Notes

Contribution from Rocketdyne, A Division of Rockwell
International Corporation, Canoga Park, California 91303

Tetramethylammonium Salts of ClF_4^-, BrF_4^-, and BrF_6^-

William W. Wilson and Karl O. Christe*

Received March 6, 1989

Chlorine trifluoride and its ionic ClF_2^+ and ClF_4^- salts are powerful oxidizers and generally either explode with or ignite hydrocarbons and many halocarbons.[1-4] Although BrF_3 is a less violent and vigorous fluorinating agent than ClF_3, it nevertheless reacts explosively with either water or hydrocarbons.[4] Therefore, it is not surprising that previously no salts or adducts of these compounds with organic materials have been reported. Thus, the only cations known to form ClF_4^- salts were Cs^+, Rb^+, K^+, NO^+, and NO_2^+. In the case of BrF_4^-, combinations with Na^+, Ag^+, and Ba^{2+} were also known, but again no mention of salts containing organic counterions has previously been made.[1,4]

Previous reports by Meinert had suggested that BrF_5 is less reactive than BrF_3, can be handled in CH_3CN solution,[5,6] and forms stable $[N(CH_3)_4]^+BrF_6^-$ and $[N(C_2H_5)_4]^+BrF_6^-$ salts.[7] In view of the brevity of the latter report, the lack of characterizing data for the $NR_4^+BrF_6^-$ salts, and a recent comment on the hazard of BrF_5–CH_3CN solutions,[8] it was desirable to verify Meinert's $NR_4^+BrF_6^-$ synthesis and to examine whether a similar approach could possibly be applied to the syntheses of $[N(CH_3)_4]^+$ salts of BrF_4^- and ClF_4^-.

Experimental Section

Caution! Any combination of organic materials with chlorine or bromine fluorides is potentially hazardous and should be carried out only on a small scale and with adequate safety precautions including safety shields, face masks, and protective clothing and gloves.

Materials. The CH_3CN (Baker, Bio-analyzed, having a water content of 10 ppm) was stored over P_2O_5, freshly distilled prior to its use, and handled either on a vacuum line or in the drybox. The BrF_5 (Matheson) was treated with 35 atm of F_2 at 100 °C for 24 h and then purified by fractional condensation through traps kept at −64 and −95 °C, with the material retained at −95 °C being used. The $CsBrF_6$,[9,10] $CsBrF_4$,[11] $CsClF_4$,[10,12] $KClF_4$,[10] and $[N(CH_3)_4]F$[13] were prepared by literature methods.

Apparatus. Volatile halogen fluorides were handled in stainless-steel vacuum lines[14] equipped with Teflon–FEP U-traps, 316-stainless-steel bellows-seal valves, and a Heise Bourdon tube-type pressure gauge. The lines and other hardware were passivated with ClF_3 prior to their use. The CH_3CN was handled on a flamed-out Pyrex vacuum line equipped with Teflon stopcocks. Reactions were generally carried out in Teflon–FEP ampules, closed by stainless-steel valves. For the metathetical reactions, a previously described[15] apparatus was used, consisting of two Teflon–FEP U-traps interconnected through a coupling containing a porous Teflon filter. Nonvolatile materials were handled in the dry N_2 atmosphere of a glovebox.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer using the 488-nm exciting line of an Ar ion laser or the 647.1-nm line of a Kr ion laser, respectively. The ^{19}F NMR spectra of CH_3CN solutions contained in heat-sealed, 5 mm o.d. Teflon–FEP tubes (Wilmad Glass Co.) were recorded at 84.6 MHz on a Varian Model EM390 spectrometer equipped with a variable-temperature probe. X-ray diffraction patterns of the powdered samples in sealed 0.5-mm quartz capillaries were obtained by using a General Electric Model XRD-6 diffractometer, Ni-filtered Cu Kα radiation, and a 114.6 mm diameter Philips camera. DSC measurements were carried out with a Perkin-Elmer Model DSC-1B instrument using crimp-sealed aluminum pans and a heating rate of 10 °C/min.

Preparation of $[N(CH_3)_4]ClF_4$. Inside the drybox, $[N(CH_3)_4]F$ (1.779 mmol) and $CsClF_4$ (1.779 mmol) were placed into the bottom half of a prepassivated double U-tube metathesis apparatus[15] containing a Teflon-coated magnetic stirring bar. On a flamed-out glass vacuum line, dry CH_3CN (11 mL of liquid) was condensed at −196 °C into the apparatus. The mixture was allowed to warm to room temperature and was stirred for 45 min. The white precipitate was separated from the clear colorless solution by filtration through the Teflon filter using 2 atm of dry N_2 for pressurization. The CH_3CN was removed from the filtrate by pumping at 25 °C for 15 h, leaving behind 300 mg of $[N(CH_3)_4]ClF_4$ (weight calculated for 1.779 mmol of $[N(CH_3)_4]ClF_4$ = 330 mg, corresponding to a 90.7% yield), which was identified by ^{19}F NMR, infrared, and Raman spectroscopy. The white filtercake (293 mg, weight calculated for 1.779 mmol of CsF = 270 mg) consisted mainly of CsF containing about 9 mol % of $[N(CH_3)_4]ClF_4$ as an impurity.

Preparation of $[N(CH_3)_4]BrF_4$. The preparation of this material from $[N(CH_3)_4]F$ and $CsBrF_4$ was carried out exactly as that described above for $[N(CH_3)_4]ClF_4$, except for the use of only 6 mL of CH_3CN as a solvent. As a result, the amount of $[N(CH_3)_4]BrF_4$ retained on the CsF filtercake increased to about 25 mol % and the yield of isolated $[N(CH_3)_4]BrF_4$ decreased to 75%.

Preparation of $[N(CH_3)_4]BrF_6$. The preparation of this material from $[N(CH_3)_4]F$ and $CsBrF_6$ was carried out exactly as that described above for $[N(CH_3)_4]ClF_4$ with 13.5 mL of CH_3CN used as a solvent. Again, the material balance was essentially quantitative, and the yield of isolated $[N(CH_3)_4]BrF_6$ was 98%.

Results and Discussion

Syntheses of the $[N(CH_3)_4]^+$ Salts of BrF_6^-, BrF_4^-, and ClF_4^-. All three salts were prepared by metathetical reactions between $[N(CH_3)_4]F$ and the corresponding cesium polyfluorohalate salts in dry CH_3CN solution at room temperature.

$$[N(CH_3)_4]F + CsHalF_n \xrightarrow{CH_3CN} CsF\downarrow + [N(CH_3)_4]HalF_n$$

The solubility of CsF in CH_3CN is low (3.465×10^{-4} mol/L at 29.0 °C) whereas those of the $[N(CH_3)_4]HalF_n$ salts and of the starting materials are much higher. For example, the solubility of $CsClF_4$ in CH_3CN at 23.5 °C was found to be 4.915×10^{-2} mol/L and those of the $[N(CH_3)_4]HalF_n$ salts were typically within the range 0.1–0.2 mol/L. To obtain high yields of the $[N(CH_3)_4]HalF_n$ salts in the above metathetical reactions, it is, therefore, necessary to use a sufficient amount of solvent to avoid partial precipitation of the desired product.

The above metathesis based on the precipitation of CsF is similar to that previously employed by Meinert and Gross[7]

$$[N(CH_3)_4]Cl + AgBrF_6 \xrightarrow{CH_3CN} AgCl\downarrow + [N(CH_3)_4]BrF_6$$

---

(1) Stein, L. In *Halogen Chemistry*; Gutmann, V., Ed.; Academic Press: New York, 1967; Vol. 1, p 133.
(2) Christe, K. O. Unpublished observations.
(3) Brower, K. R. *J. Fluorine Chem.* **1986**, *31*, 333.
(4) Rhein, R. A.; Miles, M. H. Technical Report 6811; Naval Weapons Center: China Lake, CA, 1988.
(5) Meinert, H.; Gross, U. *Z. Chem.* **1969**, *9*, 190.
(6) Gross, U.; Meinert, H. *Z. Chem.* **1971**, *11*, 431.
(7) Meinert, H.; Gross, U. *Z. Chem.* **1971**, *11*, 469.
(8) Stein, L. *Chem. Eng. News* **1984**, *62*(28), 4.
(9) Bougon, R.; Charpin, P.; Soriano, J. *C. R. Seances Acad. Sci., Ser. C* **1971**, *272*, 565.
(10) Whitney, E. D.; MacLaren, R. O.; Fogle, C. E.; Hurley, T. J. *J. Am. Chem. Soc.* **1964**, *86*, 2583.
(11) Christe, K. O.; Schack, C. J. *Inorg. Chem.* **1970**, *9*, 1852.
(12) Christe, K. O.; Sawodny, W. *Z. Anorg. Allg. Chem.* **1970**, *374*, 306, and references cited therein.
(13) Wilson, W. W.; Christe, K. O. To be submitted for publication.
(14) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Synth.* **1986**, *24*, 5.
(15) Christe, K. O.; Wilson, W. W.; Schack, C. J.; Wilson, R. D. *Inorg. Synth.* **1986**, *24*, 44.

0020-1669/89/1328-4172$01.50/0

Table I. ^{19}F NMR Parameters for the ClF_4^-, BrF_4^-, and BrF_6^- Salts

species	chem shifts[a]	solvent	temp, °C	line width, Hz	solutes
ClF_4^-	66.8	CH_3CN	−40	16	$[N(CH_3)_4]ClF_4$
BrF_4^-	−37	CH_3CN	−40	7[b]	$[N(CH_3)_4]BrF_4$, $CsBrF_4$
BrF_6^-	94	CH_3CN	−60 to +40	80	$CsBrF_6$, $[N(CH_3)_4]BrF_6$
HF	−184	CH_3CN	25	4	HF
F^-	−73.7	CH_3CN	25	2.2	$[N(CH_3)_4]F$
	−117	H_2O	25	40	$[N(CH_3)_4]F$
HF_2^-	−145.6	CH_3CN	25	3[c]	$[N(CH_3)_4]HF_2$

[a] Chemical shifts are given in ppm with negative values being upfield from the external standard $CFCl_3$. All signals were singlets except for that for HF_2^-. [b] These signals exhibited significant line broadening with increasing temperature. [c] Doublet with J_{HF} = 122 Hz.

but avoids the disadvantages of using the costly and light sensitive silver salts.

For $[N(CH_3)_4]BrF_6$ we have also studied the use of direct syntheses from $[N(CH_3)_4]F$ and BrF_5 in either CH_3CN, $CFCl_3$, or an excess of liquid BrF_5 as a solvent.

$$[N(CH_3)_4]F + BrF_5 \xrightarrow{\text{solvent}} [N(CH_3)_4]BrF_6$$

In all cases, the conversion of $[N(CH_3)_4]F$ to its BrF_6^- salts was incomplete, requiring multiple treatments. Furthermore, $[N(CH_3)_4]BrF_4$ was always formed as a byproduct, and when BrF_5 was used as the solvent, extreme care had to be taken to avoid violent reactions or explosions. Consequently, the direct synthesis is inferior to the metathesis in CH_3CN. This is not surprising since generally anions are weaker oxidizers than their parent molecules and, therefore, attack organic compounds to a lesser extent.

Properties. The $[N(CH_3)_4^+$ salts of ClF_4^-; BrF_4^-, and BrF_6^- are white crystallinic solids that are stable at room temperature. Their thermal stabilities were determined by DSC. The $[N(CH_3)_4]BrF_4$ salt was found to be most stable. It undergoes a highly exothermic decomposition at about 257 °C and exhibits a reversible weak endotherm at 80 °C that is attributed to a phase change in the solid. The $[N(CH_3)_4]BrF_6$ salt is somewhat less stable and undergoes exothermic decomposition at about 220 °C. The higher stability of the BrF_4^- salt relative to its BrF_6^- analogue is also manifested by the fact that on storage of $[N(CH_3)_4]BrF_6$ at 35 °C for 6 months most of the BrF_6^- had been reduced, most likely by the cation, to BrF_4^-. Therefore, $[N(CH_3)_4]BrF_6$ should not be stored over longer time periods at ambient temperature. As expected, $[N(CH_3)_4]ClF_4$ is the least stable salt in this series and undergoes a highly exothermic decomposition at about 100 °C, but showed no signs of decomposition during storage at 35 °C for 6 months.

Surprisingly, $[N(CH_3)_4]ClF_4$ was found to be insensitive to shock. A sample, when crimpsealed in an aluminum pan and placed on a steel plate, could not be detonated by repeated hard blows with a hammer. When the flattened aluminum pan was cut open and water was added, the sample explosively reacted with the water, indicating that no decomposition had occurred prior to the contact with water.

^{19}F NMR Spectra. The relatively high solubility of $CsBrF_4$ and $CsBrF_6$ and of the $[N(CH_3)_4]^+$ salts of ClF_4^-, BrF_4^-, and BrF_6^- in CH_3CN offered the possibility to study their ^{19}F NMR spectra. With the exception of BrF_4O^-,[16] essentially no NMR data have previously been reported for any chlorine or bromine fluoride anions due to the lack of compatible, nonexchanging solvents. The HF and BrF_5 solvents that are commonly used for the study of the corresponding halogen fluoride cations tend to undergo rapid exchange with the anions and, therefore, could not be used.

Table II. Shift Differences (ppm) from Parent Molecules for Chlorine and Bromine Fluoride Anions and Cations

species (shift)	shift difference from parent molecule	ref
	Anions	
ClF_4^- (67)	1 upfield	a
BrF_4^- (−37)	7 upfield	a
BrF_4O^- (104)	43 upfield	16
BrF_6^- (94)	72 upfield	a
	Cations	
BrF_2O^+ (199)	52 downfield	16
BrF_4^+ (197)	31 downfield	20
ClF_2O^+ (272)	10 downfield	21
ClF_4^+ (265)	15 upfield	21
$ClF_2O_2^+$ (310)	103 upfield	21
ClF_2^+ (−23)	91 upfield	21

[a] This work.

The ^{19}F NMR spectra of CH_3CN solutions of the ClF_4^-, BrF_4^-, and BrF_4^-, and BrF_6^- salts have been recorded, and the results are summarized in Table I. The signals of ClF_4^- and BrF_4^- were narrow singlets as expected from their known[11,12,17-19] square-planar structures containing four equivalent fluorine atoms. The BrF_6^- signal was also a narrow singlet with a relatively constant line width of about 80 Hz between −60 and +40 °C.

A comparison of the chemical shifts of chlorine or bromine fluoride anions and cations with those of their parent molecules does not show uniform trends (see Table II). This suggests that a simple shielding argument, i.e. that the addition of a fluoride anion to a parent molecule should add electron density and thereby result in increased shielding whereas removal of a fluoride ion should have the opposite effect, is insufficient to explain the observed data, particularly for the chlorine fluorides. Obviously, a better understanding of the nature of the ^{19}F NMR shifts is required.

Since the ClF_4^-, BrF_4^-, and BrF_6^- signals do not exhibit any unique fine splittings, it was necessary to record the NMR spectra of the potential impurities, i.e. F^-, HF_2^-, and HF, under the same conditions (see Table I). Whereas our data for HF and HF_2^- are in excellent agreement with previous reports,[22,23] our value for F^- in CH_3CN solution is are outside the range of −114 to −160 ppm previously given[22] for F^- in different solvents. In particular, the shift of −150.6 ppm listed[22] for $[N(C_2H_5)_4]F$ in aqueous CH_3CN is difficult to reconcile with our results for $[N(CH_3)_4]F$. In our study, the chemical shift of F^- in dry CH_3CN was found to be −74 ppm. Upon addition of about 10% of water, two layers formed with the aqueous layer containing essentially all the fluoride ion with a chemical shift of −117 ppm. It thus appears that the data in ref 22 have been flawed by the presence of impurities such as HF, HF_2^-, and H_2O. The correctness of our data is also supported by a plot of $\delta(^{19}F^-)$ versus $\delta(^{35}Cl^-)$ shifts for various solvents given in a recent paper by Symons.[24] On the basis of his plot, the chemical shifts of F^- in different solvents are strongly solvent dependent and cover a range from −73 ppm for dimethyl sulfoxide to about −148 ppm for CH_3OH.

Vibrational Spectra. The infrared and Raman spectra of the solid $[N(CH_3)_4]^+$ salts of ClF_4^-, BrF_4^-, and BrF_6^- are shown in Figures 1–3. and the observed frequencies and their assignments are summarized in Table III. The observed spectra are in excellent agreement with previous reports on the separate ions and confirm the above given ionic formulations for these salts. The assignments for the $[N(CH_3)_4]^+$ cation are based on the previous work by Heyns and DeBeer[25] and Berg[26] and do not require further comment. The bands due to the anions are denoted in the figures

---

(16) Gillespie, R. J. Spekkens, P. *J. Chem. Soc., Dalton Trans.* **1976**, 2391.

(17) Popov, A. I.; Kiselev, Yu. M.; Sukhoverkhov, V. F.; Chumaevskii, N. A. *Zh. Neorg. Khim.* **1988**, *33*, 1395.

(18) Sly, W. G.; Marsh, R. E. *Acta Crystallogr.* **1957**, *10*, 378.

(19) Edwards, A. J.; Jones, G. R. *J. Chem. Soc. A* **1969**, 1936.

(20) Christe, K. O.; Sawodny, W. *Inorg. Chem.* **1973**, *12*, 2879.

(21) Christe, K. O.; Hon, J. F.; Pilipovich, D. *Inorg. Chem.* **1973**, *12*, 84.

(22) Hudlicky, M. *J. Fluorine Chem.* **1985**, *28*, 461.

(23) Martin, J. S.; Fujiwara, F. Y. *Can. J. Chem.* **1971**, *49*, 3071.

(24) Carmona, C.; Eaton, G.; Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1987**, 873.

(25) Heyns, A. M.; DeBeer, W. H. J. *Spectrochim. Acta, Part A* **1983**, *39A*, 601.

(26) Berg, R. W. *Spectrochim. Acta, Part A* **1978**, *34A*, 655.

Table III. Vibrational Data for Solid $[N(CH_3)_4]ClF_4$, $[N(CH_3)_4]BrF_4$, and $[N(CH_3)_4]BrF_6$ and Their Assignments

obsd freq, cm^{-1} (rel intens)						assgnts (point group)		
$[N(CH_3)_4]ClF_4$		$[N(CH_3)_4]BrF_4$		$[N(CH_3)_4BrF_6$				
Raman	IR	Raman	IR	Raman	IR	$HalF_4^-$ (D_{4h})	BrF_6^- (O_h)	$[N(CH_3)_4]^+$ (T_d)
	3048 m		3045 m		3048 m			$\nu_{13}(F_2)\ \nu_{as}(CH_3)$, $\nu_5(E)\ \nu_{as}(CH_3)$, $\nu_{14}(F_2)\ \nu_s(CH_3)$, $\nu_1(A_1)\ \nu_s(CH_3)$, and combination bands
3030 (1.5)		3025 (2)		3022 (3)				
2975 sh	2975 w	2980 (0.5)	2973 vw	2970 (0.5)	2970 vw			
2948 (1)		2943 (1.5)		2945 (1.6)				
2905 (0+)		2908 (0+)		2905 (0+)				
2800 (0+)		2800 (0+)		2800 (0+)				
	2581 vw		2580 vw		2583 vw			$2\nu_{17}$ ($A_1 + E + F_2$)
	2481 vw		2480 vw		2484 vw			($\nu_{17} + \nu_7$) ($F_1 + F_2$)
	1491 ms		1491 ms		1489 ms			$\nu_{15}(F_2)\ \delta_{as}(CH_3)$
1479 (2)		1478 (3)						$\nu_6(E)\ \delta_{as}(CH_3)$
1469 (3)		1462 (3)		1465 (4)				$\nu_2(A_1)\ \delta_s(CH_3)$
1414 (1)	1418 m	1411 (1.5)	1416 m	1413 (1)	1417 m			$\nu_{16}(F_2)\ \delta_s(CH_3)$
1290 (0.5)	1290 mw	1285 (0.5)	1288 mw	1285 (0.5)	1286 mw			$\nu_{17}(F_2)\ \delta_{rock}(CH_3)$
1179 (0.5)		1179 (0.6) 1169 (0.5)		1170 (1)				$\nu_7(E)\ \delta_{rock}(CH_3)$
			1050 m					
952 (6)	953 s	948 (6)	951 s	945 (6)	949 s			$\nu_{18}(F_2)\ \nu_{as}(CN_4)$
	926 w		925 w		915 w			$2\nu_{19}$ ($A_1 + E + F_2$)
760 (6)		754 (6)		750 (5)				$\nu_3(A_1)\ \nu_s(CN_4)$
755 sh		750 sh		740 sh				$2\nu_8(A_1)$
	719 w		710 w		704 w			
553 (1)								
	550 vs, br		480 vs, br			$\nu_6(E_u)\ \nu_{as}$		
508 (100)		520 (100)				$\nu_1(A_{1g})\ \nu_s$ (in phase)		
				562 (59)			$\nu_1(A_{1g})\ \nu_s$ (in phase)	
					490 vs, br		$\nu_3(F_{1u})\ \nu_{as}$	
478 sh								
458 (4)	465 w	472 (6)		488 (4) 465 sh				$\nu_{19}(F_2)\ \delta(CN_4)$
443 (1)								
				451 (100)			$\nu_2(E_g)\ \nu_s$ (out of phase)	
	425 m		315 m			$\nu_2(A_{2u})\ \delta_s$ (out of plane)		
415 (85)		448 (60)				$\nu_4(B_{2g})\ \nu_s$ (out of phase)		
375 (1)		370 (1)						$\nu_8(E)\ \delta(CN_4)$
278 (6)		240 (10)				$\nu_3(B_{1g})\ \delta_s$ (in plane)		
				239 (9)			$\nu_5(F_{2g})\ \delta_s$	
				129 (1)				
				79 (2)				

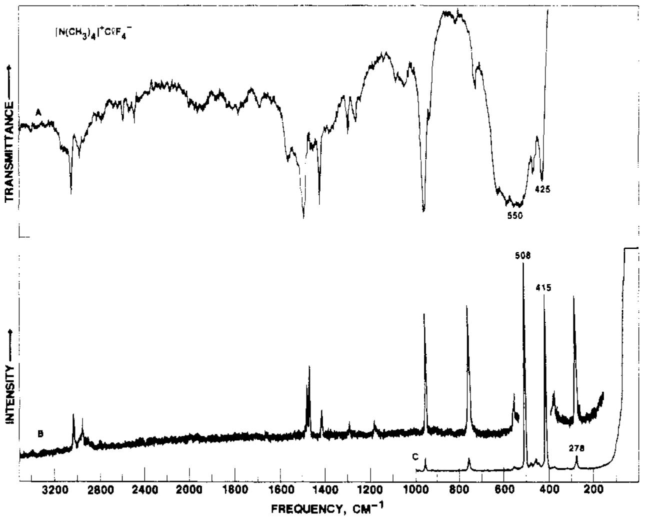

Figure 1. Vibrational spectra of solid $[N(CH_3)_4]ClF_4$: trace A, infrared spectrum as an AgCl disk; traces B and C, Raman spectra at two different sensitivity levels. The bands marked by frequency values are due to the anion.

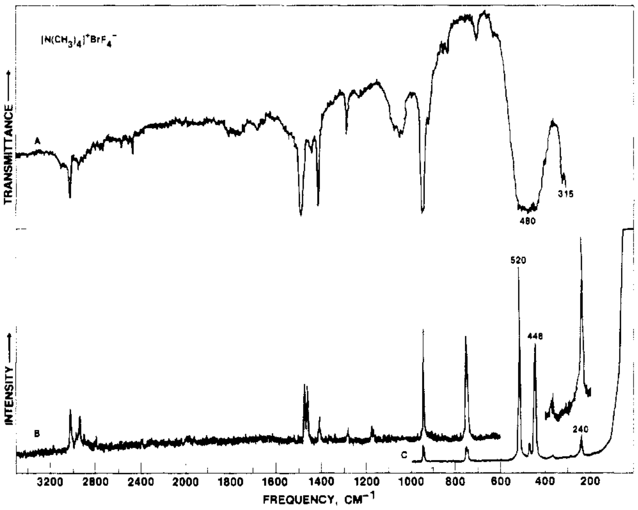

Figure 2. Vibrational spectra of solid $[N(CH_3)_4]BrF_4$.

by their frequency values and were assigned by analogy to those of their alkali-metal salts.[9,11,12,17] The fact that the observed spectra indicate no significant symmetry lowering for the anions is not surprising in view of the high symmetry of the tetramethylammonium cation.

Conclusion. The powerful oxidizer and incendiary ClF_4^- has been combined for the first time with an organic counterion. The resulting $[N(CH_3)_4]^+ClF_4^-$ salt has been isolated as a stable, nonsensitive solid. The known $[N(CH_3)_4]^+BrF_6^-$ salt and the new

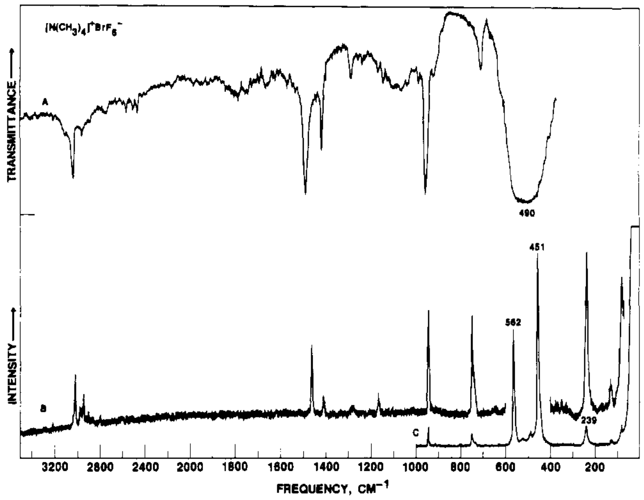

Figure 3. Vibrational spectra of solid $[N(CH_3)_4]BrF_6$.

$[N(CH_3)_4]^+BrF_4^-$ salt have also been prepared and characterized.

Acknowledgment. We are grateful to Dr. C. J. Schack and R. D. Wilson for their help and to the Air Force Astronautics Laboratory, Edwards AFB, for financial support.

Registry No. $[N(CH_3)_4]ClF_4$, 122821-59-4; $[N(CH_3)_4]F$, 373-68-2; $CsClF_4$, 15321-04-7; $[N(CH_3)_4]BrF_4$, 122821-60-7; $CsBrF_4$, 15705-88-1; $[N(CH_3)_4]BrF_6$, 35064-02-9; $CsBrF_6$, 26222-92-4.

Contribution from Rocketdyne, A Division of Rockwell
International Corporation, Canoga Park, California 91303

Anion Exchange in NF_4^+ Salts Using Graphite Salts as an Oxidizer- and Acid-Resistant Anion-Exchange Medium

Karl O. Christe* and Richard D. Wilson

Received May 19, 1989

Although a large number of NF_4^+ salts are presently known,[1] only two of these salts, NF_4SbF_6[2] and NF_4BiF_6,[3] are readily accessible by direct synthesis from NF_3, F_2, and the corresponding Lewis acid at elevated temperatures and pressures. Since the SbF_6^- and BiF_6^- anions are heavy and do not significantly contribute to the performance of these salts in applications such as NF_3–F_2 gas generators[4] and energetic formulations,[5] it is necessary to replace the SbF_6^- anion in NF_4SbF_6 by lighter and/or more energetic anions.[4] In the past, this has been achieved mainly by a metathetical exchange of the anion at low temperature in anhydrous HF or BrF_5 as a solvent.[6]

$$NF_4SbF_6 + CsBF_4 \rightarrow CsSbF_6\downarrow + NF_4BF_4 \qquad (1)$$

The main drawbacks of reaction 1 include the following: the purity of the resulting NF_4BF_4 is only about 92%, unless repeated recrystallizations from HF and BrF_5 solutions are used;[2] the yields of NF_4BF_4 are less than quantitative (typically ~80%, due to losses during the recrystallizations and hold up of mother liquor on the filter cake); and the process is a batch process that requires troublesome low-temperature filtration steps involving anhydrous HF or BrF_5 solutions. It was, therefore, desirable to develop an improved process for exchanging the anion in NF_4SbF_6, which ideally would result in quantitative yields and high purities of the desired NF_4^+ salts in a simple, one-step process under ambient conditions. In this paper we describe such a process that had been discovered in our laboratory 8 years ago but could not be reported earlier due to the classification of a patent.[7]

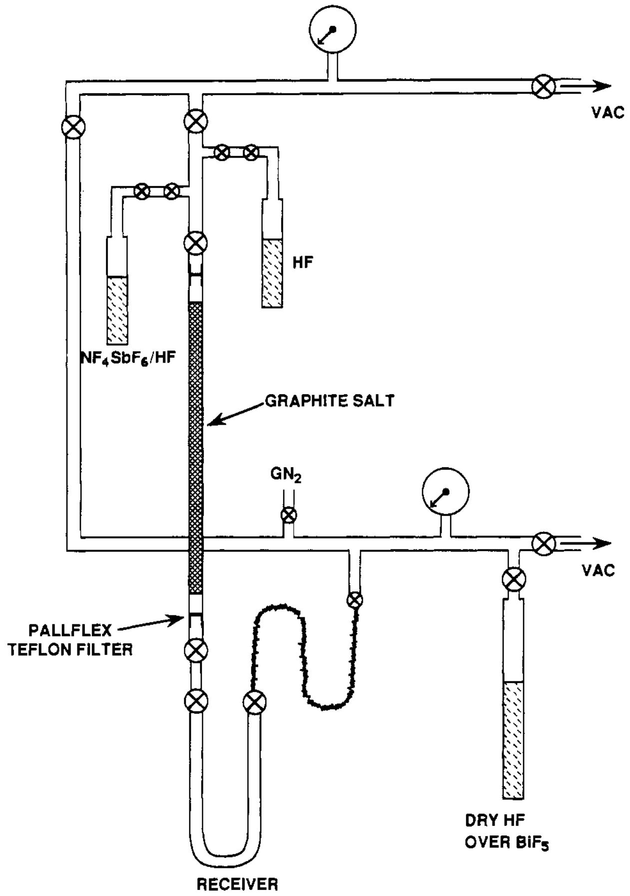

Figure 1. Apparatus used for the ion-exchange reactions between graphite salts and NF_4SbF_6.

Experimental Section

Starting Materials. Three different types of graphite were used in the course of this study. The first one consisted of spectrographic graphite (SG) electrodes, manufactured by the National Carbon Co., a Division of Union Carbide. The second one was a pyrolytic graphite (PG) slab for use in rocket nozzles, obtained from Hercules, and the third one was highly oriented pyrolytic graphite (HOPG) with a mirrorlike surface, obtained from Union Carbide by courtesy of Dr. A. Moore. All three types of graphite were ground in a mortar, classified according to particle size by the use of sieves, dried in a dynamic vacuum at 300 °C, and treated with 2 atm of F_2 pressure at room temperature for several hours prior to their use.

Hydrogen fluoride (Matheson) was dried by storage over BiF_5.[8] Arsenic pentafluoride (Ozark Mahoning), BF_3 and PF_5 (Matheson) were purified by fractional condensation prior to their use. The F_2 (Air Products) was passed through a NaF scrubber for removal of any HF. The preparations of NF_4SbF_6[6] and O_2AsF_6[9] have previously been described. The SO_2ClF (Ozark Mahoning) was pretreated at −78 °C with $O_2^+AsF_6^-$, followed by fractional condensation in a dynamic vacuum through a series of −78, −112, and −196 °C traps, with the material retained at −112 °C being used.

Caution! Anhydrous HF causes severe burns. Elemental fluorine and NF_4^+ salts are strong oxidizers and must be handled with the safety precautions previously described.[6]

Apparatus. Volatile materials were handled in stainless-steel–Teflon–FEP vacuum lines as previously described.[10] Nonvolatile materials

---

(1) For a recent review on NF_4^+ chemistry see: Nikitin, I. V.; Rosolovskii, V. Ya. *Russ. Chem. Rev.* (*Engl. Transl.*) **1985**, *54*, 426.

(2) Christe, K. O.; Schack, C. J.; Wilson, R. D. *J. Fluorine Chem.* **1976**, *8*, 541 and references cited therein.

(3) Wilson, W. W.; Christe, K. O. *J. Fluorine Chem.* **1988**, *40*, 59 and references cited therein.

(4) Christe, K. O.; Wilson, W. W. *Inorg. Chem.* **1982**, *21*, 4113 and references cited therein.

(5) Christe, K. O. U.S. Pat. 4,207,124, 1980.

(6) Christe, K. O.; Wilson, W. W.; Schack, C. J.; Wilson, R. D. *Inorg. Synth.* **1986**, *24*, 39.

(7) Christe, K. O. U.S. Pat. 4,683,129, 1987.

(8) Christe, K. O.; Wilson, W. W.; Schack, C. J. *J. Fluorine Chem.* **1978**, *11*, 71.

(9) Shamir, J.; Binenboym, J. *Inorg. Chim. Acta* **1968**, *2*, 37.

0020-1669/89/1328-4175$01.50/0