

electron-transfer reaction,  $k_3$ , must be considerably larger than  $k_{\text{obsd}}$ , since  $K_2$  must be small. In the nitrate reductase enzymes, the preliminary displacement of a ligand by  $\text{NO}_3^-$  might either be unnecessary or be much more favorable, accounting for the rapid enzymatic reduction rates.

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**Registry No.**  $\text{NO}_3^-$ , 14797-55-8;  $(\text{NH}_4)_2\text{MoOCl}_5$ , 17927-44-5; DMF, 68-12-2.

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## X-Ray Photoelectron Spectroscopic Study of Volatile Vanadium Compounds

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Vapor-phase core electron binding energies were determined by X-ray photoelectron spectroscopy for nine vanadium compounds. Vanadium  $2p_{3/2}$  binding energies were correlated using CHELEQ atomic charges and the "transition-state" point charge potential equation. Excellent correlation was obtained for compounds which are well represented by a single valence-bond structure. In the case of the other compounds, information regarding the relative contributions of various resonance structures and the importance of back-bonding was obtained by comparison of experimental and calculated binding energies.

## Introduction

The CHELEQ electronegativity equalization procedure for calculating atomic charges has been successfully used, in conjunction with the point charge potential equation, to correlate core electron binding energies for a wide range of simple organic and inorganic compounds.<sup>1,2</sup> The method has been parameterized for transition metal compounds and has been used to a limited extent for such compounds,<sup>2,3</sup> but no systematic study has been made of the applicability of the method outside the main-group elements. In this paper we report gas-phase core electron binding energies determined by X-ray photoelectron spectroscopy for nine vanadium compounds and we discuss the nature of the bonding in these compounds as deduced from the data. This work is the first gas-phase XPS study of a series of compounds of a transition metal in which a wide range of metal oxidation states is spanned.

## Experimental Section

Standard high-vacuum and inert-atmosphere techniques were employed. The organometallic vanadium compounds were handled under argon. All metal and glassware used in manipulation of the vanadium halides and oxyhalides were flamed under high vacuum and pretreated with the compound to be handled. Vanadium pentafluoride was prepared by the thermal disproportionation of  $\text{VF}_4$  (Orion) in a steel bomb.<sup>4</sup> The  $\text{VF}_5$  was twice treated with activated  $\text{NaF}^5$  and was stored in a bulb containing activated  $\text{NaF}$ . Vanadyl trifluoride (Alfa) was used without further purification. Vanadyl trichloride (ROC/RIC) was distilled through traps at 0, -78, and -196°. The clear liquid collected at -78° had a vapor pressure at 0° of 4.2 Torr (lit.<sup>6</sup> 4.4 Torr). Vanadium tetrachloride (Orion) was distilled through traps at 0, -78, and -196°. The dark red liquid

collected at -78° was stored at -78° until used. Tris(hexafluoroacetylacetonato)vanadium,<sup>7,8</sup>  $\text{V}(\text{hfacac})_3$ , was prepared by the method of Morris et al.<sup>8</sup> and purified by sublimation (mp 75.5–76.5°, lit.<sup>7</sup> 76°). The  $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$  (Strem) (mp 139.5–140.5°, lit.<sup>9</sup> 139°) was used without further purification. Its infrared spectrum agreed with the literature.<sup>9</sup> Vanadium hexacarbonyl was prepared from  $[\text{Na}(\text{diglyme})_2][\text{V}(\text{CO})_6]$  (Orion) by the method of King.<sup>10</sup> It was stored in the dark at -78° over  $\text{P}_2\text{O}_5$  and resublimed immediately before use. The  $(\pi\text{-C}_7\text{H}_7)\text{V}(\text{CO})_3$  was prepared from  $\text{V}(\text{CO})_6$  and cycloheptatriene by the method of Werner and Manastyrskyj<sup>11</sup> and was purified by sublimation. The product melted at 133–134° (lit.<sup>11</sup> 134–137°) and exhibited an infrared spectrum in agreement with the literature.<sup>11</sup> The  $(\pi\text{-C}_7\text{H}_7)\text{V}(\pi\text{-C}_5\text{H}_5)$  was prepared from  $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$  and cycloheptatriene by the method of King and Stone<sup>12</sup> and was purified by sublimation at 120°.

**X-Ray Photoelectron Spectra.** Spectra were obtained using the Berkeley iron-free, double-focusing magnetic spectrometer.<sup>13</sup> The halides, oxyhalides, and vanadium hexacarbonyl were irradiated in a gold-plated chamber with a volume of 300  $\text{cm}^3$ , a 0.5-mm exit slit, and an aluminum X-ray window. Tris(hexafluoroacetylacetonato)vanadium,  $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ , and  $(\pi\text{-C}_7\text{H}_7)\text{V}(\text{CO})_3$  were irradiated using a slit plug described by Banna.<sup>14</sup> The sample and reference gas were handled in a system constructed of 0.5-in. stainless steel pipe. This system was assembled and secured while back-flushing with argon gas as in standard Schlenk manipulation. The vapor of the compound passed to the irradiation chamber through a 15-in. length of tubing constructed of Pyrex glass and stainless steel. The samples of  $\text{VCl}_4$  and  $\text{V}(\text{CO})_6$  were held at 0° during data collection to minimize decomposition. The  $(\pi\text{-C}_7\text{H}_7)\text{V}(\pi\text{-C}_5\text{H}_5)$  was held in a heated chamber<sup>14</sup> at ca. 100°.

Magnesium  $K\alpha$  X-rays (1253.6 eV) were used for all spectra. Argon or neon at a partial pressure of 20–40  $\mu$  was introduced with the sample to the irradiation chamber, and the Ar  $2p_{3/2}$  line ( $E_B = 248.45$  eV) or the Ne 1s line ( $E_B = 870.21$  eV) was used as a reference.

Table I. Experimental Binding Energies

Compd	$E_B$ , eV				
	V 2p <sub>3/2</sub>	C 1s	O 1s	F 1s	Cl 2p <sub>3/2</sub>
VF <sub>5</sub>	528.9 (1.22) <sup>a</sup>			692.6	
VOF <sub>3</sub>	527.1 (1.24)		539.8	692.4	
VOCl <sub>3</sub>	524.8 (1.10)		538.7		205.9
VCl <sub>4</sub>	523.7 (1.47)				205.8
V(hfacac) <sub>3</sub>	522.3 (2.66)	298.6 (CF <sub>3</sub> ) 293.7 (CO) 290.9 (CH)	538.6	694.3	
( $\pi$ -C <sub>5</sub> H <sub>5</sub> )V(CO) <sub>4</sub>	519.6 (0.92)	292.2 (CO) 290.5 (CH)	538.7		
V(CO) <sub>6</sub>	518.9 (1.56)	292.0	539.7		
( $\pi$ -C <sub>7</sub> H <sub>7</sub> )V(CO) <sub>3</sub>	518.8 (1.41)	291.7 (CO) 290.3 (CH)	538.6		
( $\pi$ -C <sub>7</sub> H <sub>7</sub> )V( $\pi$ -C <sub>5</sub> H <sub>5</sub> )	518.5 (1.26)	289.8 <sup>b</sup>			

<sup>a</sup> FWHM values in parentheses. <sup>b</sup> Only one C 1s line observed; FWHM = 1.02 eV.

Sample and reference data were collected alternately. In the case of V(hfacac)<sub>3</sub>, ( $\pi$ -C<sub>5</sub>H<sub>5</sub>)V(CO)<sub>4</sub>, ( $\pi$ -C<sub>7</sub>H<sub>7</sub>)V(CO)<sub>3</sub>, and ( $\pi$ -C<sub>7</sub>H<sub>7</sub>)V( $\pi$ -C<sub>5</sub>H<sub>5</sub>), the reference was measured relative to the strongest peak in the compound and the other binding energies were determined relative to the strongest peak in a run with no reference gas present. Binding energies were determined by a least-squares fitting of the data to lorentzian line shapes. The relative accuracy of the peak positions is about  $\pm 0.1$  eV. The reported binding energies correspond to absolute free-molecule ionization potentials.

**Parameters for CHELEQ Calculations.** Bond distances from electron diffraction studies were used for VF<sub>5</sub>,<sup>15</sup> VOCl<sub>3</sub>,<sup>16</sup> and VCl<sub>4</sub>.<sup>17</sup> Bond distances from X-ray diffraction data were used for ( $\pi$ -C<sub>5</sub>H<sub>5</sub>)V(CO)<sub>4</sub><sup>18</sup> and ( $\pi$ -C<sub>7</sub>H<sub>7</sub>)V( $\pi$ -C<sub>5</sub>H<sub>5</sub>).<sup>19</sup> Bond distances for V(CO)<sub>6</sub>, VOF<sub>3</sub>, and ( $\pi$ -C<sub>7</sub>H<sub>7</sub>)V(CO)<sub>3</sub> were estimated.

## Results and Discussion

Table I lists the observed binding energies. The vanadium 2p<sub>3/2</sub> binding energies span a range of about 10 eV. The relative ordering of the chemical shifts is that expected on the basis of the vanadium oxidation states and the electronegativities of the substituent atoms. The large difference, 5.2 eV, between the vapor phase V 2p<sub>3/2</sub> binding energy of C<sub>7</sub>H<sub>7</sub>VC<sub>5</sub>H<sub>5</sub> and that reported by Groenenboom et al.<sup>20</sup> is probably due to the referencing problems associated with solids.<sup>21</sup> The extraordinarily large FWHM value found for the V 2p<sub>3/2</sub> line of tris(hexafluoroacetylacetonato)vanadium is perhaps due to unresolved multiplet splitting; the complex contains two unpaired electrons.

The "transition-state" point charge potential method corresponds to a correlation of the binding energies with valence electron distributions halfway between those of the initial-state and core-ionized molecules and has proved useful in correlating and calculating core binding energies.<sup>2</sup> In eq 1,  $E_B$  is the binding energy for a particular core level in the

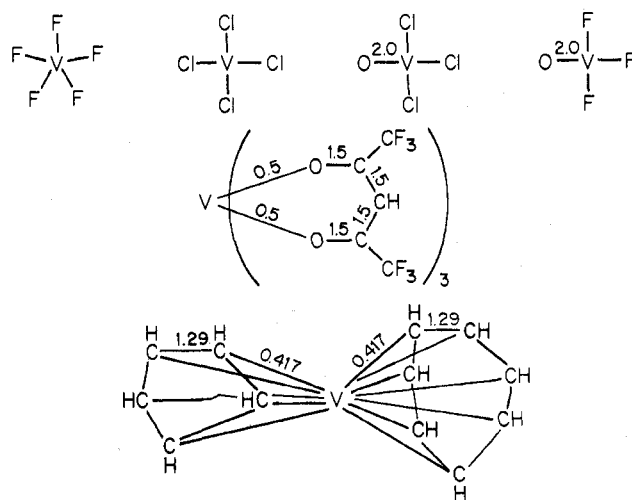
$$E_B = k(Q + Q_f - 1)/2 + (V + V_f)/2 + l \quad (1)$$

ionized atom,  $Q$  is the initial charge on this atom,  $V$  is the coulombic potential energy due to the other charged atoms in the molecule, and  $k$  and  $l$  are empirical constants determined by a least-squares fit.  $Q_f$  and  $V_f$  are the values of  $Q$  and  $V$  for the core-ionized molecule; these values can be estimated using the principle of equivalent cores.<sup>22</sup>

The vanadium 2p<sub>3/2</sub> binding energies can be correlated with CHELEQ atomic charges using eq 1. By applying the rules which we have previously outlined<sup>2</sup> for writing valence-bond structures we obtained a good correlation for all the compounds except the three carbonyl compounds. The latter compounds were ignored in the least-squares evaluation of the parameters  $k$  and  $l$ .

The valence-bond structures for the six compounds used in

evaluating  $k$  and  $l$  for V 2p<sub>3/2</sub> are as follows.



Because separate electronegativity parameters for the valence  $d$ ,  $s$ , and  $p$  orbitals of vanadium are not known (average parameters are used), we have not distinguished between the stereochemically different fluorine atoms in VF<sub>5</sub>. This procedure is reasonable in view of the facts that all five V-F distances are equal<sup>15</sup> and that only one F 1s line is observed. However, it was found that the F 1s line of VF<sub>5</sub> is considerably broader than that of VOF<sub>3</sub> (FWHM values of 1.88 and 1.25 eV, respectively); the increased line width is probably due to unresolved lines for the two types of fluorine atoms in VF<sub>5</sub>.

In the structures, bond orders other than unity are indicated by numbers next to the bonds. (However, in C<sub>5</sub>H<sub>5</sub>VC<sub>7</sub>H<sub>7</sub>, only one bond order in each set of equivalent bonds is so indicated.) The one common feature of the structures is the zero formal charge on the vanadium atoms. In tris(hexafluoroacetylacetonato)vanadium, zero formal charge on the vanadium was achieved by allowing a total of only three electron pairs to be donated to the vanadium atom, corresponding to six V-O bonds of bond order 0.5. This compound could also be well fit to the binding energy data by assuming six V-O  $\sigma$ -donor bonds of bond order unity and six V-O  $\pi$  back-bonds of bond order 1/6. However, the latter description of the bonding is unrealistic for two reasons. First, the fact that transition metal acetylacetonates are generally high-spin complexes<sup>23</sup> is inconsistent with extensive back-bonding in the compounds. Second, we have measured the core binding energies of several other metal hexafluoroacetylacetonates and have found that the oxygen and carbon 1s binding energies do not vary within experimental error. If back-bonding were significant in these compounds, the degree of back-bonding and the charge on the ligand atoms would be expected to

Table II. Calculated Atomic Charges and Comparison of Experimental and Calculated Binding Energies

	$Q_o$	$E_B(\text{exptl}) - E_B(\text{calcd}), \text{eV}$		$Q_o$	$E_B(\text{exptl}) - E_B(\text{calcd}), \text{eV}$
$\text{VF}_5$	1.122	-0.1	$\text{VCl}_4$	0.702	-0.3
$\text{VF}_3$	-0.224	0.3	$\text{VCl}_3$	-0.176	0.0
$\text{VOF}_3$	0.995	-0.3	$\text{V}(\text{hfacac})_3$	0.774	0.9
$\text{VOF}_3$	-0.228	0.1	$(\pi\text{-C}_7\text{H}_7)\text{V}(\pi\text{-C}_5\text{H}_5)$	0.464	-0.2
$\text{VOF}_3$	-0.310	-0.8	$(\pi\text{-C}_7\text{H}_7)\text{V}(\pi\text{-C}_5\text{H}_5)$	-0.054	-0.8
$\text{VOCl}_3$	0.829	-0.1	$(\pi\text{-C}_7\text{H}_7)\text{V}(\pi\text{-C}_5\text{H}_5)$	-0.054	-0.1
$\text{VOCl}_3$	-0.170	0.1	$\text{V}(\text{CO})_6$	0.347	0.0
$\text{VOCl}_3$	-0.319	-0.3			

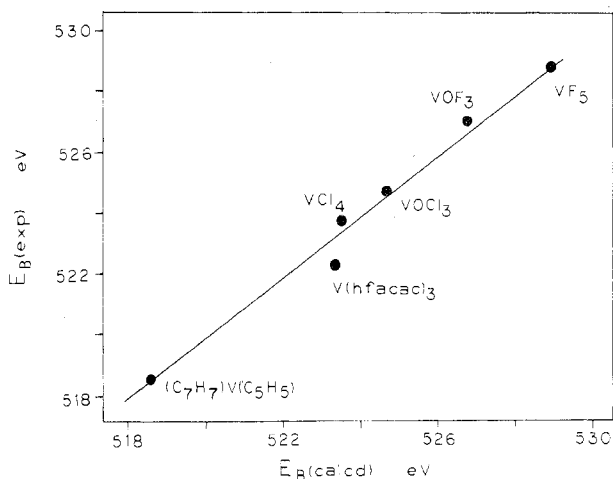


Figure 1. Plot of experimental vanadium  $2p_{3/2}$  binding energies vs. binding energies calculated by eq 1. Standard deviation 0.46 eV; correlation coefficient 0.992.

change markedly, resulting in substantial chemical shifts.

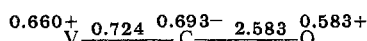
In  $(\pi\text{-C}_7\text{H}_7)\text{V}(\pi\text{-C}_5\text{H}_5)$  the carbon–vanadium distances are all equal within experimental error<sup>19</sup> and the C 1s photoelectron spectrum gave only one narrow line (FWHM = 1.02 eV). Consideration of these data led us to assume a bonding model in which each carbon–vanadium bond has the same bond order,  $5/12$ , involving a  $\sigma$ -donor bond of order  $5/24$  and a  $\pi$  back-bond of order  $5/24$ .

Figure 1 shows a plot of calculated vs. experimental V  $2p_{3/2}$  binding energies. The calculated values were obtained from eq 1 using the least-squares evaluated parameters  $k = 22.98$  and  $l = 514.30$ . At first sight, the value of  $k$  seems rather high (compare, for example, the similarly evaluated  $k$  values of 18.24 and 15.87 for chlorine and germanium respectively).<sup>2</sup> However, it must be remembered that, according to simple theory,<sup>24</sup>  $k$  is expected to be inversely proportional to atomic radius, and, because the  $k$  value for vanadium was determined using compounds in which the vanadium atoms have high oxidation states and low effective radii, we believe the  $k$  value is reasonable.

Table II lists the calculated atomic charges and the differences between the experimental and calculated binding energies for the vanadium atoms and the ligand atoms in some of the compounds. The ligand atom binding energies were calculated using  $k$  and  $l$  values which had been previously determined from data for a large number of compounds.<sup>2</sup> The fact that the binding energies calculated for the ligand atoms are in good agreement with the experimental values is strong support for the validity of the bonding assumptions and the CHELEQ charges.

The most straightforward model for the bonding in  $\text{V}(\text{CO})_6$  employs a full  $\sigma$  bond and a  $5/12$   $\pi$  back-bond, the maximum possible, in each vanadium–carbon bond. This model places a 3.5– formal charge on the vanadium atom and leads to a calculated vanadium binding energy much more negative than the experimental value. The calculated and experimental binding energies can be brought into exact agreement by

decreasing the carbon–vanadium  $\sigma$ -bond order to 0.307 while maintaining the  $\pi$ -bond order at  $5/12$ , or 0.417. The formal charges and overall bond orders in this model are



By making similar arbitrary, but reasonable, assumptions regarding the bonding in  $\text{C}_7\text{H}_7\text{V}(\text{CO})_3$ , it is possible to obtain agreement between the observed and calculated V  $2p_{3/2}$  binding energies. However, in the case of  $\text{C}_5\text{H}_5\text{V}(\text{CO})_4$ , such agreement can only be obtained by assuming a rather high formal charge on the vanadium atom. We have no explanation for the anomalously high V  $2p_{3/2}$  binding energy in the latter compound.

The fact that in the case of  $\text{V}(\text{CO})_6$  we found it necessary to assume that the V–C  $\sigma$ -bond order is less than the V–C  $\pi$ -back-bond order whereas in the case of  $\text{C}_7\text{H}_7\text{VC}_5\text{H}_5$  we obtained a good fit assuming equal bond orders for the V–C  $\sigma$  and  $\pi$  bonds is consistent with modern ideas regarding the bonding in transition metal carbonyls and organometallic compounds. It is generally agreed that the CO ligand is a stronger back-acceptor than the  $\pi\text{-C}_5\text{H}_5$  group.<sup>25,26</sup> Indeed both theoretical<sup>27</sup> and experimental<sup>28</sup> results indicate that metal–olefin bonds are essentially nonpolar, whereas theoretical calculations<sup>29</sup> indicate that the metal atoms in metal carbonyls have quite positive charges.

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**Registry No.**  $\text{VF}_5$ , 7783-72-4;  $\text{VOF}_3$ , 13709-31-4;  $\text{VOCl}_3$ , 7727-18-6;  $\text{VCl}_4$ , 10049-16-8;  $\text{V}(\text{hfacac})_3$ , 15695-77-9;  $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ , 12108-04-2;  $\text{V}(\text{CO})_6$ , 14024-00-1;  $(\pi\text{-C}_7\text{H}_7)\text{V}(\text{CO})_3$ , 12083-16-8;  $(\pi\text{-C}_7\text{H}_7)\text{V}(\pi\text{-C}_5\text{H}_5)$ , 12636-68-9.

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## Novel Onium Salts. Synthesis and Characterization of the Difluoroammonium Cation, $\text{NH}_2\text{F}_2^+$

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The syntheses and properties of  $\text{NH}_2\text{F}_2^+\text{SbF}_6^-$  and  $\text{NH}_2\text{F}_2^+\text{AsF}_6^-$ , the first known examples of difluoroammonium salts, are reported. The  $\text{NH}_2\text{F}_2^+$  cation was characterized by  $^{19}\text{F}$  and  $^1\text{H}$  NMR and vibrational spectroscopy. At room temperature the  $\text{NH}_2\text{F}_2^+$  salts are metastable and undergo spontaneous exothermic decomposition by HF elimination. Attempts were unsuccessful to prepare either  $\text{NHF}_3^+$  salts by protonation of  $\text{NF}_3$  at temperatures as low as  $-78^\circ$  or fluorine-substituted ammonium salts by direct fluorination of  $\text{NH}_4^+\text{AsF}_6^-$  in HF solution in the temperature range  $-78$  to  $+25^\circ$ .

### Introduction

Recent studies in our laboratory demonstrated that several novel onium salts can be prepared by protonation of less acidic compounds in  $\text{HF}-\text{MF}_5$  ( $\text{M} = \text{Sb}, \text{As}$ ) solutions. Thus, protonation of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  produced<sup>1,2</sup> the surprisingly stable  $\text{OH}_3^+\text{MF}_6^-$  and  $\text{SH}_3^+\text{SbF}_6^-$  salts, respectively. In this paper, we report on the protonation of  $\text{HNF}_2$  and  $\text{NF}_3$ .

Whereas salts containing the  $\text{NH}_4^+$  ion had been described already in the early part of the fourteenth century,<sup>3</sup> fluorine-substituted salts were unknown until 1965. Disproving earlier theoretical computations<sup>4,5</sup> that  $\text{NF}_4^+$  salts should be thermodynamically unstable, these salts were synthesized<sup>6,7</sup> in 1965 and shown to be of high thermal stability. Since then, numerous papers dealing with  $\text{NF}_4^+$  salts<sup>8-18</sup> and the thermally unstable  $\text{NF}_3^+$  radical cation<sup>17</sup> have appeared. Of the mixed  $\text{NH}_n\text{F}_{4-n}^+$  cations, the  $\text{NH}_3\text{F}^+$  cation has previously been described,<sup>19,20</sup> but no data on the remaining two members in this series, i.e.,  $\text{NH}_2\text{F}_2^+$  and  $\text{NHF}_3^+$ , have been published. This is not surprising, since from comparison with the highly shock-sensitive  $\text{HNF}_2$  molecule and its  $\text{CsF}$  adduct,<sup>21</sup> one might expect these more highly fluorinated mixed ammonium salts to be very susceptible to HF elimination. The adduct formation of  $\text{HNF}_2$  with the Lewis acids  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{PF}_5$ , and  $\text{SO}_2$  has been studied<sup>22</sup> at  $-196^\circ$  by infrared spectroscopy, but no evidence was found for ion formation. The thermal stability of these adducts was rather low with (in some cases irreversible) decomposition occurring at about  $-80^\circ$ .

### Experimental Section

**Caution!** Difluorammine is highly explosive<sup>21</sup> and protective shielding should be used during handling operations. The compound was always condensed at  $-142^\circ$  and the use of a  $-196^\circ$  bath should be avoided.<sup>23</sup> In the course of the present study five explosions of both  $\text{NH}_2\text{F}_2^+\text{AsF}_6^-$  and  $\text{NH}_2\text{F}_2^+\text{SbF}_6^-$  in HF solution occurred, when these solutions were kept between  $-50$  and  $+25^\circ$  for extended periods of time. However, the appearance of the ruptured Kel-F or Teflon-FEP containers indicated pressure explosions (probably caused by HF elimination with  $\text{N}_2$  formation and by the small ullage above the liquid phase) rather than rapid explosive decomposition. The rate of decomposition of these  $\text{NH}_2\text{F}_2^+$  salt solutions varied strongly from sample to sample, indicating catalysis by trace impurities. The exothermic irreversible decomposition of solid  $\text{NH}_2\text{F}_2^+$  salts appeared to proceed without explosion on a millimolar scale, provided the volume of the container was large enough to avoid overpressurization. When working with such solutions in containers with small ullage, we, therefore, re-

commend removing the volatile decomposition products by quick pumping at  $-78^\circ$  every time before handling the sample.

The experimental techniques used in this study have previously been described.<sup>1</sup> Difluorammine was prepared from difluoroarene.<sup>24</sup> Nitrogen trifluoride (99.9%, Rocketdyne) and  $\text{NH}_4^+\text{HF}_2^-$  (Braun Chemical Co.) were used without further purification. Difluorammine was handled in a Pyrex, the other reactants in a Monel Teflon-FEP, vacuum system.

**Preparation of  $\text{NH}_2\text{F}_2^+\text{AsF}_6^-$ .** In a typical experiment, dry HF (50 mmol) and  $\text{AsF}_5$  (1.74 mmol) were combined at  $-196^\circ$  in a passivated (with  $\text{ClF}_3$ ) thin-walled Kel-F capillary. The mixture was shortly warmed to room temperature to obtain a homogenous solution. Difluorammine (2.0 mmol) was added to the ampoule at  $-142^\circ$ . The mixture was warmed to  $-78^\circ$  and a white solid was formed which was completely soluble in the HF solvent at  $20^\circ$ . Unreacted  $\text{NHF}_2$  and HF solvent were removed under dynamic vacuum between  $-78$  and  $0^\circ$ , leaving behind 420 mg of a white solid. This weight is in excellent agreement with that (423 mg) expected for 1.74 mmol of  $\text{NH}_2\text{F}_2^+\text{AsF}_6^-$ .

For the preparation of the NMR samples, an excess of  $\text{AsF}_5$  was used and not pumped off to suppress exchange between the cation and the HF solvent.

**Decomposition of  $\text{NH}_2\text{F}_2^+\text{AsF}_6^-$ .** A sample of solid  $\text{NH}_2\text{F}_2^+\text{AsF}_6^-$ , contained in a Teflon-FEP ampoule, was allowed to warm slowly from  $-78$  to  $+20^\circ$ . After about 20 min at  $20^\circ$ , the solid started to melt and spontaneously decomposed with gas and heat evolution (*caution!*). The decomposition products were separated by fractional condensation and identified by infrared spectroscopy or mass spectroscopy. The main constituents were  $\text{AsF}_5$ , HF, and  $\text{N}_2$ , in addition to some  $\text{NF}_3$  and *trans*- $\text{N}_2\text{F}_2$ .

**Preparation of  $\text{NH}_2\text{F}_2^+\text{SbF}_6^-$ .** In a typical experiment,  $\text{SbF}_5$  (1.70 mmol) and dry HF (150 mmol) were combined at  $-196^\circ$  in a passivated Teflon-FEP ampoule. The mixture was warmed to  $25^\circ$  to obtain a homogenous solution. Difluorammine (2.02 mmol) was added to the ampoule at  $-142^\circ$  and the mixture was warmed to  $-78^\circ$ . A white solid formed when the starting materials melted. On warm-up toward  $0^\circ$ , the solid completely dissolved in the excess HF. The unreacted  $\text{NHF}_2$  and the HF solvent were pumped off between  $-45$  and  $0^\circ$  leaving behind a white solid residue (499 mg). This weight agrees well with that (493 mg) expected for 1.70 mmol of  $\text{NH}_2\text{F}_2^+\text{SbF}_6^-$ .

**Decomposition of  $\text{NH}_2\text{F}_2^+\text{SbF}_6^-$ .** A sample of  $\text{NH}_2\text{F}_2^+\text{SbF}_6^-$  (1.70 mmol), when kept at  $25^\circ$  for about 1 hr, underwent spontaneous exothermic decomposition with melting and gas evolution. The decomposition products, volatile at  $-78^\circ$ , consisted of  $\text{N}_2$  (0.56 mmol) and  $\text{NF}_3$  containing a small amount of *trans*- $\text{N}_2\text{F}_2$  (0.58 mmol total). The residue ( $\sim 410$  mg; weight calculated for 1.70 mmol of  $\text{HF}\cdot\text{SbF}_5$  402 mg) was warmed to  $25^\circ$  under dynamic vacuum. A small amount of white solid stable at  $25^\circ$  was obtained which, based on its infrared