Conversion of a CFCs, HFCs and HCFCs waste mixture via reaction with methane

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A B S T R A C T

The gas-phase reaction of a mixture of waste refrigerant gases, namely R22 ($CHClF_2$), R12 (CCl_2F_2) and R134a (CH_2FCF_3) with CH_4 has been investigated over the temperature range of 873–1133 K. The investigation was undertaken as an initial assessment of the viability of this process as a treatment option for waste mixtures of hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFC), chlorofluorocarbons (CFCs) and as a potential route for the synthesis of $CH_2{=}CF_2$ (VDF). During the reaction, $CH_2{=}CF_2$ is observed as the major product formed and a 43% selectivity to $CH_2{=}CF_2$ is obtained at 1073 K. A detailed mechanism is developed based on the mechanistic analysis from kinetic modeling, with the initiation reaction involving the formation of Cl radicals from CCl_2F_2. Good agreement is achieved between the predictions and experimental results. Based on a mechanistic analysis, a summary of the major reaction pathways is proposed, which is consistent with the experimental observations.

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1. Introduction

Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) are the substances responsible for the ozone depletion (ODS). Developed countries are committed to the phase-out of these substances by 2010 in the case of CFCs and 2030 for HCFCs. However, these gases are used in a diverse range of applications such as refrigeration, air-conditioning, foam blowing, aerosol, fire protection and electronics. In Australia alone, it is estimated that the quantity of gas currently in use is around 30.6 Mt of CO_2-e of ODS and SGGs (synthetic greenhouse gases), with a total GWP (global warming potential) of approximately 49.7 Mt of CO_2-e [1]. Following the end of use of equipment items that use the gases or when the working gases are replaced by other environmentally benign substitutes, the collection and accumulation of these gas mixture pose significant disposal problems.

In response to the challenges associated with management of these compounds, in 1995, Australia established Refrigerant Reclaim Australia (RRA), an industry-based not-for-profit organization who developed and instigated a stewardship program that provides rebates based on the mass of refrigerant gas returned for destruction, to manage the collection, recovery and reprocessing of these used ODSs and SGGs. Table 1 presents the quantity and composition of refrigerants recovered in Australia between 2004 and 2008 [1]. As Table 1 shows, there has been strong growth in total volume of reclaimed CFCs, HCFCs and HFCs (hydrofluorocarbons)

over this period. Among the compounds collected, R12 (CCl_2F_2), R22 ($CHClF_2$) and R134a (CH_2FCF_3) are the major components.

With respect of the disposal of these substances, the currently used treatment option adopted involves the pyrolysis of the waste in an argon plasma at very high temperatures, typically between 10,000 and 30,000 K [2,3]. In 2006, Australia destroyed a total of 332.6 metric tonnes of recovered refrigerants, which had an aggregated GWP of 0.452 Mt CO_2-e [1], using the well known PLAS-CON process technology, developed by Australia's Commonwealth Scientific and Industrial Research Organisation (CSIRO) and SRL Plasma Ltd [4].

In addition to high temperature plasma pyrolysis, intensive research on other treatment options has focused on catalytic hydrodehalogenation, especially as a process for treatment of CFCs [5–7]. However, HFCs such as CH_2F_2 and CHF_3, are produced during the hydrodehalogenation of CFCs and HCFCs, which themselves are potent greenhouse gases, with high GWPs. Furthermore, catalysts usually suffer severe deactivation during the hydrodehalogenation either because of poisoning of the active phase, or formation of carbonaceous deposits and sintering of the active phase. Using this process, formation of corrosive HCl and HF gases is inevitable, and it is a significant challenge to find a durable catalyst which can operate effectively under these reaction conditions.

Recently, we reported that $CBrClF_2$, CCl_2F_2 and CHF_3 can be converted into vinylidene fluoride ($CH_2{=}CF_2$, VDF) via a reaction with CH_4 [8–12]. However, only single fluorochemical reactant was targeted during each of these studies. As mentioned early, the refrigerant waste is usually a mixture containing HFCs, HCFCs and CFCs and thus, it is more practical and necessary to examine the reaction of CH_4 with a wider range of fluorides, especially the

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Table 1
The amount and composition of refrigerants recovered in Australia [1]. [a]

Year	CFC (%)			HCFC (%)		HFC (%)						HC [b]	Other	Total
	R11	R12	R115	R22	R124	R125	R134a	R152a	R32	R143a	R23	(%)	(%)	(kg)
2004	8.84	8.79	1.39	57.58	0.28	2.08	12.07	3.30	1.35	3.21	0.33	0.41	0.37	236570
2005	7.41	7.71	0.83	56.69	0.20	3.52	14.40	1.84	2.40	3.75	0.14	0.60	0.52	264530
2006	4.42	6.44	0.18	55.95	0.28	5.50	18.59	2.68	2.68	1.75	0.01	0.64	0.88	332618
2007	4.33	4.49	0.25	56.84	0.22	6.68	17.11	4.49	4.16	0.05	0.02	0.56	0.80	411018
2008	3.85	5.04	0.26	55.30	0.23	7.44	14.97	5.56	4.90	1.21	0.01	0.40	0.83	461886

[a] R11: CCl_3F; R12: CCl_2F_2; R115: CF_3CClF_2; R22: $CHClF_2$; R124: C_2HClF_4; R125: CHF_2CF_3; R134a: CH_2FCF_3; R152a: CHF_2CH_3; R32: CH_2F_2; R143a: CH_3CF_3; R23: CHF_3.

[b] Hydrocarbon.

mixture which includes the typical and widely used fluorinated refrigerants. In this work, we report on the reaction of CH_4 with mixtures of $CHClF_2$, CF_2Cl_2 and R134a under various conditions. The quantities of $CHClF_2$, CF_2Cl_2 and CH_2FCF_3 in the mixture are a typical blend of refrigerants being stockpiled and accumulated for disposal, as Table 1 shows.

VDF is a useful monomer for the preparation of a variety of fluorocarbon polymers, which have excellent weathering and chemical resistance properties [13]. A number of processes for the manufacturing of VDF have been reported [14], which usually involve gaseous pyrolysis reactions at temperatures between 573 and 1273 K with CH_3CF_2Cl, CH_2ClCF_2Cl or CH_3CHF_2 as source materials. Although with lower selectivity to VDF and formation of other by-products, the process presented in this study provides another potential option for the treatment of waste refrigerants and route for the synthesis of VDF.

2. Experimental

A tubular high purity (99.99%) alumina reactor (i.d. 7.0 mm) was employed for all experiments. Flow rates of $CHClF_2$ (>98%, Core Gas) or HCFC and CFC mixtures, CH_4 (>99%, Linde), and N_2 (BOC gases, 99.99%) were controlled by mass flow controllers (Brooks) to give a total flow rate of 220 mmol h^{-1} with CFC and HCFC mixtures or pure $CHClF_2$ and CH_4 accounting for 10% of the total volume flow. HCl and HF formed during reaction were trapped by a caustic scrubber (NaOH solution) before the reactor effluent reached an online micro gas chromatograph. Carbon containing products were identified by a GC/MS (Shimadzu QP5000) equipped with an AT-Q column, and quantified with a micro GC (Varian CP-2003) equipped with molecular sieve 5A and PoraPLOT Q columns. Relative molar response (RMR) factors of fluorocarbons for TCD detection were experimentally obtained from standard gas mixtures, and quantification of halogenated hydrocarbons was performed with diluted halogenated hydrocarbons in nitrogen. Quantification of other species where standard gas mixtures were not available was estimated from published correlations [15].

The concentration of HF and HCl trapped with 0.1 M NaOH solution during the reaction was determined by ion chromatography (IC) (Dionex-100) equipped with an IonPAS14A column (4 mm×250 mm).

3. Chemical kinetic modeling

The reactions of HFCs, HCFCs and CFCs with CH_4 have been modeled using the commercial software Cosilab [16]. During simulations, the steady state material balance for each species was performed, using the computer code, "Plug-Flow Reactor", available in the commercial software package Cosilab. Typically, the simulation involves the use of an existing chemical kinetic mechanism representing gas-phase reactions, although in some cases, surface reactions are also included. In separate experiments, alumina chips (the same material as that used for the reactor) were

charged into the reactor. It was found that alumina chips had a negligible effect on the reactions, and therefore, no surface reactions were considered or included in the mechanism.

4. Results and discussion

4.1. Reaction of waste mixture ($CHClF_2$, CCl_2F_2 and CH_2FCF_3) with CH_4

The reaction of mixture containing $CHClF_2$, CCl_2F_2 and CH_2FCF_3 (with a molar ratio of 9:8:1) with CH_4 (flow rate of mixture/flow rate of CH_4 = 1, more specifically, 10% mixture and 10% CH_4 with N_2 balance) commences at temperatures below 900 K. The major products detected are $CH_2=CF_2$, C_2F_4, CH_3Cl, HF and HCl under all conditions studied with minor products including CHF_3, CH_2F_2 C_2H_2, C_2H_3F, C_2HF_3, CCl_3F, CH_2CClF, CF_2CClF. Trace amounts of C_3F_6, $C_2H_2F_4$, $CF_3CH=CF_2$, $CHF=CClF$ and $CF_2=CHCl$ were detected at elevated temperatures, as well as some yet unidentified species. Following the reaction, buildup of carbonaceous deposits on the inner surface of the reactor tube was observed. In addition, polymer-like solids were found suspended in the scrubber solution, which are suggested to be arising from the polymerization of unsaturated reaction products, such as C_2F_4 and $CH_2=CF_2$. Consequently, not all the elements in the feed are recovered in the reaction products, as summarized in Table S1 of supplementary data. Generally, mass balances are reasonable (>95%) at relatively low temperatures, but drop to roughly 60% when the temperature is increased to 1073 K. In contrast to carbon and fluorine, mass balance of 97% for chlorine is achieved over the entire temperature range. As presented in Table S1 of supplementary data, unlike fluorine and carbon, which are included in various reaction products, most chlorine is recovered in the form of HCl.

Fig. 1 illustrates the conversion of $CHClF_2$, CCl_2F_2, CH_2FCF_3 during reaction with CH_4 at different temperatures. As expected, conversion levels increase with temperature and among all the reactants, the conversion level of $CHClF_2$ is always higher than CCl_2F_2 or CH_2FCF_3. At temperatures above 1000 K, >99.99% conversion is achieved for $CHClF_2$. CH_2FCF_3 appears to be the most stable reactant and its conversion is significantly below that of CH_4 and CCl_2F_2, especially at low temperatures.

Fig. 2 presents the rate of formation of major products, namely, C_2F_4, $CH_2=CF_2$ and CH_3Cl and minor products, such as C_2H_3F, C_2H_2, CHF_3, C_2HF_3, CH_2F_2, C_3F_6 and CCl_3F as a function of temperature. At temperatures below 973 K, the rate of formation of C_2F_4 increases with temperature, and dominates the product spectrum, while above this temperature, its formation rate drops and eventually its concentration decreases to almost zero at 1073 K. The formation of $CH_2=CF_2$ increases monotonically with temperature and its rate of formation exceeds that of C_2F_4 at 1000 K. With further increase in temperature, $CH_2=CF_2$ becomes the predominant product species detected. Similar to C_2F_4, CH_3Cl reaches
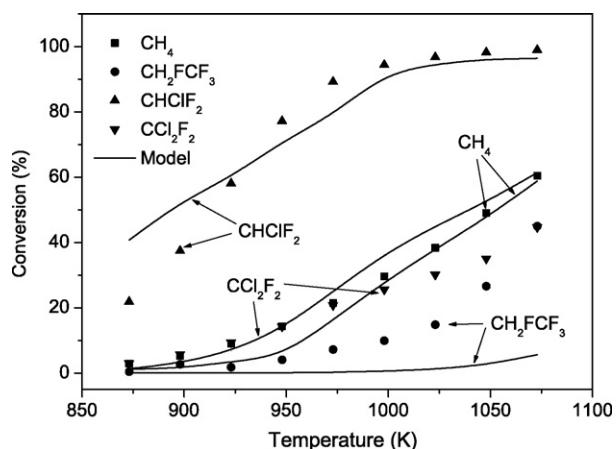
Fig. 1. Conversion of $CHClF_2$, CCl_2F_2, CH_2FCF_3 and CH_4 as a function of temperature for the reaction of HFC, HCFC and CFC mixture with CH_4. Ratio of CH_4, $CHClF_2$, $CClF_2$, and CH_2FCF_3 is 18:9:8:1 in feed. Reactions were conducted at 1.01 bar and at a residence time of 0.5 s.

Fig. 3. Selectivity of target product, $CH_2=CF_2$ as a function of temperature for the reaction of HFC, HCFC and CFC mixture with CH_4. Ratio of CH_4, $CHClF_2$, $CClF_2$, and CH_2FCF_3 is 18:9:8:1 in feed. Reactions were conducted at 1.01 bar and at a residence time of 0.5 s.

its maximum rate of formation at 1025 K, but its concentration drops at higher temperatures. All the minor products follow a similar trend, reaching their maximum yields between 1000 and 1050 K.

Under conditions approached for synthesis of $CH_2=CF_2$, it was reported that 53% selectivity to $CH_2=CF_2$ can be achieved via reaction of CH_3Br with $CHClF_2$[17]. CH_3Br and $CHClF_2$ are considered to be excellent sources of CH_3 and CF_2, which are the key intermediates for the formation of $CH_2=CF_2$ during reaction of fluorocarbons with hydrocarbons [18]. As shown in Fig. 3, a 43% selectivity to $CH_2=CF_2$ is obtained with the mixed refrigerant waste during reaction with CH_4 under similar conditions.

4.2. Reaction of individual refrigerant components with CH_4

To facilitate the understanding of the title reaction, individual reactions (CCl_2F_2 with CH_4, $CHClF_2$ with CH_4 and CH_2FCF_3 with CH_4) are investigated separately.

Uddin et al. studied the conversion of CCl_2F_2 in the absence and presence of CH_4 as a function of reaction temperature [8]. The results showed that conversion of CCl_2F_2 increased significantly following the introduction of CH_4, especially at higher temperatures. In contrast to the reaction of $CHClF_2$, the presence of CH_4 facilitates the consumption of CCl_2F_2, where it was observed that the conversion level almost doubled when CH_4 is present and the reaction takes place at 1123 K [8].
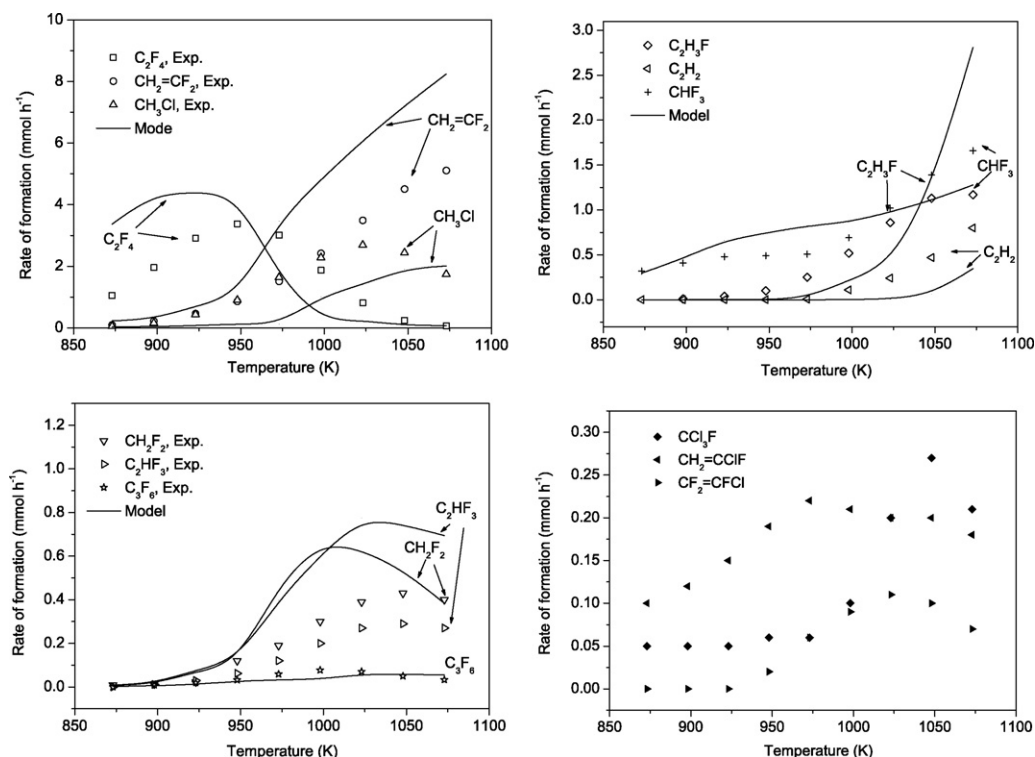
Fig. 2. Rate of formation of major and minor products as a function of temperature for the reaction of HFC, HCFC and CFC mixture with CH_4. Ratio of CH_4, $CHClF_2$, $CClF_2$, and CH_2FCF_3 is 18:9:8:1 in feed. Reactions were conducted at 1.01 bar and at a residence time of 0.5 s.

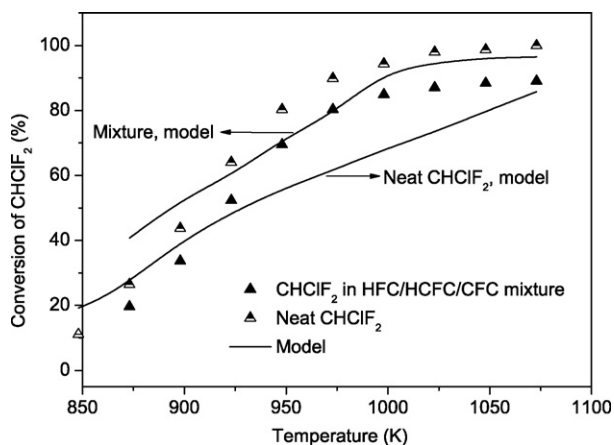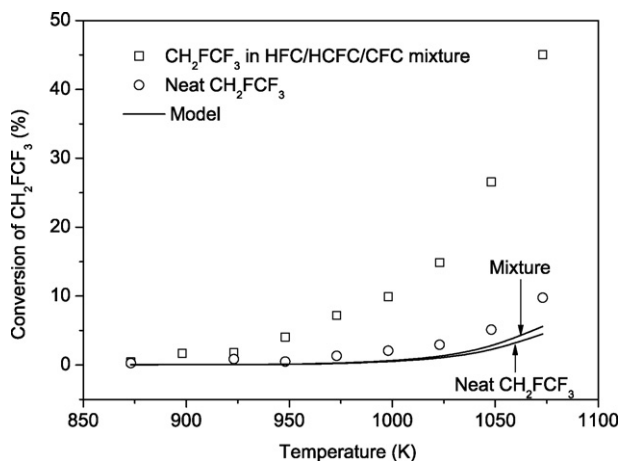**Fig. 4.** Comparison of $CHClF_2$ during reaction (1): HFC, HCFC and CFC mixture with CH_4. Ratio of CH_4, $CHClF_2$, $CClF_2$, and CH_2FCF_3 is 18:9:8:1 in feed; and reaction (2): pure $CHClF_2$ with CH_4 (1:1). Both reactions were conducted at 1.01 bar and at a residence time of 0.5 s.

Figs. 4 and 5 present the conversion levels of $CHClF_2$ and CH_2FCF_3 during their reaction with CH_4. The conversion levels of $CHClF_2$ and CH_2FCF_3 increase with temperature and conversions of 90% and 10% are achieved at 1073 K. During the reaction of the fluorochemical mixture with CH_4, as illustrated in Figs. 4 and 5, the conversion levels of $CHClF_2$ and CH_2FCF_3 are enhanced significantly. At 1073 K, close to 100% conversion for $CHClF_2$ and 45% for CH_2FCF_3 are observed. Apparently, the reaction mechanism of $CHClF_2$, CCl_2F_2 and CH_2FCF_3 mixtures is quite different to their reactions with CH_4 as individual components.

4.3. Mechanistic analysis

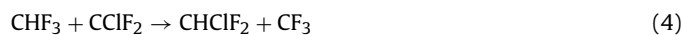#### 4.3.1. Conversion of CCl_2F_2, $CHClF_2$, CH_2FCF_3 and CH_4

The pyrolysis of $CHClF_2$ has been well studied, and the key step in the reaction involves the intramolecular elimination of HCl to form difluorocarbene [$:CF_2$], which subsequently dimerizes into C_2F_4 (TFE) [19,20]. In a separate investigation, we have found that, following introduction of CH_4 into the feed, the conversion of $CHClF_2$ is similar to that observed during pyrolysis conducted under N_2 diluted conditions, which suggests that the initial step, even in the presence of CH_4, is thermal dehydrochlorination (R1). However, as Fig. 4 shows, in the presence of CCl_2F_2 and CH_2FCF_3, the conversion

Fig. 5. Comparison of CH_2FCF_3 during reaction (1): HFC, HCFC and CFC mixture with CH_4. Ratio of CH_4, $CHClF_2$, $CClF_2$, and CH_2FCF_3 is 18:9:8:1 in feed; and reaction (2): pure CH_2FCF_3 with CH_4 (1:1). Both reactions were conducted at 1.01 bar and at a residence time of 0.5 s.

levels of $CHClF_2$ are considerably higher than that observed during the reaction of pure $CHClF_2$ with CH_4. Apparently, in addition to thermal dehydrochlorination of reaction of R1, there are other reaction steps which are also involved in the conversion of $CHClF_2$.

$$CHClF_2 \rightarrow CF_2 + HCl \tag{1}$$

$$CHClF_2 + Cl \rightarrow CClF_2 + HCl \tag{2}$$

$$H + CHClF_2 \rightarrow CHF_2 + HCl \tag{3}$$

$$CHF_3 + CClF_2 \rightarrow CHClF_2 + CF_3 \tag{4}$$

Unlike during pyrolysis and the reaction with CH_4, the presence of CCl_2F_2 provides additional steps for the consumption of $CHClF_2$ via reactions R2, R3 and the reverse reaction of R4. We suggest that reaction R3 and reverse reaction of R4 play a minor role because of the relatively high activation energies associated with these reactions. Furthermore, in the present work, the low concentration of H and CF_3 radicals ensures these reactions takes place only to a minimal extent. In contrast, it was found that activation energy of reaction of R2 is only 21.5 kJ mol^{-1}[21] which is much lower than that of reaction R1 whose activation energy is around 168 kJ mol^{-1}[22]. Along with reaction R1, R2 is a key reaction pathway for the consumption of $CHClF_2$ when CCl_2F_2 is also present in the reaction mixture.

It is worth mentioning that in the absence of $CHClF_2$ and CCl_2F_2, CH_4 remains inactive under all conditions studied. Therefore, it is unlikely that CH_4 initiates the radical formation reactions directly. Among many possible processes that a radical can be initiated for the activation of CH_4, reaction R5 is the most likely initiation step, at least at low temperatures.

$$CCl_2F_2 \rightarrow CClF_2 + Cl \tag{5}$$

$$CH_4 + CClF_2 \rightarrow CHClF_2 + CH_3 \tag{6}$$

$$Cl + CH_4 \rightarrow CH_3 + HCl \tag{7}$$

$$CCl_2F_2 + CH_3 \rightarrow CClF_2 + CH_3Cl \tag{8}$$

$$CClF_2 + CClF_2 \rightarrow CClF_2CClF_2 \tag{9}$$

$$Cl + Cl \rightarrow Cl_2 \tag{10}$$

When $CClF_2$ and Cl radicals react with CH_4 molecules, they abstract a H atom producing CH_3, $CHClF_2$ and HCl. Subsequently, CH_3 can react with CCl_2F_2 to form a $CClF_2$ radical and CH_3Cl, acting as chain propagating steps which together represent the primary pathways for the decomposition of CCl_2F_2. In the absence of CH_4, reactions (R6)–(R8) do not occur, resulting in a net lower conversion level of CCl_2F_2.

$$CH_2FCF_3 \rightarrow C_2HF_3 + HF \tag{11}$$

$$CH_2FCF_3 \rightarrow CF_3 + CH_2F \tag{12}$$

$$CH_2FCF_3 + Cl \rightarrow HCl + CF_3CHF \tag{13}$$
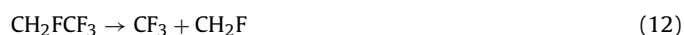
CH_2FCF_3 can be decomposed via reactions R11 to R13. However, higher energy barriers (280 kJ mol^{-1} and 386 kJ mol^{-1}) for reactions R11[23] and R12[24] result in the conversion of CH_2FCF_3 being much lower than that of $CHClF_2$ and CCl_2F_2. Reaction R13 has relatively low activation energy, and we suggest that this reaction is the main reaction responsible for the conversion of CH_2FCF_3[25]. This is consistent with the comparison of conversion level of CH_2FCF_3 during reaction of $CHClF_2$, CCl_2F_2 and CH_2FCF_3 mixture with CH_4 and the separate reaction of CH_2FCF_3 with CH_4. Similar to $CHClF_2$, the presence of Cl (derived from CCl_2F_2) increases the conversion level of CH_2FCF_3 significantly (see Fig. 5).

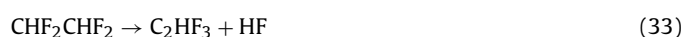**Fig. 6.** Reaction pathways for the formation of major and minor products for the reaction of $CHClF_2$, CCl_2F_2 and CH_2FCF_3 mixture with CH_4 at 998 K. Major products and pathways are in bold.

4.3.2. Formation of reaction products

As discussed earlier, it has been well documented that the primary pathway for the formation of C_2F_4 is the dimerization of CF_2 formed via reaction R1. This process has been adopted by industry for the manufacture of TFE (C_2F_4) commercially. In the presence of CH_4 and CCl_2F_2, the yield of C_2F_4 drops dramatically with temperature after achieving maximum rate of formation at 948 K. One possible explanation for this observation is that C_2F_4 reacts to form other products, such as C_3F_6 and C_4F_8[26]. However, the very low A factors and high activation energy barriers (109 cm^3 mol^{-1} s^{-1} and 34 kJ mol^{-1} for C_3F_6 and 10^{10} cm^3 mol^{-1} s^{-1} and 96 kJ mol^{-1} for C_4F_8) suggest these reactions play only a minor role in the observed decreasing rate of formation of C_2F_4. Yu et al. suggested that CF_2 can combine with CH_3 producing $CH_2=CF_2$ and H and the rate constant for R15 can be approximated by the expression of 2.1×10^{13} $T^{0.207}$ cm^3 mol^{-1} s^{-1} over temperature range of 700–2000 K. This reaction rate is more than 10 times higher than that of CF_2 dimerization, although the activation energies of both reactions are close to zero [27]. At high temperatures, reactions R6 and R7 provide large quantities of CH_3 radicals to the reaction pool, and subsequently, a sharp decrease of C_2F_4 formation and considerable increase of $CH_2=CF_2$ formation were observed (see Fig. 2). Similar results were found during the reaction of CHF_3 with CH_4, where C_2F_4 begins to drop at high temperatures due to the increasing concentration of CH_3 radicals.

$$CF_2 + CF_2 \rightarrow C_2F_4 \tag{14}$$

$$CF_2 + CH_3 \rightarrow CH_2 = CF_2 + H \tag{15}$$

$$CF_3 + CH_3 \rightarrow CH_3CF_3 \tag{16}$$

$$CH_3CF_3 \rightarrow CH_2 = CF_2 + HF \tag{17}$$

$$CH_3 + CClF_2 \rightarrow CH_3CClF_2 \tag{18}$$

$$CH_3CClF_2 \rightarrow CH_2 = CF_2 + HCl \tag{19}$$

In addition to reaction R15, reactions R16 and R17 also lead to the formation of $CH_2=CF_2$[28]. We suggest that R16 and R17 play a minor role in $CH_2=CF_2$ formation, as the concentration of CF_3 is relatively low in the present study and activation energy of R17 is as high as 300 kJ mol^{-1}. However, reactions R18 and R19 are believed to play an important role in the formation of $CH_2=CF_2$ because both

CH_3 and $CClF_2$ are available at relatively high concentrations at high temperatures.

$$CH_3 + Cl \rightarrow CH_3Cl \tag{20}$$

$$CH_3 + CCl_2F_2 \rightarrow CH_3Cl + CClF_2 \tag{R8}$$

$$CH_3 + CClF_2 \rightarrow CH_3Cl + CF_2 \tag{21}$$

$$CH_3 + CClF_3 \rightarrow CH_3Cl + CF_3 \tag{22}$$

The possible pathways leading to the formation of CH_3Cl include reactions R8, R20 to R22. As shown in Fig. 2, rate of formation of CH_3Cl decreases with temperature after a maximum rate was observed. Similar trends for CH_3Br and CH_3Cl have been detected when studying the reaction of halon 1121 ($CBrClF_2$) and CCl_2F_2 with methane [8,10]. This suggests that CH_3Cl undergoes further decomposition reactions, and at high temperatures, the reverse reactions of R8 and R20 to R22 contribute to the consumption of CH_3Cl.

A mechanism which represents the pathway for formation of CH_2F_2 is represented in reactions R23 to R27. The key intermediate, CHF_2, comes primarily from the reaction between CF_2 and HCl, since both species are abundant in the reaction pool. We suggest that reaction R27 plays a relatively minor role, as activation energy for reaction R27 is estimated to be between 143 and 171.2 kJ mol^{-1} theoretically [29], which is much higher than those for the self-combination of CF_2 or abstraction Cl from $CHClF_2$ by H radicals.

$$CHF_2 + HCl \rightarrow CH_2F_2 + Cl \tag{23}$$

$$CHF_2 + CH_4 \rightarrow CH_2F_2 + CH_3 \tag{24}$$

$$CHF_3 + CHF_2 \rightarrow CH_2F_2 + CF_3 \tag{25}$$

$$2CHF_2 \rightarrow CH_2F_2 + CF_2 \tag{26}$$

$$H_2 + CF_2 \rightarrow CH_2F_2 \tag{27}$$

Potential channels leading to the formation of C_2H_3F and C_2HF_3 are summarized in reaction R11 and reactions R28 to R33. These reactions are included in the NIST HFC mechanism and generally they predict the formation of C_2H_3F and C_2HF_3 satisfactorily [29].

$$CH_2FCF_3 \rightarrow C_2HF_3 + HF \tag{R11}$$

$$CH_4 + CF_2 \rightarrow CH_2 : CHF + HF \tag{28}$$

Table 2
Reaction model for the reaction of $CHClF_2$, CCl_2F_2 and CH_2FCF_3 mixture with CH_4. Reaction steps from GRI-Mech and NIST HFC mechanisms are not listed here for the purpose of brevity. [a]

Reaction	A (s^{-1}) or ($cm^3 mol^{-1} s^{-1}$)	n	E (kJ mol^{-1})	Reference
$CHF_2Cl \rightarrow CF_2 + HCl$	1.46×10^{15}	0	168	[22]
$HCl + F \rightarrow HF + Cl$	4.42×10^{12}	0	0.07	[31]
$CH_2F + HCl \rightarrow CH_3F + Cl$	5.50×10^{11}	0	10.2	[32]
$CHF_2 + HCl \rightarrow CH_2F_2 + Cl$	5.76×10^{11}	0	10.2	[32]
$C_2H_3 + HCl \rightarrow C_2H_4 + Cl$	5.26×10^{11}	0	0.83	[33]
$CH_3 + HCl \rightarrow CH_4 + Cl$	5.26×10^{11}	0	12.9	[32]
$CH_3 + Cl \rightarrow CH_3Cl$	3.00×10^{13}	0.30	−0.45	[32]
$CHF_2Cl + Cl \rightarrow CF_2Cl + HCl$	9.00×10^{11}	2.92	21.48	[21]
$CHF_2 + Cl \rightarrow CHF_2Cl$	1.54×10^{14}	0	0	[32]
$H + CHF_2Cl \rightarrow CHF_2 + HCl$	5.65×10^{14}	0	64.2	[32]
$CH_2 + HCl \rightarrow Cl + CH_3$	1.73×10^{12}	0	3.62	[32]
$CF_2Cl + CH_4 \rightarrow CHF_2Cl + CH_3$	6.00×10^{11}	0	0.24	[32]
$3CHF_2Cl \rightarrow 2CHF_3 + CHCl_3$	4.00×10^{23}	0	210	[32]
$CF_2Cl_2 + CF_3 \rightarrow CF_3Cl + CF_2Cl$	2.30×10^{11}	0	56.30	[34]
$CF_2Cl_2 + CH_3 \rightarrow CH_3Cl + CF_2Cl$	1.30×10^{12}	0	47.3	[35]
$CF_2Cl_2 CF_2Cl + Cl$	8.00×10^{16}	0	264	[32]
$CF_3Cl + Cl \rightarrow CF_3 + Cl_2$	1.80×10^{14}	0	131	[36]
$CF_3Cl + H \rightarrow CF_3 + HCl$	1.70×10^{13}	0	36.8	[37]
$CF_3Cl + CH_3 \rightarrow CH_3Cl + CF_3$	3.00×10^{10}	2.34	41.57	[38]
$CF_3Cl \rightarrow CF_3 + Cl$	9.16×10^{19}	1.25	372	[39]
$CF_2Cl + F \rightarrow CF_3 + Cl$	7.16×10^{14}	0	0	[40]
$CF_2Cl + CF_2Cl \rightarrow CF_2Cl - CF_2Cl$	1.86×10^{13}	0	1.94	[32]
$CF_2Cl + CF_2Cl \rightarrow CF_2Cl_2 + CF_2$	2.06×10^{16}	0	39.49	[32]
$CHF_3 + CF_2Cl \rightarrow CHF_2Cl + CF_3$	7.98×10^{11}	0	57.2	[41]
$Cl + Cl \rightarrow Cl_2$	2.00×10^{09}	0	−6.82	[32]
$CHF_3 + Cl \rightarrow CF_3 + HCl$	9.30×10^{12}	0	13.2	[32] [b]
$C_2H_6 + Cl \rightarrow C_2H_5 + HCl$	2.30×10^{13}	0.7	−0.97	[42]
$CH_3CF_2Cl \rightarrow CH_2 : CF_2 + HCl$	5.00×10^{13}	0	230	[43]
$CH_3CF_2Cl \rightarrow CH_2 : CFCl + HF$	1.30×10^{13}	0	272	[43]
$CH_3 + CF_2Cl \rightarrow CH_3CF_2Cl$	1.80×10^{33}	6.64	21	[43]
$c - C_3F_6 \rightarrow CF_2 : CF_2 + CF_2$	1.80×10^{13}	0	182.0	[44]
$c - C_3F_6 \rightarrow C_3F_6$	6.80×10^{14}	0	268.8	[44]
$CHF_2 + CH_3 \rightarrow CF_2 + CH_4$	3.00×10^{13}	0	3.4	NIST
Replaced by				
$CH_4 + CF_2 \rightarrow CH_3 + CHF_2$	1.00×10^{13}	0	159.5	[45]
$CH_3 + CF_2 \rightarrow CH_2CF_2 + H$	6.00×10^{12}	0	14.6	NIST
Replaced by	2.10×10^{13}	−0.20	0	[18]

[a] The rate constants of forward reactions are $k = AT^n \exp(-E/RT)$, where A is in pre-exponential factor, E is activation energy and R is the ideal gas constant.

[b] The estimation is made by referring to the analogous reactions in literature ($CHF_3 + CClF_2 \rightarrow CHClF_2 + CF_3$ and $CH_2F + HCl \rightarrow CH_3F + Cl$).

$$CH_4 + CF \rightarrow CH_2 : CHF + H \quad (29)$$

$$CH_3 + CHF_2 \rightarrow CH_2 : CHF + HF \quad (30)$$

$$CH_2 = CF_2 + H \rightarrow CH_2 : CHF + F \quad (31)$$

$$2CHF_2 \rightarrow CHF_2CHF_2 \quad (32)$$

$$CHF_2CHF_2 \rightarrow C_2HF_3 + HF \quad (33)$$

4.4. Chemical kinetic modeling

Based on the above analysis, a detailed mechanism is developed to model the product distribution of the present study. The mechanism comprises three reaction schemes: (1) GRI-Mech for the reaction of hydrocarbons [30]; (2) NIST HFC mechanism [29] and (3) the reaction scheme developed in this study. The reactions containing oxygen in scheme (1) and (2) are omitted since there is no oxygen involved in our investigation. For the purpose of brevity, only reactions in scheme (3) are listed in Table 2.

Fig. 1 shows a comparison of conversion of feed species with modeling results as a function of temperature. Generally, the conversion levels of $CHClF_2$, CCl_2F_2 and CH_4 are reproduced satisfactorily over the entire temperature range studied. In contrast, a low conversion level of CH_2FCF_3 is predicted, which is significantly lower than that observed experimentally. Under the conditions of this study, similarly to $CHClF_2$ and CCl_2F_2, CH_2FCF_3 can also be attacked by Cl and other reactive radicals. However, many of these reactions are absent from the reaction mechanism due to the lack

of thermo-kinetic data of these reactions, since these data have not been obtained either experimentally or theoretically.

It was noted that the prediction of conversion of CCl_2F_2 is higher than that observed experimentally, especially at elevated temperatures. Because the kinetic parameters listed in Table 2 are adopted directly from literature, careful re-assessment of these data is necessary in order to reproduce the experimental data. In some cases, different values were reported for the same reaction step, and assessing the rate parameters which are most suitable is difficult when it is combined to a mechanism containing several hundred reaction steps.

Comparison of the rates of formation of major carbon containing products is presented in Fig. 2. The major species predicted are C_2F_4, $CH_2=CF_2$ and CH_3Cl, which is in good agreement with the experimental results. Satisfactory prediction of the trends of rates of formation of these products is obtained based on the proposed mechanism, although the discrepancy tends to increase with temperature. A maximum rate of formation of C_2F_4 is predicted at around 900–925 K, which is slightly lower than the experimental result, namely 950 K. It seems that the highest rate of formation of CH_3Cl is predicted to be at temperature above 1073 K, while the rate of CH_3Cl was observed to start to decrease at 1025 K. The results of experiments and modeling both show that the rate of formation of $CH_2=CF_2$ increase with temperature, although the predictions are generally higher than experimental measurements.

The observed increase in the rate of formation of minor products, such as C_2H_3F, C_2HF_3, C_2H_2, CH_2F_2, CHF_3 and C_3F_6 are predicted reasonably well as a function of temperature. At high tempera-

tures, the rates predicted are usually higher than experimental observations, except in the case of C_3F_6. We suggest that one possible reason for this discrepancy is that our proposed mechanism does not include pathways which lead to the formation of other C_3 and C_3^+ species, such as $CF_3CF=CH_2$, $CF_3CH=CF_2$, and $C_4H_2F_4$. These products were detected in trace amounts during experiments. The temperature at which we predict maximum rates of C_2HF_3 and CH_2F_2 are 25–50 K higher than those observed experimentally.

Although the model can predict the formation of many other minor species, CCl_3F, CH_2CClF, CF_2CClF and $C_2H_2F_4$, quantitative comparison is less satisfactory. This especially true for those minor products containing chlorine. To obtain better agreement for these products, further analysis and study is necessary.

4.5. Reaction pathway analysis

To obtain a qualitative understanding of the chemistry involved in the reaction of $CHClF_2$, CCl_2F_2 and CH_2FCF_3 with CH_4, pathway analysis is used to elucidate the reaction mechanism. Based on the information obtained from the analysis, a pathway analysis for the reaction of $CHClF_2$, CCl_2F_2 and CH_2FCF_3 mixture with CH_4 is developed and is summarized in Fig. 6. Since the reactions are dependent on reaction conditions, pathway analysis was carried out at 998 K and a reaction time of 0.5 s with a feed ratio of CH_4, $CHClF_2$, $CClF_2$ and CH_2FCF_3 of 18:9:8:1. Only the pathways leading to the formation of major and most of minor products are illustrated in Fig. 6.

5. Conclusions

Reactions of recovered refrigerants waste mixtures, namely $CHClF_2$, CCl_2F_2 and CH_2FCF_3 with CH_4 have been conducted over the temperature range of 873–1133 K. The major products of reaction of $CHClF_2$, CCl_2F_2 and CH_2FCF_3 with CH_4 are $CH_2=CF_2$, C_2F_4, CH_3Cl, HF and HCl under all conditions studied. Minor products include CHF_3, CH_2F_2 C_2H_2, C_2H_3F, C_2HF_3, CCl_3F, CH_2CClF, CF_2CClF. Trace amounts of C_3F_6, $C_2H_2F_4$, $CF_3CH=CF_2$, $CHF=CClF$ and $CF_2=CHCl$ were detected at elevated temperatures. At temperatures below 973 K, the rate of formation of C_2F_4 increase with temperature and dominates the products, and above this temperature, its rate drops sharply, and is close to zero at 1073 K. The rate of formation of $CH_2=CF_2$ increases with temperature monotonically and exceeds that of C_2F_4 at 1000 K. With a further increase in temperature, $CH_2=CF_2$ becomes the major product observed and a 43% selectivity to $CH_2=CF_2$ was obtained at 1073 K. A detailed mechanism was developed based on the mechanistic analysis for the kinetic modeling. In particular, chlorine radicals produced from R12 play an important role in initiating the decomposition of R134a in mixture of refrigerants. Good agreement was achieved between the predictions and experimental results. Finally, based on the mechanistic analysis, a summary of reaction pathways is proposed, which is found to be consistent with the experimental observations.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.08.095.

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