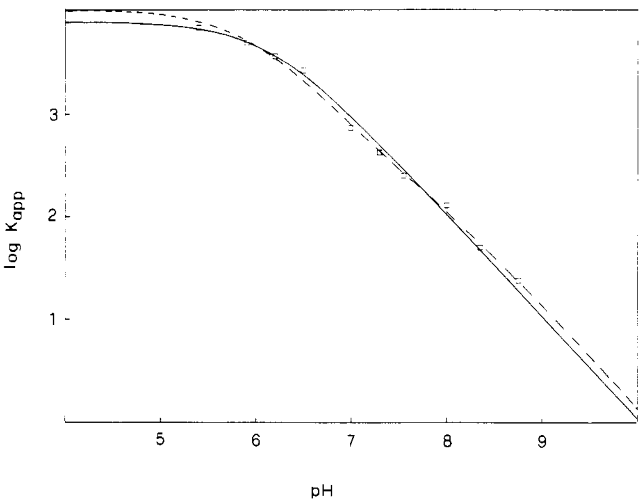

Figure 2. pH dependence of the apparent affinity constant of nitrate ion for cobalt(II)-substituted bovine carbonic anhydrase II in HEPES buffered water solutions at 20 °C. The data are fitted to a single pK_a (full line) assuming a negligible affinity for the high-pH species (best fitting parameters: $pK_a = 6.14$, $\log K = 3.09$) and microconstant values reported in Table I (best fit parameters: $\log K_1 = 4.01$, $\log K_2 = 2.40$) (dashed line).

increases with percent of Me_2SO, pK_2 increases from pure water to 5% Me_2SO and then essentially levels off. Such behavior, that is of course reflected in the pk_1 and pk_2 pair with respect to the pk_3 and pk_4 pair, seem scarcely related to the increase of pK_w in the various solvent mixtures. Possibly these patterns bear a further chemical meaning with respect to the thermodynamic parameters of the various dissociation processes; however, a further discussion of the data may become unsound, also because of the relatively large errors.

The presence of the two acidic groups in the active site of CoCA should also be reflected in the pH dependence of the apparent affinity constant of anions. Again this has been suggested by Lindskog through activity measurements on the zinc enzyme inhibited by iodide.[8] We have measured through spectrophotometric titrations the apparent affinity constants of NO_3^- against bovine CoCA II both in the absence of buffering species and anions and in the presence of the noncoordinating HEPES buffer.[5] The k_{app} values were found virtually the same in the two cases.

The pH dependence of such affinity constants is shown in Figure 2. A qualitative inspection of the data indicates that (i) there is very little evidence of two inflections in the pH dependence of the NO_3^- affinity and (ii) the main pK_a value can be located around pH 6.0. Indeed, the data can be satisfactorily fitted to a single pK_a of 6.14 ± 0.06 (full line in Figure 2); such a value should be compared with the apparent pK_a of 5.9 in Table I. A deeper insight can be obtained by fitting the data using the microconstant values of Table I to estimate the affinity of NO_3^- for the two water-containing species, assuming the affinity for the hydroxo species to be negligible. Such fitting (dashed line in Figure 2) provides values of $\log k = 4.01 \pm 0.02$ and 2.40 ± 0.04 for the affinity constant of NO_3^- for the (H-His)E(OH_2) and (His)E(OH_2) species, respectively. However, there is no significant improvement in the goodness of the fitting with respect to the single pK_a case. This means that, if it were not for the independent characterization of the ionization process of the system, the pH dependence of NO_3^- binding would have given no evidence of more than one acid-base equilibrium. Indeed, the second acid-base process has always escaped detection from inhibitor binding measurements, even in the absence of competing anions or buffering species.[6] In any case, it appears that the affinity of NO_3^- for the diprotonated species is much higher than that for the monoprotonated species, providing a rationalization of all the anion-binding data that in the past have always indicated a lower pK_a value than that obtained from the midpoint of variation of the spectral and catalytic properties of the enzyme.

The above findings bear a chemical significance well beyond the understanding of the acid-base properties of carbonic anhydrase: The present enzyme is usually reported to have much higher affinity for anions than any other zinc- or cobalt(II)-substituted enzyme with related function, and much higher than expected from the coordination chemistry of small model complexes. It appears now that such enhancement of anion affinity is largely brought about by protonation of a nearby histidine side chain, which increases by 1 unit the positive charge in the active site cavity. Interestingly, a similar behavior is shown by carboxypeptidase A, which also undergoes two active site ionizations and shows a dramatic increase in anion-binding affinity on passing from the monoprotonated to the diprotonated species.[22]

Registry No. His, 71-00-1; NO_3, 14797-55-8.

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Contribution from Rocketdyne, A Division of
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Lewis Acid Induced Intramolecular Redox Reactions of Difluoramino Compounds

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Received March 30, 1984

It is shown that strong Lewis acids, such as AsF_5 or SbF_5, which are good fluoride ion acceptors, strongly catalyze an intramolecular redox reaction of difluoramino compounds, such as CF_3NF_2, SF_5NF_2, $ClNF_2$, CF_3ONF_2, and SF_5ONF_2. In the $ClNF_2$–AsF_5 system a thermally unstable intermediate is formed at −78 °C, which on the basis of its Raman spectra is the fluorine-bridged donor–acceptor adduct $ClNF_2{\cdot}AsF_5$. The nature of the final decomposition products can be rationalized in terms of their stability. In connection with the low-temperature Raman studies, an unidentified, unstable, blue-green species was observed that gives rise to a resonance Raman spectrum with $\nu = 177$ cm^{-1} and that is also formed from $Cl_3^+AsF_6^-$ and excess Cl_2. For NF_2Cl, ^{14}N–^{19}F spin–spin coupling was observed in its ^{19}F NMR spectrum.

Introduction

During experiments aimed at the oxidative fluorination of CF_3NF_2 to $CF_3NF_3^+AsF_6^-$ by $KrF^+AsF_6^-$, an unusual observation was made. Besides the NF_3 and CF_4 products expected for an oxidative fission of the C–N bond, significant amounts of gaseous *trans*-N_2F_2 and solid $N_2F^+AsF_6^-$ were obtained. Since KrF^+ is the strongest oxidative fluorinating agent presently known[1] and N_2F_2 is a reduction product of CF_3NF_2, KrF^+ was unlikely to cause the observed N_2F_2 formation. Since $KrF^+AsF_6^-$ is thermally unstable and decomposes to Kr, F_2, and AsF_5,[2] we have considered

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the possibility that the strong Lewis acid AsF_5 might induce this decomposition of CF_3NF_2. Many difluoramino compounds are thermodynamically unstable toward decomposition reactions involving the formation of multiply bonded nitrogen species, such as N_2F_2 or N_2, and more highly fluorinated byproducts. Therefore, these difluoramino compounds are only kinetically but not thermodynamically stable, and their kinetic stability is determined by the activation energy barrier toward decomposition. Hence, it would not be surprising that complexing with a strong Lewis acid could lower this activation energy barrier.

Previous reports on the interaction of difluoramino compounds with Lewis acids or bases are scarce. Although the instability of HNF_2 in the presence of alkali-metal fluorides, for example, is well documented,[3,4] only one detailed study on the interaction of difluoramino compounds with Lewis acids has been published.[5] It was found that, with HNF_2 and alkyldifluoramines, BF_3 forms unstable, $N \rightarrow B$ bridged, donor-accepted complexes, which on warming reversibly decompose to the starting materials. With $ClNF_2$, BF_3 was found to be only weakly associated below -78 °C, and with NF_3, a large positive deviation from Raoult's law was observed,[6] indicating no association. For PF_5, a positive interaction was reported only with HNF_2 and CH_3NF_2, and the resulting adducts underwent irreversible decomposition on warming.[5] Although low-temperature infrared spectra of the $HNF_2 \cdot PF_5$ adduct were recorded, they were very complex and did not permit any conclusions concerning the nature of the adduct.[5] In view of the paucity of the available information and our above mentioned observations, a more systematic study of the interaction of difluoramino compounds with strong Lewis acids was of interest.

Experimental Section

Caution! Some difluoramino compounds are known to be sensitive, and appropriate safety precautions should be used when working with larger amounts of these materials.

Materials and Apparatus. Literature methods were used for the syntheses of KrF_2,[7] $KrFSbF_6$,[1] CF_3NF_2,[8] SF_5NF_2,[9] CF_3ONF_2,[10,11] $ClNF_2$,[12] $N_2F_3^+AsF_6^-$,[13] SF_5Br,[14] and SF_5ONF_2.[11] For some of the compounds the previously reported product yields were significantly improved: for CF_3NF_2 from 70 to 99% by carrying out the fluorination of CF_3N_3 with a fourfold excess of F_2 in a Monel cylinder at 70 °C for 24 h; for SF_5ONF_2 from 60 to 84% by carrying out the UV photolysis of equimolar amounts of SF_5OF and N_2F_4 in a flamed-out quartz bulb at 1.5-atm pressure for 16 h with water-filtered radiation from a 140-W medium-pressure mercury arc lamp; for SF_5NF_2 from 30 to 78% by UV photolysis of equimolar amounts of N_2F_4 and SF_4 in a stainless-steel cell equipped with a sapphire window, using the water-filtered radiation from a 1-kW Oriel Model 6141 HgXe lamp and an irradiation time of 2 h. HF (Matheson Co.) was dried by storage over BiF_5,[15] AsF_5 (Ozark-Mahoning Co.) was purified by fractional condensation prior to use, SbF_5 (Ozark-Mahoning Co.) was purified by distillation, and SO_2 (Matheson Co.) was used as received.

Volatile materials were manipulated in a well-passivated (with ClF_3) stainless-steel Teflon-FEP vacuum system.[16] Solids were handled in the dry N_2 atmosphere of a glovebox.

The ^{19}F NMR spectra were recorded on a Varian Model EM390 spectrometer at 84.6 MHz using Teflon-FEP sample tubes (Wilmad Glass Co.) with positive shifts being downfield from the external standard, $CFCl_3$.

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer. Gas spectra were recorded with a Teflon cell of 5-cm path length equipped with AgCl windows. Spectra of solids were recorded as dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded either on a Cary Model 83 spectrophotometer using the 4880-Å exciting line of an Ar ion laser, a Claassen filter[17] for the elimination of plasma lines, and sealed melting point capillaries as sample containers or on a Spex Model 1403 spectrophotometer using the 6471-Å exciting line of a Kr ion laser. The low-temperature spectra were recorded by using a previously described device.[18]

SF_5NF_2–$KrFSbF_6$ System. KrF^+–SbF_6^- (2.14 mmol) was placed in the drybox into a prepassivated (with ClF_3 and HF) Teflon-FEP ampule closed by a stainless-steel valve. The ampule was connected to the vacuum line, and HF (1 mL, liquid) and SF_5NF_2 (4.63 mmol) were added at -196 °C. The mixture was warmed to ambient temperature for 18 h, and the volatile products were separated by fractional condensation. They consisted of SF_6 (4.4 mmol), Kr, and a mixture (4.1 mmol) of NF_3 and *trans*-N_2F_2. The residue in the ampule consisted of SbF_5 and polyantimonate salts of N_2F^+ [19] and small amounts of $N_2F_3^+$.[13]

SF_5NF_2–$KrFAsF_6$ System. A reaction between $KrF^+AsF_6^-$ (2.65 mmol) and SF_5NF_2 (5.31 mmol) in HF solution was carried out at -31 °C for 6.5 h in the same manner as described for the SF_5NF_2–$KrFSbF_6$ system. The volatile products consisted of SF_6 (5.2 mmol), Kr, and a mixture (3.3 mmol) of mainly NF_3 and some *trans*-N_2F_2, whereas the solid residue was $N_2F^+AsF_6^-$ (0.95 mmol).

CF_3NF_2–$KrFSbF_6$ System. The reaction was carried out at 25 °C for 3 h as described for the SF_5NF_2–$KrFSbF_6$ system by using CF_3NF_2 (3.55 mmol) and $KrFSbF_6$ (1.94 mmol) in HF (2 mL, liquid). The volatile products (5.27 mmol) consisted of CF_4, NF_3, and *trans*-N_2F_2, and the white solid residue (429 mg) was a mixture of N_2F^+ and NF_4^+ polyantimonates. The formation of NF_4^+ from NF_3 and KrF^+ in HF solution has previously been reported.[1]

CF_3NF_2–KrF_2–AsF_5 System. KrF_2 (2.29 mmol), CF_3NF_2 (6.89 mmol), and AsF_5 (1.23 mmol) were condensed at -196 °C into a passivated 10-mL nickel cylinder. The cylinder was allowed to warm slowly to -78 °C and then to 25 °C by the use of a liquid N_2–CO_2 slush bath and was then heated in an oven to 50 °C for 6 h. The volatile products consisted of a mixture (10.4 mmol) of NF_3 and CF_4, *trans*-N_2F_2 (0.43 mmol), and AsF_5. A white solid residue, left behind in the cylinder, consisted of $N_2F^+AsF_6^-$ (0.65 mmol).

SF_5NF_2–AsF_5 System. SF_5NF_2 (2.31 mmol) and AsF_5 (2.31 mmol) were combined at -196 °C in a prepassivated Teflon-FEP ampule and kept at -78 °C for 1.75 h. At this point the pressure in the ampule was 373 torr, and a white solid had precipitated out of the liquid phase. The volatile materials were separated by fractional condensation and consisted of SF_6 (2.3 mmol), AsF_5 (1.5 mmol), and *trans*-N_2F_2 (0.3 mmol). The white solid residue consisted of $N_2F^+AsF_6^-$ (0.8 mmol).

When SF_5NF_2 (1.90 mmol) and AsF_5 (0.11 mmol) were kept in a sapphire tube at 25 °C for 20 h, the reaction products consisted of SF_6 (0.95 mmol), *trans*-N_2F_2 (0.30 mmol), unreacted SF_5NF_2 (0.90 mmol), and solid $N_2F^+AsF_6^-$ (0.11 mmol).

CF_3NF_2–AsF_5 System. CF_3NF_2 (6.32 mmol) and AsF_5 (6.32 mmol) were combined in a Teflon-FEP ampule and kept at -78 °C. The vapor pressure of the mixture at -78 °C steadily increased and was measured as a function of time (P in torr, t in h): 348, 0.17; 365, 0.67; 495, 1.17; 507, 1.67; 520, 2.67; 871, 20; 911, 21.5; 924, 22. The pressure calculated from the known vapor pressures of the pure compounds[20,21] and Raoult's law is 447 torr. After 22 h, the reaction was stopped. The volatile products that were separated consisted of AsF_5 (5.91 mmol) and a mixture (6.71 mmol) of CF_3NF_2, CF_4, *trans*-N_2F_2, and small amounts of NF_3. The white solid residue consisted of $N_2F^+AsF_6^-$ (0.21 mmol).

When a mixture of CF_3NF_2 (3.00 mmol) and AsF_5 (3.00 mmol) was kept at room temperature for 3 days, all the CF_3NF_2 had decomposed, producing solid $N_2F^+AsF_6^-$ (0.10 mmol), *trans*-N_2F_2 (1.4 mmol), CF_4 (3.0 mmol), and AsF_5 (2.90 mmol). However, when CF_3NF_2 (3.27 mmol) and AsF_5 (0.33 mmol) were kept at ambient temperature for 20 h, no significant decomposition of CF_3NF_2 was observed and the starting materials were recovered unchanged.

SF_5ONF_2–AsF_5 System. SF_5ONF_2 (3.99 mmol) and AsF_5 (3.99 mmol) were combined in a Teflon-FEP ampule and kept for 2 h at -78

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°C. The volatile materials consisted of SF_6 (3.83 mmol) and AsF_5 (0.14 mmol). The white solid residue in the ampule consisted of $NO^+AsF_6^-$ (2.44 mmol). Some $NO^+AsF_6^-$ had deposited in the vacuum-line section and therefore could not be recovered.

CF_3ONF_2–AsF_5 System. CF_3ONF_2 (0.49 mmol) and AsF_5 (0.49 mmol) were combined at −196 °C in a flamed-out 3-mm-o.d. quartz tube. The mixture was kept at −78 °C for 3.5 h. Separation of the products resulted in CF_4 (0.46 mmol), CF_3ONF_2 (0.03 mmol), and solid $NOAsF_6$ (0.42 mmol).

SF_5Br–AsF_5 System. SF_5Br (2.28 mmol) was condensed into a passivated sapphire tube at −196 °C, and its vapor pressure at −79 °C was measured to be 11 ± 1 torr. The vapor pressure of liquid AsF_5 under the same conditions was found to be 182 torr. The tube was cooled back to −196 °C, and AsF_5 (2.38 mmol) was added. The mixture was warmed to −79 °C, and the vapor pressure above the resulting clear liquid was determined as 75 ± 1 torr (calculated vapor pressure for an ideal mixture based on Raoult's law = 100 torr). All material could be removed from the sapphire tube by pumping at −79 °C.

$ClNF_2$–AsF_5 System. The vapor pressures of pure $ClNF_2$ and pure AsF_5 were measured at −79 °C and found to be 405 and 182 torr, respectively. Then equimolar amounts (5.65 mmol each) of $ClNF_2$ and AsF_5 were combined at −196 °C in a passivated Teflon-FEP U-trap. The trap was allowed to slowly warm from −196 to −79 °C by means of a liquid N_2–dry ice slush bath. At −79 °C, the tube contained a white solid with a pressure of about 220 torr above it. The tube was cooled to −196 °C, and 0.16 mmol of noncondensable material (N_2) was pumped off. The tube was warmed again to −79 °C, and the pressure above the solid was 120 torr. In addition to a white solid, some yellow solid was also formed, particularly at temperatures slightly higher than −79 °C. Most of these solids were unstable at ambient temperature, and fractional condensation of the volatile decomposition products through a series of traps kept at −78, −126, −156, −196, and −210 °C showed NF_3, N_2F_4, *trans*-N_2F_2, AsF_5, and Cl_2. Smaller amounts of a stable white solid residue, left behind at room temperature, were shown by vibrational spectroscopy to be a mixture of $N_2F_3^+AsF_6^-$ [13] and $N_2F^+AsF_6^-$.[19]

More accurate material balances for this system were obtained by using different ratios of starting materials and either sapphire or flamed-out quartz reactors and by recording low-temperature Raman spectra of the intermediate unstable products formed in this system. With a 1:1 mole ratio of $ClNF_2$ and AsF_5, a typical material balance was as follows: starting materials, $ClNF_2$ and AsF_5 (2.59 mmol each); products, NF_3 (1.50 mmol), AsF_5 (2.4 mmol), Cl_2 (1.3 mmol), N_2 (0.35 mmol), *trans*-N_2F_2 (0.10 mmol), and N_2FAsF_6 + $N_2F_3AsF_6$ (0.10 mmol). For $ClNF_2$ (3.60 mmol) and AsF_5 (1.25 mmol), the products consisted of NF_3 (2.28 mmol), N_2 (0.40 mmol), Cl_2 (1.78 mmol), AsF_5 (1.07 mmol), *trans*-N_2F_2 (trace), and $N_2F_3AsF_6$ + N_2FAsF_6 (0.17 mmol). For $ClNF_2$ (3.67 mmol) and AsF_5 (0.037 mmol), the products were $ClNF_2$ (2.40 mmol), NF_3 (0.26 mmol), N_2 (0.06 mmol), N_2F_4 (0.43 mmol), Cl_2 (0.62 mmol), and N_2FAsF_6 + $N_2F_3AsF_6$ (0.03 mmol).

Cl_2–AsF_5 System. An equimolar mixture of Cl_2 and AsF_5, when kept at −79.0 °C in a sapphire tube, resulted in a clear yellow liquid exhibiting a vapor pressure of 115 torr (calculated vapor pressure for an ideal mixture based on Raoult's law = 121 torr). All material could be removed from the sapphire tube by pumping at −78 °C.

Results and Discussion

A study of the binary CF_3NF_2–AsF_5 system showed that in the presence of AsF_5 the normally stable CF_3NF_2 undergoes even at −78 °C a slow decomposition according to (1). Since N_2F_2 exists

$$2CF_3NF_2 \xrightarrow{AsF_5} 2CF_4 + N_2F_2 \qquad (1)$$

as two isomers, cis and trans, and since only the cis isomer forms an adduct with AsF_5[22]

$$cis\text{-}N_2F_2 + AsF_5 \rightarrow N_2F^+AsF_6^- \qquad (2)$$

the observation of both, gaseous *trans*-N_2F_2 and solid $N_2F^+AsF_6^-$, can readily be rationalized by the formation of both N_2F_2 isomers in reaction 1.

Therefore, the surprising observation of *trans*-N_2F_2 and $N_2F^+AsF_6^-$ in the $KrF^+AsF_6^-$–CF_3NF_2 reaction system can be attributed to a Lewis acid promoted intramolecular redox reaction of CF_3NF_2 in which the CF_3 groups are oxidized to CF_4 and the NF_2 groups are reduced to N_2F_2.

To test the generality of this Lewis acid promoted intramolecular redox reaction, we have also studied the effect of AsF_5 on $ClNF_2$, SF_5NF_2, CF_3ONF_2, and SF_5ONF_2, which, in the absence of strong Lewis acids, are all thermally stable compounds.[10–12,23] It was found that AsF_5 strongly affects the decomposition of all of these difluoramino compounds. Thus, SF_5NF_2 undergoes an analogous, albeit faster and quantitative, decomposition according to (3) and (2). It should be pointed out

$$2SF_5NF_2 \xrightarrow{AsF_5} 2SF_6 + N_2F_2 \qquad (3)$$

that the SF_6 and N_2F_2 products formed in (3) are different from those (S_2F_{10} and N_2F_4) formed in the uncatalyzed thermal decomposition of SF_5NF_2.[23]

For CF_3ONF_2 and SF_5ONF_2, the addition of AsF_5 also promoted an intramolecular redox reaction at low temperatures. After several hours at −78 °C almost quantitative CF_4 or SF_6 elimination was observed for stoichiometric mixtures of either CF_3ONF_2 or SF_5ONF_2 with AsF_5. However, the solid byproduct was not $N_2F^+AsF_6^-$, but $NO^+AsF_6^-$:

$$RONF_2 + AsF_5 \rightarrow RF + NO^+AsF_6^- \qquad (4)$$

Thus, the $RONF_2$ compounds also exhibit a Lewis acid promoted intramolecular redox reaction, analogous to those found for the RNF_2 compounds. Again R– is oxidized to RF while –ONF_2 is reduced to FNO. Since FNO readily forms with AsF_5 a stable $NO^+AsF_6^-$ salt, this salt is the only observed coproduct. In the case of $RONF_2$, however, the products, RF and FNO, are identical with those[10,11] observed for the uncatalyzed thermal decomposition of these compounds.

Of the difluoramino compounds investigated in this study, $ClNF_2$ is the least stable. Therefore, it was not surprising that $ClNF_2$ rapidly reacts with AsF_5. Under carefully controlled conditions, an unstable, white, solid, 1:1 intermediate is formed at −78 °C, which at slightly higher temperature starts to decompose with AsF_5, Cl_2, N_2, and NF_3 evolution. In addition to these products, smaller amounts of *trans*-N_2F_2, N_2F_4, $N_2F^+AsF_6^-$, and $N_2F_3^+AsF_6^-$ are formed. On the basis of the observed reaction stoichiometry, the principal reaction is (5), with some contributions from (6) and (7).

$$6ClNF_2 \xrightarrow{AsF_5} 3Cl_2 + N_2 + 4NF_3 \qquad (5)$$

$$4ClNF_2 \xrightarrow{AsF_5} 2Cl_2 + N_2F_2 + 2NF_3 \qquad (6)$$

$$2ClNF_2 \xrightarrow{AsF_5} 2Cl_2 + N_2F_4 \qquad (7)$$

The mechanism of the above described AsF_5-aided decomposition of difluoramino compounds presents an interesting problem. The Lewis acid AsF_5 could interact with RNF_2 molecules through either the R or the NF_2 group. Interaction through R (R = CF_3, SF_5, or Cl) is unlikely because compounds such as CF_4 or SF_6 do not form adducts with AsF_5. However, if in SF_6 one fluorine ligand is replaced by a group of very low electronegativity, such as CH_3, the SF_5 group can become basic enough to donate a fluoride ion to AsF_5 with formation of an ionic RSF_4^+ salt, such as $CH_3SF_4^+AsF_6^-$.[24] To show that with SF_5NF_2 the formation of such a salt, i.e. $F_2NSF_4^+AsF_6^-$, as an intermediate is unlikely, we have studied the interaction of SF_5Br with AsF_5. Since Br and NF_2 have comparable electronegativities, the fluoride donor abilities of SF_5Br and SF_5NF_2 should be similar. Measurements of the vapor pressure at −79 °C above a roughly stoichiometric mixture of SF_5Br and AsF_5, however, revealed only a very weak negative deviation from Raoult's law, indicating little or no interaction. Similarly, the vapor pressure of a stoichiometric mixture of Cl_2 and AsF_5 at −79 °C deviated only slightly from Raoult's law. Therefore, we can limit the following discussion to a consideration of the interaction of the NF_2 group with AsF_5.

The NF_2 group could interact with AsF_5 through a free valence-electron pair on either nitrogen or fluorine. If fluorine is

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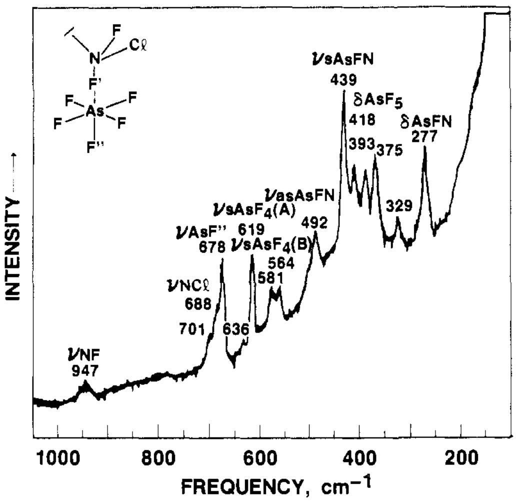
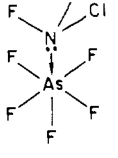


Figure 1. Raman spectrum of the low-temperature 1:1 adduct between NF_2Cl and AsF_5, prepared at −78 °C. Conditions: −130 °C, 6471-Å excitation, and spectral slit width of 8 cm^{-1}.

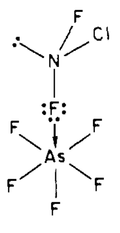
the donor, either a fluorine-bridged, covalent, donor–acceptor complex or a predominantly ionic adduct, $RNF^+AsF_6^-$, could be formed, depending on which product is kinetically and energetically more favorable. Analogies can be cited for both types of interaction. Thus, HNF_2 has previously been shown to form with BF_3 a $>N:\rightarrow B<$ type, covalent, donor–acceptor complex.[5] On the other hand, it is well-known that N_2F_4 forms with AsF_5 the ionic salt $N_2F_3^+AsF_6^-$.[13,22] In view of these alternatives, an extensive effort was made to establish by experiment the nature of the RNF_2–Lewis acid intermediate involved in the above described decomposition reactions. Since even at −78 °C CF_3NF_2 and SF_5NF_2 do not form a solid adduct with AsF_5, whereas $ClNF_2$ does, we have concentrated our studies on the $ClNF_2$ system.

^{19}F NMR studies of equimolar mixtures of $ClNF_2$ and AsF_5 in anhydrous HF at −78 °C and of $ClNF_2$ and SbF_5 in SO_2 at −60 °C showed that in both cases $ClNF_2$ had undergone decomposition. In the absence of AsF_5 or SbF_5, $ClNF_2$ was stable in both solvents. Its NMR spectra showed signals at ϕ 141 in SO_2 at −60 °C and at ϕ 137 in HF at −80 °C. In both cases, a partially resolved triplet was observed due to nitrogen–fluorine spin–spin coupling $J_{^{14}N^{19}F} = 120$ Hz. To our knowledge, no N–F spin–spin coupling has previously been reported for $ClNF_2$.

In view of the instability of $ClNF_2$ in solutions containing AsF_5 or SbF_5, Raman spectra of the solid 1:1 adduct formed between $ClNF_2$ and AsF_5 at −78 °C were recorded at −130 °C. A typical spectrum is shown in Figure 1. On the basis of the large number of observed bands and the absence of the characteristic AsF_6^- vibrations,[13] an ionic $ClNF^+AsF_6^-$ structure can be ruled out. Of the two possible covalent, donor–acceptor complexes, structure II is preferred, on the basis of a comparison with the Raman spectrum of the known N-donor adduct $CH_3CN\rightarrow AsF_5$. The intense Raman bands at 492, 439, and 277 cm^{-1} can only be reconciled satisfactorily with structure II. The observed frequencies and their tentative assignments for II are given in Figure 1. In the spectra a weak band of variable intensity was also observed at about 1060 cm^{-1}, which could be due to small amounts of N_2F^+.[19] However, the possibility cannot be ruled out that this band represents the NF stretching mode. Then, the 947-cm^{-1} band must be assigned to the NCl stretching mode and the 710- and 688-cm^{-1} bands to the doubly degenerate antisymmetric AsF_4 stretching mode.



I



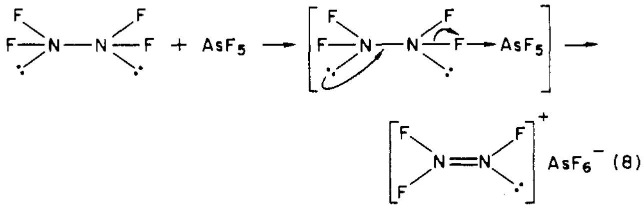
II

Several interesting observations were made in connection with these Raman studies. When the sample was warmed to above −78 °C, the white solid decomposed and an unstable yellow solid formed, which was shown by Raman spectroscopy to contain $Cl_3^+AsF_6^-$.[26] During its decomposition in a closed system, a blue-green unstable material also formed, which with 6471-Å excitation gave a resonance Raman spectrum with its fundamental at 177 cm^{-1}. After pumping off all material volatile at room temperature, a small amount of a white solid was left behind, which on the basis of its Raman and infrared spectra was a mixture of $N_2F^+AsF_6^-$ and $N_2F_3^+AsF_6^-$. The origin of the unstable blue-green species was shown to be due to $Cl_3^+AsF_6^-$ and an excess of Cl_2. A sample of $Cl_3^+AsF_6^-$, when warmed in the presence of an excess of Cl_2 to temperatures slightly above −78 °C, produced the same blue-green species. Possible candidates for this species could be the unknown Cl_5^+ cation or Cl_3 radical, but the frequency of 177 cm^{-1} appears rather low for either one of these, and attempts were unsuccessful to isolate a $Cl_3^+Cl_{2n}AsF_6^-$ species from $Cl_3^+AsF_6^-$ and an excess of Cl_2 at temperatures as low as −95 °C. It should be noted that the 177-cm^{-1} band, which previously has also been reported[26] for $Cl_3^+AsF_6^-$ as an unassigned band of 20% intensity at 170 cm^{-1}, most likely does not belong to $Cl_3^+AsF_6^-$. In our study, this band was completely absent in some of the $Cl_3^+AsF_6^-$ spectra and was observed with variable intensity in others.

The possibility of attributing the complexity of the Raman spectrum of Figure 1 to a polyanion, such as $As_2F_{11}^-$,[27] was also investigated but rejected. When AsF_5 was reacted with a large excess of $ClNF_2$, the solid residue at −78 °C exhibited a spectrum identical with that in Figure 1.

Another interesting question was whether catalytic amounts of AsF_5 suffice to decompose these RNF_2 type compounds. It was found that, for example, 6 mol % of AsF_5 resulted in the decomposition of 53 mol % of the SF_5NF_2 starting material and in the formation of 6 mol % of $N_2F^+AsF_6^-$. It thus appears that the SF_5NF_2 decomposition requires only catalytic amounts of AsF_5 but that the relatively slow SF_5NF_2 decomposition reaction comes to a halt when all the available AsF_5 is converted by *cis*-N_2F_2 in a faster reaction to solid $N_2F^+AsF_6^-$. For the $RONF_2$ type compounds, obviously larger amounts of AsF_5 are required because of the quantitative formation of FNO and its fast and quantitative conversion to solid $NO^+AsF_6^-$. The fact that only AsF_5, but not AsF_6^-, catalyzes the RNF_2 decomposition was demonstrated by the fact that $ClNF_2$ was recovered unchanged when exposed to a stoichiometric amount of $N_2F_3^+AsF_6^-$ for 2 days at ambient temperature.

Finally, the different behavior of N_2F_4 and the difluoramino compounds toward strong Lewis acids needs to be discussed. Whereas the difluoramino compounds of this study appear to form fluorine-bridged donor–acceptor complexes, N_2F_4 forms ionic $N_2F_3^+AsF_6^-$. This different behavior is attributed to the fact that in N_2F_4 removal of a fluoride anion is greatly facilitated by the availability of a free valence-electron pair on the vicinal N atom. This free pair can migrate to form an N═N double bond, thus yielding an energetically favorable, stable cation (eq 8). In the



case of CF_3NF_2 and SF_5NF_2, the C and S atoms, respectively, do not possess a free valence-electron pair that by migration could stabilize a corresponding $R{=}NF^+$ cation. Therefore, for RNF_2

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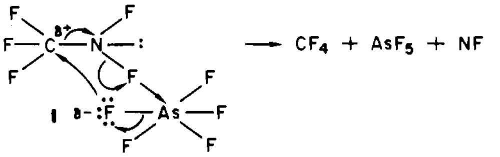
the reaction analogous to (8) stops at the thermally unstable intermediate donor-acceptor stage, which on warm-up can decompose to the observed products by attack of a negatively polarized fluorine atom bound to As on the positively polarized central atom of the R group (eq 9). Such a mechanism, involving



(9)

the formation of NF radicals, could explain the formation of both *cis*- and *trans*-N_2F_2 isomers and could also account for the observation of side reactions, as in the case of $ClNF_2$.

In summary, this study has shown that (i) strong Lewis acids, which are good fluoride acceptors, catalyze the decomposition of difluoramino compounds, (ii) the thermally unstable intermediates, which are initially formed, appear for RNF_2 compounds with highly electronegative R groups to be fluorine-bridged donor-acceptor complexes, and (iii) the exact nature of the final products is governed by their relative stabilities.

Acknowledgment. The authors are grateful to Dr. L. R. Grant for his help and to the Office of Naval Research and the Army Research Office for financial support.

Registry No. II, 93782-55-9; SF_5NF_2, 13693-10-2; $KrFSbF_6$, 52708-44-8; $KrFAsF_6$, 50859-36-4; CF_3NF_2, 335-01-3; KrF_2, 13773-81-4; AsF_5, 7784-36-3; SF_5ONF_2, 14521-09-6; CF_3ONF_2, 4217-93-0; $ClNF_2$, 13637-87-1; SF_5Br, 15607-89-3; Cl_2, 7782-50-5.

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Kinetics of Reduction of Nickel(III) Complexes by Iron(II) and Vanadium(IV) in Aqueous Acidic Perchlorate Media

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Received March 29, 1984

The kinetics of the reduction of a series of nickel(III) macrocycle complexes by $Fe(H_2O)_6^{2+}$ and $VO^{2+}(aq)$ have been studied in acidic aqueous media. An inverse $[H^+]$ rate dependence observed in the reductions by $VO^{2+}(aq)$ is attributed to a dominant $VO(OH)^+$ pathway. Applications of the Marcus theory relationship to the cross-reactions yield estimated self-exchange rate constants of 10^{-3}–10^{-2} M^{-1} s^{-1} for $Fe(H_2O)_6^{2+/3+}$ and 10–10^3 M^{-1} s^{-1} for $VO(OH)^{+/2+}$. These values are larger than the corresponding rate constants derived from metal polypyridine cross-reactions, and the differences are interpreted in terms of the structural and electronic properties of the oxidants. A comparison is made between the behavior of the $Fe(H_2O)_6^{2+}$ and $VO(OH)^+$ ions as reductants. Estimated self-exchange rate constants of $Fe(H_2O)_6^{2+/3+}$ and $VO(OH)^{+/2+}$ are compared with those of other transition-metal aquo ion couples.

Introduction

There has been considerable interest recently in the study of nickel complexes in the trivalent state.[1,2] Numerous nickel(III) complexes have been reported, the majority of these containing tetraaza macrocyclic[3,4] or polypyridine ligands.[5,6] The aqueous redox chemistry of these species is also of interest. While Ni(III) complexes display considerable stability in nonaqueous media, in aqueous solution these species are relatively unstable with respect to reduction. Kinetic studies of the oxidation of metal aquo ions by Ni(III) macrocyclic complexes in aqueous solution are limited to only a few examples.[7,8]

In this paper we report data on the kinetics of the oxidation of Fe^{2+} and VO^{2+} aquo ions by a series of Ni(III) macrocyclic complexes in acidic perchlorate media. The oxidants used in this study include both tetraaza macrocycle complexes, with labile axial coordination sites, and the substitution-inert, bis(triaza macrocycle) complexes of nickel(III). The results of these kinetic investigations are discussed in terms of outer-sphere vs. inner-sphere electron-transfer mechanisms, employing the Marcus theory relationships.[9] Also examined, with regard to the current investigation and others, is the parallel behavior of the Fe(II) and V(IV) aquo ions as reductants, a relationship first reported by Rosseinsky.[10]

Experimental Section

Stock solutions of iron(II) perchlorate were prepared by the oxidation of powdered iron metal (Fisher) in perchloric acid. The iron(II) concentration was determined by titration against standard $KMnO_4$ and by spectrophotometry as $Fe(phen)_3^{2+}$ (510 nm, ϵ = 11 100 M^{-1} cm^{-1}) following complexation with excess 1,10-phenanthroline. The acidity of the stock solution was determined by titration against standard NaOH using methyl orange as the indicator.

Stock solutions of vanadium(IV) perchlorate were prepared by the addition of a stoichiometric amount of barium perchlorate to a solution of vanadyl sulfate (Fisher), followed by removal of precipitated barium sulfate by decantation and filtration. The concentration of VO^{2+} was determined by titration against ammonium cerium(IV) nitrate in acetic acid using a ferroin indicator.

$Ni(cyclam)^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) (Chart I), $Ni(Me_2cyclam)^{2+}$ (Me_2cyclam = *C-meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane), $Ni(tet\text{-}c)^{2+}$ (tet-c = *rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), $Ni(tet\text{-}d)^{2+}$ (tet-d = *meso*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), $Ni(Me_2diene)^{2+}$ (Me_2diene = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene), $Ni(Me_6diene)^{2+}$ (Me_6diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene), $Ni(non)_2^{2+}$ (non = 1,4,7-triazacyclononane), and $Ni(dec)_2^{2+}$ (dec = 1,4,7-triazacyclodecane) were prepared as perchlorate salts as described previously.[11-14] The corresponding Ni(III) complexes were prepared in situ by the oxidation of the Ni(II) complex with a stoichiometric deficiency of $Co(aq)^{3+}$, just prior to their use in kinetic experiments.

The stopped-flow apparatus and data acquisition system have been

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