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# FLUORINATION OF ACTIVATED HALOGENS WITH KF IN POLYETHYLENE GLYCOL-ACETONITRILE SYSTEM

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Polyethylene glycol (mol. wei. 300-600) was found to be effective as a phase-transfer catalyst on the fluorination of activated halogen compounds with potassium fluoride in acetonitrile. Carboxylic and sulfonic acid chlorides were readily converted into their fluorides in high yields.

Solid-liquid phase transfer catalysts such as crown ethers have been studied over the years and the utilization of "naked" anions has become active research interest in organic syntheses.[1] In the field of organic fluorine chemistry, the utility of 18-crown-6 ether to catalyze reactions involving fluoride ion has been demonstrated by several workers. These reactions include (1) displacement of other halogens by fluorine or elimination of hydrogen halides,[2] (2) formation of sulfonyl fluorides from sulfonyl chlorides,[3] (3) oligomerization of perfluoroolefins,[4] and reaction of perfluoro-2-methyl-2-pentene with acid to yield acid fluoride in an aprotic polar solvent.[5] On the other hand, Yanagida and his co-workers recently reported on the property of polyethylene glycol concerning with its ability of metal ion complexation.[6]

We now wish to report a very facile and convenient method to generate a "naked" fluoride ion employing polyethylene glycols in acetonitrile. Aliphatic and aromatic carboxylic acid chlorides and aromatic sulfonic acid chlorides were converted into corresponding fluorides with KF in the presence of polyethylene glycols, even at room temperature, while benzyl bromide and 2,4-dinitrochlorobenzene reacted with sluggishness even at reflux. Cyclohexyl bromide in a similar reaction gave cyclohexene in a good yield. These results indicate that the presence of polyethylene glycols in the reaction system has a substantial effect on activation of fluoride ion, though it is less effective than that of crown ethers.

Among the polyethylene glycols of various molecular weights, the liquid-catalysts such as PEG 200, 300, 400, and 600 are much more efficient than those of solid-catalysts such as PEG 4000 or 6000. As these solid-catalysts with higher molecular weights are almost insoluble in acetonitrile, the solubilities of polyethylene glycols in polar solvents seem to be an important factor to accelerate the reactions. In conculsion, the polyethylene glycols soluble in the solvent are found to be an efficient agent for the nucleophilic enhancement of the fluoride ion in acetonitrile and to be useful catalysts from practical point of view.

Preparation : benzoyl fluoride. To a mixture of freshly dried acetonitrile (10 ml) and PEG 400 (1.0 g), which had been dried over molecular sieve 4A, was added calcined potassium fluoride (1.16 g, 20 mmol) at room temperature. After stirring the heterogenerous system for 1 h, benzoyl chloride (1.41 g, 10 mmol) was added, and the mixture was stirred for 3 h at room temperature. The reaction mixture was then poured into a 10% aqueous HCl solution, and the oily material was distilled under reduced pressure, giving benzoyl fluoride, bp 86-88 °C/ 100 mmHg, in a 92% yield.

Benzenesulfonyl fluoride. Benzenesulfonyl chloride (1.77 g, 10 mmol), polyethylene glycol 300 (1.0 g) and potassium fluoride (1.16 g, 20 mmol) were worked up similarly. Benzenesulfonyl fluoride, bp 92-94 °C/ 18 mmHg, was obtained in an 86% yield.

Table 1. Reaction of Activated Halides with KF/MeCN

$$\underset{(10\ \mathrm{mmol})}{\text{R-X}} \quad + \quad \underset{(20\ \mathrm{mmol})}{\text{KF}} \quad \xrightarrow[\text{MeCN (10 ml)}]{\text{PEG (1.0 g)}} \quad \text{R-F} \quad + \quad \text{KX}$$

| R-X | Catalyst | Temp °C | Time h | Product | Yield[a] % |
|---|---|---|---|---|---|
| PhCOCl | ——— | 20 | 3 | PhCOF | 19 |
| 〃 | PEG 200[b] | 20 | 3 | 〃 | 97 |
| 〃 | 300 | 20 | 3 | 〃 | 96 |
| 〃 | 400 | 20 | 3 | 〃 | 98 |
| 〃 | 600 | 20 | 3 | 〃 | 96 |
| 〃 | 4000 | 20 | 3 | 〃 | 48 |
| $C_3H_7COCl$ | ——— | 20 | 3 | $C_3H_7COF$ | 13 |
| 〃 | PEG 600 | 20 | 3 | 〃 | 97 |
| 〃 | 4000 | 20 | 3 | 〃 | 61 |
| $PhSO_2Cl$ | ——— | 20 | 3 | $PhSO_2F$ | 5 |
| 〃 | PEG 400 | 20 | 3 | 〃 | 98 |
| 〃 | 600 | 20 | 3 | 〃 | 97 |
| p-$MeC_6H_4SO_2Cl$ | ——— | 20 | 3 | p-$MeC_6H_4SO_2F$ | 11 |
| 〃 | PEG 300 | 20 | 3 | 〃 | 86 |
| 〃 | 400 | 20 | 3 | 〃 | 90 |
| $PhCH_2Br$ | ——— | Refl. | 6 | $PhCH_2F$ | 0 |
| 〃 | PEG 300 | 〃 | 6 | 〃 | 19 |
| 〃 | 400 | 〃 | 6 | 〃 | 21 |
| Cyclo-$C_6H_{11}Br$ | ——— | Refl. | 6 | $C_6H_{10}$[c] | 0 |
| 〃 | PEG 300 | 〃 | 6 | 〃 | 76 |
| 〃 | 400 | 〃 | 6 | 〃 | 81 |
| 2,4-$(O_2N)_2C_6H_3Cl$ | ——— | Refl. | 24 | 2,4-$(O_2N)_2C_6H_3F$ | 0 |
| 〃 | PEG 300 | 〃 | 24 | 〃 | 56 |
| 〃 | 400 | 〃 | 24 | 〃 | 41 |

a) Yields were determined from the relative intensities of $^{19}F$ nmr signals, using $PhCF_3$ as reference.

b) Polyethylene glycols of various molecular weights were gifted from Neos Co. (Osaka), and dried by azeotropic distillation with benzene or by keeping them over molecular sieve 4A.

c) Cyclohexene was formed and no fluorinated product was observed.

## References

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