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ENHANCED EFFECT OF SPRAY-DRIED POTASSIUM FLUORIDE ON FLUORINATION

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Spray-dried potassium fluoride was found to be much less hygroscopic and much more effective as a fluorinating agent than usual calcine-dried potassium fluoride. Organic compounds containing an activated halogen atom were readily fluorinated in acetonitrile with spray-dried potassium fluoride.

Although some sorts of metal fluorides generating "naked" fluoride ion, such as potassium and cesium fluorides, are known to be a useful fluorinating agent,[1-4)] it is not easy to handle these fluorides because of their highly hygroscopic property. Solid-supported potassium fluoride[5,6)] and "freeze-dried" potassium fluoride[7,8)] have recently been reported to be less hygroscopic than usual calcine-dried potassium fluoride, which have an enhanced catalytic effect on the hydrogen-bond assisted organic reactions. However, these types of potassium fluoride have no effect on the fluorination of organo halogen compounds.

The background like this prompted us to find out other active types of potassium fluoride, and we now wish to report the fluorination with "spray-dried" potassium fluoride, which is prepared easily and is much less hygroscopic and much more effective on the fluorination than calcine-dried potassium fluoride.

Experimental results are as follows: After one hour of exposure to an atmosphere, calcine-dried potassium fluoride was found to have absorbed as much humidity as 26% of its weight, while spray-dried one has absorbed only 3%. When each of the potassium fluorides was used for the fluorination of p-chloronitrobenzene in refluxing dimethylsulfoxide,[9)] the reaction proceeded as shown in Fig. 1. By using spray-dried potassium fluoride, the halogen-exchange reaction affording p-fluoronitrobenzene proceeded much faster than the case of using calcine-dried potassium fluoride.

Other organo chlorine compounds such as acyl, aroyl, and sulfonyl chlorides, and alkyl halides were also subjected to the fluorination with spray-dried potassium fluoride using acetonitrile as a solvent. The results (Table 1) show that carboxylic and sulfonic acid chlorides are readily converted into the corresponding fluorides even at room temperature. Activated halogen atoms of alkyl or aryl halides also gave corresponding fluorides in considerably good yields.

The strong contrast of spray-dried to calcine-dried potassium fluoride as a fluorinating agent is apparently ascribed to the difference in the particle size, i.e., in their surface area of their crystals. Several physical figures of both potassium fluorides were determined as shown in Table 2. These figures prove that spray-dried crystals have expectedly much smaller particle size, much larger surface area and are much more bulky compared with calcine-dried potassium fluoride crystals. However, both crystals have almost similar water contents so that the much less hygroscopic property of spray-dried crystals is difficult to understand from their particle size. The variety in these hygroscopic properties should be ascribed to the difference of surface structures of the crystals and the X-ray analysis of the surface is now under way.

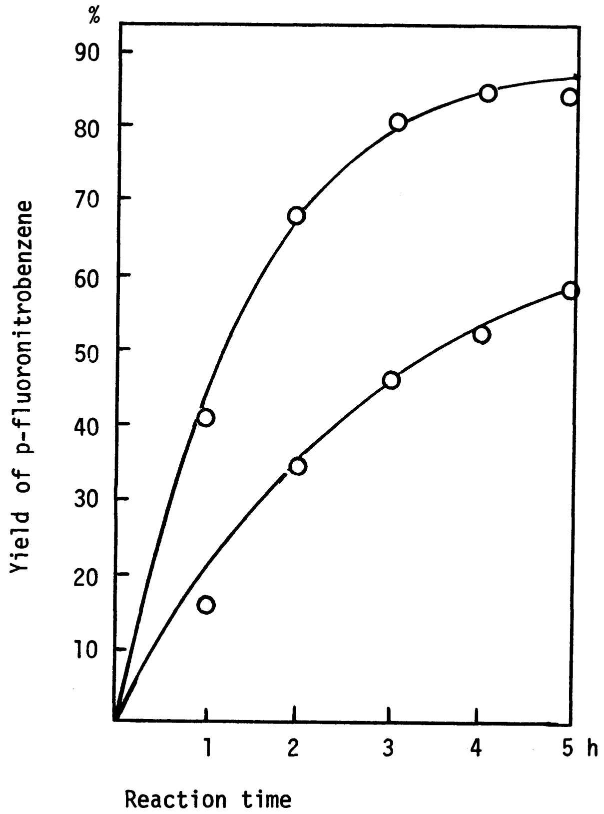

Fig. 1. Fluorination of p-chloronitrobenzene with KF in refluxing DMSO using equimolar KF to p-CNB. The yields were determined by glc analysis.

Table 2 Some physical properties of potassium fluoride

Drying method	Particle size[a] (μm)	Specific surface area[b] (m^2/g)	Bulk density (g/ml)	H_2O content[c] (%)
spray	10 - 50	1.3	0.3 - 0.7	0.24
calcine	200 - 300	0.1	1.4 - 1.6	0.30

a) By a microscopic observation. b) By the BET method. c) By the Karl-Fischer's method.

Table 1 Fluorination of organo halogen compounds with spray-dried KF in acetonitrile

$$RX + KF \xrightarrow{MeCN} RF + K\text{-}X$$

RX	Temp.	Time (h)	Product	Yield (%)
CH_3COCl	r.t.	3	CH_3COF	83[a], 78[b]
$i\text{-}C_3H_7COCl$	"	3	$i\text{-}C_3H_7COF$	96[a]
C_3H_7COCl	"	3	C_3H_7COF	83[a] (13)[c]
C_4H_9COCl	"	3	C_4H_9COF	92[a]
PhCOCl	"	3	PhCOF	89[a], 84[b] (19)[c]
$PhSO_2Cl$	"	24	$PhSO_2F$	81[a], 74[b] (5)[c]
$C_8H_{17}Br$	refl.	10	$C_8H_{17}F$	65[a]
$PhCH_2Br$	"	10	$PhCH_2F$	68[a] (-)[c]
$ClCH_2CO_2Et$	"	24	FCH_2CO_2Et	47[a]
$2,4\text{-}(O_2N)_2C_6H_3Cl$	"	10	$2,4\text{-}(O_2N)_2C_6H_3F$	58[a] (-)[c]
$cyclo\text{-}C_6H_{11}Br$	"	10	$cyclo\text{-}C_6H_{10}$[c]	82[a] (-)[c]

a) Yield determined from the relative intensities of ^{19}F NMR signals, using $PhCF_3$ as internal reference. b) Isolated yield. c) The figures in parentheses give the yields obtained by using calcine-dried potassium fluoride. d) Cyclohexene was formed and no fluorinated product was observed.

Experimental

Spray-dried KF : Into a stainless-steel spray-drier, an aqueous solution (30 wt% concn.) of commercially available potassium fluoride was introduced as spray at the rate of 3 kg/h, and dried by the stream of heated air (300 - 500 ^{o}C). Instantly dried potassium fluoride came out at the rate of ~820 g/h as a bulky mass (d. 0.41 g/ml), giving a yield of 91%.

Calcine-dried KF : Commercially available potassium fluoride was finely ground and dried at 250 - 300 ^{o}C by baking it for 2 - 3 h with occasional grinding.

Fluorination : A mixture of benzoyl chloride (2.82 g, 20 mmol), spray-dried potassium fluoride (2.32 g, 40 mmol), and dried acetonitrile (20 ml) was stirred for 3 h at room temperature. Inorganic material was removed by filtration and the filtrate was poured into an aqueous solution of hydrochloric acid. An oily material was separated and subjected to distillation, giving benzoyl fluoride (84%), b.p. 84 - 86 ^{o}C/ 98 mmHg.

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