PROCESS FOR CONVERSION OF SURPLUS HALONS, CFCs AND CONTAMINATED HFCs INTO FLUOROELASTOMER PRECURSORS

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ABSTRACT

In this study, the gas-phase reaction of halons, CFCs and targeted HFCs with methane was undertaken over a temperature range of 773 to 1173 K in a plug-flow reactor. The effect of reaction temperature and feed composition (ODS:CH_4 ratio) on the product profile was investigated. At lower temperatures (below 923 K), $CHClF_2$ and CH_3Br were produced as major products, during which the conversion of $CBrClF_2$ was <50%. At elevated temperatures (>1073 K), complete conversion of $CBrClF_2$ was achieved, with the initial products $CHClF_2$ and CH_3Br replaced by $CF_2{=}CH_2$. A single-pass yield of 63% $CF_2{=}CH_2$ was achieved at 1173 K for the feed composition of 1211:CH_4 = 1:2. We suggest that the methylation of [$CClF_2$] radicals derived from $CBrClF_2$ is the most likely pathway for the formation of $CF_2{=}CH_2$. Minor species formed at elevated temperatures include several C_1-C_3 fluoro- and hydrofluorocarbons and C_2 hydrochlorofluorocarbons such as CHF_3, C_2F_2, C_2H_3F, $C_3H_3F_5$, C_2H_2ClF and C_2HClF_2. Mineral acids (HF, HCl and HBr) are produced as inorganic halogenated products, and soot formation was observed at higher temperatures. Compared to existing extremely high temperature technologies currently used to destroy halons, this process produces valuable chemicals, with an overall energy loading an order of magnitude lower, and thus offers important environmental and economic advantages.

Introduction

Over the past three decades, the depletion of the ozone layer by anthropogenic sources of chlorine and bromine has received significant global attention. Chlorofluorocarbons (CFCs) and bromofluorocarbons and bromochlorofluorocarbons (halons) have been identified as major contributors to ozone depletion. Under the Montreal Protocol, production of halon fire suppressants was phased out in industrialised countries in 1994 and production of chlorofluorocarbons (CFCs) was banned in 1996 and strict import-export and recycling controls came into effect throughout the world. [1]

A wide range of safe and effective alternatives to halons, CFCs, and other ozone depleting chemicals have been developed and are in broad use in dozens of industrial, consumer, and military applications. As a result of these developments, large volumes of surplus, unusable stockpiles of ozone depleting chemicals have accumulated around the world, particularly halon 1211 which had been used as a fire suppressant in hand-held extinguishers. Many techniques have been identified that can effectively destroy stockpiles of ozone depleting chemicals, typically involving extremely high temperatures[2]. Conversion as a treatment technique has attracted considerable research interest because its aim is to convert the CFCs and halons into useful or environmentally benign products.[3-8]

Thermal hydrodehalogenation (THD) is a conversion technique where halons and CFCs react with hydrogen or hydrogen donor molecules at high temperature to form a mixture of hydrofluorocarbons (HFCs), hydrocarbons, perfluorocarbons and mineral acids as products.

Recently THD has emerged as a promising halon treatment process, since many HFCs are being considered as replacements for CFCs.

We have investigated the THD of halon 1301 ($CBrF_3$) in both H_2 and CH_4 over the temperature range of 773 – 1073 K.[9-11] It was found that the addition of H_2 or CH_4 to the reactant stream resulted in a substantial increase in the conversion level of $CBrF_3$ compared to the thermal decomposition of $CBrF_3$. Regardless of whether the reaction was carried out with H_2 or CH_4 as hydrogen donor reactants, the major HFC product is CHF_3 in both cases. The importance of this finding is that a process has been developed in which CHF_3 is converted to CF_3I (also known as halon 13001).[12] CF_3I is a chemically active fire suppressant that can be used as a replacement for halon 1301.

While there are a number of processes for conversion of $CBrF_3$ to useful products, the same cannot be said for halon 1211, $CBrClF_2$. The presence of both Cl and Br in the halon structure greatly complicates the hydrodehalogenation process, resulting in the production of a wide variety of halogenated and nonhalogenated species under most conditions.[13] We studied the hydrodehalogenation of $CBrClF_2$ in some detail to find out that the initial products of the gas-phase reaction of $CBrClF_2$ with CH_4 were $CHClF_2$ and CH_3Br, which were replaced by $CF_2{=}CH_2$ at higher temperatures.[14] Although these (previous) studies have demonstrated the possibility of production of $CF_2{=}CH_2$ (a potential HFC), further study of the effects of the reaction parameters such as feed composition and temperatures (>1073 K) was necessary in order to optimise the production of $CF_2{=}CH_2$.

This paper reports the results of a detailed, systematic study of the gas-phase reaction of halon 1211 ($CBrClF_2$) with methane at elevated temperatures (773 – 1173 K) with the aim of maximising the yield of $CF_2{=}CH_2$. Detailed (quantitative) analyses of mineral acids (HF, HCl and HBr) are also presented. These data provide the information needed to develop a novel process for the conversion of the existing stockpiles of halon 1211 to a useful hydrofluorocarbon ($CF_2{=}CH_2$) for fluoroelastomer production, using methane as methylating agent. Indeed, it appears that a wide variety of chemicals, including halons CFC, HFCs and PFCs can be treated via this route.

Experimental

Gas-phase reaction of $CBrClF_2$ with CH_4 was carried out in a plug flow alumina reactor (I.D. 0.65 cm) under atmospheric pressure. Details of the experimental facility have been described previously.[8] In a typical experiment, the reactor is heated in flowing N_2 to the desired reaction temperature. The reaction commenced when a reaction mixture of $CBrClF_2$ and CH_4 diluted with nitrogen in a volumetric flow rate of 65.3 cm^3/min was fed into the reactor having a reaction zone volume of 1 cm^3 over the temperature range of 773 to 1173 K. Therefore, the residence time was varied in the range of 0.2 - 0.3 s. The exhaust gases were passed through a caustic (0.1 M NaOH) scrubber and a tube packed with silica gel to remove mineral acids (HF, HCl, HBr) and moisture, respectively. Reaction products were analysed with an on-line micro GC (Varian ChrompaK) equipped with Poraplot Q and Molecular sieve columns and TCD detector. A QP5000 (Shimadzu) GC-MS equipped with a Poraplot U capillary column and quadruple mass spectrometer was used for product identification. Quantitative analysis of the product halocarbons was performed using relative molar response (RMR) factors estimated from published correlations for TCD detectors.[15] The amount of mineral acids trapped in the NaOH scrubber over a fixed, predetermined time period was analysed with an ion chromatograph (DIONEX DX-100) furnished with an IonPac AS14A analytical column.

Results and Discussions

The stoichiometric gas-phase reaction of $CBrClF_2$ with CH_4 was conducted over the temperature range of 773 to 1173 K with a $CBrClF_2/CH_4/N_2$ volumetric flow ratio of 5.4:5.4:54.6 and 5.4:10.8:49 cm^3/min (STP). Figure 1 shows that the conversion of both $CBrClF_2$ and CH_4 increases with the temperature and complete conversion of $CBrClF_2$ occurs at 973 K. Compared to the case of equimolar feed of $CBrClF_2$ and CH_4, an increase in the partial pressure of CH_4 in the feed has no significant effect on the conversion level of $CBrClF_2$. It is worth mentioning that the conversion of $CBrClF_2$ is much lower at a given temperature when the reaction was carried out in the absence of CH_4. For instance, the conversion of $CBrClF_2$ was less than 2% at 873 K in the absence of CH_4, increases to 15% in the presence of CH_4, and in the absence of $CBrClF_2$, methane was unreactive over the range of temperature studied (773-1173 K).

Figure 2 shows a detailed profile of the rate of feed consumption and formation of all identified major and minor products as a function of temperature for equimolar feed of $CBrClF_2$ and CH_4. At lower temperatures (below 973 K), $CHClF_2$, CH_3Br and $CF_2{=}CH_2$ are the major reaction products as shown in Figure 2(a). The formation $CHClF_2$ and CH_3Br can be explained by the following cycle mechanism (Scheme 1) with initiation steps being the homolytic dissociation of $CBrClF_2$ into $CClF_2$ and Br radicals: $CBrClF_2 \rightarrow CClF_2 + Br$, with subsequent propagation steps:

$CClF_2 + CH_4 \rightarrow CHClF_2 + CH_3$

$CBrClF_2 + CH_3 \rightarrow CH_3Br + CClF_2$.

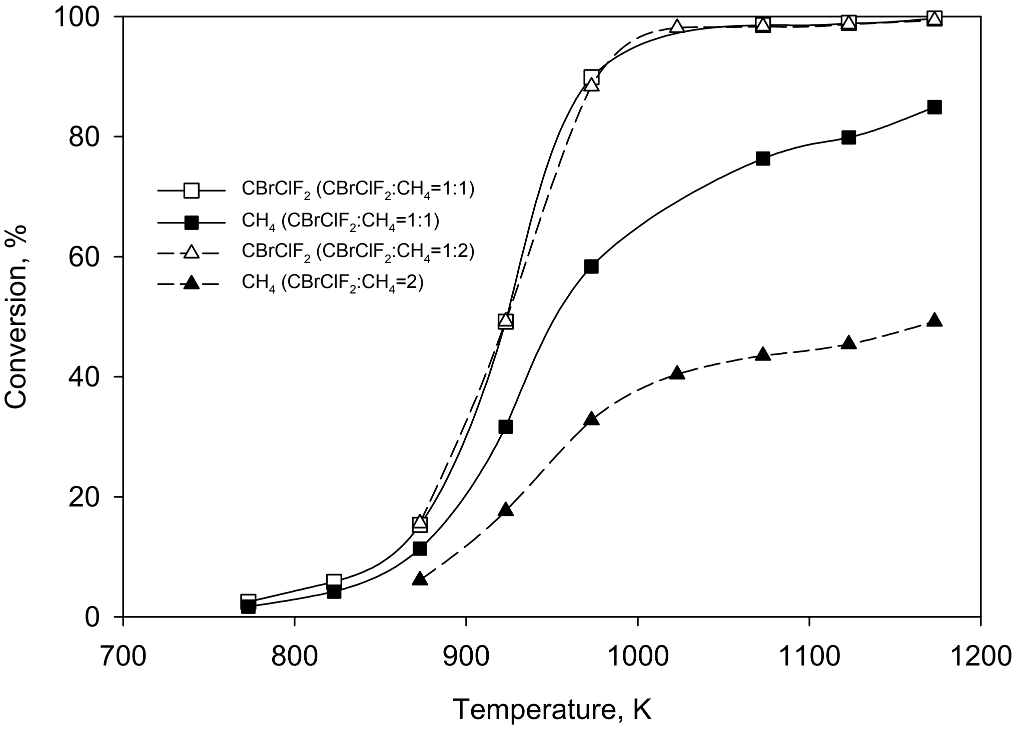


Figure 1: Gas-phase reaction of $CBrClF_2$ with CH_4 over the temperature range of 773 - 1173 K.

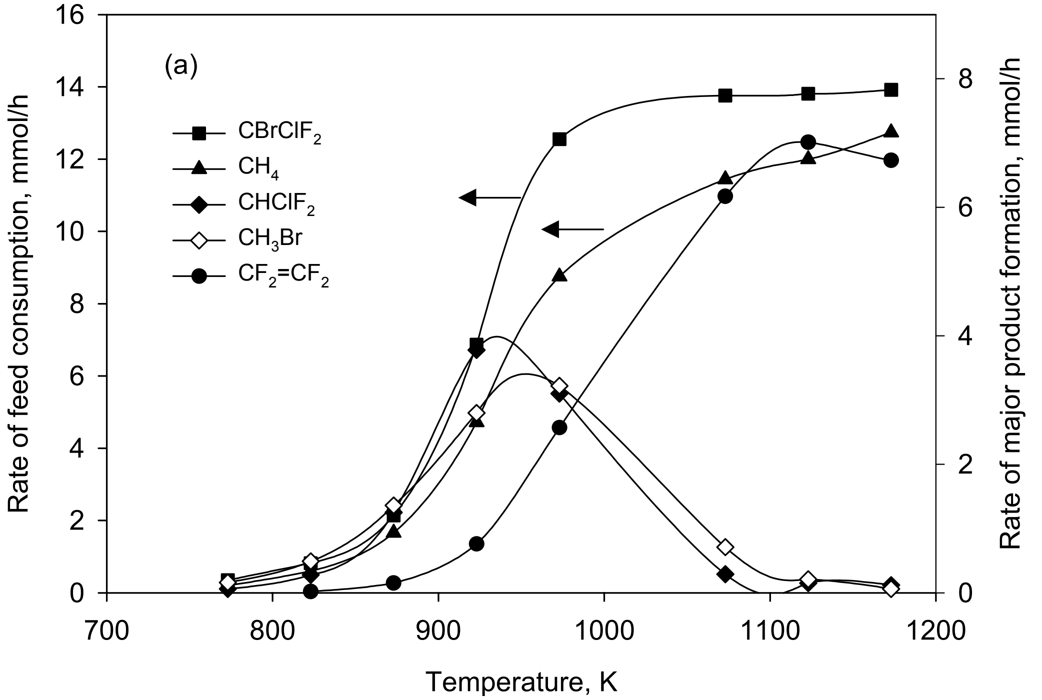
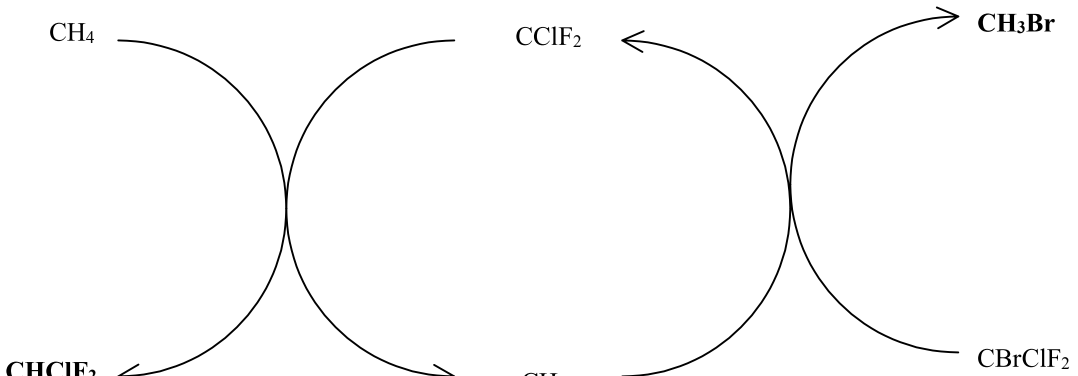


Figure 2a : Rate of formation of major products during the gas-phase reaction of $CBrClF_2$ with CH_4. $CBrClF_2$: CH_4 in feed = 1:1.



Scheme 1: Low temperature (<923K) reaction mechanism for the formation of $CHClF_2$ and CH_3Br by gas-phase reaction of $CBrClF_2$ and CH_4.

In addition to the major products, a wide variety of minor products are also formed. The rates of formation of the minor products are shown in Figure 2(b). The significant minor species produced at lower temperatures are CCl_2F_2 and CBr_2F_2, which may have formed by dismutation of $CBrClF_2$:

$2CBrCl_2F_2 \rightarrow CCl_2F_2 + CBr_2F_2$.

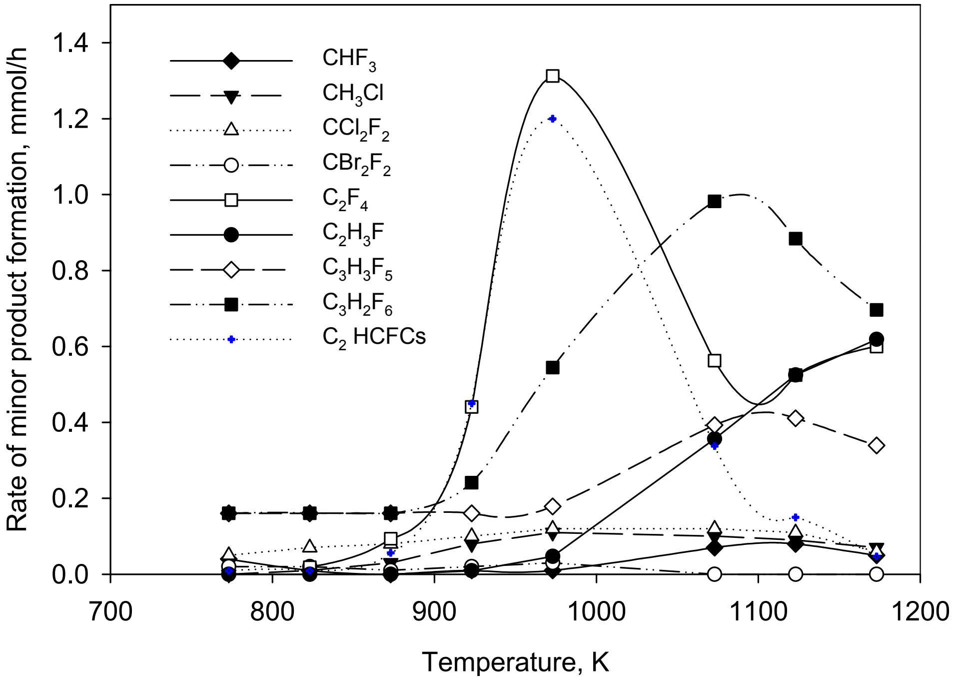


Figure 2b : Rate of formation of minor products during the gas-phase reaction of $CBrClF_2$ with CH_4. $CBrClF_2$: CH_4 in feed = 1:1.

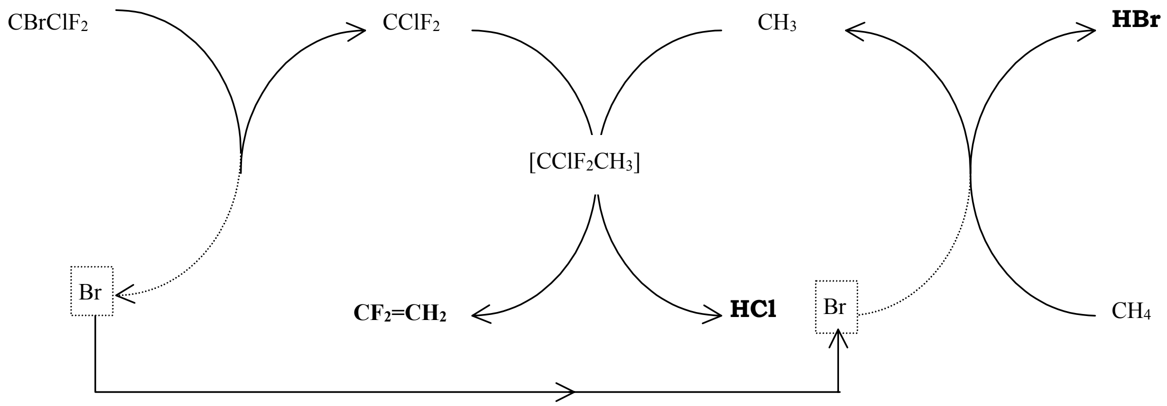
Other minor species formed at elevated temperatures include several C_1-C_3 fluoro- and hydrofluorocarbons and C_2 hydrochlorofluorocarbons such as CHF_3, C_2F_2, C_2H_3F, $C_3H_3F_5$, C_2H_2ClF and C_2HClF_2. We suggest that the difluorocarbene (CF_2:) species that is formed by the dissociation of $CHClF_2$ ($CHClF_2 \rightarrow CF_2$: + HCl) could act as a source for the production of some of the minor products. C_2F_4 is thought to be produced by direct coupling of two difluorocarbene (CF_2:) species while C_2H_3F may be formed by the reaction of CF_2: and CH_4.

$CF_2: + CH_4 \rightarrow\rightarrow C_2H_3F + HF$.

Formation of CHF_3 can be explained by the following reaction:

$CF_2: + HF \rightarrow CHF_3$.

Increasing the temperature of the reaction above 973 K, the formation of both $CHClF_2$ and CH_3Br decreases, whereas the formation of CF_2=CH_2 increases significantly over the entire temperature range studied, becoming the major product at high temperatures. The formation of CF_2=CH_2 can be elucidated by the following reaction scheme (Scheme 2)



Scheme 2: High temperature (>973) reaction pathway for the formation of $CF_2{=}CH_2$ from $CBrClF_2$ and CH_4.

We suggest that the methylation of $CClF_2$ species with CH_3 species forms an unstable $[CClF_2CH_3]$ intermediate which undergoes rapid dissociation to $CF_2{=}CH_2$ and HCl.

The C_2 hydrochlorofluorocarbons are formed primarily at elevated temperatures. Chlorination of the difluoroethylene ($CF_2{=}CH_2$) with hydrogen chloride (HCl) could be a possible pathway for their formation:

$$CF_2{=}CH_2 + HCl \rightarrow C_2H_2ClF + HF$$

$$CF_2{=}CH_2 + HCl \rightarrow C_2HClF_2 + H_2.$$

The carbon balance between the feed and product stream was found be significantly less than 100 % at higher temperatures (above 873 K). The difference between the carbon number in the feed and the products is attributed to carbonaceous species and shown in Table 1 as "missing carbon" as a % of feed carbon. A significant amount of carbonaceous species (not quantified) and estimated by "difference" was observed during the reaction at higher temperatures. However, the unbalanced portion of product may include some polymeric species which are formed at elevated temperatures. The amount of coke reaches 24 % of the feed carbon at 1173 K. Although the amount carbonaceous species at higher temperature is related to the loss of feed as byproducts, but it could be beneficial when considering the high gas-phase selectivity of the target product ($CF_2{=}CH_2$) and resulted in a significant reduction in unwanted gas-phase by-products at elevated temperatures.

The effect of CH_4 concentration in the feed was investigated using a $CBrClF_2$:CH_4 ratio of 1:2 over the temperature range of 873 – 1173 K. Figure 3 shows the rate of production of all major and minor products at various reaction temperatures. At lower temperatures the profile of major products for 1:2 feed ratio is very similar to that of 1:1 feed ratio. Initially (at lower temperatures) $CHClF_2$ and CH_3Br are produced in a mole ratio of approximately 1. The formation of $CHClF_2$ reaches a maximum at around 923K and then starts to decline, while the formation of CH_3Br remains quite high even at 1023 K and then decreases slowly with temperature. On the other hand, the rate of formation of $CF_2{=}CH_2$ starts to increase sharply from 923 K and reaches 8.83 mmol/h at 1173 K which is equivalent to yield of 62.5% based on the $CBrClF_2$ feed. The maximum yield of $CF_2{=}CH_2$ for the feed ratio 1:1 was 50% at 1173 K. These results suggest that an increase in partial pressure of CH_4 in the feed enhanced the yield of $CF_2{=}CH_2$ by providing a high concentration of CH_3 species available for coupling with $CClF_2$.

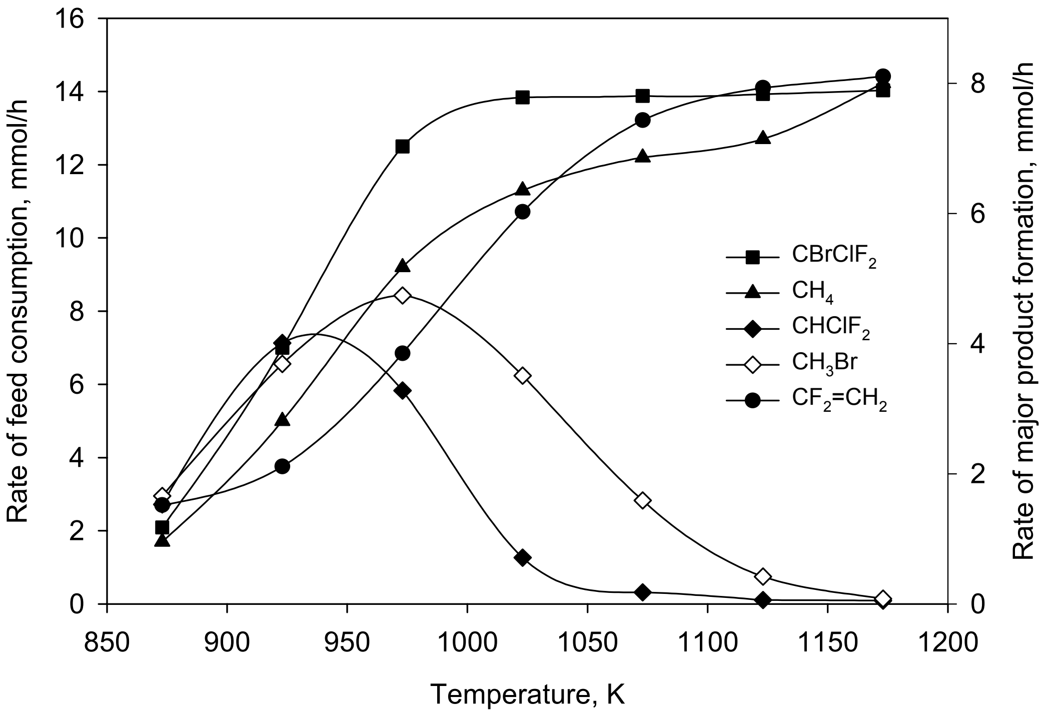


Figure 3a: Rate of formation of major products during the gas-phase reaction of $CBrClF_2$ with CH_4. $CBrClF_2$: CH_4 in feed = 1:2.

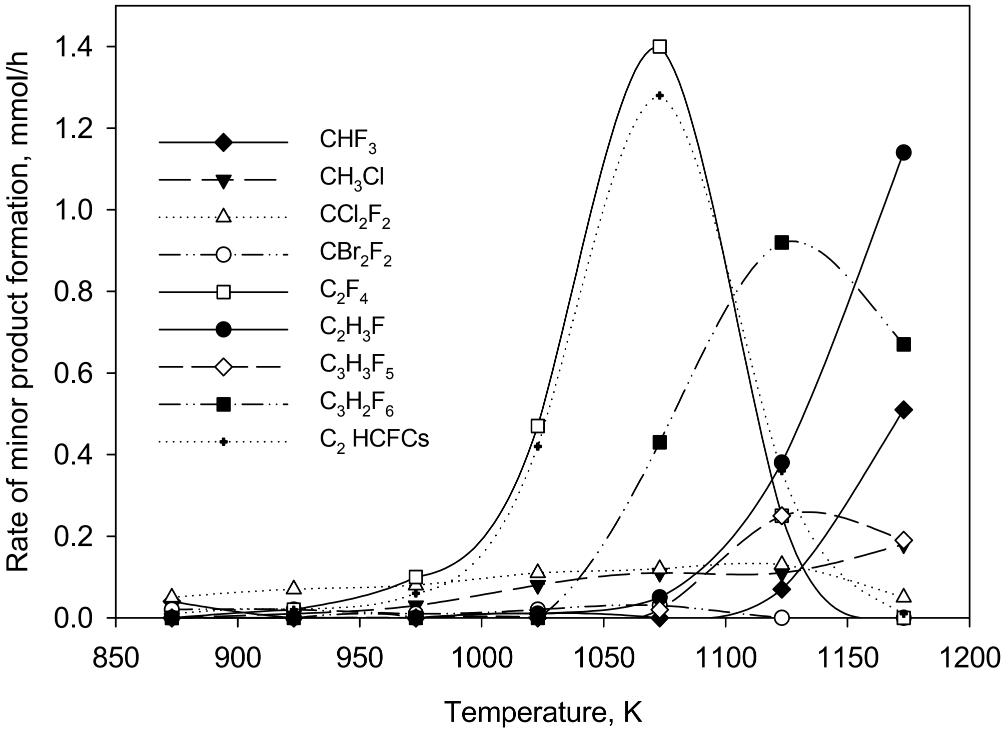


Figure 3b: Rate of formation of minor products during the gas-phase reaction of $CBrClF_2$ with CH_4. $CBrClF_2$: CH_4 in feed = 1:2.

Table 2 shows the representative halogen (F, Cl and Br) balance for the reaction of $CBrClF_2$ with CH_4 (Feed ratio 1:1) performed over 973 to 1173 K. This table compares the rate of halogen-in with the feed ($CBrClF_2$) to the rate of halogen-out in the reactor effluent stream. The rate of halogen-out is based on a number of reactions: a) halogen in product HFC gases which is determined from the molecular formula of all identified halogen containing organic compounds and their rate of formation; b) halogen captured in NaOH scrubber, which is repeated the rate of formation of mineral acids (HBr, HCl and HF) as determined by ion chromatograph; c) halogen in unreacted feed, which is estimated from the unreacted portion of $CBClF_2$ in the reactor effluent. As can be seen in the table, a fluorine (F) balance of about 81% with respect to the feed was achieved, of which 85 – 95% is in the gaseous products. The amount of F captured in NaOH scrubber (as HF) ranged between 10 – 20%. On the other hand, only 35 – 47% Br balance was achieved between 973 and 1173 K. A chlorine (Cl) balance of 75 – 91% with respect to the feed is accomplished between 973 and 1173 K. Out of which, approximately 30% was accounted for the major product ($CHClF_2$) and 38% was captured in the NaOH scrubber as mineral acid (HCl). In the temperature range of 1073 – 1173 K, 87 – 96% of the chlorine accounted for in the outlet stream was captured as mineral acid in the NaOH scrubber.

Conclusions

Thermal hydrodehalogenation/methylation of halon 1211 ($CBrClF_2$) with methane was carried out in the temperature range of 773 to 1173 K in a plug-flow reactor. $CHClF_2$ and CH_3Br were produced as major products at lower temperatures. At elevated temperatures (>1073 K), feed $CBrClF_2$ was converted completely, while the initial products $CHClF_2$ and CH_3Br were replaced by $CF_2{=}CH_2$. An increase in partial pressure of CH_4 enhances the yield of hydrogenated and methylated products. A single-pass yield of 63% $CF_2{=}CH_2$ was achieved at 1173 K for the feed composition of $CH_4/CBrClF_2$= 2.0. Methylation of $CClF_2$ radicals derived from $CBClF_2$ is thought to be the most likely pathway for the formation of $CF_2{=}CH_2$. Other minor species formed at elevated temperatures include several C_1-C_3 fluoro- and hydrofluorocarbons and C_2 hydrochlorofluorocarbons such as CHF_3, C_2F_2, C_2H_3F, $C_3H_3F_5$, C_2H_2ClF and C_2HClF_2. Mineral acids (HF, HCl and HBr) are produced as inorganic halogenated products. Soot formation was observed at higher temperatures. The results demonstrate a viable chemical pathway to efficiently convert halon 1211 into environmentally benign and potentially valuable fluorochemicals. Compared to existing destruction technologies, these conversion processes can be used to dispose of surplus ozone depleting chemicals while retaining the valuable carbon-fluorine bonds. Of equal importance is that the process can be conducted using far less energy, thereby resulting in significantly reduced greenhouse gas emissions.

Table 1: Thermal hydrodehalogenation of halon 1211 ($CBrClF_2$) with methane (CH_4)

Reactant	Temperature	Consumption		Rate of Formation (mmol/h)													"Missing Carbon" as % of Feed
(mmol/h) $CBrClF_2$:CH_4	(K)	(mmol/h)		Major Products			Minor Products										
		$CBrClF_2$	CH_4	$CHClF_2$	CH_3Br	$C_2H_2F_2$	CHF_3	CH_3Cl	CCl_2F_2	CBr_2F_2	C_2F_4	C_2H_3F	$C_3H_3F_5$	$C_3H_2F_6$	C_2H_2ClF	C_2HClF_2	
14.0: 15.0	773	0.35	0.20	0.06	0.16	trace	0.04	trace	0.05	0.02	tarce	nd	nd	nd	nd	0.01	0.7
	823	0.82	0.60	0.28	0.49	0.02	0.01	0.01	0.07	0.02	0.02	nd	nd	nd	nd	0.01	1.5
	873	2.14	1.66	1.25	1.36	0.15	0.00	0.03	0.08	0.01	0.10	nd	nd	nd	nd	0.06	1.6
	923	6.87	4.72	3.78	2.80	0.76	0.01	0.08	0.10	0.02	0.47	0.01	trace	0.09	0.05	0.43	3.8
	973	12.55	8.75	3.10	3.22	2.57	0.01	0.11	0.12	0.03	1.40	0.05	0.02	0.43	0.22	1.06	9.5
	1073	13.76	11.44	0.29	0.71	6.17	0.07	0.10	0.12	trace	0.25	0.38	0.26	0.92	0.15	0.21	20.9
	1123	13.81	12.0	0.15	0.21	7.01	0.08	0.09	0.11	nd	0.56	0.56	0.28	0.81	0.10	0.06	18.3
	1173	13.92	12.74	0.12	0.06	6.73	0.05	0.07	0.06	nd	0.64	0.66	0.20	0.60	0.03	0.02	26.7
14.1: 28.0	873	2.09	1.70	1.53	1.66	0.19	0.04	trace	0.05	0.02	trace	nd	nd	nd	nd	0.01	0.3
	923	7.00	5.00	4.01	3.69	0.97	trace	0.01	0.07	0.02	0.02	nd	nd	nd	nd	0.02	5.2
	973	12.50	9.20	3.28	4.74	3.25	nd	0.03	0.08	0.01	0.10	nd	nd	nd	nd	0.06	16.0
	1023	13.84	11.30	0.71	3.51	6.10	0.01	0.08	0.11	0.02	0.47	0.01	trace	trace	trace	0.42	15.2
	1073	13.88	12.20	0.18	1.59	7.95	trace	0.11	0.12	0.03	1.40	0.05	0.02	0.43	0.22	1.06	3.2
	1123	13.93	12.70	0.06	0.42	8.60	0.07	0.11	0.13	nd	0.25	0.38	0.25	0.92	0.15	0.21	7.5
	1173	14.03	14.23	0.05	0.08	8.83	0.51	0.18	0.05	nd	trace	1.14	0.19	0.67	0.01	trace	11.5

*nd: not detected

Table2: Halogen balance for the gas-phase reaction of $CBrClF_2$ with CH_4 at 973 – 1173 K (feed ratio; $CBrClF_2$:CH_4 = 1:1)

Temperature (K)	Halogen in feed (mmol/h)			Halogen in product gas			Halogen in NaOH scrubber			Halogen in unreacted feed			Total halogen out			Missing Halogen as % of Feed		
				(mmol/h)														
	F	Cl	Br	F	Cl	Br	F	Cl	Br	F	Cl	Br	F	Cl	Br	F	Cl	Br
973	28	14	14	19.5	5.0	3.3	0.3	4.0	0.2	2.9	1.5	1.5	22.7	10.5	5.0	19	26	65
1073				21.6	1.2	0.7	0.8	10.1	4.2	0.4	0.2	0.2	22.8	11.5	5.1	18	18	64
1173				20.6	0.5	0.1	1.7	12.2	6.5	0.2	0.1	0.1	22.5	12.7	6.7	20	9	52

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