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Technical Note

Simultaneous conversion of $CHClF_2$ and CH_3Br to CH_2CF_2

Hai Yu, Eric M. Kennedy *, John C. Mackie, Bogdan Z. Dlugogorski

Process Safety and Environment Protection Research Group, School of Engineering, The University of Newcastle, Callaghan, NSW 2308, Australia

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Abstract

Gas phase reaction of $CHClF_2$ with CH_3Br in an alumina tube reactor at 773–1123 K as a function of various input ratios of CH_3Br to $CHClF_2$ is presented. The major products detected include C_2F_4, CH_2CF_2, and CH_4. Minor products include CH_3Cl, CHF_3, C_2H_4, C_2H_2, $CH_2CF–CF_3$, and C_2H_3F. The reaction produces a high yield of CH_2CF_2 (53% based on $CHClF_2$ feed) at 1123 K and an input molar ratio of CH_3Br to $CHClF_2$ of 1.8, suggesting that the reaction potentially can be developed as a process to convert two ozone depleting substances ($CHClF_2$ and CH_3Br) to a highly valuable chemical, CH_2CF_2. The reaction of $CHClF_2$ with CH_3Cl and CH_3I was also investigated under similar reaction conditions, to assist in understanding the reaction chemistry involved in the reaction of $CHClF_2$ with CH_3Br.

Keywords: $CHClF_2$; CH_3Br; CH_2CF_2; Ozone depleting substance; Fluoroelastomers

1. Introduction

The implementation of the Montreal and Kyoto Protocols has intensified research aimed at securing alternative gaseous agents and developing technologies capable of treating the growing stockpiles of saturated halocarbons, including hydrofluorocarbons, chlorofluorocarbon, halons (brominated fluorocarbons or brominated chlorofluorocarbons), hydrochlorofluorocarbons, perfluorocarbons, and methyl bromide.

At present, there are two commercially established treatment technologies, thermal incineration and thermal plasma arc pyrolysis, both of which are destructive and highly energy intensive. In addition, the emission of carcinogenic or toxic by-products such as dioxins and phosgene produced from these processes will pose environmental and health concerns. Conversly, many halocarbons possess valuable C–F bonds, are manufactured at high costs, and are available as relatively pure chemicals in large quantities, which make them attractive chemical feedstock for production of useful chemicals. Clearly, there is a need for the development of energy efficient processes suitable for the conversion of the wide variety of halocarbons to useful and environmentally benign products.

We have recently discovered that CCl_2F_2, $CBrClF_2$, and CHF_3 can be converted into unsaturated hydrofluorocarbons such as CH_2CF_2 through their gas phase reaction with CH_4 (Uddin et al., 2003; Yu et al., 2005; Yu et al., 2006a). CH_2CF_2 is a valuable commodity, widely used in the fluoroelastomer and semiconductor industries. It is 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).

In this communication, we report the reaction of $CHClF_2$ with CH_3Br as a possible option for simultaneous conversion of two ozone depleting substances to CH_2CF_2. CH_3Br is a versatile chemical, used in a wide range of applications including soil fumigation and quarantine treatment. $CHClF_2$ is the world's most widely used refrigerant, introduced as a short term alternative to halons, for

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* Corresponding author. Tel.: +61 2 4921 6177; fax: +61 2 4921 6920.
E-mail address: eric.kennedy@newcastle.edu.au (E.M. Kennedy).

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both residential and commercial applications. However, both halocarbons are ozone depleting substances and the phaseout of these chemicals is underway under the Montreal Protocol.

2. Experimental

The experimental facility used in this study has been described in detail elsewhere (Yu et al., 2004). Briefly, the apparatus consists of a tubular high purity (99.99%) alumina reactor (i.d. 8.5 mm) with the reactor zone maintained uniformly by a three zone furnace. Carbon containing species were identified with 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 Thermal Conductivity Detector detection were experimentally obtained from standard gas mixtures and quantification of halogenated hydrocarbons was performed with a diluted mixture of $CHClF_2$ (>99%, Actrol), CH_3Cl (99.5%, Aldrich) and CH_3Br (>99%, BOC Gases) in nitrogen. For other species, RMR values were estimated from published correlations (Height et al., 1999). Hydrogen halides formed during reaction was trapped with 0.1 M NaOH solution and the concentration of fluoride determined with an ion chromatograph (Dionex-100) equipped with an IonPac AS14A column (4×250 mm). CH_3I was purchased from Aldrich and has a purity of 99%.

The reactions of $CHClF_2$ with CH_3Br and other chemicals were performed under the conditions summarised in Table 1.

Table 1
Summary of reaction conditions considered in this investigation ($P = 101$ kPa; Reactor volume $= 1.35$ cm^3)

Condition	Reaction	Input molar flow rate (mmol h^{-1})	T (K)
1	$CHClF_2 + CH_3Br$	N_2:150 $CHClF_2$:8.1 CH_3Br:8.7	773–1123
2	$CHClF_2 + CH_3Cl$	N_2: 150 $CHClF_2$:8.3 CH_3Cl:8.7	773–1123
3	$CHClF_2 + CH_3I$	N_2:150 $CHClF_2$:8.3 CH_3I:13.8[a]	773–973
4	$CHClF_2 + CH_3Br$	N_2:150 $CHClF_2$:6 0 or 4.8 CH_3Br:8.7	973–1123

[a] During the reaction of $CHClF_2$ with CH_3I, the gas mixture of N_2 and $CHClF_2$ was passed through a saturator which contains liquid CH_3I and cooled at temperatures between −18 and −20 °C using a mixture of 23.3 wt% NaCl and 76.7 wt% of ice. Since we are not able to quantify CH_3I, the molar flow rate of CH_3I is estimated, based on its vapour pressure at −18 °C. For the same reason, we did not calculate the conversion of CH_3I.

3. Results and discussion

The gas phase reaction of $CHClF_2$ with CH_3Br commences at 773 K under conditions listed in Table 1. The major products are C_2F_4, CH_2CF_2, CH_4, and HX ($X = Br$, Cl and F). Minor products include CH_3Cl, C_2H_2, C_2H_4, C_2H_3F, CH_2CFCF_3, and CHF_3. The products detected at trace amounts include CO_2, $CHBrF_2$, C_2HF_3, and CH_2Br_2. Some unidentified species are produced at high temperatures. Coke formation is observed on the surface of reactor and on exposed thermocouple sheaths. Mass balances are estimated by determining the ratio of the total number of mol of element per unit time in the gas species at the outlet of the reactor to total number of mol of elements per unit time in the feed. Generally, the mass balances of all elements decreases according to the following trend $H > Br \approx Cl > F > C$. For example, at 1123 K under Condition 1 listed in Table 1, the mass balances are estimated to be 93% for H, 91% for Br, 90% for Cl, 80% for F, and 69% for C. This suggests that some species including solid and liquid products, which were formed during reaction but not included in the mass balance analysis, are rich in C and F, probably PVDF, $(CH_2{=}CF_2)_n$.

Fig. 1 shows the conversion of $CHClF_2$ and CH_3Br, and the rate of formation of important products vs temperature under Condition 1 in Table 1. The conversion of $CHClF_2$ is always higher than that of CH_3Br until temperature reaches 1123 K when complete conversion (>99%) of both $CHClF_2$ and CH_3Br is achieved. The rates of formation of C_2F_4 and CH_4 increase initially and attain maximum levels at ca. 950 K and 1000 K, respectively, after which the rates decline. The rate of formation of CH_2CF_2, the targeted product, increases with temperature, and a single pass yield of 42% based on $CHClF_2$ feed is obtained at $T = 1123$ K. The rates of formation of minor products, CHF_3, C_2H_3F, and C_2H_4, increase while the rates of formation of CH_3Cl, C_2H_2, and CH_2CFCF_3 increase initially and decrease after reaching maximum values.

We suggest that the initial step during the reaction of $CHClF_2$ with CH_3Br is molecular elimination of HCl from $CHClF_2$, producing HCl and CF_2. The subsequent combination of CF_2 leads to the formation of C_2F_4. The pyrolysis of CH_3Br has been investigated by several researchers (Kiss et al., 1977; Barthel and Senkan, 1994). It is generally believed that the initial steps at low temperatures include the following reactions, which can generate CH_3 radicals.

$$CH_3Br \rightarrow CH_3 + Br \tag{1}$$

$$CH_3Br + Br \rightarrow CH_3 + Br_2 \tag{2}$$

$$CH_3Br + CH_3 \rightarrow CH_2Br + CH_4 \tag{3}$$

$$CH_2Br + CH_3Br \rightarrow CH_2Br_2 + CH_3 \tag{4}$$

The conversion level of $CHClF_2$ is higher than that of CH_3Br under conditions investigated, which is due to the higher activation barrier (approximately 66.9 kcal mol^{-1}) for (1) than that for the molecular elimination of $CHClF_2$

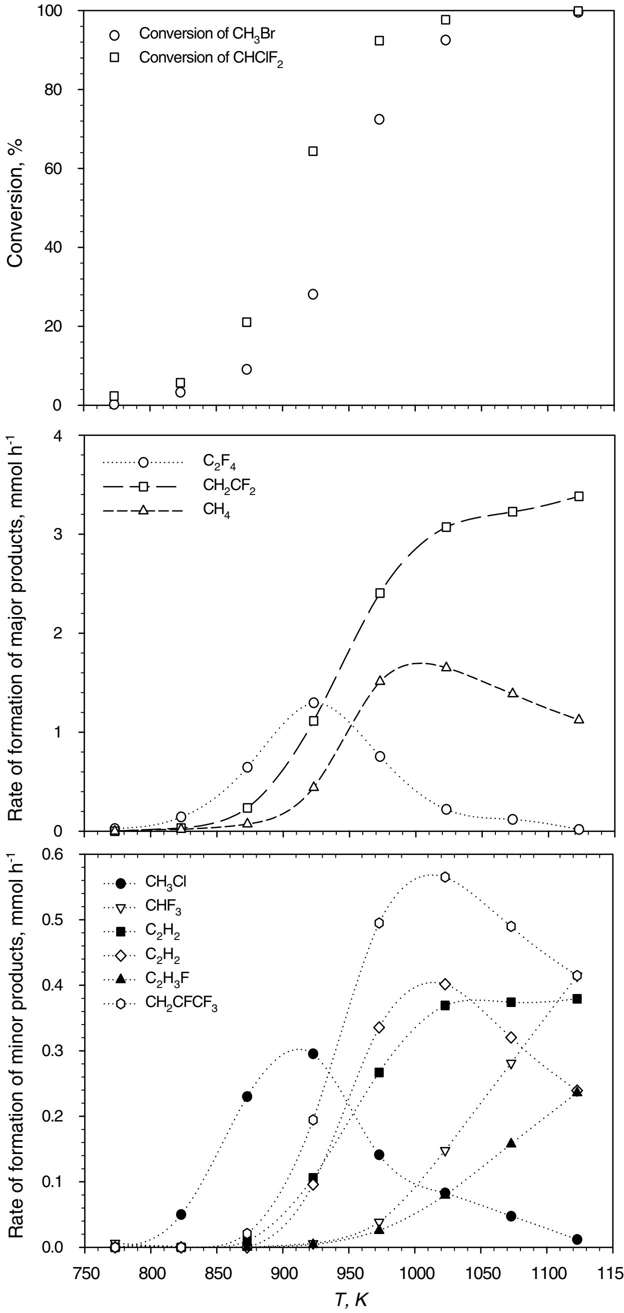

Fig. 1. The conversion and rate of formation of products as a function of temperature during the reaction of $CHClF_2$ with CH_3Br under Condition 1 in Table 1.

(53.5 kcal mol^{-1}) (Sehon and Szwarc, 1951; Kushina et al., 1972). We suggest that the coupling of CF_2 (from $CHClF_2$) with CH_3 (from CH_3Br) is responsible for the formation of CH_2CF_2, which is supported by both the computational and experimental work conducted in our research group. Our recent quantum chemical study of this reaction suggests that the reaction of CF_2 and CH_3 can occur readily, producing CH_2CF_2 and H. Over the temperature range of 700–2000 K, the rate constant for $CF_2 + CH_3 \rightarrow CH_2CF_2 + H$ can be well approximated by the expression $2.1 \times 10^{13}\ T^{-0.207}$ cm^3 mol^{-1} s^{-1} (Yu et al., 2006b).

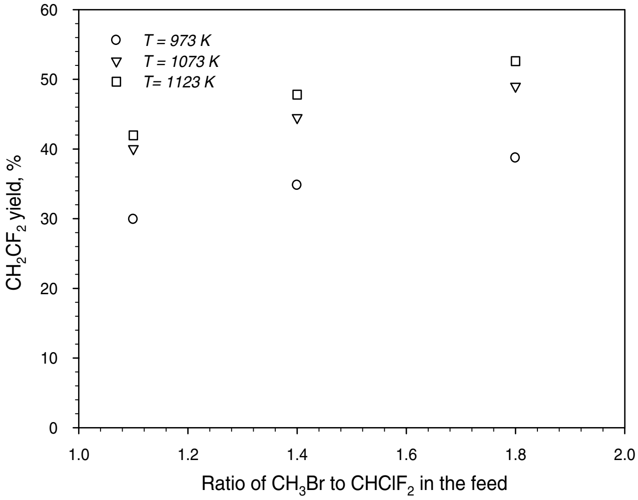

Fig. 2. Effect of input ratio of CH_3Br to $CHClF_2$ on the yield of CH_2CF_2 during the reaction of $CHClF_2$ with CH_3Br under Conditions 1 and 4 in Table 1.

Additional experiments were carried out on the reaction of $CHClF_2$ with CH_3Br at various input ratio and reaction of $CHClF_2$ with CH_3Cl or CH_3I. These experiments result in an increase or decrease in the concentration of CH_3 in the coupling reaction, in order to probe its effect on the formation of CH_2CF_2. As shown in Fig. 2, an increase in the ratio of CH_3Br to $CHClF_2$ in the feed can increase yield to CH_2CF_2 and a single pass yield of 53% is achieved at 1123 K at an input ratio of CH_3Br to $CHClF_2$ of 1.8. The experimental results obtained on the reaction of $CHClF_2$ with CH_3Cl and CH_3I conducted under similar conditions to that for the reaction of $CHClF_2$ with CH_3Br (see Table 1) show that the rate of CH_2CF_2 formation is enhanced with CH_3I and reduced with CH_3Cl (results are not presented), which is also consistent with our proposed CH_2CF_2 formation pathway.

4. Conclusions

The gas phase reaction of $CHClF_2$ with CH_3Br was investigated in an alumina tube reactor at 773–1123 K and various input ratios of CH_3Br to $CHClF_2$. The major products detected are C_2F_4, CH_2CF_2, CH_4, and HX (X = Br, Cl, and F). A single pass yield of 53% is achieved for CH_2CF_2 (based on $CHClF_2$) at 1123 K and an input ratio of CH_3Br to $CHClF_2$ of 1.8. It is suggested that the targeted product, CH_2CF_2, is formed via the reaction pathway involving the reaction of CH_3 with CF_2.

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