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# Fluoride-catalyzed hydroalkoxylation of hexafluoropropene with 2,2,2-trifluoroethanol

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**Abstract**

Trifluoroethoxylation of hexafluoropropene with 2,2,2-trifluoroethanol (TFE) were conducted using an alkali metal fluoride catalyst to produce $CF_3CHFCF_2OCH_2CF_3$. KF exhibited the highest yield and selectivity of $CF_3CHFCF_2OCH_2CF_3$, whereas LiF and NaF were inactive for the trifluoroethoxylation reaction. The same reaction also proceeded well in the presence of RbF or CsF, but yielded large amounts of olefinic and high molecular weight side products, implying that the size of alkali metal cation or the degree of MF dissociation plays an important role in determining the activity and the product composition. FT-IR and NMR experiments revealed that CsF interacts with TFE more strongly than KF through a hydrogen bonding. The experimental and spectroscopic results suggest that the degree of MF dissociation should be in the medium range for the selective production of $CF_3CHFCF_2OCH_2CF_3$ in high yield and selectivity.

*Keywords:* Hydrofluoroethers; CFC alternatives; Hydroalkoxylation; Alkali metal fluoride

## 1. Introduction

In spite of broad applications in various areas including chemical, mechanical, and semiconductor industries, chlorofluorocarbons (CFCs) and chlorofluorohydrocarbons (HCFCs) are doomed to be phased out due to their high ozone deleting potential (ODP) and high global warming potential (GWP) [1–4]. As the second generation of CFC alternatives, hydrofluorocarbons (HFCs) were newly introduced, but soon turned out to possess high GWP [5,6]. For this reason, a number of silicone, nitrogen, and oxygen-containing molecules with zero ODP and low GWP were proposed as the third generation CFC alternatives [7–9]. Based on the theoretical and experimental results reported so far, oxygen atom-containing hydrofluoroethers (HFEs) seem to possess most favorable physical and chemical properties comparable to CFCs, such as low surface tension, nonflammability, and excellent solvating ability [10–12].

Various HFEs were prepared by the alkylation of acyl halides using a sulfonic acid ester as an alkylating agent in the presence of anhydrous KF [13,14]. However, the alkylation method suffered from the relatively high cost of raw material and the difficulty in handling the toxic acyl fluorides. Recently, Matsukawa et al. [15] reported that the hydroalkoxylation of fluoroolefins in the presence of a $Pd^0$ complex, $[Pd(PPh_3)_4]$ was highly active for producing HFEs in high yield and selectivity. This is a great finding because the formation of commonly observed olefinic side products can be completely suppressed, but the use of an expensive Pd complex seems to be a major obstacle in the commercial application of this process [14]. As a more economical process, alkali metal fluoride-catalyzed hydroalkoxylation, discovered by Dow Chemical Company, is particularly attractive because the process required a small amount of inexpensive catalyst [16]. However, detailed investigation on the role of alkali metal fluoride (MF) was never been attempted.

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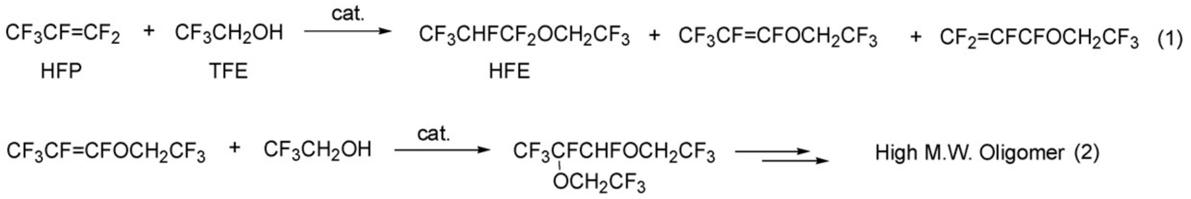


$$\underset{\text{HFP}}{CF_3CF{=}CF_2} + \underset{\text{TFE}}{CF_3CH_2OH} \xrightarrow{\text{cat.}} \underset{\text{HFE}}{CF_3CHFCF_2OCH_2CF_3} + CF_3CF{=}CFOCH_2CF_3 + CF_2{=}CFCFOCH_2CF_3 \quad (1)$$

$$CF_3CF{=}CFOCH_2CF_3 + CF_3CH_2OH \xrightarrow{\text{cat.}} \underset{\displaystyle OCH_2CF_3}{CF_3CFCHFOCH_2CF_3} \longrightarrow \text{High M.W. Oligomer} \quad (2)$$

Scheme 1. Reaction scheme of hexafluoropropene (HFP) with 2,2,2-trifluoroethanol (TFE).

In this paper, we report our study on the role of metal fluoride for the hydroalkoxylation of hexafluoropropylene (HFP) with 2,2,2-trifluoroethanol (TFE) by means of FT-IR and NMR spectroscopic methods.

## 2. Results and discussion

The hydroalkoxylation of HFP with TFE was conducted in the presence of MF. As shown in Table 1, LiF and NaF were inactive for the hydroalkoxylation of HFP. On the contrary, the use of RbF and CsF resulted in almost quantitative conversion of TFE. Among MF tested, KF exhibited the highest selectivity to the desired product, $CF_3CHFCF_2OCH_2CF_3$, but RbF and CsF produced large amounts of side products. GC–mass and $^1H$ NMR analysis showed that the side products contained three olefinic HFEs (*cis*/*trans* $CF_3CF{=}CFOCH_2CF_3$ and $CF_2{=}CFCFOCH_2CF_3$) and higher molecular weight HFEs, which are believed to be produced by further hydroalkoxylation of olefinic HFEs with HFP as depicted in Scheme 1.

In general, the solubility and dissociation of alkali metal fluoride in polar organic solvents increase with increasing size of the cation, and therefore, the higher activity of MF with a larger size of cation strongly suggests that the hydroalkoxylation proceeds in a homogeneous way. The formation of the side product seems to be largely affected by the degree of dissociation (or the nucleophilicity) of MF. This is supported by an experiment using 18-crown-6-ether, which is known to completely dissociate KF into $K^+$ and $F^-$ [17]. When KF was used together with 18-crown-6-ether, quantitative conversion was obtained, but with the formation of large quantities of side products.

To have a better understanding of the role of MF, the interaction of MF with TFE was investigated in $CH_3CN$ by means of a FT-IR spectroscopy. As shown in Fig. 1, the peak at 3452 $cm^{-1}$ corresponds to the O–H stretching frequency of TFE. Since KF is an active catalyst for the hydroalkoxylation of TFE, KF was expected to interact with TFE through the hydroxyl group. Contrary to our expectation, the O–H peak remained unchanged when KF was added to a solution of TFE in $CH_3CN$, possibly due to the extremely low solubility of KF in $CH_3CN$. However, the O–H peak shifted to a lower frequency from 3452 to 3447 $cm^{-1}$ upon interaction with CsF, suggesting a strong interaction between CsF and HFE through a hydrogen bond between hydroxyl group and $F^-$ [19] (Fig. 1).

The interaction of TFE with CsF can be more clearly seen in $^1H$ NMR spectra in Fig. 2. The peak corresponding to the hydroxyl group of TFE shifted slightly downfield by the interaction with KF from 3.89 to 4.51 ppm at the molar ratio of TFE/KF = 5. The peak shift was much more pronounced when interacted with CsF. The degree of peak shift increased with increasing amount of CsF.

Besides the interaction with TFE, MF is also known to interact with HFP to form metal alkoxide and $CF_3CHFCF_3$ as shown in Eq. (3). Thus formed metal akoxide is proposed as an

Table 1
Effect of MF on the hydroalkoxylation of TFE and HFP[a]

| Entry | MF | Conversion of TFE (%) | Yield (%)[b] | Selectivity (%)[b] |
|---|---|---|---|---|
| 1 | LiF | – | – | – |
| 2 | NaF | Trace | Trace | Trace |
| 3 | KF | 85.3 | 83.2 | 97.2 |
| 4 | KF[c] | 96 | 79.4 | 79.7 |
| 5 | RbF | 93 | 75.8 | 81.5 |
| 6 | CsF | 100 | 71.1 | 71.1 |

[a] Reaction conditions: $CF_3CH_2OH$ (TFE, 50 mmol), $CF_3CF = CF_2$ (HFP, 100 mmol), solvent ($CH_3CN$, 30 mL), MF (0.1 mmol), r.t., 1 h.

[b] Yield and selectivity of $CF_3CHFCF_2OCH_2CF_3$.

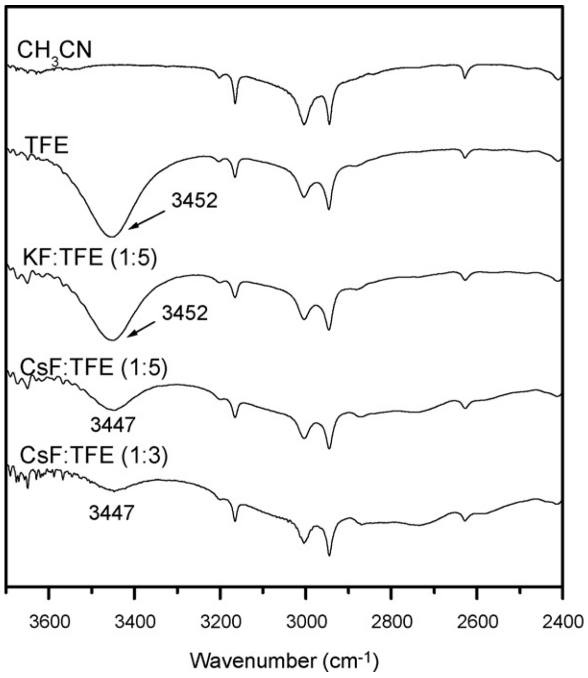


Fig. 1. FT-IR spectra showing the interaction of metal fluoride with $CF_3CH_2OH$ (TFE).

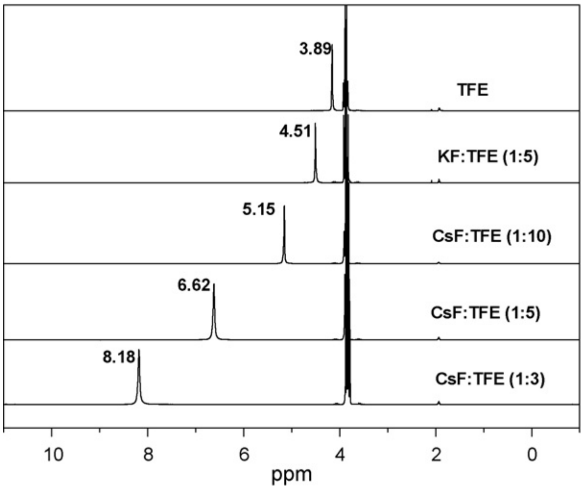


Fig. 2. NMR spectra showing the interaction of MF with $CF_3CH_2OH$ (TFE).

active species for the hydroalkoxylation [15,18].

$$CF_3CF = CF_2 \xrightarrow{MF} (CF_3)_2CF^-M^+ \xrightarrow{CF_3CH_2OH} CF_3CHFCF_3 + CF_3CH_2O^-M^+ \qquad (3)$$

In fact, the formation of $CF_3CHFCF_3$ was also observed in our experiment, implying that the interaction between MF and HFP might play an important role in the catalysis. The concentration of $CF_3CHFCF_3$ increased with increasing size of the cation of MF.

The hydroalkoxylation of HFP was significantly affected by the polarity of solvent employed. As listed in Table 2, the reaction in a less polar solvent such as toluene and ethyl acetate gave poor TFE conversion, whereas the reaction in a polar solvent like acetone, DMF, DMSO, and $CH_3CN$ showed much higher conversion of TFE. Interestingly, the amount of side products were higher in carbonyl or sulfoxide-containing solvents such as acetone, DMF, and DMSO, implying that the dissociation of KF can be facilitated through the interaction with the functional groups, C=O or S=O.

Table 2
Effect of solvent for the hydroalkoxylation of TFE with HFP[a]

| Entry | Solvent | Conversion of TFE (%) | Yield (%)[b] | Selectivity (%)[b] |
|---|---|---|---|---|
| 1 | Toluene | 4.5 | 2.3 | – |
| 2 | Ethyl acetate | 5.7 | 3.8 | 1.9 |
| 3 | Acetone | 91.4 | 74.1 | 81.0 |
| 4 | $CH_3CN$ | 85.3 | 83.2 | 97.2 |
| 5 | DMF | 100 | 83.6 | 83.6 |
| 6 | DMSO | 100 | 71.5 | 71.5 |

[a] Reaction conditions: $CF_3CH_2OH$ (TFE, 50 mmol), $CF_3CF=CF_2$ (HFP, 100 mmol), solvent (30 mL), catalyst (0.1 mmol), r.t., 1 h.
[b] Yield and selectivity of $CF_3CHFCF_2OCH_2CF_3$.

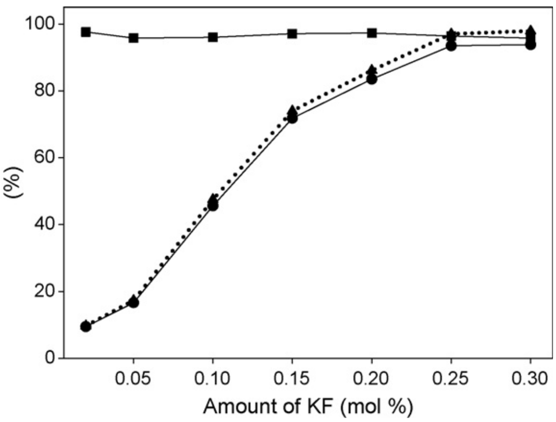
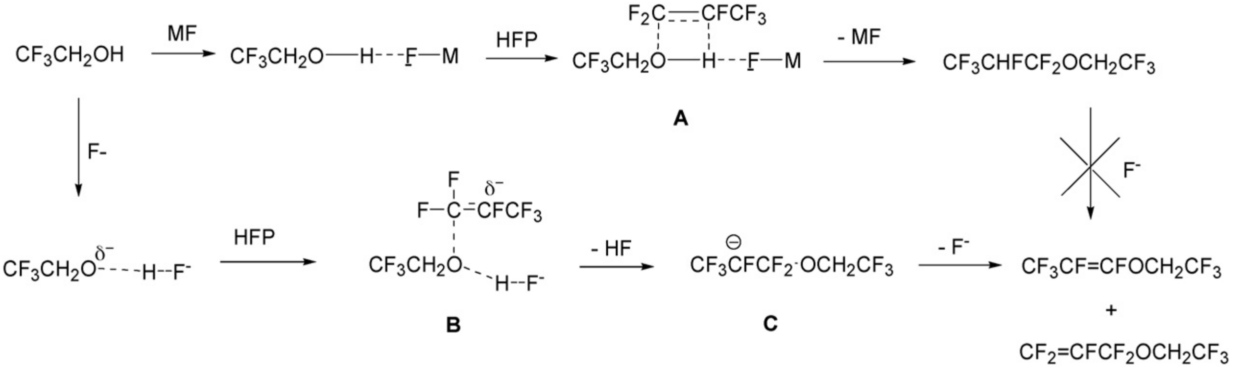


Fig. 3. Effect of the amount of KF for the hydroalkoxylation of 2,2,2-trifluoroethanol (TFE) to hexafluoropropene (HFP). Reaction conditions: $CF_3CH_2OH$ (TFE, 50 mmol), $CF_3CF=CF_2$ (HFP, 100 mmol), solvent (30 mL), r.t., 1 h.

To optimize the amount of the catalyst, the concentration of KF was varied from 0.02 to 0.3 mol.% with respect to the amount of TFE. As shown in Fig. 3, the conversion of TFE and yield of $CF_3CHFCF_2OCH_2CF_3$ increased continuously with the increase the amount of KF up to 0.25 mol.% KF and then remained constant on further increase of the catalyst concentration. Interestingly, the selectivity of $CF_3CHFCF_2OCH_2CF_3$ was maintained at approximately 96%, regardless of the catalyst concentration.

On the basis of experimental and spectroscopic results, two mechanistic pathways were proposed for the hydroalkoxylation of HFP with TFE. The first mechanism is based on the activation of TFE by MF as depicted in Scheme 2. TFE is likely to be activated by either MF or $F^-$. The MF-activated TFE would then react with HFP to form a transient intermediate A,



Scheme 2. Proposed mechanism for the production of saturated and unsaturated ether.

which in turn transforms into $CF_3CHFCF_2OCH_2CF_3$ with the regeneration of MF. Since the olefinic compounds were not produced from the reaction of $CF_3CHFCF_2OCH_2CF_3$ with MF in $CH_3CN$ at 80 °C in the absence of TFE and HFP, the abstraction of H atom from $CF_3CHFCF_2OCH_2CF_3$ by MF is unlikely. As an alternative, the activation of TFE by free $F^-$ can be considered as the most plausible route to the formation of olefinic side products. $F^-$-activated TFE will then interact with HFP to form an intermediate species, B. The abstraction of HF from B will generate the anionic species, C. The subsequent elimination of $F^-$ from C would produce olefinic compounds.

Alternatively, $CF_3CHFCF_2OCH_2CF_3$ can be produced through a carbanionic mechanism involving the formation of $(CF_3)_2CF^-M^+$, as described in the previous papers by Sekiya et al. [15,18].

Even though the exact mechanism cannot be precisely defined, each mechanism seems to be functioning in the formation of $CF_3CHFCF_2OCH_2CF_3$. It is also obvious that MF with higher dissociation constant produces larger amounts of olefinic side products.

## 3. Conclusions

Various alkali metal fluorides were tested as catalysts for the hydroalkoxylation of HFP with TFE. The catalytic activity of MF and the formation of side products were found to increase with increasing size of $M^+$. Spectroscopic and experimental results showed that MF interacts with TFE through a hydrogen bond. MF with larger sized $M^+$ was found to interact more strongly with the OH group of TFE and consequently produces larger amounts of side products. Among the fluorides tested, KF with a medium-sized cation exhibited the highest yield and selectivity of $CF_3CHFCF_2OCH_2CF_3$. The formation of $CF_3CHFCF_3$ was also observed, implying that the hydroalkoxylation reaction could proceed through a carbanionic mechanism.

In summary, MF (M = K, Rb, Cs) are highly effective for the hydroalkoxylation of HFP, but some improvement in the catalytic system is strongly demanded to minimize the side product formation.

## 4. Experimental

### 4.1. Materials

TFE and solvents were purchased from Aldrich Chemical Co. and stored over molecular sieve 4A. Anhydrous alkali metal fluorides were obtained from Aldrich Chemical Co. and stored in a glove box. HFP was obtained from Ulsan Chemical Co. and used as received.

### 4.2. Hydroalkoxylation of HFP

In a 100 mL stainless-steel reactor, TFE (50 mmol, 5 g), a catalyst, dibutyl ether as an internal standard and a solvent were placed. After purging the reactor with Ar (99.9%), HFP (100 mmol, 15 g) was introduced and stirred for 1 h at room temperature. After completion of the reaction, the product mixture was analyzed using a Gas chromatograph equipped with a FID detector and HP-FFAP column (OD = 0.32 mm, $L$ = 30 m). The identification of the product mixtures was conducted using an Agilent 6890-5973 MSD GC–mass spectrometer and $^1H$ NMR spectrometer (Varian 300 Unity plus).

### 4.3. FT-IR and $^1H$ NMR studies

Samples for the IR measurements were prepared as follows: MF was dissolved in TFE, and then 0.5 g of the resulting solution was mixed with 3 mL of anhydrous $CH_3CN$. In the case of $^1H$ NMR experiment, 0.05 g of MF–TFE mixture was dissolved in 1 mL of $CD_3CN$. FT-IR measurements were performed on a PerkinElmer Spectrophotometer GX 1 using a PerkinElmer Horizontal Attenuated Total Reflectance Accessory. $^1H$ NMR spectra were recorded on a Varian 300 Unity plus.

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