

A Novel Synthetic Route for the Preparation of Ammonium & Alkali Metal Tetrafluoroborates & Alkyl Substituted Ammonium Tetrafluoroborates using Pyridinium Tetrafluoroborate as the Precursor

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Ammonium and alkali metal tetrafluoroborates have been prepared by the cation exchange reaction of pyridinium tetrafluoroborate with the corresponding hydroxides/halides. The reaction of pyridinium tetrafluoroborate with primary, secondary and tertiary alkyl amines at room temperature gives rise to mono-, di- and tri-alkylammonium tetrafluoroborates, respectively. The yields are good and the samples are of high purity. The products have been characterised by elemental analysis, IR and PMR spectroscopy. The spectral data for most of the compounds are reported for the first time.

Tetrafluoroborates salts are widely used both in research and industry. Some of the applications are in electrolytic polishing of ammonium¹, metal finishing operations², bright dipping solutions for Sn-Pb alloys in printed circuits and other electrical components³, catalyst in organic synthesis^{4,5}, high temperature fluxes, battery components and boriding of steel surfaces⁸. The availability of pure salts is of decided advantage for the applications mentioned above. However, the methods so far reported for their preparation are not satisfactory as regards purity of products, simplicity of methods employed and yields. We report here a simple, one-step procedure for the synthesis of title compounds at room temperature, employing pyridinium tetrafluoroborate for exchange reactions.

Materials and Methods

All the reagents employed in the present study were of LR/AR grade.

The precursor, pyridinium tetrafluoroborate ($C_5H_5NHBF_4$) was synthesised by the reaction of pyridinium poly(hydrogen fluoride) with boric oxide or boric acid⁹. Recrystallized samples, m.p. 210°C, when treated with ammonium and alkali metal hydroxide/chlorides underwent cation exchange and formed the corresponding ammonium and alkali metal tetrafluoroborates. This preparative mode has been extended to the preparation of alkyl substituted ammonium tetrafluoroborates in good yields and high purity.

The infrared spectra of the compounds were recorded both in nujol mull and KBr using a Perkin Elmer 599 spectrophotometer, ¹H (TMS standard) and ¹⁹F (CFCl₃ standard) NMR spectra were recorded on Varian T60 and Varian FT 80A (74-84 MHz) NMR spectrometers using D₂O or DMSO-*d*₆ as solvents. ¹³C NMR spectra were recorded on a Bruker WH-270 MHz F-T NMR, X-ray powder diffraction patterns were recorded with a Phillips 1050/70 X-ray diffractometer using Cu Kα radiation.

Preparation of ammonium tetrafluoroborate

To a solution of pyridinium tetrafluoroborate, (5 g) was added a very slight excess of ammonium hydroxide (1:1) solution dropwise. Pyridine was found to be liberated and was extracted with chloroform thrice. The aqueous solution was filtered and evaporated slowly on a water-bath at 60°-70°C when a solid was obtained, it was dried *in vacuo* over phosphorus pentoxide, yield 92%.

Preparation of alkali metal (Na, K, Rb and Cs) tetrafluoroborates

To a solution of pyridinium tetrafluoroborate (5 g) was added calculated amount of sodium hydroxide solution (30 ml, 1.0 N), potassium chloride (2.5 g in 10 ml of water), rubidium bromide (2.0 g in 5 ml of water) or cesium bromide (1.5 g in 5 ml of water). Pyridine was found to be liberated in the process. In the case of sodium tetrafluoroborate the pyridine was extracted with chloroform and the solution concentrated. The yield was 94%. In the other cases, the precipitate formed was filtered, washed with alcohol-water mixture

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and dried in a hot air oven ($\sim 105^\circ\text{C}$). The yield was 96%, 96% and 90% for the potassium, rubidium and cesium salts respectively.

The compounds have been characterised by chemical analysis (Table 1) and X-ray powder diffraction pattern (Table 2). The BF_4^- and the boron contents of all the compounds were estimated gravimetrically using nitron acetate as precipitant¹⁰ and titrimetrically by the method of Tatarskii *et al*¹¹.

Table 1 – Analytical and Infrared Spectra data of Ammonium and Alkali Metal Tetrafluoroborates

MBF ₄	Found(calc.), %		IR frequencies (cm ⁻¹)	Probable assignments
	BF ₄ ⁻	Boron		
			3330 s 1430 s 1295 m	$\nu(\text{N-H})$ $\delta(\text{N-H})$
NH ₄ BF ₄ *	82.01 (82.82)	—	1100-1000 b,vs 765 w, 720 w 530 s, 520 s	$\nu_3(\text{F}_2): \nu(\text{B-F})$ $\nu_4(\text{F}_2): \delta(\text{B-F})$ $\nu_3(\text{F}_2): \nu(\text{B-F})$
NaBF ₄	77.86 (79.05)	9.72 (9.84)	1100-1040 b,vs 770 w, 1305 w 527 m, 516 m	$\nu_4(\text{F}_2): \delta(\text{B-F})$ $\nu_3(\text{F}_2): \nu(\text{B-F})$
KBF ₄	68.31 (68.99)	8.55 (8.58)	1080-1300 b,vs 770 m, 740 w 530 s, 518 s	$\nu_4(\text{F}_2): \delta(\text{B-F})$ $\nu_3(\text{F}_2): \nu(\text{B-F})$
RbBF ₄	50.16 (50.40)	6.19 (6.27)	1075-1025 b,vs 765 w 525 s, 518 s	$\nu_4(\text{F}_2): \delta(\text{B-F})$ $\nu_3(\text{F}_2): \nu(\text{B-F})$
CsBF ₄	39.55 (39.51)	4.90 (4.92)	1090-1000 b,vs 530 m, 517 s	$\nu_2(\text{F}_2): \delta(\text{B-F})$

* Nitrogen estimation : calc. = 13.36% : found = 13.25%.

Table 2 – X-ray Powder Diffraction Pattern Data of Ammonium and Alkali Metal Tetrafluoroborates (in Å)

NH ₄ BF ₄		NaBF ₄		KBF ₄		RbBF ₄		CsBF ₄	
<i>d</i> _{obs}	<i>d</i> _{lit}	<i>d</i> _{obs}	<i>d</i> _{lit}	<i>d</i> _{obs}	<i>d</i> _{lit}	<i>d</i> _{obs}	<i>d</i> _{lit}	<i>d</i> _{obs}	<i>d</i> _{lit}
5.75	5.70	3.41	3.41	3.88	3.88	3.99	3.98	4.82	4.83
4.53	4.50	3.39	3.39	3.49	3.50	3.85	3.84	4.65	4.66
3.88	3.84	2.85	2.84	3.40	3.40	3.63	3.62	4.21	4.20
3.67	3.65	2.32	2.31	3.27	3.26	3.53	3.52	4.08	4.08
3.58	3.55	2.15	2.14	3.07	3.07	3.37	—	3.82	3.82
3.11	3.18	2.04	2.03	2.81	2.80	3.18	3.17	3.74	3.73
2.93	2.89	2.01	2.00	2.75	2.74	2.89	2.88	3.55	3.55
2.87	2.84	1.84	1.83	2.33	2.32	2.81	2.83	3.36	3.35
2.56	2.53	1.82	1.81	2.21	2.20	2.53	2.52	3.05	3.04
2.34	2.33	1.56	1.56	2.08	2.08	2.40	2.38	2.95	2.96
2.30	2.28	1.51	1.50	2.03	2.02	2.35	2.33	2.52	2.52
2.48	2.16			1.83	1.82	2.33	2.32	2.47	2.46
1.66	1.65					2.27	2.27	2.39	2.39
						2.16	2.15	2.31	2.30
								2.27	2.27
								2.24	2.23

Preparation of monoalkly ammonium tetrafluoroborates

Pyridinium tetrafluoroborate (5 g) dissolved in 15 ml of water was kept in ice-cooled water. To this solution was added 2.6 ml of propylamine dropwise with stirring. Pyridine was found to be liberated which was extracted with chloroform. The aqueous solution was concentrated to dryness on a water-bath maintained at 50-60°C and the solid so obtained dried over P₄O₁₀. The yield of *n*-propylammonium tetrafluoroborate was 91%.

Six other monoalkylammonium tetrafluoroborates were prepared in a similar manner employing methyl amine (25/30%), ethyl amine (40%), isopropyl amine, *n*-butyl amine, *t*-butyl amine, benzyl amine and cyclohexyl amine.

All the monoalkylammonium tetrafluoroborates were found to be hygroscopic and were preserved over P₄O₁₀. The analytical results are given in Table 3.

Preparation of di- and tri-alkylammonium tetrafluoroborates

Dimethyl-, diethyl- and trimethyl-ammonium tetrafluoroborates were prepared by adopting the same procedure as described for monoalkylammonium tetrafluoroborates. For the other di- and tri-alkylammonium salts a modified procedure was adopted.

Pyridinium tetrafluoroborate (5 g) was taken in a beaker and cooled in an ice-bath; to it was added di-*n*-propyl amine (4.5 ml) dropwise. The reaction was instantaneous and exothermic. For

Table 3 – Preparation and Analyses of Mono-alkylammonium Tetrafluoroborate (RNH₃BF₄)

Compound prepared	Yield (%) (M.P., °C)	Found (calc.), %	
		Nitrogen	BF ₄ ⁻
CH ₃ NH ₃ BF ₄	98 (180)	11.72 (11.78)	72.24 (73.06)
C ₂ H ₅ NH ₃ BF ₄	95 (146)	10.50 (10.54)	64.98 (65.36)
<i>n</i> -C ₃ H ₇ NH ₃ BF ₄	91 (150)	9.37 (9.53)	58.53 (59.13)
<i>i</i> -C ₃ H ₇ NH ₃ BF ₄	90 (100)	9.59 (9.53)	58.39 (59.13)
<i>n</i> -C ₄ H ₉ NH ₃ BF ₄	93 (194)	8.64 (8.71)	53.09 (53.98)
<i>t</i> -C ₄ H ₉ NH ₃ BF ₄	93 (174)	8.72 (8.70)	53.68 (53.98)
C ₆ H ₁₁ NH ₃ BF ₄	94 (134)	7.44 (7.49)	45.98 (46.47)
C ₆ H ₅ CH ₂ NH ₃ BF ₄	90 (126)	7.10 (7.18)	44.28 (44.56)

about 30 min, the solution was stirred and maintained at 0-5°C. The liberated pyridine was extracted with ether, the precipitate filtered off on suction, washed well with ether till free from pyridine. The compound was dried over P₄O₁₀; yield 90%.

The other salts were prepared in a similar manner, making use of calculated amounts of amines and the prepared salts were stored over P₄O₁₀. Analytical results are given in Table 4, Table 5 gives the ¹H NMR data for the alkylammonium tetrafluoroborates.

Results and Discussion

Ammonium and alkali metal tetrafluoroborates

The analytical data and spectral data (Tables 1 and 2) indicate that the products are of high purity.

The infrared spectra of NH₄BF₄ and other alkali metal fluoroborates (Table 1) show a very strong broad absorption in the region 1100-1000 cm⁻¹ which is characteristic of the tetrafluoroborate ion and a sharp doublet in the region 515-530 cm⁻¹. The former strong band has been assigned to ν₃ (B-F stretching) and the latter doublet to ν₄ (B-F bending) of the tetrahedral BF₄ ion. The splitting of ν₄ and the appearance of the other bands are attributed to the lowering of site symmetry of the anion¹². In addition to the above absorptions, NH₄BF₄ shows two more peaks; one at 3330 cm⁻¹ and the other at 1430 cm⁻¹ which are due to the ammonium ions. The X-ray powder diffraction pattern results (Table 2) are in good agreement with the values reported in literature¹³ indicating the purity of the compounds.

Alkyl substituted ammonium tetrafluoroborates

Tables 3 and 4 indicate that yields are good and the products are of high purity. The PMR spectral data are presented in Table 5. The IR data (spectra available with the authors) for all the salts show a medium split band in the region 500-530 cm⁻¹ and a characteristic broad band in the region 1150-1000 cm⁻¹. These can be assigned (as with the alkali metal salts) to ν₃ (B-F stretching) and ν₄ (B-F bending) frequencies of the BF₄⁻ ion.

In the infrared spectra of alkylammonium tetrafluoroborates, a strong broad absorption in the region 3200-3800 cm⁻¹ is observed. This has been assigned to the merging of the N-H and C-H stretching vibrations, both of which occur in this region. In dialkylammonium salts, the N-H stretching vibrations appear in the region

Table 4 - Analytical Data of Di- and Tri-alkylammonium Tetrafluoroborates

Compounds prepared	Yield (%) (M.P., °C)	Found (calc.), %	
		Nitrogen	BF ₄ ⁻
(CH ₃) ₂ NH ₂ BF ₄	94 (220)	10.62 (10.54)	65.03 (65.36)
(C ₂ H ₅) ₂ NH ₂ BF ₄	93 (169)	8.58 (8.70)	54.09 (53.98)
(<i>n</i> -C ₃ H ₇) ₂ NH ₂ BF ₄	90 (235)	7.32 (7.40)	45.84 (45.98)
(<i>n</i> -C ₄ H ₉) ₂ NH ₂ BF ₄	88 (235)	6.28 (6.45)	39.93 (40.04)
(<i>i</i> -C ₄ H ₉) ₂ NH ₂ BF ₄	84 (235)	6.38 (6.45)	40.25 (40.04)
(C ₆ H ₅ CH ₂) ₂ NH ₂ BF ₄	85 (186)	4.90 (4.91)	30.28 (30.48)
(O)C ₄ H ₈ NH ₂ BF ₄	91 (141)	8.00 (8.01)	49.24 (49.65)
(CH ₃) ₃ NHBF ₄	90 (204)	9.50 (9.54)	59.03 (59.13)
(C ₂ H ₅) ₃ NHBF ₄	92 (106)	7.37 (7.41)	46.02 (45.97)

3160-3270 cm⁻¹. In trialkylammonium salts, the ν(N-H) and ν(C-H) appear below 3000 cm⁻¹. Several other bands in the region 2800-2300 cm⁻¹ might be due to the amine salt combination bands¹⁴. The other absorptions are due to the organic moieties present in the molecule.

The ¹H NMR spectra (DMSO-*d*₆ solvent, TMS-internal standard) (Table 5) of all the alkylammonium tetrafluoroborates identify the organic moieties. The N-H resonances were identified by deuterium exchange. In some cases, the α-protons were found to couple with the N-H protons and these couplings were found to be relieved on deuterium exchange.

It is of interest to mention that other methods so far reported do not give such high yields or purity. The methods reported for the preparation of substituted (alkyl or aryl) ammonium tetrafluoroborates are: (i) decomposing the adducts of boron trifluoride and amines¹⁵, (ii) reaction between ether solution or the amine with boron trifluoride etherate¹⁶, and (iii) by the reaction of tetrafluoroboric acid (HBF₄) and amines¹⁷⁻¹⁹. The tetrafluoroboric acid is found to be always in equilibrium with its hydrolysis products, BF₄⁻ + H₂O → [BF₃OH]⁻ + HF. Equilibrium constant is 2.8 × 10⁻³ at 25°C (ref. 20). The salts prepared by using this acid would, therefore, be associated with these impurities. The present method has the advantage of eliminating the drawbacks of the earlier methods such as the presence of difficultly removable impurities, the poor yields and

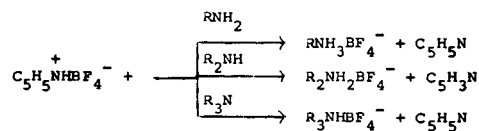
Table 5 - ^1H NMR Data of Mono-, Di- and Tri-alkylammonium Tetrafluoroborates [δ (ppm)]

$\text{CH}_3\text{NH}_3\text{BF}_4$	$\text{C}_2\text{H}_5\text{NH}_3\text{BF}_4$	$n\text{-C}_3\text{H}_7\text{NH}_3\text{BF}_4$	$i\text{-C}_3\text{H}_7\text{NH}_3\text{BF}_4$	$n\text{-C}_4\text{H}_9\text{NH}_3\text{BF}_4$
2.5 s (-CH ₃)	1.23 t (-CH ₃)	1.0 t (CH ₃)	1.3 d ($\begin{matrix} \text{CH}_3 \\ \\ - \\ \\ \text{CH}_3 \end{matrix}$)	0.9 (-CH ₃)
7.08 s (-NH ₃)	2.92 q (-CH ₂ -)	1.66 mlt ($\beta\text{-CH}_2$)	3.3 mlt (-CH<)	1.43 mlt (β and $\gamma\text{-CH}_2$)
4.21 (-NH ₃) on deuteration	7.23 b, s (-NH ₃)	2.83 t ($\alpha\text{-CH}_2$)	7.26 s (-NH ₃)	2.8 t ($\alpha\text{-CH}_2$)
	5.47 s (-NH ₃) on deuteration	6.46 s (-NH ₃)	5.56 s (-NH ₃) on deuteration	7.3 b (-NH ₃)
		4.66 s (-NH ₃) on deuteration		4.0 b (-NH ₃) on deuteration
$t\text{-C}_4\text{H}_9\text{NH}_3\text{BF}_4$	$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3\text{BF}_4$	$\text{C}_6\text{H}_{11}\text{-NH}_3\text{BF}_4$	$(\text{CH}_3)_2\text{NH}_2\text{BF}_4$	$(\text{C}_2\text{H}_5)_2\text{NH}_2\text{BF}_4$
1.33 s ($\begin{matrix} \text{CH}_3 \\ \\ \text{CH}_3 \\ \\ \text{CH}_3 \end{matrix}$)	4.01 s (-CH ₂ -) 7.4 s (C ₆ H ₅ -)	1.66 b (10 ring protons except α -proton)	2.63 s (-CH ₃) 7.7 b (-NH ₂)	1.23 t (-CH ₃) 2.96 q (-CH ₂)
7.16 s (-NH ₃)	7.56 s (-NH ₃)	2.96 mlt (α -proton)	4.53 (-NH ₂) on deuteration	7.53 b (-NH ₂)
4.5 s (-NH ₂) on deuteration		7.23 b (-NH ₃)		4.86 (-NH ₂) on deuteration
		5.16 b (-NH ₃) on deuteration		
$(n\text{-C}_3\text{H}_7)_2\text{NH}_2\text{BF}_4$	$(n\text{-C}_4\text{H}_9)_2\text{NH}_2\text{BF}_4$	$(i\text{-C}_4\text{H}_9)_2\text{NH}_2\text{BF}_4$	$(\text{O})\text{C}_4\text{H}_8\text{NH}_2\text{BF}_4$	
1.0 t (-CH ₃)	0.95 (-CH ₃)	1.0 d ($\begin{matrix} \text{CH}_3 \\ \\ - \\ \\ \text{CH}_3 \end{matrix}$)	3.16 mlt ($\text{N} \begin{matrix} \text{CH}_2 \\ / \\ \text{CH}_2 \end{matrix}$)	
1.7 mlt ($\beta\text{-CH}_2$)	1.58 mlt (β and $\gamma\text{-CH}_2$)	2.0 mlt (-CH<)	3.8 mlt ($\text{O} \begin{matrix} \text{CH}_2 \\ / \\ \text{CH}_2 \end{matrix}$)	
2.9 b ($\alpha\text{-CH}_2$ - coupled with NH ₂ protons)	2.9 t ($\alpha\text{-CH}_2$) 6.73 b (-NH ₂ -)	2.76 d (-CH ₂ -CH<)	7.63 s (-NH ₂ -)	
2.9 t (ondeuteration)	4.16 b (-NH ₂ -) on deuteration	NH absorption was not seen	4.5 s (-NH ₂ -) on deuteration	
8.06 b (-NH ₂)				
$(\text{C}_6\text{H}_5\text{CH}_2)_2\text{NH}_2\text{BF}_4$	$(\text{CH}_3)_3\text{NHF}_4$	$(\text{C}_2\text{H}_5)_3\text{NHF}_4$		
4.16 s (-CH ₂ -)	2.86 s (-CH ₃)	1.3 t (-CH ₃)		
7.43 s (C ₆ H ₅ -)	NH was not observed	3.16 mlt (-CH ₂ -) coupled with >NH		
NH ₂ absorption was not seen clearly		3.16 q (-CH ₂) on deuteration		
		NH was not observed		

s - singlet, q - quartet, d - doublet, mlt - multiplet, t - triplet, b - broad.

the necessity of employing elaborate experimental procedures. This novel procedure is simple, one-pot reaction, occurring at room temperature (25°C).

The pK_a values of the alkyl amines (8.7-11.2) employed are higher than that of pyridine (5.17) and therefore they displace pyridine from pyridinium tetrafluoroborate with great ease. The displacement reactions could be summarised in terms of the following scheme:



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