Journal of Fluorine Chemistry, 67 (1994) 211–214

A study of the synthesis of Group I and Group II metal fluorides with pyridinium poly(hydrogen fluoride), PPHF

Ram Niwas Singh and D.K. Padma*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012 (India)

(Received February 11, 1993; accepted June 11, 1993)

Abstract

Alkali and alkaline earth metal fluorides, hydrogen fluorides and complex fluorides have been prepared by the reaction of the corresponding metal chloride, oxide and carbonate with pyridinium poly(hydrogen fluoride) at room temperature. The resulting compounds have been characterized by chemical analysis, IR and NMR (^{1}H, ^{13}C, ^{19}F) spectroscopy and XRD methods. The interesting feature is the formation of normal fluorides by lithium, calcium and magnesium, while sodium, potassium, rubidium, caesium, strontium and barium form fluoride complexes with HF, and beryllium gives rise to a pyridinium tetrafluoroberyllate salt. This salt has been synthesized and characterized for the first time.

Introduction

Several studies carried out in our laboratories have shown that pyridinium poly(hydrogen fluoride), PPHF, is a good fluorinating and complexing reagent [1–3]. Hence, it was of interest to treat alkali and alkaline earth metal compounds with this reagent to study the role of the central metal atom in determining the type of fluoride formed.

Experimental

Materials and methods

All reagents were Analar grade. Pyridinium poly(hydrogen fluoride), (PPHF), was prepared by mixing pyridine and HF in a 3:7 mole ratio [4] and storing in polyethylene bottles at −5 °C.

Infrared spectra were recorded on an FTS-7 Bio-Rad spectrometer over the spectral range 4000–200 cm^{-1} (CsI disc) using neat samples or Nujol mulls, while NMR spectra were measured on a Bruker Model AC-200 spectrometer at 200 MHz for ^{1}H, 188.3 MHz for ^{19}F and 50.323 MHz for ^{13}C nuclei. Samples were referenced externally with respect to tetramethylsilane/trifluoromethylbenzene with positive shifts downfield from the standards.

Thermograms were recorded on a Perkin–Elmer TGS-2 Thermogravimetric Analyzer while X-ray diffractograms were measured on a vertical goniometer Philips MDL PW 1050/70 diffractometer, using Fe Kα, Co Kα and Cu Kα targets.

Syntheses

In all cases studied, PPHF was held in a polyethylene flask fitted with a sodium fluoride scrubber and the solution stirred with a Teflon-coated magnetic pellet. The reactants were cooled in an alcohol–liquid nitrogen slush bath (−30 °C to −40 °C). The starting material was added (Table 1) in small portions over a period of 20 min. After addition was complete, stirring was

TABLE 1. Syntheses of metal fluorides, metal hydrogen fluorides and pyridinium tetrafluoroberyllate

Starting material (A)	Amount taken		Product formed	
	A (g)	PPHF (ml)	Formula	Yield (%)
Li_2CO_3	3.291	5	LiF	90
Na_2CO_3	4.257	8	$NaHF_2$	88
NaCl	5.389	8	$NaHF_2$	89
K_2CO_3	4.101	8	KHF_2	94
KCl	4.010	8	KHF_2	88
RbCl	1.000	3	$RbF\cdot 3/2HF$	87
CsCl	1.000	3	$CsF\cdot 3/2HF$	89
BeO	2.998	55	$(pyH)_2BeF_4$	86
MgO	2.802	5	MgF_2	94
$CaCO_3$	3.078	6	CaF_2	95
$SrCO_3$	4.194	8	$SrHF_3$	84
$BaCO_3$	4.166	8	$BaHF_3$	96

---

*Author to whom correspondence should be addressed.

SSDI 0022-1139(93)02965-H

continued, the contents were allowed to warm up to room temperature and stirred for another 0.5 h in all cases except for the beryllium sample (3 h). At the end of the reaction the products were generally soluble but partial precipitation of salts occurred in the case of barium and strontium. The barium salt was separated by decantation and the remaining PPHF removed by washing with acetone. In the case of strontium, the salt formed was partially soluble in PPHF, so the mixture was treated with chloroform and the PPHF layer separated using a separating funnel. The lower layer containing the salt was treated with acetone, the separated salt washed with acetone and dried. The remaining homogeneous solutions were treated with acetone (50–100 ml) and the precipitated salts filtered under suction, washed several times with acetone, dried under vacuum (20 mm Hg), weighed, stored under nitrogen and characterized by IR, NMR and XRD methods and by chemical analysis. All operations were carried out in an inert atmosphere.

Characterization

The hydrogen fluoride content of HF-containing salts (Table 2) was determined by titrimetry using standard sodium hydroxide solution [5]. With the insoluble strontium and barium hydrogen fluorides, titration with sodium hydroxide was completed by warming the titrants to ensure complete reaction of HF. The final products, insoluble SrF_2 and BaF_2, were isolated and identified by XRD [6a, b]. Pyridinium fluoroberyllate was characterized by IR and NMR spectroscopy, and by chemical analysis (pyridine (%): Calc.: 64.52; Found: 64.26). The metathetic reaction with sodium chloride formed the well-known Na_2BeF_4 which was identified by IR spectroscopy [7] and XRD [6c] methods.

Results and discussion

Table 1 lists the compounds studied and their reaction products and Table 2 gives the analytical results for the associated hydrogen fluoride.

TABLE 2. Analysis of metal hydrogen fluorides

Compound	Amount taken (g)	Associated HF		% HF	
		Found (mg)	Calc. (mg)	Found	Calc.
$NaHF_2$	0.2280	71.25	73.58	31.25	32.27
KHF_2	0.2025	51.98	51.86	25.67	25.61
$RbF\cdot 3/2HF$	0.1873	41.28	41.81	22.04	22.32
$CsF\cdot 3/2HF$	0.1678	28.19	27.69	16.80	16.50
$SrF_2\cdot HF$	0.1762	17.67	24.19	10.03	13.73
$BaF_2\cdot HF$	0.2107	21.60	21.58	10.25	10.24

In the infrared spectra of $NaHF_2$, KHF_2, $RbF\cdot 3/2HF$ and $CsF\cdot 3/2HF$, the presence of a band at *c.* 1500 cm^{-1} (broad) and another at *c.* 1200 cm^{-1} indicates the presence of the HF_2^- ion [8]. For the strontium and barium salts, a broad band occurs between 1630 and 1785 cm^{-1} together with two peaks at *c.* 1185 and 1160 cm^{-1}, again indicating the presence of the HF_2^- ion [9a] as supported by X-ray analysis [9b].

The IR spectrum of pyridinium tetrafluoroberyllate together with assignments based on previous reports for other pyridinium salts [10, 11] is given in Table 3. The ν_3 splitting has been explained as arising from the interaction of the ions in the unit cell and/or because of the low-site symmetry of the ion in the crystal lattice [12].

The presence of the pyridinium ion has also been observed in the NMR spectrum as characteristic multiplets occurring at 8.10 ppm, at a lower field than those in pyridine (7.54 ppm). The ^{13}C NMR spectrum indicated a downfield shift of β- and γ-carbon atoms from 123.94 to 129.95 ppm and from 136.14 to 149.53 ppm, respectively, whereas an upfield shift of the α-carbon atom occurred from 149.70 to 143.75 ppm [10, 13, 14]. These ^{13}C shifts were critically dependent on both charge transfer and variations in the bond-order parameters.

The ^{19}F NMR spectrum of aqueous $(C_5H_5NH)_2BeF_4$ solution exhibited a chemical shift δ -104.80 ppm with respect to trifluoromethylbenzene as external standard ($\delta_{CFCl_3} = -167.8$ ppm) (close to the value of 163 ppm

TABLE 3. Infrared spectrum of $(pyH)_2BeF_4$

Frequencies (cm^{-1})	Assignments
3204 (m); 3146 (m); 3117 (sh); 3085 (m); 3049 (s); 2950 (m); 2911 (m); 2880 (m)	C—H stretching and N—H stretching vibrations
1629 (m); 1599 (s); 1527 (vs); 1477 (s)	symmetric and antisymmetric in-plane ring deformation, the result of C=C and C=N interactions
1365 (vw); 1327 (m); 1236 (m); 1185 (w); 1151 (vw); 1050 (m)	aromatic in-plane hydrogen deformation vibrations
1027 (w); 993 (w)	ring breathing and C—H out-of-plane vibrations
924 (m); 817 (m)	ν_{Be-F} stretching
741 (s); 672 (s)	ring vibrations (out-of-plane and in-plane)
607 (m)	δ_{Be-F} bending
426 (w)	ring deformation

TABLE 4. X-Ray diffraction data for rubidium and caesium hydrogen fluorides

RbF·3/2HF				CsF·3/2HF			
h k l	I/I_0	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	*h k l*	I/I_0	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)
1 1 1	30	4.8973	4.8794	1 1 1	21	5.1617	5.1564
2 0 0	51	4.2081	4.2257	2 0 0	47	4.4567	4.4656
2 2 0	100	2.9798	2.9880	2 2 0	100	3.1542	3.1576
3 1 1	6	2.5384	2.5482	2 2 2	57	2.5777	2.5782
2 2 2	65	2.4336	2.4397	4 0 0	34	2.2311	2.2328
4 0 0	44	2.1116	2.1128	4 2 0	34	1.9977	1.9971
4 2 0	19	1.8892	1.8898	4 2 2	32	1.8261	1.8231
4 2 2	18	1.7239	1.7251	5 1 1 3 3 3	10	1.7171	1.7188
5 1 1 3 3 3	20	1.6240	1.6265	4 4 0	14	1.5796	1.5788
4 4 0	12	1.4950	1.4940	6 0 0 4 4 2	20	1.4890	1.4885
6 0 0 4 4 2	6	1.4093	1.4086	6 2 0	21	1.4127	1.4121
6 2 0	12	1.3374	1.3363	6 2 2	10	1.3468	1.3464
6 2 2	8	1.2745	1.2741	4 4 4	7	1.2881	1.2891

TABLE 5. X-Ray diffraction data of pyridinium tetrafluoroberyllate

d (Å)	I/I_0	*d* (Å)	I/I_0
11.3315	100	3.1311	19
9.3439	21	3.0368	4
6.5815	8	2.8872	2
6.0266	9	2.8216	2
5.6464	11	2.7255	3
5.1840	17	2.6865	5
4.8102	10	2.5301	3
4.5126	7	2.4696	2
4.3848	11	2.4327	2
4.0724	44	2.3289	3
3.8698	4	2.2827	3
3.7502	10	2.1436	3
3.6021	9	2.0790	2
3.5099	12	1.9364	2
3.4217	24	1.8279	2
3.3192	3	1.7774	3
3.2036	21		

reported for $(NH_4)_2BeF_4$ [15]) with a well-resolved quartet with a coupling constant $J_{Be-F}=39.02$ Hz. Hence, the ^{19}F spectrum clearly indicates the presence of the $BeF_4{}^{2-}$ anion. Its metathetical product Na_2BeF_4, obtained by treating with sodium chloride, was identified by XRD [6c] and IR spectroscopy [7].

The thermograms obtained showed a sharp weight loss corresponding to the decomposition of $SrHF_3$ at 120 °C while $BaHF_3$ decomposed at 168 °C with loss of HF. The final products, SrF_2 [6a] and BaF_2 [6b], were identified by XRD. RbF·3/2HF exhibited a slow decomposition from 50 °C (onwards) which was incomplete up to 350 °C, while the CsF·3/2HF compound exhibited a major weight loss between 40 °C and 100 °C and thereafter a slow weight loss which remained incomplete up to 350 °C.

The compounds LiF, MgF_2, CaF_2, $NaHF_2$, KHF_2 and $BaHF_3$ were further identified by XRD which gave good agreement with reported values [6d–i].

The XRD of $SrHF_3$ showed the presence of small amounts of free SrF_2. Chemical analysis also indicated that the amount of associated HF was less than that required by the formula $SrHF_3$ perhaps due to decomposition.

For RbF·3/2HF and CsF·3/2HF (formulated on the basis of the amount of associated HF, see Table 2), since XRD data were not available indexing was achieved by adopting a general procedure [16] with the XRD data being listed in Table 4. RbF·3/2HF and CsF·3/2HF have been found to have face centred cubic lattices, $a = 8.4514$ and 8.9312 Å; respectively. The XRD data for $(C_5H_5NH)_2BeF_4$ are listed in Table 5.

Because of the high charge/radius ratio of the cations and very high lattice energies [17], the final products in the case of Li, Mg and Ca were the corresponding fluorides, whereas HF was associated in the case of Na, K, Rb, Cs, Sr and Ba, such associations have been previously reported [18–20]. As a result of small size, high ionization enthalpy and vacant p orbitals, beryllium has a tendency to form covalent compounds. Hence coordination of fluoride occurs and in the presence of the pyridinium cation this leads to the formation of pyridinium fluoroberyllate.

Acknowledgement

The authors gratefully acknowledge the financial assistance of The Department of Atomic Energy.

References

1 H.P. Sampath Kumar and D.K. Padma, *J. Fluorine Chem., 51* (1991) 171.

2 K.S. Mohamed and D.K. Padma, *Q. Chem. Rev. (India), 1* (1985) 1.

3 R.G. Kalbandkeri, K.S. Mohamed, D.K. Padma and A.R.V. Murthy, *Polyhedron, 4* (1985) 787.

4 G.A. Olah, J.T. Welch, Y.D. Vankar, M. Nojima, I. Kerekes and J.A. Olah, *J. Org. Chem., 44* (1979) 3872.

5 I.G. Ryss, *The Chemistry of Fluorine and its Inorganic Compounds,* State Publishing House for Scientific, Technical and Chemical Literature, Moscow, 1956, AEC-Tr-3927 (Part 1), p. 115.

6 *Powder Diffraction File, Inorganic Phases,* International Center for Diffraction Data, Swarthmore, PA, 1990: (a) 6-262; (b) 4-452; (c) 21-1103; (d) 4-857; (e) 6-290; (f) 35-816; (g) 6-479; (h) 1-1095; (i) 35-1378.

7 R.D. Peacock and D.W.A. Sharp, *J. Chem. Soc. A,* (1959) 2764.

8 J.A.A. Ketelaar, C. Haas and J.V.D. Elsken, *J. Chem. Phys., 24* (1956) 624.

9 (a) A. Lautie, F. Romain, M.H. Limage, A. Novak, H. Prevost-Czeskleba and J. Moret, *J. Mol. Struct., 118* (1984) 227; (b) V.W. Massa and E. Herdtweck, *Acta Crystallogr., Sect. C, 39* (1983) 509.

10 K.S. Mohamed and D.K. Padma, *Spectrochim. Acta, 44A* (1988) 325.

11 (a) D. Cook, *Can. J. Chem., 39* (1961) 2009; (b) N.S. Gill, R.H. Nuttall, D.E. Scaife and D.W.A. Sharp, *J. Inorg. Nucl. Chem., 18* (1961) 79.

12 R.S. Halford, *J. Chem. Phys., 14* (1946) 8.

13 K.S. Mohamed and D.K. Padma, *Spectrochim. Acta, 41A* (1985) 725.

14 R.G. Pugmire and D.M. Grant, *J. Am. Chem. Soc., 90* (1968) 697.

15 J.C. Kotz, R. Schaeffer and A. Clouse, in J.W. Emsley, J. Feeney and L.H. Sutcliffe (eds.), *Progress in NMR Spectroscopy,* Pergamon, New York, 1971, p. 497.

16 L.V. Azaroff and M.J. Buerger, *The Powder Method in X-ray Crystallography,* McGraw-Hill, New York, 1958, p. 79 and p. 106.

17 (a) J.C. Bailar (ed.), *Comprehensive Inorganic Chemistry,* Pergamon, Oxford, 1973, Vol. 1, pp. 346, 409 and 629; (b) H.J. Emeleus (ed.), *Advances in Inorganic Chemistry and Radiochemistry,* Academic Press, New York, 1959, Vol. 1, pp. 190, 199 and 210.

18 G.H. Cady, *J. Am. Chem. Soc., 56* (1934) 1431.

19 K.R. Webb and E.B.R. Prideaux, *J. Chem. Soc.,* (1939) 111.

20 A.F. Clifford and A.G. Morris, *J. Inorg. Nucl. Chem., 5* (1957) 71.