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Research Note

Ionic liquid-assisted hydroalkoxylation of hexafluoropropene with 2,2,2-trifluoroethanol: A mechanistic consideration

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ABSTRACT

$CF_3CHFCF_2OCH_2CF_3$ (1,1,2,3,3,3-hexafluoropropyl-2′,2′,2′-trifluoroethylether), one of the third generation CFC alternatives, was obtained in high yield and selectivity from the hydroalkoxylation reaction of hexafluoropropene with 2,2,2-trifluoroethanol conducted in the presence of a catalytic system consisting of a potassium salt and an ionic liquid, 1-butyl-3-methylimidazolium chloride ([BMIm]Cl). The formation of commonly observed olefinic side products in the hydroalkoxylation catalyzed by potassium salts was greatly reduced by the co-presence of [BMIm]Cl. Theoretical calculations and mechanistic studies suggested that potassium ion is largely responsible for the formation of olefinic side products.

1. Introduction

The development of alternatives to chlorofluorocarbons (CFCs) has received great attention due to the adverse environmental impacts of CFCs on the stratospheric ozone layer and global warming [1,2]. Among the CFC alternatives so far developed, hydrofluoroethers (HFEs) have been considered as the most environmentally friendly alternatives for their zero ozone depleting potential and low global warming potential as well as for their excellent performance similar to CFCs [3–6].

A number of methods to synthesize HFEs have been reported including the fluorination of dialkyl ether with F_2 [7,8] or metal fluoride [9] and the alkylation of acyl halides alkylation of acyl halides using dialkylsulfate in the presence of KF [10,11]. However, these methods suffer from either the low product selectivity or the difficulty in handling the toxic and reactive raw materials. HFEs with a structure of R_FCHFCF_2OR' ($R_F = F$ or perfluorinated alkyl group) can be conveniently synthesized from the hydroalkoxylation reaction of fluorinated olefin with an alcohol in the presence of a strong base [12–15], but producing large amounts of olefinic by-products that are difficult to remove from the saturated HFEs. Recently, Matsukawa et al. discovered an elegant process to completely suppress the olefinic side products by employing a Pd^0 complex as the catalyst for the hydroalkoxylation of fluoroolefins [16], but the use of an expensive novel metal complex would be a major obstacle in the commercial application of this process.

Herein, we report that a catalytic system consisting of and K_3PO_4 and an ionic liquid, 3-butyl-1-methylimidazolium chloride ([BMIm]Cl) is highly effective for drastically reducing the formation of unsaturated hydrofluoroethers in the hydroalkoxylation reaction of hexafluoropropene (HFP, **1**) with 2,2,2-trifluoroethanol (TFE, **2**) while producing $CF_3CHFCF_2OCH_2CF_3$ (**3**) in high yield and selectivity. The mechanistic pathways to the formation of major and side products were also discussed on the basis of theoretical calculations.

2. Experimental

2.1. Chemicals

KH_2PO_4, K_2HPO_4, K_3PO_4, *t*-BuOK, 1-methylimidazole, *n*-butylchloride, and *N*,*N*-dimethylacetamide (DMAc) were purchased from Aldrich Chemical Co. and used as received. TFE was obtained from TCI Co. and used without further purification. HFP was purchased from Ulsan Chemical Co. [BMIm]Cl was prepared by modifying literature procedures [17]. In a 100 mL high pressure reactor, 1-methylimidazole (8.2 g, 0.1 mol) was reacted with *n*-butylchloride (13.9 g, 0.15 mol) at 100 °C for 10 h. After the completion of the reaction, the excess *n*-butylchloride was evaporated and the product mixture was washed with diethyl ether 3 times. The crude product was recrystallized in acetonitrile/ethyl acetate after washing with diethyl ether 3 times (yield: 94.1%).

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Table 1
Activities of various catalysts for the hydroalkoxylation of HFP.[a]

Entry	Catalyst	TFE conversion (%)	Yield (%)		
			3	**4–6**	**7–8**
1	KH_2PO_4	1.3	1.2	0.1	–
2	K_2HPO_4	71.7	60.9	10.5	0.3
3	K_3PO_4	77.8	69.8	8.0	–
4	$[BMIm]BF_4$	0.6	0.5	0.1	–
5	$[BMIm]PF_6$	0.7	0.6	0.1	
6	[BMIm]Cl	1.0	0.8	0.1	0.1
7	[BMIm]Cl	3.3	2.9	0.3	0.1
8	*t*-BuOK	99.7	90.8	8.9	–
9	KCl	0.2	0.2	–	–

[a] Molar ratio of TFE/catalyst = 100, solvent = DMAc (10 mL), temperature = 25 °C, reaction time = 1 h.

2.2. *Hydroalkoxylation of HFP*

All the reactions were conducted in a 100 mL stainless-steel autoclave reactor equipped with a magnet bar, a thermocouple, and a pressure gauge. The reactor was charged with an appropriate catalyst and TFE and reacted under a pressure of HFP. After the completion of the reaction, the product mixture was analyzed using a Hewlett Packard 6890 gas chromatograph equipped with a flame ionized detector and a HP-FFAP capillary column (30 m × 0.32 mm × 0.25 μm) and a Hewlett Packard 6890-5973 MSD GC-mass spectrometer equipped with a HP-FFAP capillary column (30 m × 0.32 mm × 0.25 μm).

3. Results and discussion

The hydroalkoxylation reaction of HFP with TFE was investigated in the presence of a potassium phosphate in DMAc for 1 h at an ambient temperature and at the molar ratio of TFE/phosphate = 100. As listed in Table 1, KH_2PO_4 was almost inactive for the hydroalkoxylation, whereas K_2HPO_4 and K_3PO_4 exhibited moderate activities, producing **3** in yields of 60.9 and 69.8%, respectively. In addition to **3**, large amounts of olefinic compounds (*cis*-$CF_3CF{=}CFOCH_2CF_3$ (**4**), *trans*-$CF_3CF{=}CFOCH_2CF_3$ (**5**), and $CF_2{=}CFCF_2OCH_2CF_3$ (**6**)) were also co-produced as side products, which are hard to separate from **3** due to their close boiling points. The formation of side products was higher in the presence of K_2HPO_4.

Surprisingly, the formation of olefinic side products, **4**–**6** were greatly reduced when K_2HPO_4 or K_3PO_4 was used along with [BMIm]Cl. For instance, the combined use of K_3PO_4 and [BMIm]Cl ($[BMIm]Cl/K_3PO_4 = 3$) decreased the yields of **4**–**6** down to 0.2%, while increasing the yield of **3** to 97.9%. This is a significant advance because such small amounts of olefinic compounds in **3** could be easily removed by using an adsorbent like molecular sieves.

From the above experimental result, it is likely that active species are newly generated *in situ* from the reaction of K_3PO_4 with [BMIm]Cl as shown in Eqs. (1)–(3).

$$K_3PO_4 + [BMIm]Cl \rightarrow [BMIm][K_2PO_4] + KCl, \tag{1}$$

$$K_3PO_4 + 2[BMIm]Cl \rightarrow [BMIm]_2[KPO_4] + 2KCl, \tag{2}$$

$$K_3PO_4 + 3[BMIm]Cl \rightarrow [BMIm]_3[PO_4] + 3KCl. \tag{3}$$

In this context, the reduced formation of **4**–**6** by the copresence of [BMIm]Cl can be ascribed to the transformation of active K_3PO_4 into presumably inactive KCl, which is hardly dissociable in DMAc. In fact, as listed in Table 1, KCl was completely inactive for the hydroalkoxylation (entry 9). It is therefore assumed that K^+ is largely responsible for the formation of olefinic side products as long as K^+ participates in the reaction.

Table 2
Effect of added [BMIm]Cl on the hydroalkoxylation of HFP catalyzed by a potassium salt.[a]

Entry	Catalyst	Molar ratio ([BMIm]Cl/ K salt)	TFE conversion (%)	Yield (%)		
				3	**4–6**	**7–8**
1	K_3PO_4-[BMIm]Cl	2	87.4	84.4	2.9	0.1
2	K_3PO_4-[BMIm]Cl	3	100	97.9	0.2	1.9
3	K_3PO_4-[BMIm]Cl	4	100	98.4	0.3	1.3
4	K_3PO_4-[BMIm]Cl	6	100	98.6	0.3	1.1
5	K_2HPO_4-[BMIm]Cl	1	93.1	86.0	4.8	2.3
6	K_2HPO_4-[BMIm]Cl	2	100	96.0	2.1	1.9
7	*t*-BuOK-[BMIm]Cl	3	100	97.8	0.2	2.0
8[b]	*t*-BuOK-[BMIm]Cl	3	99.3	97.5	0.3	1.5

[a] Molar ratio of TFE/catalyst = 100, solvent = DMAc (10 mL), temperature = 25 °C, reaction time = 1 h.

[b] The reaction was carried out with the solution obtained from the reaction of *t*-BuOK and [BMIm]Cl in DMAc after the filtration of KCl.

To support our postulate that the K^+ is playing a major role in the production of **4**–**6**, the hydroalkoxylation was carried out in the presence of potassium *tert*-butoxide (*t*-BuOK) with or without [BMIm]Cl. The strong basicity and high solubility of *t*-BuOK in DMAc is expected to facilitate its reaction with [BMIm]Cl to produce [BMIm][*t*-BuO] and KCl. As shown in Tables 1 and 2, *t*-BuOK resulted in almost quantitative conversion of TFE irrespective of the presence of [BMIm]Cl, but the yield of **4**–**6** was greatly reduced to about 40 times from 9.3 to 0.2% when [BMIm]Cl was co-present. This is a clear indication that K^+ is responsible for the formation of **4**–**6** because K^+ in *t*-BuOK can be easily transformed into inactive and hardly dissociable KCl upon interaction with [BMIm]Cl. In fact, the interaction of *t*-BuOK with [BMIm]Cl in DMAc produced white precipitates, which was identified as KCl by elemental analysis and FT-IR spectroscopy. Even though the characterization of the remaining imidazolium species after the filtration of KCl was not successful possibly due to the decomposition during the isolation, the species is believed to be [BMIm][*t*-BuO]. As expected, the DMAc solution containing the imidazolium species exhibited similar activity to *t*-BuOK-[BMIm]Cl.

As can be seen in Table 2, the yield of **3** increased slowly with increasing molar ratio of $[BMIm]Cl/K_3PO_4$, whereas the combined yields of **4–6** was not varied much with the molar ratio of $[BMIm]Cl/K_3PO_4$ in the range 3–6. However, the formation of doubly alkoxylated side products, $CF_3CHFCF(OCH_2CF_3)_2$ (**7**) and $CHF(CF_2OCH_2CF_3)_2$ (**8**), was more pronounced at the molar ratios of $[BMIm]Cl/K_3PO_4$ above 2. The reason is not clear at the moment, but the imidazolium salts seem to be more effective for the further hydroalkoxylations of **4**–**6** than potassium phosphate.

To have a better insight into the mechanism for the formations of **3** and side products, theoretical calculations were conducted with K_3PO_4 as the catalyst at the B3LYP (6-31+G† for H, C, O and F, and LanL2DZ with ECP for P and K) level of the theory using Gaussian 03 program. It is assumed that $CF_3CH_2O^-$ is generated *in situ* from the interaction of TFE with strongly basic K_3PO_4 in an aprotic polar solvent like DMAc (see Eq. (4)).

$$CF_3CH_2OH + PO_4^{3-} \rightarrow CF_3CH_2O^- + HPO_4^{2-}, \quad \Delta G^{\ddagger} \approx 0\ \mathrm{kcal\,mol^{-1}}, \tag{4}$$

$$CF_3CH_2O^- + HFP \rightarrow A, \quad \Delta G^{\ddagger} \approx -23.9\ \mathrm{kcal\,mol^{-1}}. \tag{5}$$

Fig. 1(a) is the optimized structure of the carbanionic intermediate **A**, formed from the nucleophilic attack of $CF_3CH_2O^-$ on the double bond of HFP (see Eq. (5)). The free energy of formation of **A** was calculated as $\Delta G \approx -23.9\ \mathrm{kcal\,mol^{-1}}$. The desired product **3** seems to be formed from the interaction of **A** with TFE (see Eq. (6)).

$$\mathbf{A} + CF_3CH_2OH \rightarrow \mathbf{3} + CF_3CH_2O^-, \quad \Delta G^{\ddagger} \approx 0\ \mathrm{kcal\,mol^{-1}}. \tag{6}$$

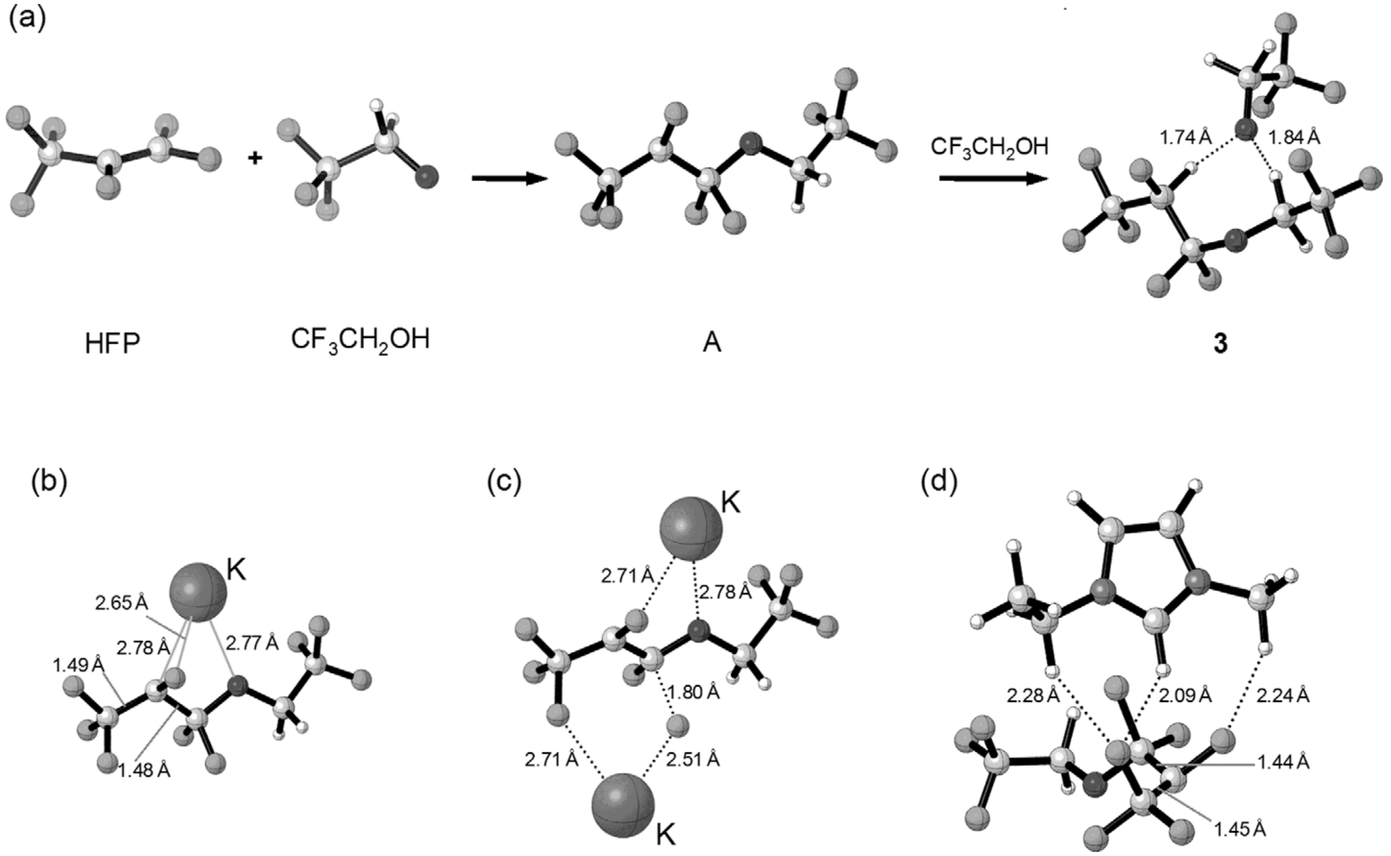

Fig. 1. Optimized structures of (a) the reaction between HFP and CF_3CH_2OH via intermediate A, (b) the intermediate interacting with K^+, (c) the transition state of the reaction abstracting F^- from the intermediate, (d) the intermediate interacting with $[EMIm]^+$.

Alternative pathway to the formation of **3** from the interaction between **A** and HPO_4^{2-}, formed from the interaction of K_3PO_4 with TFE, is rather unlikely because $\Delta G^\ddagger$ for the reaction between more acidic $H_2PO_4^-$ and **A** is calculated to be 4.9 kcal mol^{-1}.

In addition to the interaction with TFE, the carbanionic species **A** is also capable of interacting with K^+. Fig. 1(b) is the optimized structure showing the multi-interactions of K^+ with carbanion, F, and oxygen atoms of **A**. The carbanionic species **A** seems to be stabilized by the interaction with K^+ through carbanion and oxygen atom, thereby prohibiting the protonation at the carbanion and consequently providing sufficient time for the abstraction of F^- from either CF_2 or CF_3 group. Three different isomers can be produced depending on the site of F^- abstraction. ΔG for the formations of *trans*-$CF_3CF{=}CF(OCH_2CF_3)$, *cis*-$CF_3CF{=}CF(OCH_2CF_3)$, and $CF_2{=}CFCF_2(OCH_2CF_3)$ were calculated to be −9.2, −9.2, and −1.2 kcal mol^{-1}, respectively, suggesting that the formation of *cis* and *trans* isomers are equally feasible. However, as shown in Fig. 1(c), it is noteworthy that both CF_2 and CF_3 groups are arranged in favorable positions to produce *trans*-$CF_3CF{=}CF(OCH_2CF_3)$ by the attack of another K^+ from the opposite side of the first K^+ ($\Delta G^\ddagger = 2.0$ kcal mol^{-1}).

The olefinic isomers can be further hydroalkoxylated with TFE. Among doubly hydroalkoxylated products, germinal diether $CF_3CHFCF(OCH_2CF_3)_2$ (**7**) was found to be more stable than the vicinal diethers, by 9–16 kcal mol^{-1}. These computational results on the composition of side products are in good agreement with the experimental results.

To have a clue to the role of imidazolium cation in the reduction of side products, theoretical investigation was also conducted for the interaction between the carbanionic species and an imidazolium cation. For simplicity, 1-ethyl-3-methylimidazolium cation ($[EMIm]^+$) was employed instead of $[BMIm]^+$. Fig. 1(d) shows the optimized structure showing the interaction between $[EMIm]^+$ with **A**. Unlike the structure with K^+ shown in Fig. 1(b), the carbanion remains intact without interacting with $[EMIm]^+$, thereby providing enough space and time for the interaction between carbanion and CF_3CH_2OH to produce **3**. Furthermore, CF_2 group is heavily protected by a bulky $[EMIm]^+$ and thus the abstraction of F^- is prohibited to a great extent. This is probably the reason for the reduced formation of olefinic side products, **4**–**6**.

Based on the theoretical and experimental results, plausible pathways for the formation of **3** and side products in the presence of a catalytic system consisting of K_3PO_4 and [BMIm]Cl are suggested (see Scheme 1 in the supplementary material). $[BMIm]_3[PO_4]$ is likely to be formed first from the interaction between K_3PO_4 and [BMIm]Cl. TFE is then activated by PO_4^{3-} to generate $CF_3CH_2O^-$ and HPO_4^{2-}. Following reaction of $CF_3CH_2O^-$ with HFP would produce a carbanionic intermediate **A**, which in turn rapidly transforms into **3** upon interaction with TFE, along with the regeneration of $CF_3CH_2O^-$. Small amounts of olefinic side products, **4**–**6** can also be produced as the result of the interaction between **A** and $[BMIm]^+$, even though the interaction is not very strong to abstract F^- from **A**. Further alkoxylation of **4**–**6** with TFE would proceed similarly to the alkoxylation of TFE.

4. Conclusions

The catalytic system consisting of K_3PO_4 and [BMIm]Cl was highly effective for reducing the formation of olefinic side products in the hydroalkoxylation reaction of HFP with TFE, while producing 1,1,2,3,3,3-hexafluoropropyl-2′,2′,2′-trifluoroethylether in high yield and selectivity. Experimental and computational studies revealed that K^+ is largely responsible for the formation of olefinic side products.

We expect these novel catalytic systems could find applications in the hydroalkoxylation of various olefins.

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Supplementary material

The online version of this article contains additional supplementary material.

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References

[1] A. McCulloch, P.M. Midgley, P. Ashford, Atmos. Environ. 37 (2003) 889.
[2] R.L. Powell, J. Fluor. Chem. 114 (2002) 237.
[3] A.R. Ravishankara, A.A. Turnipseed, N.R. Jensen, S. Barone, M. Mills, C.J. Howard, S. Solomon, Science 263 (1994) 71.
[4] A. Sekiya, S. Misaki, J. Fluor. Chem. 101 (2000) 215.
[5] W.-T. Tsai, J. Hazard. Mater. A 119 (2005) 69.
[6] J. Murata, S. Yamashita, M. Akiyama, J. Chem. Eng. Data 47 (2002) 911.
[7] H.S. Huang, D.F. Persico, R.J. Lagow, J. Org. Chem. 53 (1988) 78.
[8] A. Sekiya, K. Ueda, Chem. Lett. (1990) 609.
[9] M. Brandwood, P.L. Coe, C.S. Ely, J.C. Tatlow, J. Fluor. Chem. 5 (1975) 521.
[10] R.M. Flynn, M.W. Grenfell, G.L. Moore, J.G. Owens, WO 22356 (1996).
[11] S.H. Hwang, J.R. Kim, S.D. Lee, H. Lee, H.S. Kim, H. Kim, J. Ind. Eng. Chem. 13 (2007) 537.
[12] J.A. Young, P. Tarrant, J. Am. Chem. Soc. 72 (1950) 1860.
[13] A.L. Henne, M.A. Smook, J. Am. Chem. Soc. 72 (1950) 4378.
[14] J.D. Park, W.M. Sweeney, S.L. Hopwood Jr., J.R. Lacher, J. Am. Chem. Soc. 78 (1956) 1685.
[15] R.E.A. Dear, E.E. Gilbert, J. Chem. Eng. Data 14 (1969) 493.
[16] Y. Matsukawa, J. Mizukado, H. Quan, M. Tamura, A. Sekiya, Angew. Chem. Int. Ed. 44 (2005) 1128.
[17] J.S. Wilkes, J.A. Levisky, R.A. Wilson, C.L. Hussey, Inorg. Chem. 21 (1982) 1263.