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On the Existence of Pentacoordinated Nitrogen

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The thermal decomposition of NF_4HF_2 was studied by using ^{18}F-labeled HF_2^-. The observed distribution of ^{18}F among the decomposition products indicates that within experimental error the attack of HF_2^- on NF_4^+ occurs exclusively on fluorine and not on nitrogen, contrary to the predictions based on bond polarities. These results confirm the previous suggestion that the lack of pentacoordinated nitrogen species is due mainly to steric reasons.

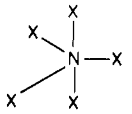
Introduction

Hypervalency, hypercoordination, and formal expansion of the valence octet for first-row elements are and have been the subject of considerable interest and controversy.[2] Whereas hypercoordinated carbon[3] or boron[4] species are well-known, convincing experimental evidence has not been presented so far for the existence of hypercoordinated nitrogen.

It was speculated that pentacoordinated NF_5 is formed either from NF_3–F_2 by fission-fragment radiolysis at room temperature[5] or irradiation with 3-MeV bremsstrahlung[6] at −196 °C or from NF_4AsF_6 by pyrolysis at 175 °C.[7] However, all attempts have failed to confirm these speculations by either matrix isolation experiments,[7,8] low-temperature photolysis,[9] kinetic studies[10] or isotopic exchange studies.[11]

A second pentacoordinated nitrogen species that has been studied experimentally is NH_5. On the basis of hydrogen–deuterium exchange experiments between either molten NH_4^+ salts and LiD or ND_4^+ salts and LiH, the possible intermediacy of pentacoordinated NH_4D or ND_4H was postulated.[12] However, it was subsequently shown that the observed H_2 to D_2 ratios greatly exceeded those expected for the formation of an intermediate NH_4D or ND_4H, and a catalytic isotope exchange reaction of the formed HD gas must be involved.[13]

Theoretical calculations have been carried out for NF_5,[14,15] NH_3F_2,[16] and NH_5.[12,17,18] In all cases it has been found that the pentacoordinated NX_5 species are unstable with respect to decomposition to $NX_3 + X_2$ and are less stable than the corresponding ion pairs $NX_4^+X^-$. Of the various geometries possible for a pentacoordinated NX_5 species, the trigonal-bipyramidal D_{3h} structure with two symmetrical axial bonds, i.e.



was generally found to be most favorable. Interestingly, however, it was found for NH_3F_2 that the D_{3h} geometry is only a saddle point and that the molecule is stabilized by relaxation to a C_{3v} structure that essentially is an ion pair $NH_3F^+F^-$ with only one F atom in the first coordination sphere and the second F atom at 2.00 Å from the nitrogen atom.[16] This behavior suggests that there is not enough space around nitrogen for five ligands and that steric reasons are mainly responsible for the nonexistence of a pentacoordinated nitrogen.[19]

In view of the previous failures of the experimentalists and the above conclusions by the theoreticians, the existence of a stable pentacoordinated nitrogen species is unlikely. This, however, would not preclude the possible existence of a pentacoordinate nitrogen species as a short-lived unstable intermediate, provided nitrogen could sterically accommodate five ligands. Consequently, we sought to obtain a conclusive answer to the question of whether nitrogen can sterically accommodate five ligands in its first coordination sphere.

Experimental Section

A Teflon–FEP ampule equipped with a Kel-F valve was passivated with F_2, and NF_4PF_6[9] (0.854 mmol) and dry CsF[20] (0.809 mmol) were added in the drybox. Fluorine-18 labeled HF was prepared by combining a Ne/[^{18}F]F_2 mixture, which was accelerator produced under conditions previously described[21] except for using a 15-MeV beam, with 1 atmosphere of H_2 at −196 °C in a 150-mL nickel can containing unlabeled anhydrous[22] HF (2.35 mmol). The H_2 and Ne were pumped off at −196 °C, and the radioactivity of the HF was measured. The labeled HF was condensed at −196 °C into the Teflon reactor, and its contents were warmed first to room temperature. While the reactor was gradually warmed to 100 °C over 1 h, the volatile products were pumped through a $^1/_4$-in. Teflon–FEP cold trap kept at −130 °C, followed by a soda lime scrubber and a second Teflon–FEP cold trap kept at −210 °C. The −130

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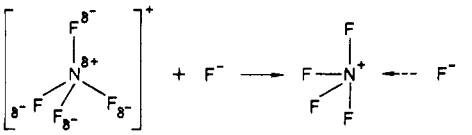
°C trap contained the HF and the −210 °C trap the NF_3, and the soda lime scrubber absorbed the F_2. The relative activity distribution, corrected for the elapsed time, was continuously monitored during the course of the experiment. The quantitative nature of the reaction was confirmed in a separate experiment by its material balance using unlabeled reagents under identical conditions.

Results and Discussion

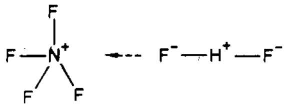
A major drawback of the previously studied NH_4^+–H^- system[12] is the unfavorable polarity of the N–H bonds. Since in NH_4^+ the positive charge resides on the protons and the negative one on the nitrogen, the negatively charged H^- anion should attack on a proton ligand and not on the nitrogen as required for a pentacoordinated nitrogen transition state. This conclusion has been confirmed by an ab initio study, which showed that in the hydrogen abstraction reaction the pentacoordinated D_{3h} structure does not intervene either as an intermediate or a transition state. The H^- ion can abstract a proton from NH_4^+ along a continuous downhill energy path.[17]

This drawback of unfavorable bond polarities can be overcome by the NF_4^+–F^- system. In NF_4^+ the N–F bonds have the desired polarity for an attack of F^- on nitrogen, i.e.



(1)

Since $NF_4^+F^-$ is unknown[23] and because in the solvents known to be compatible with NF_4^+, such as HF or halogen fluorides, the F^- forms complex fluoro anions, we have studied the attack of a complex fluoro anion on NF_4^+. The HF_2^- anion appeared to be the ideal candidate because of the low thermal stability of its NF_4^+ salt[20] and its linear, highly polar structure presenting no additional steric hindrance compared to a free F^- anion, i.e.



The $NF_4^+HF_2^-$ salt can be generated from NF_4PF_6 and $CsHF_2$ in a minimal amount of anhydrous HF as a solvent.

$$NF_4PF_6 + CsHF_2 \xrightarrow{HF} CsPF_6 + NF_4HF_2 \qquad (2)$$

The NF_4HF_2, which is stable at room temperature in an excess of HF, decomposes on removal of HF in a dynamic vacuum between 25 and 100 °C with NF_3 and F_2 evolution.[20]

$$NF_4HF_2 \xrightarrow[\Delta T]{\text{vacuum}} NF_3 + F_2 + HF \qquad (3)$$

By the use of ^{18}F labeled HF_2^- and a radioassay of the decomposition products, one then can distinguish between attack of HF_2^- on nitrogen or fluorine of NF_4^+. If there is no steric hindrance, i.e. if nitrogen can coordinate to five fluorine atoms, the HF_2^- should attack on nitrogen because of the more favorable Coulomb forces, and hence this should result in statistical scrambling of the ^{18}F among NF_3, F_2, and HF. If, however, nitrogen can coordinate to only four fluorine atoms, then HF_2^- must attack NF_4^+ at a fluorine ligand. In this case all the activity should be found in F_2 and HF and none in the NF_3. Since the PF_6^- anion can readily exchange with the labeled HF_2^- anion in HF solution, the $CsPF_6$ residue which is left after completion of steps 2 and 3 should also contain a statistical amount of activity.

Table I. Distribution of ^{18}F in the Reaction Products from the Pyrolysis of $NF_4F{\cdot}2.9HF$

	^{18}F activity, mCi		
		calcd for attack on	
product	found	N	F
F_2	2.85	4.2	2.95
HF	8.2	6.1	8.55
$CsPF_6$	17.6	12.6	17.7
NF_3	1.2×10^{-3}	6.3	0
tot. activity	28.6	29.2	29.2

The results of our study are summarized in Table I. As can be seen, the ^{18}F balance is excellent and the observed data are compatible only with attack of HF_2^- on the fluorine and not the nitrogen atom of NF_4^+. The fact that a small activity reading was observed for NF_3 should not be interpreted as a small contribution of competing attack on nitrogen but is rather due to slight variation of the radiation background level and the associated difficulty in measuring relatively small radiation values.

In conclusion, it can be stated that within experimental error the HF_2^- attack on NF_4^+ occurs exclusively on the fluorine atoms. Since the polarities of the bonds in both NF_4^+ and HF_2^- would favor attack on nitrogen, the lack of attack on nitrogen is attributed to steric reasons. In view of the small size of fluorine and its ability to achieve maximum coordination numbers for most elements, the existence of pentacoordinated nitrogen species containing ligands other than fluorine must be judged even less likely, except for hydrogen, which has a smaller covalent radius than fluorine.

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Registry No. NF_4HF_2, 71485-49-9; F_2, 7782-41-4; HF, 7664-39-3; $CsPF_6$, 16893-41-7; NF_3, 7783-54-2; $CsHF_2$, 12280-52-3; NF_4PF_6, 58702-88-8.

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