

On the instability of salts containing the trifluoride anion

Karl O. Christe¹

Rocketdyne Division of Rockwell International Corporation, 6633 Canoga Ave., Canoga Park, CA 91309, USA

Received 30 March 1994; accepted 8 May 1994

Abstract

Elemental fluorine does not form a stable $[\text{N}(\text{CH}_3)_4]^+ \text{F}_3^-$ salt with solutions of $\text{N}(\text{CH}_3)_4\text{F}$ in either CH_3CN at -31°C or CHF_3 at -142°C .

Keywords: Salt instability; Trifluoride anion; IR spectroscopy

1. Introduction

The trifluoride anion, F_3^- , has been the subject of numerous theoretical calculations [1–4] ranging from SCF (Self Consistent Field) to CCSDT (Coupled Cluster Single Double Triple). The most sophisticated methods [3] duplicated well the vibrational frequencies observed by Ault and Andrews [5] for the Cs^+F_3^- and Rb^+F_3^- ion pairs in argon matrices at 15 K. The best estimates for the stability of F_3^- indicate that F_3^- is thermodynamically more stable than $(\text{F}_2 + \text{F}^-)$ by about 110 kJ mol^{-1} [3]. This value is comparable to those found for Br_3^- ($D_0 = 105 \text{ kJ mol}^{-1}$) and I_3^- ($D_0 = 109 \text{ kJ mol}^{-1}$) and larger than that of Cl_3^- ($D_0 = 75 \text{ kJ mol}^{-1}$). Since the Cl_3^- , Br_3^- and I_3^- anions are all well known, both in solution and in the solid state, and anhydrous $[\text{N}(\text{CH}_3)_4]\text{F}$ provides a source of soluble fluoride anions in the presence of a large and oxidizer-resistant cation [6], it was interesting to examine whether $[\text{N}(\text{CH}_3)_4]^+ \text{F}_3^-$ can be prepared on a macroscopic scale using experimental techniques which have recently provided novel anions such as XeF_5^- [7], IOF_6^- [8], $[\text{TeOF}_6]^{2-}$ [9], PF_4^- [10] and ClF_6^- [11].

2. Experimental details

The possibility of preparing $[\text{N}(\text{CH}_3)_4]^+ \text{F}_3^-$ was examined by pressurizing solutions of $[\text{N}(\text{CH}_3)_4]^+ \text{F}^-$ with up to 500 Torr of F_2 in either CH_3CN at -31°C or CHF_3 at -142°C . (**Caution! These experiments**

are potentially hazardous and appropriate safety precautions must be used at all times.) The resulting mixtures were gently agitated for about 2 h, followed by removal of all material which was volatile at these low temperatures in a dynamic vacuum. The solid residues were then allowed to warm in the closed Teflon–FEP reaction vessels to room temperature. No fluorine evolution was observed during these warm-up steps. The non-volatile residues were characterized from the observed material balances and their IR vibrational spectra.

3. Results and discussion

In the case of the CHF_3 solution, the low-temperature product was the known $[\text{N}(\text{CH}_3)_4]^+ \text{F}^- \cdot n\text{CHF}_3$ adduct [6] which decomposed at higher temperature to $[\text{N}(\text{CH}_3)_4]\text{F}$ and CHF_3 . In the case of the CH_3CN solution, the solid product was $[\text{N}(\text{CH}_3)_4]^+ \text{HF}_2^-$ formed by slow attack of the solvent by both F_2 and F^- [12]. The absence of an oxidizing species in the solid products was also demonstrated by their inability to liberate iodine from aqueous KI solutions.

These results demonstrate that, despite the large and strongly stabilizing $[\text{N}(\text{CH}_3)_4]^+$ counterion, F_2 does not form a stable F_3^- salt with $[\text{N}(\text{CH}_3)_4]^+ \text{F}^-$ in either CH_3CN or CHF_3 solutions at low temperatures. The failure of F_3^- formation under the above conditions, despite the bond energy of F_2 and the dissociation energy of F_3^- being comparable to those of I_2 and I_3^- , respectively, is surprising and may be attributed to the high solvation energies of F^- in highly polar

¹ Present address: Hughes STX, Phillips Laboratory, Edwards Air Force Base, CA 93524-7001, USA.

solvents such as CHF_3 or CH_3CN . Reactions between $[\text{N}(\text{CH}_3)_4]\text{F}$ and F_2 in the absence of a solvent were not studied due to the experimental difficulties expected in controlling the reaction.

Acknowledgement

The author thanks the US Army Research Office and the US Air Force Phillips Laboratory for financial support of this work.

References

- [1] P.A. Cahill, C.E. Dykstra and J.C. Martin, *J. Am. Chem. Soc.*, **107** (1985) 6359.
- [2] J.J. Novoa, F. Mota and S. Alvarez, *J. Phys. Chem.*, **92** (1988) 6561.
- [3] G.L. Heard, C.J. Marsden and G.E. Scuseria, *J. Phys. Chem.*, **96** (1992) 4359.
- [4] C. Sosa, C. Lee, G. Fitzgerald and R.A. Eades, *Chem. Phys. Lett.*, **211** (1993) 265.
- [5] B.S. Ault and L. Andrews, *Inorg. Chem.*, **16** (1977) 2024; B.S. Ault and L. Andrews, *J. Am. Chem. Soc.*, **98** (1976) 1591.
- [6] K.O. Christe, W.W. Wilson, R.D. Wilson, R. Bau and J. Feng, *J. Am. Chem. Soc.*, **112** (1990) 7619.
- [7] K.O. Christe, E.C. Curtis, D.A. Dixon, H.P. Mercier, J.C.P. Sanders and G.J. Schrobilgen, *J. Am. Chem. Soc.*, **113** (1991) 3351.
- [8] K.O. Christe, D.A. Dixon, A.R. Mahjoub, H.P.A. Mercier, J.C.P. Sanders, K. Seppelt, G.J. Schrobilgen and W.W. Wilson, *J. Am. Chem. Soc.*, **115** (1993) 2696.
- [9] K.O. Christe, D.A. Dixon, J.C.P. Sanders, G.J. Schrobilgen and W.W. Wilson, *Inorg. Chem.*, **32** (1993) 4089.
- [10] K.O. Christe, D.A. Dixon, H.P.A. Mercier, J.C.P. Sanders, G.J. Schrobilgen and W.W. Wilson, *J. Am. Chem. Soc.*, **33** (1994) 4911.
- [11] K.O. Christe, W.W. Wilson, R.V. Chirakal, J.C.P. Sanders and G.J. Schrobilgen, *Inorg. Chem.*, **29** (1990) 3506.
- [12] W.W. Wilson, K.O. Christe, J. Feng and R. Bau, *Can. J. Chem.*, **67** (1989) 1898.