

Received: January 19, 1983; accepted: March 9, 1983

THERMOCHEMISTRY OF NF_4^+ SALTS. ON THE ENTHALPY OF FORMATION OF NF_4XeF_7 AND THE $\text{NF}_4\text{SbF}_6\text{-BrF}_3$ SYSTEM

K.O. CHRISTE^a, W.W. WILSON^a, R.D. WILSON^a, R. BOUGON^b and T. BUI HUY^b

^aRocketdyne Division of Rockwell International, Canoga Park, CA 91304 (USA)

^bCentre d'Etudes Nucléaires de Saclay, 91191 Gif-sur-Yvette Cedex (France)

SUMMARY

The thermal decomposition of NF_4XeF_7 was studied by differential scanning calorimetry. From the observed enthalpy of decomposition, a value of -491 kJ mol^{-1} was calculated for $\Delta H_f^\circ(\text{NF}_4\text{XeF}_7(\text{s}))$. The reaction of NF_4^+ salts with BrF_3 , previously suggested [1] for the determination of more precise thermochemical values for NF_4^+ salts by solution calorimetry, was shown to be infeasible.

INTRODUCTION

In a previous paper [2] thermochemical data were summarized for NF_4BF_4 , NF_4PF_6 , NF_4AsF_6 , NF_4SbF_6 , NF_4GeF_5 and $(\text{NF}_4)_2\text{GeF}_6$. In this paper we would like to report thermochemical data for the recently synthesized [3] NF_4XeF_7 which is of particular interest due to its exceptionally high energy content. Furthermore, we would like to comment on several suggestions, recently made by Woolf [1], concerning the thermochemistry of NF_4^+ salts.

EXPERIMENTAL

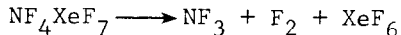
The synthesis of NF_4XeF_7 [3] and the DSC method [2] have previously been described. Based on its elemental analysis [3] the purity of the NF_4XeF_7 sample used in this study was 98.0 weight percent with a total of two percent of NF_4SbF_6 and CsSbF_6

being present as impurities. Since these impurities are thermally much more stable [4] than NF_4XeF_7 [3], they did not interfere with the DSC measurements, and a simple 2 percent correction of the starting weights was made.

The reaction of NF_4SbF_6 [5] with BrF_3 (The Matheson Company) was carried out in a well-passivated (with ClF_3) Teflon FEP ampule connected to a 314-stainless steel Teflon FEP vacuum system. The NF_4SbF_6 was treated with a tenfold excess of BrF_3 at 25°C for 2 hours. The volatile products were separated by fractional condensation and consisted of mainly unreacted BrF_3 and a small amount of HF and NF_3 . No evidence for the formation of either BrF_5 or F_2 was observed. The solid residue had changed only little in weight and based on its Raman spectrum consisted mainly of NF_4SbF_6 , a small amount of Br_2^+ and possibly some BrF_2^+ salts.

RESULTS AND DISCUSSION

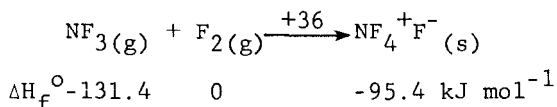
Enthalpies of Decomposition and Formation of NF_4XeF_7 In a previous study [3] it was shown that the thermal decomposition of NF_4XeF_7 proceeds according to



Although $(\text{NF}_4)_2\text{XeF}_8$ is the logical intermediate in this decomposition, this compound could only be isolated by selective laser photolysis [3]. The observation of a shoulder at 107°C on the main decomposition endotherm of NF_4XeF_7 (onset at 80°C) supports a two step decomposition mechanism for NF_4XeF_7 and suggests the formation of $(\text{NF}_4)_2\text{XeF}_8$ as an intermediate. Unfortunately, a large enough sample of pure $(\text{NF}_4)_2\text{XeF}_8$ was not available to measure the decomposition enthalpy of the second step separately. For the overall decomposition enthalpy of NF_4XeF_7 a value $\Delta H_{\text{dec}} = 64.6 \pm 5 \text{ kJ mol}^{-1}$ (1σ) was found. From the known enthalpies of formation of NF_3 [6] and XeF_6 [7] the enthalpy of formation of NF_4XeF_7 is calculated as $\Delta H_{\text{f}}^{\circ}(\text{NF}_4\text{XeF}_7(\text{s})) = -490.7 \text{ kJ mol}^{-1}$. A comparison of this value with those previously found [2] for a series of NF_4^+ salts containing other complex fluoro anions clearly demonstrates that NF_4XeF_7 is by far the most energetic of these salts.

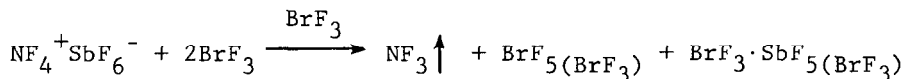
Comments on the Paper by Woolf In a recent paper by Woolf [1] the interesting observation was made that the experimentally determined enthalpies of formation of several NF_4^+ salts [2] closely correspond to those estimated for the corresponding NO_2^+ salts [1]. Furthermore, it was extrapolated that this relationship for salts with anion dominated lattices should also hold for the cation dominated lattice salts NF_4^+F^- and NO_2^+F^- , deriving the enthalpy of formation of NF_4^+F^- from an estimate for NO_2^+F^- [1]. Criticizing the admittedly substantial uncertainties in the known experimental data [2], Woolf preferred his values derived from the same data, but extended by estimates and extrapolations. In our opinion, this is unwarranted.

In spite of the above criticism, it is most gratifying that Woolf's estimated value of -91 kJ mol^{-1} for the enthalpy of formation of solid NF_4^+F^- [1] is almost identical to that (-95 kJ mol^{-1}) derived from our previous data [2]



Unfortunately, the commentary in [1] could easily be misinterpreted. After listing an exothermic value of -91 kJ mol^{-1} for the enthalpy of formation of NF_4^+F^- , reference is made [1] to "the previous prediction of instability" of this compound. Obviously, in both papers [1,2] almost identical exothermic values are obtained for the enthalpy of formation of solid NF_4^+F^- . However, as stressed in [2], solid NF_4^+F^- is unstable with respect to decomposition to NF_3 and F_2 by about 36 kJ mol^{-1} .

In [1], solvolysis of NF_4^+ salts in BrF_3 according to



was suggested as a method of obtaining more precise thermochemical values for NF_4^+ salts, and a heat of reaction of about 70 kJ mol^{-1} was anticipated for this reaction. A study of the $\text{NF}_4\text{SbF}_6\text{-BrF}_3$ system carried out in our laboratory shows that this reaction does not proceed as postulated and therefore is of no practical

usefulness. No BrF_5 formation was observed, and the evolution of some NF_3 , accompanied by some Br_2^+ and HF formation, is indicative of experimental difficulties with undesired side reactions, even in well-passivated Teflon-stainless steel equipment. The discrepancy between the predicted [1] 70 kJ mol^{-1} exothermicity and the observed unreactivity of the above system might be attributed to the previous neglect of taking the strong association of liquid BrF_3 into account. If the left side of the equation is corrected for ΔH_{vap} of BrF_3 ($42.84 \text{ kJ mol}^{-1}$) [8], the heat of reaction becomes endothermic by about 15 kJ mol^{-1} and agrees with the observed lack of reactivity.

ACKNOWLEDGEMENTS

The authors are indebted to the Office of Naval Research, the Army Research Office and la Direction des Recherches Etudes et Techniques for financial support, and to Drs. C. J. Schack and L. R. Grant for helpful discussions.

REFERENCES

- 1 A. A. Woolf, J. Fluorine Chem., 20 (1982) 627.
- 2 R. Bougon, T. Bui Huy, J. Burgess, K. O. Christe and R. D. Peacock, J. Fluorine Chem., 19 (1982) 263.
- 3 K. O. Christe and W. W. Wilson, Inorg. Chem., in press.
- 4 K. O. Christe, R. D. Wilson and I. B. Goldberg, Inorg. Chem., 18, (1979) 2572.
- 5 W. W. Wilson and K. O. Christe, J. Fluorine Chem., 15 (1980), 83, and references cited therein.
- 6 'JANAF Interim Thermochemical Tables', The Dow Chemical Company, Midland, Michigan, 1965 and subsequent revisions.
- 7 B. Weinstock, E. E. Weaver and C. P. Knop, Inorg. Chem., 5 (1966) 2189.
- 8 G. D. Oliver and J. W. Grisard, J. Amer. Chem. Soc., 74 (1952) 2705.