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Short Communication

Gas-phase reaction of CCl_2F_2 (CFC-12) with methane

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Abstract

Gas-phase reaction of CFC-12 (CCl_2F_2) with methane was carried out in a plug flow reactor over the temperature range of 873–1123 K. The major organic halocarbons formed during the reaction were C_2F_4, $C_2H_2F_2$, $CHClF_2$, CH_3Cl, $C_3H_2F_6$ and CCl_3F. The formation of all products except $C_2H_2F_2$ decreased with temperature, while the selectivity to $C_2H_2F_2$ (difluoroethylene) increased with temperature and reached ≈80% at 1123 K. Under these reaction conditions, methane acts as hydrogen and carbon source, resulting in the formation of an unsaturated C_2 hydrofluorocarbon from two C_1 precursors.

Keywords: CFC-12; Methane; Dehydrohalogenation; Difluoroethylene

1. Introduction

Restrictions on the use of ozone depleting chemicals such as chlorofluorocarbons (CFCs) and brominated chlorofluorocarbons or brominated fluorocarbons (halons) have initiated intensive research into methods for disposal of stockpiled CFCs and halons. The hydrodehalogenation reactions of these chemicals constitute the core of processes for their conversion to hydrofluorocarbon replacements. For example, the catalytic hydrodechlorination of CFCs with hydrogen over supported palladium catalysts has been studied widely for the production of hydrofluorocarbons (Takita et al., 1990; Coq et al., 1993; Karpinski et al., 1996; Malinowski et al., 1998; Early et al., 1999; Ahn et al., 2000; Moulijn et al., 2000). However, the major drawback of catalytic hydrodechlorination is the lack of stability of catalysts under the severe (acidic) reaction conditions (Moon et al., 1998; Wiersma et al., 1998). We have reported the gas-phase hydrodehalogenation of halon 1301 (CF_3Br) and halon 1211 ($CBrClF_2$) with methane, where methane was used as a hydrogen donor and/or methylating agent (Li et al., 1999; Li et al., 2000; Howe et al., 2002). The products of the reaction between $CBrF_3$ and methane were CHF_3 and CH_3Br, while the reaction between $CBrClF_2$ and methane produced mainly $CHClF_2$ and CH_3Br at lower temperatures with $C_2H_2F_2$ forming with high selectivity at more elevated temperatures.

In this study, we report for the first time the gas-phase reaction of CCl_2F_2 with methane. This novel gas-phase reaction presents a potentially new pathway for the conversion of CFCs to hydrofluorocarbons using methane as a hydrogen donor and/or methylating agent. The major reaction product, $C_2H_2F_2$, is a highly valued precursor for the production of Viton, a temperature and corrosion resistant fluoropolymer.

2. Experimental

2.1. Materials

CFC-12 (CCl_2F_2) was obtained from ACTROL (Australia) having a purity of >99%. CH_4 (99.5%) and

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N_2 (99.99%) were purchased from BOC GASES. All gases were used in the reaction without further purification.

2.2. Gas-phase reaction of CCl_2F_2 with methane

The gas-phase reaction of CCl_2F_2 with methane was carried out in an alumina plug flow reactor over the temperature range of 873–1123 K at atmospheric pressure. A reactant gas stream (CH_4:CCl_2F_2:N_2 = 1:1:10) passed through the reactor at a total flow rate of approximately 65 cm^3/min (STP). The volume of the reaction zone was maintained at 1 cm^3 such that the residence time varied from 0.29 to 0.22 s for 873 to 1123 K. Gaseous halocarbon products were analysed with an on-line micro GC and an off-line GC/MS after passing through a NaOH scrubber. The amount of mineral acids (HF and HCl) liberated during the reaction was quantified periodically with an off-line ion chromatograph.

3. Results and discussion

Fig. 1 shows the conversion of CCl_2F_2 and CH_4 against the reaction temperature. The conversion of CCl_2F_2 commenced at around 923 K and increased with temperature. In the absence of CH_4, the conversion of CCl_2F_2 was approximately 25% at 1123 K, while CCl_2F_2 conversion increased to 43% in the presence of CH_4 at the same temperature. The conversion of CH_4 was approximately at the same level as that of CCl_2F_2. It is worth mentioning that in the absence of CCl_2F_2, methane remained inactive over the entire range of temperature studied (873–1123 K). Similar results were observed in the gas-phase reaction of methane with halon 1211 ($CBrClF_2$) (Tran et al., 2001).

Fig. 2 shows the selectivity of reaction products and the rate of formation of mineral acids (HF and HCl).

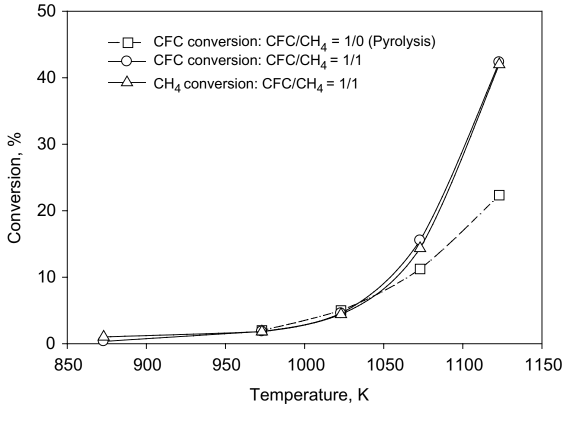

Fig. 1. Gas-phase reaction of CCl_2F_2 with CH_4.

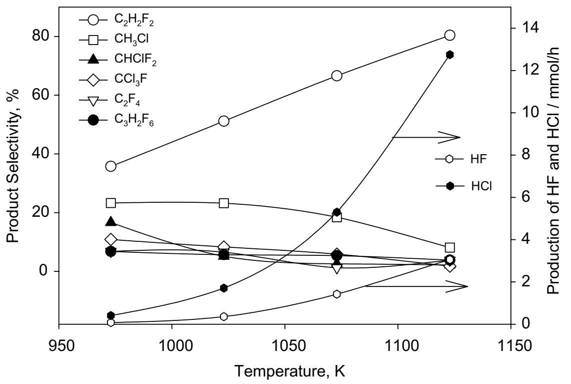

Fig. 2. Product selectivity for the gas-phase reaction of CCl_2F_2 with CH_4. CCl_2F_2:CH_4:N_2 = 1:1:10, total flow rate = 65 cm^3/min (molar feed rate of CCl_2F_2 = 14.50 mmol/h).

The halocarbon products formed during the pyrolysis of CCl_2F_2 (not shown in Fig. 2) were $CClF_3$, CCl_3F and $C_2Cl_2F_2$ at 923 K and selectivity of both $CClF_3$ and $C_2Cl_2F_2$ increased and that of CCl_3F decreased with temperature. In the presence of methane, the major products formed include C_2F_4, CCl_3F, $C_2H_2F_2$, $CHClF_2$, CH_3Cl, and $C_3H_2F_6$. In addition to organic halocarbons, mineral acids (HF and HCl) are also formed during the reaction. With the increase of reaction temperature, production of all other halocarbon species except $C_2H_2F_2$ declined, while the selectivity to $C_2H_2F_2$ increased and reached ≈80% at 1123 K. Although not quantified, trace amount of hydrocarbons such as C_2H_4 and C_2H_6 were detected in the product and at higher temperature carbon deposition inside the reactor was also observed. The ion chromatographic results reveal that in excess of 90% of the fluorine is retained in the hydroflurorcarbon products whereas ≈80% of the chlorine in feed CCl_2F_2 is released as HCl. Although the actual reactions involved in this gas-phase process are not clear at this stage, we suggest the following pathways for the formation of the major compounds (in bold):

$CCl_2F_2 \rightarrow CClF_2^{\cdot} + Cl^{\cdot}$ (initiation step)

$Cl^{\cdot} + CH_4 \rightarrow CH_3^{\cdot} + \mathbf{HCl}$ (methane activation step)

$CClF_2^{\cdot} + CH_3^{\cdot} \rightarrow [CClF_2CH_3] \rightarrow \mathbf{C_2H_2F_2} + \mathbf{HCl}$
(major pathway at elevated temperatures)

Other reactions which also occur include:

$CClF_2^{\cdot} + CH_4 \rightarrow \mathbf{CHClF_2} + CH_3^{\cdot}$

$CH_3^{\cdot} + Cl^{\cdot} \rightarrow \mathbf{CH_3Cl}$

$CClF_2^{\cdot} + CH_3^{\cdot} \rightarrow [CClF_2CH_3] \rightarrow CF_2: + \mathbf{CH_3Cl}$

$2CF_2: \rightarrow \mathbf{C_2F_4}$

In other related studies of the gas-phase reaction of halons (1211 and 1301) with methane, we found that halons are more readily hydrodehalogenated than CFCs, most probably due to the facile cleavage of C–Br bonds leading to the formation of active species which react with methane.

4. Conclusions

Gas-phase reaction of CFC-12 (CCl_2F_2) with methane was carried out in a plug flow reactor over the temperature range of 873–1123 K. The major organic halocarbons formed during the reaction were C_2F_4, $C_2H_2F_2$, $CHClF_2$, CH_3Cl, $C_3H_2F_6$ and CCl_3F. The formation of all products except $C_2H_2F_2$ decreased with temperature, while the selectivity to $C_2H_2F_2$ increased with temperature and reached ≈80% at 1123 K. Under these reaction conditions, methane acts as hydrogen and carbon source, resulting in the formation of an unsaturated C_2 hydrofluorocarbon from two C_1 precursors.

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