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SYNTHESIS AND PROPERTIES OF $(NF_4)_2SiF_6$ AND INTERACTION OF SiF_4 WITH ANHYDROUS HF AND $CsHF_2$

WILLIAM W. WILSON and KARL O. CHRISTE

Rocketdyne, a Division of Rockwell International
Canoga Park, Calif. 91304 (U.S.A.)

SUMMARY

The scope of the metathetical process for the production of NF_4^+ salts from HF solutions was extended to the synthesis of salts derived from Lewis acids which are weaker than the HF solvent. The new salt $(NF_4)_2SiF_6$ was prepared by this process and was characterized. The solubility of SiF_4 in anhydrous HF and the reversibility of the $Cs_2SiF_6 + 2HF \rightarrow 2CsHF_2 + SiF_4$ reaction were demonstrated.

INTRODUCTION

Highly energetic NF_4^+ salts containing multiply charged light anions are of significant interest for solid propellant NF_3-F_2 gas generators [1] and high detonation pressure explosives[2]. Whereas NF_4^+ salts containing triply charged anions are unknown, the following NF_4^+ salts containing doubly charged anions have been prepared: $(NF_4)_2GeF_6$ [3], $(NF_4)_2SnF_6$[4], $(NF_4)_2TiF_6$ [5], $(NF_4)_2NiF_6$[6], and $(NF_4)_2MnF_6$[7].

Since the fourth main group elements Sn and Ge are known to form stable $(NF_4)_2MF_6$ salts [3,4], the synthesis of the more energetic $(NF_4)_2SiF_6$ salt seemed also possible. However, previous attempts were unsuccessful to prepare an NF_4^+ salt derived from SiF_4 by either direct methods, such as low-temperature uv-photolysis [3], or by indirect methods, such as a standard metathesis between NF_4SbF_6 and Cs_2SiF_6 in anhydrous HF solution. The metathetical approach failed because anhydrous HF displaces SiF_4 from hexafluorosilicates[8] according to

$$M_2SiF_6 + 2HF \rightarrow 2MHF_2 + SiF_4 \qquad (1)$$

Since recent studies [9] in our laboratory had shown that under suitable reaction conditions even very weak Lewis acids, such as WF_6, UF_6 or XeF_6, can form stable NF_4^+ salts, an extension of this method to SiF_4 was investigated.

In connection with this study previous reports [8] were reexamined that SiF_4 is insoluble in and does not react with liquid anhydrous HF, a seemingly surprising behavior in view of the well established existence of H_2SiF_6 in aqueous HF solution.

EXPERIMENTAL

Apparatus

Volatile materials used in this work were handled in a stainless steel-Teflon FEP vacuum line. The line and other hardware used were well passivated with ClF_3 and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox. Metathetical reactions were carried out in HF solution using an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter [4]. Thermal decomposition measurements were carried out in a previously described [10] sapphire reactor.

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 Company). Spectra of gases were obtained by using a Teflon cell of 5 cm path length equipped with AgCl windows.

Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line of an Ar-ion laser and Claassen filter [11] for the elimination of Plasma lines. Sealed glass, Teflon FEP, or Kel-F tubes were used as sample containers in the transverse-viewing transverse-excitation mode. Lines due to the Teflon or Kel-F sample tubes were suppressed by the use of a metal mask.

Elemental analyses were carried out as previously described [12].

Materials

Literature methods were used for the syntheses of NF_4SbF_6 [13] and NF_4HF_2 solutions in HF [14]. Hydrogen fluoride (Matheson) was dried by storage over BiF_5 to remove the H_2O [15]. Silicon tetrafluoride (Matheson) was used as received. Cesium fluoride (KBI) was dried by fusion in a platinum crucible and ground in the drybox.

Interaction of SiF_4 with Anhydrous HF

Anhydrous HF (80 mmol) was condensed into a sapphire tube equipped with a metal valve and a pressure transducer (Validyne). The tube was cooled to -78°C and briefly pressurized with 997 torr of SiF_4. The value was quickly closed and during a 5 minute time period the pressure inside the tube dropped to 320 torr. The tube was pressurized again briefly with SiF_4 to 902 torr, and after closing the valve the pressure inside the tube gradually decreased during the next ten minutes to 509 torr. When the sapphire tube was warmed from -78° to 25°C, the pressure inside the tube increased to 1472 torr. For no interaction or solubility of SiF_4 in HF, the amount of added SiF_4 (3.50 mmol) should have resulted in a total pressure of 2675 torr. A Raman spectrum of the liquid phase in the sapphire tube at 25° showed only bands due to HF and SiF_4. An infrared spectrum of a mixture of HF and SiF_4 in the gas phase also showed only the bands characteristic for HF and SiF_4.

Preparation of Cs_2SiF_6 from CsF and SiF_4 in HF

Dry CsF (33.4 mmol) was loaded into a 50 ml Telfon tube containing a Teflon coated magnetic stirring bar. Anhydrous HF (316 mmol) was added to the tube on the vacuum line at -196°C. The tube was warmed to -78°C and the CsF was dissolved in the HF. The tube was cooled again to -196°C and SiF_4 (37.0 mmol) was added. The mixture was allowed to warm up to ambient temperature with stirring. The material volatile at 25°C was pumped off, separated by fractional condensation through -126° and -196°C traps, and consisted of SiF_4 (34.9 mmol) and HF. The residue consisted of a mushy solid and the tube had gained 1.696 g in weight. This residue was pressurized for 2.5 hours with 720 torr of SiF_4 at 25°C which resulted in an exothermic reactior and the formation of a white crystalline solid. The material volatile at 25°C was pumped off and consisted of HF and unreacted SiF_4. The white solid residue (6.7 g, weight calcd for 16.7 mmol of Cs_2SiF_6 6.8 g) was shown by infrared and Raman spectroscopy to be Cs_2SiF_6 [16], and did not exhibit any bands due to SiF_5^- [17], HF_2^- or any HF adducts [14]. A third treatment of the solid with SiF_4 did not result in any further weight uptake, HF evolution or change in the spectra of the solid.

Preparation of $(NF_4)_2SiF_6$.

A mixture of CsF (29.1 mmol) and NF_4SbF_6 (29.17 mmol) was loaded in the drybox into one half of a prepassivated Teflon double U metathesis apparatus. Dry HF (20 ml liquid) was added on the vacuum line and the mixture was stirred for 15 minutes at 25°C. After cooling the apparatus to -78°C, it was inverted and the NF_4HF_2 solution was filtered into the other half of the apparatus. Most of the HF solvent was pumped off during warm-up towards 0°C until the first signs of decomposition of NF_4HF_2 were noted. The resulting residue was cooled to -196° and SiF_4 (32.7 mmol) was added. The mixture was allowed to warm to ambient temperature while providing a 912 ml ullage in the vacuum line. During warm-up of the apparatus the SiF_4 evaporated first and upon melting of the $NF_4HF_2 \cdot nHF$ phase a significant reduction in the SiF_4 pressure was noted, resulting in a final pressure of 400 torr. A clear colorless solution was obtained with no sign of solid formation. The material volatile at 0°C was pumped off, separated by fractional condensation through -210° and -126°C traps, and consisted of SiF_4 (22.6 mmol) and HF (75 mmol). The residue, a white fluffy solid, was treated at 25°C with 400 torr of SiF_4 (15.6 mmol) for 24 hours. The volatile material was pumped off at 24°C for 3 hours and consisted of SiF_4 (13.2 mmol) and HF (14 mmol). The white solid residue was treated one more time at 25°C with SiF_4 (17.4 mmol) for 14 hours. The materials volatile at 25°C were pumped off and consisted of SiF_4 (16.7 mmol) and HF (0.7 mmol). Since the vibrational spectra of the solid residue still showed the presence of HF type material, the solid was transferred to a sapphire tube and heated in a dynamic vacuum at 50°C for a total of 28 hours until no further HF evolution was noted. A total of 9 mmol of HF, but only traces of NF_3 and SiF_4 were collected during this pyrolysis. The white solid residue (3.759 g, 80% yield) was shown by vibrational spectroscopy to consist mainly of $(NF_4)_2SiF_6$ with small amounts of SbF_6^- as the only detectable impurity. Based on its elemental analysis, the product had the following composition (weight %): $(NF_4)_2SiF_6$, 95.5; $CsSbF_6$, 2.2; NF_4SbF_6, 2.3 Anal. Calcd: NF_3, 42.6; Cs, 0.79; Si, 8.3; Sb, 1.6. Found: NF_3, 42.6; Cs, 0.78; Si, 8.3; Sb, 1.6.

The filter cake from the metathetical preparation of the NF_4HF_2 solution consisted of 11.1 g of $CsSbF_6$ (weight calcd for 29.1 mmol of $CsSbF_6$ 10.7 g), containing small amounts of $(NF_4)_2SiF_6$, formed by hang-up of some mother liquor on the filter cake and its subsequent conversion to $(NF_4)_2SiF_6$ during pressurization of the apparatus with SiF_4.

Thermal Decomposition of $(NF_4)_2SiF_6$

The thermal decomposition of $(NF_4)_2SiF_6$ in a constant-volume sapphire reactor was studied by total pressure measurements using a Validyne pressure transducer and a strip chart recorder. In order to minimize the effect of changes in the sample size during a given experiment, the largest feasible sample (1.55 g) and the smallest available reactor volume (27.8 mL) were used. In this manner, less than 0.4 percent of the sample was decomposed in any given experiment. Analysis of the gaseous decomposition products showed NF_3, F_2 and SiF_4 in a 2.0:2.0:1.0 mol ratio.

RESULTS AND DISCUSSION

Interaction of SiF_4 with HF and $CsHF_2$

In agreement with previous reports [8], a large excess of anhydrous HF was found to quantitatively displace SiF_4 from Cs_2SiF_6

$$Cs_2SiF_6 + 2HF \xrightarrow{HF} 2CsHF_2 + SiF_4 \qquad (2)$$

However, experiments using $CsHF_2$ and a large excess of SiF_4 showed that reaction (2) is actually an equilibrium which can be shifted all the way to the left by a large excess of SiF_4 and removal of the evolved HF. During these experiments it was also noted that, contrary to previous literature reports [8], SiF_4 exhibited a pronounced solubility in anhydrous HF. This observation was confirmed in a study of the binary HF-SiF_4 system at -78° and 25°C. Infrared spectra of a mixture of gaseous HF and SiF_4 and Raman spectra of liquid HF pressurized with two atmospheres of SiF_4 at 25°C showed only the presence of bands due to HF and SiF_4, but no evidence for H_2SiF_6. It therefore appears that under the given conditions SiF_4 dissolves in liquid HF, but does not form H_2SiF_6 to an easily observable extent.

Synthesis of $(NF_4)_2SiF_6$

Based on the above observations for the $CsHF_2$-SiF_4 system, the synthesis of $(NF_4)_2SiF_6$ wassuccessfully carried out by first preparing a solution of NF_4HF_2 in HF according to

$$NF_4SbF_6 + CsF \xrightarrow[-78^{o}C]{HF} CsSbF_6\downarrow + NF_4HF_2 \qquad (3)$$

followed by removal of as much HF as possible from the system without decomposing NF_4HF_2, and finally repeatedly pressurizing the resulting residue with SiF_4 and pumping off any displaced HF

$$2NF_4HF_2\cdot nHF + SiF_4 \longrightarrow (NF_4)_2SiF_6 + 2(n+1)HF \qquad (4)$$

The yield of $(NF_4)_2SiF_6$ (based on the limiting reagent CsF) was 80 mol percent, with the lost materials being principally due to hang up of mother liquor on the $CsSbF_6$ filter cake during reaction (3). The purity of the product was 95.5 mol percent which is typical for similar metathetical reactions [9, 18]. Purification by recrystallization from either HF or BrF_5 solution was not possible owing to displacement of SiF_4 by HF and low solubility in BrF_5.

Contrary to $(NF_4)_2GeF_6$, for which treatment with an excess of GeF_4 resulted in NF_4GeF_5 formation [3]

$$(NF_4)_2GeF_6 + GeF_4 \rightarrow 2\ NF_4GeF_5 \tag{5}$$

$(NF_4)_2SiF_6$ when treated with an excess of SiF_4, did not exhibit any tendency to form a stable NF_4SiF_5 salt. This reluctance of SiF_4 to form a stable NF_4SiF_5 salt might also account for the failure to obtain NF_4SiF_5 by low-temperature uv-photolysis of NF_3-F_2-SiF_4 mixtures [3].

Properties of $(NF_4)_2SiF_6$

$(NF_4)_2SiF_6$ is a white crystalline solid stable at ambient temperature. It slowly decomposes at 90°C according to

$$(NF_4)_2SiF_6 \rightarrow 2NF_3 + 2F_2 + SiF_4 \tag{6}$$

Its rate of decomposition was studied by total-pressure measurements at 88.3°C and 99.3°C. For all experiments, plots of log pressure versus log time resulted in a straight line with a slope corresponding to a 1.12 fractional reaction order. Assuming x to be the amount of $(NF_4)_2SiF_6$ at any time, the rate of decomposition equals

$$\frac{-dx}{dt} = kx^{1.12} \tag{7}$$

Substituting x in this equation by $x_o - \frac{PV}{5RT}$ where V is the reactor volume and x_o the amount of $(NF_4)_2SiF_6$ at the beginning of the experiment, (7) becomes

$$\frac{V}{5RT}\ \frac{dP}{dt} = k(x_o - \frac{PV}{5RT})^{1.12} \tag{8}$$

and

$$k = \frac{V}{5RT(x_o - \frac{PV}{5RT})^{1.12}}\ \frac{dP}{dt} \tag{9}$$

From (9) and the observed dP/dt decomposition rates at a given decomposition pressure P the following global kinetic constants were calculated, k(88.3°C)=

$1.03\text{X}10^{-7}$ $\text{mol}^{-0.12}\text{sec}^{-1}$ and $k(99.3^{o}\text{C}) = 3.08\text{X}10^{-7}$ $\text{mol}^{-0.12}\text{sec}^{-1}$. From the Arrhenius relation, a global decomposition activation energy E = 26.6 kcal mol^{-1} was obtained which compares favorably with the corresponding value of 36.6 kcal mol^{-1} previously obtained [10] for the considerably more stable NF_4BF_4 salt.

The ionic structure of $(NF_4)_2SiF_6$ was established by the infrared and Raman spectra of the solid. The observed spectra are shown in Figure 1, and the assignment of the bands to NF_4^+ and SiF_6^{2-} is summarized in Table 1. The splittings observed for some of the degenerate modes and violation of some of the selection rules indicate that the actual site symmetries of NF_4^+ and SiF_6^{2-} in the crystal are actually lower than T_d and O_h, respectively, which were used for simplicity in Table 1.

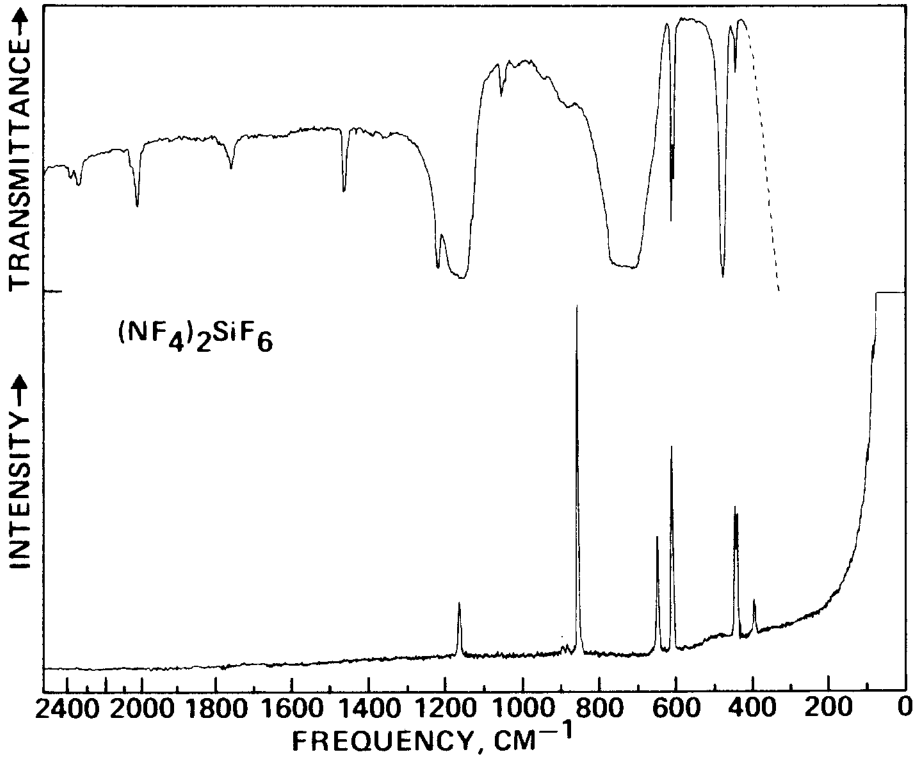

Fig. 1. Infrared and Raman Spectra of Solid $(NF_4)_2SiF_6$.
The broken line indicates absorption due to the AgCl window material.

TABLE I

Vibrational Spectra of Solid $(NF_4)_2SiF_6$

obsd freq, cm^{-1}, and rel intens[a]		assignment (point group)[b]	
IR	RA	$NF_4^+(T_d)$	$SiF_6^{2-}(O_h)$
2350 sh 2310 vw		$2\nu_3(A_1+E+F_2)$	
2010 w		$\nu_1+\nu_3(F_2)$	
1760 vw		$\nu_3+\nu_4(A_1+E+F_2)$	
1468 w		$\nu_1+\nu_4(F_2)$	
1223 mw		$2\nu_4(A_1+E+F_2)$	
1165 vs	1164 (1.5)	$\nu_3(F_2)$	
1060 vw 1050 sh		$\nu_2+\nu_4(F_1+F_2)$	
890	895(0+) 885(0+)	$2\nu_2(A_1+A_2+E)$	
	859(10)	$\nu_1(A_1)$	
735 vs, br			$\nu_3(F_{1u})$
	649(3.2)		$\nu_1(A_{1g})$
614 m 609 mw	611(5.8)	$\nu_4(F_2)$	
478 s			$\nu_4(F_{1u})$
448 w	447 441 (3.8)	$\nu_2(E)$	$\nu_2(E_g)$
	398(1.0)		$\nu_5(F_{2g})$

(a) Uncorrected Raman intensities.

(b) The splitting observed for $\nu_4(F_2)$ indicates that the actual site symmetry of NF_4^+ is lower than T_d.

CONCLUSION

The scope of the metathetical NF_4^+ salt process in HF solution has been extended to the synthesis of salts, derived from Lewis acids which are weaker than the HF solvent. This modified process has been demonstrated for the synthesis of $(NF_4)_2SiF_6$, a new salt not accessible by previously known direct [3] or indirect [15,19] methods.

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REFERENCES

1 K. O. Christe, R. D. Wilson, and C. J. Schack, Inorg. Chem., 16, 937 (1977) and references cited therein.

2 K. O. Christe, U. S. Patent 4,207,124 (1980).

3 K. O. Christe, C. J. Schack, and R. D. Wilson, Inorg. Chem., 15, 1275 (1976).

4 K. O. Christe, C. J. Schack, and R. D. Wilson, Inorg. Chem., 16, 849 (1977).

5 K. O. Christe and C. J. Schack, Inorg. Chem., 16, 353 (1977).

6 K. O. Christe, Inorg. Chem., 16, 2238 (1977).

7 K. O. Christe, W. W. Wilson, and R. D. Wilson, Inorg. Chem., 19, 3254 (1980).

8 I. G. Ryss, 'The Chemistry of Fluorine and its Inorganic Compounds,' AEC-Translat. -3927, page 370 (1960).

9 W. W. Wilson and K. O. Christe, unpublished results.

10 K. O. Christe, R. D. Wilson, and I. B. Goldberg, Inorg. Chem., 18, 2572 (1979).

11 H. H. Claassen, H. Selig, and J. Shamir, J. Appl. Spectrosc., 23, 8 (1969).

12 R. Rushworth, C. J. Schack, W. W. Wilson, and K. O. Christe, Anal. Chem., 53, 845 (1981).

13 K. O. Christe, C. J. Schack, and R. D. Wilson, J. Fluorine Chem., 8, 541 (1976).

14 K. O. Christe, W. W. Wilson, and R. D. Wilson, Inorg. Chem., 19, 1494 (1980).

15 K. O. Christe, W. W. Wilson, and C. J. Schack, J. Fluorine Chem., 11, 71 (1978).

16 H. Siebert, 'Anwendungen der Schwingungsspektroskopie in der Anorganishe Chemie' Springer-Verlag, Berlin and New York (1966).

17 H. C. Clark and K. R. Dixon, Chem. Commun., 717 (1967); H. C. Clark, K. R. Dixon, and J. G. Nicolson, Inorg. Chem., 8, 450 (1969).

18 W. W. Wilson, R. D. Wilson, and K. O. Christe, J. Inorg. Nucl. Chem., 43, 1551 (1981).

19 K. O. Christe, C. J. Schack, and R. D. Wilson, J. Fluorine Chem., 8, 541 (1976).