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THE LOW TEMPERATURE INFRARED SPECTRUM OF THIAZYL FLUORIDE AND THE ADDITION COMPOUNDS OF THIAZYL FLUORIDE WITH BORON TRIFLUORIDE, PHOSPHORUS PENTAFLUORIDE AND ARSENIC PENTAFLUORIDE

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SUMMARY

The low temperature infrared spectra of the solid addition compounds of thiazyl fluoride, NSF, with the Lewis acids  $\text{BF}_3$ ,  $\text{PF}_5$ , and  $\text{AsF}_5$  were interpreted in terms of ionic compounds containing the thiazyl cation,  $(\text{NS})^+$ . The low temperature infrared spectrum of thiazyl fluoride itself was indicative of an unionized form in the solid state.

INTRODUCTION

Emken reported the existence of the thiazyl cation,  $(\text{NS})^+$ , in explaining the significant shift to a higher wave number of the N-S stretching vibration in  $\text{NSCl}_{(s)}$  ( $1397 \text{ cm}^{-1}$ ) as compared to that in  $\text{NSCl}_{(g)}$  ( $1324 \text{ cm}^{-1}$ ) [1]. He proposed the shift to be the result of the ionization of  $\text{NSCl}_{(g)}$  to  $(\text{NS})^+\text{Cl}^-$  ions in the solid state. Glemser and Koch prepared the thiazyl cation by reacting NSF with  $\text{AsF}_5$  and  $\text{SbF}_5$  [2,3]. The Raman spectra of these adducts suggested the formulation  $(\text{NS})^+(\text{XF}_6)^-$ , X=As or Sb.

This work investigates the gas and solid state infrared spectra of thiazyl fluoride, NSF. The observed infrared shift for the N-S vibration in  $\text{NSF}_{(g)}$  versus  $\text{NSF}_{(s)}$  was small, indicating little or no change in the N-S force constant of NSF in the solid state. The addition compounds of NSF, with the Lewis acids  $\text{BF}_3$  [4],  $\text{PF}_5$ , and  $\text{AsF}_5$  [2,3] were also studied. The preparation and infrared spectra of these compounds suggest they can be formalized as ionic compounds and can be expressed as  $(\text{NS})^+(\text{MF}_x)^-(\text{MF}_x^- = \text{BF}_4^-, \text{PF}_6^-, \text{AsF}_6^-)$ . Hitherto no infrared spectra of  $\text{NSF} \cdot \text{BF}_3$ , and  $\text{NSF} \cdot \text{PF}_5$ , or a low temperature infrared spectra of any of the above compounds have been reported.

## EXPERIMENTAL

Materials

N-Fluoroformyliminosulfur difluoride,  $F_2SNOF$ , was prepared using the procedure suggested by Clifford and Kobayashi [5]. Mercury(II) fluoride (Ozark Mahoning) was used directly from the container. The color was light cream to white indicating the absence of  $HgO$ . Bis(imidosulfur difluoride)mercury(II),  $Hg(NSF_2)_2$ , was prepared using the procedure of Glemser, Mews, and Roesky [6]. Boron trifluoride (Baker), arsenic pentafluoride (Ozark Mahoning) and phosphorus pentafluoride (Matheson) were used directly from the cylinders.

Apparatus

A glass-metal vacuum system was employed in the manipulation of volatile materials which are sensitive to air and moisture. The metal portion of the system consisted of a Heise-Monel Bourden tube vacuum gauge connected to the glass portion of the vacuum line with 1/4-inch Monel tubing. All joints and stopcocks were lubricated with Fluorolube G.R.-90 (Fisher Scientific Co.).

Infrared Spectra

Infrared spectra were studied using a Perkin-Elmer model 521 spectrophotometer (a reproducibility of  $\pm 2 \text{ cm}^{-1}$  was obtained throughout the range studied). Gaseous samples were investigated in a 10-cm glass cell fitted with sodium chloride windows. The spectra of  $NSF_{(s)}$  and the solid adducts  $NSF \cdot BF_3_{(s)}$ ,  $NSF \cdot PF_5_{(s)}$ , and  $NSF \cdot AsF_5_{(s)}$  were studied in a low temperature cell [1,7]. A copper block, connected to a cold finger and fitted with a KBr window, was cooled with liquid nitrogen. The cell was attached to the vacuum line and  $NSF_{(g)}$  or the dissociated adduct was introduced into the cell; contact with the liquid nitrogen-cooled center window formed a thin film. The cell was then mounted in the infrared spectrophotometer and the spectrum was taken.

## Preparation

Thiazyl fluoride,  $\text{NSF}_{(g)}$ , was prepared by placing a hot water bath around a reaction vessel containing  $\text{Hg}(\text{NSF}_2)_2$  while the vessel was connected to the vacuum line and under reduced pressure [6,8]. Thiazyl fluoride was prepared only as needed since it readily polymerizes. The adducts of NSF with  $\text{AsF}_5$ ,  $\text{BF}_3$ , and  $\text{PF}_5$  were formed by direct contact of NSF with the respective Lewis acid [2,3,4]. Thiazyl fluoride and an excess of the appropriate acid were condensed into a glass vessel at  $-195^\circ$ . The reactor was warmed to  $-23^\circ$  to promote contact and reaction, followed by cooling to  $-63^\circ$ . At that point, the excess volatile components were removed by vacuum transfer leaving an off-white ( $\text{NSF}\cdot\text{BF}_3$ ) or yellow ( $\text{NSF}\cdot\text{PF}_5$ ,  $\text{NSF}\cdot\text{AsF}_5$ ) crystalline solid.

## Properties

### (a) NSF

Thiazyl fluoride gas at room temperature and low pressure displayed the infrared spectrum shown in Figure 1. The low temperature spectrum obtained for  $\text{NSF}_{(s)}$  is also illustrated in Figure 1. Assignments are detailed in Table 1 [9,10,11].

TABLE 1

Infrared absorption position of gaseous and solid NSF

Compound	$\text{cm}^{-1}$	Assignment [10,11]	Other bands
NSF (gas)	1372	$\nu_1$	{1255, 905, 709} ( $\text{SOF}_2$ )
	642	$\nu_2$	{1030} ( $\text{SiF}_4$ )
	366 [9,10]	$\nu_3$	
NSF (solid)	1380	$\nu_1$	1305?
	588	$\nu_2$	
	372	$\nu_3$	

(b) NSF·BF<sub>3</sub>

Thiazyl fluoride (1.2 mmol) when mixed with BF<sub>3</sub> (2.5 mmol) consumed 1.11 mmol of BF<sub>3</sub> indicating a product mole ratio, NSF·BF<sub>3</sub>, of 1.08:1. A low pressure infrared spectrum of the volatiles removed at -63° produced peaks characteristic of only BF<sub>3</sub>(g). A molecular weight of 66.50 was determined from vapor density measurements of the volatiles above a sample of solid adduct at room temperature. The calculated value for a 1:1 mixture of NSF to BF<sub>3</sub> is 66.44. The low temperature infrared spectrum recorded for NSF·BF<sub>3</sub>(s) is shown in Figure 1. Assignments are listed in Table 2. A low pressure infrared spectrum of the volatiles produced from the dissociation of the solid adduct at room temperature showed peaks characteristic of only NSF(g) and BF<sub>3</sub>(g). Attempts to measure the equilibrium dissociation pressure of the adduct, in the metal section of the vacuum line, failed to provide reproducible data.

(c) NSF·PF<sub>5</sub>

Thiazyl fluoride (4.0 mmol) contacted with PF<sub>5</sub> (8.0 mmol) consumed 3.91 mmol of PF<sub>5</sub> giving a product mole ratio, NSF·PF<sub>5</sub>, of 1.02:1. The low pressure infrared spectrum of the volatiles removed depicted peaks characteristic of only PF<sub>5</sub>(g). The recorded low temperature infrared spectrum for NSF·PF<sub>5</sub>(s) is shown in Figure 1. Assignments are given in Table 2. Equilibrium dissociation measurements of the adduct produced erratic data.

(d) NSF·AsF<sub>5</sub>

Thiazyl fluoride (5.0 mmol) contacted with AsF<sub>5</sub> (5.5 mmol) consumed 4.68 mmol of AsF<sub>5</sub> giving a product mole ratio, NSF·AsF<sub>5</sub>, of 1.07:1. The low temperature spectrum obtained for NSF·AsF<sub>5</sub>(s) is shown in Figure 1. Assignments are detailed in Table 2.

## DISCUSSION

The infrared spectrum of gaseous NSCl has previously been investigated [1]. The three fundamental vibrations,  $\nu_1$  (NS stretch),  $\nu_2$  (S-Cl stretch) and  $\nu_3$  (bending) were directly observed at 1324.0, 417.8, and 271 cm<sup>-1</sup>, respectively. Nitrogen, sulfur and chlorine isotopes were used to verify the assignments. In addition, the infrared spectrum of solid films of NSCl on various substrates cooled with liquid nitrogen has been investigated [1]. The investigation showed the existence of two forms of the

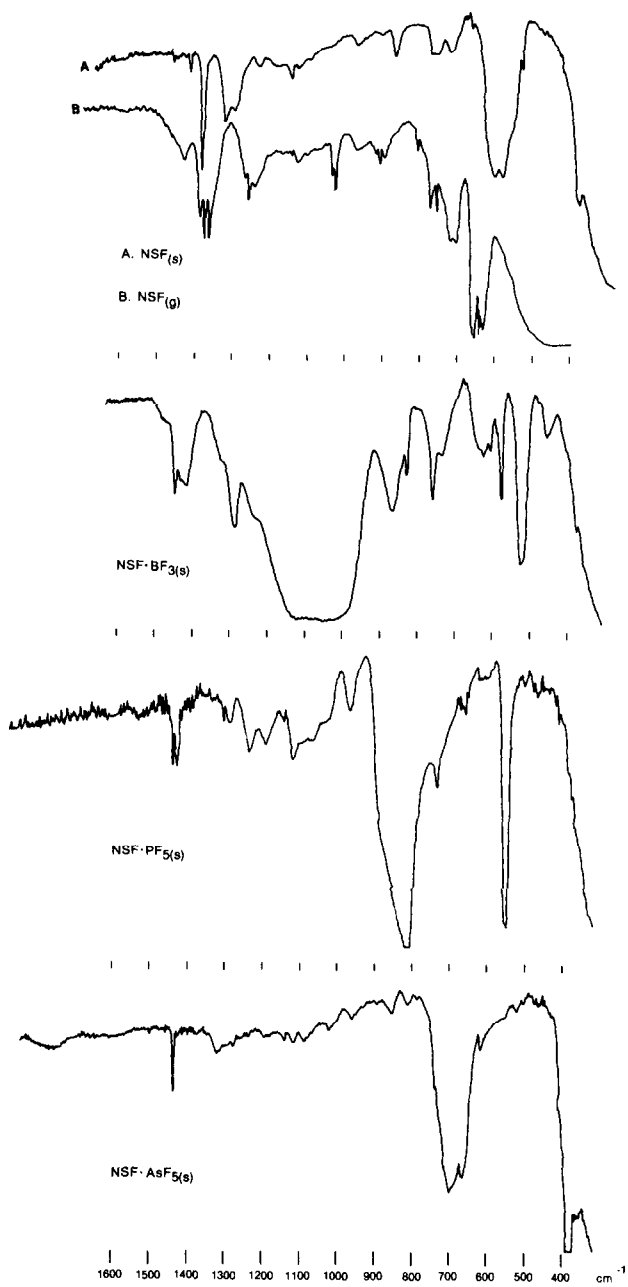


Fig. 1. Infrared spectra of NSF and NSF adducts.

TABLE 2

Infrared frequencies and assignments for  $\text{NSF}\cdot\text{BF}_3(\text{s})$ ,  $\text{NSF}\cdot\text{PF}_5(\text{s})$  and  $\text{NSF}\cdot\text{AsF}_5(\text{s})$

$\text{NSF}\cdot\text{BF}_3(\text{s})$ $\text{cm}^{-1}$	$\text{NSF}\cdot\text{PF}_5(\text{s})$ $\text{cm}^{-1}$	$\text{NSF}\cdot\text{AsF}_5(\text{s})$ $\text{cm}^{-1}$	Assignment
1443 m	1443 m	1442 m	$\text{NS}^+[1,2,3,]$
1060 vs			$\text{BF}_4^- [7,12,13]$
	820 vs		$\text{PF}_6^- [12,14]$
763 m			$\text{BF}_4^-$
		704 s 668 s	$\text{AsF}_6^- [2,3,7,14]$
	555 s		$\text{PF}_6^-$
528 s 520 s			$\text{BF}_4^-$
		387 vs	$\text{AsF}_6^-$
Other bands			
1420 m	1430 m		(?)
	1240 w		(?)
	1200 w 1120 m 970 m		Ke1-F Grease
878 m			$\text{BF}_3 [13]$
	740 m		(?)
632 w			$\text{BF}_3$
579 m			(?)
460 w			$\text{BF}_3$

solid  $\text{NSCl}$  films: one form with main peaks at 1346, 350, and  $256\text{ cm}^{-1}$ ; and another form with main peaks at 1397.0, 205, and  $140\text{ cm}^{-1}$ . In both, the highest wave number was assigned to the N-S stretching vibration. The latter form was interpreted in terms of the existence of the thiazyl cation,  $(\text{NS})^+$ , while the other was interpreted in terms of a "molecular" form. Film appearance, band size and shapes, and isotopic substitution were used to verify those interpretations.

The observed shift to a higher wave number of the N-S stretching vibration in  $\text{NSF}_{(s)}$  ( $1380 \text{ cm}^{-1}$ ) as compared to that in  $\text{NSF}_{(g)}$  ( $1372 \text{ cm}^{-1}$ ) is only about one-tenth that reported for the  $\text{NSCl}$  solid form interpreted in terms of the thiazyl cation,  $(\text{NS})^+$ . Therefore the  $\text{NSF}_{(g)}$  does not appear to ionize in the solid state as does the  $\text{NSCl}$ .

Thiazyl fluoride forms adducts with the Lewis acids  $\text{PF}_5$ ,  $\text{BF}_3$ , and  $\text{AsF}_5$  in a one-to-one molecular ratio of  $\text{NSF}$  to acid. The magnitudes of the dissociation pressures of the adducts imply that the order of thermal stability is  $\text{NSF}\cdot\text{AsF}_5 > \text{NSF}\cdot\text{BF}_3 > \text{NSF}\cdot\text{PF}_5$ . This same stability trend has been observed for the  $\text{CF}_3\text{SF}_3$  adducts with the same acceptors [7].

The low temperature infrared spectra of the solid adducts  $\text{NSF}\cdot\text{BF}_3(s)$ ,  $\text{NSF}\cdot\text{PF}_5(s)$  and  $\text{NSF}\cdot\text{AsF}_5(s)$  showed in each case peaks which can be assigned to the appropriate anions. It is interpreted that the adducts exist as ionic solids which can be formulated as  $(\text{NS})^+(\text{MF}_x)^-$ .

The  $\text{NSF}\cdot\text{BF}_3(s)$  spectrum shows a broad band centered at  $1050 \text{ cm}^{-1}$  which is assigned to  $\nu_3$  of the  $\text{BF}_4^-$  anion [7,12]. The doublet with peaks at  $520$  and  $528 \text{ cm}^{-1}$  are attributed to  $^{10}\text{B}$  and  $^{11}\text{B}$   $\nu_4$  modes of the  $\text{BF}_4^-$  anion [13]. The band at  $763 \text{ cm}^{-1}$  is in the region expected for the  $\nu_1$  fundamental of the  $\text{BF}_4^-$  anion. The narrow peak appearing at  $1443 \text{ cm}^{-1}$  is assigned to the thiazyl cation,  $(\text{NS})^+$  [1,2,3].

In the  $\text{NSF}\cdot\text{AsF}_5(s)$  spectrum the peaks appearing at  $704$  and  $668 \text{ cm}^{-1}$  are assigned to  $\nu_3$  and  $\nu_1$  of the  $\text{AsF}_6^-$  anion [2,3], while the peak at  $378 \text{ cm}^{-1}$  is believed to result from  $\nu_4$  of  $\text{AsF}_6^-$  [12,14]. The  $\nu_2$  vibrational band of  $\text{AsF}_6^-$  was not observed. It is normally degenerate and infrared inactive ( $\nu_2 \sim 565 \text{ cm}^{-1}$ ) [9]. The sharp peak located at  $1442 \text{ cm}^{-1}$  is in the region expected for the  $(\text{NS})^+$  ion.

The  $\text{NSF}\cdot\text{PF}_5(s)$  spectrum has bands centered at  $555$  and  $820 \text{ cm}^{-1}$  which are in the region expected for  $\nu_3$  and  $\nu_2$  of the  $\text{PF}_6^-$  anion [12,14]. The sharp peak at  $1443 \text{ cm}^{-1}$  is assigned to the  $(\text{NS})^+$  ion.

The infrared spectra of the volatiles above the adducts  $\text{NSF}\cdot\text{BF}_3(s)$  and  $\text{NSF}\cdot\text{PF}_5(s)$  suggest that the adducts are completely dissociated in the gas phase. The process of adduct formation and dissociation can be described for  $\text{NSF}\cdot\text{BF}_3$  as  $\text{NSF} + \text{BF}_3 \rightleftharpoons (\text{NS})^+(\text{BF}_4)^-(s)$ .

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