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Potential Hazards Relating to Pyrolysis of c-C_4F_8 in Selected Gaseous Diffusion Plant Operations

L. D. Trowbridge

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LOCKHEED MARTIN ENERGY RESEARCH CORPORATION
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ABSTRACT

As part of a program intended to replace the present evaporative coolant at the gaseous diffusion plants (GDPs) with a non-ozone-depleting alternate, a series of investigations of the suitability of candidate substitutes is under way. One issue concerning a primary candidate, c-C_4F_8, is the possibility that it might produce the highly toxic perfluoroisobutylene (PFIB) in high temperature environments. This study was commissioned to determine the likelihood and severity of decomposition under two specific high temperature thermal environments, namely the use of a flame test for the presence of coolant vapors and welding in the presence of coolant vapors. The purpose of the study was to develop and evaluate available data to provide information that will allow the technical and industrial hygiene staff at the GDPs to perform appropriate safety evaluations and to determine the need for field testing or experimental work.

The scope of this study included a literature search and an evaluation of the information developed therefrom. Part of that evaluation consists of chemical kinetics modeling of coolant decomposition in the two operational environments. The general conclusions are that PFIB formation is unlikely in either situation but that it cannot be ruled out completely under extreme conditions. The presence of oxygen, moisture, and combustion products will tend to lead to formation of oxidation products (COF_2, CO, CO_2, and HF) rather than PFIB.

1. INTRODUCTION

The phase out of the production of chlorofluorocarbons (CFCs) has led to plans to replace CFC-114 at the gaseous diffusion plants (GDPs) with a fully fluorinated coolant, cycloperfluorobutane (also known as FC-c318 or by its chemical formula, c-C_4F_8). This report documents investigations into the thermal stability of c-C_4F_8 coolant at conditions expected to apply during specific high temperature operations at the Portsmouth and Paducah Gaseous Diffusion Plants. Under conditions at which c-C_4F_8 could thermally degrade (above a few hundred degrees Celsius), potentially hazardous unsaturated fluorocarbon compounds may form, most notably perfluoroisobutylene (PFIB; also known as perfluoroisobutene, octafluoroisobutene, and octafluoroisobutylene, or by its chemical formula, i-C_4F_8 or iso-C_4F_8).

GDP coolant losses occur to the atmosphere through both leaks and during maintenance activities and through leaks into the UF_6 process gas stream and into the cooling water. At process gas conditions, c-C_4F_8 is even more stable than CFC-114, though a small degree of reaction can be expected. The fluorinating potential of UF_6 guarantees to a good degree of confidence that within the process gas stream, any unsaturated fluorocarbons will be destroyed virtually as soon as produced. The coolant reaction products in the process gas stream are thus unlikely to be more hazardous than the parent compound. Hydrolysis of coolant leaking into the cooling water stream should be lower than that of CFC-114. At ambient temperatures, c-C_4F_8 is inert in air. Manufacturer's literature obtained in the late 1980s (DuPont n.d., "Physical Properties..."; DuPont n.d. "Electrical Insulating...") suggests that the onset of pyrolysis could occur in the temperature range 250 to 600°C (the lower temperatures applying only when reaction is catalyzed by certain metals). This is far outside temperatures normally encountered in the diffusion plants except for a few special conditions. These include electrical arcs and open flames (e.g., during welding or accidental fires) and also the operating conditions of the Portsmouth Freon degrader. The Freon degrader, however, has not operated recently, and even when operating, should provide an excess of fluorine, plausibly minimizing the formation of hazardous unsaturated fluorocarbons. A further specialized high temperature environment is that of a propane torch test used to detect coolant vapors in air.

Hazardous levels of PFIB and other less toxic unsaturated compounds are available in the industrial safety literature. For safety analysis purposes, the issue that must be addressed is the degree to which c-C_4F_8 reacts to form PFIB or other toxic compounds when exposed to the range of conditions that might occur in or near localized high temperatures and flames. Definitive information on these points was not located (nor intensively sought) during the CFC replacement campaign of the late 1980s and early 1990s. It would, however, be very beneficial to be able to use some basis for setting limits for coolant concentrations other than the (extremely conservative) assumption of 100% conversion to PFIB.

The purpose of this report is to find and interpret available information to provide a technical basis to the industrial hygiene and safety analysis organizations charged with evaluating the suitability and protective measures to be taken when this new coolant is introduced at the GDPs. This report itself is not intended of to constitute that safety evaluation.

More specifically, this study reviews scientific literature relevant to the question of thermal decomposition of c-C_4F_8 in order to improve the technical basis for the safety evaluation of the specific operations previously mentioned short of actual experimental simulation of the operations. As part of this study, a thorough literature search was conducted to uncover the available information and to indicate those areas where further information may be desirable.

Qualitative information on conditions conducive and not conducive to PFIB formation was found, as was an extensive literature on the chemical kinetics of the pyrolysis of perfluorocarbons. Kinetic information on these subjects is evaluated, and the specific operations of concern evaluated on the basis of chemical kinetics by use of a small scale reaction rate model for coolant pyrolysis.

2. LITERATURE SEARCH

This section summarizes the more pertinent material found in the literature search; it cannot provide a complete discussion of all references that have any bearing on the subject. A working annotated bibliography developed during this search is ~ 90 pages long.

The generation of toxic decomposition products has long been a concern in the plastics industry and in fire prevention circles. Consequently, work sponsored by that industry is the source of most of the information discovered. No complete and comprehensive answer was found to the question of a safe limit for gaseous c-C_4F_8 in high temperature environments similar to those of concern at the diffusion plants, but a great deal of suggestive and circumstantial information is available. Discussion of the material found in the literature search is categorized into three areas:

1. *Toxicity*. Toxicity of fluorocarbon decomposition fumes, including comment on specific tests where the products were not characterized other than by their toxicity. Brief mention is also made of protective measures, including PFIB removal methods and antidotes.

2. *Descriptive chemistry*. Experiments yielding product composition produced under specified conditions. These are primarily integrated results of tests of pyrolysis or fires. Such studies can give some indication of conditions under which PFIB can be produced and factors that promote or inhibit its formation.

3. *Chemical kinetics*. Experimental information giving rates of elementary or composite reaction steps, such as the following: c-$C_4F_8 \rightarrow 2\, C_2F_4$. This is the sort of information needed to model the decomposition of coolant and formation of toxic products.

2.1 TOXICITY

Current regulations establish a threshold limit value of 0.01 ppm for occupational exposure to PFIB to prevent acute pulmonary effects (Anon 1990). Dose-response studies include those of Smith et al., (1982). The toxicity of PFIB in past coolant replacement activities at the diffusion plants has been considered, but primarily on the basis of the content in source material (Covert and Hays 1992). PFIB is not the only toxic product that may form in the decomposition or combustion of c-C_4F_8, but the others (notably HF and COF_2) are more familiar and have considerably higher limiting values.

Given the high level of toxicity of PFIB, considerable attention has been given to the mechanism of injury (Arroyo and Keeler 1997; Lehnert et al., 1993; Nold et al., 1991), to protective measures and to the development of antidotes for exposure such as n-acetylcysteine (Lailey et al., 1991; Lailey 1997).

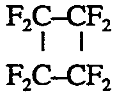
PFIB can be removed from a gas by use of activated charcoal (Hall. Lawston and Tinsley 1989). The moisture content of the charcoal or surface treatment can be important parameters in the effectiveness of charcoal (Karwacki and Stickel 1991). This is the sort of material generally used in respirator cartridges. Other methods are used for PFIB removal from gas streams, including bubbling the gas stream though methanol (Treat 1979; England and Krespan 1966; Brice et al., 1953), passing it through a heated alumina-supported alkali metal hydroxide catalyst (Weeks 1972) or passing it though strong alkaline solutions (Brice et al., 1953).

A number of references to tests were found in which polytetrafluoroethylene (PTFE) or related fluoropolymers were heated or burned and test animals subjected to the fumes. No reference to similar tests with c-C_4F_8 or other vapor phase fluorocarbons were found. The physical conditions in these tests are usually not well defined (as to temperature, contact time, flow rate, oxygen depletion, etc.). In PTFE, the primary low temperature toxic component is a polymer fragment (Waritz and Kwon 1968; Seidel et al. 1991). Temperatures at which this is important (below 450°C) and the relatively low degree of polymerization during c-C_4F_8 pyrolysis suggest that this is not likely to be a problem with c-C_4F_8. At higher temperatures, PTFE pyrolysis products are very similar to those of c-C_4F_8, so some relevant qualitative comparisons might be drawn.

2.2 DESCRIPTIVE CHEMISTRY

Studies discussed here are those that are primarily qualitative in nature, for example experiments that exposed fluorocarbons to certain physical conditions and evaluated the products or effects in a general way but not at the level of detail allowing one to follow the rate of formation of products. The more detailed category is discussed in section 2.3. Physical conditions of interest can be categorized as *pyrolysis* (thermal decomposition at high temperature in the absence of reactive species such as O_2); *pyrolysis in air or oxygen* (high temperature in the presence of air or O_2); or *flame* (high temperature in the presence of combustion conditions – oxygen, fuel and reaction products).

The pyrolytic decomposition of c-C_4F_8 to C_2F_4 is something of a standard reaction in fluorocarbon chemical kinetics. Since rate information is available from several sources, these are discussed primarily in section 2.3. For now, it is sufficient to note that the thermal decomposition of c-C_4F_8 (in the absence of air or O_2) produces first C_2F_4 and then (at higher temperatures and longer times) a variety of other species including C_3F_6, 2-C_4F_8, PFIB (i-C_4F_8), and CF_2. Other than the parent compound c-C_4F_8, which is a (strained) four-member ring with the structure



and the biradical CF_2, the remainder of these are unsaturated fluorocarbons with chemical structures $F_2C{=}CF_2$, $F_2C{=}CF{-}CF_3$, $F_3C{-}FC{=}CF{-}CF_3$, and $(CF_3)_2C{=}CF_2$, respectively. At higher temperatures or longer times, additional products appear, including saturated fluorocarbons such as CF_4 and C_2F_6 and polymers or solids of lower fluorine content (see, for example, Gray and Pritchard 1956; Atkinson and Atkinson 1957; Butler 1962; Lifshitz, Carroll and Bauer 1963; Simmie et al. 1969; Lifshitz et al. 1982; Buravtsev et al. 1985; Fedurtsa and Kushina 1987; Buravtsev 1994; Bauer and Javanovic 1998).

Studies of the decomposition of compounds other than c-C_4F_8 can be useful when their products are the same as are those of c-C_4F_8. For example, HFC-227ea (CF_3-CFH-CF_3), exposed to temperatures above 800°C for 1 to 2 s first decomposes to C_3F_6, then subsequently to several other products, including PFIB (Ritter 1997). When heated to temperatures ranging from 650 to 775°C in inert gas, HCFC-124 (CF_3-CFHCl) produced a variety of compounds including C_2F_4, C_3F_6, CFC-114a, 1- and 2-C_4F_8, and minor quantities of PFIB. The same experiment performed in a hydrogen environment produced a complex mixture of hydrofluorocarbons (Difelice and Ritter 1996). A similar study on HCFC-22 (CF_2HCl) between 500 and 750°C yielded primarily C_2F_4 and C_3F_6 at the lower temperatures but also produced traces of c-C_4F_8 and PFIB (in addition to several chlorofluorocarbons) at the higher temperatures. The addition of H_2 or CH_4 shifted the product mix away from unsaturated species (such as C_2F_4, C_3F_6, and PFIB) toward hydrofluorocarbons (Defilice and Ritter 1993). A similar study on thermal decomposition of CF_3H between 830 and 1030°C (contact times from 20 ms to 2 s) began with elimination of HF to yield CF_2 and subsequently the familiar products C_2F_4, C_3F_6, and c–C_4F_8. PFIB was not mentioned (Politanskii 1969).

One study directed at determination of the mechanism of PFIB formation examined the pyrolysis products of C_2F_4 and C_3F_6 alone and in various mixtures at temperatures between 730 and 770°C for times on the order of a second. The mixture gave somewhat higher yields of PFIB than did either compound alone, though the effect was not extremely large (Zaitsev et al. 1990).

A deliberate pyrolytic synthesis for PFIB is described (Young et al. 1967) in which pure C_3F_6 is circulated for 24 h through a carbon-lined reactor held at 750°C. Conversion was approximately 50% efficient under these conditions.

A general reference on combustion (Gad and Anderson 1990) contains a few pages with brief summaries of combustion or pyrolysis tests of PTFE and related polymers. The results vary widely, but the general trends are as follows:

- *Pyrolysis with no O_2.* Saturated and unsaturated gaseous perfluorocarbon decomposition products appear, including C_2F_4, C_3F_6, PFIB, and c-C_4F_8

- *Pyrolysis in air.* Fewer perfluorocarbons are produced; toxic gaseous products are primarily COF_2 and CF_3OF.

- *Pyrolysis in O_2:* Products are primarily COF_2 and CF_4

In another pyrolysis study, decomposition of various perfluoro polymers was examined in N_2, air, and O_2. Gaseous products were characterized as "major," "medium," or "minor" without further quantification. Temperatures examined ranged from 485 to 535°C. PFIB was produced as a "medium" product at the highest temperatures in N_2 and as a "low" product in air at those temperatures, while COF_2 was found in high concentration in air or O_2 at the highest temperatures (Molero-Meneses et al 1981).

PTFE pyrolysis tests in air at 500 to 650°C identified only COF_2 as a toxic product. The analytical method might have been unable to detect PFIB or distinguish COF_2 from HF, but the effective toxicity of the fumes was consistent with the level of COF_2 determined (Scheel et al. 1968; Coleman et al. 1968). Arito studied the pyrolysis of PTFE between 450 and 650°C. Product identification was by gas chromatograph/mass spectroscopy, but only qualitative analyses ("present" or "absent") were reported. PFIB was detected in a dry N_2 purge experiment, but was not seen in humid or O_2-containing conditions. When O_2 was present, COF_2 formed, as did CF_3OF. However, COF_2 disappeared at high temperatures due to disproportionation to CF_4 and CO_2, and also when moisture is present due to hydrolysis to HF and CO_2 (Arito and Soda 1977).

Although it will burn in oxygen, c-C_4F_8 will not sustain combustion in air, (Fletcher and Kittleson 1968). Studies of this system, however, did not provide product analysis. A similar study of the direct combustion of C_2F_4 in O_2 near the lower (O_2-poor) flame limit gave primarily COF_2 as a reaction product; at the maximum flame temperature, the products were mainly CF_4 and CO_2 (Duus 1955).

Fire studies involving c-C_4F_8 (used a fire suppressant) have been reported, but they are not useful for our purposes since no reaction product information is provided (Trees et al. 1995; Grosshandler et al. 1995). A few related studies (CF_2HBr, PTFE) did include product analysis.

None observed PFIB in products (though in some cases the analytical technique could not have detected it even if it were present). The product mix is likely to be a strong function of detailed conditions of the fire. (One can imagine scenarios in which the fire radiantly heats nearby areas so that thermal decomposition is more appropriate.)

PTFE fire studies that combined toxicity tests with product analysis found lethal responses consistent with the HF, CO, and COF_2 levels observed in the fire (Clarke et al. 1992). PFIB could not have been detected even if present by the gas analysis method used, PFIB did not seem to contribute to the mortality rate of the test animals.

A series of PTFE fire studies (Baker and Kaiser 1991; Seidel et al. 1991), was conducted in an attempt to duplicate earlier very high toxicity results (Levin et al. 1982). Baker and Seidel concluded that the National Bureau of Standards toxicity was due to the formation of toxic particulates under fairly special conditions, namely those in which polymer degradation fumes are heated and reheated in a hot furnace without an actual flame. In a normal fire, moisture and combustion products are present and tend to destroy toxic products like particulates and PFIB. The compounds HF, CO, and COF_2 were considered the main toxic hazards in a fire involving PTFE.

One detailed fire study (Biordi et al. 1978) reported products of CF_3Br in a methane flame. Flame temperatures ranged from about 570 to 1670°C. Various product species were detected by mass spectrometry, including CF_2, HF, CO, and COF_2. Though the analytical method was sensitive enough to detect C_3F_6 or PFIB, no species containing more than two carbons was detected. The main products were CO, CO_2, COF_2, HF, H_2O and Br. While the precursor compound is not c-C_4F_8, once dissociated to CF_2, the flame chemistry in this system is likely very similar to that of a flame involving c-C_4F_8.

Related and possibly useful reaction information has been located during this literature search. One such area is that of the fluorination of c-C_4F_8 by F_2 or ClF_3. (Fletcher and Ambs 1964; Levy and Kennedy 1974; Fletcher and Hindemann 1983; Trowbridge and Angel 1992). While not directly relevant to this study, the work on the reactions of F_2 with several unsaturated perfluorocarbons indicates that the rate of fluorination is sufficiently rapid, even at room temperature, that such compounds (including PFIB) will not survive contact with F_2 (Rodgers 1963; Rodgers 1965).

Several references relating to photolytic, radiolytic, and arc- and electric discharge-induced breakdown of c-C_4F_8 and related compounds were found. Such conditions, however, appear to yield product mixes quite different from those of thermal decomposition (including some species less thermally stable than those that appear in high temperature pyrolysis). Since these studies seem only distantly related to the problem at hand, they are not discussed further.

Reviews of PFIB chemistry are to be found in Zeifman (1984) and England and Krespan (1966), dealing largely with its use in organic syntheses.

Analytical techniques are not the focus of this work, but some potentially useful references to gas chromatograph, infrared spectroscopic, and mass spectrometric analysis of perfluorocarbons (PFCs) and PFIB in particular are to be found in several sources (O'Mahony 1993a and 1993b; Marhevka et al. 1982; Shih et al. 1990; Kochetkova et al. 1987; Bright and Matula 1968; Brice et al. 1953)

To summarize the descriptive chemical literature, it may be instructive to list the conditions under which PFIB has been observed to form. An early synthesis was the pyrolysis of c-C_4F_8 at 700 to 725°C. Brice reported producing about 30 g/h by this method, though the details of the operation (pressure, dwell time in the reactor) were not mentioned (Brice et al. 1953). Similar synthetic methods use other compounds in the pyrolysis system. Young prescribed a pyrolytic synthesis whereby C_3F_6 heated to 750°C for 24 h produced PFIB in high yield (Young et al. 1967). More detailed studies indicate that PFIB forms at elevated temperatures by a mechanism now regarded to involve reaction of C_3F_6 with CF_2. (See more detailed discussion of kinetics that follow.) PFIB was obtained in high yield from C_2F_4 for times >30 s at 650°C, and from c-C_4F_8 for times >15 s at 700°C (Atkinson and Atkinson 1957). In both cases, the starting materials had generated some C_3F_6. When C_3F_6 was used alone as a starting material PFIB was produced in quantity at temperatures from 600 to 675°C. Higher temperatures tend to speed the rate of PFIB formation, but soon PFIB decomposition reactions become significant. In the Atkinson studies, at temperatures between 700 and 750°C, PFIB decomposition to form primarily C_2F_6 and solids (approximate composition $C_{1.25}F$) dominated (Atkinson and Trentwith 1953; Atkinson and Atkinson 1957).

PFIB is very unlikely to form in an environment containing elemental fluorine. Though a rate for the reaction of PFIB with F_2 was not found, unsaturated PFCs in general react very quickly with fluorine.

All sources seem to indicate that in the presence of O_2, the production of PFIB is at least somewhat suppressed compared with pyrolysis in the absence of O_2. Similarly, the presence of H_2O always appears to reduce formation of PFIB relative to formation in its absence. A few of the previously mentioned sources, however, do indicate PFIB formation under conditions that at least initially contained O_2. These involved the pyrolysis of solid fluorocarbon polymers, which represent a high density sources of reactant (compared with O_2 in the gas phase); therefore, the possibility of local oxygen depletion exists in such experiments.

2.3 KINETICS

2.3.1 Pyrolysis Reactions

Pyrolysis of c-C_4F_8 and other fluorocarbons has been studied and reported extensively in the literature. Several studies have directly addressed the question of mechanism and rate of c-C_4F_8 decomposition in the absence of air, and over the years a consensus has developed as to the mechanisms leading from c-C_4F_8 to other perfluoroolefins, including PFIB. The major reaction steps are now generally considered to be:

1. $c\text{-}C_4F_8 \leftrightarrow 2\,C_2F_4$,

2. $C_2F_4 \leftrightarrow 2\,CF_2$,

3. $C_3F_6 \leftrightarrow CF_2 + C_2F_4$,

and

4. $i\text{-}C_4F_8 \leftrightarrow CF_2 + C_3F_6$.

(see for example Bauer et al. 1969 or Buravtsev et al. 1985). Earlier studies postulated the reaction step:

$$c\text{-}C_4F_8 \leftrightarrow C_3F_6 + CF_2 \quad .$$

(Atkinson and Atkinson 1957; Butler 1962). This step has been disputed (Politanskii 1969; Buravtsev et al. 1985; Baklanov and Ushakova 1989) and fairly convincingly demonstrated not to participate in the overall mechanism (Fedurtsa and Kushina 1987). However, it is still included in some recent kinetics models (Bauer and Javanovic 1998). All these are reversible reactions, and all species involved have the basic formula $(CF_2)_n$ (if not that structure). Therefore, to a degree, studies involving any of the stable starting materials (that is, all but the biradical CF_2) can be potentially useful to the present study. The equilibrium will not be affected by the choice of starting materials.

Direct studies of the dissociation or formation of c-C_4F_8 are numerous (Lacher et al. 1952; Atkinson and Trentwith 1953; Gray and Pritchard 1956; Atkinson and Atkinson 1957; Butler 1962; Lifshitz, Carroll, and Bauer 1963; Drennan and Matula 1968; Simmie et al. 1969; Lifshitz et al. 1982; Buravtsev et al. 1985; Fedurtsa and Kushina 1987; Bauer and Javanovic 1998), with the level of detail increasing in the more recent research. Similar studies on other compounds in the system have also have been reported; for example, C_3F_6 (Atkinson and McKeegan 1966; Buravtsev et al. 1989a), C_2F_4 (Atkinson and Atkinson 1957; Modica and LaGraff 1966; Carlson 1971; Schug and Wagner 1978; Buravtsev 1989b), and PFIB (i-C_4F_8) (Zaitsev et al. 1990). Other species are minor products in this reaction system, notably the linear butene 2-C_4F_8 (Buravtsev et al. 1989b).

Recent work on this system is bringing the study to a new level of detail in the examination of radical intermediates (e.g., CF_3-CF**:** and •F_2C-CF_2•) (Buravtsev 1994, Buravtsev et al. 1996, and Buravtsev and Kolbanovskii 1998). However, the system seems incomplete from a modeling standpoint at this time, and that degree of detail was not pursued in this study.

Additional side reactions also can intrude into the simple reaction system previously outlined. Particularly at higher temperatures, disproportionation of the fluorocarbons to species of higher and lower fluorine content begins, though the mechanisms are not as well understood in detail. For example (and as earlier alluded to), PFIB (or at least the reaction system under conditions where PFIB was present in quantity) produced a mix of products at higher temperatures including solids of low fluorine content (average formula apparently approximately $C_{1.25}F$) plus saturated fluorocarbons such as C_2F_6 and CF_4 (Atkinson and Atkinson 1957). In the decomposition of C_3F_6, at higher temperatures where PFIB and 2-C_4F_8 were formed, a considerable fraction of the reactant was lost to formation of solids of reduced fluorine content (Matula 1968).

In the process of developing these mechanisms, many rate constant equations have been proposed. Rate constants are typically presented in a form such as:

$$k_1 = 10^{17} \exp(-331 \text{ kJ mol}^{-1} / RT) \text{ s}^{-1} \quad ,$$

where k_1 (in this case, from Buravtsev et al. 1985) applies to the rate of reaction 1 per the rate equation

$$-d [c\text{-}C_4F_8]/dt = k_1 [c\text{-}C_4F_8] \quad ,$$

where [c-C_4F_8] indicates the concentration of c-C_4F_8. All rate constant parameter values found are not enumerated here, but the ones selected for use in modeling are listed in Table 1 in section 3.3.

Rate constant parameters for reactions 1 and 2 are fairly well established and most of the later proposed values agree fairly well by the standards of chemical kinetics (at 1000°C, rate constants from most of the references cited varying by less than a factor of 4 for reaction 1 and by about an order of magnitude for reaction 2). Many of these rates were derived from experiments that cover the range of physical conditions of interest in this application and thus should not suffer from problems of extrapolation.

Rates are most reliable when they are directly measured, that is, measured under circumstances in which that rate (or its reverse) is the most important reaction occurring. Rate constants derived under circumstances in which other reactions play a major role are harder to determine accurately. Reaction 3 has fewer proposed rate constants and they vary by about 1½ orders of magnitude at 1000°C, the variability probably caused by this factor. Frequently, kinetics models are used to assist in establishing values of rate constants. The model attempts to duplicate the overall evolution of species observed experimentally, and rate constant values are adjusted to achieve this duplication. This can be a great aid in elucidating and bounding rate constants in moderately complicated systems; however, used uncritically this can easily lead one seriously astray. A case in point is a model involving thermal decomposition of CHF_2Cl that incorporates all the major reaction steps previously listed. Apparently, experimental results were used to fit the rate constant parameters, but with results at great variance with the rest of the literature (Broyer et al. 1988). For example, the decomposition and formation rate listed for c-C_4F_8 (reaction 1 and its reverse) are 10 to 12 orders of magnitude lower than other researchers report, and many other (but not all) rates reported in that work suffer similarly. In short, literature rates should not be used uncritically.

A very important rate constant for our purposes is that of reaction 4, as it is the step leading directly to formation of PFIB. Two expressions for the rate constant were found for this reaction as written (Buravtsev et al. 1989b; Bauer and Javanovic 1998), and two other sources (Atkinson and Atkinson 1957; Matula 1968) gave overall rate information for decomposition of C_3F_6 to PFIB plus other products. These last two were heated reactor experiments done at temperatures in the range of 550 to 675°C for times ranging from tens of minutes to hours, and the rate constants are in good agreement with one another in that range. Bauer's rate is part of a kinetics model used to simulate experimental data from a fast flow-through reactor at temperatures ranging from 670 to 770°C and for times from 0.07 to 10 s. Buravtsev's rate similarly is part of a kinetics model used to explain experimental results, but for conditions found in a piston compression system that are much faster (times on the order of 1 ms) and hotter (temperatures ranging from 880 to 1500°C).

Each of these rates duplicates observed PFIB formation rates for conditions in their own time-temperature-composition regime. Extrapolated to other conditions, however, the rates are less accurate. Extrapolated to a common temperature, the rate derived from the lowest temperature range (Matula 1968) gives the highest rate constant and that from the highest range (Buravtsev et al. 1989b) gives the lowest, a trend suggesting the current state of knowledge is incomplete in regard to this system. The best that can probably be done is to use the rate constant derived from the conditions most closely resembling the physical conditions of interest. Buravtsev's rate is probably the most appropriate to use for fast high temperature systems (e.g. a flame – oxygen ignored – or other systems involving rapid heating and cooling of gas). Matula's is probably most appropriate for lower temperature long-duration heating.

Subjectively, Buravtsev's rate seems to be on sounder ground than Bauer's, if only because his articles appear to more critically evaluate each rate used within his kinetics model. Bauer's model, at least in the context of the discussion in the article, offers no explanation for the source of the rates used in his kinetics model. Many are clearly well accepted values for well-established reaction steps, but a few reactions are included that have been generally dismissed or do not appear in the literature. These reactions, however, are included with rates that are plausible on thermodynamic grounds and which do no apparent harm to the overall result. One example was the earlier cited decomposition of c-C_4F_8 directly to CF_2 and C_3F_6, and another is an additional route to PFIB:

$$2\,C_2F_4 \leftrightarrow \text{i-}C_4F_8\quad.$$

No other reference to this reaction was found in either this literature search or that cited by Bauer. This reaction would require quite a bit of bond rearrangement, and thus seems mechanistically less plausible than reaction 4. The rate constant given is about the same as for reaction 4, so its presence in a reaction model should not greatly affect the predicted net PFIB formation. It is not adopted in the model used in the present study.

Despite these criticisms, we will, in general, use Bauer's rate for reaction -4 as our base case, more for conservatism than for any particular subjective opinion as to its superiority. Scenarios that clearly involve longer time and lower temperature will also be examined using the Matula rate.

Other reactions may also be important in that they lead to alternate products (and thus may reduce PFIB formation). Among these are

5. $\text{i-}C_4F_8 \rightarrow C_2F_6 + C_XF$

a "high temperature" (above 700°C) decomposition route for PFIB (Atkinson and Atkinson 1957),

6. $\text{2-}C_4F_8 \leftrightarrow 2\,C_2F_4$

and

7. $\text{2-}C_4F_8 \leftrightarrow C_3F_6 + CF_2$

from Buravtsev et al. (1989b). Similar reactions producing the other linear butene, 1-C_4F_8, are reported to have much lower rates. An alternative expression for the formation of C_3F_6

8. $1\tfrac{1}{2}\;C_2F_4 \rightarrow C_3F_6$,

(Buravtsev et al. 1985) was included in the available list of reactions for comparison purposes but had no major effect on model results and is not used in the simulations discussed later.

Numerous other reaction steps involving fluorocarbon species were found in the literature search, including reactions that lead to the formation of saturated fluorocarbons, e.g.

$$CF_2 \leftrightarrow CF + F$$

and

$$CF_2 + F \leftrightarrow CF_3$$

as well as reactions of the class

$$2\ C_nF_{2n+1} \leftrightarrow C_{2n}F_{2n+2}$$

(see, for example, Kerr 1981). Such reactions would have to be balanced by reactions leading to the formation of compounds (probably solids) with an F-to-C ratio lower than 2. The rates of many of these reactions were examined at the physical conditions of interest in the present study and found to be generally much slower than those forming the various low molecular weight fluorocarbons previously discussed. To minimize complication in modeling, and because the details of evolution of such species is outside the bounds of what is needed to achieve the goals of this study, reactions in this class were not explored. These classes of products will be idealized by the products found in reaction 5 and by inclusion of part of the product distribution (in addition to PFIB) reported by Matula (1968).

From the above-listed rates it is possible to generate order-of-magnitude predictions of degradation and product buildup for a specified set of physical conditions (concentrations, time, temperature). Decomposition of c-C_4F_8 is something of a standard reaction in the literature (though the later stages leading to PFIB are not), so there are opportunities to compare model results with experimental results. Such comparisons, however, will apply to conditions in which the fluorocarbon is not mixed with significant quantities of other reactive materials (such as O_2 or H_2O).

2.3.2 Oxidation Reactions

Rate information on thermal or chemical degradation of fluorocarbons in the presence of air, oxygen, or water vapor is much less complete. It is clear that degradation of c-C_4F_8 in air will begin in the same manner as in the absence of air, with decomposition to C_2F_4. That implies that the temperature of onset of degradation will be similar. Once C_2F_4 is produced, the presence of water or oxygen creates new reaction paths leading to products other than PFIB, such as COF_2, CO, HF, and CO_2. Unlike the case of pure thermal decomposition of c-C_4F_8, most experimental work (Duus 1955; Fletcher and Kittelson 1968; Matula et al. 1970; McHale et al. 1971) does not include time evolution of products, but only their final composition.

The most comprehensive study of high temperature oxidation reaction kinetics was conducted by Keating and Matula (1977). They used shock tube methods to examine the kinetics of the system of C_2F_4 and O_2 between 1400 and 2230°C. They regarded the primary reaction as consisting of

$$C_2F_4 \leftrightarrow 2\ CF_2\ .$$

$$CF_2 + O_2 \rightarrow COF_2 + O\ ,$$

and

$$COF_2 \rightarrow COF + F\ .$$

A model incorporating some 20 reactions was used to duplicate the major features of combustion at these conditions. Bauer also studied the $C_2F_4 + O_2$ system in a shock tube. The temperature range was somewhat lower (930 to 1730°C). Major products were CO, COF_2, CF_4, and C_2F_6. The major reaction steps suggested include

$$C_2F_4 \leftrightarrow 2\,CF_2\,,$$

$$CF_2 + O_2 \rightarrow COF_2 + O\,,$$

and

$$C_2F_4 + O \rightarrow COF_2 + CF_2\,,$$

plus other reaction steps that produce CF_3 and CF_4. (Bauer et al. 1969). In another shock tube experiment, the system $C_2F_4 + O_2$ is described as proceeding by

$$C_2F_4 \leftrightarrow 2\,CF_2$$

and

$$CF_2 + O_2 \rightarrow CO + 2\,F$$

with rate constants for these two reactions given for temperatures between 1230 and 2030°C (Modica and LaGraff 1965). In that work, COF_2 was not observed.

Once one begins to consider the fate of the initial oxidation products of CF_2 (that is, CO, FCO, and COF_2), an expanding network of reactions makes the system more and more complex. Using kinetic information found in Keating and Matula (1977) or Kerr (1981), the rates of some of the reactions that are the next steps in oxidation were examined, for example

$$CO + F_2 \leftrightarrow FCO + F\ ,$$

$$FCO + M \leftrightarrow CO + F + M\,,$$

$$COF_2 + F \leftrightarrow FCO + F_2\,,$$

$$COF_2 + M \leftrightarrow FCO + F + M\,,$$

and

$$CF_3 + O \rightarrow COF_2 + F.$$

This examination suggested that once oxidized, CF_2 will not be regenerated in quantity. A more and more complicated treatment of oxidation of CF_2 would not be realistic if it neglected the presence of hydrogen-containing compounds (either as fuel or combustion products in a flame or humidity in the air), and the treatment discussed in section 3 of this report stops after the initial stages of oxidation.

3. KINETICS MODELING

Evaluation of the interaction of numerous chemical species via several chemical reaction steps generally involves some sort of mathematical modeling. For the present study, a simple model of chemical kinetics was developed and used to evaluate the possibility of formation of PFIB under various conditions representative of those of interest to the coolant replacement program. The model is described in more detail in Appendix A.

Application of the model to a specific problem requires attention to two additional topics: the selection of chemical species and reactions pertinent to the problem and the definition of the physical and chemical conditions that apply.

The two operational issues in question, namely formation of PFIB in a propane burner and formation during welding operations, each require definition of plausible or at least bounding conditions as to initial gas composition as well as time-temperature-gas mass flow histories for each scenario. The physical conditions assumed in these scenarios are described as each problem is discussed.

Kinetics modeling can be very complex (as in atmospheric chemistry or combustion modeling), requiring supercomputer-grade computational resources. This model was developed for a specific problem and runs on a personal computer and thus is somewhat limited in terms of the degree of complexity it can practically handle (i.e., number of reactions and species, and degree of "stiffness" of problem, a term relating to the variation in rates between fastest and slowest). The model was written to focus on formation of PFIB from pyrolysis products of c-C_4F_8, and as such, the reaction sets used for the various scenarios neglect or idealize species and reactions that are not directly pertinent to the formation of PFIB.

In the literature review section, the reaction mechanism for the formation of PFIB was discussed, as were the general conditions under which PFIB has been observed to form. Those are primarily pyrolysis conditions – high temperature but lacking other reactants such as water vapor or oxygen. Though a flame environment does not appear to be conducive to PFIB formation, to bound the possible formation rate of PFIB, scenarios were examined in which c-C_4F_8 was subjected to the thermal environment, but not to the chemical species present (i.e., oxygen and water vapor and, for flame scenarios, common combustion radicals such as HO_2, O, OH, and CO). In other runs, oxygen reactions were included in an attempt to more realistically depict the chemical environment as well.

3.1 METHOD

The basic strategy of the model is to straightforwardly numerically integrate a set of chemical kinetics equations to track the time evolution of chemical species. The kinetics model is designed to follow the composition of a packet of gas that passes through a specified time-temperature history, as in a streamline passing through a flame or heated zone. The chemical result at the end of this timeline may be that desired for a particular scenario or a portion of that result, as in the case of the burner flame, in which the results of several timelines representing different streamlines are integrated to give a composite result. It should be noted that the time-temperature history is an externally specified function in this model. There is no internal feedback between degree of reaction and temperature. Heat of reaction (which might warm or cool the gases) is not considered. We are examining scenarios in which the inclusion of coolant is a minor perturbation on other events that thermally dominate the system (e.g. burning of propane). Details of the model are discussed in Appendix A.

3.2 DEFINING A "BASE" SET OF REACTIONS

From the literature, a set of reaction steps was selected for the pyrolysis of c-C_4F_8 with emphasis on the formation and destruction of PFIB (i-C_4F_8). The reaction steps included are as follows:

1 $\quad$ c-$C_4F_8 \rightarrow 2\,C_2F_4$,

-1 $\quad$ $2\,C_2F_4 \rightarrow$ c-C_4F_8 ,

2 $\quad$ $C_2F_4 \rightarrow 2\,CF_2$,

-2 $\quad$ $2\,CF_2 \rightarrow C_2F_4$,

3 $\quad$ $CF_2 + C_2F_4 \rightarrow C_3F_6$,

-3 $\quad$ $C_3F_6 \rightarrow CF_2 + C_2F_4$,

4 $\quad$ i-$C_4F_8 \rightarrow C_3F_6 + CF_2$,

-4 $\quad$ $C_3F_6 + CF_2 \rightarrow$ i-C_4F_8 ,

5 $\quad$ i-$C_4F_8 \rightarrow C_2F_6 + (CF)_n$,

6 $\quad$ 2-$C_4F_8 \rightarrow 2\,C_2F_4$,

-6 $\quad$ $2\,C_2F_4 \rightarrow$ 2-C_4F_8 ,

7 $\quad$ 2-$C_4F_8 \rightarrow C_3F_6 + CF_2$,

-7 $\quad$ $C_3F_6 + CF_2 \rightarrow$ 2-C_4F_8 ,

8 $\quad$ $1\frac{1}{2}\,C_2F_4 \rightarrow C_3F_6$, and

9 $\quad$ $C_3F_6 \rightarrow {}^{3}/_{8}$ i-C_4F_8 $+ {}^{3}/_{16}$ 2-C_4F_8 $+ {}^{3}/_{4}\,(CF)_n$.

In these reactions, $(CF)_n$ represents fluorinated carbon solids of indeterminate composition, and C_2F_6, while the major saturated fluorocarbon observed, is not the only one (CF_4, C_3F_8, and n-C_4F_{10} being others observed in various studies).

The model is constructed so that a subset of the reactions listed can be selected in order to compare the results of different postulated mechanisms or rate constant values. For each reaction, a formula for the rate constant was chosen from those found in the literature search. The parameters for these formulae are listed in Table 1. Where several rate constant formulae were available, the basis for choosing a particular one was based on judgment regarding the credibility of that rate for the conditions of interest. In a few cases, there was considerable variability of rates with no clear way to distinguish their relative merits. In such cases, alternate formulations are included, the intent being to choose one rate or the other and compare the outcomes of otherwise identical scenarios. Reactions 8 and 9 fall into this category. Similarly, two rate constant formulae for reaction −4 are included in the model from two sources, giving disparate rate constant parameters for the same reaction step. The base set of reactions actually used in the pyrolysis runs included reactions 1 through 7 and their reverse reactions. The base case rate constant used for reaction −4 was that due to Bauer and Javanovic (1998), listed as "−4a" in Table 1.

3.3 REACTIONS INVOLVING O_2

The previously described reaction set treats decomposition purely as a pyrolysis process — that is, it does not include reactions involving H, OH, O, HO_2, etc. In descriptive chemistry references, the general indication is that an actual flame environment (as opposed to pure heating) suppresses formation of PFIB, so presumably full inclusion of combustion reactions would lead to a lower PFIB formation rate than quoted here. Pyrolysis cases (using reactions from the set 1 through 9) should, however, give an upper limit to the formation of PFIB and may be at least potentially representative of what might occur in an environment in which oxygen had been fully depleted – for example, a fuel-rich flame.

Inclusion of a complete set of reactions for the pyrolysis, oxidation, and (for the propane burner) fuel combustion would be an extremely complex task, far beyond the intended scope or available resources of this effort. To capture some of the effect of oxygen on the formation of PFIB, it is therefore necessary to focus on a limited number of key reaction steps and dismiss those that are not significant. About three dozen reaction steps involving fluorocarbons and atomic or molecular oxygen were examined within the context of the range of compositions and temperatures of interest. It was clear that the most important reactions involved the oxidation of the CF_2 radical.

Table 1. Reaction rate constant parameters

ID	Reaction	E_A (J/mol)	A^a	n^b	References
1	$c\text{-}C_4F_8 \rightarrow 2C_2F_4$	331,000	1.000E+17	0	Buravtsev et al. 1985
–1	$2C_2F_4 \rightarrow c\text{-}C_4F_8$	131,000	2.512E+12	0	Buravtsev et al. 1985
2	$C_2F_4 \rightarrow 2CF_2$	285,000	2.800E+15	0	Schug and Wagner 1978
–2	$2CF_2 \rightarrow C_2F_4$	9,145	4.740E+11	0	Schug and Wagner 1978
3	$C_3F_6 \rightarrow C_2F_4 + CF_2$	345,971	1.580E+13	0	Bauer and Javanovic 1998
–3	$CF_2 + C_2F_4 \rightarrow C_3F_6$	31,400	6.457E+09	0	Kerr 1981
4	$i\text{-}C_4F_8 \rightarrow C_3F_6 + CF_2$	384,920	1.200E+16	0	Bauer and Javanovic 1998
–4	$CF_2 + C_3F_6 \rightarrow i\text{-}C_4F_8$	238,000	3.981E+12	0	Buravtsev et al. 1989b
–4a	$CF_2 + C_3F_6 \rightarrow i\text{-}C_4F_8$	123,014	8.385E+07	1	Bauer and Javanovic 1998
5	$i\text{-}C_4F_8 \rightarrow C_2F_6 + (CF)_n$	346,017	1.100E+14	0	Atkinson and Atkinson 1957
6	$2\text{-}C_4F_8 \rightarrow 2C_2F_4$	417,000	2.512E+11	0	Buravtsev et al. 1989b
–6	$2C_2F_4 \rightarrow 2\text{-}C_4F_8$	166,000	2.512E+12	0	Buravtsev et al. 1989b
7	$2\text{-}C_4F_8 \rightarrow C_3F_6 + CF_2$	380,000	2.512E+13	0	Buravtsev et al. 1989b
–7	$CF_2 + C_3F_6 \rightarrow 2\text{-}C_4F_8$	121,000	7.943E+10	0	Buravtsev et al. 1989b
8	$1.5\ C_2F_4 \rightarrow C_3F_6$	188,000	3.162E+10	0	Buravtsev et al. 1985
9	$C_3F_6 \rightarrow i\text{-}C_4F_8, 2C_4F_8, (CF)_n$	197,485	1.202E+08	0	Matula 1968
10	$CF_2 + O_2 \rightarrow COF_2 + O$	110,876	2.000E+13	0	Keating and Matula 1977
11	$CF_2 + O_2 \rightarrow CO + 2F + O$	62,760	2.000E+12	0	Kerr 1981
12	$CF_2 + O \rightarrow CO + 2F$	0	1.000E+13	0.5	Keating and Matula 1977[c]
13	$F + C_2F_4 \rightarrow \frac{1}{2}\ C_2F_6 + CF_2$	0	2.300E+13	0	Kerr 1981[c]
14	$CO + O_2 \rightarrow CO_2 + O$	159,000	3.100E+11	0	Kerr 1981
15	$2O \rightarrow O_2$	0	2.400E+10	–0.5	Keating and Matula 1977[d]

[a] Rates are in units of $(cm^3/mol)^{(N-1)}/s$, where N is the number of moles of reactants in the chemical reaction equation.

[b] Rate equations are of the form $k = AT^n \exp(-E_A / R\,T)$.

[c] Reaction products are idealized; see text for explanation.

[d] Rate is treated as second order, although original data was for a third-order reaction with an inert participant. Effect of inert participant was taken to be constant and subsumed into A.

This occurs via the following reactions:

10. $CF_2 + O_2 \rightarrow COF_2 + O$,

11. $CF_2 + O_2 \rightarrow CO + 2\,F + O$,

and

12. $CF_2 + O \rightarrow FCO + F$.

These reaction steps are critical because they remove CF_2 from availability, essentially permanently, as the reverse reactions are not rapid in the range of physical conditions of interest. The CF_2 thus removed is unavailable to form PFIB.

An initial attempt was made to explore the product split between oxidized carbon products and fluorinated products by adding reactions 10 and 12 to the pyrolysis set and, for simplicity, treating the FCO + F in reaction 12 as forming exclusively COF_2 . The results predicted that, when oxygen is in excess, CF_2 is virtually all oxidized (in that scheme, to COF_2, although that compound should be considered to represent all subsequent products of oxidation, such as CO and CO_2). Little CF_2 survived to recombine as the gas cooled to form higher fluorocarbons, including PFIB. While it is useful to conclude that PFIB would not form in quantity in the presence of pyrolyzing conditions and oxygen, COF_2 is also a toxic compound. At the sponsor's request, the reaction set was carried a step further to explore the product distribution among the various oxidation products of carbon by inclusion of additional reaction steps. The following discussion covers only this extension, and the earlier more limited oxygen reaction set is not further discussed.

Numerous reaction steps for which kinetic information was available were considered for inclusion in this extended set. Relative reaction rates were calculated over the range of temperatures and reagent concentrations of interest, and those reaction steps that had the fastest rates were retained, while those relatively slower involving the same reagents were discarded. For example, C_2F_4 will react directly with atomic O, but at a rate several orders of magnitude lower than the CF_2 + O reaction Consequently, the former reaction was not included. The reaction set that was retained included reactions 10 through 12 plus:

13. $F + C_2F_4 \rightarrow C_2F_5$,

14. $CO + O_2 \rightarrow CO_2 + O$,

and

15. $2\,O + M \rightarrow O_2 + M$.

Reaction 13 is somewhat faster than many similar reactions of atomic fluorine with unsaturated fluorocarbons. In this reaction model, rather than adding numerous reactions of fluorocarbon radicals leading to saturated perfluorocarbon products, C_2F_5 is taken to be equivalent to ½ C_2F_6 + CF_2, a simplification in keeping with the earlier treatment regarding C_2F_6 as representing all saturated perfluoroalkanes. Reaction 12 produces FCO, and FCO participates in numerous additional reactions, generally leading to CO or COF_2. On examination of the relative rates of the available reactions steps at the conditions of interest, it was determined that nearly all FCO would decompose to CO rather than COF_2. Rather than including an additional species and several additional reactions (to a reaction set already bogging down the kinetics model), Reaction 12 was idealized as:

$$12'.\quad CF_2 + O \rightarrow CO + 2F$$

As before, the parameters used to calculate these rate constants are listed in Table 1.

3.4 PROPANE FLAME (HALOGEN TESTER)

A propane torch with a special "Halide Leak Detector" burner tip (manufactured by BenzOmatic of Medina, New York) is presently used to test for the presence of coolant in the air. It functions by mixing propane with air (the air possibly containing coolant vapor) and burning it with the flame directed at a heated copper disk. Color changes in the flame are indicative of the presence of halogen-containing gases. The problem at hand is to estimate (or at least to bound) the production of PFIB in the exhaust gas from this torch. Details of the physical model of this propane flame are described in Appendix B. Briefly, temperature vs. time profiles were devised to approximate the thermal history the gas would experience as it transits the burner flame in each of a limited series of streamlines at several radial intervals. The specific parameters used in the model are listed in Table 2. In each streamline, the gas entering the flame front is assumed to instantly rise from ambient temperature to T_{max}, remain at that temperature for 0.002 s, and then decline at the listed rate until it reaches 123°C (400 K). The results for each streamline are taken to represent the effect on the gas passing through an annular region within ± 10% of the burner tip radius of streamline's radius. For example, the "30%" streamline, results are applied to all gas flowing in an annulus between 20 and 40% of the burner tip radius).

Table 2. Parameters for temperature-vs-time profile used for streamlines in propane flame

Streamline at X% of tip radius	Fraction of flow	T_{max} (°C)	T decline (°C/s)
10%	7.84%	1785	–20,000
30%	21.60%	1785	–27,900
50%	29.60%	1785	–52,600
70%	28.00%	1670	–80,000
90%	12.96%	1477	–101,000

A specific inlet concentration of coolant (and, if appropriate, oxygen) is postulated. For species initially absent, a starting composition greater than zero must be specified for computational reasons. This value was set at 1 ppb or lower in all runs.

The chemical kinetics model is run for each of these time-temperature-composition cases, and the computed exiting gas composition recorded. Each streamline is given a weighting factor based on mass flow in its radial interval (listed as "fraction of flow" in Table 2), and the average exiting composition of gas is computed, from which mass flow factors for each compound are calculated.

3.4.1 Pyrolysis Cases

The chemical kinetics model was first run for a series of temperature profiles simulating a pure pyrolysis environment representative of the thermal (but not necessarily the chemical) environment experienced in a propane flame.

Evolution of reaction products is depicted graphically in Figure 1 for a brief period at the beginning of the run for the base case (5000 ppm coolant), using the temperature profile defined for the streamline at 30% of the burner tip radius. This figure illustrates some important features of a flame temperature environment as regards fluorocarbon pyrolysis. In a very short time (about 10 ns), most of the starting coolant decomposes to CF_2. Secondary and tertiary products reach their equilibrium values at fairly low concentrations in 10 to 60 ns. PFIB declines from its initial 1 ppb level over a time scale longer than depicted on this graph. It has reached its high temperature equilibrium by the time the temperature begins to decline at 2 ms. Basically, it can be seen from this figure that flame temperature does not favor formation of PFIB. Only when the gas cools sufficiently for formation of C_3F_6 does the PFIB increase in concentration.

Figure 2 shows the evolution of products for the same run up to 0.1 s. As the gas cools, the level of C_2F_4 increases, allowing for further formation of other species. As the temperature declines, various reaction rates decline to the point that different products cease being formed. Between 1200 and 700°C, most product compositions cease changing until, at the final temperature (500°C), only the slow combination of remaining trace levels of CF_2 to form C_2F_4 persists. This suggests that in a pyrolysis environment, the maximum temperature is not critical if it exceeds a certain level (perhaps 1400°C). It is the time spent within a critical temperature range that favors the formation of PFIB.

Similar runs at 10, 50, 70 and 90% of burner radius were carried out, and the results of each weighted as previously described. The predicted PFIB production in this case was 0.7 ppm. Output summaries for all cases are in Tables C-1 through C-3 of Appendix C.

The results are more succinctly summarized in Table 3. Column 1 indicates how many streamlines were included in the flow weighting. For a few sensitivity cases, only a single

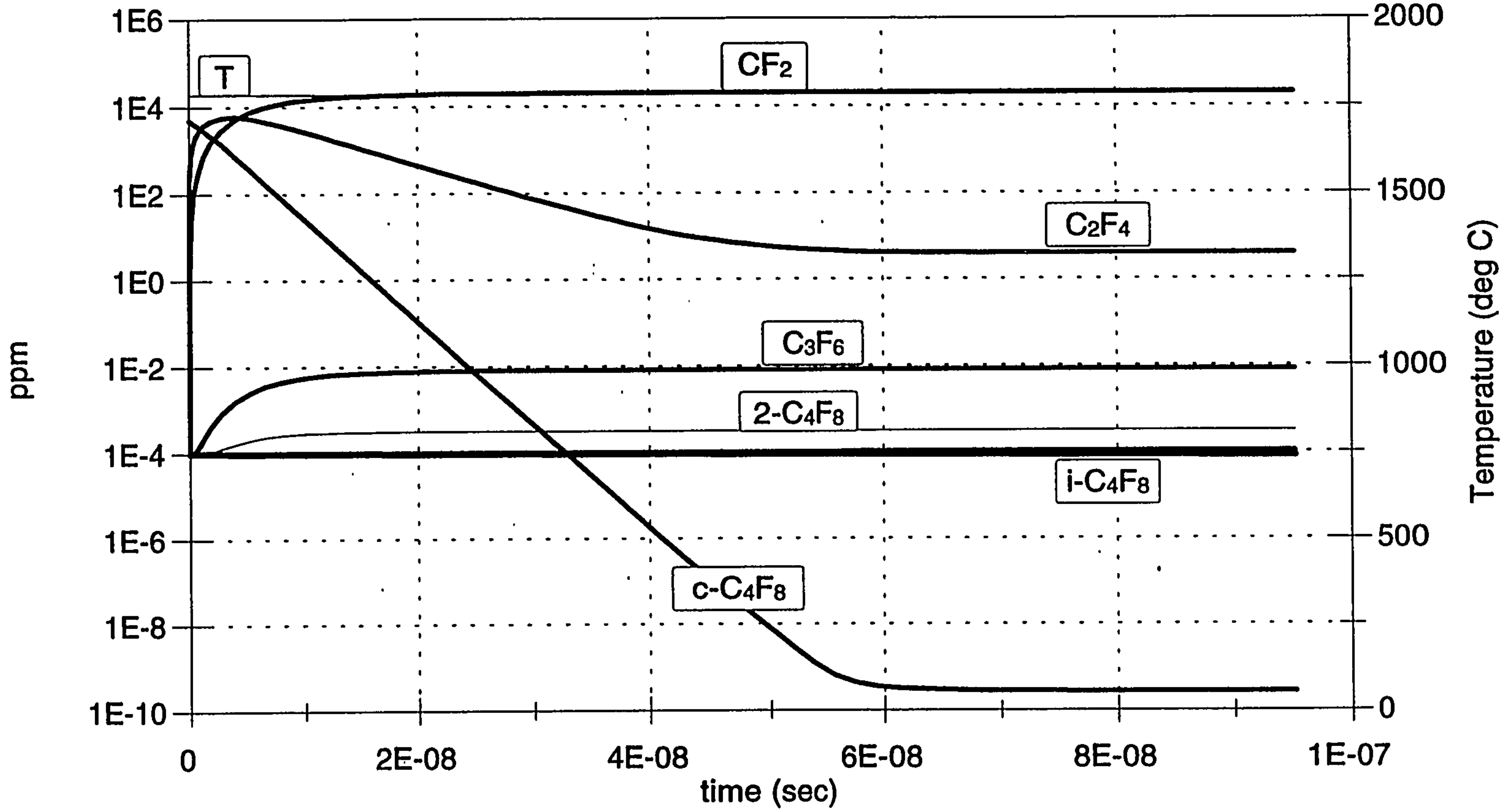


Figure 1: Kinetics model predictions for early phases of propane flame in the 30%-of-radius streamline. (Base reaction set used; oxygen reactions ignored)

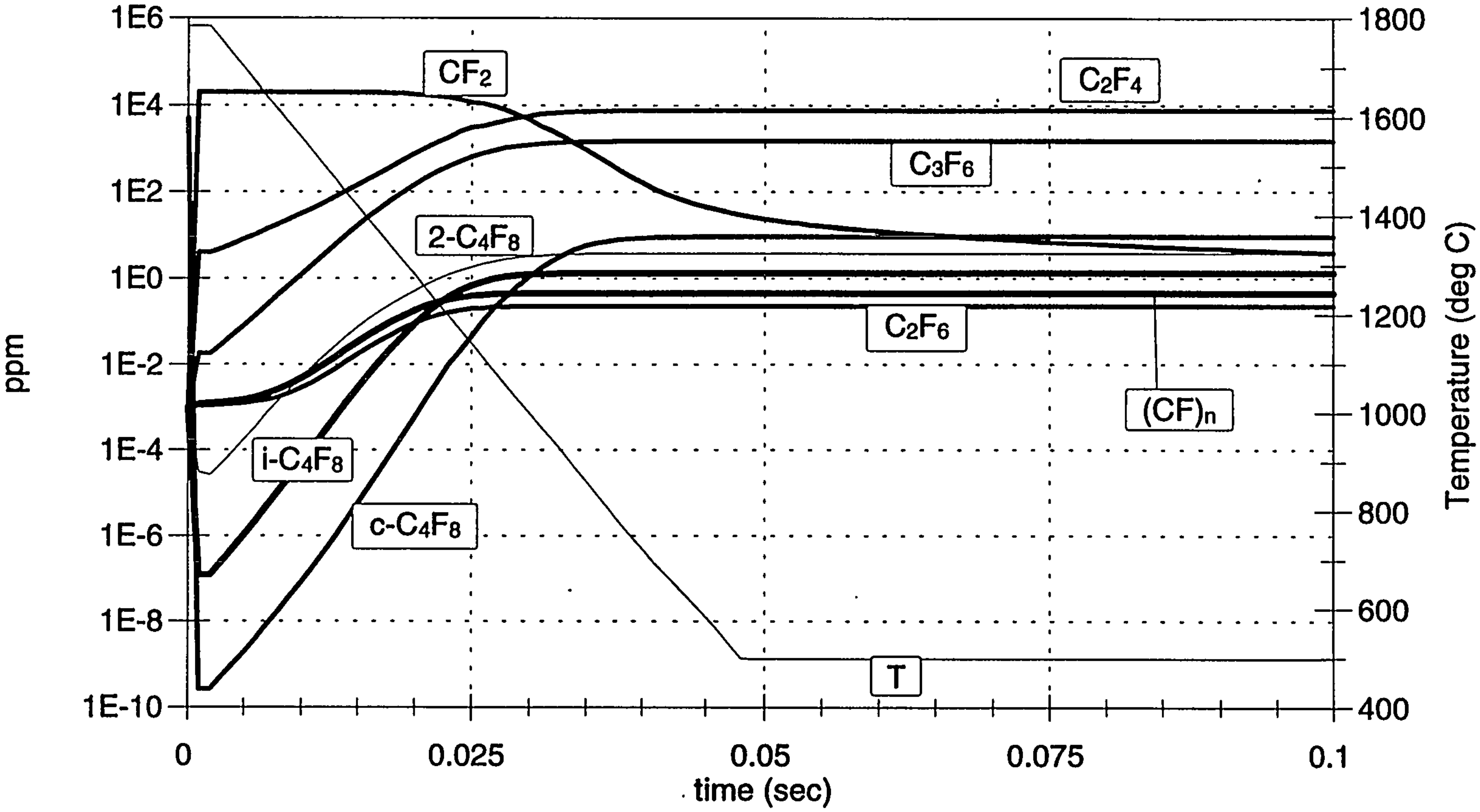


Figure 2: Kinetics model predictions for later phases of propane flame in the 30%-of-radius streamline. (Base reaction set used; oxygen reactions ignored)

Table 3. Summary of results for propane burner cases

Case	Rate set	Initial		Final			Production rate			Notes[a]
		c-C_4F_8 (ppm)	Oxygen (ppm)	PFIB (ppm)	COF_2 (ppm)	CO (ppm)	PFIB (sccm)	COF_2 (sccm)	CO (sccm)	
				Pyrolysis cases						
5 streamlines	Base	1,000	0	0.0035	—	—	7.6E–07			
5 streamlines	Base	5,000	0	0.69	—	—	0.00015			
5 streamlines	Base	20,000	0	28	—	—	0.0061			
5 streamlines	Buravtsev	5,000	0	0.0022	—	—	4.8E–07			*b*
5 streamlines	Buravtsev	20,000	0	0.19	—	—	4.1E–05			*b*
9 streamlines	Base	5,000	0	0.69	—	—	0.00015			
30% SL	Matula	5,000	0	9.5	—	—	0.0021			*b,c*
30% SL	Base	5,000	0	1.3	—	—	0.00028			*c*
30% SL	Buravtsev	5,000	0	0.0048	—	—	1.05E–06			*b,c*
				Oxygen cases						
5 streamlines	Base	20,000	27,000	< 1 ppb	9,160	42,700	< 2E–07	2.0	9.3	*a*
30% SL	Base	5,000	27,000	< 1 ppb	3,730	15,700	< 2E–07	0.8	3.4	*a,c*
30% SL	Base	20,000	200,000	< 1 ppb	14,800	50,600	< 2E–07	3.2	11.0	*a,c*
30% SL	Base	20,000	5,000	19	1,880	8,120	0.0041	0.4	1.8	*a,c*

[a] Production rates for CO and COF_2 provide an indication of the likely ratio of these products but are not likely to be quantitatively realistic, as combustion products of the propane fuel are not included.

[b] Cases whose rate set is designated as Matula used Reaction 9 for formation of PFIB but not reaction –4 (see text). Cases designated as Buravtsev used the rate constant labeled –4 in Table 1; base rate sets used entry –4a (Bauer and Javanovic 1998).

[c] Single streamline (at 30% of radius). Production rate entries assume all gas experiences this thermal environment in these cases.

streamline is used (at 30% of radius). Comparison of the single streamline results with the average results for the same case indicates that the production rate is exaggerated in the single streamline case by this simplification.

The second column indicates the reaction set used. The base set is the one previously discussed, using the Bauer-derived PFIB production rate. The Buravtsev set is identical except for the substitution of Buravtsev's rate for reaction −4. The Matula reaction set used the alternate reaction (reaction 9) for production of PFIB. These are discussed in the following sections.

The third and fourth columns indicate the initial quantities of coolant and oxygen (if any) in that case. The next three columns give the final concentration of PFIB, COF_2, and CO. The final three translate these concentrations into production terms by multiplying by the number of standard cubic centimeters per minute of gas entering the flame (218 sccm).

The first three cases vary the initial concentration of coolant. Evidently, the combined kinetics of this system results in PFIB production higher than first order (in fact, varying as about the 2.8 power) in the initial quantity of $c\text{-}C_4F_8$, though this certainly overstates the case at some point. In this calculation series, the flame temperature– time profile is taken as a constant. However, when 2% of the incoming gas is coolant, there will be significant cooling due to reaction and simply to the heat capacity of the gas. At some point, the coolant will behave more as a fire-extinguishing agent than as a fuel impurity, but this factor is not taken into account in this study.

3.4.1.1 Sensitivity cases

A number of variations on these cases were run to explore the sensitivity of the predictions to uncertain parameters. Two involved use of the alternate rate equations found for the formation of PFIB. As indicated in the literature review section, two formulae (Buravtsev et al. 1989b; Bauer and Javanovic 1998) were found for reaction −4 with reaction rates between a factor of 10 and 100 apart. As discussed earlier, Bauer's rates were derived from somewhat lower-temperature longer-contact-time experiments. Buravtsev's physical conditions (temperatures spanning flame temperatures and contact times on the order of milliseconds) are probably a closer match to the time and temperature environment in this flame and hence is the more appropriate rate. The rate for PFIB formation given by Matula (1968) was also used and predicts higher PFIB formation than the base case, but is derived from experiments at physical conditions far removed from the time and temperature history experienced in a gas flame and is thus likely inappropriate.

Other sensitivity runs explored the effect of variations on the baseline temperature profile, including alternate cooldown rates, peak temperatures, and grid sizes. The peak temperature chosen for the base case, 1785°C, was taken as a plausible temperature for a slightly rich or lean propane-air flame. The peak temperature could be lower due to poorer fuel-air stoichiometry or the presence of coolant. At the dwell time used, equilibrium (and nearly complete dissociation to CF_2) was established very quickly. No effect of reduced peak temperature was observed until the peak was below about 1400°C, at which point PFIB production falls. As these cases yielded results identical to the base case, they are not listed in the tables.

3.4.1.2 Variations on the Base Case

Since PFIB requires CF_2 and C_3F_6 to form and, in the center of the flame, the fluorocarbon is largely decomposed to CF_2, it seemed possible that conditions for formation of PFIB would be more favorable near the edge of the flame (near the walls of the burner). Statements in the literature also suggest that PFIB can best be formed within a fairly narrow temperature range. A few variations on the base case were run to explore this possibility:

1. Finer grid near the outer radius of the flame. The base case grid divided the flame into five zones, each running over 20% of the radius of the burner tip. The finer radial grid used the standard radial zones (20% wide up to 80% of the radius), then a zone of 16% of the radius, then four zones (from 96% to 100% of the radius) of 1 % each. The "finer grid" case in Table C-1 and the "9 streamline" entry in Table 3 depict this case.

2. Different T(r) function. Within the outer 4%, the peak temperature vs radius was not very well defined in the Lewis and von Elbe textbook (1951). The base case simply extrapolated the $T_{max}(r)$ trend that applied throughout the flame out to the wall, while this alternate case linearly interpolates between $T_{max}(96\% \ r)$ and the wall temperature (~400K).

Neither temperature distribution is probably realistic, but they should bound the true behavior. A series of runs was carried out for these two variations and the results integrated over all the radial zones, weighting by fraction of mass flow, as before. In neither case did the PFIB formed increase over the base case. In most zones, the initial trace quantity (1 ppb) of PFIB assumed to be present never increased. There were some indications of a slightly higher local PFIB concentration in a narrow temperature range, but that effect was overwhelmed by the decline in mass flow as a function of radius.

3. Slower cooldown rate. As mentioned in Appendix B, rates of temperature decline for the various streamlines were taken from contour plots depicting streamline direction, velocity, and temperature (Lewis and von Elbe 1951). Actual dwell times at temperature could be somewhat different than the base assumption, so a series of runs explored the effect of this parameter on PFIB production. The post-burn rate of temperature decline was varied from 5000 to 80,000 deg/s, with 20,000 deg/s being the probable correct value at the center of the flame. This range of decline rates clearly spans the rates that can explain the visible flame structure. A rate of decline of 5000 deg/s for the mass flow and size of the propane flame in question would lead to a visible flame much longer than is actually observed and 80,000 deg/s should conversely lead to a much shorter flame. PFIB production was computed to be roughly proportional to the time spent in the favorable temperature range. A rate of 5000 deg/s produced about 3 times as much PFIB as 20,000 deg/s while an 80,000 deg/s decline produced about 11% as much.

3.4.2 Cases Including Oxygen Reactions

Addition of a reasonably complete set of combustion reactions (fuel, oxygen, etc.) to the pyrolysis model would be a great deal of work and was not planned as part of this project. Since, however, for the higher possible concentrations of c-C_4F_8, the PFIB production predicted from the pure pyrolysis model may be too high to ignore, some effort was spent in assessing the effect of oxygen. The reaction set used for the oxygen runs consisted of the base pyrolysis set (using the Bauer equation for reaction −4, and excluding reactions 8 and 9), plus reactions 10 through 15. As before, a radial grid was used to calculate the behavior in each of five streamlines and a flow-weighted sum performed to calculate average product formation and mass production rate.

A variable difficult to quantify in this case is the oxygen content. In air, oxygen is on the order of 20%, but after combustion, it will be much lower, or even virtually absent, depending on the details of the fuel-air ratio, temperature, dwell time, etc. In these calculations, the fuel-air reaction is idealized as simply providing an elevated temperature environment, without reference to the chemical species that might be present due to the fuel. A value for oxygen of 2.7% was chosen for the base cases in this series. This represents the oxygen that would be unconsumed by a propane-air flame that was slightly fuel lean, but not so much as to greatly affect the peak temperature.

Most of the cases also used an initial concentration of coolant of 2% (20,000 ppm). Nominally, 2.7% O_2 would be inadequate to completely combust 2% c-C_4F_8, leading to the possibility of complete consumption of oxygen and the potential for formation of PFIB from the surviving CF_2. Depending on the fuel-air mix, the available post-burn concentration might be higher or lower than this level. The flame in the burner tip is predominantly a premixed flame (that is, the fuel and oxidizer are mixed prior to burning). However, the structure of the tip provides a good supply of additional air at the edge of the flame that can diffuse into the flame if there is an oxygen deficit. Overall, an oxygen-poor environment is not likely.

In the model runs, the oxygen was indeed depleted, but most of the carbon ended up in the form of CO, COF_2, or C_2F_6 (which should be taken to represent numerous other saturated fluorocarbons not included in the reaction set). In addition to the fluorocarbon products, COF_2 and CO are listed as major products. Direct participation of combustion products or reactions is, as previously discussed, not part of this calculation, so the CO and COF_2 values listed are not very credible quantitatively. The ratio may be a more reliable reflection of the product distribution to be expected, however. In the various oxygen runs, CO and COF_2 were produced in a ratio ranging from 3:1 to 10:1 and each appeared at the percent level in the product mix. In the reaction scheme used, free atomic fluorine was also present in the product mix, which is unlikely to occur in the real event, as it would react readily with water vapor and other combustion products to form HF or other fluorinated species.

Figures 3 and 4 depict the early and later stages of one of the oxygen streamline cases (again, the 30%-of-radius streamline). The early stage is much like that of the pure pyrolysis case, in that rapid decomposition of c-C_4F_8 to C_2F_4 and then to CF_2 takes place within a short period of time (10 to 60 ns). Species that are the result of oxygen reactions (CO, COF_2, F) appear at the 1 ppm level and are rising at 0.1 µs. They eventually grow to dominate the product mix at the expense of the fluorocarbon species. As the gas cools, reactions cease, but by that time, only CF_2 survives at above a parts-per-million level. The remainder of the fluorocarbons, including PFIB (i-C_4F_8 in the graphs) have fallen to essentially zero from their nominal initial 1 ppb concentration. A lower coolant level was included in an alternate single-streamline case (0.5% coolant, as in the pyrolysis base cases). The results were similar to the 2.0% coolant case. Two additional single streamline cases were run in which a 2% coolant concentration reacted with both higher and lower concentrations of oxygen (0.5 and 20%). Only in the lowest oxygen case did PFIB production occur, a case trending toward the results of the pyrolysis cases.

3.4.3 Propane Burner -- Summary and Conclusions

The PFIB generation predicted in these calculations ranges from nil to fairly small but is not in all cases completely trivial. Due apparently to the limited time at temperatures at which the PFIB precursors CF_2 and C_3F_6 are simultaneously stable, the very high concentrations reported in some pyrolytic synthesis techniques do not appear even in the pure pyrolysis cases. Due to the interactions with other combustion products, it is very unlikely that PFIB could be produced at levels even comparable to those predicted here. The presence of oxygen at pyrolytic temperatures, though only incompletely analyzed, appears to suppress formation of PFIB.

If the PFIB formation rates predicted here give cause for concern, then it would be advisable to experimentally evaluate the system. Of the many factors that were not taken into account in this modeling study, most will tend to reduce PFIB production. Consequently, an experimental study would have a good chance of determining that productions levels were safe in this propane burner environment. The kinetics results presented here would suggest that the environment most likely to produce PFIB would involve an oxygen depleted environment, high concentration of coolant, and long contact times at temperatures in the range of 700 to 1000°C.

This analysis has concentrated on the fate of c-C_4F_8 in a flame environment, but it is quite likely that very similar results would have been obtained were the same analysis done with CFC-114 as the coolant. The C-Cl bond is weaker than the C-F bond, so it would tend to dissociate first. At flame temperatures, CFC-114 very likely would decompose largely to CF_2, just as c-C_4F_8 does. As the gas cools, a similar mix of products should form, though with the addition of HCl and

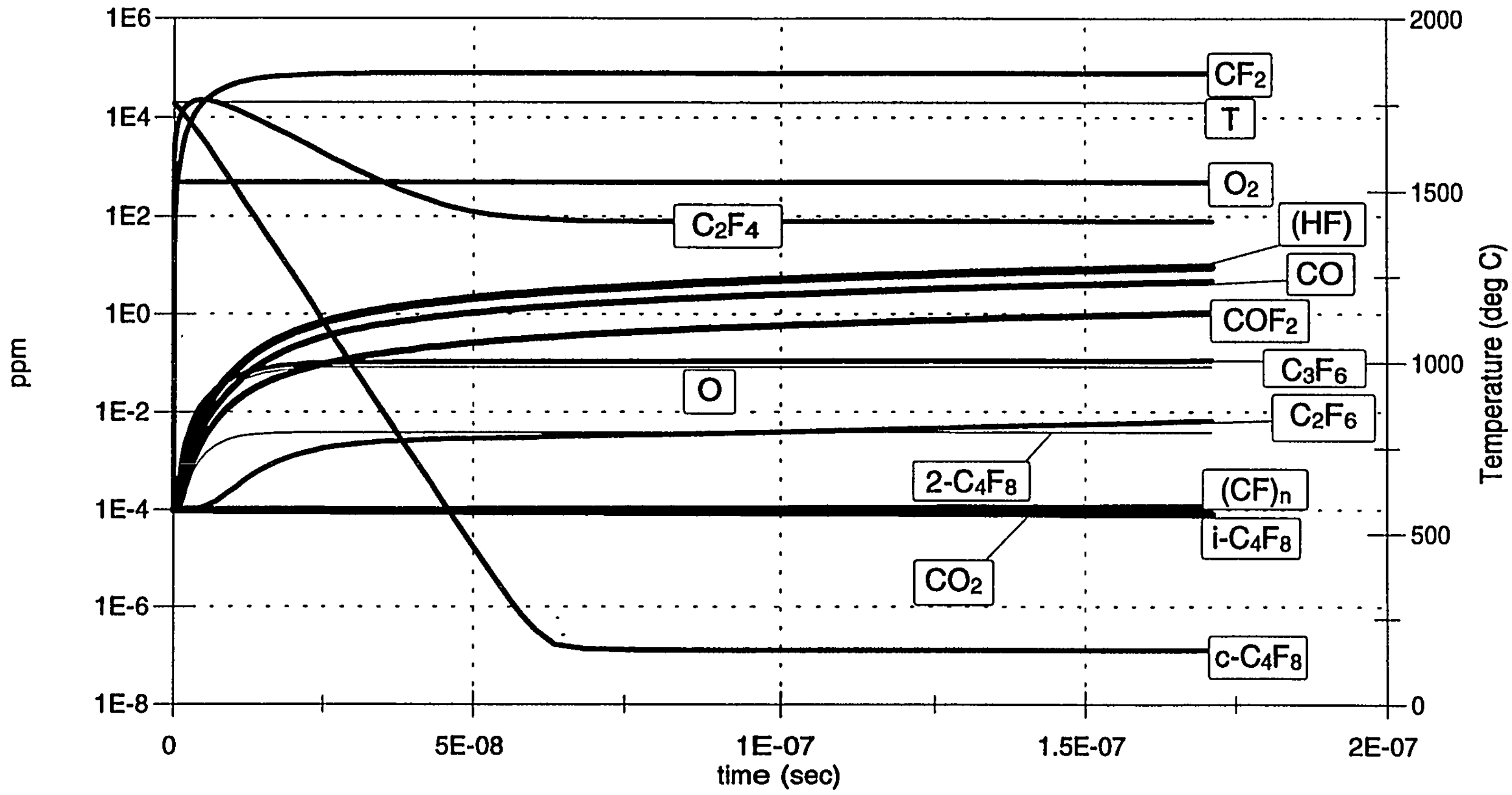


Figure 3: Kinetics model predictions for early phases of propane flame in the 30%-of-radius streamline. (Base reaction set used; oxygen reactions are considered; F from model shown as HF)

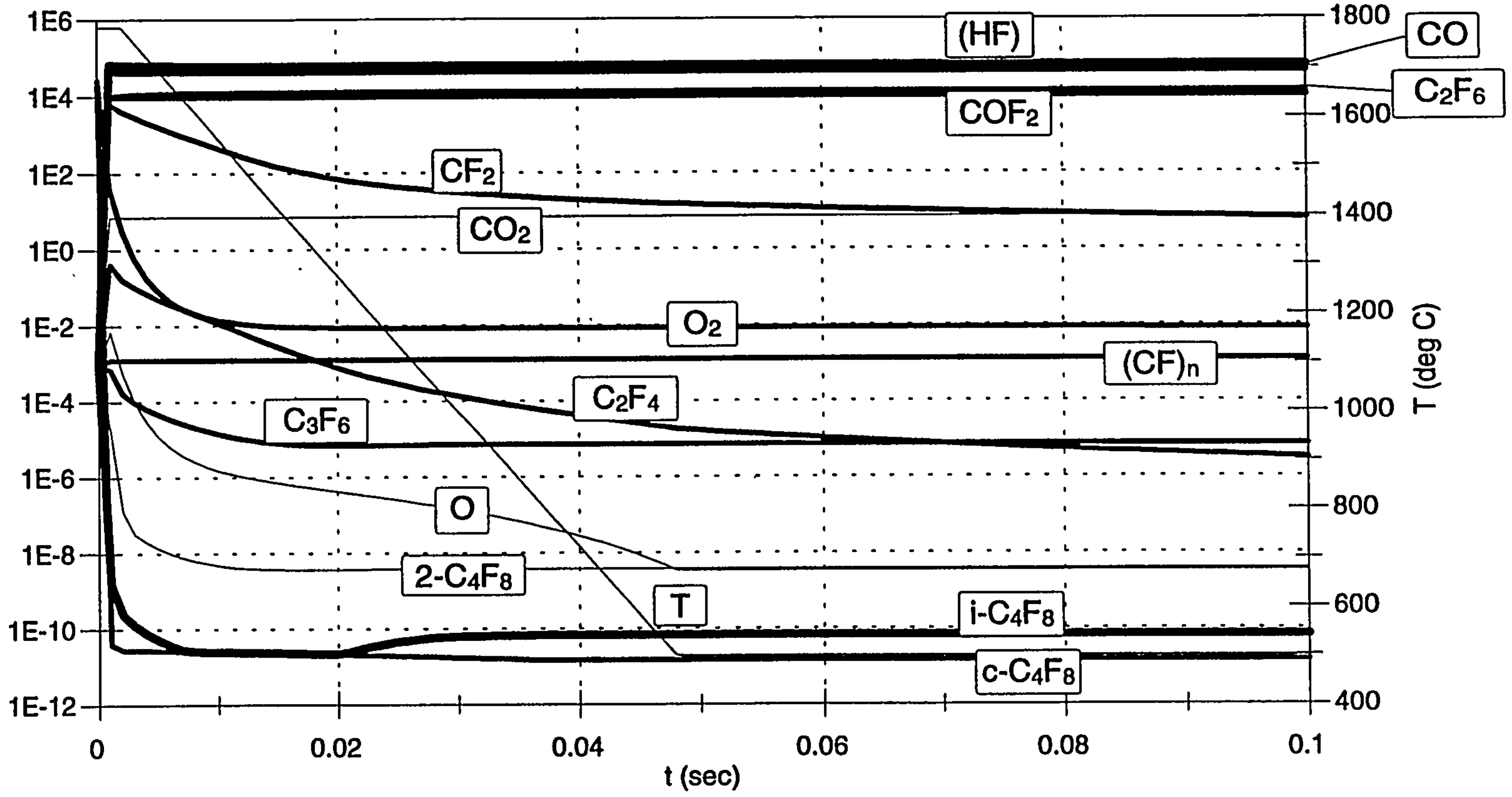


Figure 4: Kinetics model predictions for later phases of 30%-of-radius streamline in propane flame scenario. (Base reaction set used; oxygen reactions are considered; F from model shown as HF)

some chlorofluorocarbon species.

3.5 Metal Inert Gas WELDING SCENARIOS

The second arena in which coolant vapor may be exposed to high temperatures is in welding, especially of coolant systems. Here, the concern is that residual levels of coolant in the ambient air could be heated and decompose. The type of welding under consideration is termed Metal-Inert Gas (MIG) welding. It is a variety of arc welding in which an inert cover gas (usually a mix of argon and carbon dioxide) floods the region being welded, preventing oxygen in the air from reaching and reacting with the hot metal.

Two MIG welding scenarios were defined (with many variations used to explore variability or uncertainty in operating parameters). The two scenarios are intended to depict the environment on the "weld side" (that is, where the welding is taking place) and on the "trans-weld" side (that is, the side of the plate or pipe opposite the welding). For each scenario, time vs temperature profiles were defined based, where possible, on historical measurements and on welding literature.

3.5.1 Trans-Weld Cases

The chemical environment on the side opposite the weld is fairly easy to define. A variable quantity of coolant vapor will be present in ambient air (or possibly an inert purge gas). This will be in contact with a hot spot near the region of the weld. The temperature at any given location on the weld trajectory will rise fairly quickly to a maximum, then fall more slowly as the welding passes its location. The trans-weld scenario is the least likely to result in direct exposure of personnel (being on the inside of welded equipment) but is the closest to the conditions known to produce PFIB in quantity.

During a cylinder repair campaign, trans-weld surface temperature measurements were made during MIG welding of $^{5}/_{16}$ in steel plate. These temperature measurements recorded maximum temperatures between 420 to 480°C (Underwood 1996). This range is consistent with more general temperature vs distance guidance provided by standard welding references (Weisman 1976). To allow for variations in thickness of material, rate of weld progression, etc., a wide range of peak temperatures was examined. The time history of the heating followed a fairly consistent pattern. A typical temperature profile is shown in Table 4.

The temperature rose within a few seconds to its peak value, remained there a few seconds, then declined to ambient temperature at an approximately exponential rate with a half-life of about 30 s. This behavior is idealized for this analysis to assume an instantaneous rise to the maximum temperature, then a fall to ambient at a constant rate, reaching ambient in 1 min. One of Underwood's time vs. temperature profiles is listed in Table 4 along with the corresponding idealized version. Since the major chemical activity occurs at the highest temperatures, detailed representation of the low temperature portion of the temperature decline was not important.

Table 4. Temperature-vs-time profile for trans-weld scenario

Time (s)	Measured T[a] (°C)	Idealized T (°C)
0	21	21
5	43	21
6	414	462
9	462	462
13	426	433
18	371	396
24	317	352
33	259	286

[a] Underwood 1996.

The peak temperature will vary with technique, so a wide range of temperatures was considered. Cases were run with peak temperatures ranging from 400 to 1250°C.

Since this scenario is primarily one of heating ambient air,.oxygen was considered in most of the runs, with its initial value set at 20% by volume (200,000 ppm). Since high coolant levels lead to higher PFIB production, the initial coolant level was considered to be 2% (20,000 ppm) in all runs. This was the highest coolant level discussed during project planning, but inside coolant piping, much higher levels are possible, so the results of this analysis may not be bounding.

Kinetics model results were computed using the base reaction set only. Results are listed in Table 5. In no case involving oxygen was PFIB produced; rather, the tendency was for it to be destroyed. Only for runs at 700°C and above were there significant destruction of coolant and formation of COF_2, CO, and CO_2. High temperature runs also resulted in formation of large quantities of atomic fluorine, an unrealistic artifact of the set of reactions and species considered. In this reaction system, the excess F would most likely end up in CF_4 (at the expense of C_2F_6 and the generic fluorocarbon solid $(CF)_n$ used in the this model), in conversion of some CO to COF_2, and, if water vapor were present, as HF. Note that at normal humidity levels, air may contain moisture levels on the order of 1 to 3% by volume, which is sufficient to consume atomic fluorine up to 2 to 6% (20,000 to 60,000 ppm), more than is listed for most of these runs.

High temperature runs (700°C and above) were terminated early, because they were taking very long to compute (days long in some cases). At termination, the program was busily calculating rapid forward and reverse reactions of very low concentration species, a problem with the kinetics program that could perhaps have been remedied given more time for development. These runs were terminated after the meaningful chemical action had ceased, and the results are unlikely to have been much different had they continued for the full duration of the run.

The most realistic peak temperatures are probably in the range of 400 to 500°C, not the higher temperatures (which are, incidentally, incandescent temperatures). The 500°C case resulted in 1 ppm c-C_4F_8 destroyed, no PFIB production, and formation of 3 ppb COF_2, 1 ppm CO, and "excess F" (in this case plausibly interpreted as HF) of 1 ppm. These concentrations would form in a volume of gas of the general size of the hottest region of metal, that is perhaps a few cubic centimeters. To convert this to a production source term, consider that approximately 1 std cm^3 of gas (occupying 3 cm^3 volume) produces 1 ppm CO in 1 min, or about 10^{-6} sccm CO. Roughly speaking, then, 1 ppm produced (as listed in Table 5) corresponds to 10^{-6} sccm of that material produced.

To bound PFIB production, three further cases were run using the pyrolysis reactions only (i.e. with no oxygen). These cases might depict the situation in which the piping had been purged with an inert gas (e.g., dry nitrogen) rather than air and also allow for the possibility that the oxidizing reaction rates overstate the actual reaction rates at low temperature. The first case used a peak temperature of 500°C and thus can be considered the most plausible based on the temperature information available. This case produced no PFIB and slightly under 1 ppm of C_2F_4. The temperature was not high enough for the precursors of PFIB to form in quantity in this case. The second pyrolysis case used a maximum temperature of 700°C. About half of the initial c-C_4F_8 was pyrolyzed, producing largely C_2F_4 and C_3F_6, but also 0.4 ppm PFIB. The third case used a temperature of 1000°C. This case resulted in near-complete decomposition of c-C_4F_8, with formation of large quantities of various unsaturated fluorocarbons, mostly C_2F_4 and C_3F_6, but including about 150 ppm PFIB.

Except for the presence of oxygen, this "trans-weld" time-temperature environment most closely resembles the conditions conducive to formation of PFIB (lower temperatures and longer contact times). For this reason, the lower temperature cases were rerun using the PFIB formation rate published for reaction 9 (Matula 1968). In the two cases involving oxygen (500 and 700°C), PFIB production was, as in the base case, essentially nil. Three cases were run without the presence of oxygen. The lowest temperature case (and probably the most likely to be correct) at 500°C produced no PFIB, as in the base case. The higher temperature cases (peak temperatures of 700 and 1000°C) produced substantially more than the base cases (about 27 and 800 ppm, respectively). In the absence of oxygen and for these peak temperatures, these cases may represent the best estimate of PFIB formation in this situation.

Table 5. MIG weld scenarios—trans-weld scenarios (side opposite the weld)
(concentrations in ppm unless otherwise indicated)

		Rate set by maximum temperature, °C													
		Base cases									Matula cases				
	T_{max},°C	400	450	500	700	1000	1250	500	700	1000	500	700	500	700	1000
Initial quantity	O_2	200,000	200,000	200,000	199,917	190,024	200,000	0	0	0	200,000	199,998	0	0	0
	c-C_4F_8	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000
Final quantity	CF_2	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	0.0014	0.14	0.02	< 1 ppb	0.0056	0.0014	0.14	0.054
	C_2F_4	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	0.77	7,330	150	< 1 ppb	< 1 ppb	0.77	7,330	95
	C_3F_6	< 1 ppb	< 1 ppb	< 1 ppb	0.0013	1.44	< 1 ppb	0.001	8,680	24,100	< 1 ppb	0.0012	0.001	8,610	1,320
	c-C_4F_8	20,000	20,000	20,000	9,470	< 1 ppb	< 1 ppb	20,000	9,800	0.27	20,000	9,480	20,000	9,800	0.1
	2-C_4F_8	< 1 ppb	< 1 ppb	< 1 ppb	0.001	0.0038	< 1 ppb	< 1 ppb	25	1,350	< 1 ppb	0.001	< 1 ppb	39	7,500
	i-C_4F_8	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	0.37	149	< 1 ppb	0.001	< 1 ppb	27	792
	C_2F_6	0.0017	0.013	0.39	10,500	22,300	18,800	< 1 ppb	0.001	348	0.39	10,500	< 1 ppb	0.0017	3,590
	$(CF)_n$	< 1 ppb	< 1 ppb	< 1 ppb	0.001	0.0015	0.0015	< 1 ppb	0.001	696	< 1 ppb	0.001	< 1 ppb	54	35,500
	O_2	200,000	200,000	200,000	189,000	162,000	160,000				200,000	189,000			
	O	0.003	0.016	0.063	0.083	1.4	26				0.067	0.34			
	COF_2	0.001	0.0011	0.0033	261	1,700	3,870				0.0033	259			
	CO	0.0034	0.025	0.77	20,600	13,700	11				0.77	20,600			
	F	0.0044	0.026	0.77	20,500	22,800	39,300				0.77	20,500			
	CO_2	< 1 ppb	0.001	0.001	172	20,000	38,500				0.001	164			

Note 1: The duration of most runs was 30 s. Because of excessive computation time, runs at 700, 1000, and 1250°C were stopped at 24, 22, and 9 s, respectively. No significant net chemical changes were occurring at the time these run terminated.

Note 2: Cases whose rate set is designated as Matula used Reaction 9 for formation of PFIB but not reaction –4 (see text). Reaction 9 was derived from long-duration, lower-temperature experiments, conditions somewhat similar to the conditions postulated here.

It may be helpful to relate these temperatures to common experience. Metal will begin to glow dull red at about 600°C. It glows cherry red at 900°C, then orange at about 1000°C, and yellow at about 1100°C (Lange 1964). Temperatures at which there is significant coolant decomposition will tend to be ones where the metal surface in question is visibly glowing and, of course, where coolant can contact those surfaces.

The general conclusion to be drawn from these cases is that, within the limits of the available information and of the kinetics calculations, at reasonable temperatures, little or no PFIB should be produced in air from this environment. It should be noted that the highest concentration coolant considered was 2%. Much higher concentrations (up to pure coolant vapor) could occur in unpurged systems.

3.5.2 Weld-Side Cases

The situation on the welded side of a MIG weld is the hardest to physically define in a convincing manner, because the cover gas, intended to prevent oxygen from reaching the welded region, will also keep coolant from the hottest region (which must be above the melting point of iron at 1535°C). The gas flow used is on the order of 840 std L/h, so the cover gas near the weld will be moving at a velocity on the order of a meter per second. No meaningful penetration of ambient air to the molten welded region or the arc will occur under these conditions. (Otherwise the cover gas would not be fulfilling its function.) The gases departing the weld region will be hot, however, and eventually air containing oxygen and coolant will mix with this departing cover gas. Since the coolant is presumed to be in the air and neither oxygen nor coolant are present in the cover gas, a wide range of compositions may exist but there will tend to be a fixed ratio of coolant to oxygen. Because c-C_4F_8 (and CFC-114) are larger, heavier molecules than O_2, their diffusion into the hot inert gas will be slower than that of O_2, which could lead to some slight variation in this ratio. The main effect, however, will be simple mixing of the (perhaps hot) cover gas with cold air/coolant mixture. The hottest gas, considered simply on a dilution basis, would contain the smallest air/coolant fraction.

A series of cases was defined using a very wide range of temperatures to span this environment. Rather than explore a large multidimensional parameter space, a fixed composition (with a probably unrealistically large fraction of air/coolant mix, namely 50%) was chosen. Coolant is taken to be 1% by volume, and oxygen, 10% by volume (i.e., originally from a mix of 2% coolant in air). This ratio will always provide excess oxygen beyond what is needed to fully combust the coolant.

The time vs temperature profile for these cases was somewhat arbitrarily defined but is based on gas flow rates and dimensions of the weld and gas flow. An instantaneous temperature rise is followed by 10 ms at the defined maximum temperature, then by a 100 ms decline to 500°C. This would represent the thermal environment within first 10 to 20 cm of the gas flow path. Peak temperatures chosen ranged from 700 to 1500°C. All cases used the base oxygen reaction set.

The results of these runs are listed in Table 6. At 700°C, most of the coolant survives the environment, but for runs of 900°C and above, the coolant is completely reacted. In no case is PFIB formed; rather, the tendency is for it to be destroyed.

As the peak temperature increases, COF_2 appears in increasing quantities and CO appears at about 1.7% in all the higher temperature runs. In the kinetics results, atomic fluorine appears at an increasing level as the temperature increases. Again, this is an unrealistic result brought on by the choice of a limited number of species and reactions. The presence of atomic fluorine as a kinetically stable species suggests that, had slower reactions and additional species been included, more CF_4, HF, and perhaps COF_2 would form.

Table 6. MIG weld scenarios—weld-side scenario results
(concentrations in ppm unless otherwise indicated)

		Base case by maximum temperature, °C			
		700	900	1200	1500
Initial quantity	O_2	100,000	99,961	99,200	93,400
	c-C_4F_8	10,000	10,000	10,000	10,000
Final quantity	CF_2	0.031	< 1 ppb	< 1 ppb	< 1 ppb
	C_2F_4	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb
	C_3F_6	0.0012	0.2	1.7	< 1 ppb
	c-C_4F_8	9,640	< 1 ppb	< 1 ppb	< 1 ppb
	2-C_4F_8	< 1 ppb	0.0011	0.01	< 1 ppb
	i-C_4F_8	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb
	C_2F_6	358	10,600	9,870	2,360
	$(CF)_n$	< 1 ppb	0.001	0.0014	0.0012
	O_2	99,600	90,500	88,300	69,100
	O	0.12	0.9	3.1	7.2
	COF_2	8.6	633	1,670	4,880
	CO	706	18,100	17,000	17,100
	F	696	15,200	17,400	56,100
	CO_2	0.16	78	1,620	13,300

Because establishing a convincing mass flow value for any of these cases is quite difficult, no attempt was made to deduce production terms for COF_2 and CO . Obviously, the concentrations derived from this modeling would apply to a gas flow that is a small fraction of the cover gas flow (which is about 14 std L/min), but how small a fraction is uncertain. Far more convincing would be to physically monitor the gas departing a MIG welding operation for HF or other reactive halogens (e.g., COF_2) and for CO.

3.5.3 Conclusions Regarding Weld Scenarios

In neither weld scenario set was PFIB formation predicted when oxygen was considered. On both the side of the material being welded and the side opposite the weld, coolant will apparently be present only when mixed with air. Oxygen depletion is not the uncertainty it was in the propane flame case. Only if welding occurred opposite a container with very high coolant concentrations (a situation outside the realm analyzed here) or one purged with an inert gas would PFIB formation be predicted. If extensive decomposition of the coolant occurs in the presence of oxygen, the major toxic species of concern would be COF_2 and HF, which have similar toxicity levels.

4. CONCLUSIONS

Indications from the literature suggest that PFIB formation occurs within a restricted range of temperatures (hot enough for partial decomposition of fluorocarbons, but not so hot as to eliminate all C_3F_6) and requires relatively long-term contact (many seconds to hours). The presence of air and humidity tends to reduce or eliminate formation of PFIB but will allow the formation of other toxic compounds such as HF, CO, and COF_2. A flame environment seems to suppress formation of PFIB.

Kinetics results point to the same conclusions. An anaerobic environment allows formation of PFIB within the proper temperature range. Temperatures found in a flame environment are too high for significant formation of PFIB, however, and would tend to dissociate any PFIB previously present. Only on cooling can PFIB form. Additionally, nearby regions heated to the ideal temperature range by flame might also form PFIB. The time and temperature combination in a flame environment is not conducive to PFIB formation even ignoring the effect of oxygen and other combustion products. When these factors are taken into consideration, PFIB (and other fluorocarbons) oxidize to COF_2, CO and CO_2..

While the kinetics and most chemical literature suggest that PFIB should not form in the presence of O_2, there are two factors that point toward the possibility of PFIB formation. First, some descriptive chemistry literature indicated that PFIB was found in fluorocarbon polymer pyrolysis experiments involving air (though always at a lower level than in an inert gas environment). Conditions in these experiments were never sufficiently defined, however, to rule out the possibility of local oxygen depletion. This leads, though to the second point: in the operational scenarios examined here, an environment in which oxygen depletion might occur cannot be absolutely ruled out in the most extreme cases.

Although the decomposition or oxidation of CFC-114 was not specifically covered in either literature reports or in the kinetics modeling performed here, the fact that closely related compounds seem to thermally decompose to form products very similar to those of c-C_4F_8 suggests that the toxic fluorocarbon decomposition products of the two species would be quite similar in similar environments.

More definitive results would require much more extensive kinetic analysis and would always suffer from the possibility that something important may have been overlooked. Experimentation is a surer guide to reality, though it can rarely span all possible combinations of conditions. The trends and conclusions obtained from chemical reaction modeling appear generally favorable, but if definite confirmation is needed, experimentation ought to be performed. The kinetics and literature search can guide the experimental search toward those conditions most likely to be a problem. Specifically, conditions that should be most closely examined are those involving high concentrations of coolant, relatively long contact time in the ideal temperature range, and little or no oxygen or moisture.

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Appendix A

KINETICS MODEL DESCRIPTION

A chemical kinetics model was devised for the purpose of examining c-C_4F_8 thermal decomposition. The basic strategy is the straightforward numeric integration of a set of chemical kinetics equations so as to track the time evolution of chemical species.

Two versions were created in parallel, one a spreadsheet version (Corel Quattro Pro) and the other written and compiled in Borland's Turbo Pascal (6.0). The first version can do only a limited number of time steps but displays all intermediate calculations and will graph the result directly, allowing aberrant behavior to be seen at a glance. It was used primarily for testing modifications and for displaying the initial short-time-span results. The compiled version can, in principle, run for an indefinite period but prints results only at fixed intervals (and thus may miss rapid changes). It runs much faster than the spreadsheet.

The general algorithm of both is an only slightly sophisticated brute force time integration method. At each iteration, the model computes the current temperature from a user-specified time vs temperature function. At the current temperature, it calculates the value of each rate constant and then the rate of each reaction based on the rate constant and current concentrations of reactants. It also calculates a predicted pseudo-equilibrium value for each species based on the current level of that species and the rates of reactions creating and destroying that species. It selects the largest time interval which will not allow any species to grow or decline at a greater rate than a user-specified rate (e.g., 25% of the present value) or approach its apparent equilibrium more closely than another user-specified parameter. The change in each species is then calculated by multiplying all rates by that time interval. Quantities are updated and the next time interval begins.

As currently written, the program treats the active species as a perturbation on externally imposed physical conditions. Although concentrations are expressed in parts per million, the pressure is treated as a constant, and neither pressure nor concentrations are adjusted for the increase or decrease in the total moles of gas. Energy balance is not considered either. Heat of reaction does not enter into the temperature of the system, which is an externally imposed function of time. Neither of these approximations will be important when considering low concentrations of reactants in a much higher background of unreacting gas, but the approximations, of course, have their limits of validity.

Testing of the model was done largely by examining results for internal consistency (mass balance, proper performance in limiting cases) and by comparing the two versions on identical cases. A few comparisons of the pyrolysis data set were run against similar calculations or experimental results from the literature. For example, Bauer (1998) developed a similar model with which to examine c-C_4F_8 pyrolysis. While the rate equations he used were not in all cases identical to the ones used here (he included some reactions generally regarded by many workers as not occurring directly, and others that do not contribute meaningfully to the results), results published in his article on the destruction of c-C_4F_8 and production of C_2F_4 and C_3F_6 at 950 K and 1000 K gave results within a factor of 3 or better of the results of the base pyrolysis reaction set used for most of the calculations presented in this report. A test series using Bauer's reaction rate set duplicated his published results for 10 s pyrolysis within 2% at 950 K and 20% at 1000 K. A second test series was run to attempt to duplicate the experimental end product mix reported by Zaitsev (1990) for the pyrolysis of mixtures of C_2F_4 and C_3F_6 at 770°C. At the relatively low temperatures and moderate contact times in that study (0.8 to 1.3 s), the experimental results were most closely duplicated by use of the PFIB formation rate for reaction 9 (Matula 1968), with the major final products (C_2F_4 and C_3F_6) duplicated within 2% and 40%, respectively, and the minor species listed in Zaitsev's article (c-C_4F_8 and PFIB) varying by a factor of 4 from the model results.

Algorithm for kinetics model:

After reading in the required input data and establishing the initial conditions, the following algorithm is used. At each time interval, the program

1. Calculates T(t)
2. Calculates each rate constant k(T)
3. Calculates the rate, d{rxn}/dt, of each reaction as entered in the input data
   (e.g., for the reaction A+ B to give products, it calculates k[A][B])
4. Calculates rate of change in each species d[X]/dt caused by each reaction
5. From the results of step 4, three composite rates of change are calculated for each species:
   a. Net d[X]/dt for each compound (sum of all d[X]/dt)
   b. Gross increases (sum of all positive d[X]/dt for each compound)
   c. Gross decreases (sum of all negative d[X]/dt for each compound)
6. Calculates [X]eq , the pseudo-equilibrium level of [X] based on current level of [X] and the gross rate increases and decreases from 5b and 5c
7. Calculates the largest time increment (dt) which keeps all changes (increases, decreases, and approach to equilibrium) less than the user-specified fractional changes for all species
8. Selects as dt the smallest value from (a) dt calculated in 7, (b) a user-specified maximum dt, or (c) the time remaining to the next print interval
9. Calculates the quantities of all compounds at the end of the current period as
   $[X](t+dt) = [X](t) + d[X]/dt \times dt$
10. If the time is at a print interval, prints the current time, temperature, and concentrations

Regarding the time-temperature profile, the model is designed to examine temperature histories that start at some level, remain constant for a period of time, and then decline linearly to a minimum temperature, after which the temperature remains constant. This is a reasonable approximation of the temperature history of gas in the types of problem considered in this study.

Appendix B

IDEALIZED MODEL OF PYROLYSIS CONDITIONS IN A PROPANE FLAME

To develop a reasonable time vs temperature profile for coolant-containing gas passing though the propane burner (used for coolant negative testing), an examination of the flame characteristics of that device was conducted.

The halide gas detector used for testing for the presence of CFC-114 in system air after purging consists of a fairly standard propane torch but with a specially adapted burner tip. A schematic of the burner tip is displayed in Fig. 5. The air being sampled is delivered to the fuel inlet line upstream of the combustion zone via a plastic tube. The flame chamber contains a burner tip approximately 1.65 cm in diameter, with an insert dividing this opening into a series of holes each smaller than the quench distance of propane air mixtures (ca 3 mm), thereby preventing propagation of the flame back toward the fuel source. The burner tip is contained within a larger cylindrical shield 3 cm in diameter. The shield is open at the top and attached at the bottom to the fuel/air inlet line. It also has a series of openings at the bottom which allow additional air into the interior of the shield. The shield has a side port for viewing the flame (not shown in the diagram). Intercepting the flame is an insulated, slitted copper disk. If halogens are present in the flame's air supply, they will interact with the copper disk (presumably by forming slightly volatile copper halides) and color the flame above the slit in the copper disk.

In operation, the flame is attached to the burner tip and is essentially all contained inside the shield. Per the manufacturer's directions, the flame should be set so as to just touch the slitted copper disk, which is located in the path of the flame and thermally insulated from its mount on the shield. Photographs of operation at Paducah Gaseous Diffusion Plant suggest that the technique in practice may use somewhat higher gas flows, and this produces longer flames. Higher gas flows have the advantage of moving the sample gas into the flame faster, hence giving a better response time.

It is evident from test operation of the device that most of the air required for burning comes from the sample line (shutting off the inlet tube nearly extinguishes the flame), though the vent holes at the base of the shield allow air to be drawn into the shield chamber. It is reasonable, in any case, to treat this propane burner flame as a pre-mixed flame (as opposed to a diffusion flame). Furthermore, the stable flame structure indicates it produces primarily a laminar flame. On this basis, parameters were developed for estimating the physical conditions that would be experienced by a molecule passing though the flame.

The best description of the level of complexity needed here is provided by Lewis and von Elbe (1951). In that reference, burner flames were described for several fuels. The greatest detail was provided for natural gas–air flames of comparable dimensions to the propane flame of immediate concern here. Detailed temperature and velocity profiles were given for a number of streamlines passing through the flame. Table B-1 gives a summary of parameters deduced from those diagrams.

Table B-1. Analysis of gas velocity and temperature for natural gas–air flame[a]

Streamline	Location (% of radius)	Velocity, preburn (cm/s)	Velocity, postburn (cm/s)	Peak temp. (°C)	Temp. decline (°C/s)	Time near max temp. (ms)
0	0.0	225	219	1758	20,000	2.5
2	15.8	219	288	1758	19,000	3.2
4	30.8	203	247	1754	15,000	2.3
6	47.9	173	208	1751	33,000	1.5
8	68.5	118	164	1660	83,000	2.7
10	95.9	19	55	1400	—	—
Outer edge	100.0	0	0	400		

[a] Lewis and von Elbe 1951.

A brief description of gas passing through a burner flame is as follows:

a. The gas may be slightly preheated in the burner tube (as determined by the temperature of the tube itself).

b. A flame front forms at the tip of the burner (roughly conical in shape, the precise angle determined by the ratio of the gas flow velocity downstream and the speed of propagation of the flame front upstream). As gas passes through this flame front, its temperature rises from the inlet temperature to near the maximum value within a space of tenths of a millimeter and times of tens of microseconds. Most of the combustion (and heat release) occurs here.

c. The gas remains at near maximum temperature for 1 to 3 ms as heat generated by completion of reaction and loss by radiation balance. Beyond this point, the gas cools at a more or less linear rate at least through the region at which luminescence (visible flame) is prevalent, eventually reaching ambient temperature. This process can take tens of ms.

Throughout the process, the gas velocity initially has a parabolic profile (as per fully developed laminar flow) with a peak velocity of about 230 cm/s. The gas velocity after passing the flame front is approximately 50 cm/s faster than pre-burn velocity up to at least 96% of the burner radius. Heating, of course, has resulted in a large volume expansion of the gas, but the excess volume manifests itself mostly as expansion of the radius of the flame and only slightly increases the velocity of gas.

The above characteristics were idealized to the temperature vs time vs radius parameters described in Table 2. A peak temperature of 1785°C was used in the center of the flame, a value chosen a bit higher than the natural gas-air maximum flame temperature of 1758°C in the Lewis flame analysis (Lewis and von Elbe 1951) due to the slightly higher energy content of propane. Cooling rates increase toward the outer edge of the flame. Cooling rates beyond about 70% of the radius were extrapolated from the trend inside that radius. According to the general principles of flame propagation, a flame cannot be sustained within a certain distance of a heat sink (that is the burner tube), as heat conduction to that sink is too rapid to allow the combustion to accelerate to ignition temperature. Thus there will be a transition zone near the edge of the burner in which the flow velocity goes from a low value at the flame boundary to zero at the wall (normal laminar velocity profile) and the maximum temperature of the gas goes from flame temperature to burner wall temperature. Since this is a small fraction of the radial area of the burner and the gas velocity is low, the fraction of gas passing through this zone is a very small fraction of the total (between 96 and 100% of radius, the mass flow of gas is approximately 0.7% of the total mass flow through the burner). We do not have information on the temperature in this zone other than its limits, but we should be able to bound its behavior, as we know the endpoints (the 96 and 100% values), and the decline should be monotonic. One of the sets of sensitivity cases discussed in the text attempts to bound behavior in this region.

That and other references indicate that the characteristics of premixed laminar flames will differ only a little for related hydrocarbon fuels operated at near stoichiometric mixtures with air. For example, the measured maximum flame temperatures for several fuels are provided in Table B-2.

Table B-2. Empirical maximum flame temperature and burning velocity for optimum air-fuel mixtures[a]

	T_{max} (°C)	V_b (cm/s)
methane-air	1875	45
ethane-air	1895	40
propane-air	1925	43
butane-air	1895	38

[a] Perry 1950.

These values are for optimum fuel-air mixtures, and the flame temperatures will decrease as the mix deviates from the ideal composition. From kinetics model runs, it became evident that even considerable differences in peak temperatures above a certain level (about 1400°C – incidentally the approximate boundary of the visible portion of the flame) had little effect on the model results. Above that temperature, the coolant (and, if it had formed earlier, any PFIB) was fully dissociated to CF_2 radicals.

The results from each streamline are multiplied by a weighting factor proportional to the cross-sectional area (perpendicular to the gas velocity) in a zone ± 10% of that radius and the gas velocity at that radius, as determined by a parabolic velocity distribution. The overall mass flow entering the flame was derived from information supplied by Keith Potter of Paducah Gaseous Diffusion Plant, who measured propane consumption in the halide test at 0.9 g/min. At an assumed gas mix of 3.5 vol % propane in air, the bulk gas flow will be 320 cm^3/s at an inlet temperature of 400 K, yielding an average gas velocity of 150 cm/s entering the flame front in the 1.65 cm diameter burner tip. This is well within the range of stable flames (bulk gas velocities between two and five times the burning speed of the gas mix -- approximately 43 cm/s for this propane air mixture). This is a further indication that the parameters used (and hence the gas velocities and dwell times) are reasonable for the type of flame considered.

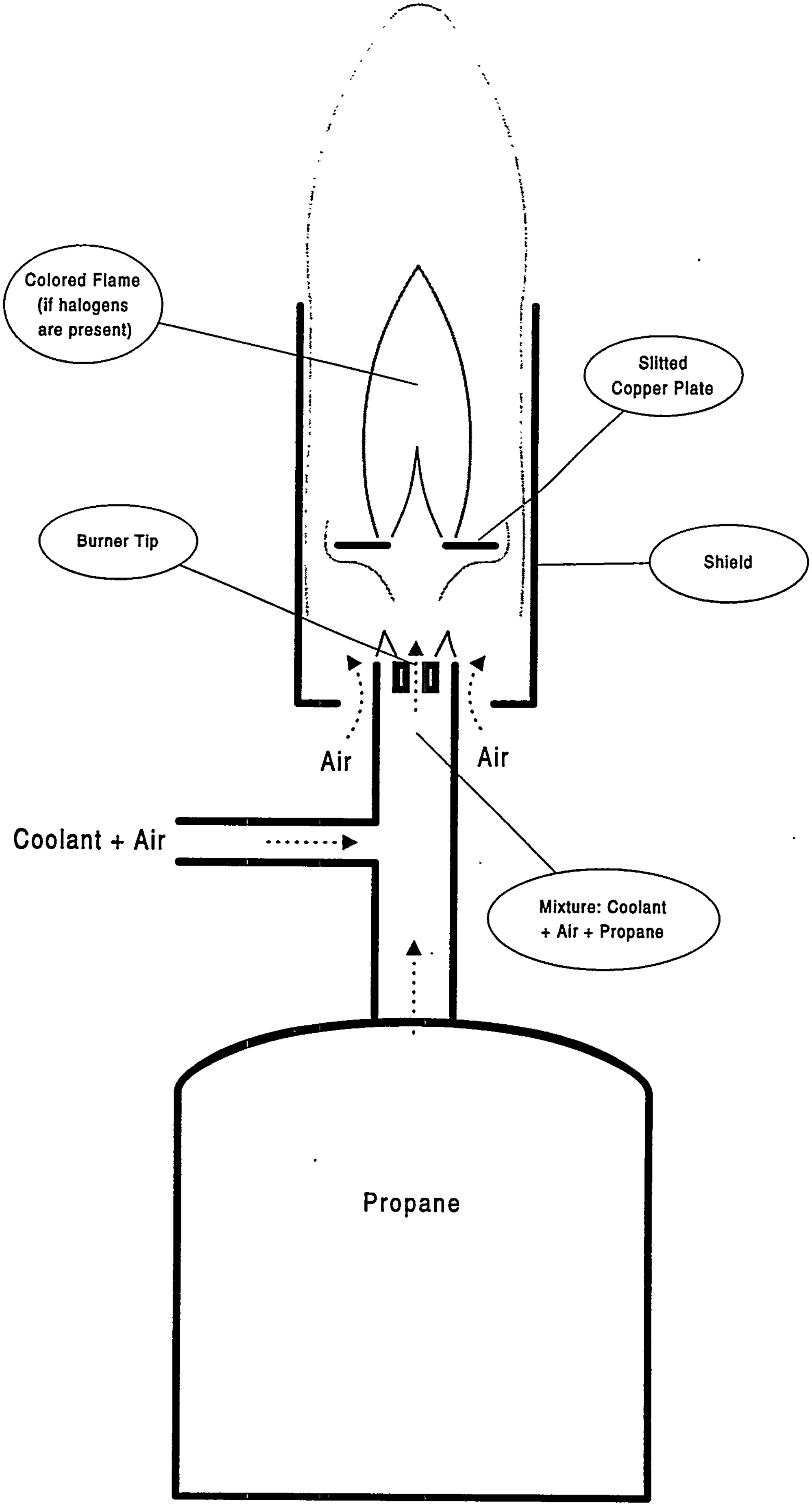

Figure 5: Schematic of propane burner used for halogen testing

Appendix C

KINETICS MODEL RESULTS FOR PROPANE BURNER SCENARIO

Table C-1. Results for propane burner kinetic modeling cases—pyrolysis base cases (no oxygen)
(concentrations in ppm; x% SL indicates time-temperature profile for streamline at x% of flame radius)

Base cases

Description		10% SL	30% SL	50% SL	70% SL	90% SL	Weighted sum
Rate set		Base	Base	Base	Base	Base	
Max T (°C)		1785	1785	1785	1670	1477	
				Medium concentration			
Initial quantity	O_2	0	0	0	0	0	
	c-C_4F_8	5,000	5,000	5,000	5,000	5,000	5,000
Final quantity	CF_2	0.41	0.39	0.38	0.38	0.37	0.38
	C_2F_4	7,140	7,740	8,630	9,040	9,210	8,510
	C_3F_6	1,880	1,480	894	629	517	975
	c-C_4F_8	11	11	9.6	8.5	7.9	9.5
	2-C_4F_8	5.8	3.9	1.8	1.1	0.92	2.3
	i-C_4F_8	2.1	1.3	0.5	0.25	0.17	0.69
	C_2F_6	0.44	0.23	0.062	0.026	0.023	0.11
	$(CF)_n$	0.87	0.45	0.12	0.052	0.044	0.22
				High concentration			
Initial quantity	O_2	0	0	0	0	0	
	c-C_4F_8	20,000	20,000	20,000	20,000	20,000	20,000
Final quantity	CF_2	0.38	0.38	0.38	0.38	0.39	0.38
	C_2F_4	14,100	17,100	23,000	26,800	28,500	22,800
	C_3F_6	16,800	14,900	11,100	8,620	7,470	11,200
	c-C_4F_8	46	57	75	82	84	72
	2-C_4F_8	243	167	80	49	44	98
	i-C_4F_8	58	46	26	16	12	28
	C_2F_6	39	24	8.2	3.9	3.8	12
	$(CF)_n$	78	47	16	7.8	7.5	24
				Low concentration			
Initial quantity	O_2	0	0	0	0	0	
	c-C_4F_8	1,000	1,000	1,000	1,000	1,000	1,000
Final quantity	CF_2	0.53	0.51	0.49	0.49	0.48	0.5
	C_2F_4	1,890	1,910	1,950	1,960	1,970	1,940
	C_3F_6	73	56	32	23	20	36
	c-C_4F_8	0.67	0,56	0.41	0.33	0.29	0.42
	2-C_4F_8	0.084	0.056	0.028	0.017	0.013	0.033
	i-C_4F_8	0.012	0.0069	0.0022	0.0011	0.0007	0.0035
	C_2F_6	0.0022	0.0016	0.0012	0.0011	0.0012	0.0013
	$(CF)_n$	0.0033	0.0022	0.0014	0.0013	0.0013	0.0017

Table C-2. Results for propane burner kinetic modeling cases—pyrolysis sensitivity cases (no oxygen)
(measured in ppm unless otherwise indicated)

Sensitivity cases

1. Finer grid at outer radius of flame

Description		10% SL	30% SL	50% SL	70% SL	88% SL	96.5% SL	97.5% SL	98.5% SL	99.5% SL	Weighted sum
Rate set		Base	Base	Base	Base	Base	Base	Base	Base	Base	
Max T (°C)		1785	1785	1785	1670	1496	1269	1020	772	524	
Initial quantity	O_2	0	0	0	0	0	0	0	0	0	
	c-C_4F_8	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000	5,000
Final quantity	CF_2	0.41	0.39	0.38	0.38	0.37	0.37	0.37	0.45	0.001	0.38
	C_2F_4	7,140	7,740	8,630	9,040	9,220	9,200	9,500	65	0.023	8,500
	C_3F_6	1,880	1,480	894	629	509	524	320	0.023	< 1 ppb	973
	c-C_4F_8	11	11	9.6	8.5	7.8	7.3	7.9	4,970	5,000	17
	2-C_4F_8	5.8	3.9	1.8	1.1	0.89	0.92	0.62	0.001	< 1 ppb	2.3
	i-C_4F_8	2.1	1.3	0.5	0.25	0.17	0.24	0.018	< 1 ppb	< 1 ppb	0.69
	C_2F_6	0.44	0.23	0.062	0.026	0.02	0.027	0.001	< 1 ppb	< 1 ppb	0.11
	$(CF)_n$	0.87	0.45	0.12	0.052	0.04	0.053	0.001	< 1 ppb	< 1 ppb	0.22

Table C-2 (continued)

2. Alternate PFIB reaction rates (single streamline cases)

Description		30% SL	30% SL	30% SL
Rate set		Matula	Base	Buravtsev
Max T (°C)		1785	1785	1785
Initial quantity	O_2	0	0	0
	c-C_4F_8	5,000	5,000	5,000
Final quantity	CF_2	0.39	0.39	0.39
	C_2F_4	7,690	7,740	7,660
	C_3F_6	1,480	1,480	1,540
	c-C_4F_8	11	11	11
	2-C_4F_8	14	3.9	3.8
	i-C_4F_8	9.5	1.3	0.0048
	C_2F_6	1.8	0.23	0.0067
	$(CF)_n$	46	0.45	0.012

Table C-2 (continued)

3. Variations in temperature decline rate (single streamline cases)

Description		10% SL	10% SL	10% SL
Rate set		5,000K/s	50,000K/s	80,000K/s
Max T (°C)		1785	1785	1785
Initial quantity	O_2	0	0	0
	c-C_4F_8	5,000	5,000	5,000
Final quantity	CF_2	10	0.72	0.67
	C_2F_4	3,880	8,540	9,010
	C_3F_6	4,010	961	646
	c-C_4F_8	7.1	8.6	7.3
	2-C_4F_8	32	1.9	1.1
	i-C_4F_8	10	0.57	0.26
	C_2F_6	< 1 ppb	< 1 ppb	< 1 ppb
	$(CF)_n$	< 1 ppb	< 1 ppb	< 1 ppb

Table C-2 (continued)

4. Alternate reaction rate set (PFIB formation rate for reaction –4 uses Buravtsev rate rather than Bauer rate for same reaction.)

Description		10% SL	30% SL	50% SL	70% SL	90% SL	Weighted sum
Rate set		Buravtsev	Buravtsev	Buravtsev	Buravtsev	Buravtsev	
Max T (°C)		1785	1785	1785	1670	1477	
				High concentration			
Initial quantity	O_2	0	0	0	0	0	
	c-C_4F_8	20,000	20,000	20,000	20,000	20,000	20,000
Final quantity	CF_2	0.38	0.38	0.38	0.38	0.39	0.38
	C_2F_4	13,700	16,600	22,500	26,300	28,100	22,300
	C_3F_6	17,200	15,300	11,400	8,940	7,750	11,500
	c-C_4F_8	43	53	71	79	81	68
	2-C_4F_8	245	168	80	49	44	99
	i-C_4F_8	0.4	0.31	0.17	0.1	0.082	0.19
	C_2F_6	1.3	0.8	0.28	0.14	0.17	0.42
	$(CF)_n$	2.7	1.6	0.56	0.29	0.34	0.85
				Medium concentration			
Initial quantity	O_2	0	0	0	0	0	
	c-C_4F_8	5,000	5,000	5,000	5,000	5,000	5,000
Final quantity	CF_2	0.41	0.39	0.38	0.38	0.37	0.38
	C_2F_4	7,040	7,660	8,580	9,000	9,180	8,460
	C_3F_6	1,950	1,540	933	654	536	1,010
	c-C_4F_8	11	11	9.5	8.4	7.8	9.4
	2-C_4F_8	5.8	3.8	1.8	1.1	0.89	2.2
	i-C_4F_8	0.0077	0.0048	0.0018	< 1 ppb	< 1 ppb	0.0022
	C_2F_6	0.011	0.0067	0.0034	0.0027	0.0028	0.0044
	$(CF)_n$	0.021	0.012	0.0059	0.0043	0.0046	0.0078

Table C-3. Results for propane burner kinetic modeling cases—oxygen reactions

A. Base case (high coolant concentration)

Description		10% SL	30% SL	50% SL	70% SL	90% SL	Weighted sum
Rate set		Base - O	Base - O	Base - O	Base - O	Base - O	
Max T (°C)		1785	1785	1785	1670	1477	
Initial quantity	O_2	27,003	27,003	27,003	27,009	27,017	
	c-C_4F_8	20,000	20,000	20,000	20,000	20,000	20,000
Final quantity	CF_2	6.6	6.3	6	5.2	< 1 ppb	5.1
	C_2F_4	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb
	C_3F_6	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	1	0.13
	c-C_4F_8	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb
	2-C_4F_8	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	0.014	0.0018
	i-C_4F_8	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb
	C_2F_6	13,000	13,000	13,000	13,300	20,200	14,000
	$(CF)_n$	0.0013	0.0013	0.0013	0.0016	0.0027	0.0016
	O_2	0.0028	0.0084	0.048	328	7,210	1,030
	O	< 1 ppb	< 1 ppb	< 1 ppb	< 1 ppb	0.45	0.058
	COF_2	10,100	10,100	10,100	8,980	5,300	9,160
	CO	43,800	43,800	43,800	44,300	34,200	42,700
	F	61,700	61,700	61,700	62,000	28,000	57,400
	CO_2	7.2	7.2	7.2	17	33	13

B. Variable oxygen-to-coolant ratio (single streamline cases)

Description		30% SL	30% SL	30% SL
Rate set		Base - O	Base - O	Base - O
Max T (°C)		1785	1785	1785
Initial quantity	O_2	27,000	200,000	5,000
	c-C_4F_8	5,000	20,000	20,000
Final quantity	CF_2	< 1 ppb	< 1 ppb	3.4
	C_2F_4	< 1 ppb	< 1 ppb	14,100
	C_3F_6	< 1 ppb	< 1 ppb	8,330
	c-C_4F_8	< 1 ppb	< 1 ppb	34
	2-C_4F_8	< 1 ppb	< 1 ppb	58
	i-C_4F_8	< 1 ppb	< 1 ppb	19
	C_2F_6	67	495	8,130
	$(CF)_n$	< 1 ppb	0.0012	13
	O_2	16,700	153,000	< 1 ppb
	O	225	504	< 1 ppb
	COF_2	3,730	14,800	1,880
	CO	15,700	50,600	8,120
	F	32,100	127,000	< 1 ppb
	CO_2	413	13,600	0.1

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