Journal of Fluorine Chemistry, 57 (1992) 155–158

Room temperature synthesis of metal fluorides and pyridinium fluorometallate complexes by the direct reaction of metals with pyridinium poly(hydrogen fluoride)

K. R. Muddukrishna, Ram Niwas Singh and D. K. Padma*
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012 (India)

Abstract

Metal powders (Pb, Cu, Zn, Mn, Al, Fe, Sn, Cr) are found to react directly with pyridinium poly(hydrogen fluoride) (PPHF) at room temperature to form metal fluorides/pyridinium fluorometallates and hydrogen The reaction rate is dependent on the particle size of the metals and stirring conditions.

Introduction

It is well known that anhydrous hydrogen fluoride in both the gaseous and liquid states reacts only superficially with metals at room temperature (20–30 °C). An adherent film of the corresponding metal fluoride formed passivates and protects the base metal from further attack by hydrogen fluoride. The reaction is enhanced at high temperatures and pressures to give the corresponding metal fluoride and hydrogen [1]. Interestingly, the present observation is that the corresponding reaction is promoted at room temperature in the presence of pyridinium poly(hydrogen fluoride). The metals Pb, Cu, Zn and Mn react to form hydrogen and the corresponding metal fluorides generally in their most stable oxidation state. In the case of Al, Fe, Sn and Cr, the metal fluoride formed complexes further with the excess fluoride present to form the pyridinium fluorometallate salt. Such type of complex fluoride formation has been observed earlier [2–5].

Experimental

Metal powders (1–3 g) are treated with pyridinium poly(hydrogen fluoride) (35 ml) in a polyethylene flask fitted with a sodium fluoride scrubber which strips off anhydrous hydrogen fluoride vapour and also

---

*Author to whom correspondence should be addressed allows the escape of hydrogen. The reactants are well shaken at room temperature for 5–6 days or until the metal powder is completely consumed. In the case of the metals Pb, Cu, Zn and Mn, the formed metal fluoride precipitates to a certain extent, while with the metals Al, Fe, Sn and Cr, the corresponding pyridinium fluorometallates formed remain in solution. On addition of 200–300 ml dry acetone, the precipitation of the fluoride salts in both cases goes to completion. This precipitate is filtered, dried and stored under nitrogen in a polyethylene desiccator, as the pyridinium salts are hygroscopic. Results in Table 1 indicate an overall yield of >90%. Pyridinium analysis (Table 2) indicates a high purity for the salts. Table 3 gives the XRD data for the metal fluorides. The X-ray diffractograms were recorded on a Phillips X-ray diffractometer and the IR spectra on a Perkin Elmer Model 599 spectrometer.

Results and discussion

The metals Pb, Cu, Zn and Mn gave air-stable products which could be identified as lead (II) fluoride, copper (II) fluoride, zinc fluoride and

TABLE 1

Reaction of metals with PPHF (product yields)

Metal	Starting amounts (g)	Yield of salt		
		Obtained (g)	Calculated (g)	%
Pb	3.0	3.4	3.55	95.7
Cu	2.5	5.1	5.40	94.3
Zn	2.0	2.9	3.16	91.7
Mn	2.7	4.3	4.57	94.1
Al	1.0	13.1	14.12	92.8
Fe	1.0	7.0	7.34	95.4
Cr	1.0	7.1	7.80	90.9
Sn	2.0	6.4	6.62	96.7

TABLE 2

Analysis of pyridinium fluorometallates

Salt	Pyridinium (%)	
	Obtained	Calculated
$(C_5H_5NH)_3AlF_6$	61.00	62.99
$(C_5N_5NH)_3FeF_6$	56.98	58.55
$(C_5N_5NH)_3CrF_6$	58.14	59.11
$(C_5N_5NH)_2SnF_6$	40.68	40.74

TABLE 3

XRD data of metal fluorides (d values)

Metal fluoride	Found	Reported [6(a)–(d)]
MnF_2	3.43, 2.72, 2.38 1.82, 1.72, 1.65	3.45, 2.74, 2.39 1.82, 1.72, 1.65
$CuF_2 \cdot 2H_2O$	4.76, 3.68, 3.15 2.97, 2.71, 2.54	4.78, 3.71, 3.15 2.98, 2.71, 2.55
ZnF_2	3.33, 2.61, 2.28 1.75, 1.67, 1.40	3.33, 2.61, 2.29 1.75, 1.67, 1.40
β-PbF_2	3.41, 2.95, 2.09 1.79, 1.71, 1.48	3.43, 2.97, 2.10 1.79, 1.72, 1.49

manganese(II) fluoride by comparison with reported X-ray diffraction data [6, a–d] (Table 3).

The highly hygroscopic salts were identified as pyridinium fluorometallate salts based on pyridinium analysis and their IR spectra. The salts, $(C_5H_5NH)_3AlF_6$, $(C_5H_5NH)_3FeF_6$, $(C_5H_5NH)_2SnF_6$ and $(C_5H_5NH)_3CrF_6$ exhibit the reported characteristic IR absorption frequencies of the pyridinium cation at 3040, 1620, 1595, 1520, 1475, 1245, 1150, 990 and 745 cm^{-1} for all the salts [2] and the ν(M–F) is in agreement with reported values [7] for AlF_6^{3-} at 599, FeF_6^{3-} at 485, SnF_6^{2-} at 555 and CrF_6^{3-} at 540 cm^{-1}. Attempts to obtain single crystals for structural analysis have so far failed. However, by metathetic reaction the corresponding alkali salts have been prepared and identified by their reported X-ray data [6(e)–(f)].

$$(C_5H_5NH)_3FeF_6 + 3KCl \longrightarrow K_3FeF_6 + 3C_5H_5NHCl$$

$$(C_5H_5NH)_3CrF_6 + 3NaCl \longrightarrow Na_3CrF_6 + 3C_5H_5NHCl$$

A representative reaction scheme can be expressed as follows:

$$Zn + C_5H_5NH(HF)_xF \longrightarrow ZnF_2 + H_2$$

$$Fe + 3C_5H_5NH(HF)_xF \longrightarrow (C_5H_5NH)_3FeF_6 + H_2$$

The continuous corrosion of the fluoride-passivated metal is attributed to a similar complexing nature of the metal fluoride with ammonia and pyridine [8] and AsF_5 in anhydrous HF medium [9, 10]. The presence of pyridine in anhydrous HF (PPHF) seems to facilitate solubility of the metal fluorides, although stable adducts were isolated only for Cr, Fe, Al and Sn while the metals, Cu, Zn, Pb and Mn gave rise to their respective metal fluorides on precipitation by acetone.

Acknowledgement

One of the authors (K.R.M.) thanks CSIR for a Senior Research Fellowship.

References

1 E L Muetterties and J E Castle, *J Inorg Nucl Chem* , *18* (1961) 148
2 K Syed Mohamed and D K Padma, *J Fluorine Chem* , *35* (1986) 411
3 H P Sampath Kumar and D K Padma, *J Fluorine Chem* , *51* (199) 171
4 H M Haendler, F A Johnson and D S Crocket, *J Am. Chem Soc* , *80* (1958) 2662
5 D. S Crocket and H M Haendler, *J Am Chem Soc.*, *82* (1960) 4158
6 *Powder Diffraction File, Inorganic Phases*, International Center for Diffraction Data, Swarthmore, PA, USA, 1990, (a) 24 727 (b) 6–143 (c) 7-214 (d) 6–251 (e) 22–1223 (f) 27–675
7 R D Peacock and D W A Sharp, *J Chem Soc* , *(A)* (1959) 2764
8 I G Ryss, *The Chemistry of Fluorine and its Inorganic Compounds*, United States Atomic Energy Commission Technical Information Services, Moscow–Leningrad, U S S R , 1960, Part II, p 642
9 B Frlec and D Gantar, *J Fluorine Chem* , *19* (1982) 485
10 B Frlec, D Gantar and J H Holloway, *J Fluorine Chem* , *20* (1982) 385