

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 $\text{CF}_3\text{CHF}_2\text{OCH}_2\text{CF}_3$. KF exhibited the highest yield and selectivity of $\text{CF}_3\text{CHF}_2\text{OCH}_2\text{CF}_3$, 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 $\text{CF}_3\text{CHF}_2\text{OCH}_2\text{CF}_3$ in high yield and selectivity.

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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

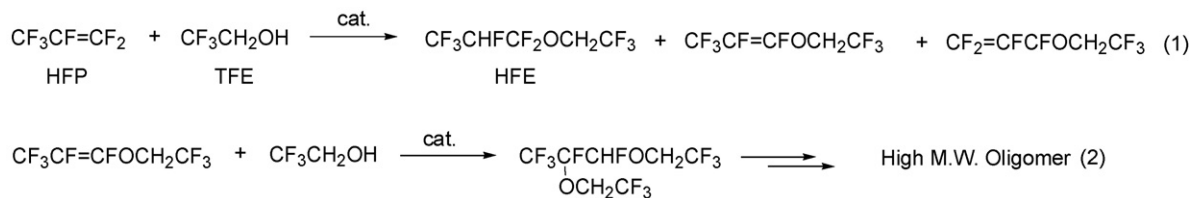
physical and chemical properties comparable to CFCs, such as low surface tension, nonflammability, and excellent solvating ability [10–12].

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, $[\text{Pd}(\text{PPh}_3)_4]$ 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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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, $\text{CF}_3\text{CHF}\text{CF}_2\text{OCH}_2\text{CF}_3$, 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* $\text{CF}_3\text{CF}=\text{CFOCH}_2\text{CF}_3$ and $\text{CF}_2=\text{CFCFOCH}_2\text{CF}_3$) 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 $\text{CF}_3\text{CHF}\text{CF}_3$ as shown in Eq. (3). Thus formed metal alkoxide 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: $\text{CF}_3\text{CH}_2\text{OH}$ (TFE, 50 mmol), $\text{CF}_3\text{CF}=\text{CF}_2$ (HFP, 100 mmol), solvent (CH_3CN , 30 mL), MF (0.1 mmol), r.t., 1 h.

^b Yield and selectivity of $\text{CF}_3\text{CHF}\text{CF}_2\text{OCH}_2\text{CF}_3$.

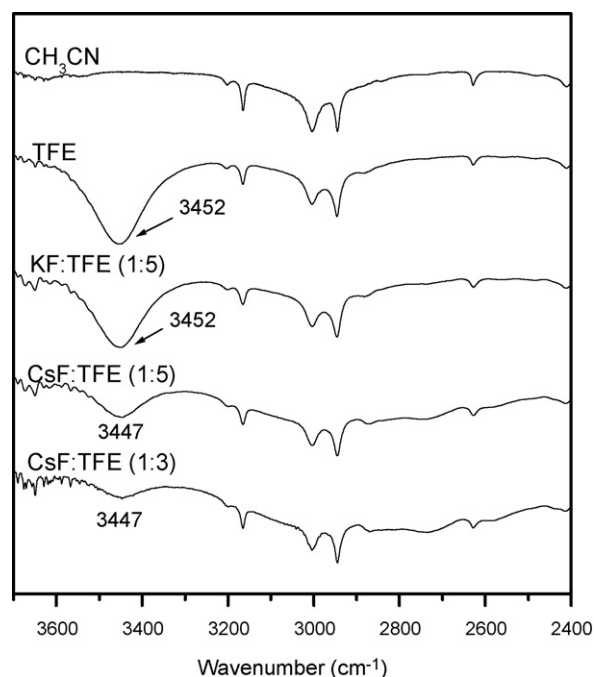


Fig. 1. FT-IR spectra showing the interaction of metal fluoride with $\text{CF}_3\text{CH}_2\text{OH}$ (TFE).

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