	0.	!ref
CHF:CF2	+ F	= CF2:CF2	+ H	2.00E12	0.00	0.	!ref

Fluoroethylenes: H Atom Abstraction by H							
CH2:CHF	+ H	= CHF:CH-Z + H2	0.33E06	2.53	12241.	!ref	
CH2:CHF	+ H	= CHF:CH-E + H2	0.33E06	2.53	12241.	!ref	
CH2:CHF	+ H	= CH2:CF + H2	0.33E06	2.53	12241.	!ref	
CH2:CF2	+ H	= CF2:CH + H2	0.67E06	2.53	12241.	!ref	
CHF:CHF-Z	+ H	= CHF:CF-Z + H2	0.33E06	2.53	12241.	!ref	
CHF:CHF-E	+ H	= CHF:CF-E + H2	0.33E06	2.53	12241.	!ref	
CHF:CF2	+ H	= CF2:CF + H2	0.33E06	2.53	12241.	!ref	
Fluoroethylenes: Oxidation by O							
CH2:CHF	+ O	= CH2F + HCO	5.30E09	1.00	1310.	!fit	87CVE
CHF:CHF-Z	+ O	= CH2F + CF:O	7.00E09	1.00	1590.	!fit	87CVE
CHF:CHF-E	+ O	= CH2F + CF:O	8.00E09	1.00	1320.	!fit	87CVE
CH2:CF2	+ O	= CHF2 + HCO	4.30E09	1.00	1490.	!fit	87CVE
CHF:CF2	+ O	= CHF2 + CF:O	6.00E09	1.00	1150.	!fit	87CVE
CF2:CF2	+ O	= CF2 + CF2:O	1.90E09	1.00	0.	!fit	87CVE
CH2:CHF	+ O	= CH3 + CF:O	5.30E09	1.00	2300.	!ref+1	74SLA/GUT
Fluoroethylenes: H Atom Abstraction by OH							
CH2:CHF	+ OH	= CHF:CH-Z+ H2O	2.00E06	2.00	2850.	!ref	-6
CH2:CHF	+ OH	= CHF:CH-E+ H2O	2.00E06	2.00	2850.	!ref	-6
CH2:CHF	+ OH	= CH2:CF + H2O	1.00E06	2.00	2850.	!ref	-10
CHF:CHF-Z	+ OH	= CHF:CF-Z+ H2O	2.00E06	2.00	2850.	!ref	-5
CHF:CHF-E	+ OH	= CHF:CF-E+ H2O	2.00E06	2.00	2850.	!ref	-5
CH2:CF2	+ OH	= CF2:CH + H2O	2.00E06	2.00	2850.	!ref	
CHF:CF2	+ OH	= CF2:CF + H2O	1.00E06	2.00	2850.	!ref	+ 1
Fluorovinyls: Oxidation by O2							
CH2:CF	+ O2	= CH2O + CF:O	4.48E26	-4.55	5480.	!ref	direct
CHF:CH-Z	+ O2	= CHF:O + HCO	4.48E26	-4.55	5480.	!ref	direct
CHF:CH-E	+ O2	= CHF:O + HCO	4.48E26	-4.55	5480.	!ref	direct
CHF:CF-E	+ O2	= CHF:O + CF:O	4.48E26	-4.55	5480.	!ref	direct
CHF:CF-Z	+ O2	= CHF:O + CF:O	4.48E26	-4.55	5480.	!ref	direct
CF2:CH	+ O2	= CF2:O + HCO	4.48E26	-4.55	5480.	!ref	direct
CF2:CF	+ O2	= CF2:O + CF:O	4.48E26	-4.55	5480.	!ref	direct
CH2:CF	+ O2	= CH2O + CF:O	1.05E38	-8.22	7030.	!ref	a/s
CHF:CH-Z	+ O2	= CHF:O + HCO	1.05E38	-8.22	7030.	!ref	a/s
CHF:CH-E	+ O2	= CHF:O + HCO	1.05E38	-8.22	7030.	!ref	a/s
CHF:CF-E	+ O2	= CHF:O + CF:O	1.05E38	-8.22	7030.	!ref	a/s
CHF:CF-Z	+ O2	= CHF:O + CF:O	1.05E38	-8.22	7030.	!ref	a/s
CF2:CH	+ O2	= CF2:O + HCO	1.05E38	-8.22	7030.	!ref	a/s
CF2:CF	+ O2	= CF2:O + CF:O	1.05E38	-8.22	7030.	!ref	a/s
Fluorovinyls: Oxidation by O							
CH2:CF	+ O	= CH2CO + F	3.00E13	0.00	0.	!ref	
CHF:CF-E	+ O	= CHF:CO + F	3.00E13	0.00	0.	!ref	
CHF:CF-Z	+ O	= CHF:CO + F	3.00E13	0.00	0.	!ref	
CF2:CF	+ O	= CF2CO + F	3.00E13	0.00	0.	!ref	
CHF:CH-E	+ O	= CHF:CO + H	3.00E13	0.00	0.	!ref	
CHF:CH-Z	+ O	= CHF:CO + H	3.00E13	0.00	0.	!ref	
CF2:CH	+ O	= CF2CO + H	3.00E13	0.00	0.	!ref	

Fluorovinyls: Oxidation by OH

CH2:CF	+ OH	= CH2CO + HF	3.00E13	0.00	0.	!ref
CHF:CH-E	+ OH	= CH2CO + HF	3.00E13	0.00	0.	!ref
CHF:CH-Z	+ OH	= CH2CO + HF	3.00E13	0.00	0.	!ref
CHF:CF-E	+ OH	= CHFCO + HF	2.00E13	0.00	0.	!ref
CHF:CF-Z	+ OH	= CHFCO + HF	2.00E13	0.00	0.	!ref
CF2:CF	+ OH	= CF2CO + HF	1.00E13	0.00	0.	!ref
CH2:CF	+ OH	= CH3 + CF:O	3.00E13	0.00	0.	!ref
CHF:CH-E	+ OH	= CH2F + HCO	3.00E13	0.00	0.	!ref
CHF:CH-Z	+ OH	= CH2F + HCO	3.00E13	0.00	0.	!ref
CHF:CF-E	+ OH	= CH2F + CF:O	4.00E13	0.00	0.	!ref
CHF:CF-Z	+ OH	= CH2F + CF:O	4.00E13	0.00	0.	!ref
CF2:CF	+ OH	= CHF2 + CF:O	5.00E13	0.00	0.	!ref

Fluoroethynes: H Atom Addition/Stabilization

C2HF	+H (+M)	= CH2:CF (+M)	2.80E12	0.00	2410.	!ref
C2HF	+H (+M)	= CHF:CH-Z (+M)	1.40E12	0.00	2410.	!ref
C2HF	+H (+M)	= CHF:CH-E (+M)	1.40E12	0.00	2410.	!ref
	LOW/0.67E27	-3.5			2410./	
	H2/2./	CO/2./	CO2/3./	H2O/5./		
C2F2	+H (+M)	= CHF:CF-Z (+M)	2.80E12	0.00	2410.	!ref
C2F2	+H (+M)	= CHF:CF-E (+M)	2.80E12	0.00	2410.	!ref
	LOW/1.33E27	-3.5			2410./	
	H2/2./	CO/2./	CO2/3./	H2O/5./		

Fluoroethynes: Oxidation

C2HF	+ O	= FCCO-E + H	1.00E07	2.00	1900.	!ref*2 MB A077
C2F2	+ O	= FCCO-E + F	1.00E07	2.00	1900.	!ref*2 MB A077
C2HF	+ OH	= CHFCO + H	2.18E-4	4.50	-1000.	!ref MB A089
C2HF	+ OH	= CH2F + CO	2.50E-4	4.00	-2000.	!ref/2 MB A090
C2HF	+ OH	= HCCO + HF	2.50E-4	4.00	-2000.	!ref/2 MB A090
C2F2	+ OH	= CF2CO + H	2.18E-4	4.50	-1000.	!ref MB A089
C2F2	+ OH	= FCCO-E + HF	2.50E-4	4.00	-2000.	!ref MB A090

Fluoroketenes, Fluoroketyl

CHFCO	+ H	= CH2F + CO	1.13E13	0.00	3428.	!ref MB A094
CF2CO	+ H	= CHF2 + CO	1.13E13	0.00	3428.	!ref MB A094
CHFCO	+ H	= FCCO-E + H2	5.00E13	0.00	8000.	!ref MB A095
CHFCO	+ O	= CHF:O + CO	1.00E13	0.00	8000.	!est
CF2CO	+ O	= CF2:O + CO	1.00E13	0.00	8000.	!est
CHFCO	+ OH	= FCCO-E + H2O	7.50E12	0.00	2000.	!ref MB A097
HCCO	+ F	= CHF + CO	3.00E13	0.00	0.	!ref MB A101
FCCO-E	+ F	= CF2 + CO	3.00E13	0.00	0.	!ref MB A101
FCCO-E	+ H	= CHF + CO	1.00E14	0.00	0.	!ref MB A101
FCCO-E	+ O	= CF:O + CO	1.00E14	0.00	0.	!ref MB A102

F Atom Reactions

CH3OH	+ F	= CH3O	+ HF	2.62E09	1.44	-205.	!91GLA/KOS	
CH3OH	+ F	= CH2OH	+ HF	4.62E07	1.97	-300.	!91GLA/KOS	
CH2O	+ F	= HCO	+ HF	6.00E13	0.00	2000.	!ref	-45
CHF:O	+ F	= CF:O	+ HF	2.65E13	0.00	1800.	!90FRA/ZHA	-35
CH3O	+ F	= CH2O	+ HF	3.00E13	0.00	0.	!est	-114
HCO	+ F	= CO	+ HF	1.00E13	0.00	0.	!est	-120
C2H3	+ F	= C2H2	+ HF	2.00E13	0.00	0.	!ref	
CH2:CF	+ F	= C2HF	+ HF	2.00E13	0.00	0.	!ref	
CHF:CH-Z	+ F	= C2HF	+ HF	2.00E13	0.00	0.	!ref	
CHF:CH-E	+ F	= C2HF	+ HF	2.00E13	0.00	0.	!ref	
CHF:CF-Z	+ F	= C2F2	+ HF	2.00E13	0.00	0.	!ref	
CHF:CF-E	+ F	= C2F2	+ HF	2.00E13	0.00	0.	!ref	
CF2:CH	+ F	= C2F2	+ HF	2.00E13	0.00	0.	!ref	
CHF:CF-Z	+ F	= CHF	+ CF2	1.00E13	0.00	0.	!ref	
CHF:CF-E	+ F	= CHF	+ CF2	1.00E13	0.00	0.	!ref	
CF2:CF	+ F	= CF2	+ CF2	2.00E13	0.00	0.	!ref	
CF2:CF2	+ F	= CF3	+ CF2	3.00E13	0.00	0.	!ref	-18

NOTATION

$$k = AT^b e^{-E/RT}$$

A: prefactor (s⁻¹, etc.)

b: temperature dependence (dimensionless)

E: activation energy (J/mol/4.18)

H: heat of reaction (kJ/mol/4.18)

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