EXPERIMENTAL AND COMPUTATIONAL STUDIES OF REACTION OF HALON 1211 ($CBrClF_2$) WITH METHANE

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ABSTRACT

In this study, the gas-phase reaction of halon 1211 ($CBrClF_2$) with methane was studied experimentally and computationally over a temperature range of 773 to 1173 K in a plug-flow reactor. At lower temperatures (below 923 K), during which the conversion of $CBrClF_2$ was below 50 %, $CHClF_2$ and CH_3Br were produced as major products. At elevated temperatures (>1073 K), complete conversion of $CBrClF_2$ was achieved, with the initial products $CHClF_2$ and CH_3Br replaced by $CH_2{=}CF_2$. The effect of the ratio of $CBrClF_2$ to CH_4 was also studied and a single-pass yield of 63 % of $CH_2{=}CF_2$ was achieved at 1173 K for the feed composition of $CBrClF_2{:}CH_4 = 1{:}2$.

A chemical reaction scheme involving 91 species and 435 reactions was developed and used to model the reaction of $CBrClF_2$ with CH_4. The predicted conversion of $CBrClF_2$ and rate of production of $CHClF_2$ are in a good agreement with the experimental values while the predicted CH_4 conversion and rate of production of other species are less satisfactory.

INTRODUCTION

One of the major consequences of *The Montreal Protocol on Substances that Deplete the Ozone Layer* has been to intensify research efforts aimed at developing methods for disposal of stockpiled CFCs and halons *(1)*. Many techniques have been identified that can destroy stockpiles of ozone depleting chemicals. However, these destructive techniques typically require extremely high temperatures and thus are energy inefficient *(2, 3)*. Conversion, in contrast to destructive technologies, is attracting considerable interest with most research effort focused on hydrodehalogenation of ozone depleting substance (ODSs). Hydrodehalogenation involves reactions of ODSs with hydrogen with the resultant products being normally a mixture of hydrofluorocarbons (HFCs), hydrocarbons and mineral acids *(4-10)*. Unfortunately, HFCs are powerful synthetic greenhouse gases (GHGs) and emission of HFCs is now being regulated by the *Kyoto Protocol (11)*. As a result, the application of hydrodehalogenation is a limited or at best short-term solution to CFC and halon treatment. Clearly, there is the need for the development of a process suitable for the conversion of a wide variety of CFCs, halons, HFCs, and other ODSs and GHGs to useful and environmentally benign products.

Recently, we have discovered that hydrodehalogenation of halon and CFCs using CH_4 rather than hydrogen could be used to produce unsaturated hydrofluorocarbons such as vinylidene fluoride ($CH_2{=}CF_2$). $CH_2{=}CF_2$ is an environmentally benign chemical, widely used in the fluoroelastomer and semiconductor industries. It is also the key monomer for the synthesis of a variety of products, most notably poly(vinylidene fluoride) (PVDF), Viton® (produced by Dupont Corporation) and KEL-F® (produced by 3M). The market demand for $CH_2{=}CF_2$ is high and increasing, which has led 3M to sign an agreement with Solvay Fluoropolymers Inc. in 2002, which allows 3M to have access to Solvay's newly built 2,300 metric tonnes/year PVDF plant, and its 50% interest in Alventia, a joint venture with 3M, which produces 5,000 metric tonnes $CH_2=CF_2$ per year *(12)*.

In previous experimental studies, we investigated the hydrodehalogenation of $CBrClF_2$ with methane in some detail. It has been found 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 $CH_2=CF_2$ at higher temperatures *(13)*. However, the reaction mechanism involved in this novel chemistry is far from being fully elucidated. Further study of the effects of the reaction parameters such as feed composition and temperatures (>1073 K) is also necessary in order to optimise the production of $CH_2=CF_2$.

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). A kinetic reaction scheme has developed and used to model the reaction of $CBrClF_2$ with methane.

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 *(9)*. In a typical experiment, the reactor was 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 an AT-Q capillary column and quadrupole 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 *(14)*. 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.

CHEMICAL KINETIC MODELLING

The reaction of $CBrClF_2$ with CH_4 in the tubular reactor was modelled using a commercial software package PLUG *(15)*. The Chemical Application PLUG is a Fortran-based computer code developed for the analysis of plug flow reactors which can include gas phase and surface chemistry. More specifically, the code is designed to model the non-dispersive, one-dimensional flow of a chemically reacting ideal gas mixture in a conduit of essentially arbitrary geometry. The application makes use of the gas-phase kinetics and surface kinetics preprocessors to handle gas-phase and heterogeneous kinetics as well as thermodynamics properties.

The mechanism developed here comprises 435 elementary reactions. The development requires intensive examination of the existing literature for kinetic parameters for each reaction step and careful investigation of analogous reaction systems. Polynominial coefficients describing the thermodynamic data were taken directly from the existing database including THERM (the default thermochemical database in Chemkin 3.7.1), NASATHERM (NASA Complex Chemical Equilibrium Programme database) and BURCAT *(16)*. For species whose information is not available, a software package (THERM) was used to generate the polynomial coefficients *(17)*. In this case, standard state enthalpy, standard state entropy and temperature dependant specific heats were required as input and obtained from the literature.

RESULTS AND DISCUSSION

EXPERIMENTAL RESULTS

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). A detailed analysis of the experimental results has been published elsewhere *(18)*. A brief description of these results is included here.

Figure 1 shows that the conversion of both $CBrClF_2$ and CH_4 increases with the temperature and complete conversion of $CBrClF_2$ occurs above 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 $CBrClF_2$. In separate experiments, it has been found 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 (results are not included in this paper). For instance, the conversion of $CBrClF_2$ was less than 2% at 873 K in the absence of CH_4, increasing to 15% in the presence of CH_4, while in the absence of $CBrClF_2$, methane did not react over the range of temperature studied (773-1173 K).

At lower temperatures (below 973 K), $CHClF_2$, CH_3Br and $CH_2{=}CF_2$ are the major reaction products as shown in Figure 2(a). In addition to the major products, a wide variety of minor products are also formed. The significant minor species produced at lower temperatures are CCl_2F_2 and CBr_2F_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_4, C_2H_3F, $C_3H_3F_5$, C_2H_2ClF and C_2HClF_2 *(18)*.

Increasing the temperature of the reaction above 973 K decreases the concentration of both $CHClF_2$ and CH_3Br, whereas the formation of $CH_2{=}CF_2$ increases significantly over the entire temperature range studied, becoming the dominant product at high temperatures.

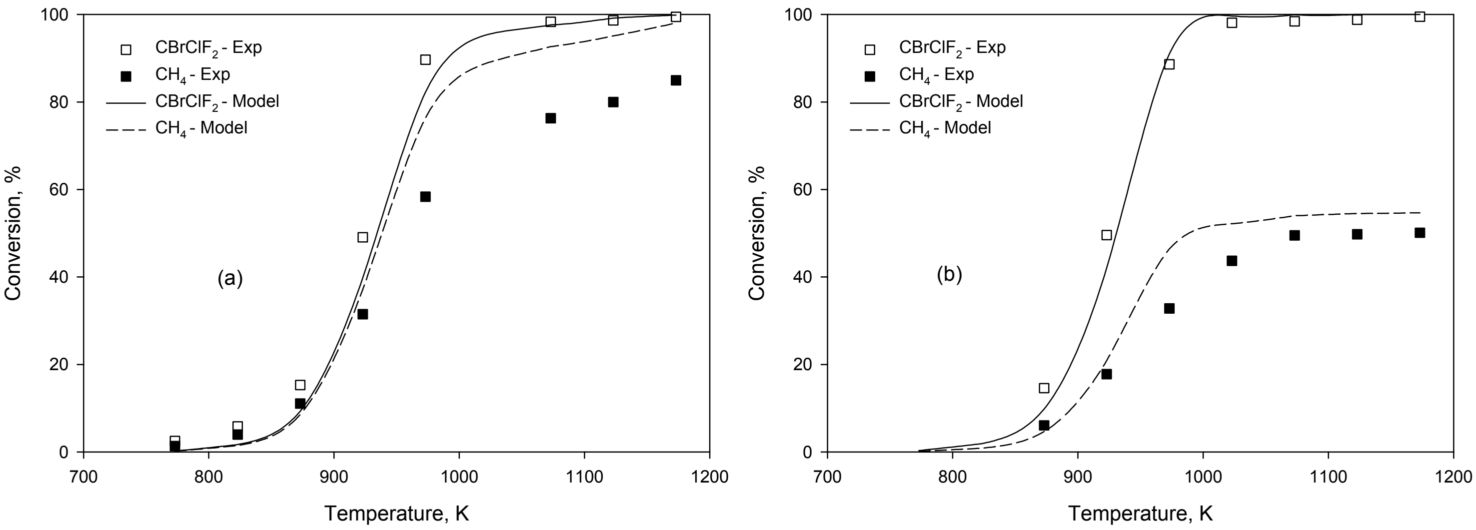

Figure 1. Conversion of $CBrClF_2$ and CH_4 as a function of temperature during the reaction of $CBrClF_2$ with CH_4. (a) $CBrClF_2$:CH_4 in feed = 1:1; (b) $CBrClF_2$:CH_4 in feed = 1:2.

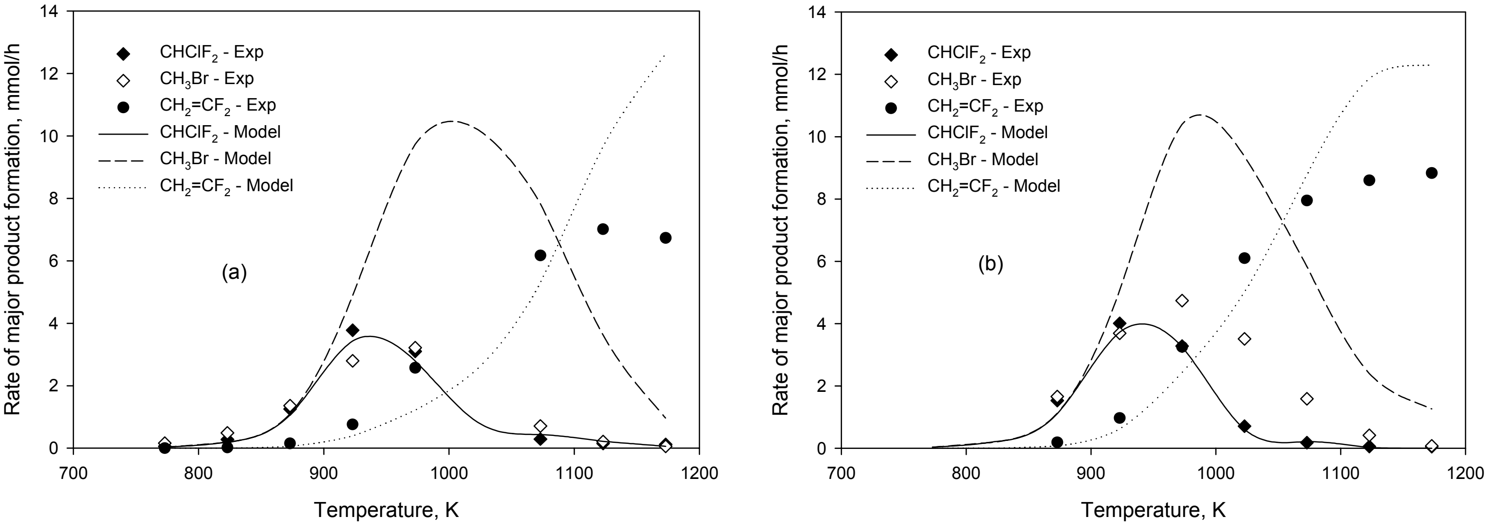

Figure 2. Rate of formation of major products during the gas-phase reaction of $CBrClF_2$ with CH_4. (a) $CBrClF_2$:CH_4 in feed = 1:1; (b) $CBrClF_2$:CH_4 in feed = 1:2.

The carbon balance between the feed and product stream was found to be significantly less than 100% at higher temperatures (above 873 K). The unbalanced portion of product may include some polymeric species which are formed at elevated temperatures. The amount of coke, estimated on the basis of mass-balance considerations, reaches 24% of the feed carbon at 1173 K. Although the amount of carbonaceous species at higher temperature is related to the loss of feed as byproducts, it could be beneficial when considering the high gas-phase selectivity of the target product (CH_2=CF_2) as it results 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 mixture of $CBrClF_2$ and CH_4 at the ratio of 1:2 over the temperature between 873 and 1173 K. At lower temperatures the profile of major products for 1:2 feed ratio is very similar to that of 1:1 feed ratio (Figure 2). 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 923 K 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 $CH_2{=}CF_2$ 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, while for the feed ratio 1:1, the yield of $CH_2{=}CF_2$ was 50% 1173 K.

MECHANISTIC ASPECTS

The formation of $CHClF_2$ and CH_3Br, the two major products at low temperatures, can be explained by a free radical chain reaction mechanism which is summarized as follows:

$CBrClF_2 \rightarrow CClF_2 + Br$ Initiation step (R1)
$Br + CH_4 \rightarrow CH_3 + HBr$ (R2)
$CClF_2 + CH_4 \rightarrow CHClF_2 + CH_3$ Propagation step (R3)
$CBrClF_2 + CH_3 \rightarrow CH_3Br + CClF_2$ Propagation step (R4)
$CH_3 + Br \rightarrow CH_3Br$ Termination step (R5)

Minor products, CCl_2F_2 and CBr_2F_2, may have been formed primarily via reactions (R6) and (R7), as discussed in our previous study of the thermal pyrolysis of $CBrClF_2$ *(19)*.

$CClF_2 + CBrClF_2 \rightarrow CCl_2F_2 + CBrF_2$ (R6)
$CBrF_2 + CBrClF_2 \rightarrow CBr_2F_2 + CClF_2$ (R7)

One possible reaction pathway leading to the formation of the target product, $CH_2{=}CF_2$, is via the methylation of $CClF_2$ species with CH_3 species, forming an unstable CCH_3ClF_2 intermediate, which then undergoes repaid dissociation to produce $CH_2{=}CF_2$ and HCl (R8).

$$CClF_2 + CH_3 \rightarrow [CH_3CClF_2] \rightarrow CH_2{=}CF_2 + HCl \qquad (R8)$$

Jones et al. studied the reaction of $CClF_2$ and CH_3 radicals and found that, the reaction can form chemically activated CH_3CClF_2 molecules which may subsequently eliminate HCl to produce $CH_2{=}CF_2$ and HCl (R9) or be stabilized by collision *(20)*.

$$CClF_2CH_3 \rightarrow CH_2{=}CF_2 + HCl \qquad (R9)$$

At the pressure of 1 atm, only 10% $CClF_2CH_3$ undergoes the dissociation step (R9). The dissociation of CH_3CClF_2 has been investigated by many authors *(21-23)* and the activation energy for (R9) has been estimated to be ca. 55 kcal/mol, which is higher than the dissociation energy of $CHClF_2$ (R10) (ca. 53 kcal/mol) *(23, 24)*.

$$CHClF_2 \rightarrow CF_2 + HCl \qquad (R10)$$

Clearly, if the reaction (R8) were the major pathway for the formation of $CH_2{=}CF_2$, we would expect to detect CH_3CClF_2 during reaction. However, no $CClF_2CH_3$ was detected under all conditions studied, and we therefore suggest other reactions play an important role in the formation of $CH_2{=}CF_2$.

We propose that the reaction of CF_2 with CH_3 (R11) is the primary reaction pathway leading to the formation of $CH_2{=}CF_2$.

$$CH_3 + CF_2 \rightarrow [CH_3CF_2] \rightarrow CH_2{=}CF_2 + H \qquad (R11)$$

Both CF_2 and CH_3 are present at relatively high concentrations during reaction. CF_2 can be easily formed from the dissociation of $CHClF_2$ (R10) while CH_3 can be generated from (R2), (R3) or (-R5), the reverse reaction of (R5).

A detailed quantum chemical study of reaction of CF_2 with CH_3 which is to presented elsewhere, suggests that this reaction can lead to the formation of $CH_2{=}CF_2$ with an activation energy of almost zero and takes place at a relatively fast rate *(25)*. Our proposal is also supported by the experimental observation. At temperatures above 973 K, the formation of both $CHClF_2$ and CH_3Br decreases, indicating that secondary reactions, involving the consumption of $CHClF_2$ and CH_3Br, are enhanced. $CHClF_2$ and CH_3Br most likely undergo the dissociation reactions (R10) and (-R5). As a result, the concentrations of CF_2 and CH_3 are higher and the rate of production of $CH_2{=}CF_2$ increases accordingly. In addition, an increase in partial pressure of CH_4 in the feed enhanced the yield of $CH_2{=}CF_2$ by providing a high concentration of CH_3 moiety available for coupling with CF_2.

The presence of CF_2 is also suggested by the production of some of the minor products. C_2F_4 is believed to be produced by direct coupling of two difluorocarbene (CF_2) species (R12) while C_2H_3F may be formed by the reaction of CF_2 and CH_4 (R13).

$$CF_2 + CF_2 \rightarrow C_2F_4 \qquad (R12)$$
$$CF_2 + CH_4 \rightarrow C_2H_3F + HF \qquad (R13)$$
$$CF_2 + HF \rightarrow CHF_3 \qquad (R14)$$

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

$$CH_2{=}CF_2 + HCl \rightarrow C_2H_2ClF + HF \qquad (R15)$$
$$CH_2{=}CF_2 + HCl \rightarrow C_2HClF_2 + H_2 \qquad (R16)$$

CHEMICAL KINETIC MODELLING

To better understand the reaction mechanism involved in the reaction of $CBrClF_2$ with methane, the first attempt has been made to develop a kinetic reaction scheme, which comprises four reaction sub models: (1) GRI-MECH hydrocarbon mechanism *(26)*; (2) NIST fluorocarbon mechanism *(27)*; (3) the reaction scheme developed in our previous study of hydrodehalogenation of $CBrClF_2$ with hydrogen *(28)*; (4) the reaction scheme developed in this study. Species and reactions containing oxygen are removed from GRI-MECH and NIST mechanisms since there is no oxygen involved in our study. For the purpose of brevity, only reaction steps in scheme (4) are listed in Table 1. Wherever possible for a given reaction, kinetic data are taken from the literature in which the reaction has been studied in detail. Otherwise, kinetic parameters are estimated by referring to analogous reactions. It should be pointed out that the reaction mechanism reported here constitutes work in progress. At this stage, the mechanism does not include $C_3H_3F_5$, $C_3H_2F_6$, C_2H_2ClF and C_2HClF_2 which are detected as minor species at relatively high temperatures. Formation of coke is also not considered in the current reaction scheme.

Figure 1 shows a comparison of conversion of $CBrClF_2$ and CH_4 as a function of temperature at two feed ratios. The predicted conversion level of $CBrClF_2$ is in good agreement with the experimental value under all conditions. The conversion level of CH_4 is predicted very well at temperatures below 923 K while overpredicted at temperatures above 923 K.

Figures 2 show a comparison of rates of production of major carbon containing species as a function of temperature at two feed ratios. The major carbon containing species are $CHClF_2$, CH_3Br and CH_2=CF_2, which are in good agreement with the experimental results obtained. Satisfactory prediction of the rate of production of $CHClF_2$ is given by the proposed mechanism. However, a significant discrepancy between experimental and modelling values is observed for the rate of production of CH_3Br and CH_2=CF_2. CH_3Br is over-predicted under all conditions while CH_2=CF_2 is underpredicted below 1073 K and overpredicted above 1073 K. The proposed model can predict the formation of many of minor species, including CBr_2F_2, CCl_2F_2, C_2F_4 and CH_3Cl, but the quantitative comparison is less satisfactory.

The discrepancy between experimental and modelling results could be ascribed to a number of factors including: (1) the kinetic data for many reaction steps have been estimated and thus refinement of some parameters may be required; (2) reaction pathways for the formation of minor species should be elucidated and included in the reaction scheme; (3) more importantly, substantial amounts of carbon and halogen are missing. The composition of these missing materials and the reaction pathways leading to these species are unknown, which undoubtedly limits the efficacy of the current model. Further efforts will be made to address these issues and achieve a better agreement between the experimental and modelling results.

Although the model need further improvement to better fit the experimental results, it does suggest that the reaction of $CF_2 + CH_3 \rightarrow CH_2{=}CF_2 + H$ is the primary reaction pathway leading to formation of CH_2=CF_2 as discussed previously. If this step were removed from the proposed scheme, only trace amounts of CH_2=CF_2 would be predicted, while the removal of $CClF_2 + CH_3 \rightarrow CH_3CClF_2 \rightarrow CH_2{=}CF_2 + HCl$ has little effect on the amount of CH_2=CF_2 predicted.

CONCLUSIONS

Reaction 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 CH_2=CF_2. An increase in partial pressure of CH_4 enhanced the yield of CH_2=CF_2. A single-pass yield of 63% CH_2=CF_2 was achieved at 1173 K for the feed composition of $CH_4/CBrClF_2$= 2.0.

A chemical reaction scheme involving 91 species and 435 reactions has been developed and used to model the reaction of $CBrClF_2$ with CH_4. The predicted conversion of $CBrClF_2$ and the rate of production of $CHClF_2$ are in a good agreement with the experimental values while the predicted CH_4 conversion and the rate of production of other species are less satisfactory.

The results demonstrate a viable chemical pathway to efficiently convert $CBrClF_2$ into environmentally benign and potentially valuable solid fluorochemicals. Compared to the existing destruction technologies, the present conversion process can be used to dispose of surplus ozone depleting chemicals while retaining the valuable carbon-fluorine bonds. Of equal importance is that the process requires far less energy than destruction technologies, thereby resulting in significantly reduced greenhouse gas emissions.

Table 1. Reaction model for hydrodehalogenation of $CBrClF_2$ with CH_4. The complete reaction scheme comprises four reaction sub schemes: (1) GRI-MECH hydrocarbon mechanism *(26)*; (2) NIST fluorocarbon mechanism *(27)*; (3) the reaction scheme developed in our previous study of hydrodehalogenation of $CBrClF_2$ with hydrogen *(28)*; (4) the reaction scheme developed in this study. For the purpose of brevity, only reaction steps in scheme (4) are listed in this table except for reaction $CH_2 + CF_2 \rightarrow CH_2{=}CF_2 + H$, whose kinetic parameters follow from our quantum chemical study.

Reaction	*A*	*n*	*E*	Reference
$CH_3 + CF_2 \rightarrow CH_2{=}CF_2 + H$	2.1E13	-0.207	0.0	25
$CH_3 + CHClF_2 \rightarrow CClF_2 + CH_4$	5.8E11	0.0	10.0	29
$CBrF_2 + CH_4 \rightarrow CH_3 + CHBrF_2$	9.5E11	0.0	11.0	{27}
$CClF_2 + CH_3 \rightarrow CH_3CClF_2$	1.8E33	-6.64	5.0	{27}
$CH_3CClF_2 \rightarrow CH_2CF_2 + HCl$	1.0E13	0.0	55.2	21
$CH_3Br + H \rightarrow CH_3 + HBr$	5.1E13	0.0	5.8	30

The rate coefficients of the forward reaction is $k = AT^n \exp(-E/RT)$, where A is in s^{-1} or $cm^3\ mol^{-1}\ s^{-1}$, as appropriate, the activation energy is in kcal/mol, n denotes the temperature exponent, and R stands for the ideal gas constant.

{}: The estimation is made by referring to the analogous reaction in the literature.

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