

Conversion of CHF_3 to $\text{CH}_2=\text{CF}_2$ via reaction with CH_4 in the presence of CBrF_3 : An experimental and kinetic modelling study

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ABSTRACT

Gas-phase reaction of CHF_3 (HFC 23) with CH_4 in the presence of CBrF_3 (halon 1301) to produce $\text{CH}_2=\text{CF}_2$ (VDF) is presented. Experiments were carried out in a plug-flow reactor at temperatures between 873 and 1173 K. Under these conditions, $\text{CH}_2=\text{CF}_2$ was a dominant product observed, with CH_2F_2 , C_2H_2 , CH_2CHF , C_2F_4 , C_2H_6 and CHF_2CF_2 also detected. In the presence of less than 6000 ppm of CBrF_3 , the rate of formation of $\text{CH}_2=\text{CF}_2$ is significantly enhanced, and a much lower rate of formation of the major by-product, C_2F_4 is observed. Further increasing the proportion of CBrF_3 in the feed resulted in an even higher rate of formation of $\text{CH}_2=\text{CF}_2$. Experimental results are fitted very well by a model derived from the NIST and GRI-Mech 3.0 mechanisms, modified to include additional published kinetic data.

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1. Introduction

Hydrofluorocarbons (HFCs) are widely used as substitutes for halons, chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), although there is concern over the high global emission of HFCs, which is estimated to reach 5.5 million tonnes by 2015 [1]. During the 2009 Copenhagen Climate Summit, USA and a number of other attendee countries suggested that the phase-out plan implemented for CFCs and HCFCs should be considered for application to HFCs. In particular, the EU concluded that new incentives for HFC-23 destruction should be found, and the existing clean development mechanism (CMD) projects should be honoured as outlined in EU Council Conclusions on EU Position for the Copenhagen Climate Conference [2]. HFC-23 (CHF_3) is the second most potent greenhouse gas, whose global warming potential (GWP) is 11,700 times higher than CO_2 . According to the UNFCCC (United Nations Framework Convention on Climate Change), around 20 projects have been registered for the oxidative destruction of CHF_3 under the clean development mechanism (CDM) by 2009 which aims to reduce CHF_3 emissions by about 82.6 million tonnes of equivalent CO_2 [3]. However, the oxidative processes operate at temperatures as high as 1473 K and produce large quantities of HF which requires additional treatment.

Recently, technologies such as catalytic decomposition and thermal pyrolysis have been proposed for the destruction of

CHF_3 [4–8]. Alternatively, we have discovered that CCl_2F_2 , CBrClF_2 , CHClF_2 and CHF_3 can be converted into the unsaturated hydrofluorocarbon, $\text{CH}_2=\text{CF}_2$ via reaction with CH_4 or CH_3Br [9–13]. Vinylidene difluoride, $\text{CH}_2=\text{CF}_2$, is a monomer for the synthesis of poly(vinylidene difluoride), pVDF which is a thermoplastic that exhibits a variety of piezo-, pyro- and ferroelectrical properties, is inert to various solvents, oils, acids and shows low permeabilities to gases and liquids [14]. Other fluoroelastomers, produced by co-polymerising VDF with other monomers, are finding favour as performance requirements become more stringent and demanding. Fluoroelastomers offer the advantages of long-term, maintenance-free service in severe environments and more reliable protection of the environment [15].

Commercial synthesis of the VDF monomer involves the gaseous pyrolysis of $\text{CH}_3\text{CF}_2\text{Cl}$, $\text{CH}_2\text{ClCF}_2\text{Cl}$, CH_3CF_3 and the reaction of CH_3CHF_2 with Cl_2 at temperatures between 573 and 1273 K [16]. The challenges associated with the preparation of these C_2 sources significantly increase the cost of production of $\text{CH}_2=\text{CF}_2$.

As previously reported, CHF_3 can be converted to VDF (vinyl difluoride), $\text{CH}_2=\text{CF}_2$, via gas-phase reaction with CH_4 [11]. However, low CH_4 conversion levels inhibit a high subsequent yield of VDF. In order to activate CH_4 , CaBr_2 was introduced to the reaction mixture because it possesses a relatively weak Ca–Br bond [10]. However, the results showed that CaBr_2 can react with CHF_3 as well as CH_4 at elevated temperatures. In the present study, CBrF_3 is chosen as a promoter for the reaction of CHF_3 with CH_4 . As CBrF_3 has a relatively weak C–Br bond and can provide Br radicals at relatively low temperatures, it is expected that the Br radicals can activate

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Table 1
Summary of reaction conditions studied in this investigation.

Condition	Reaction	Input molar flow rate (mmol h ⁻¹)	Temperature (K)
1	CH ₄ + CHF ₃	N ₂ : 200 CH ₄ : 18.4 CHF ₃ : 17.6	873–1173
2	CH ₄ pyrolysis	N ₂ : 200 CH ₄ : 18.2	873–1173
3	CHF ₃ pyrolysis	N ₂ : 200 CHF ₃ : 18.1	873–1173
4	CH ₄ + CHF ₃ + CBrF ₃	N ₂ : 200 CH ₄ : 18.6 CHF ₃ : 17.4 CBrF ₃ : 1.4	873–1173
5	CH ₄ + CHF ₃ + CBrF ₃	N ₂ : 200 CH ₄ : 19.45 CHF ₃ : 18.4 CBrF ₃ : 7.31 or 16.4	1073

$P = 1.01$ bar, residence time = 0.5 s.

CH₄ readily [17–20], facilitating the formation of CH₃ radicals and thus improving the yield of CH₂=CF₂.

2. Experimental details

This experimental facility has been described in detail elsewhere [18,21]. Briefly, the apparatus consists of a tubular, high purity (99.99%) 7.0 mm ID alumina reactor. 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 hydrocarbons for TCD detection were experimentally obtained from standard gas mixtures, and quantification of halogenated hydrocarbons was performed with diluted halogenated hydrocarbons in nitrogen. Other species where standard gas mixture was not available were estimated from published correlations [22].

The feed gas was composed of nitrogen (99.999%, BOC), CH₄ (99.97%, Linde), CHF₃ (>98%, Coregas) and CBrF₃ (98.5%, 1.4% N₂, Coregas). All gases were metered with mass flow rate controllers (Brooks). Prior to the effluent gas reaching the GC, mineral acids and moisture were captured by a caustic scrubber and sodium hydroxide (in the form of pellets) trap. The concentration of the trapped hydrogen halides formed during the reaction was determined with an ion chromatograph (Dionex-100) equipped with an Ion-Pac AS14A column (4 × 250 mm).

The reaction conditions explored in this investigation are summarised in Table 1.

3. Chemical kinetic modelling

The reactions involving CHF₃, CH₄ and CBrF₃ during the gas-phase have been modelled using the computer code, “Plug-Flow Reactor”, available in the commercial software package Cosilab. It is a comprehensive tool used for numerical simulation of a variety of chemically reactive flows [23]. 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. For the current investigations, relevant energy balance equations were neglected because all experiments were conducted under essentially isothermal conditions. In separate experiments, α -alumina chips (the same material as that used for the reactor) were charged into the reactor. It was found that α -alumina chips had a negligible effect on the reactions, and there-

fore, no surface reactions were considered or included in surface mechanism.

The elementary reaction scheme used in this study is based on the NIST mechanism, which comprises two distinct reaction schemes: (1) fluorocarbons (HFCs) and (2) bromofluorocarbons (CBrF₃) [24] for fluorocarbon reactions as well as the GRI-Mech 3.0 mechanism [25] combined with the other literature [11,26] for hydrocarbon reactions. The complete mechanism used in the present study includes 350 reactions and 72 species.

Sensitivity and pathway analysis were performed using the sensitivity analysis code and reaction pathway analysis code available in the Cosilab software. Sensitivity and pathway analysis can enhance the understanding of reaction mechanisms and identify rate-limiting steps.

4. Results and discussion

4.1. Experimental results

The gas-phase reaction of CHF₃ with CH₄ was examined under condition (1) as outlined in Table 1. Similar to previous research results [11], the reaction commences at roughly 1023 K with CH₂=CF₂, C₂F₄ and HF detected as major products, and C₂H₂, CH₂F₂, C₂H₃F, C₂HF₃ and C₃F₆ as minor products (see Table S1, Supplementary data). Even at temperatures as high as 1113 K, the conversion level of CH₄ is below 10%, as shown in Fig. 1. Under the same reaction conditions, a conversion level of 30% for CHF₃ is achieved. Separate CH₄ pyrolysis experiments, conducted under condition 2 in Table 1, illustrate how stable CH₄ is even at temperatures as high as 1173 K. There is no detectable conversion of CH₄ and subsequently no reaction products are observed for all the pyrolysis experiments.

With the aim of enhancing the rate of reaction between CH₄ and CHF₃, it is critical to explore ways which facilitate activation of CH₄. Following the study of reaction of CHF₃ with CH₄, relatively small amounts of CBrF₃ (less than 10% of the level of CH₄ in the feed) were introduced into the reactor with the aim of using it as an initiator for CH₄ activation. Fig. 1 shows the level of conversion of CH₄, CHF₃ and CBrF₃ as a function of temperature (as described under condition 4 in Table 1). Compared with the reaction of CHF₃ with CH₄ in the absence of CBrF₃, the conversion level of CH₄ increased considerably upon addition of the CBrF₃ to the feed CH₄/CHF₃. In the absence of CBrF₃, conversion of CH₄ is detected at 1023 K and increases slowly with temperature, although the CHF₃ conversion level remains essentially unchanged except for a small increase between 1013 and 1113 K.

In a 1:13 feed with CH₄, CBrF₃ starts to decompose at relatively low temperatures, and almost complete conversion of CBrF₃ is achieved at temperatures above 1073 K. This is similar to previous studies of the reaction of CBrF₃ with CH₄ [26]. Decomposition of CBrF₃ is also enhanced by its reaction with CH₄ and CH₃ radicals. In the absence of CH₄, the conversion level of CBrF₃ is roughly 20% at 1073 K.

Fig. 2 presents the rate of formation of carbon-containing products as a function of temperature under conditions 1 and 4 in Table 1. Reaction products include CH₂=CF₂, C₂F₄, C₂H₂, CH₂F₂, CH₂CHF, CHF₂CF₂ and trace amounts of C₃F₆ and CHF₂CHF₂ were also detected (for details, see Table S2, Supplementary data). At higher temperatures, a number of unidentified species were detected and quantified, assuming their molar response factors are equal to that of CH₂=CF₂. In addition, CH₃Br formed as a minor product following the introduction of CBrF₃ into the reaction feed gas streams.

For both conditions, CH₂=CF₂ is the dominant product, although CBrF₃ enhances its rate of formation significantly. Upon addition

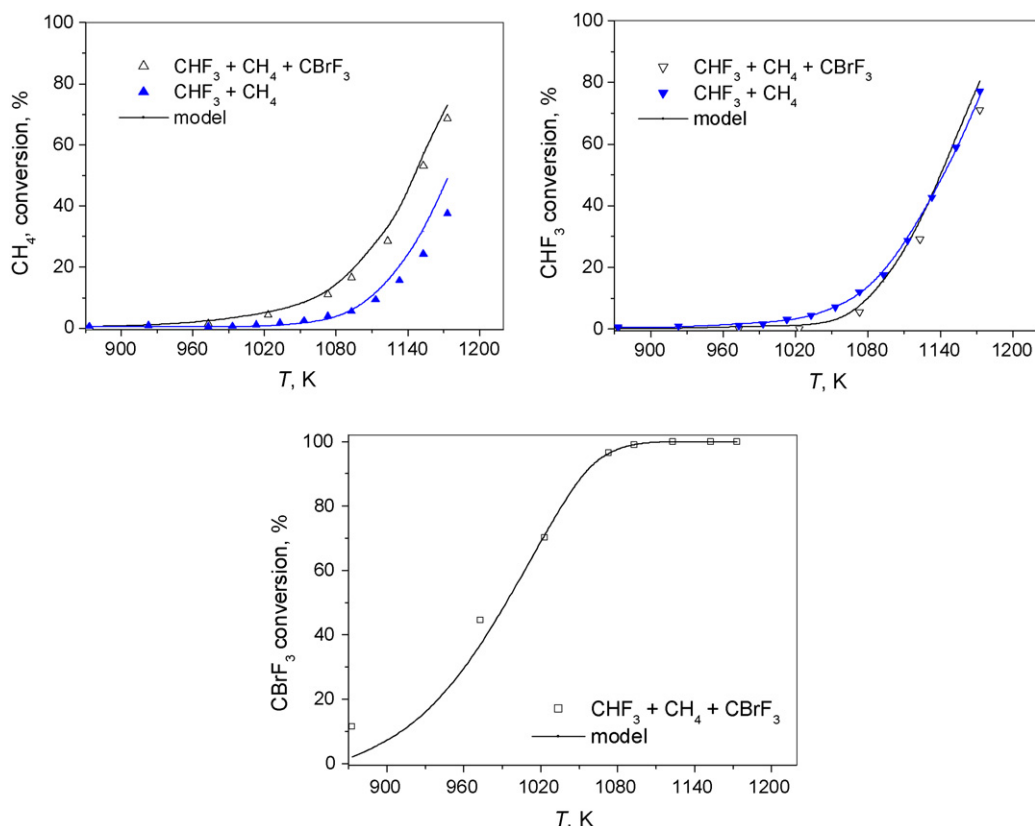


Fig. 1. Conversion levels of CHF_3 and CH_4 under condition 1 (solid symbols) and condition 4 (open symbols) listed in Table 1, each as a function of temperature.

of CBrF_3 to the feed stream, the rate of formation of $\text{CH}_2=\text{CF}_2$ increased significantly at low temperatures but to a lesser extent at higher temperatures. Another notable feature observed upon addition of CBrF_3 is the lower rate of formation of C_2F_4 compared with the reaction in the absence of CBrF_3 . Clearly, dimerization of CF_2 radicals is suppressed under condition 2 (where CBrF_3 is present). A similar trend is observed for the formation of CHF_2 and the formation of C_2H_2 , C_2H_4 and CF_2CHF are also favoured in the presence of CBrF_3 .

Formation of $\text{CH}_2=\text{CF}_2$ was also observed (as a minor product) during the reaction of CH_4 with CBrF_3 [26]. However, the contribution of CBrF_3 into $\text{CH}_2=\text{CF}_2$ in the present experiments is insignificant, even at elevated temperatures (see Supplementary data, Fig. S1). Furthermore, there are only trace amounts of CBrF_3 in our investigation, and therefore, the rate of direct conversion of CBrF_3 to $\text{CH}_2=\text{CF}_2$ is negligible.

Even higher conversion levels of CH_4 and formation rates $\text{CH}_2=\text{CF}_2$ can be achieved with a further increase in the concentration of CBrF_3 in the feed (condition 5 in Table 1), as shown in Fig. 3. The reaction of CBrF_3 with CH_4 produces CHF_3 [26], and as a result, higher concentrations of CHF_3 in the outlet than inlet was observed under high $\text{CBrF}_3/\text{CH}_4$ feed ratios.

4.2. Mechanistic analysis and modelling

The existing NIST and GRI-Mech 3.0 mechanisms, combined with other recent literature [11,26] are used to model the reactions. Generally, good agreement between model predictions and experiments were achieved for the conversion of reactants and for the rates of formation of major and minor species. As shown in Fig. 1, the conversion of CHF_3 and CH_4 is satisfactorily predicted by modified NIST mechanism. Comparing the experimental results undertaken under conditions 1, 3 and 4, similar levels of CHF_3

conversion were observed which suggests that the initial reaction involves the decomposition of CHF_3 . It is generally argued that CHF_3 decomposes through elimination of HF (R1), a process requiring relatively higher temperatures ($>1023\text{ K}$), with an activation energy in the range of $230\text{--}302\text{ kJ mol}^{-1}$ [6,27,28]. This is consistent with our observation that conversion of CHF_3 commences at 1023 K :



As shown in Fig. 1, in excess of 70% of CBrF_3 is converted at 1023 K and the conversion levels increase further until close to 100% is achieved above 1073 K . This is consistent with the presence of a labile C–Br bond in CBrF_3 [29] compared with the other reactants, CH_4 and CHF_3 , and as such, CBrF_3 decomposes first producing CF_3 and Br radicals (R2) before CH_4 or CHF_3 reacts:



Br can then react with CHF_3 [30–32] and CH_4 [32,33], which subsequently initiates a series of chain reactions. No notable enhancement or inhibition of the conversion level of CHF_3 was observed following CBrF_3 (Fig. 1) addition, whereas CH_4 conversion levels are enhanced significantly even at low temperatures, possibly due to the following reaction:



The activation energy of reaction (R3) (76 kJ mol^{-1}) is only slightly lower than that of reaction (R4) (88 kJ mol^{-1}), so the difference in conversion levels between CH_4 and CHF_3 is not a result of the difference in their reaction activation energies:



Furthermore, as shown in Fig. 1, the conversion level of CHF_3 is slightly lower between 973 and 1133 K following the addition of CBrF_3 . We suggest that apparent decrease in CHF_3 conversion

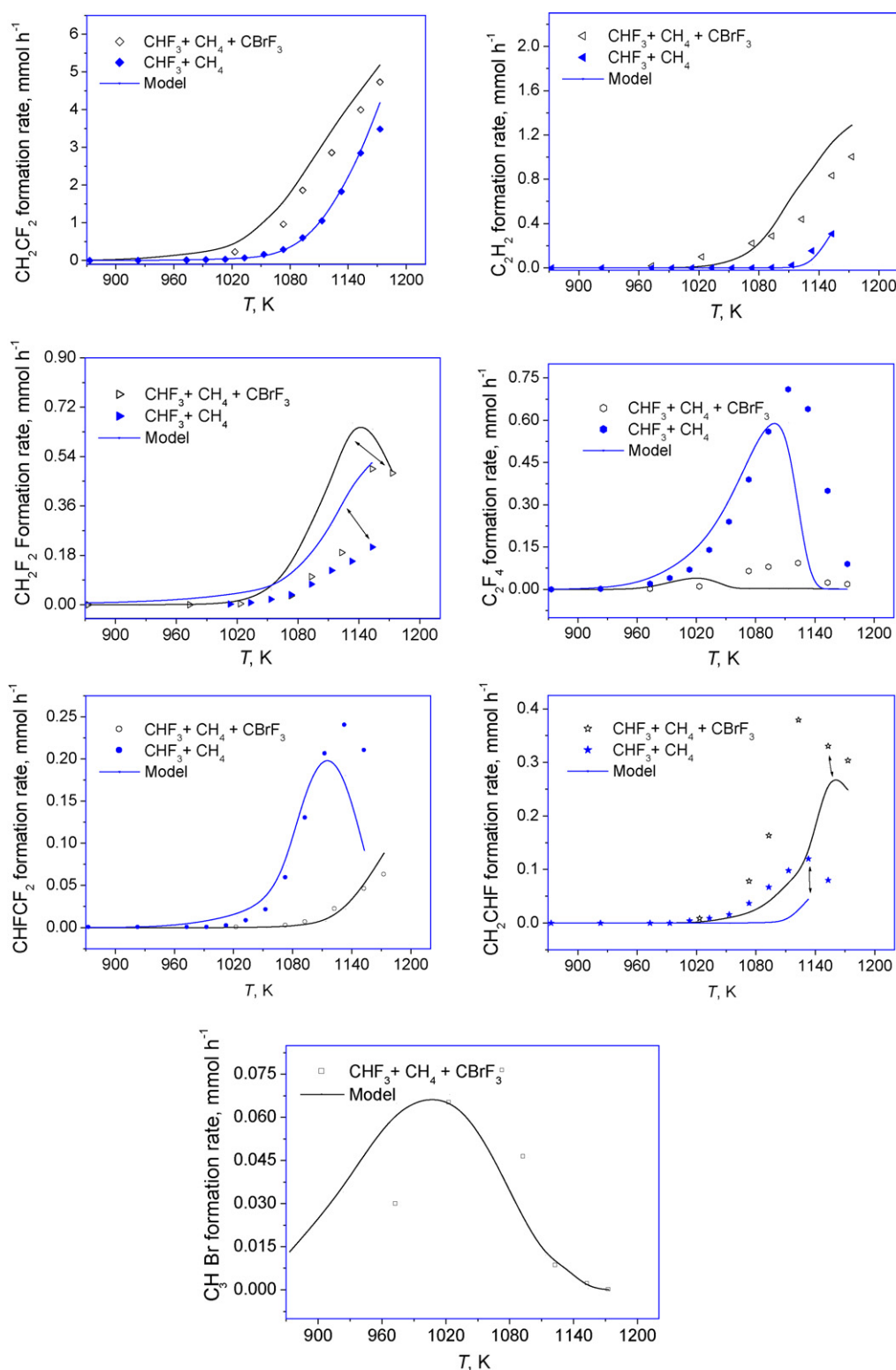


Fig. 2. Rates of formation of products under condition 1 (solid symbols) and condition 4 (open symbols) listed in Table 1, each as a function of temperature.

is a result of the reaction of CF_3 radicals with CH_4 [34]. During the reaction of CBrF_3 with CH_4 , CHF_3 was also found as a major product [18,26] and thus, in the presence of CBrF_3 , CHF_3 conversion is lower than the reaction in the absence of CBrF_3 as it is a product of the reaction of CBrF_3 with CH_4 :



The desired reaction product, $\text{CH}_2=\text{CF}_2$ can be formed through reactions (R6)–(R10). In our previous computational studies, it was shown that there is essentially no stabilisation of the intermediate, CF_2CH_3 for reaction (R6) and that the reaction between CF_2 and CH_3 leads solely to the production of CH_2CF_2 and elemental hydrogen [35]:



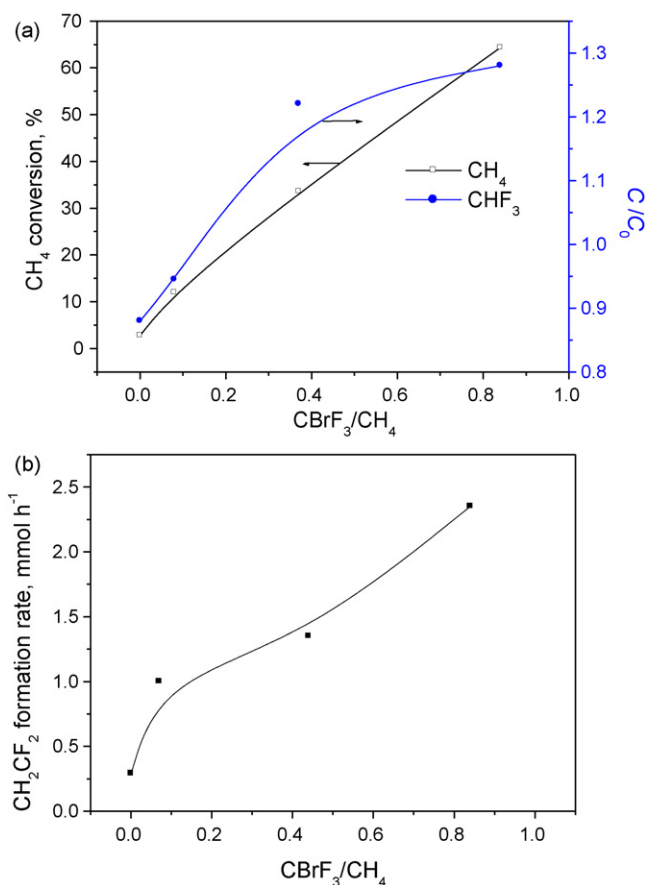


Fig. 3. Conversion of CH₄ and CHF₃ (a) and CH₂CF₂ formation rate (b) as a function of CBrF₃ to CH₄ ratio in the feed. C and C₀ is the concentration of CHF₃ in the outlet and inlet, respectively.



The other reactions involving CF₃ and CH₂ radicals play a relatively minor role in the formation of CH₂=CF₂, due to the relatively low concentration of CF₃ and CH₂ radicals in the absence of CBrF₃. In the presence of CBrF₃, in addition to the direct decomposition of CBrF₃ (R2), CF₃ can be derived from CHF₃.

To identify the primary reactions influencing CH₂=CF₂ formation in this system, sensitivity analysis was carried out using the Cosilab software and the results of this analysis are shown in Fig. 4. As expected, the elimination of HF from CHF₃ (R1) shows significant sensitivity for the formation of CH₂=CF₂, irrespective of CBrF₃ being present or absent from the reaction. However, in the absence of CBrF₃, CH₂=CF₂ formation depends strongly on the dissociation of CF₂ on the reactor surface into carbon and fluorine (R13), according to the mechanism proposed by Yu et al. [11]. Through this pathway, surface-generated fluorine is believed to be the main contributor to CH₄ activation. However, the contribution of (R11) is highly dependent on the availability of free CF₂, as CF₂ can readily dimerize under some reaction conditions:

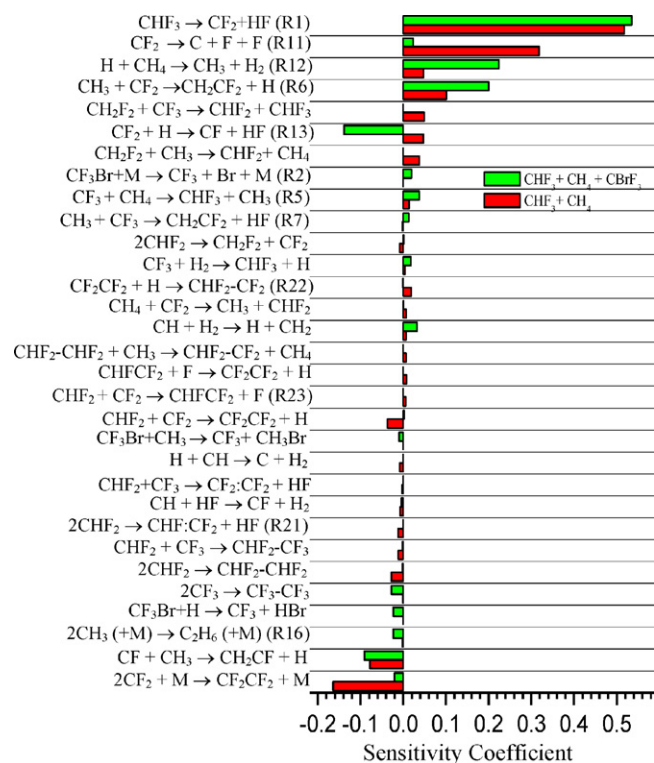


Fig. 4. Sensitivity coefficients of CH₂CF₂ molar fraction for reactions (1) CHF₃ with CH₄ and CBrF₃, and (2) CHF₃ with CH₄ at 1073 K.

In the presence of CBrF₃, the role of CF₂ dissociation is replaced by reaction (R12):



This reaction has been investigated theoretically and experimentally [36–39]. The reaction activation energy suggested by different researchers is generally between 30 and 50 kJ mol⁻¹, and is markedly lower than thermal, gas-phase dissociation of CH₄, where an activation energy of 400 kJ mol⁻¹ for dissociation of CH₄ into CH₃ and H has been reported [40].

The analysis presented in Fig. 4 confirms the importance of reaction (R6) as the predominant pathway for the formation of CH₂=CF₂ while reactions (R7)–(R10) play a relatively minor role in its formation. It can be noted that reaction (R13) inhibits formation of CH₂=CF₂, as disclosed by sensitivity analysis, following addition of CBrF₃. As discussed above, H is the main contributor to the activation of CH₄ via reaction (R14), while large amounts of H are consumed by reaction (R13). As a result, a negative sensitivity for reaction (R13) is observed on CBrF₃ addition:



Based on this assessment, the predicted rate of formation of CH₂=CF₂ agrees well with experimental results in the absence of CBrF₃, although CH₂=CF₂ concentration is slightly over predicted following the introduction of CBrF₃. According to the sensitivity analysis undertaken, the chief difference between the two cases is associated with the changing influence of reactions (R6) and (R12).

The observed sharp increase in the rate of formation of C₂H₂ following addition of CBrF₃ is a result of the contribution from the chain reactions initiated by Br and CF₃. C₂H₂ is formed via the dehydrogenation of C₂H₄ and C₂H₆. The model under predicts the rate of formation of C₂H₂ over the entire temperature range, and in the present experiments, it is also formed by reaction of other F-containing intermediates such as CH₂CHF [41], CHF and CHF:CH. Unfortunately, the lack of a detailed reaction mechanism which

includes the reactions of these species results in an under prediction in the rate of formation of C_2H_2 in our model. Sensitivity analysis discloses that the following reactions are most sensitive for formation of C_2H_4 and C_2H_2 .



One striking difference between the reactions in the absence and presence of $CBrF_3$ is the rate of formation of C_2F_4 . In the case where $CBrF_3$ is present, only trace amounts of C_2F_4 are detected. In both cases, C_2F_4 is formed through the dimerization of CF_2 . It is believed that the subsequent concentration of CF_2 formed as a result of HF elimination from CHF_3 (R1) should be similar in the two cases. However, in the presence of $CBrF_3$, the concentration of CH_3 radicals which can consume CF_2 such as (R6) and (R7) is much higher. It is estimated that rate constant for CF_2 dimerization is roughly $4 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [42,43]. Previous studies have shown that the rate constant for $CF_2 + CH_3 \rightarrow CH_2=CF_2 + H$ can be well approximated by the expression $2 \times 10^{13} T^{-0.207} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is significantly higher than that of CF_2 dimerization [35] and thus in the case where $CBrF_3$ is present, the rate of activation of CH_4 , is enhanced, the concentration of CH_3 is increased and thus the rate of formation of $CH_2=CF_2$ is higher.

As illustrated in Fig. 2, small amounts of CHF_2 and CH_2CHF are detected at elevated temperatures. Romelaer et al. studied the gas-phase pyrolysis of $CHClF_2$ and CHF_3 in the presence of hydrogen [28]. They proposed that CF_2 , which is formed by decomposition of CHF_3 and $CHClF_2$, reacts with hydrogen to produce CHF_2 , which then reacts with H_2 to produce CH_2F_2 . However, in the present study, we suggest that CHF_2 is formed via the combination of two CHF_2 radicals [44]. In addition, other possible pathways include substitution of F by H and reaction of CHF_2 with CF_2 as shown in reaction (R22) and (R23) can also contribute to its formation:



Alternatively, CHF_2 radicals can also react with CH_3 , forming CH_3CHF_2 , which is believed to be the precursor of CH_2CHF via reaction (R24). The increase in CHF_2CF_2 and CH_2CHF concentration following $CBrF_3$ addition is ascribed to the activation of CH_4 by Br and CF_3 . Therefore, reactions (R22) and (R24) are enhanced as a result of the increased concentration of CH_3 and H derived from CH_4 :

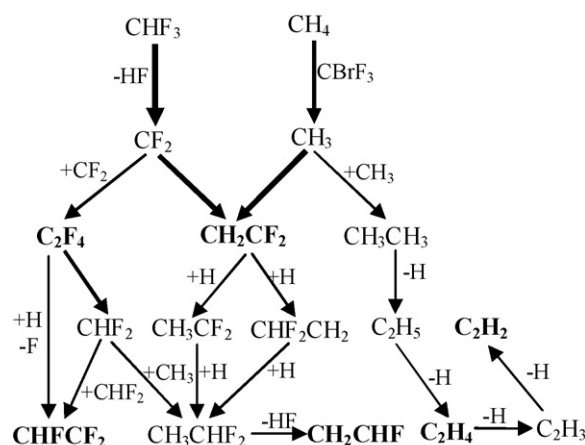


Fig. 5. Reaction pathways leading to formation of carbon-containing products during the reaction of CHF_3 with CH_4 in the presence of $CBrF_3$.

4.3. Reaction pathway analysis

Based on the data obtained from the experimental work and the mechanistic analysis, the reaction pathways leading to the formation of carbon-containing products during reaction of CHF_3 with CH_4 in the presence of $CBrF_3$ are assessed and summarised in Fig. 5. Only the most significant pathways are presented in the figure. The lack of elementary reaction steps involving some fluorine-containing species (which contribute the formation of products such as CH_2F_2 , C_2H_2 , CH_2CHF and CHF_2CF_2) from the mechanism compromises the analysis significantly. As a result, some discrepancies were observed between modelling and experimental results.

5. Conclusions

Reaction of CHF_3 with CH_4 leading to the formation of CH_2CF_2 in the absence and presence of $CBrF_3$ was studied experimentally and modelled kinetically. The study reveals that rate of formation of the target product, $CH_2=CF_2$ is improved dramatically following the addition of trace amounts of $CBrF_3$ to the feed. Compared with the neat reaction of CHF_3 with CH_4 , the addition of $CBrF_3$ enhances the conversion of CH_4 but not that of CHF_3 which results the higher yield of $CH_2=CF_2$ and lower rate of formation of the by-product, C_2F_4 . Higher $CH_2=CF_2$ formation rates can be achieved with an increase of the concentration of $CBrF_3$ in the feed.

Experimental results are modelled using a mechanism based on the NIST, GRI-Mech 3.0 mechanisms, in combination with other literature. Sensitivity analysis discloses that reactions such as the decomposition of CHF_3 into CF_2 , the decomposition of CH_4 into CH_3 and the reaction of CH_3 with CF_2 are the most sensitive steps for the formation of $CH_2=CF_2$. Finally, the reaction pathways leading to the formation of carbon-containing products during reaction of CHF_3 with CH_4 in the presence of $CBrF_3$ are elucidated.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.04.011.

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