The Protiotetramethylammonium Dication $(CH_3)_3NCH_4^{2+}$: Hydrogen/Deuterium Exchange and Calculational Studies. Search for the Parent Protioammonium Dication NH_5^{2+} [1]

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Abstract: The protonation of ammonium ions NR_4^+ (R = H, CH_3) to form the corresponding protioammonium dications HNR_4^{2+} (R = H, CH_3) was investigated by hydrogen/deuterium exchange experiments and by ab initio molecular orbital calculations. Hydrogen/deuterium exchange was observed by ^2H NMR spectroscopy at the CH_3 groups of tetramethylammonium ion $N(CH_3)_4^+$ when reacted with excess $DF:SbF_5$ superacid. On the basis of calculational results, the intermediacy of the corresponding C−H-protonated protiotetramethylammonium dication $(CH_3)_3NCH_4^{2+}$ is suggested to account for the observed exchange. Under similar conditions, no exchange was observed in the parent ammonium ion NH_4^+ in $FSO_3D:SbF_5$ superacid, although the NH_5^{2+} dication was calculated to be kinetically stable with a considerable barrier to deprotonation. The pentafluoroammonium dication NF_5^{2+} was also investigated theoretically, and the results were compared to those of neutral NF_5.

Introduction

A major step in the development of structural chemistry a century ago was the realization of the ionic rather than covalent nature of ammonium compounds.[2] Ammonium compounds, as well recognized, are tetravalent ionic (**1**) and not pentacovalent nitrogen compounds (**2**). Considerable interest and controversy have centered around hypervalency, hypercoordination, and formal expansion of the valence octet for first-row elements in the past years.[3−5] Hypercoordinated boron[6] (e.g., pentahydridoboron BH_5 **3**) and carbon[7] (e.g., the methonium ion, the parent carbonium ion CH_5^+ **4**) species are well-known and characterized. The isoelectronic pentacoordinated nitrogen compound NH_5^{2+} is so far unknown. Studies on pentavalent neutral NH_5 have also been reported.[8]
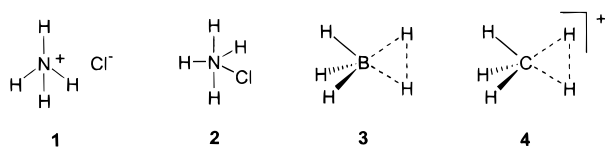
Schmidbaur et al. have recently reported[9] the preparation and subsequent X-ray analysis of the aurated azonium dication $((C_6H_5)_3PAu)_5N^{2+}$ **5**, in which the central nitrogen atom is coordinated by five gold(I) ligands. Considering the isolobal relationship[10,11] (i.e., similarity in bonding) between LAu^+ and

H^+, ion **5** represents a gold analogue of the elusive protioammonium dication NH_5^{2+}.

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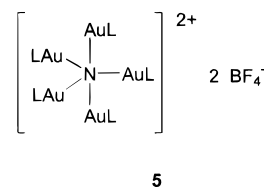
It is generally not possible to directly observe small gitonic dications[12] in solution by methods such as NMR or IR−Raman spectroscopy. There is evidence for the formation of NO_2H^{2+} and CH_3COH^{2+} in highly acidic media. ^{17}O NMR spectroscopic studies of nitronium ion in superacidic $HSO_3F:SbF_5$ medium have indicated the involvement of the protonitronium dication NO_2H^{2+}.[13] This dication has also been observed in the gas phase.[14] IR studies of the acetyl cation show significant shifts of the CO frequencies depending on the acidity of the system, indicating protosolvation.[15] Hydrogen/deuterium exchange experiments in superacids have clearly indicated the involvement of such dications as H_4O^{2+} and H_4S^{2+}.[16,17] In addition, a number of other small dications have been observed in the gas phase by charge-stripping mass spectrometry, including the smallest two-electron diatomic dication He_2^{2+}.[18] In these studies it was found that many dications, although thermodynamically extremely unstable, are kinetically stabilized by high barriers

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Protiotetramethylammonium Dication [(CH₃)₃NCH₄²⁺]

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to decomposition.[19] Theoretical calculations are a particularly powerful tool for probing these dications. In the experimentally studied superacid solutions, however, further stabilization is possible due to clustering (protosolvation) and thus charge dispersion.

Several experimental and theoretical studies have previously been reported on the possible intermediacy of pentacoordinated nitrogen compounds. On the basis of hydrogen/deuterium exchange experiments between molten NH_4^+ salts and LiD or ND_4^+ salts and LiH, Olah et al. postulated the possible intermediacy of pentacoordinated NH_4D or ND_4H.[8] It was, however, subsequently shown that the observed H_2 to D_2 ratios greatly exceeded those expected solely for the formation of an intermediate NH_4D or ND_4H, and therefore, a catalytic isotope exchange reaction of the formed HD must be also involved.[20,21] Theoretical calculations on NH_5 by Simonetta et al.[22] indicated that of the various geometries possible for NH_5, the trigonal bipyramidal D_{3h} structure is the most favorable. In addition, the study indicated that pentacoordinated NH_5 is unstable with respect to decomposition to $NH_3 + H_2$ and is less stable than the corresponding ion pair $NH_4^+H^-$. Further, it is to be considered that since no free H^- exists in the condensed phase, the observed hydrogen/deuterium exchange could be accounted for by an intermediate in which LiD is complexed with NH_4^+.

Recent ab initio calculations suggested that covalent NF_5 is a vibrationally stable molecule.[23,24] So far, however, all experimental attempts to prepare and characterize NF_5, either as a covalent molecule or as an ionic $NF_4^+F^-$ salt,[25] have failed. Christe, Schrobilgen, and Olah et al. have studied[26] the thermal decomposition of $NF_4^+HF_2^-$ by using ^{18}F-labeled HF_2^-. In these studies it was found that the attack of HF_2^- on NF_4^+ occurs exclusively on fluorine and not on nitrogen, contrary to the predictions based on bond polarities. It was thus argued that nitrogen is sterically not able to accommodate five fluorine atoms in its first coordination sphere.[26]

In the present study, we have investigated by hydrogen/deuterium exchange experiments and by ab initio molecular orbital calculations, the protonation of ammonium ions NR_4^+ (R = H, CH₃) to form the corresponding protioammonium dications HNR_4^{2+} (R = H, CH₃). Hydrogen/deuterium exchange was observed by ^{2}H NMR spectroscopy at the CH₃ groups of tetramethylammonium ion $N(CH_3)_4^+$ when reacted with excess DF:SbF₅ superacid. On the basis of calculational results, the intermediacy of the corresponding C−H-protonated gitonic[12] protiotetramethylammonium dication $CH_4N(CH_3)_3^{2+}$ is suggested to account for the observed exchange. The parent pentacoordinated NH_5^{2+} dication was calculated to be kinetically stable with a considerable barrier to deprotonation of 25.9 kcal/mol. No hydrogen/deuterium exchange was observed, however, when NH_4^+ was reacted with FSO₃D:SbF₅. The theoretical results were compared to those of the isoelectronic carbon analogue CH_5^+ as well as the neutral NH_5 molecule. The pentafluoroammonium dication NF_5^{2+} was also investigated theoretically, and the results were compared with its neutral analogue NF_5.

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Table 1. Total Energies (−au) and Zero-Point Vibrational Energies (kcal/mol)

structure	MP2(fu)/ 6-31G**// MP2(fu)/ 6-31G** (ZPE)	G2	QCISD/ 6-311G**// QCISD/ 6-311G**	NIMAG[a]
9 (C_{4v})	56.57883 (29.4[b])	56.62512	56.61391	0
11 (C_{3v})	56.53648 (28.2[b])	56.58392		1
12 (C_{2v})	56.57660 (29.0[b])	56.62225		1
NH_3^{2+} (D_{3h})	55.17674 (17.0[b])	55.23075	55.21603	0
NH_4^+ (T_d)	56.73765 (29.7[b])	56.78348	56.77186	0
H_2	1.15766 (6.1[b])	1.16643	1.16834	0
13 (T_d)	213.49363 (98.6[c])			0
14 (C_S)	213.50781 (101.5[c])			0
15 (C_S)	551.11298 (10.7[c])			0
16 (D_{3h})	352.02840 (8.9[c])			0
F_2	199.03883 (1.6[c])			0

[a] NIMAG (number of imaginary frequencies) at the MP2(fu)/6-31G**//MP2(fu)/6-31G** level. [b] ZPE at MP2(fu)/6-31G**//MP2(fu)/6-31G** scaled by a factor of 0.93. [c] ZPE at HF/6-31G*//HF/6-31G* level scaled by a factor of 0.8929.

Results and Discussion

In order to investigate small gitonic azonium dications, high-level ab initio calculations were carried out on the parent monocations NH_4^+ and $N(CH_3)_4^+$ and their protonated dications, as well as on dication NF_5^{2+} and its parent monocation NF_4^+. Geometry optimizations were performed at MP2(fu)/6-31G** (fu = full) and/or QCISD/6-311G** level. Frequency calculations were carried out to characterize the structures as minimum, saddle point, or transition structure and to evaluate zero-point vibrational energies (ZPE). Improved energies were obtained with the Gaussian-2 (G2) method. The G2 theory is a composite method based on MP2(fu)/6-31G* geometry which is treated in single-point calculations with a variety of basis sets at the post-SCF level.[27] Atomic charges were obtained using the natural bond orbital analysis (NBO)[28] method. Unless otherwise stated, MP2(fu)/6-31G** structures and charges and G2 energies will be discussed in the text. Similar to previous[29] calculations on the parent carbonium ion CH_5^+, we have considered a number of symmetry-constrained structures for the geometry optimization of pentacoordinated nitrogen compounds, including the C_s forms **6** and **7**, the C_{2v} form **8**, the square pyramidal C_{4v} form **9**, and the trigonal bipyramidal D_{3h} form **10**. Total energies (−au) and zero-point vibrational energies (kcal/mol) of the ions are summarized in Table 1. Optimized geometries are given in Figures 1−3.

6 (C_S)   7 (C_S)   8 (C_{2v})

9 (C_{4v})   10 (D_{3h})
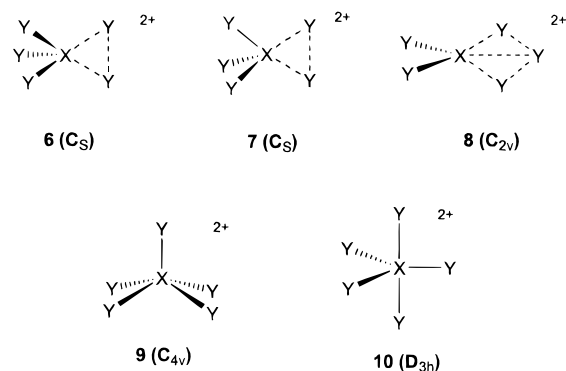
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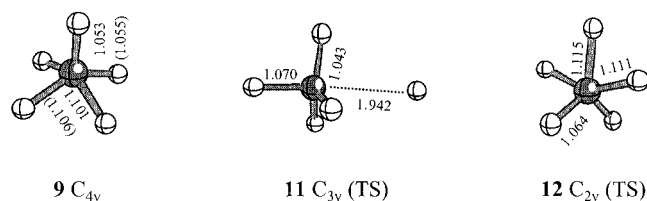
9 C_{4v} **11** C_{3v} (TS)   **12** C_{2v} (TS)

Figure 1. MP2(fu)/6-31G**-optimized geometries of **9**−**12** (QCSID/6-311G**).

13 (C_S)   **14** (T_d)
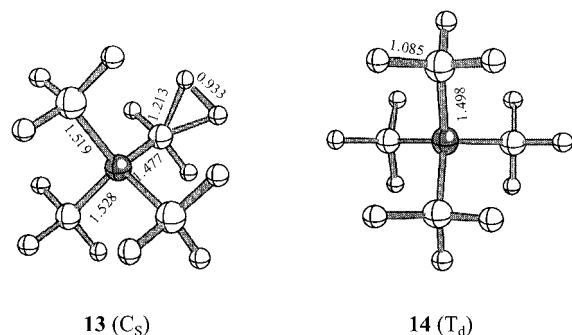
Figure 2. MP2(fu)/6-31G**-optimized geometries of $CH_4N(CH_3)_3{}^{2+}$ and $N(CH_3)_4{}^+$ ions **13** and **14**, respectively.
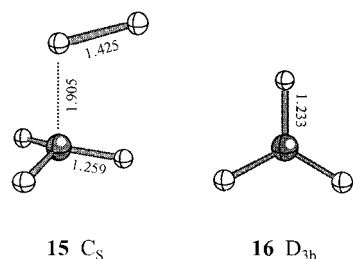

15 C_S **16** D_{3h}

**Figure 3.** MP2(fu)/6-31G**-optimized geometries of $NF_5{}^{2+}$ and $NF_3{}^{2+}$ dications **15** and **16**, respectively.

In experimental studies, we have reacted $NH_4{}^+$ and $N(CH_3)_4{}^+$ ions with excess deuterated superacids, such as $FSO_3D{:}SbF_5$ and $DF{:}SbF_5$, in order to probe hydrogen/deuterium exchange or its absence. Under these extremely acidic conditions, ammonium ions do not show any deprotonation equilibria with their neutral amines. In fact, 1:1 molar mixtures of $FSO_3D{:}SbF_5$ ($H_0 = -21$) and $DF{:}SbF_5$ ($H_0 = -25$) are among the strongest superacid systems known, in which no free amine can be present.[30] Thus, if observed, hydrogen/deuterium exchange in $NH_4{}^+$ and $N(CH_3)_4{}^+$ ions cannot proceed via a deprotonation−reprotonation mechanism, but would involve the corresponding protonated gitonic dications as intermediates.

Protioammonium Dication $NH_5{}^{2+}$. At both MP2(fu)/6-31G** and QCISD/6-311G** levels, structure **9** (C_{4v} symmetry) was found to be the single minimum on the potential energy surface of $NH_5{}^{2+}$. Structures **6**−**8** and **10** are not minimum structures at these levels of theory. The optimized structure of $NH_5{}^{2+}$ **4** was characterized by a slightly longer axial (1.106 Å) and slightly longer equatorial (1.055 Å) N−H bonds compared to the N−H bonds of the $NH_4{}^+$ ion (1.022 Å). NBO charges of the ion **9** were calculated to be −1.19 au on the central nitrogen atom, 0.57 au on the axial hydrogen atom, and 0.65 au on the equatorial hydrogen atoms. Similar NBO charges were obtained at QCISD/6-311G** level (−1.39, 0.62, and 0.69 au, respectively).

The dissociation of **9** into $NH_4{}^+$ and H^+ is expectedly highly exothermic by 99.1 kcal/mol. We have identified the transition

state **11** for the dissociation reaction which lies 25.9 kcal/mol above minimum structure **9**. Thus, dication **9** has a considerable kinetic barrier to dissociation. However, it should be taken into consideration that these data refer to the isolated idealized gas phase and that in the condensed phases electrophilic (protolytic) solvation or clustering effects may have great influence. Particularly in small dications such interactions should diminish the effect of charge−charge repulsion and thus could bring the cations into a thermodynamically more feasable range. On the other hand, it may also lower the kinetic barrier to deprotonation. Counterions may also play a considerable role in the protonation equilibria. In superacid systems, however, exceedingly delocalized and weak nucleophiles like $SbF_6{}^-$ or related $Sb_2F_{11}{}^-$ anions might not compete efficiently with the rather localized lone pairs of the mono- or dications. Transition state **11** has C_{3v} symmetry and is characterized by one long (1.942 Å) and one short (1.070 Å) axial C−H bond. We have also identified the transition state **12** for hydrogen scrambling in dication **9**. The barrier for hydrogen scrambling between two C_{4v} structures through **12** is calculated to be only 1.0 kcal/mol. Thus, hydrogen scrambling in $NH_5{}^{2+}$ should be very facile. This type of facile hydrogen scrambling has also been calculated for methonium dications $CH_4{}^{2+}$, $CH_5{}^+$, and $CH_6{}^{2+}$.[7]

Significantly, we also found that the gas phase reaction of $NH_3{}^{2+}$ dication with H_2 forming $NH_5{}^{2+}$ **9** is highly exothermic by 143.0 kcal/mol.

$$NH_3{}^{2+} + H_2 \longrightarrow NH_5{}^{2+}$$
$$\mathbf{9}$$
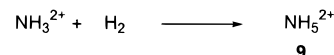
The $NH_3{}^{2+}$ dication has previously been observed in the gas phase by charge-transfer mass spectrometry (CTMS) and has also been studied theoretically.[31] Our calculations indicate that it might be possible to observe the $NH_5{}^{2+}$ dication **9** in the gas phase by reacting $NH_3{}^{2+}$ and H_2.

As mentioned, Olah et al. have observed H/D exchange when reacting $NH_4{}^+$ with LiD or $ND_4{}^+$ with LiH.[8] The intermediacy of neutral NH_5 was suggested to explain the exchange reactions. It was, however, subsequently pointed out that exchange reaction with HD formed in deprotonation can explain much of the exchange. Simonetta et al. have previously[22] calculated the reaction of $NH_4{}^+$ salts with LiH forming NH_5. In these studies, pentacoordinated NH_5 was found to be a stable structure with D_{3h} symmetry at the 4-31G level. We were able to reproduce Simonetta's calculations at the 4-31G level, but found that the reported D_{3h} structure is a transition state rather than a minimum structure on the NH_5 potential energy surface. Furthermore, we found that at correlated MP2(fu)/6-31G** level NH_5 spontaneously dissociates into $NH_4{}^+$ and H^- ions. Similar to its isoelectronic carbon analogue $CH_5{}^-$, neutral NH_5 has not been observed experimentally. $CH_5{}^-$ has been calculated to be thermodynamically and kinetically unstable,[32,33] in accord that 10 electrons in the carbon valence shell cannot give a stable species (in contrast to $CH_5{}^+$, which is an 8 electron species).

Attempts to observe hydrogen/deuterium exchange in ammonium ion $NH_4{}^+$ when treated with excess deuterated superacid were unsuccessful. Ammonium chloride $NH_4{}^+Cl^-$ was reacted with $DSO_3F{:}SbF_5$ solution at 100 °C. No hydrogen/deuterium exchange was observed by ^2H NMR even after 14 days.

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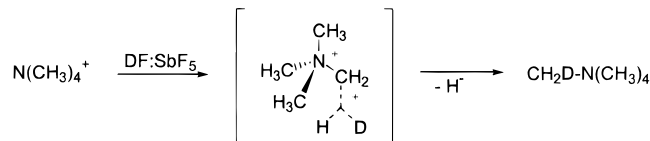(33) Cremer, D.; Kraka, E. *J. Phys. Chem.* **1986**, *90*, 33.

$$NH_4^+ \xrightarrow[\times]{DSO_3F:SbF_5} NH_4D^{2+} \xrightarrow[-H^+]{} NH_3D^+$$
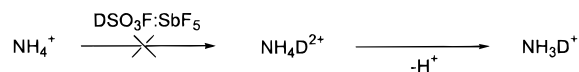
Similarly, ammonium-d_4 chloride $ND_4^+Cl^-$ was also reacted with $FSO_3H:SbF_5$ solution at 100 °C. Again, no deuterium/hydrogen exchange was observed by ^2H NMR after 2 weeks.

$$ND_4^+ \xrightarrow[\times]{HSO_3F:SbF_5} NHD_4^{2+} \xrightarrow[-H^+]{} NHD_3^+$$
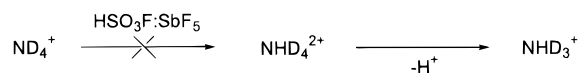
The lack of hydrogen/deuterium exchange in NH_4^+ suggests that the protioammonium dication NH_5^{2+} **9** does not form under the experimental conditions in the studied superacid medium. However, the use of methods such as charge-stripping mass spectrometry[18] allowing the reaction of NH_3^{2+} and H_2 might be successful to observe the elusive NH_5^{2+} dication in the gas phase.

Protiotetramethylammonium Dication. Tetramethylammonium tetrafluoroborate $N(CH_3)_4^+BF_4^-$ was reacted with DF:SbF_5 at 20 °C, and the solution was analyzed by ^1H and ^2H NMR spectroscopy ($\delta(^1H)$ 2.26 s). At 20 °C, no decomposition of the ion was observed. We observed hydrogen/deuterium exchange in $N(CH_3)_4^+$ of the methyl protons ($\delta(^1H)$ 2.26 s) with the simultaneous appearance of a peak at $\delta(^2H)$ 2.28 whose intensity increased with time (Figure 4). Up to 2% deuterium incorporation at the CH_3 groups in **14** was observed during 14 days at 20 °C. No evidence was found for any protonation of the central nitrogen atom in $N(CH_3)_4^+$. The intermediacy of the C—H-deuterated tetramethylammonium dication is considered to account for the observed exchange at the methyl protons in $N(CH_3)_4^+$ **14**:

$$N(CH_3)_4^+ \xrightarrow{DF:SbF_5} \left[\begin{array}{c} CH_3 \\ H_3C\cdots \overset{+}{N} \diagdown CH_2 \\ H_3C \quad \diagdown \overset{+}{\diagup} \\ H \quad D \end{array} \right] \xrightarrow{-H^-} CH_2D\text{-}N(CH_3)_4$$

An alternative mechanism involving deprotonation of $(CH_3)_4N^+$ to trimethylammonium methylide is unlikely under these highly acidic conditions. It has been shown previously that even deprotonation equilibria of the *tert*-butyl cation to isobutylene is not possible under these conditions.[34,35] Yet another possible mechanism involving free methyl cation (CH_3^+) transfer to fluoride ion F^- leading to CH_3F also seems less probable because of the exceedingly high acidity of HF:SbF_5 medium ($H_0 = -25$ to -30). Furthermore, the bulk of the hydrogen fluoride in this medium exists in the form of H_2F^+.[30] The residual BF_4^- anion will also be extremely non-nucleophilic due to its complexation with SbF_5. Furthermore, we have not detected any CH_3F:SbF_5 complexes or its facile proton/deuterium exchange by NMR spectroscopy. If there were such a cleavage, we should have observed the formation of trimethylammonium ion $(CH_3)_3NH^+$. However, no such cleavage was ever detected.

To probe the mechanism of the observed hydrogen/deuterium exchange in tetramethylammonium ion under superacid conditions, we have carried out ab initio calculations. Protonation of the tetramethylammonium ion $N(CH_3)_4^+$ may result in two different dications: N-protonated gitonic[12] dication $HN(CH_3)_4^{2+}$ and C—H-protonated dication $(CH_3)_3NCH_4^{2+}$ **13**.

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(a)
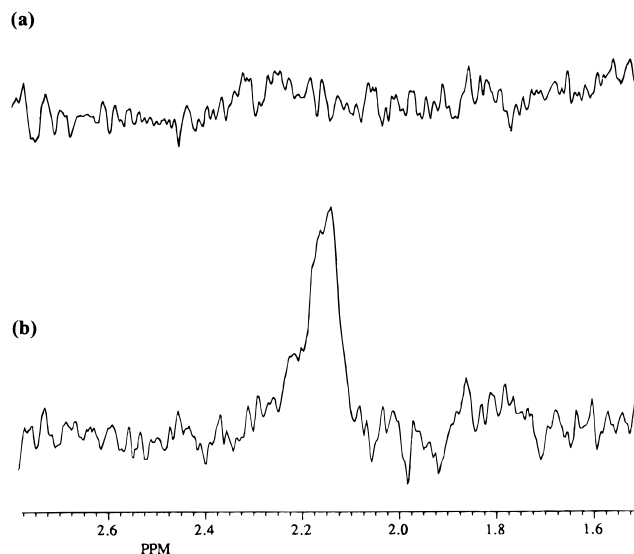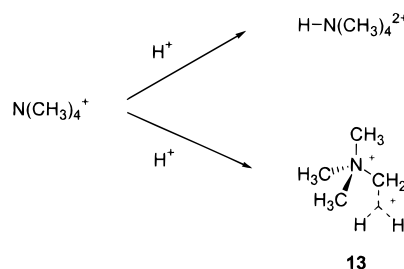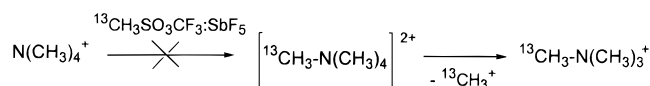
(b)

Figure 4. ^2H NMR Spectrum of $(CH_3)_4N^+$ in DF:SbF_5: (a) after 12 h and (b) after 14 days.

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No minimum structure could be located for pentacoordinated nitrogen dication $HN(CH_3)_4^{2+}$ because of its spontaneous dissociation upon optimization. The C—H-protonated form **13**, however, was found to be a stable minimum at MP2(fu)/6-31G** level with a three-center two-electron bond at the CH_3 carbon (Figure 2). Protonation of tetramethylammonium ion $N(CH_3)_4^+$ **14** forming $CH_4N(CH_3)_3^{2+}$ **13** dication was further calculated to be slightly exothermic by 6.0 kcal/mol at the MP2-(fu)/6-31G** + ZPE level. These results are in line with previous studies in which alkyl cations, such as *tert*-butyl[34] and 2-propyl cations,[35] as well as acylium ions[36] were found to undergo C—H protonation to form highly electron deficient, *superelectrophilic*[12] protioalkyl and protioacyl dications, respectively.

We have also attempted to observe $CH_3/^{13}CH_3$ exchange in $N(CH_3)_4^+$ ion. Tetramethylammonium tetrafluoroborate $N(CH_3)_4^+BF_4^-$ was reacted with $^{13}CH_3SO_3CF_3$:SbF_5 (1:1 molar solution) at 50 °C. Periodic monitoring by ^{13}C NMR over a period of 1 week, however, did not indicate any $CH_3/^{13}CH_3$ exchange in the $N(CH_3)_4^+$ cation. In addition, attempts to find a stable minimum structure at MP2(fu)/6-31G** level for the $N(CH_3)_5^{2+}$ dication failed, because of its spontaneous dissociation into $N(CH_3)_4^+$ and CH_3^+ cations upon optimization.

$$N(CH_3)_4^+ \xrightarrow[\times]{^{13}CH_3SO_3CF_3:SbF_5} \left[^{13}CH_3\text{-}N(CH_3)_4 \right]^{2+} \xrightarrow[-^{13}CH_3^+]{} ^{13}CH_3\text{-}N(CH_3)_3^+$$

Both our experimental and theoretical results suggest that the nitrogen atom in $N(CH)_4^+$ ion is sterically unable to accommodate any further ligand (H^+ or CH_3^+) to form pentacoordinated azonium dications $HN(CH_3)_4^{2+}$ or $N(CH_3)_5^{2+}$, respec-

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tively. Instead, protonation of $N(CH_3)_4^+$ leads to the thermodynamically more favorable C–H-protonated dication $CH_4N(CH_3)_3^{2+}$ **13**.

Pentafluoroammonium Dication NF_5^{2+}. Geometry optimization of NF_5^{2+} at MP2(fu)/6-31G** level gave a single minimum structure **15** (C_S symmetry), resembling a complex between NF_3^{2+} **16** and F_2 with a long N–F bond (1.905 Å, see Figure 3). Previous[26] calculations on the neutral NF_5 molecule have also resulted in a complex of NF_3 and F_2 rather than a pentacoordinated species. NF_4^+ when reacted with $^{18}F^-$ gave only $^{19}F^{18}F$, but no fluorine exchange of NF_4^+. We have also optimized NF_3^{2+} dication **16**, and its geometry is given in Figure 3. The reaction of NF_3^{2+} dication with F_2 forming NF_5^{2+} dication was calculated to be exothermic by 28.5 kcal/mol at the MP2(fu)/6-31G** + ZPE level.

There have apparently been no prior experimental studies of NF_3^{2+} dication **16** in the gas phase, although previous[24] calculations have shown that NF_3^{2+} is a structurally stable molecule with a trigonal planar geometry. Our calculations indicate that it might be possible to observe NF_5^{2+} dication **16** in the gas phase. Similar to neutral NF_5, however, NF_5^{2+} does not contain a pentacoordinated central nitrogen atom but can be visualized as a complex of NF_3^+ and F_2. This further suggests that the nitrogen atom is sterically unable to accommodate five fluorine atoms in its first coordination sphere.

Conclusions

The protonation of ammonium ions NR_4^+ (R = H, CH_3) to the corresponding protioammonium dications HNR_4^{2+} (R = H, CH_3) was investigated by hydrogen/deuterium exchange experiments and by ab initio molecular orbital calculations. Hydrogen/ deuterium exchange was observed by ^2H NMR spectroscopy at the CH_3 groups of tetramethylammonium ion $N(CH_3)_4^+$ when reacted with excess DF:SbF$_5$ superacid. On the basis of the calculated results, the intermediacy of the corresponding C–H-protonated gitonic protiotetramethylammonium dication $(CH_3)_3$-NCH_4^{2+} is suggested to account for the observed exchange. Lack of similar exchange in parent NH_4^+ ion indicates the inability to form the NH_5^{2+} dication in superacids. Protonation of NH_4^+ is highly endothermic by some 99.8 kcal/mol. However, NH_5^{2+} was calculated to be kinetically stable with a considerable barrier to deprotonation (25.9 kcal/mol). The theoretical results were also compared to those of the isoelectronic carbon analogue CH_5^+ as well as to neutral NH_5. NF_5^{2+} dication was also investigated theoretically and found to be a stable molecule at MP2(fu)/6-31G** level. Similar to neutral NF_5, however, its structure does not resemble a pentacoordinated nitrogen compound, but rather a complex between NF_3^{2+} and F_2. These results are in line with previous[26] studies, which suggested that nitrogen is sterically unable to accommodate five fluorine atoms in its first coordination sphere (although it can accommodate five hydrogens).

Experimental Section

Ammonium chloride, ammonium-d_4 chloride (99.9 atom % D), tetramethylammonium tetrafluoroborate, $CH_3SO_3CF_3$, $^{13}CH_3SO_3CF_3$ (99 atom % ^{13}C), D_2SO_4 (98 wt %, 99.5 atom % D; Acros), anhydrous NF (Setic Labo), D_2O (99.9 atom %; Acros), and benzoyl chloride (Lancaster) were purchased from Aldrich if not indicated otherwise and were used as received. SbF$_5$ (Allied-Chemical) and FSO$_3$H (3M) were doubly distilled prior to use. DF was prepared from benzoyl

fluoride and D_2O as reported.[37] Benzoyl fluoride was prepared from benzoyl chloride and anhydrous HF as described in the literature.[38]

^1H and ^2H NMR spectra were obtained on a Bruker AM 400 spectrometer equipped with a variable temperature probe at 400 and 61.4 MHz, respectively. ^{13}C NMR spectra were taken on a Varian Associates Model Unity-300 spectrometer at 75.4 MHz. Quartz NMR tubes (5 mm) were used for samples containing DF. NMR spectra were obtained with respect to TMS by using an acetone-d_6 capillary as external standard.

All calculations were carried out using the Gaussian 94[39] package of programs.

Preparation of FSO$_3$D. Doubly distilled FSO$_3$H (14.8 mL, 0.26 mol) were placed into a flask equipped with a magnetic stirrer under nitrogen atmosphere. The solution was cooled to 0 °C, and 14 mL (0.26 mol) of D_2SO_4 (98 wt %) were added. The ensuing mixture was stirred at room temperature for a period of 24 h. Distillation yielded 16.6 g (0.16 mol) of FSO$_3$D (bp = 165 °C). ^2H NMR of the distillate indicated a deuterium enrichment of approximately 90 atom % D (δ-(^2H) 9.59 s).

H/D Exchange in $N(CH_3)_4^+$ with DF:SbF$_5$. $N(CH_3)_4^+BF_4^-$ (150 mg) was placed into a Kel-F tube and cooled to −78 °C in a dry ice/ acetone bath. Approximately 2 mL of DF:SbF$_5$ (2.5:1 molar solution) was added to the solution at −78 °C. The ensuing mixture was vigorously stirred (Vortex stirrer) under periodic cooling. After the sample was characterized by ^1H and ^2H NMR spectroscopy at −15 °C, it was kept at room temperature for 14 days and periodically monitored by ^1H and ^2H NMR spectroscopy.

Attempted H/D Exchange in NH_4^+ (ND_4^+) with FSO$_3$D:SbF$_5$ (FSO$_3$H:SbF$_5$). $NH_4^+Cl^-$ ($ND_4^+Cl^-$) (30 mg) was placed into an NMR tube and cooled to −78 °C in a dry ice/acetone bath. Approximately 0.5 mL of a 1:1 molar solution of FSO$_3$D:SbF$_5$ (FSO$_3$H:SbF$_5$) was added to the solution at −78 °C. The ensuing mixture was vigorously stirred (Vortex stirrer) under periodic cooling until the $NH_4^+Cl^-$ (salt was completely dissolved. The sample was characterized by ^1H and ^2H NMR spectroscopy and subsequently heated in an oil bath to 100 °C. Periodic monitoring by ^1H and ^2H NMR over a period of 14 days did not indicate any H/D exchange in NH_4^+ (ND_4^+) cation.

Attempted $CH_3/^{13}CH_3$ Exchange in $N(CH_3)_4^+$ with $^{13}CH_3SO_3CF_3$: SbF$_5$. $N(CH_3)_4^+BF_4^-$ (50 mg) was dissolved in approximately 0.5 mL of $CH_3SO_3CF_3$:SbF$_5$ (1:1 molar solution) in an NMR tube and cooled to −78 °C in a dry ice/acetone bath. Subsequently, 2 drops of ^{13}C-enriched $^{13}CH_3SO_3CF_3$ were added to the solution, and the ensuing mixture was vigorously stirred (Vortex Stirrer). After the sample was characterized by ^{13}C NMR spectroscopy, it was heated to 50 °C in an oil bath. Periodic monitoring by ^{13}C NMR over a period of 1 week did not indicate any $CH_3/^{13}CH_3$ exchange in $N(CH_3)_4^+$ cation.

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