Journal of Fluorine Chemistry, 51 (1991) 171–177

Received: April 20, 1990; accepted: October 4, 1990

A CONVENIENT AND HIGH-YIELD SYNTHESIS FOR PYRIDINIUM AND METAL HEXAFLUOROCOMPLEXES OF VANADIUM, CHROMIUM, IRON AND COBALT

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SUMMARY

Pyridinium poly(hydrogen fluoride) reacts with the oxide of vanadium(V) and chlorides of chromium(III), iron (III) and Co(II) at room temperature forming the pyridinium salts of hexafluoro vanadate(V), hexafluorochromate(III), hexafluoroferrate(III) and hexafluorocobaltate(II) in near quantitative yields (80%). These pyridinium salts are the precursors for the preparation of the alkali metal hexafluorometallates by metathetic reactions in acetonitrile medium with the corresponding metal chlorides. The prepared salts have been identified by their infrared spectral data and elemental analysis.

INTRODUCTION

Hexafluorometallates of vanadium, chromium, iron and cobalt have been synthesised by a variety of methods [1,2] including hydrogen fluoride as a fluorinating reagent, which has its drawback due to its low boiling point (19.6^{0}C). Secondly, for each salt, the reported methods and conditions are different.

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[*] This paper was presented at the Fluorine Chemistry session at the South East Regional Meeting of the American Chemical Society at Winston - Salem, North Carolina, Oct. 11, 1989.

0022-1139/91/$3.50

Presently, a general procedure has been evolved based on the synthetic route developed for several other fluoro complexes of non-metals and metals, making use of pyridinium poly(hydrogen fluoride). This reagent, (Bpt 55°C), is a rich reservoir of fluoride ions, capable of fluorinating both chlorides and oxides of metal and non-metals at room temperature [3,4,5]. Preliminary investigations indicated that transition metal chlorides undergo facile conversions to the corresponding pyridinium fluoride salts. A general procedure has been standardised. Details are given below.

EXPERIMENTAL

All reagents used were AR/Analar grade. Pyridinium poly(hydrogen fluoride) was prepared [3] and stored in polyethylene bottles at -20°C.

All operations were carried out in polyethylene and teflon ware, in a nitrogen atmosphere using Schlenk technique inside a fume cupboard. The IR spectral data of the solid samples were recorded on a Perkin Elmer 599 spectrophotometer.

General Procedure

A known weight of the metal oxide/chloride (anhydrous) (5.23 g of V_2O_5; 5.06 g of $CrCl_3$; 5.26 g $FeCl_3$; 4.9 g of $CoCl_2$) were added in portions, separately, into cooled (0°C) pyridinium poly(hydrogen fluoride), PPHF, (70 ml) taken in polyethylene Erlenmeyer flasks containing a magnetic follower and connected to sodium fluoride absorption towers. The added solid dissolved with vigorous reaction. After completion of the addition, the reaction mixture was stirred for four to six hours at room temperature and then 2 aliquots (100 ml each) of dry chloroform was introduced and well stirred. The chloroform layer extracts out the unassociated pyridine. The hydrogen fluoride layer and the chloroform layer were separated in a separating funnel and to the HF layer was added 100 ml of dry acetone when a white solid precipitated out. This was filtered under suction and washed well with dry acetone in a glove box under dry nitrogen. The salt was then further dried under vacuum (polyethylene vacuum desiccator) and later stored under nitrogen. The yields of the respective pyridinium hexafluorometallates (V, Cr, Fe & Co) were 11.9 g, 11.4 g, 10.6 g and 12.7 g respectively, corresponding to a percentage yield of 85, 88, 80 and 89, based on the metal oxide/chloride taken. All these salts after hydrolysis were analysed by standard procedures [6-11] for their pyridine, fluoride and metal content. It is to be pointed out that all the salts gave negative chloride test and exhibited insolubility in most organic solvents except in acetonitrile in which they were sparingly soluble.The analytical results as well as IR spectral data are given in Table 1. Only one typical result is given though analysis was carried out on five to six samples of each hexafluoro salt.

RESULTS AND DISCUSSION

The analytical results in Table 1 indicate that these salts have a purity of more than 99%. Their IR spectra indicate that all of them are pyridinium salts and the metal is hexacoordinated with fluoride (the presence of one ν M-F (broad) band is consistant with an O_h anion), on comparison of the spectra with that reported for other hexacoordinated species such as, pyridinium hexafluorotitanate(12) and hexafluorometallate of potassium (KVF_6(V) and other metal salts)[13-16]. The number of pyridinium cations associated in the salt matches up the oxidation

TABLE I

Analytical and spectral data for pyridinium hexafluorometallates

Compound (colour)		Chemical Analysis(%)			IR Spectral data in cm^{-1}	
		Pyridine	Fluoride	Metal	Pyridinium cation (s)	MF_6^- (anion) (s,br)
$(C_5H_5NH)VF_6$ (white)	Calcd	32.3	46.5	20.8	3040,1620,1595 1520,1475,1245, 1150,990,745	ν_{V-F} = 660
	Found	32.1	45.9	20.7		
$(C_5H_5NH)_3CrF_6$ (white with green tinge)	Calcd	58.5	28.1	12.8	3040,1620,1595 1520,1475,1245, 1050.990,745	ν_{Cr-F}=540
	Found	57.5	27.5	12.7		
$(C_5H_5NH)_3FeF_6$ (white)	Calcd	57.8	27.8	13.7	3040,1620,1600 1520,1478,1245, 1050,990,745	ν_{Fe-F}=485
	Found	56.8	27.3	13.5		
$(C_5H_5NH)_4CoF_6$ (white with blue tinge)	Calcd	64.1	23.1	12.0	3400,1620,1590, 1520,1470,1250 1045,990,745	ν_{Co-F}=440
	Found	62.6	21.6	11.7		

s = strong and s,br = strong and broad

state of the metal in the starting metal oxide/chloride. This is understandable as PPHF has a capacity to furnish HF for fluorinations and so the mode is similar to HF fluorinations wherein the oxidation state of the metal is retained in the salt.

The overall synthesis reaction could be represented as:

$$V_2O_5 + 2C_5H_5NH(HF)_xF \longrightarrow 2\ C_5H_5NHVF_6 + 5H_2O \qquad (1)$$

$$CrCl_3 + 3C_5H_5NH(HF)_xF \longrightarrow (C_5H_5NH)_3CrF_6 + 3HCl \qquad (2)$$

$$FeCl_3 + 3C_5H_5NH(HF)_xF \longrightarrow (C_5H_5NH)_3FeF_6 + 3HCl \qquad (3)$$

$$CoCl_2 + 4C_5H_5NH(HF)_xF \longrightarrow (C_5H_5NH)_4CoF_6 + 2HCl \qquad (4)$$

These pyridinium salts are stable and can be stored under nitrogen. Making use of these salts as precursors the corresponding alkali metal salts have been prepared by a procedure adopted for the silver salts of hexafluorophosphate, tetrafluoro borate and hexafluorosilicates (rather than the aqueous procedure adopted for the alkali metal salts) [17-20]. They have been identified by their IR spectra [2,1,16]. To prevent the formation of any oxyfluorometallates, moisture should be strictly avoided during filtration and storage. It is to be mentioned that water formed as one of the products during synthesis does not hydrolyse the formed fluoro salts in presence of anhydrous hydrogen fluoride. Perhaps, due to its greater association with HF.

It has been reported that VF_5 in anhydrous hydrogen fluoride does not indicate the presence of VF_6^- species in solution [21] and that in presence of pyridine, VF_5 undergoes reduction to form $VF_4(C_5H_5N)$[22]. Therefore, it is very interesting to see that the pyridinium ion in pyridinium poly(hydrogen fluoride) stabilizes the formed VF_5 in HF to form $C_5H_5NH^+VF_6^-$. This indicates that VF_5 exhibits a capacity to accept F^- ions in solution. In the case of chromium, iron and cobalt also the maximum coordination number of the central atom is invoked during fluorination and the original oxidation state of the metal is retained while the species undergoes salt formation with the requisite amount of the pyridinium cation. All the salts have been obtained in good yields and purity. It is to be mentioned that these pyridinium salts have not been earlier reported though other salts of these hexafluorometallates are very well known. Pyridinium ion being easily exchangeable, undergoes ready exchange with alkali metal ions to yield the corresponding well known alkali metal hexafluorometallates. This synthesis establishes pyridinium poly(hydrogen fluoride) as a convenient fluorinating reagent at room temperature for high yield synthesis of transition fluorometallates.

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