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PRELIMINARY NOTE

Polymer-Supported Potassium Fluoride - A Versatile Fluorination Reagent

HANFAN LIU*

Institute of Chemistry, Academia Sinica, Beijing 100080(China)

PING WANG and PENGNIAN SUN

Department of Biology, University of Science and Technology
of China, Hefei (China)

SUMMARY

The nucleophilic reactivity of potassium fluoride was found to be appreciably enhanced via the despersion of KF onto an inert polymeric support. This crosslinked polystyrene was conveniently synthesized with high surface area and porosity.

Fluoride salts have been extensively used for different purposes in synthetic chemistry in recent years [1,2]. However, the low solubility of alkali fluorides in aprotic solvents impedes their wide application. Many attempts have been made to mitigate this problem, usually by phase-transfer catalysis [3].

An alternative approach to improving the reactivity is the use of supported reagents [4], which owe much of their improved reactivity to increased reagent surface area. A variety of inorganic support materials such as alumina, silica, Celite and zeolite [5] have been impregnated with fluoride salts for this purpose, but the reactivity of the reagents as a source of nucleophilic fluorine is very low presumably because of surface OH-F^- hydrogen bonding. Clark et al, [6] and Ichihara and co-

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workers [7] recently reported the successful application of non-surface hydroxylated high-surface-area calcium fluoride in organofluorination. The surface area of the 'effective' calcium fluoride is ca. 10 m^2/g which is much greater than that of normal KF (0.1 m^2/g) or natural fluorite, but much less than that of more conventional supports (about 500 m^2/g). On the other hand, an organic polymer offers several advantages as a support: (1) unlike metal oxide surfaces, polymeric hydrocarbons are nearly inert and have no surface hydroxyl groups; (2) compared with calcium fluoride, polymers can be easily prepared with large specific surface area and porosity. We have therefore examined the possibility of using a high-surface-area inert organic support material for enhancing the reactivity of potassium fluoride in fluorination reactions.

The porous polymers were made in spherical bead form by a two-phase dispersion polymerization in monomer-water suspension [8]. Divinylbenzene (DVB)-styrene, with or without a polar third monomer, was copolymerized in the presence of a diluent. Two kinds of crosslinked polymer composed of 70% of DVB and 30% of 2-N-vinylpyrrolidone (designated as Poly4) or 50% of DVB and 50% of styrene (Poly1) were prepared with specific surface areas of 760 m^2/g or 680 m^2/g respectively. A supported reagent, KF-Poly, was prepared by slowly adding an aqueous solution of potassium fluoride to a suspension of the polymer in dioxane under vigorous agitation; the mixture was then filtered, and the doped polymer dried at ca. 100°C under reduced pressure for 2 hours. The supported reagent routinely has a weight ratio of KF to polymer of 1:4.

The polymer-supported potassium fluoride reagent was successfully used in the preparation of various acid fluorides. Typical examples, combined with literature data, are listed in Table 1. The reactivities of KF-Poly and KF-CaF_2 are comparable but KF-Poly is slightly better. Fluorination of carboxylic and sulphonic acid chlorides proceeded smoothly with this KF-Poly reagent in acetonitrile or dioxane at room temperature, the reaction was complete within a few hours. Under the same conditions nucleophilic substitution hardly occurred when KF powder alone was used (see Table 2).

TABLE 1

Fluorination using polymer-supported KF and KF-CaF_2

Substrate	Reagent	Solvent	Temperature/°C	Time/h	Product	Yield[a]/%
MeCOCl	KF-Poly4	Dioxane	Room temp.	1	MeCOF	90
MeCOCl	KF-CaF_2[b]	Sulpholane	30	0.2	MeCOF	74
EtCOCl	KF-Poly4	Dioxane	Room temp.	0.2	EtCOF	100
PhCOCl	KF-Poly4	Dioxane	Room temp.	0.2	PhCOF	95
PhCOCl	KF-CaF_2[b]	Sulpholane	19	0.2	PhCOF	71
p-BrPhCOCl	KF-Poly1	Dioxane	34	4.5	p-BrPhCOF	99
p-BrPhCOCl	KF-Poly1	Dioxane	60	0.15	p-BrPhCOF	99
$PhCH_2COCl$	KF-Poly1	Dioxane	45	0.5	$PhCH_2COF$	90
p-$MePhSO_2Cl$	KF-Poly1	MeCN	Room temp.	1	p-$MePhSO_2F$	100
p-$MePhSO_2Cl$	KF-CaF_2[c]	MeCN	Room temp.	4	p-$MePhSO_2F$	100

Reaction conditions: substrate, 5 mmol; KF-Poly, 2.5g (8 mmol KF); solvent, 15 ml.

[a] G.l.c. conversion.

[b] Data from reference 6.

[c] Data from reference 7.

TABLE 2

Fluorination of carboxylic chloride with KF-Poly and KF

Substrate	Reagent	Temp./°C	Time/h	Yield[a]/%
MeCOCl	KF-Poly4	Room temp.	1	90
MeCOCl	KF	Room temp.	1	Trace
EtCOCl	KF-Poly4	Room temp.	0.2	100
EtCOCl	KF	Room temp.	0.2	Trace
PhCOCl	KF-Poly4	Room temp.	0.2	95
PhCOCl	KF	Room temp.	1.3	10
p-BrPhCOCl	KF-Poly1	34	4.5	99
p-BrPhCOCl	KF	60	4.5	16

Reaction conditions: solvent, dioxane; otherwise as in Table 1.

[a] G.l.c. conversion.

We also conducted the fluorination of $PhCH_2Br$ with KF-Poly1, but in this case the reactivity of KF-Poly1 was inferior to KF-CaF_2 ($PhCH_2Br \xrightarrow[\text{MeCN reflux, 16h}]{\text{KF-Poly1}} PhCH_2F$, yield 32%; _cf_. 68% yield with KF-CaF_2 used by Clark's group [6]).

It is clear that the presence of the polymer enhances the reactivity of KF in the fluorination reaction. We believe that the improvement in reactivity is because of the dispersion of KF on the inert surface of the polymer support. No chemical interaction between KF and the polymer is apparent.

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