

Received: September 28, 1983; accepted: December 5, 1983

NOVEL AMMONIUM HEXAFLUOROARSENATE SALTS FROM REACTION OF $(CF_3)_2NH$, $CF_3N(OCF_3)H$, $CF_3N(OCF_3)_2H$, CF_3NHF AND SF_5NHF WITH THE STRONG ACID HF/AsF_5 .

DARRYL D. DESMARTEAU, WILLIAM Y. LAM, BRIAN A. O'BRIEN AND SHI-CHING CHANG

Department of Chemistry, Clemson University, Clemson, South Carolina 29631 (USA)

SUMMARY

Reactions of the fluorinated amines $(CF_3)_2NH$, $CF_3N(OCF_3)H$, $CF_3N(OCF_3)_2H$, CF_3NHF and SF_5NHF with the strong acid HF/AsF_5 form the corresponding ammonium salts $R_f^1R_f^2NH_2^+AsF_6^-$ and $R_fNHF_2^+AsF_6^-$ in high yield. [$R_f^1=CF_3$, $R_f^2=CF_3$, CF_3O , $(CF_3)_2CFO$; $R_f=CF_3$, SF_5] The colorless crystalline solids are stable for prolonged periods at 22°C in sealed FEP containers. They have dissociation pressures at 22°C ranging from ~5 torr ($R_fNHF_2^+AsF_6^-$) to ~50 torr [$CF_3N(OCF_3)_2H_2^+AsF_6^-$]. ^{19}F NMR and Raman spectroscopy were used to identify the compounds.

INTRODUCTION

Fluoroammonium salts of the type NFH_3^+ , $NH_2F_2^+$ and NF_4^+ are well known and $NH_2F_2^+$ can be prepared directly from NF_2H by protonation in superacid media HF/MF_5 ($M=As, Sb$) [2,3]. On the other hand, NF_3 cannot be converted to NF_3H^+ in the same way. Similarly, it is well known that fluorocarbon amines such as $(CF_3)_3N$ and $(CF_3)_2NH$ have very low basicity, but there do not appear to have been any attempts to protonate these and related compounds in superacid media.

During investigations of the chemistry of $\text{CF}_2=\text{NF}$ [4], we attempted to form a cation of the imine by removal of a fluoride ion with AsF_5 . Instead of the desired salt, $\text{CF}_2=\text{NF}$ and AsF_5 formed a weak molecular complex at lower temperature which was completely dissociated at 22°C . While attempting to characterize this complex by NMR, we inadvertently prepared $\text{CF}_3\text{NFH}_2^+$ in fluorosulfuric acid solution. This result prompted us to investigate the obvious question as to whether fluorocarbon amines would form stable ammonium salts. Using several fluorocarbon amines available from on-going research, we report here the facile formation of ammonium hexafluoroarsenate salts by reaction of $(\text{CF}_3)_2\text{NH}$, $\text{CF}_3\text{N}(\text{OCF}_3)\text{H}$, $\text{CF}_3\text{N}[\text{OCF}(\text{CF}_3)_2]$, CF_3NFH and SF_5NHF with the strong acid HF/AsF_5 .

EXPERIMENTAL

General

All volatile compounds were handled in glass or stainless steel vacuum systems equipped with glass-Teflon and severe service stainless steel valves, respectively. Amounts of materials were measured by PVT measurements or direct weighing. Pressures were measured with a Wallace and Tiernan differential pressure gauge, series 1500. Temperatures were measured with a digital-indicating iron-constantan thermocouple.

Infrared spectra were taken on a Perkin-Elmer 1430 instrument with a 3600 Data Station. Spectra involving HF were taken with 5 cm stainless steel or 10 cm Teflon-Kel-F cells fitted with AgCl windows. Other spectra were taken in 10 cm glass cells fitted with KCl or AgCl windows. ^{19}F NMR spectra were taken on Varian XL-100-15, JEOL C-60-HL or JEOL FX-90Q spectrometers with external CFCl_3 as a reference. Chemical shifts are in ppm relative to external CFCl_3 , with high field shifts having a negative sign. Solutions

involving HF were contained in 4 mm OD thin wall Kel-F tubes inserted in a standard 5 mm glass NMR tube. The Kel-F tubes were filled by vacuum transfer and sealed before inserting them into the glass NMR tube. Raman spectra were taken using thin wall FEP tubes for sample containers, utilizing a Spex 14018 double monochromator with photon-counting detection. Excitation was via the 514.5-nm line of an Ar⁺ ion laser.

Reagents

The amines (CF₃)₂NH [5], CF₃N(OCF₃)H, CF₃N[OCF(CF₃)₂]H, CF₃NHF [6] and SF₅NHF [7], and the imines CF₂=NF [4] and SF₄=NF [7] were prepared by literature methods. Hydrogen fluoride was obtained from Air Products Inc. and was purified by distillation. Arsenic pentafluoride was prepared by heating reagent grade As₂O₅ with excess fluorine at 200° in a Monel bomb.

Synthesis of ammonium salts

In a typical reaction, 1 ml of HF was distilled into a 10 ml FEP reactor at -196°C, followed by 3.0 mmol of AsF₅. The mixture was warmed to 22°C to form a solution of AsF₅ in HF. The reactor was then cooled to -196° and perfluoromethanimine (3.0 mmol) was added. The mixture was warmed to 22°C and let stand for 1 h. It was then cooled to -70°C and pumped on through an FEP U-trap. Pumping to constant weight at this temperature resulted in a fine white crystalline solid corresponding to 94% yield of CF₃NH₂⁺AsF₆⁻ based on the starting CF₂=NF. Similar results were obtained starting with CF₃NHF. Other salts were prepared from the amines using similar procedures. When pumped on at -78°C to remove excess HF, the yields were quantitative within experimental error. All the salts sublimed readily at 22°C in sealed FEP containers to form large transparent crystals.

$\text{CF}_3^{\text{A}}\text{NF}_2^{\text{B}}\text{H}^+\text{AsF}_6^-$: $P_{22^\circ\text{C}} \approx 7$ torr; NMR (HF, -34°C) A -74.5 (d), B -92.2 (q); $J_{\text{AB}} = 17.5$ Hz; Raman(s) 1291(w), 1200(w), 961(w), 773(vw), 667(s), 639(w), 493(w), 451(s), 442(sh), 394(m), 340(w), 288(vw) cm^{-1} .

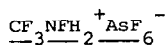
$\text{F}_4^{\text{A}}\text{SF}_4^{\text{B}}\text{NF}_2^{\text{X}}\text{H}^+\text{AsF}_6^-$: $P_{22^\circ\text{C}} \approx 7$ torr; NMR (HF, -52°C) A 52(m), B 51.7(m), X -68.9 (br, s); $J_{\text{AB}} \approx 150$, J_{BX} and J_{AX} not readily determined; Raman(s) 1064(m), 753(s), 692(s), 666(m), 564(w), 521(w), 449(m), 379(w), 371(m), 119(w), 79(w) cm^{-1} .

$\text{CF}_3\text{N}(\text{OCF}_3)_2\text{H}^+\text{AsF}_6^-$: $P_{22^\circ\text{C}} \approx 50$ torr; NMR not determined; Raman (s, -196°C) 1245(vw), 1185(vw), 1162(vw), 1054(w), 909(s), 773(w), 709(s), 690(sh), 685(s), 574(m), 333(w), 297(w), 221(w), 192(vw) cm^{-1} .

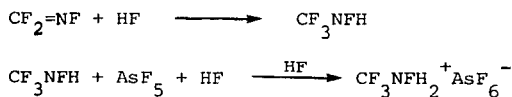
$(\text{CF}_3^{\text{A}})_2\text{NH}_2^+\text{AsF}_6^-$: $P_{22^\circ\text{C}} \approx 20$ torr; NMR (HF, -28°C) A -58.3 (s); Raman not determined.

$\text{CF}_3\text{N}[\text{OCF}(\text{CF}_3)]_2\text{H}^+\text{AsF}_6^-$: $P_{22^\circ\text{C}} \approx 10$ torr; other data not determined.

RESULTS AND DISCUSSION



The formation of fluorotrifluoromethylammonium hexafluoroarsenate, $\text{CF}_3\text{NFH}_2^+\text{AsF}_6^-$, occurs in high yield on reaction of either $\text{CF}_2=\text{NF}$ or CF_3NFH with a stoichiometric amount of AsF_5 in excess liquid HF at or below 22°C . Excess AsF_5 can also be employed with similar results.



Removal of the excess HF at -70°C gives a nearly quantitative yield of the ammonium salt. The HF can also be removed near 0°C with a resulting lower yield of the salt. At this temperature, the salt

already has a measurable dissociation pressure and some of the starting amine and AsF_5 are removed along with HF. At 22°C , the dissociation pressure is ≈ 7 torr and the IR spectrum of the equilibrium vapor is that of CF_3NFH and AsF_5 . At this pressure the HF is not visible, but its presence is readily discernible by its attack on glass forming SiF_4 .

Support for the structure of $\text{CF}_3\text{NFH}_2^+\text{AsF}_6^-$ comes from the Raman and ^{19}F nmr spectra. Raman spectra were only of marginal quality because of strong fluorescence in all samples under a variety of conditions, including low temperature Kel-F, FEP or Pyrex sample containers, HF solutions and varying the wavelength of the laser excitation. Nevertheless, sufficient quality spectra could be obtained to readily assign ν_1 of AsF_6^- at 667 cm^{-1} as the most intense band in the spectrum of the solid. This value compares favorably with related AsF_6^- salts of NF_2H_2^+ and NF_4^+ [8]. * Other observed bands are reasonable for the salt but no effort was made to assign them.

The strongest support for the cation $\text{CF}_3\text{NFH}_2^+$ comes from its ^{19}F NMR. In HF solution, $\text{CF}_3\text{NFH}_2^+\text{AsF}_6^-$ shows a doublet for the CF_3 (-74.5) and a quartet for the fluorine on nitrogen (-92.2) with $^3J_{\text{FF}} = 17.5\text{ Hz}$. Cooling to as low as -70°C did not result in any observable J_{HF} coupling. This is in contrast to the free amine in CFCl_3 , where a doublet of doublets is observed for the CF_3 (-74.2) and a doublet of quartets for the NF (-126.7), with $^3J_{\text{FF}} = 26.7$, $^2J_{\text{H-NF}} = 9.5$ and $^3J_{\text{H-CF}_3} = 9.5\text{ Hz}$ [6]. Clearly, $\text{CF}_3\text{NFH}_2^+$ is exchanging protons with the solvent HF and the concentrations of both $\text{CF}_3\text{NFH}_2^+$

* The ν_1 band for $\text{NF}_2\text{H}_2^+\text{AsF}_6^-$ occurs at 714 and 674 cm^{-1} and a frequency of 667 cm^{-1} for $\text{CF}_3\text{NFH}_2^+\text{AsF}_6^-$ is very reasonable. See ref. 2 and references therein.

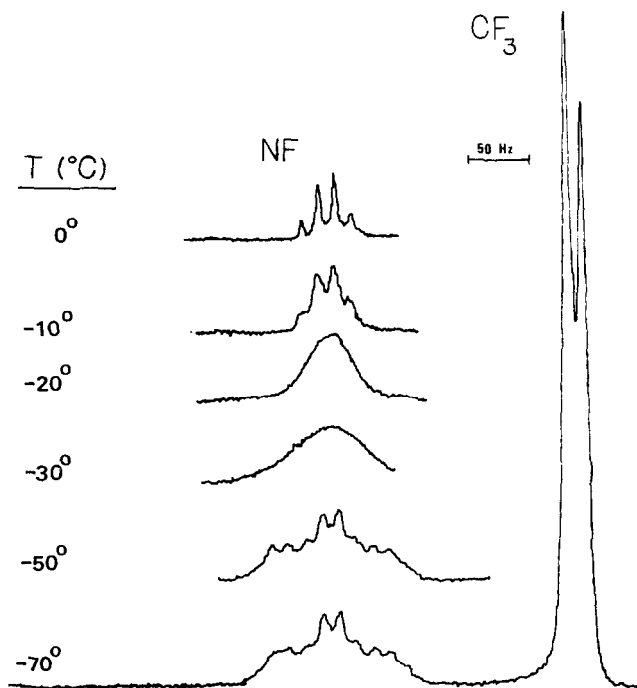


Fig. 1. ^{19}F NMR OF $\text{CF}_3\text{NH}_2^+\text{AsF}_6^-$ in HOSO_2F . 1000 Hz sweep width. Relative area $\text{NF}:\text{CF}_3=1.0:3.0$. CF_3 signal shows little change with temperature.

and CF_3NHF may be comparable*. The latter conclusion is supported by the ^{19}F NMR of $\text{CF}_3\text{NH}_2^+\text{AsF}_6^-$ in fluorosulfuric acid. The temperature dependent spectrum is shown in Figure 1. The doublet of relative area 3 due to the CF_3 (-69) and the triplet of quartets of relative area 1, due to the NF (-65) can be explained by $^3J_{\text{FF}} = 14$ and $^2J_{\text{H-NF}} \approx 42$ Hz**. The large change in the chemical shift of the NF group, and the observable $^2J_{\text{HF}}$ coupling, clearly imply that the species is

* Proton exchange of $\text{NH}_2\text{F}_2^+\text{AsF}_6^-$ in HF could be suppressed by addition of excess AsF_5 to the solution (ref. 2). We attempted this with $\text{CF}_3\text{NH}_2^+\text{AsF}_6^-$ without success.

** In a sample of $\text{CF}_3\text{NH}_2^+\text{AsF}_6^-$ in HOSO_2F at 30°C , the AsF_6^- anion is visible as a very broad signal near -63 ppm.

predominantly the $\text{CF}_3\text{NFH}_2^+$ cation in HOSO_2F and its exchange of protons with the solvent is slow on the NMR time scale at lower temperatures. This is in contrast to HF as a solvent where the exchange is fast and where CF_3NHF is probably a major species. If the latter is true, the chemical shift of the NF group in HF might be expected somewhere between that of pure CF_3NHF (-126.7) in CFC_2Cl_3 and $\text{CF}_3\text{NFH}_2^+$ (-65) in HOSO_2F . Fortuitously, it is found at -92, very near the average of the two values.

Other examples of fluorinated ammonium salts

Other ammonium salts can be similarly formed from $(\text{CF}_3)_2\text{NH}$, $\text{CF}_3\text{N}(\text{OCF}_3)\text{H}$, $\text{CF}_3\text{N}[\text{OCF}(\text{CF}_3)_2]\text{H}$ and $\text{SF}_4=\text{NF}$ or SF_5NHF . The least stable salt was observed with $\text{CF}_3\text{N}(\text{OCF}_3)\text{H}$, which exhibited the highest dissociation pressure at 22°C. The stability of $\text{SF}_5\text{NFH}_2^+\text{AsF}_6^-$ was similar to that of $\text{CF}_3\text{NFH}_2^+\text{AsF}_6^-$. The Raman spectra for $\text{CF}_3\text{N}(\text{OCF}_3)_2\text{H}_2^+\text{AsF}_6^-$ and $\text{SF}_5\text{NFH}_2^+\text{AsF}_6^-$ both contained strong bands assignable to ν_1 of AsF_6^- at 690 and/or 685, and 692 and/or 666 cm^{-1} , respectively. The ^{19}F NMR spectra of $(\text{CF}_3)_2\text{NH}_2^+\text{AsF}_6^-$ and $\text{SF}_5\text{NFH}_2^+\text{AsF}_6^-$ in HF solution are similar to that of $\text{CF}_3\text{NFH}_2^+\text{AsF}_6^-$ in HF. The $^3\text{J}_{\text{HF}}$ coupling readily observed in $(\text{CF}_3)_2\text{NH}$ is absent in the solution of the ammonium salt and the chemical shift of CF_3 groups is only slightly different from that of the free amine (-58.3 vs. -57.1). Similarly, $^2\text{J}_{\text{HF}}$ is not observable for $\text{SF}_5\text{NFH}_2^+\text{AsF}_6^-$. As with CF_3NHF , a substantial change is observed for the NF chemical shift in $\text{SF}_5\text{NFH}_2^+$ (-68.9) vs. pure SF_5NHF (-74.7). The shift in the axial S-F fluorines of SF_5 group is even larger (52 vs. 64.6), whereas the equatorial fluorines show little change (51.7 vs. 52.6).

CONCLUSION

The facile formation of fluorinated alkyammonium hexafluoroarsenate salts has been demonstrated by reaction of fluorinated amines with AsF_5/HF . While only a few examples have been prepared it seems clear that a variety of amines of the type R_fNFH and $\text{R}_f^1\text{R}_f^2\text{NF}$ will react similarly. It would be of interest in the future to determine if related compounds such as R_fNF_2 , $(\text{R}_f)_2\text{NF}$ and $(\text{R}_f)_3\text{N}$ will also form ammonium salts under similar conditions.

ACKNOWLEDGEMENTS

The financial support of this research by the U.S. Army Research Office (DAAG 29-82-KO188) and the National Science Foundation (CHE-8217217) is gratefully acknowledged. DDD also acknowledges the Alexander von Humboldt Foundation for a fellowship during part of this research and Professor K. Seppelt for helpful assistance.

REFERENCES

- 1 V. Grakauskas, A. H. Remanick and K. Baum, *J. Am. Chem. Soc.*, 90 (1968) 3839.
- 2 K. O. Christe, *Inorg. Chem.*, 14 (1975) 2821.
- 3 K. O. Christe, G. P. Guertin and A. E. Pavlath, *Inorg. Nucl. Chem. Lett.*, 2 (1966) 83. W. E. Tubberg, R. T. Rewick, R. S. Stringham and M. E. Hill, *ibid*, 2 (1966) 79.
- 4 A. Sekiya and D. D. DesMarteau, *J. Org. Chem.*, 46 (1981) 1277.
- 5 J. A. Young, S. N. Tsoukalas and R. D. Dresdner, *J. Am. Chem. Soc.*, 80 (1958) 3604.
- 6 A. Sekiya and D. D. DesMarteau, *J. Fluorine Chem.*, 15 (1980) 183.
- 7 D. D. DesMarteau, H. H. Eysel, H. Oberhammer and H. Günther, *Inorg. Chem.*, 21 (1982) 1607.
- 8 K. O. Christe and D. Pilipovich, *Inorg. Chem.*, 10 (1971) 2803. ν_1 of AsF_6^- in $\text{NF}_4^+\text{AsF}_6^-$ = 685 cm^{-1} .