GAS PHASE REACTION OF HALON 1301 (CBRF₃) WITH PROPANE

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ABSTRACT

Nonoxidative gas-phase reaction of Halon 1301 (CBrF₃) with propane in a nitrogen bath was investigated using a tubular plug flow reactor. Experiments were performed at atmospheric pressure, over a range of temperatures from 500 to 700 °C and residence times between 0.7 and 4.0 s. Pyrolysis of propane was **also** investigated to examine the effect of added Halon 1301 on the pyrolysis reaction. Experimental data suggest that CF₃ and Br radicals formed via the thermal cleavage of CBrF₃ react with products of the decomposition of C_3H_8, producing a wide range of species. In addition to HBr, the major products formed during the reaction included CHF₃, CH_4, C_2H_4, C_3H_6 and H₂. Minor product species including C_2H_2, C_3H_4, $C_2H_3F_3$, $C_3H_3F_3$, CH_2F_2 were detected. Coke formation was also observed on the surface of the reactor. **A** reaction mechanism for formation of major and important minor species is presented and discussed.

INTRODUCTION

The Montreal protocol, with later London (1990) and Copenhagen (1992) Amendments, has mandated a ban on the production of halons (bromine-containing fluorocarbons and chlorofluorocarbons), CFCs (chloroflurocarbons), and other ozone-depleting substances in industrialized countries. This restriction on the use of ozone-depleting chemicals has sparked a worldwide research effort to develop treatment processes for the growing stockpiles of halons and CFCs.

Although it is Halon 1211 that accumulates as waste material in halon banks around the world, most of the interest in halon conversion has focused on the synthesis of CF₃I (also known as Halon 1301) from Halon 1301. This is because there is a growing acceptance of CF₃I as a viable replacement for Halon 1301, especially for application in unoccupied spaces. It is generally acknowledged that CF₃I has fire retardant properties that are very similar to those of Halon 1301. Although CF₃I is itself classified **as** a halon, its relatively short atmospheric lifetime ensures that it decomposes in the troposphere and has no effect on stratospheric ozone [1].

With the emergence of the growing demand for CF₃I, new processes have been developed for its synthesis. For example, there **is** a recently patented process for the direct conversion of CBrF₃ to CF₃I [2], which **is** based on a complex initial electrochemical reaction where CBrF₃ is converted to CF₃ZnBr. This reaction takes place in the solvent dimethyl formamide (DMF). Subsequent steps involve the reaction of the CF₃ZnBr organometallic with IBr, producing CF₃I and ZnBr₂. A series of separation, purification, and recycling steps are then needed to complete the overall process.

A Japanese patent **[3]** has described a process for conversion of CHF₃ to CF₃I via the catalytic reaction of CF₃I with I₂. While the reaction mechanism is not well understood, the overall reaction is suggested to be:

$$3CHF_3 + I_2 \rightarrow 2CF_3I + 3HF + C$$

An oxidative process has been patented, where the yield of CF₃I was enhanced over existing synthesis techniques by minimizing the formation of undesirable reaction side products, especially carbon [4].

We have recently studied the reaction of Halon 1301 with hydrogen and methane [5, 6, 7], and were able to produce hydrofluorocarbons as reaction products (which are widely used as CFC replacements) selectively and under relatively mild reaction conditions. We have been able to produce CHF₃ from Halon 1301, which can now be used as an intermediate for the production of CF₃I. The significance of this discovery is that it shows that it is possible to produce compounds from halon, which are environmentally benign and possess substantial economic value.

In this paper, we examined the reaction of Halon **1301** with propane as the hydrogen donor. The reaction was investigated over a range of temperature from 500 to 700 °C at the ambient pressure. The pyrolysis of propane under similar conditions was also conducted to examine the effect of added Halon 1301 on the pyrolysis reaction and to shed light on mechanistic aspects of the reaction of CBrF, with propane.

EXPERIMENTAL

The apparatus (Figure 1) used for these studies included a temperature controlled plug flow reactor with an analysis train consisting of an online micro gas chromatograph (GC) for product quantification, an on-line GC-8A chromatograph for H_2 quantification (argon as carrier gas), and an offline GC/MS for product identification. The reactor was operated at a nominal pressure of 1 atm. Three gases—N, (99.99%), CBrF, (98.5%, 1.5% N_2), and propane (99.5%)—were metered with electronic mass flow controllers (Brooks). A 3-zone electrical tube furnace was employed to heat the 7 mm ID, 10 mm OD reactor tube.
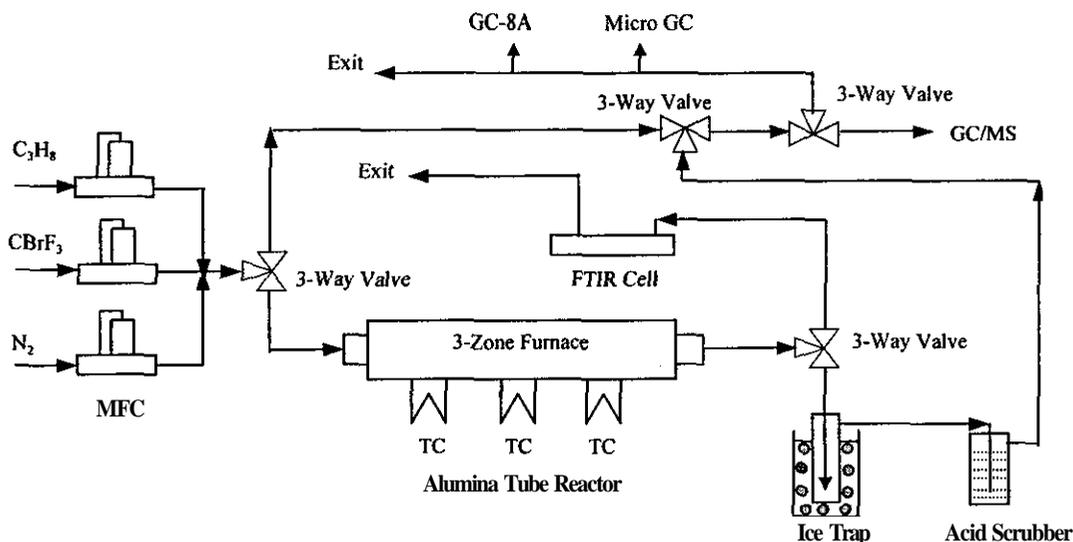
Figure 1. Schematic of the experimental facility

The reactor effluent first passed through a three-way valve. One branch of the effluent stream was directed through a liquid trap (0 °C), then through a caustic scrubber (0.1 M NaOH), to the online Micro GC (equipped with dual thermal conductivity detectors) and then **to** the online GC-8A. The alternative branch of reactor effluent was directed to a FTIR gas cell, which was removed and the gas in the cell analyzed by FTIR for the identification and quantification of HF and HBr. Using the above facility, all major gas phase product species were determined.

Response factors used for quantification of CBrF, and all other hydrocarbons were determined experimentally from standard gas. For response factors of other species identified by GC/MS, the equation developed by Barry and Rosie **[8]** was used.

$$RMR_i = \left[\frac{\dfrac{\sigma_i + \sigma_I}{\sigma_I}}{\dfrac{\sigma_\phi + \sigma_I}{\sigma_I}} \right] \left[\frac{M_i - M_I}{M_\phi - M_I} \right]^{1/4} \times 100 \tag{1}$$

$$\sigma = 2.36(T_c / P_c)^{1/3} \tag{2}$$

where σ is molecular diameter (Å), M denotes molecular weight, T_C is critical temperature (K), P_C stands for critical pressure (atm), and scripts i, I, and ϕ refer to the species 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.

For a given inlet concentration, experiments were performed over a range of reaction temperatures (500–700 "C). Residence times were varied by adjusting gas flow rate of reactant while keeping the concentration of reactant constant. The reproducibility of *2%* was achieved between replicate runs.

RESULTS AND DISCUSSION

PYROLYSIS OF PROPANE

Experiments were conducted over a range of temperature from 500 to 650 °C at residence times between 1.0 and 4.0 s with a constant input volumetric ratio of N_2 to propane of 10:4.

There is much published information in the literature on the thermal decomposition of propane over a wide of range of temperatures. The data available on product distribution at temperatures between 500 and 900 °C indicate the main products **as** methane, ethylene, propylene, and hydrogen [9, 10, 11, 12, 13]. At temperatures between 530 and 670 °C, methane, ethylene, propylene, and hydrogen are formed in approximately equal amounts [10, 11]. Most researchers have assessed the reaction to be first order.

Our experimental results also confirmed that the major products included methane, ethylene, propylene, and hydrogen, with ethane produced in minor amounts. At higher temperatures, traces of acetylene, butane, and butadiene were also detected. The distribution of main products and ethane is shown in Figure 2. It is clear that, with the increase of propane conversion, product yields increased correspondingly. The yields of methane, ethylene, propylene, and hydrogen were very similar to the trend reported in the previous work [10, 11]. Kershenbaum and Martin [9] suggested the overall stoichiometry **of** the major reactants may be summarized as follows:

$$C_3H_8 \rightarrow C_3H_6 + H_2 \quad (A{=}1.52{\times}10^{11}\ s^{-1}, E{=}52.5\ kcal/mole) \tag{R1}$$
$$C_3H_8 \rightarrow CH_4 + C_2H_4 \quad (A{=}9.26{\times}10^{10}\ s^{-1}, E{=}51.7\ kcal/mole) \tag{R2}$$
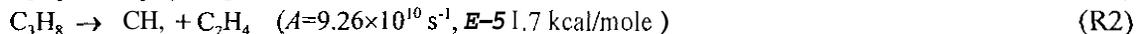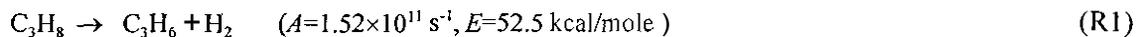
These two reactions have nearly the same A (Arrhenius frequency factor) and E (activation energy) values, suggesting that the two reactions take place at approximately the same rate. As a result, the quantity of methane, ethylene, propylene, and hydrogen is similar.
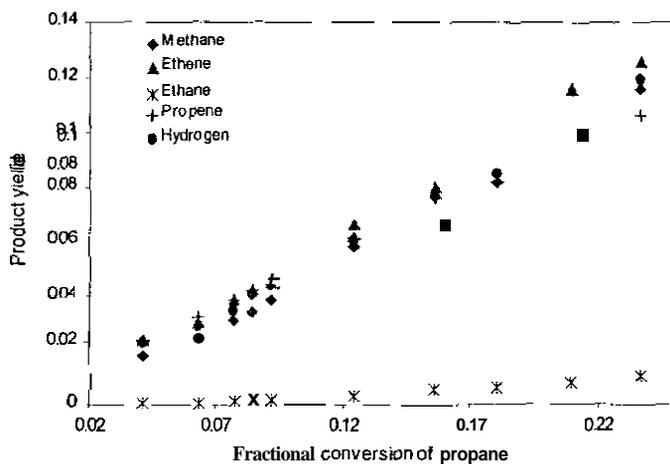
Figure 2.   Product yield versus coversion of propane. Product yield is expressed
as moles of products formed divided by moles of propane in the feed gas

From the conversion data obtained in the experiment, global reaction kinetics were estimated using the ideal plug flow equation and taking into account the changing density of the system. For ideal plug flow reactor with reaction order of unity 1, the performance equation can be written as [14]:

$$k\tau = -(1 + s_A)ln(1 - X_A) - s_A X_A \tag{3}$$

$$s_A \approx \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}} \tag{4}$$

where k is rate constant (s^{-1}), rdenotes residence time (s), s_A signifies fractional change in volume of the system between no conversion and complete conversion of reactant A (propane), and X_A is the fractional conversion of A (propane). For our experiments, the feed molar ratio of propane to nitrogen was 10:4.

Based on our experimental results, we estimated s_A to be **0.286.** At various temperatures, a plot of $-(1 + s_A)ln(1 - X_A) - s_A X_A$ versus τ is presented in Figure **3.** The results are consistent with the assumption that pyrolysis reaction follows first-order kinetics. Based on the data extracted from Figure 3, an Arrhenius plot of rate constant vs $1/T$ was produced (Figure 4) and kinetic parameters for the pyrolysis of propane were estimated as follows:

$$k_{pyrolysis} = 3.50 \times 10^{13} \ (s^{-1}) \ exp \ (-61.7 \, (kcal/mol)/RT) \tag{5}$$

Comparison with the results by other researchers is shown in Table 1.
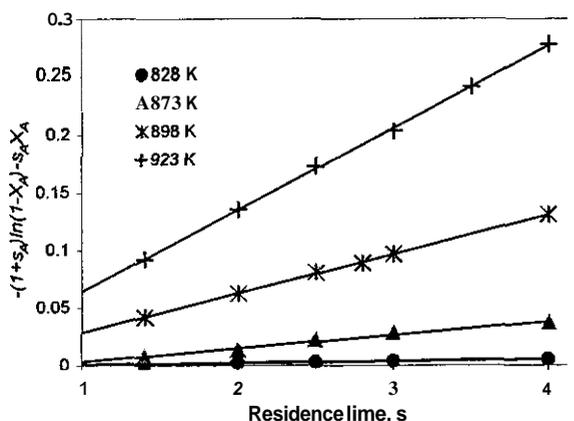
Figure 3.   Apparent first order behaviour for propane pyrolysis.
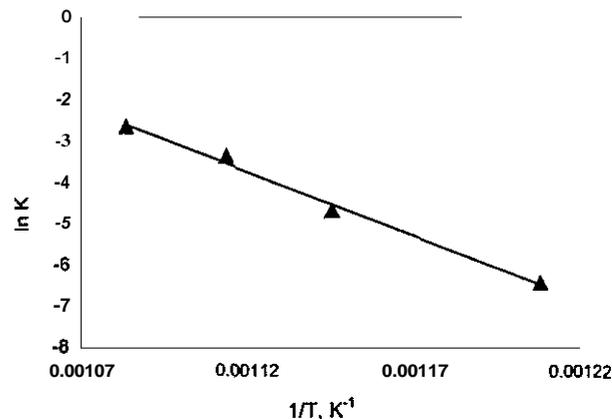
Figure 4.   Arrhenius plot for 1st order rate constant for propane pyrolysis.

TABLE 1. ARRHENIUS **KINETIC** DATA OF PYROLYSIS OF PROPANE.

Author	Laidler [10]	Kershenbaum [9]	Sundaram [12]	Present Work
A, sec-1	2.58×10^{14}	2.4×10^{11}	1.06×10^{11}	3.50×10^{11}
E, kcal/mol	67.1	52.1	50.83	61.7
Reaction temperature, °C	530-660	800-1000	720-870	500-650

A: frequency factor; E   activation energy.

EFFECT OF MOLAR RATIO OF HALON 1301 TO PROPANE ON THE REACTANT CONVERSIONS AND PRODUCT YIELDS

Maintaining a constant residence time (2 s), a series of experiments was conducted over the relatively narrow range of temperature between **575** and **650°C** to investigate the effect of Halon 1301 on the

pyrolysis reaction while minimizing the rate of coke formation. At each temperature, four different molar ratios of Halon 1301 to propane (0.1, 0.2, 0.5, and 1.0) were used, and the experimental results were compared with those obtained under similar conditions doing propane pyrolysis.

As shown in the Figure 5, following the addition of even small quantity of Halon 1301 to the reaction system (input molar ratio of propane to Halon 1301 = 1:0.1), the conversion of propane rose dramatically. At 625 °C, for example, the conversion of propane increased from less than 7% in case of prolysis of propane to 42% with the molar ratio of Halon 1301 to propane of 0.1. With a further increase in the fracture of Halon 1301, the conversion of propane continued to rise, with conversion of propane reaching 78% at molar ratio 1:1. However, the Halon 1301 conversion showed the opposite trend (Figure **6**), which was more pronounced at higher temperatures.
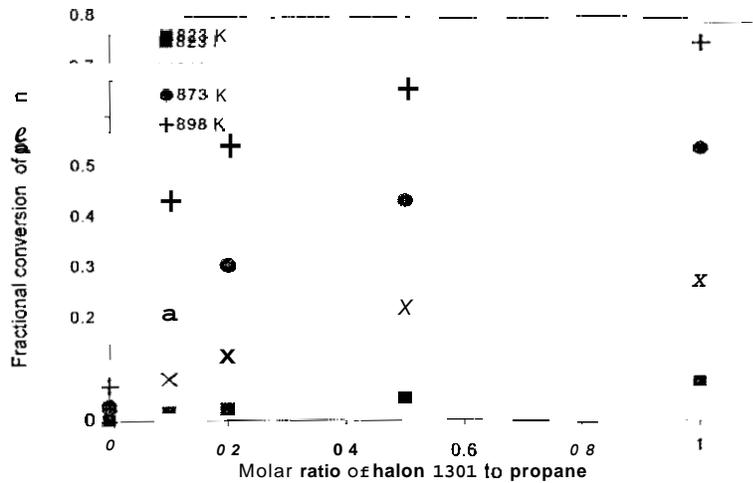
Figure 5. Propane conversion as a function of molar ratio of Halon 1301 to propane in the feed gas at various temperatures.
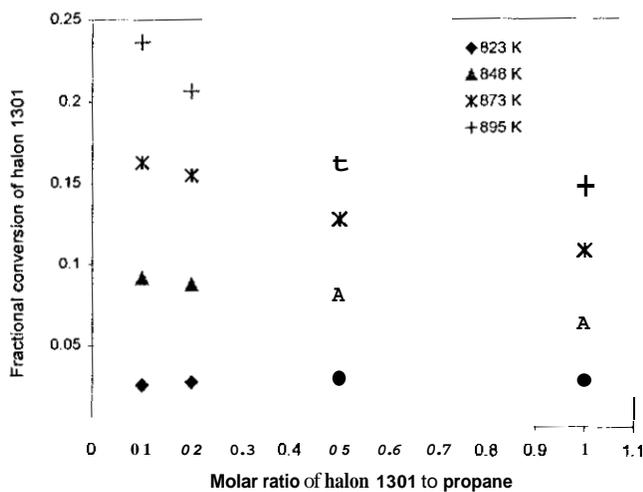
Figure 6. Halon conversion as a function of molar ratio of halon to propane in the feed gas.
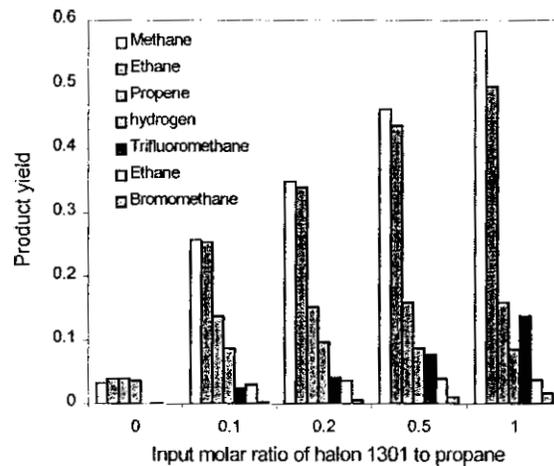
Figure 7. Product yield as a function of molar ratio of Halon 1301 to propane at a residence time of 2.0 s and reaction temperature 625 °C.

Even with the dramatic increase in the conversion level of propane, the product distribution remained quite similar to propane pyrolysis. As seen in Figure 7, the major products included CH_4, C_2H_4, C_3H_6, and H_2 with HBr and CHF, produced during reaction of Halon 1301 with propane. Figures 6 and 7 show the product yield as a function of molar ratio of reactants at 625 °C (product yield is expressed as moles of product formed divided by the initial moles of propane in the feed). Compared with pyrolysis of propane, the CH_4, C_2H_4, C_3H_6, and H_2 yields all increased dramatically. This suggests that the presence of Halon 1301 enhances both R1 and R2. With the increase in molar ratio of Halon 1301 to propane, CH,, C_2H_4, and CHF, increased rapidly. However, C_3H_6 yield showed a more moderate rate of increase while H_2 production decreased slightly following an initial increase. The major difference between Halon 1301/ propane reaction and the pyrolysis of propane was that the yields of the CH, and C_2H_4 are much larger than those of C_3H_6 and H_2 in the Halon 1301 propane reaction, while yields of CH, and C_2H_4 are similar to those of C_3H_6 and H_2 in case of pyrolysis of propane.

MECHANISTIC ASPECTS OF THE REACTION OF PROPANE WITH HALON 1301

Additional experiments were conducted over a wider range of temperature between 500 and 700 "C. The input volumetric ratio was fixed (N_2:$CBrF_3$:C_3H_8=11:1:1). At each temperature, four residence times (0.7, 1.0, 2.0, 4.0 s) were investigated. The conversion levels of Halon 1301 and propane as the function of temperature and residence time are shown in Figures 8-10. As expected, reactant conversions are influenced by reaction temperature and residence time. With an increase of temperature and residence time, the conversion of both propane and Halon 1301 correspondingly increased.
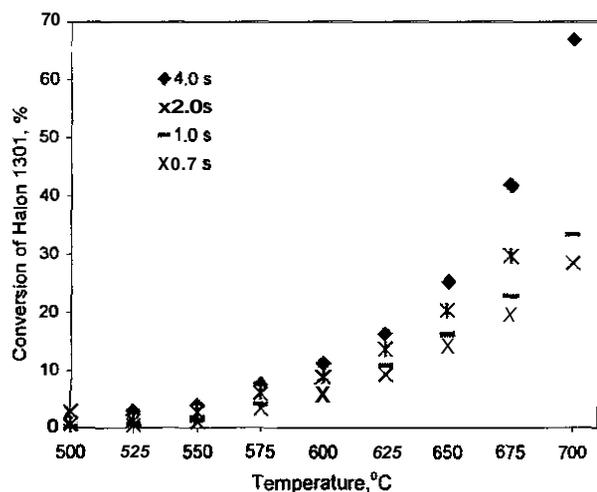
Figure 8. Conversion of Halon 1301 as a function of temperature at various residence times; Volumetric ratio of reactant feed: N_2:$CBrF_3$:C_3H_8=11:1:1.
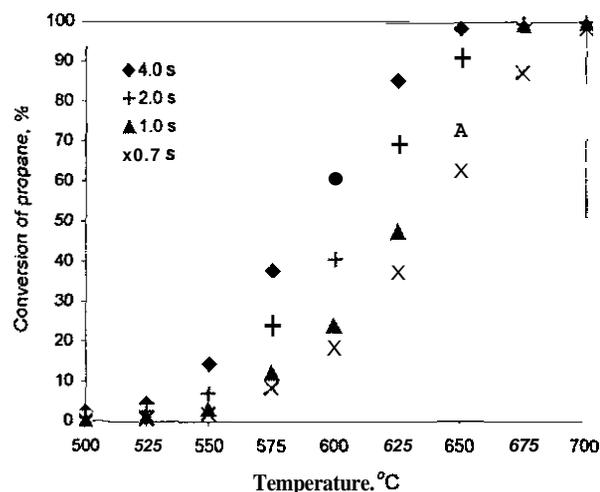
Figure 9. Conversion of propane as a function of temperature at various residence time; Volumetric ratio of reactant feed: N_2:$CBrF_3$:C_3H_8=11:1:1.

The reaction of propane with Halon 1301 commenced at approximately 500 °C at a residence time of 4 s. At the lower temperatures, the conversion of propane and Halon 1301 is very slow, and the conversion level of both species is very similar. However, the difference in conversion level increases as reaction temperature increases, when the conversion of propane is consistently much higher than that of Halon 1301. At reaction temperature 650 °C and residence time 4.0 s, for example, the propane was consumed completely while there was only 25% Halon 1301 taking part in the reaction.

It is generally accepted that the thermal cleavage of C-Br bond, the most labile bond in CBrF, [15], results in CF, and Br radicals. In the presence of $CBrF_3$, C_3H_8 reactivity enhances dramatically, resulting in the production of CH,, C_2H_4, C_3H_6, and H_2. The subsequent reaction of H,, CH_4, C_3H_6, and CH, with CF, and Br radicals could initiate a series of reactions. We did not detect the presence of C_3H_7Br, which
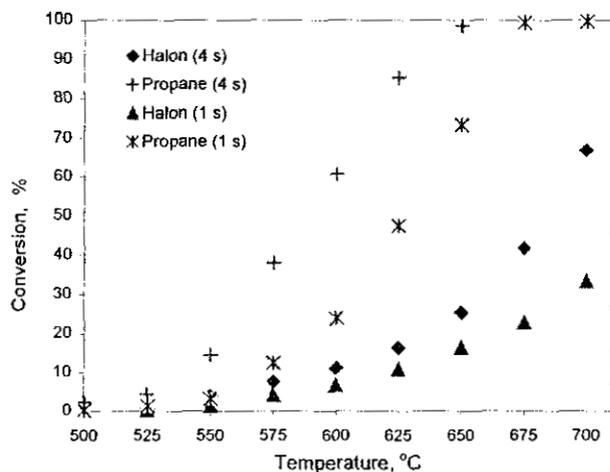
Figure 10. Comparison of propane and Halon 1301 conversions as the function of temperature at various residence times; Volumetric ratio of reactant feed $N_2:CB4F_3:C_3H_8=11:1:1$.
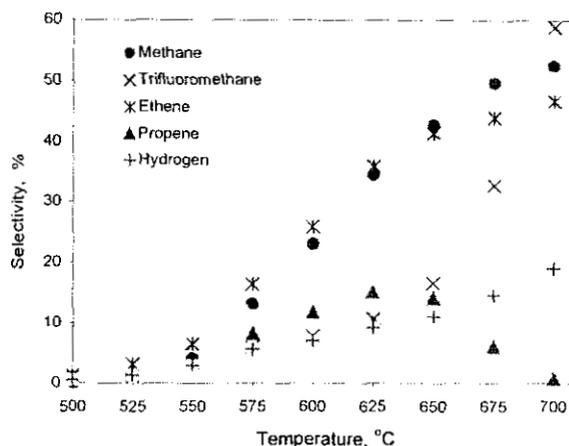
Figure 11. Major product distribution as a function of reaction temperature at a residence time of 4.0 s with product yield expressed as fractions of the initial mole fraction of $CBrF_3$; Volumetric ratio of reactant feed $N_2:CB4F_3:C_3H_8=11:1:1$.

suggests the radicals do not directly react with C_3H_8 *to* produce C_3H_7Br or that C_3H_7Br is formed transiently but decomposes readily under these reaction conditions.

In addition to HBr, the major products formed during reaction were CHF_3, CH_4, C_2H_4, C_3H_6, and H_2. *At* higher temperatures (greater than 650 °C), other product species including C_2H_2, C_3H_4, $C_2H_3F_3$, $C_3H_5F_3$, CH_2F_2, and $C_2H_3F_3$ were also detected. Coke was also observed to deposit on the surface of the reactor under elevated temperature conditions. Variation of the major products with temperature at a constant residence time of 4.0 s is shown in Figure 11. All major products, with the exception of C_3H_6, increased with temperature, while C_3H_6 conversion increased until 650 °C after which the yield of C_3H_6 dramatically dropped with the increasing temperature.

The major product, CHF_3, could be produced from the reaction of $CBrF_3$ with H_2, CH_4, or other hydrogen-containing substance. **As** for reaction of $CBrF_3$ and H_2, the following mechanism was proposed by Li et al. [5].

$$CBrF_3 \rightarrow CF_3 + Br \tag{R3}$$

$$CF_3 + H_2 \rightarrow CHF_3 + H \tag{R4}$$

$$Br + H_2 \rightarrow HBr + H \tag{R5}$$

$$CF_3 + HBr \rightarrow CHF_3 + Br \tag{R6}$$
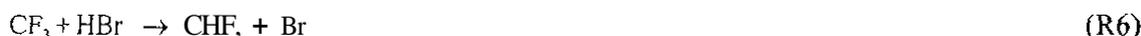
It was also suggested that, although the reaction of $CBrF_3$ and H_2 is initiated by scission of the C-Br bond (R3) rather than by the decomposition of H_2 due *to* its high decomposition energy, the process of the conversion of $CBrF_3$ into CHF_3 catalyzed by H radical (R7) becomes significant once the radical H is formed.

$$CBrF_3 + H \rightarrow CF_3 + HBr \tag{R7}$$

In other previous work [16], it was suggested that CH_4 has a similar reactivity to that of H_2 when reacting with $CBrF_3$. The process for the reaction of halon with CH_4 is as follows:

$$CF_3 + CH_4 \rightarrow CHF_3 + CH_3 \tag{R8}$$

$$CH_3 + CBrF_3 \rightarrow CH_3Br + CF_3. \tag{R9}$$

The main products from the above procedure are CHF_3 and CH_3Br. **In** our experiments only relatively minor quantities of CH_3Br were formed, which suggests that CH_4 plays a relatively minor role in the production of CHF_3 during propane Halon 1301 reactions.

With the increasing temperature, the yield of CH_4, C_2H_4, H_2 and C_3H_6 increased. At approximately **650** °C the yield of C_3H_6 dropped dramatically. We suggest this is because C_3H_6 pyrolyzes at higher temperatures in a manner similar to propane. The main products from the pyrolysis of propylene are CH_4, C_2H_4, and H_2, which also contribute to the total yield of CH_4, C_2H_4, and H_2 [I 7]. With the decrease of C_3H_6, the CHF_3 yield increased dramatically. This is probably because H_2 produced from pyrolysis of propylene also took part in the reaction with Halon 1301.

Among a number of minor products, CH_3Br was first detected approximately at a temperature of **525** °C and a residence time of 4.0 s. With the increase of temperature and residence time, the amount of CH_3Br formed increased slightly.

It is generally agreed that $C_2H_2F_2$ is formed from the combination of CH_3 and CF_3 radicals, although the specific pathways of $C_2H_2F_2$ formation are still disputed. Westbrook **[IS]** reported that the $C_2H_2F_2$ was formed directly from $CF_3 + CH_3$ through elimination of HF.

$$CF_3 + CH_3 \rightarrow C_2H_2F_2 + HF$$
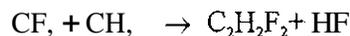
Biordi et al. [19] and Battin-Leclerc et al. [20] suggested two step mechanism leading to the formation of $C_2H_2F_2$

$$CF_3 + CH_3 \rightarrow CF_3CH_3 \tag{R11}$$

$$CF_3CH_3 \rightarrow CH_2CF_2 + HF \tag{R12}$$
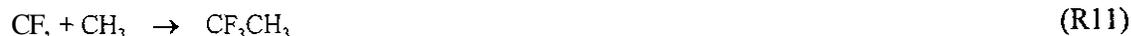
In our experiment $C_2H_3F_3$ was also detected, which suggests that the latter pathway seems plausible.

Biordi et al. [19] believed that CHF_3, the main product in our experiment, can decompose at high temperatures as follows:

$$CHF_3 + H \rightarrow HF + CHF_2 \tag{R13}$$

With CHF_2 reacting with CH_3 to produce C_2H_3F and HF

$$CHF_2 + CH_3 \rightarrow C_2H_3F + HF \tag{R14}$$

Karra and Senkan [21] suggested that presence of bromine or chlorine radicals could decrease the concentration of ethane to produce CH_4 and C_2H_2

$$C_2H_6 + Br \rightarrow C_2H_5 + HBr$$

$$C_2H_5 + H \rightarrow C_2H_4 + H_2 \tag{R16}$$

$$C_2H_4 + Br \rightarrow C_2H_3 + HBr \tag{R17}$$

$$C_2H_3 + H \rightarrow C_2H_2 + H_2$$
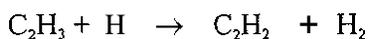
It is possible for the C_2H_3 radical to react with CF_3 to form $C_3H_3F_3$, one of minor products in the reaction.

$$C_2H_3 + CF_3 \rightarrow C_3H_3F_3 \tag{R19}$$

The process of coke formation is very complicated because the pyrolysis of ethane, propane, propylene, and other hydrocarbon **all** can produce coke at high temperatures [12, 22, 23, 24]. C_3H_4 was detected at higher temperatures, but only in trace amount. For this reason, no effort to develop a pathway for C_3H_4 was made.

CONCLUSIONS

The pyrolysis of propane and gas phase reaction of CBrF, and propane were carried out at ambient temperature, over a wide range of temperatures and at various residence times. Experiments showed that the pyrolysis of propane follows first-order kinetics with respect to propane disappearance, with activation energy of 61.7 kcal/mol and Arrhenius frequency factor of 3.50×10^{13} s^{-1}. The addition of halon into the reaction system greatly enhances the rate of pyrolysis of propane. Propane initially pyrolyzes to produce CH,, C_2H_4, C_3H_6, and H_2 **as** main products and many minor products including C_2H_6. Subsequently, we suggest that mainly H_2 reacts with CBrF, to produce HBr and CHF,. CH, can also react with CBrF, to produce CH_3Br and CHF,, but its reaction with Halon 1301 only plays a relatively minor role.

ACKNOWLEDGMENTS

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