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To: W. J. Spetnagel, X-710, Portsmouth GDP
Cy: R. L. Jones, C-710, Paducah GDP
D. F. Williams
From: L. D. Trowbridge *LD*

Subject: Evaluation of Reactivity of $c\text{-C}_4\text{F}_8$ with Cascade Impurities

Introduction

The purpose of this document is to summarize an investigation of known chemical mechanisms which might result in significant destruction of the proposed alternate coolant $c\text{-C}_4\text{F}_8$ within the isotopic or purge cascades of the gaseous diffusion plants. This investigation took the form of a literature search and analysis of the pertinent results thereof. The literature search for $c\text{-C}_4\text{F}_8$ degradation mechanisms was conducted in conjunction with a larger search on thermal decomposition mechanisms for that compound [Trowbridge 99].

The physical and chemical conditions of interest are those of the isotopic and purge cascades in the diffusion plants. The range of temperatures, pressures and gas composition may vary considerably. To avoid sensitivity about specific values, we will consider total pressures of 1 atm and temperatures ranging from 50 to 200C. In the isotopic cascade, the gas is essentially all UF_6 , though other impurities may appear at low levels as products of inleakage of air (e.g. HF , O_2 , N_2 , CO_2 , COF_2) or coolant (CFC-114 or the material in question here, $c\text{-C}_4\text{F}_8$), residual gas and reaction products in equipment after cleanup treatments (again HF , O_2 , ClF , Cl_2 , ClO_2F , ClF_3 , F_2), and residues of historical feed impurities or products of reaction with materials of construction in the fuel cycle (e.g. SiF_4 , MoF_6 , BF_3 , TcO_3F , AsF_5). The purge cascade environment is physically similar, but represents the transition region between the cascade region where UF_6 dominates and that where lighter gases dominate. Though the overall mass flows of non- UF_6 species are very small, the lighter gases separate and concentrate by molecular weight in the purge cascade, so that percent levels of impurities may appear locally.

The literature search revealed only three explicit chemical mechanisms which could lead to the destruction of $c\text{-C}_4\text{F}_8$ in the isotopic or purge cascades. In all three cases, the expected rate of destruction is very small, with the overall decomposition probably smaller than the that of the current coolant, CFC-114. The three mechanisms of destruction are (a) thermal decomposition of $c\text{-C}_4\text{F}_8$ and (b) direct fluorination and (c) radiolytic decomposition. Each mechanism will be discussed in more detail below.

Thermal decomposition of $c\text{-C}_4\text{F}_8$

The first mechanism relates to thermal decomposition of $c\text{-C}_4\text{F}_8$. The initial step in thermal decomposition is



The rate of this reaction is sufficiently low at the temperature range of interest that it has been studied only at somewhat higher temperatures (collectively in many studies, between 360 and 1200°C). There is

significant commercial interest in this reaction, as it is involved in the decomposition of PTFE (polytetrafluoroethylene). Consequently, numerous studies have appeared in the literature. A typical kinetic study, due to Butler [1962], determined the kinetics to be unimolecular, following:

$$-d [c-C_4F_8]/dt = k_1 [c-C_4F_8] \text{ s}^{-1} \quad (2)$$

where $k_1 = 6.2 \times 10^{15} \exp (-310.9 \text{ kJ/mol} / R T) \quad (3)$

Butler's experiments took place in a lower temperature range (360 to 560°C) than most other studies. Other rates, extrapolated to the mid-300s (°C) give rates varying less than an order of magnitude from this particular rate constant. Mathematically, the extrapolation from 360 to the range of interest (50 to 200°C) is fairly reliable, though chemically, one cannot guarantee that some other mechanism will not become dominant at lower temperatures. No evidence for a higher rate low-temperature mechanism was found in the literature, however.

Unsaturated compounds such as C_2F_4 are rapidly attacked by fluorinating agents such as F_2 and UF_6 , so that C_2F_4 formed in the initial decomposition step would rapidly be converted to C_2F_6 (that is, FC-116). Though a specific rate of reaction for C_2F_4 with UF_6 or F_2 was not found, C_2F_4 does react quickly with atomic F (always in equilibrium in trace quantities with F_2) [Kerr 87]. Related compounds (e.g. 2-perfluoro-butene) react quickly with F_2 [Rodgers 65] and with UF_6 [Trowbridge 92].

Extrapolation of the above rate to 200°C yields a decomposition rate of $2.9 \times 10^{-19} \text{ s}^{-1}$, which is completely inconsequential: selecting extreme numbers for the sake of discussion, if 10,000 kg/year of the coolant leaked into the cascade and if any given molecule of coolant has an average cascade residence time of 1 day, at this rate of decomposition only 0.3 µg of coolant would dissociate per year.

Direct Fluorination of c-C₄F₈:

The second mechanism by which the coolant might decompose is the direct fluorination of c-C₄F₈ to produce (primarily) n-C₄F₁₀. This kinetics of this gas-phase reaction with F_2 have been studied between 309 and 450°C [Levy 74] and found to follow a rate equation

$$-d [c-C_4F_8]/dt = k_2 [c-C_4F_8] [F_2]^{1/2} \quad (4)$$

where

$$k_2 = 4.3 \times 10^{12} \exp (-169.5 \text{ (J/mol K)} / R T) (\text{cc/mol})^{1/2} \text{ s}^{-1} \quad (5)$$

The fact that the rate appears proportional to the square root of F_2 concentration suggested to Levy that the mechanism involved dissociation of molecular fluorine to atomic fluorine. The proposed mechanism, then, involved the following steps:



The products of the C_4F_9 radical were largely n-C₄F₁₀, but also included CF_4 , C_2F_6 , and C_3F_8 . By assuming

that the rate determining step in the above mechanism is that of equation (7), the following rate equation was derived:

$$-d [c-C_4F_8]/dt = k_7 [c-C_4F_8] [F] \quad (9)$$

where

$$k_7 = 6.0 \times 10^{11} \exp (- 88.7 (J/mol K) / R T) \text{ cc mol}^{-1} \text{ s}^{-1} \quad (10)$$

Assuming this reaction mechanism is correct, any fluorinating agent which produces an equilibrium concentration of atomic fluorine would be expected to attack c-C₄F₈ via reaction (7) at the rate given by equations (9) and (10). The literature search uncovered no data on c-C₄F₈ fluorination kinetics by other agents, but thermodynamic information is available for many cascade impurities which enables estimation of their corresponding equilibrium dissociation. For example, the expected reaction rate by SiF₄ would be presumed to follow a mechanism involving



followed by reactions (7) and (8). Thermodynamic parameters for SiF₄, F, and SiF₃ (a radical species) are available to calculate the equilibrium concentration of [F] (in this case vanishingly small in the 50 to 200°C temperature range), and hence the expected loss rate of c-C₄F₈ in the presence of SiF₄. To the extent that thermodynamic data is available for impurities and their fluorine-deficient decomposition products, this can be applied to any source of atomic fluorine. This method for estimating fluorination rates is not guaranteed to be either an upper or lower limit to the true rate. It may overestimate the fluorination rate if the rate of decomposition of the source of atomic fluorine is sufficiently slow to be the rate determining step, and it may underestimate the rate if some other more rapid mechanism of fluorination also occurs.

In fact, an additional, or at least modified, reaction mechanism appears to apply at lower temperatures even for the reaction of F₂ with c-C₄F₈. Levy observed an upward deviation of rate of reaction at the lowest temperatures studied (that is, the rate declined less rapidly with temperature than equations (5) and (10) would predict). This was attributed to a heterogeneous (that is, gas-surface) component of the reaction. Other than to take measures to minimize this effect and avoid lower temperatures where it dominated, Levy did not further examine this effect. A less extensive series of experiments was conducted on the F₂ + c-C₄F₈ system at a lower temperature range (150 to 250°C) in which a high surface area fluorine-passivated sintered nickel filter material was deliberately present in the reaction zone [Trowbridge 92]. A few experiments were conducted without this high surface area material present (i.e. with only that surface area represented by the passivated nickel walls of the reaction chamber) and such experiments exhibited a rate approximately 1/3 that of the high surface area experiments -- that is, there was some surface effect, but the rate did not appear to be linearly proportional to the microscopic surface area. The temperature dependence in these experiments was weaker than for Levy's, but consistent with a surface-dissociation mechanism. Neither of the initial reactant compositions were varied in these experiments (all initial concentrations being about 10 Torr in each reactant), so the kinetic dependence on composition was not determined. Treated as first order in concentration of the fluorocarbon, the rate followed the equation

$$-d[c-C_4F_8] = k_{12} [c-C_4F_8] \quad (12)$$

where

$$k_{12} = 2.95 \exp (- 50.3 \text{ kJ/mol} / R T) \text{ s}^{-1} \quad (13)$$

Extrapolation of this rate to the higher temperature range of Levy's experiments yields a rate of the same order of magnitude as that determined by Levy. Extrapolation of Levy's rate to this lower temperature regime gives rate 10^{-6} that of the Trowbridge experiments. Taken together, the two investigations are consistent with a mechanism that is predominantly homogeneous at higher temperature, transitioning to a heterogeneous reaction around 300°C, which declines less rapidly with decreasing temperature.

This picture may be internally consistent, but we are left with the problem of how to estimate fluorination rates in the lower temperature regime, where the kinetic dependence on composition is not known. Simply putting the lower temperature kinetic results into the form used by Levy (equation 9) gives the following rate constant

$$k_{14} = 1858 \exp(+26.4 \text{ kJ/mol} / R T) \text{ cc/mol s} \quad (14)$$

Whether justified or not on kinetic grounds, this equation will reproduce the experimentally observed rate of fluorination in the lower temperature experiments. Given the apparent heterogeneous nature of the reaction in the temperature range of interest, it is more difficult to definitively and quantitatively predict the behavior of species for which rate information is unavailable. The thermodynamics of the apparent primary reactants – atomic F and $c\text{-C}_4\text{F}_8$ – will be the same regardless of the source of F, but the parent (e.g. SiF_4) and its other fragment (e.g., SiF_3) may well have different surface characteristics, i.e. different degree of coverage as a function of temperature and pressure, a different degree of dissociation, different migration rates, etc. Thermodynamics dictates that the gas phase equilibrium concentration of F should not be altered by the presence of the surface (except to extent that surface adsorption might deplete the gas-phase of the parent species) but it may change the speed of reaching equilibrium.

Extrapolation of the Levy homogeneous rate of F_2 reaction to the 50-200°C range under consideration yields inconsequentially low fluorination rates. The rate, of course, is dependent on the concentration of fluorine which, in this case, may vary from none at all to a few percent, depending on the location in the cascade and the recent history of cleanup treatments by which residual unreacted F_2 might have entered the cascade. To choose a high limit, imagine that in a location in the purge cascade, the gas composition is 5% $c\text{-C}_4\text{F}_8$ and 5% F_2 (levels higher than this would verge on flammability limits and likely would be avoided). Applying Levy's rate (k_7), extrapolated to 100°C and 200°C yields a fractional rate of conversion of 10^{-14} and 10^{-9} s^{-1} respectively. Using the adaptation of Levy's formula to the lower temperature rate data of Trowbridge (k_{14}), the fractional conversion rate of coolant at these two temperatures would be considerably higher (though still small): $5 \times 10^{-7} \text{ s}^{-1}$ at 100°C and $1.6 \times 10^{-5} \text{ s}^{-1}$ at 200°C. These figures represent the fraction of the resident 5% coolant predicted to be converted to C_4F_{10} or other products per second. What this would mean in terms of fraction of inleaking $c\text{-C}_4\text{F}_8$ reacted will further depend on the dynamics of the coolant inleakage and removal from the cascade, the rates of upflow and downflow in the region of fluorinating agent concentration, and, of course, the persistence of the fluorinating agent concentration in the region containing coolant.

Figure 1 is an attempt to display the available decomposition and fluorination data on a common basis. The fractional decomposition rates of $c\text{-C}_4\text{F}_8$ for the three referenced mechanisms are depicted, one plot showing the rate of thermal dissociation, and two plots showing rates of fluorination (one gas-phase, the other in the presence of high surface area NiF_2), the latter two calculated for a F_2 partial pressure of 0.05 bar.

No information was found on low temperature reaction rates of $c\text{-C}_4\text{F}_8$ with other fluorinating agents

beyond the negative information that in the range 150-250°C, UF_6 did not react to a measurable degree [Trowbridge 92] (at the limits of detectability in that experiment, the UF_6 rate was less than 1% of the F_2 rate). Application of the fairly sparse literature on F_2 reaction to an estimate of the reaction rates of other impurities that might act as fluorinating agents is difficult to support rigorously, but can be done mathematically. Assuming that the kinetics of fluorination involve atomic F (directly or indirectly -- perhaps adsorbed on surfaces), then any species which might serve as a fluorinating agent will have some equilibrium level of atomic fluorine at a given temperature and partial pressure, as determined by the thermodynamics of that species and its dissociation fragments. The rate of reaction of a fluorinating agent other than F_2 can be estimated from the thermodynamics of that species and the known rate of reaction with F_2 . For purposes of analysis, it will be assumed that the general kinetic form of Levy's rate (Equation 9) is followed, but with the low temperature rate constant form adapted from Trowbridge (Equation 14). The rationale for doing this is largely that it is the best that can be done with the information available rather than that it can be rigorously defended.

Thermodynamic parameters for possible impurity species and dissociation fragments are largely derived from the JANAF Thermochemical Tables [Chase 85] (F , F_2 , ClF_3 , ClO_2 , ClF , Cl , MoF_6 , MoF_5 , COF_2 , COF , HF , H , SiF_4 , SiF_3 , BF_3 , BF_2), but other sources were used for less common species (ClO_2F [Trowbridge/Gatti 92]; ClF_2 [Blauer 69]; AsF_3 , AsF_5 , [Leitnaker 88]; UF_6 , UF_5 [Leitnaker 83]). Thermodynamic data for TcO_3F was sought but is apparently not available. From these parameters, equilibrium values for atomic F were calculated for each impurity, and from that, predicted coolant reaction rates were computed. The results are listed in the following table. It is assumed that the coolant and fluorinating agent are both present at partial pressures of 0.05 bar with the exception of UF_6 , which is assumed to be present at 1 bar. The table shows the fractional rate of reaction of the coolant. The entries are sorted by their reaction rate at 200°C, and the order is a fairly good representation of the general ranking of effectiveness of these materials as fluorinating agents.

Table 1: Predicted conversion rate of $c-C_4F_8$
(fraction per second)

T (°C)	50	100	150	200
ClF_3	8.6E-08	1.1E-06	7.1E-06	3.1E-05
F_2	4.2E-08	5.2E-07	3.5E-06	1.6E-05
ClO_2F	5.6E-11	2.0E-09	3.0E-08	2.6E-07
ClF	8.8E-16	1.1E-13	4.3E-12	7.7E-11
UF_6 (*)	1.3E-18	7.1E-16	8.5E-14	3.7E-12
AsF_5	7.1E-26	4.2E-22	3.1E-19	5.8E-17
MoF_6	3.6E-26	1.6E-22	9.7E-20	1.5E-17
C_2F_6	2.7E-36	3.2E-31	2.4E-27	2.7E-24
COF_2	1.4E-38	2.8E-33	3.0E-29	4.6E-26
HF	1.0E-41	3.5E-36	6.1E-32	1.3E-28
SiF_4	2.4E-43	2.2E-37	7.8E-33	3.0E-29
BF_3	8.0E-45	1.1E-38	5.3E-34	2.6E-30

(*) UF_6 partial pressure taken as 1 bar; all other species assumed to be at a partial pressure of 0.05 bar

ClF_3 is predicted to be slightly more effective than F_2 at conversion of coolant. Species lower than ClO_2F

probably have too low a fluorinating potential to have any observable effect on $c\text{-C}_4\text{F}_8$. UF_6 is something of a special case in that the entire isotopic cascade contains UF_6 , so the exposure of inleaking coolant to reaction will be much larger. The rate, however, is such that little, if any, observable effect is likely (which is consistent with the negative observation cited earlier [Trowbridge 92]). To take an arbitrary number, if the average residence time of an inleaking coolant molecule in the cascade is 1 day (86,400 s), then at 100 and 200°C, the probability of conversion would be 7×10^{-11} and 3×10^{-7} respectively. The hypothetical 10,000 kg inleaking coolant per year used previously would produce 2 μg coolant conversion at 100°C and 8 mg at 200°C, in either case inconsequential.

The predicted rates from this analysis do not unequivocally prove that these weaker fluorinating agents could not fluorinate $c\text{-C}_4\text{F}_8$ by some other more direct mechanism, but it is not very probable that weaker agents would do what stronger agents do not. In any case, the consequences of most plausible reactions would not be of great concern. The major product of fluorination is $n\text{-C}_4\text{F}_{10}$, which will be present in small quantities as an impurity in the coolant in any case. The only difficulty it might present is that it is slightly higher in molecular weight and thus will be more slowly purged from the cascade. The rate of conversion is so small that this is unlikely to be a problem. A portion of the reacted coolant, however, will convert to lighter species which are more easily purged from the cascade than the parent species. In the presence of a fluorinating agent (which is to say, UF_6) any mechanism that attacks or breaks down the coolant will tend to lead to formation of lighter products – there should be no tendency toward polymerization.

It should be noted that the present coolant, CFC-114, ($\text{C}_2\text{F}_4\text{Cl}_2$) is itself subject to attack by fluorinating agents. In the presence of F_2 , it slowly reacts to form first CFC-115 ($\text{C}_2\text{F}_5\text{Cl}$) and then CFC-116 (C_2F_6). The rate at 150°C is about ten times that observed for $c\text{-C}_4\text{F}_8$ [Trowbridge 90].

Radiolytic decomposition

Another mechanism of decomposition is radiolysis. Under X-ray bombardment, pure $c\text{-C}_4\text{F}_8$ is decomposed to a series of lighter and heavier fluorocarbons [Heckel 1968]. The presence of O_2 , however, suppresses the formation of the heavier species, presumably terminating polymerization of radical or unsaturated species. If radiolysis were to occur in the gaseous diffusion cascade, the presence of UF_6 would probably serve even better than O_2 as a source of fluorine for preventing polymerization. For X-rays, the “G-factor” for radiolytic decomposition of $c\text{-C}_4\text{F}_8$ is 3 molecules decomposed per 100 eV deposited energy, a fairly typical value for gas phase species subject to decomposition. In the cascade environment, the primary exposure is to alpha rather than photon radiation, but G-factors commonly have similar values for different types of ionizing radiation. The highest radiation field due to decay of the U in UF_6 and its daughters will occur in that region where the isotopic enrichment is highest. Locally higher radiation fields may exist in the immediate vicinity of uranium deposits (based strictly on density, perhaps 1000 times higher), and other nuclides (e.g. Tc-99) could similarly produce locally higher fields where they occur.

A rough calculation was performed of the decomposition rate of $c\text{-C}_4\text{F}_8$ in 5% enriched UF_6 gas (with U-234 assumed enriched to 0.05%). Assuming a G-factor of 3 for all types of ionizing radiation, the fraction of $c\text{-C}_4\text{F}_8$ expected to decompose would be on the order of 10^{-17} per second. Near a deposit, if the radiation field were about 1000 times higher, the local fractional decomposition of coolant would be 10^{-14} per second. The radiolytic effectiveness of Tc-99 should be about 35 times that of the 5% assay U, so in the vicinity of Tc deposits, the local decomposition is estimated to be on the order of 10^{-13} per second. None of these rates would produce a significant effect even if the product were a polymer, but the likely effect of radiolysis is simply to (very slightly) accelerate fluorination of $c\text{-C}_4\text{F}_8$.

Summary: The expected rates of $c\text{-C}_4\text{F}_8$ fluorination, decomposition, and radiolysis are very small. The most reactive potential contaminants are F_2 and ClF_3 . ClF and ClO_2F would be weaker agents, and UF_6 is unlikely to cause any significant reaction. The limited evidence available suggests that at temperatures spanning cascade conditions, $c\text{-C}_4\text{F}_8$ will be chemically more stable than CFC-114, which itself has proven adequately chemically resistant to cascade conditions. Of course, in the presence of high concentrations of strong fluorinating agents, a flammable mixture can form [Fletcher 1968 and 1983], but this is true of CFC-114 also, and thus not unique to the alternate coolant.

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W. J. Spetnagel
April 30, 1999
page 8

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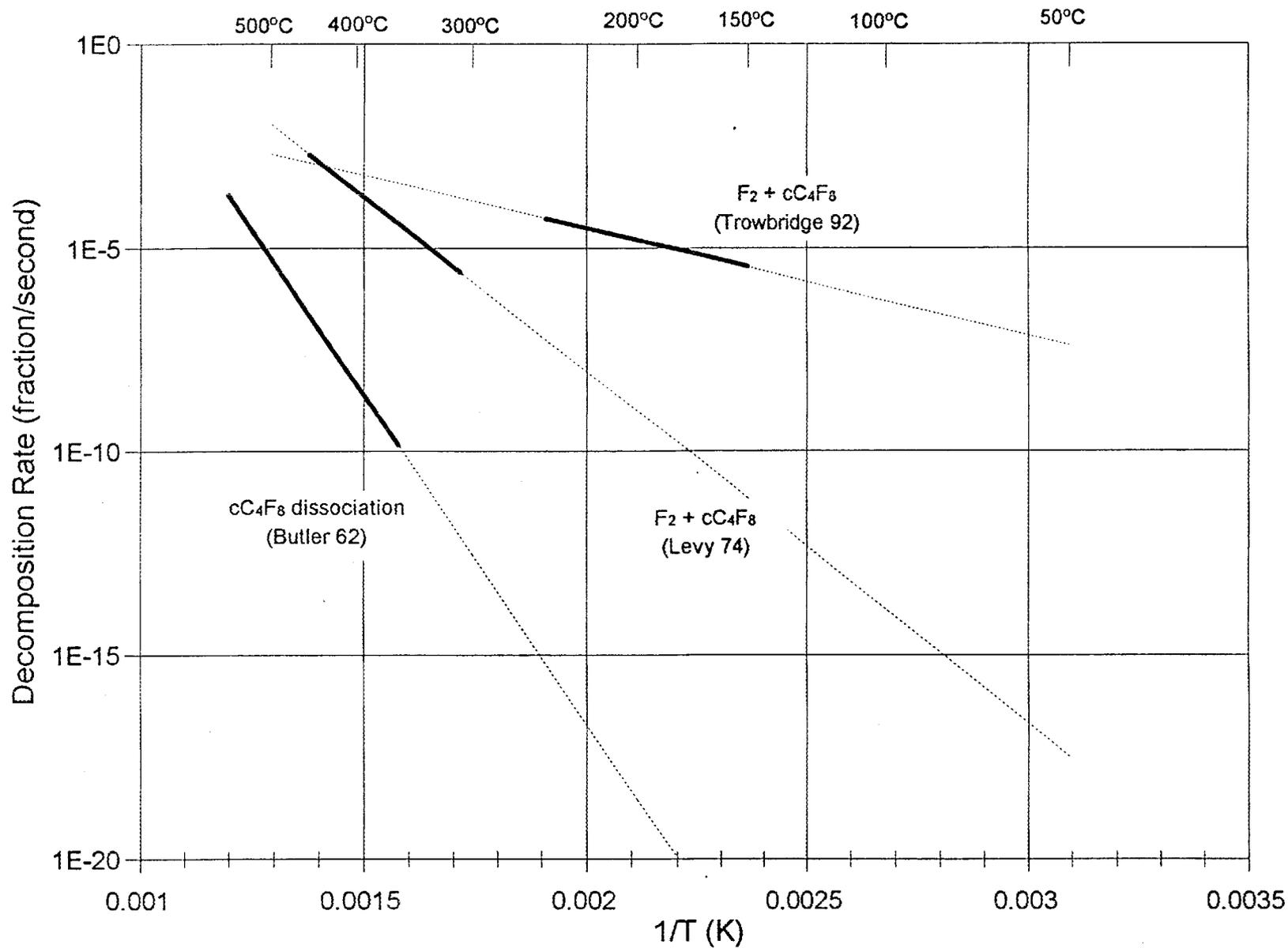


Figure 1: Comparison of $c\text{-C}_4\text{F}_8$ decomposition rates. In all cases, the rate shown is the predicted fraction decomposed per second. The “ $c\text{-C}_4\text{F}_8$ dissociation” line depicts the rate of unimolecular dissociation to form C_2F_4 . The two “ $\text{F}_2 + c\text{C}_4\text{F}_8$ ” entries show the rate of reaction with 0.05 bar fluorine. The Levy (1974) rate is for a homogeneous (i.e. gas phase) mechanism whereas the Trowbridge (1992) rate apparently involves a heterogeneous (i.e. surface) mechanism. In all cases, the heavy lines depict the temperature range over which the experimental data was taken, and the dotted lines represent extrapolations.