Selective production of difluoromethyl methyl ether from chlorodifluoromethane using alkali metal carbonates

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Abstract

CHF_2OCH_3 (HFE-152a), an important starting material for synthesizing various C_2 hydrofluoroethers and a prospective alternative to CH_3CF_2Cl (HCFC-142b), has been found to be effectively produced from the reaction of CHF_2Cl (HCFC-22) with alkali metal carbonates in methanol. Some alkali metal carbonates induce selective production of CHF_2OCH_3 with a small amount of $CH(OCH_3)_3$, a major side product. Activities of alkali metal carbonates for producing CHF_2OCH_3 are in the order of $K_2CO_3 > Na_2CO_3 > Li_2CO_3$, suggesting that the solubility and ionization tendency of alkali metal carbonate in methanol play important roles in the reaction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrofluoroether; Difluoromethyl methyl ether; Chlorodifluoromethane; Alkali metal carbonate

1. Introduction

Hydrofluoroethers (HFEs) are prospective candidates for next generation alternatives of CFCs (chlorofluorocarbons) because HFEs do not produce ozone depletion and these have very low impact on global warming [1–3]. Several theoretical and experimental reports proposed that some HFEs such as CHF_2OCHF_2, CF_3OCH_3, $CF_3CF_2OCH_3$, and $CF_3CF_2CF_2OCH_3$ have favorable physical and chemical properties as do CFCs, HCFCs (hydrochlorofluorocarbons) and HFCs (hydrofluorocarbons) [4–6].

Difluoromethyl methyl ether (CHF_2OCH_3, HFE-152a) is considered a useful starting material for synthesizing various higher-fluorinated dimethyl ethers [7] and a possible alternative refrigerant to CH_3CF_2Cl (HCFC-142b) [8]. It has been reported that CHF_2OCH_3 can be synthesized by the reaction of CHF_2Cl and CH_3ONa in which, however, a large amount of trimethylorthoformate, $CH(OCH_3)_3$, is produced as a side product which is, however, economically valueless [8–10]. Formation of $CH(OCH_3)_3$ requires competitive consumption of the reactants, CHF_2Cl and CH_3ONa. In other words, the formation of $CH(OCH_3)_3$ inevitably reduces the yield of CHF_2OCH_3.

In this paper, we report a method to suppress effectively the formation of the side product, $CH(OCH_3)_3$ by employing alkali metal carbonates instead of using CH_3ONa as a base.

2. Experimental

CHF_2Cl (purity $> 98\%$) was supplied from Ulsan Chemical Co. Methyl alcohol, sodium methoxide, alkali metal carbonates and other reagents used were purchased from Aldrich Chemical Co. All chemicals were used without further purification.

Reactions were conducted in a 100 ml stainless steel high-pressure reactor with a magnetic drive stirrer and an electrical heating jacket. Base (50 mmol), methanol (25 ml) and ethylene glycol dimethyl ether (1 g, internal standard) were charged into the reactor. After the mixture was cooled to $5°C$ with a vigorous stirring, CHF_2Cl (200 mmol) was fed to the reactor through a sampling valve. The reactor was then heated to a reaction temperature and the reactants were stirred for 2 h. After cooling the reaction mixture to $-78°C$, a sample of the liquid phase was analyzed using GC (HP 6890, HP-1, 50 m × 0.2 mm × 10 um). The formation of CHF_2OCH_3 was confirmed by GC-Mass (HP 6890-5973 MSD) and ^{19}F NMR (564.54 MHz, Varian INOVA-600) [11].

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Conversion of the base was determined by acidimetric titration of unreacted base left in the solution using 0.1N aqueous HCl with an indicator. Yields of CHF_2OCH_3 and $CH(OCH_3)_3$ were evaluated from gas chromatographic results of the liquid sample containing internal standard and the quantitative analysis of alkali metal chloride and alkali metal fluoride. Yields of CHF_2OCH_3 and $CH(OCH_3)_3$ were defined as follows:

Percent yield of CHF_2OCH_3

$$= \frac{100 \times [CHF_2OCH_{3\,produced}, mmol]}{[base_{introduced}, mmol]}$$

Percent yield of $CH(OCH_3)_3$

$$= \frac{100 \times [CH(OCH_3)_{3\,produced}, mmol]}{[base_{introduced}, mmol]}$$
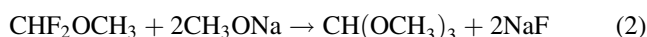
3. Results and discussion

3.1. Formation of CHF_2OCH_3 and $CH(OCH_3)_3$

In order to find out whether the variation of reaction parameters can affect the formation of the side-product, the reaction of CHF_2Cl with CH_3ONa was investigated at various temperatures and CH_3ONa concentrations. As shown in Table 1, the yields of CHF_2OCH_3 and $CH(OCH_3)_3$ increased along with the temperature, but the product ratio of $CHF_2OCH_3/CH(OCH_3)_3$ remained almost constant in the range 3.6–3.7. On the other hand, the yield of CHF_2OCH_3 decreased as the concentration of CH_3ONa increased. Even though the formation of $CH(OCH_3)_3$ was suppressed by lowering the concentration of CH_3ONa, the amount of $CH(OCH_3)_3$ was still high with respect to the formation of CHF_2OCH_3. Furthermore, the net production of the target compound, CHF_2OCH_3 also decreased with decrease in the

concentration of CH_3ONa. These results clearly indicate that the formation of $CH(OCH_3)_3$ cannot be suppressed by changing either the reaction temperature or the concentration of CH_3ONa.

Two reaction mechanisms have been proposed for the formation of CHF_2OCH_3 and $CH(OCH_3)_3$. Satoh et al. proposed a reaction mechanism, where CHF_2OCH_3 and $CH(OCH_3)_3$ are produced consecutively as in Eqs. (1) and (2) [8].

$$CHF_2Cl + CH_3ONa \rightarrow CHF_2OCH_3 + NaCl \quad (1)$$

$$CHF_2OCH_3 + 2CH_3ONa \rightarrow CH(OCH_3)_3 + 2NaF \quad (2)$$

They reported that the formation of $CH(OCH_3)_3$ is reduced by removing CHF_2OCH_3 as soon as it forms.

On the other hand, Hine and Porter proposed a different reaction mechanism in which CHF_2OCH_3 and $CH(OCH_3)_3$ were produced from the same difluorocarbene intermediate F_2 formed by the elimination of HCl from CHF_2Cl as shown in the following equations [9].

$$CHF_2Cl + CH_3ONa \rightarrow: CF_2 + CH_3OH + NaCl \quad (3)$$
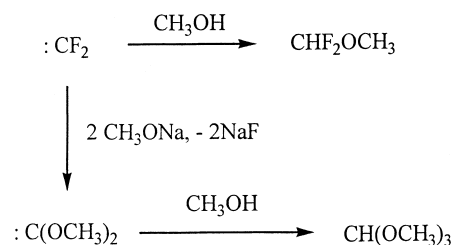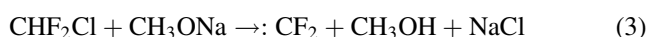
In order to have a better insight into the mechanism for the formation of $CH(OCH_3)_3$, we have conducted a reaction of CHF_2OCH_3 with CH_3ONa. The reaction of CHF_2OCH_3 and CH_3ONa at 25°C for 2 h produced only a trace amount of $CH(OCH_3)_3$, strongly implying that $CH(OCH_3)_3$ is not produced from CHF_2OCH_3.

Table 1

Effects of temperature and CH_3ONa concentration on the production of CHF_2OCH_3 from CHF_2Cl and CH_3ONa[a]

Entry	CH_3ONa (mmol)	Temperature (°C)	Conversion (%)[b]	Yield (%)		Product ratio (A/B)[d]
				A	B	
1	50	0	74.4	39.0	10.8	3.6
2	50	25	86.0	47.0	12.7	3.7
3	50	40	92.6	50.3	13.6	3.7
4	50	60	98.8	54.0	15.0	3.6
5	12.5	25	92.5	59.9	10.7	5.6
6	25	25	93.0	56.7	12.0	4.7
7	100	25	83.7	40.0	14.4	2.8
8[c]	40	25	88.2	50.8	12.4	4.1
9[c]	67	25	85.2	44.9	13.2	3.4

[a] Reaction condition: $CH_3ONa/CHF_2Cl = 1/4$, methanol 25 ml, $CH_3OCH_2CH_2OCH_3$ (internal standard) 1 g, reaction time 2 h.
[b] Conversion of base.
[c] $CHF_2Cl = 200$ mmol.
[d] A: CHF_2OCH_3; B: $CH(OCH_3)_3$.

Table 2
Effect of bases on the production of CHF_2OCH_3 from CHF_2Cl and methanol[a]

Entry	Base[b]	Temperature (°C)	Conversion (%)[c]	Yield (%)		Product ratio (A/B)[d]
				A	B	
1	KOH (15.7)	25	82.4	40.4	12.9	3.1
2	NaOH (15.7)	60	99.5	51.8	15.6	3.3
3	K_2CO_3 (10.3)	60	70.5	64.0	1.7	37.6
4	$KHCO_3$ (6.35)	100	8.4	8.0	–	–
5	$NaHCO_3$ (6.35)	100	3.5	3.2	–	–
6	CH_3CO_2Na (5)	100	1.6	1.5	–	–

[a] Reaction condition: base 50 mmol, CHF_2Cl 200 mmol, methanol 25 ml, $CH_3OCH_2CH_2OCH_3$ (internal standard) 1 g, reaction time 2 h.
[b] The values in parenthesis are pK_a's of conjugate acids [12].
[c] Conversion of base.
[d] A: CHF_2OCH_3; B: $CH(OCH_3)_3$.

3.2. Reactions of chlorodifluoromethane with various bases

In an attempt to find a more efficient base system to replace CH_3ONa, several bases having different basicities were tested for the production of CHF_2OCH_3. According to the carbene mechanism, the side product, $CH(OCH_3)_3$ can be produced only in the presence of methoxide anion. Therefore, if the base to be used has a basicity that is enough to abstract hydrogen from CHF_2Cl but too weak to form CH_3O^- from CH_3OH, then a higher yield of CHF_2OCH_3 and less formation of $CH(OCH_3)_3$ can be achieved.

Table 2 shows that KOH and NaOH exhibit similar behavior to CH_3ONa for the production of CHF_2OCH_3 and $CH(OCH_3)_3$. The formation of large amounts of $CH(OCH_3)_3$ can be ascribed to the methoxide anion (CH_3O^-) formed by the equilibrium reaction between OH^- and CH_3OH.

$$OH^- + CH_3OH \rightleftharpoons H_2O + CH_3O^- \quad K_{eq} \approx 0.50 \quad (6)$$

On the contrary, the reaction of less basic K_2CO_3 with CHF_2Cl gave the highest yield of CHF_2OCH_3 and the lowest formation of $CH(OCH_3)_3$. In the case of much weaker base, $KHCO_3$ or CH_3CO_2Na, only a few percent conversion were obtained at 100°C. These results indicate that basicity is important in enhancing the yield of CHF_2OCH_3 and in preventing the formation of $CH(OCH_3)_3$.

Table 3 shows that the reactivity of alkali metal carbonate for the production of CHF_2OCH_3 is in the order of $K_2CO_3 > Na_2CO_3 > Li_2CO_3$. The same trend is observed with alkali metal bicarbonates: $KHCO_3 > NaHCO_3$ (Table 2). These indicate that, in addition to the basicity, solubility and ionization tendency of alkali metal carbonate in methanol play important roles in determining the yield of CHF_2OCH_3.

The effect of temperature on the reaction of CHF_2Cl with alkali metal carbonate was investigated. Unlike in the case of CH_3ONa (Table 1), the yield of $CH(OCH_3)_3$ decreased with rise in reaction temperature (Table 3). However, the formation of CHF_2OCH_3 increased with the temperature rise, giving higher product ratio of $CHF_2OCH_3/CH(OCH_3)_3$.

Table 3
Effect of alkali metal carbonates on the production of CHF_2OCH_3[a]

Entry	Base	Temperature (°C)	Conversion (%)[b]	Yield (%)		Product ratio (A/B)[d]
				A	B	
1	Li_2CO_3	100	12.5	12.1	–	–
2	Na_2CO_3	60	5.9	5.7	–	–
3	Na_2CO_3	100	40.4	41.2	–	–
4	K_2CO_3	25	42.5	30.6	3.6	8.5
5	K_2CO_3	60	71.2	64.0	2.1	30.5
6	K_2CO_3	100	78.6	74.8	1.2	62.3
7	K_2CO_3[c]	100	87.7	84.2	0.8	105.3

[a] Reaction condition: alkali metal carbonate 50 mmol, CHF_2Cl 200 mmol, methanol 25 ml, $CH_3OCH_2CH_2OCH_3$ (internal standard) 1 g, reaction time 2 h.
[b] Conversion of base.
[c] K_2CO_3: 25 mmol.
[d] A: CHF_2OCH_3; B: $CH(OCH_3)_3$.

4. Conclusion

CHF_2OCH_3 (HFE-152a) can be produced by the reaction of CHF_2Cl (HCFC-22) and methanol with base. Experimental studies revealed that the formation of the valueless side-product $CH(OCH_3)_3$ was inevitable in the reaction of CHF_2Cl with CH_3ONa. Alkali metal carbonates showed remarkable activities and selectivities for CHF_2OCH_3 by suppressing the formation of $CH(OCH_3)_3$. Activities of alkali metal carbonates for producing CHF_2OCH_3 were in the order $K_2CO_3 > Na_2CO_3 > Li_2CO_3$, suggesting that solubility and ionization tendency of alkali metal carbonate in methanol play important roles in determining the yield of CHF_2OCH_3.

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