# Experimental and Computational Studies on the Gas-Phase Reaction of CBrF<sub>3</sub> with Hydrogen

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Gas-phase hydrogen dehalogenation of halon 1301 (bromotrifluoromethane, CBrF<sub>3</sub>) has been studied experimentally in a tubular alumina reactor operating at atmospheric pressure. It is found that hydrogen can accelerate the decomposition of halon 1301 and that conversion levels of CBrF<sub>3</sub> and H<sub>2</sub> increase with temperature and residence time. CBrF<sub>3</sub> conversion increases with decreasing input volume ratio of CBrF<sub>3</sub> to H<sub>2</sub>. The species produced are a complex mixture of halogenated hydrocarbons including CHF<sub>3</sub>, CH<sub>2</sub>F<sub>2</sub>, C<sub>2</sub>HF<sub>3</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>2</sub>H<sub>2</sub>F<sub>4</sub>, C<sub>2</sub>HF<sub>5</sub>, CHBrF<sub>2</sub>, CH<sub>3</sub>Br, CH<sub>2</sub>Br<sub>2</sub>, CHBr<sub>2</sub>F, and CH<sub>2</sub>BrF in addition to HBr and HF. The production yield of CHF<sub>3</sub>, the major product, increases with temperature to 1023 K, after which CHF<sub>3</sub> levels decrease with increasing temperature. Conversely, CHF<sub>3</sub> selectivity decreases with increasing temperature, residence time, or input ratio of CBrF<sub>3</sub> to H<sub>2</sub>. The initiation reaction is believed to be the rupture of the C–Br bond in  $CBrF_{3_1}$  and the radical species CF<sub>3</sub> then reacts with H<sub>2</sub> to produce H and CHF<sub>3</sub>. The key step in the process is the attack of H radical on CBrF<sub>3</sub> to produce CF<sub>3</sub> and HBr. Experimental data are compared with the model predictions, and good agreement between experimental and modeling prediction is obtained for CHF<sub>3</sub> production. However, the existing mechanism does not predict the formation of  $CHBrF_{2}$ , which is detected during the experimental study, and the concentrations of CH<sub>2</sub>F<sub>2</sub> and C<sub>2</sub>F<sub>6</sub> measured experimentally are significantly different from those predicted. Modifications to the existing NIST mechanism are suggested to improve the prediction of the quantity of these species produced.

# Introduction

CFCs (chlorfluorocarbons) and halons (bromine-containing fluorocarbons and chlorofluorocarbons) have been confirmed as stratospheric ozone-depleting agents. CFCs are a class of compounds that were used as refrigerants, aerosol propellants, foam blowing agents, and solvents in the electronics industry. In 1974, Molina and Rowland found that CFCs were major sources of chlorine-containing radicals in the stratosphere, which catalyze the destruction of ozone in the upper stratosphere (*1*). Halons such as halons 1301 (CBrF<sub>3</sub>), 1211 (CBrClF<sub>2</sub>), and 2402 (C<sub>2</sub>Br<sub>2</sub>F<sub>4</sub>) were used extensively for fire mitigation application. Halons provide a large source of stratospheric bromine radicals, which are 10-100 times as destructive to the ozone layer as chlorine on a per atom basis (*2*). The campaign to protect the stratospheric ozone layer that shields the earth from damaging UV-B radiation has led to a landmark international agreement: The Montreal Protocol on Substances That Deplete the Ozone Layer. This protocol provides deadlines for phasing out the production of several CFCs and halons and many other halocarbons. The major consequences of the phasing out of halons have been the initiation of an exhaustive effort to develop new halon replacements and the need to develop effective halon treatment processes. Generally, there are two generic approaches to treat halons: destruction or conversion.

Currently available halon destruction technology is based on thermal oxidation, including processes such as rotary kiln incineration, fluidized-bed incineration, liquid injection incineration, lime/cement kiln coincineration, molten salt incineration, plasma arc incineration, and high-temperature fluid wall destruction (3). However, at the high temperature of incineration, most fluorinated organics decompose and react to produce toxic and corrosive fluorides, primarily in the form of hydrogen fluoride (HF), which can attack the refractory of many current incinerator systems (4). The combustion inhibition properties of halons also make incineration a very unattractive disposal option, especially from an energy-consumption perspective. Furthermore, there are increasing concerns over the emission of both feed and toxic products of incomplete combustion (PICs) such as COF<sub>2</sub>, COFCl, COCl<sub>2</sub>, and perhalogenated olefins that can be produced in these processes (5). Moreover, HBr and Br<sub>2</sub> are produced during the incineration of bromine-containing compounds. Hydrogen bromide can be removed by scrubbing the exhaust gases with base, but the technology for controlling  $Br_2$  is not well developed (3). There are some reports of catalyst-aided oxidative destruction of CFCs at the bench-scale level. However, deactivation of catalysts remains an unresolved issue in the development of these technologies (6-9).

Along with the exhaustive search for halon replacements, halon conversion technology has attracted considerable research interest, where the general focus is to treat the halons through their conversion into products of economic value. Hydrodehalogenation is a nonoxidative process in which CFCs or halons react with hydrogen or hydrogen donors. A limited number of studies have been reported in the area of gas-phase hydrodehalogenation of CFCs and halons. The thermal decomposition of halon 1211 (CBrClF<sub>2</sub>) in H<sub>2</sub> has been studied, and it was found that hydrogenolysis of C-Br takes place at low temperature while the cleavage of its analogous C-Cl bond does not (10). Defluorination only occurs at high temperatures (>600  $^{\circ}$ C) and then increases significantly with temperature. A variety of products, including HCFCs, HFCs, and hydrocarbons, were detected at elevated temperatures (10). These results were in reasonable agreement with the study of the reaction of CFC 113 (CF2-ClCFCl<sub>2</sub>) with H<sub>2</sub> investigated by Ritter, although the onset temperatures of defluorination were shifted to even higher temperatures (700 °C) at comparable residence times and pressures (5). It was also noted in both studies that, in the presence of H<sub>2</sub>, dechlorination and defluorination were energetically favorable, resulting in the formation of HCl and HF. In contrast, during the reaction of CBrF<sub>3</sub> and H<sub>2</sub> in a shock tube between 1000 and 1600 K and 1.2-2.6 atm, Hidaka et al. did not detect the formation of HF, although HBr was detected (11). More work is needed to understand the thermal chemistry of hydrodehalogenation of halons and to study the product distribution as a function of temperature and residence time before it can be considered a commercially viable process.

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Alumina Tube Reactor

FIGURE 1. Schematic of the experimental apparatus: MFC, mass flow controller; TC, temperature controller.

Detailed kinetic schemes are widely used to simulate various reaction processes. The main advantage of this approach over those based on simpler empirical models lies in its wider range of application, allowing greater control over the design and optimization of reacting systems (12). Most elementary reaction mechanisms reported in the literature were developed for some specific reactions and for applications under well-defined experimental conditions. Many kinetic parameters rely on empirically determined reaction rates (some of which are not very accurate) or rate parameters estimated theoretically. Thus, every reaction mechanism should be reexamined whenever new experimental or theoretical results become available (13). To date, however, little attention has been paid to the numerical simulation of the thermal hydrodehalogenation of CFCs or halons

In this paper, we concentrate on gas-phase nonoxidative thermal reaction of  $CBrF_3$  and  $H_2$  at ambient pressure. This chemistry is numerically simulated by a NIST (National Institute of Standard and Technology) mechanism that combines the general gas-phase reaction chemistry of  $CBrF_3$ with HFC and  $CH_4$  reaction mechanisms (14). Some modifications to specific elementary reaction steps in the model are suggested to improve the agreement between experimental data and model predictions. The current study represents one component in a larger investigation to examine a range of treatment options for halons.

# **Experimental Section**

Thermal hydrodehalogenation of halon 1301 in a nitrogen bath gas was studied at ambient atmosphere in a 7.0 mm i.d. alumina (99.99%) tubular reactor. A high-purity alumina reactor rather than quartz reactor was used because the quartz tube is rapidly corroded by fluorides (*5*). The reactor was resistively heated in a three-zone electric tube furnace (Figure 1).

From examination of temperature profiles across the heated zone of the furnace, temperature gradients of <5 K were achieved. Three gases [N<sub>2</sub> (99.99%), CBrF<sub>3</sub> (98.5%, 1.5% N<sub>2</sub>), and H<sub>2</sub> (99.99%)] were metered with electronic mass flow controllers (Brooks). To maintain a constant residence time at various temperatures, the volume of thermal zone was adjusted by moving two small thermocouple sheaths (alumina, 6.0 mm o.d.) situated in the reactor.

The reactor effluent was analyzed on a MTI micro gas chromatograph (GC, Activon, M200H) with two thermal conductivity detectors. A gas chromatograph/mass spectrometer (GCMS QP5000, Shimadzu) was used for product identification. The operational conditions of the two apparatus are summarized in Table 1. Mineral acids HBr and

## TABLE 1. GC and GC/MS Operational Conditions

	GC MTI, M200H		GCMS-QP5000	
column	molecular sieves	Poraplot U	AT-Q	
carrier gas	He	He	He	
column head pressure	103 kPa	30.4 kPa	16.8 kPa	
column temperature	50 °C	100 °C	60-200 °C	
injection temperature	na <sup>a</sup>	na	230 °C	
interface temperature	na	na	230 °C	
split ratio	na	na	100	
total flow	na	na	151.9 cm <sup>3</sup> /min	
sample time	20 s	20 s	na	
sample volume	na	na	5.0 cm <sup>3</sup>	
a				

<sup>a</sup> na, not applicable.

# TABLE 2. Estimated Response Factors for Halogenated Species

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compound	RMR	compound	RMR
$CF_4$	77.7	$C_2F_6$	108.1
CHBrF <sub>2</sub>	81.6	$C_2HF_5$	103.7
$CH_2Br_2$	81.6	$C_2H_2F_2$	72.15
CH <sub>2</sub> BrF	81.6	$C_2H_2F_4$	98.5
$CH_2F_2$	66.1	$C_2H_3F_3$	90.7

HF produced were removed continuously from the gas stream by a water scrubber located at the exit of the reactor. A bypass line was designed to sample feed gases for concentration analysis.

Relative molar response (RMR) factors were determined experimentally for quantification of  $CHF_3$  (Kidde Graviner Co.),  $CH_3Br$  (BOC Gases), and all hydrocarbons (Scott Specialty Gases, Alltech). RMRs (Table 2) of other species were estimated theoretically from correlation developed by Barry and Rosie (15):

$$RMR_{i} = \left[\frac{\frac{\sigma_{i} + \sigma_{I}}{\sigma_{I}}}{\frac{\sigma_{\phi} + \sigma_{I}}{\sigma_{I}}}\right] \left[\frac{M_{i} - M_{I}}{M_{\phi} - M_{I}}\right]^{1/4} \times 100$$
(1)

$$\sigma = 2.36 (T_{\rm c}/P_{\rm c})^{1/3}$$
 (2)

where  $\sigma$  is molecular diameter (Å), *M* denotes molecular weight, *T*<sub>c</sub> is critical temperature (K), *P*<sub>c</sub> stands for critical pressure (atm), and subscripts i, I, and  $\phi$  refer to the species



FIGURE 2. Simulation of fluid flow in tubular reactor from CFD modeling assuming axisymmetric geometry for 0.1 s residence time.

under consideration, the carrier gas, and benzene (the internal standard), respectively. The factor of 100 represents the response of benzene, arbitrarily assigned a value of 100 response units per mole. Carbon mass balance of 98% ( $\pm 2\%$  error) was achieved under all reaction conditions.

For a given inlet concentration, experiments were performed at various temperatures. A series of six residence times were used at each temperature, and the residence time was determined as a function of flow rate, volume of thermal zone, and temperature. Every alternate run was repeated to examine reproducibility.

**CFD Simulation of the Tubular Reactor.** To verify the legitimacy of the plug flow idealization for the tubular reactor employed in the investigation, a series of CFD (computational fluid dynamics) simulations were performed using the FLUENT package. In this modeling, the conservation equations for transport of mass, momentum (Navier–Stocks), and energy were solved for nonreacting system at different temperatures and residence times, assuming symmetrical conditions on the axial coordinate. The results indicated that the plug flow idealization rendered a negligible error in the analysis of experimental data for long residence time (>0.7 s) and a minor though more significant error for short residence times (<0.7 s), as shown in Figure 2.

**Chemical Kinetic Modeling.** The reactor behavior was modeled through the steady-state material balances for each chemical species. The energy balance equation was neglected because all experiments were performed under essentially isothermal conditions. The calculations were carried out using a computer code PLUG (16), which is a Fortran-based program for the analysis of plug flow reactors with gas-phase and (optionally) surface chemistry. This program makes use of two other chemical kinetic software packages known as CHEMKIN-III (17) and SURFACE CHEMKIN-III (18) to handle gas-phase and heterogeneous kinetics as well as thermodynamic properties. Only CHEMKIN-III was used in the present study since possible catalytic surface reactions of the alumina reactor were shown to be negligible during experiments with alumina chips. The detailed chemical reaction scheme used in this study, called the NIST mechanism, actually incorporates (a) fluorocarbon (HFC), (b) bromofluorocarbon (CBrF<sub>3</sub>), and (c) hydrocarbon mechanisms (14). It includes 209 reactions and 44 species after all reactions and species containing oxygen were removed from the mechanism.

The conversion levels of both CBrF<sub>3</sub> and H<sub>2</sub> and the production of CHF<sub>3</sub> are satisfactorily predicted by the NIST



FIGURE 3. Conversion of CBrF<sub>3</sub> at various residence times as a function of reaction temperature; volumetric ratio of reactant feed,  $H_2$ :CBrF<sub>3</sub>: $N_2 = 1:1:11$ .

mechanism, although conversion levels observed in experiments are slightly higher than those predicted. For minor products, however, a significant deviation was noted between experimental results and model predictions. Especially, significant production of  $C_2F_4$  was predicted in the model but not detected in our experiments. The formation of a series of Br-containing products such as CHBrF<sub>2</sub>, CH<sub>2</sub>Br<sub>2</sub>, CHBr<sub>2</sub>F, and CH<sub>2</sub>BrF, which were not predicted in the model, was observed experimentally. The formation of  $C_2F_6$ , which was found in trace amounts experimentally, was predicted to be present in significant amounts in the model. On the basis of our experimental results, we have suggested modifications to the NIST mechanism, which will be discussed in detail later.

# **Results and Discussion**

**Conversion of CBrF**<sub>3</sub> and H<sub>2</sub>. With an input volumetric ratio of  $H_2$ :CBrF<sub>3</sub>:N<sub>2</sub> = 1:1:11, the conversion levels of halon 1301 and hydrogen as function of temperature are shown in Figures 3 and 4.

The conversion levels of both reactants increase with temperature and residence time. At 1053 K and a residence time of 2.0 s, both  $CBrF_3$  and  $H_2$  were consumed completely (>99%). Conversion levels of  $CBrF_3$  and  $H_2$  were virtually identical at low temperature. At high temperature, the conversion level of  $H_2$  was higher than that of  $CBrF_3$ . These results suggest that at low temperature the thermal cleavage



FIGURE 4. Conversion of H<sub>2</sub> at various residence times as a function of reaction temperature; volumetric ratio of reactant feed, H<sub>2</sub>:CBrF<sub>3</sub>:  $N_2 = 1:1:11$ .



FIGURE 5. Conversion of CBrF<sub>3</sub> as function of temperature at various CBrF<sub>3</sub>/H<sub>2</sub> ratios and a 1.0 s residence time.

of C–Br bond, the most labile bond in  $CBrF_3$  (19), initiates a radical chain reaction. The radical species Br and  $CF_3$  thus formed attack  $H_2$  or HBr to produce the major products observed:  $CHF_3$  and HBr:

$$\operatorname{CBr}F_3 \rightarrow \operatorname{CF}_3 + \operatorname{Br}$$
 (R1)

$$CF_3 + H_2 \rightarrow CHF_3 + H$$
 (R2)

$$Br + H_2 \rightarrow HBr + H \tag{R3}$$

$$CF_3 + HBr \rightarrow CHF_3 + Br$$
 (R4)

At higher temperature, however, the rate of homolysis or hydrogenolysis of the C–F bond in CF<sub>3</sub> and CBrF<sub>3</sub> increases, resulting in the production of a range of minor products, such as CHBrF<sub>2</sub>. This also leads to elevated production of HF and a slightly higher rate of consumption of H<sub>2</sub>:

$$CF_3 + H \rightarrow CF_2 + HF$$
 (R5)

$$CF_2 + HBr \rightarrow CHBrF_2$$
 (R6)

$$\operatorname{CBrF}_3 \rightarrow \operatorname{CBrF}_2 + F$$
 (R7)

$$\operatorname{CBrF}_2 + \operatorname{H}_2 \rightarrow \operatorname{CHBrF}_2 + \operatorname{H}$$
 (R8)

$$\mathbf{H} + \mathbf{F} \to \mathbf{H}\mathbf{F} \tag{R9}$$

The influence of  $H_2/CBrF_3$  feed ratio on the conversion of  $CBrF_3$  for 1.0 s residence time is shown in Figure 5.

Without  $H_2$  added in feed, the conversion of CBrF<sub>3</sub> is very low, approximately 10%, even at a temperature of 1053 K. The addition of  $H_2$  greatly accelerates the reaction of CBrF<sub>3</sub>, and this effect is more pronounced at high temperatures. As more hydrogen is added to the feed stream, the conversion of CBrF<sub>3</sub> increases, suggesting that H<sub>2</sub> accelerates the decomposition of CBrF<sub>3</sub> and has a significant influence on the decomposition kinetics of CBrF<sub>3</sub>. A similar mechanism was also reported for the reaction of CFCl<sub>2</sub>CF<sub>2</sub>Cl with hydrogen (*5*). In contrast, the reaction rate of CFCl<sub>2</sub>CF<sub>2</sub>Cl is not altered under oxidative conditions as compared with that under pyrolysis conditions (*20*). Therefore, the radicals O or OH are not energetically favorable to attack perhalogenated hydrocarbons, while the abstraction of halogen atoms by a hydrogen radical is energetically favorable. With an excess of CBrF<sub>3</sub> in the feed stream, the reaction rate of CBrF<sub>3</sub> is much slower at high temperature than that at low temperature, suggesting that H<sub>2</sub> is a more efficient sink than other hydrogen-containing products, such as CHF<sub>3</sub>.

The reaction of CBrF<sub>3</sub> and H<sub>2</sub> is initiated by the scission of the C–Br bond (R1) rather than by the decomposition of H<sub>2</sub> because of the high dissociation energy of H<sub>2</sub>. However, once the radical H is produced, the process of the conversion of CBrF<sub>3</sub> into CHF<sub>3</sub> catalyzed by H radical (R10) becomes significant, followed by R2 and R4. Obviously, reactions R2 and R10 can be enhanced by increasing the concentration of H<sub>2</sub>, which explains why the conversion level of CBrF<sub>3</sub> increases with a higher concentration of H<sub>2</sub> in the system:

$$\operatorname{CBrF}_3 + \operatorname{H} \to \operatorname{CF}_3 + \operatorname{HBr}$$
 (R10)

Hence, at low temperature, reactions R1 and R10 are the major contributors to the consumption of CBrF<sub>3</sub>.

Model predictions of the conversion levels of CBrF<sub>3</sub> and H<sub>2</sub> were also shown in Figures 3–5. The conversion levels were satisfactorily predicted by the NIST mechanism, but the experimental results were slightly higher than those calculated. This can probably be attributed to the following causes. First, models generally are not optimized to fit only one specific experimental data set, and their applicability is generally for an overall description of the reaction profile rather than the duplication of experimental data recorded over a limited parameter range (21). Second, the actual residence time of the reaction was slightly longer than that calculated for a plug flow reactor because of the circulation of reactants in the inlet section of the reactor, as depicted in Figure 2 from CFD simulation. This circulation has a greater influence at shorter residence times than at longer residence times. Third, the surface of the reactor wall may potentially affect the reaction, which is not included in the NIST mechanism. In the literature, wall effects were suggested to exist in reactors of 10.5 mm i.d. or smaller at high temperature in similar systems, which may render the global reaction rate higher than that without wall effect (22, 23). However, in this study, experiments with alumina chips indicated that there was no detectable contribution of wall reactions under the present experimental conditions.

**Product Variation.** Apart from HBr and HF (at high temperatures),  $CHF_3$  is the major product species formed under all conditions investigated. The yield and selectivity of  $CHF_3$  at various temperatures, residence times, or input  $CBrF_3/H_2$  ratios are presented in Figures 6–8.

The yield of CHF<sub>3</sub> increases with increasing temperature to 1023 K, after which it drops considerably with increasing temperature. Not unexpectedly, the selectivity of CHF<sub>3</sub> decreases with increasing temperature, and this decrease becomes more pronounced at higher temperatures. However, even at high temperatures, the selectivity of CHF<sub>3</sub> remains high (90%) among carbon-containing products. This feature is highlighted in Figure 7. At 873 K, the selectivity of CHF<sub>3</sub> decreases slightly with increasing residence time but only decreases 2% over the broad range of residence time from 0.1 to 2.0 s. This decrease reaches about 6% at 993 K, while conversion of CBrF<sub>3</sub> increases from 20.0% at 0.1 s to 92.6%



FIGURE 6. Yield and selectivity of CHF<sub>3</sub> against temperature at 1.0 s residence time; product yield expressed as fractions of the initial concentration of CBrF<sub>3</sub>; volumetric ratio of reactant feed,  $H_2$ :CBrF<sub>3</sub>:  $N_2 = 1:1:11$ .



FIGURE 7. Selectivity of CHF<sub>3</sub> against residence time at 873 and 993 K; volumetric ratio of reactant feed,  $H_2$ :CBrF<sub>3</sub>:N<sub>2</sub> = 1:1:11.



FIGURE 8. Products selectivity as a function of the input volume ratio of  $CBrF_3$  to  $H_2$  at 1.0 s residence time at 993 K.

at 2.0 s. The production of CHF<sub>3</sub> as a function of input ratio of CBrF<sub>3</sub>/H<sub>2</sub> (993 K and 1.0 s residence time) is shown in Figure 8. Both the selectivity and yield of CHF<sub>3</sub> decrease with higher concentrations of CBrF<sub>3</sub> in the feed stream. The production yield of CHF<sub>3</sub> decreases dramatically from 96.2% at a CBrF<sub>3</sub>/H<sub>2</sub> ratio of 0.1 to 9.9% at a CBrF<sub>3</sub>/H<sub>2</sub> ratio of 10 (corresponding conversion of CBrF<sub>3</sub> is reduced from 99.3% to 19.6%), while its selectivity only decreases about 20% over the same range. These results are in excellent agreement with the results of shock tube experiments performed by Hidaka's group (*11*).



FIGURE 9. Reaction pathways of minor products formed from  $CHF_3$  (34–36).

The production profile of CHF<sub>3</sub> predicted by the NIST reaction mechanism and our proposed modified mechanism is depicted in Figures 6–8. It is shown that the production profile of CHF<sub>3</sub> can be satisfactorily predicted by the NIST mechanism. Combining CHF<sub>3</sub> distribution profile with CBrF<sub>3</sub> and H<sub>2</sub> conversion profiles, we can conclude that the NIST reaction mechanism, which was optimized for CBrF<sub>3</sub> combustion chemistry, can be applied to simulate nonoxidative hydrogen reaction chemistry. However, there are some discrepancies between experimental and theoretical results for the production of secondary reaction products.

In addition to a number of  $CHF_3$  formation reactions in the NIST mechanism, we suggest an additional reaction (R11), which is also important for the formation of  $CHF_3$ :

$$H + CF_3 \rightarrow CHF_3$$
  $\Delta H = -4.31 \times 10^5 \text{ J/mol}(24)$  (R11)

Although reactions R2 and R4 are generally more important for the formation of CHF<sub>3</sub> than R11, reaction R11 is an energetically favorable reaction with no associated potential energy barriers (*24*). It seems likely it has a nonnegligible influence on the formation rate of CHF<sub>3</sub> (*25*). Our sensitivity analysis shows that approximately 6% CHF<sub>3</sub> is formed via this reaction at 973 K and 1.0 s.

A number of minor products were detected at high temperatures, including  $CH_2F_2$ ,  $C_2HF_3$ ,  $C_2F_6$ ,  $C_2H_2F_4$ ,  $C_2HF_5$ ,  $CHBrF_2$ ,  $CH_3Br$ ,  $CH_2Br_2$ , and  $CH_2BrF$ . Among these minor products,  $C_2HF_3$ ,  $CH_3Br$ ,  $C_2H_2F_4$ ,  $C_2HF_5$ ,  $CH_2Br_2$ ,  $CHBr_2F$ , and  $CH_2BrF$  are present in trace amounts (<1.00% *C*/*C*<sub>0</sub>), while  $CH_2F_2$ ,  $C_2F_6$ , and  $CHBrF_2$  were detected at higher concentrations. The pathways leading to formation of these products are shown in Figure 9. The distribution profiles of  $CH_2F_2$ ,  $C_2F_6$  and  $CHBrF_2$  as a function of temperature and residence time are presented in Figures 10 and 11.

It is seen in Figure 10 that the production yield of  $CH_2F_2$ , similar to  $CHF_3$ , increases with increasing temperature up to 1023 K, after which it decreases at higher temperatures. Although  $CHBrF_2$  is observed even at temperatures as low as 823 K, its concentration increases relatively slowly with temperature. The species  $C_2F_6$  follows a similar trend to that of  $CHBrF_2$  but was detected at a much lower concentration. The selectivity of these three minor products as a function of residence time (993 K) is displayed in Figure 11. The selectivity of  $CH_2F_2$  and  $CHBrF_2$  rises consistently with residence time, while the selectivity of  $C_2F_6$  decreases slightly with increasing residence time up to 0.5 s and then remains roughly constant at longer residence times.

The product CHBrF<sub>2</sub> is formed via two possible reaction pathways (Figure 9): (i) Br is abstracted from CBrF<sub>3</sub> by an H radical, and the subsequently formed CF<sub>3</sub> radical then reacts with H to form CF<sub>2</sub>, which reacts further with HBr. (ii) The radical CF<sub>2</sub>, suggested to be formed from the decomposition of CHF<sub>3</sub>, reacts with HBr to form CHBrF<sub>2</sub>. Although



FIGURE 10. Minor product distribution against temperature at 1.0 s residence time; product yield expressed as fractions of the initial concentration of CBrF<sub>3</sub>; volumetric ratio of reactant feed,  $H_2$ :CBrF<sub>3</sub>:  $N_2 = 1:1:11$ .



FIGURE 11. Selectivity of carbon-containing major product against residence time at 993 K; volumetric ratio of reactant feed,  $H_2$ :CBrF<sub>3</sub>:  $N_2 = 1:1:11$ .

the homolysis of a C–F bond in CBrF<sub>3</sub> is energetically unfavorable and thus negligibly slow at low temperatures, it may occur at high temperatures. In fact, CHBrF<sub>2</sub> is the initial minor species detected at 823 K experimentally, suggesting that cleavage of the C–F bond in CBrF<sub>3</sub> occurs simultaneously with the homolysis of the C–Br bond. This explanation is given added validity by the observed formation of CH<sub>3</sub>Br, CH<sub>2</sub>Br<sub>2</sub>, and CH<sub>2</sub>BrF, which were detected in trace amounts experimentally. Both these pathways are enhanced at higher temperature or at longer residence time, and thus the production of CHBrF<sub>2</sub> increases with increasing temperature or residence time.

Minor hydrofluorocarbon product species are likely to be formed from the secondary reaction of CHF<sub>3</sub> or CHBrF<sub>2</sub>. High temperatures or long residence time favors the decomposition of CHF<sub>3</sub>, leading to increased formation of CHF<sub>2</sub> and the production of CH<sub>2</sub>F<sub>2</sub>. The rate of formation of CH<sub>2</sub>F<sub>2</sub> from hydrodehalogenation of CHF<sub>3</sub> should be very slow at low temperatures, as the dissociation energy of C-F (4.86  $\times$  10<sup>5</sup> J/mol) is significantly higher than that of C–H (4.15  $\times$  10<sup>5</sup> J/mol). Hence, CH<sub>2</sub>F<sub>2</sub> formation proceeds via an alternative process. As shown in Figure 9, two mechanisms are suggested to contribute to formation of CH<sub>2</sub>F<sub>2</sub>. One is via the combination of CHF with HF, as this pathway has a lower energy barrier (19). The alternative mechanism is the hydrogenation of CHBrF<sub>2</sub>, followed by the elimination of HBr, which is energetically more favorable. On the other hand, CH<sub>2</sub>F<sub>2</sub> is an intermediate species that can react further with other radicals

to produce tertiary products such as  $C_2H_2F_{4,}$  and thus its production yield decreases at temperatures above 1023 K.

Hexafluoroethane is formed primarily via the combination of two CF<sub>3</sub> radicals. Its low concentration is attributed to its unfavorable formation kinetics. First, because of the much higher concentration of H<sub>2</sub> and HBr, reactions R2 and R4 must be much faster than R12, contributing to the low selectivity to C<sub>2</sub>F<sub>6</sub>. Second, at 1000 K, the rate constant of R11  $(k_{11} = 6.3 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} (25))$  is 100 times greater than that of R12  $(k_{12} = 6.0 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} (11))$ , so R12 is a kinetically and energetically unfavorable reaction in the presence of H<sub>2</sub>:

$$CF_3 + CF_3 \rightarrow C_2F_6 \quad \Delta H = -4.01 \times 10^5 \text{ J/mol} (26) \text{ (R12)}$$

It seems that CF<sub>3</sub> formed during the reaction would be quickly converted into CHF<sub>3</sub>, and thus only trace amounts of  $C_2F_6$ are formed. Reaction R12 is a highly exothermic reaction, but its production yield was observed to increase with increasing temperature. This feature can be explained by the study of Zitter et al. (*27*), who found that reaction R12 has a higher activation energy at low temperature and a lower activation energy at high temperature; hence, the production of  $C_2F_6$  is favored at higher temperatures.

No  $C_2F_4$  was detected in any experiment undertaken in this investigation.  $CF_2$  radicals can be produced via the decomposition of  $CHF_3$  (R13) or reaction R5. However, selfcombination of  $CF_2$  radicals rarely occurs in the presence of hydrogen, for reasons similar to that used to explain the negligible formation of  $C_2F_6$ . However,  $C_2F_4$  can also be formed via reaction of  $CF_2$  and  $CHF_3$  (R16), whose reaction rate is considerably higher than that of reaction R14, but only takes place to any significant extent above 1200 K (*28*):

$$CHF_3 \rightarrow CF_2 + HF$$
 (R13)

$$CF_2 + CF_2 \rightarrow C_2F_4 \quad \Delta H = -2.88 \times 10^5 \text{ J/mol} (24)$$
 (R14)

$$H + CF_2 \rightarrow CHF_2$$
  $\Delta H = -377 \times 10^5 \text{ J/mol} (24)$  (R15)

$$CF_2 + CHF_3 \rightarrow C_2F_4 + HF$$
 (R16)

We suggest that the formation of  $C_2F_4$  may be favored at high temperature. Indeed, Hidaka et al. (*11*) did not detect any  $C_2F_4$  below 1300 K but did observe the formation of  $C_2F_4$ above this temperature when they studied the reaction of CBrF<sub>3</sub> and H<sub>2</sub> in a shock tube between 1000 and 1600 K and at 1.2–2.6 atm. Combining our results and the results of Hidaka et al., we conclude that the self-combination of CF<sub>3</sub> or CF<sub>2</sub> only occurs to a significant extent at high temperatures during nonoxidative gas-phase reactions.

When we employed the NIST mechanism to predict the formation of minor species, we found significant discrepancy between experimental and modeling results. To improve simulation of minor species, we have incorporated some minor modifications into the NIST mechanism, outlined in the following:

reactions considered	Α	b	Ε	ref
$CH_3 + CF_3 \rightarrow CH_2 - CF_2 + HF$	5.53E+19	-1.9	1.02E+04	
replaced by	6.76E+11	0.0	0.0	(29)
$CF_3 + CF_3 \rightarrow CF_3 - CF_3$	1.63E+36	-7.3	2.95E+04	
replaced by	6.00E+11	0.0	0	(11)
$CH_3 + CF_3Br \rightarrow CF_3 + CH_3Br$	5.75E+12	0.0	1.76E+04	
replaced by	5.75E+12	0.0	2.18E+04	(30)
$CF_3Br \rightarrow CF_3 + Br$	2.00E+13	0.0	2.63E+05	
replaced by	5.50E+16	0.0	2.51E+05	(11)
$CH_3Br \rightarrow CH_3 + Br$	1.58E+13	0.0	3.00E+05	
replaced by	7.65E+13	0.0	2.96E+05	( <i>30</i> )

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in which  $k = AT^{b} \exp(-E/RT)$ , and the units are in mol cm s K, with E in J mol<sup>-1</sup>.

To predict the formation of  $CHBrF_2$  (quantities of  $CH_2BrF$ and  $CH_2Br_2$  were negligible), we have included additional reactions into the NIST mechanism. Because of the lack of thermochemical data on some Br-containing species, we have chosen to estimate data from the corresponding chlorine species or their analogues to undertake the computational study:

reaction	А	b	Е	ref
$      (R6) CF_2 + HBr \rightarrow CHBrF_2 \\       (R8) CBrF_2 + H_2 \rightarrow CHBrF_2 + H \\       (R11) H + CF_3 + M \rightarrow CHF_3 + M \\       (R17) CBrF_3 + H \rightarrow CBrF_2 + HF \\       (R18) CBrF_2 + HBr \rightarrow $	1.38E+12 5.39E+10 5.00E+13 1.10E+15 2.63E+11	0 0 0 0	4.00E+04 4.00E+04 1.67E+04 1.87E+05 1.10E+04	(31) (32) (25) (37) (33)
$CHBrF_2 + Br$				

It can be seen in Figures 10 and 11 that predictions of these minor species were somewhat improved, following the inclusions and modifications of the existing mechanism. The production of CHBrF2, which is not included in the NIST mechanism, is predicted reasonably well by the modified version. The discrepancy between predicted and measured levels of  $C_2F_4$  and  $C_2F_6$  has also been narrowed after modification of the mechanism, especially for the production of C<sub>2</sub>F<sub>6</sub>. This suggests that R12 is a dominant reaction of C<sub>2</sub>F<sub>6</sub> formation. The prediction of CH<sub>2</sub>F<sub>2</sub> production is also improved in the modified version. As shown in Figure 10, at low temperatures, the production yield of CH<sub>2</sub>F<sub>2</sub> is higher than that of CHBrF<sub>2</sub>, while the modified version predicts higher concentrations of CHBrF<sub>2</sub>. Reaction R19, which might represent a significant pathway for the consumption of CHBrF2 and the formation of CH2F2, has not been included in modified version due to the unavailability of its kinetic parameters:

$$CHBrF_2 + H_2 \rightarrow CH_2F_2 + HBr$$
 (R19)

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