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Reactivity Pattern in the Room-Temperature Activation of NH_3 by the Main-Group Atomic Ions Ga^+, Ge^+, As^+ and Se^+

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The activation of ammonia by the main-group cations Ga^+, Ge^+, As^+ and Se^+ has been explored both experimentally and theoretically. ICP/SIFT tandem mass spectrometer measurements of room-temperature kinetics have revealed a substantial variation in rates and product distributions across the Periodic Table of Elements. The main features of the observed primary chemistry include H-atom elimination, ammonia addition and a cation-assisted proton transfer to yield NH_4^+ that is second order in ammonia. These observations are shown to be completely consistent with computed potential energy surfaces for the reactions of each of the four atomic cations. Dehydrogenation by the elimination of molecular hydrogen, not observed experimentally, is shown by the calculations to be inhibited by the presence of a kinetic barrier.

Introduction

Bond activation of ammonia has been listed among the top 10 challenges for contemporary catalysis in the context of olefin hydroamination and arene oxidative amination.[1] Furthermore, developments in oxidative addition of ammonia[2] or catalytic C–H aminations[3] have formed the subject of recent feature and review articles demonstrating the extraordinary potential, as well as obstacles, associated with these and related reactions.[4] Insights into the mechanisms as well as the elementary steps of N–H bond activation brought about by bare transition-metal ions[5] as well as small metal clusters[6] have been provided over the years by detailed gas-phase experiments complemented by computational studies.[5g,5h,6e,6f,6g,7] From this extensive work, rather general concepts about the role of, e.g. electronic structures, spin states, kinetic excitation, cluster size effects and charge states of *transition-metal* containing reactants have been developed. Both experimental and theoretical works in which *main-group* elements have been employed to bring about N–H bond activation according to reaction (2) have also been reported in the literature.[8]

In the context of mechanistic studies on metal-mediated methane activation by atomic ions M^+,[9] quite recently, Bohme and co-workers reported the completely unexpected and unprecedented dehydrogenation of CH_4 by the main-group atomic cation As^+,[10] and in a DFT-based analysis a mechanism of this bond activation has been provided.[11] Hallmarks of this reaction are the following: (i) In contrast to the metal-mediated C–H bond activation by M^+, for As^+ relativistic effects[9c,12] do not matter; (ii) in the course of the ion-molecule reaction, a triplet-singlet conversion occurs along the oxidative insertion of As^+ ($^3P_0$) into the C–H bond of CH_4 to generate $[(H)As(CH_3)]^+$ in its singlet state, thus constituting a further example of a two-state reactivity scenario;[13] from this insertion intermediate dehydrogenation is brought about by a sequence of α-hydrogen migration and reductive elimination of molecular hydrogen.

Here, we will report our combined experimental and computational findings on the thermal reactions of the *main*-group cations M^+ (M = Ga, Ge, As and Se) with NH_3 obtained in a search for chemical features that change across the periodic Table.

Results and Discussion

Experimental Results: Experimental results obtained for the reactions of Ga^+, Ge^+, As^+ and Se^+ are shown in Figure 1. Table 1 summarizes the measured rate coefficients and product distributions and the derived reaction efficiencies. The reaction efficiency is taken to be equal to the ratio k/k_c, where k is the experimentally measured rate coefficient and k_c is the capture or collision rate coefficient. k_c was computed using the algorithm of the modified variational transition-state/classical trajectory theory developed by Su and Chesnavich[14] with $\alpha(NH_3) = 2.145 \times 10^{-24}$ cm^3,[15] and $\mu_D(NH_3) = 1.47$ D.[16]

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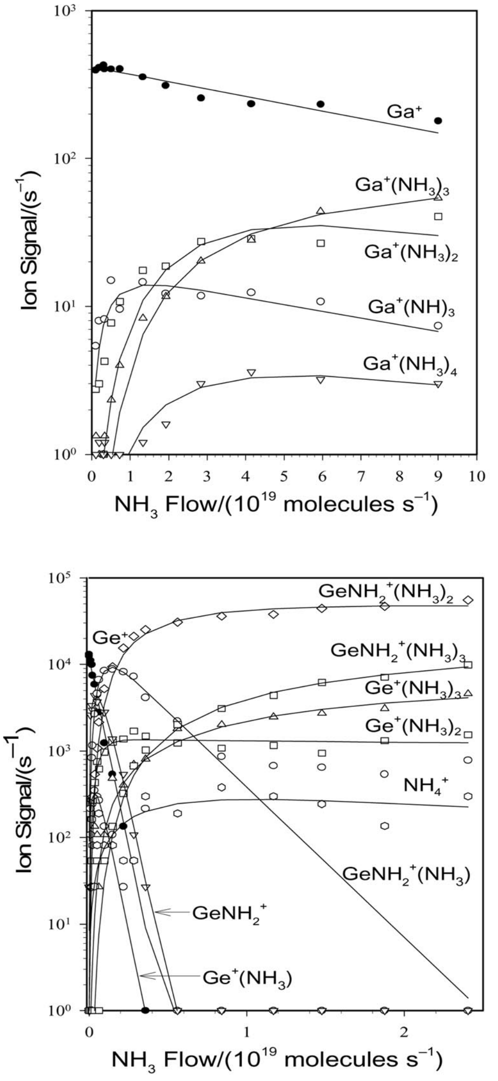


Figure 1. Composite of ICP/SIFT results for the reactions of the main-group atomic cations Ga^+, Ge^+, As^+ and Se^+ with NH_3 in helium buffer gas at 0.35 ± 0.01 Torr and 295 ± 2 K. Because of the isobaric interference with the Ar_2^+ dimer ion, special care was taken to adjust plasma conditions (the flow of nebulizer gas) to minimize the Ar_2^+ signal to $< 5\%$ of the initial Se^+ signal.

Table 1. Rate coefficients k (in units of 10^{-10} cm^3 molecule^{-1} s^{-1}), reaction efficiencies $(k/k_c)^a$, product distributions (PD) and higher-order product ions measured for reactions of main-group atomic ions M^+ with ammonia in helium at 0.35 ± 0.01 Torr and 295 ± 2 K.

M^+	k	k/k_c[a]	Primary products	PD [%]	Higher-order product ions
Ga^+	0.0063	0.00029	$Ga^+(NH_3)$	100	$Ga^+(NH_3)_{2-3}$
Ge^+	1.6	0.075	$GeNH_2^+$	88	$GeNH_2^+(NH_3)_{1-3}$
			$Ge^+(NH_3)$	10	$Ge^+(NH_3)_2$
			NH_4^+	2	$NH_4^+(NH_3)_{1,2}$
As^+	2.0	0.095	$AsNH_2^+$	100	$AsNH_2^+(NH_3)_{1-2}$
Se^+	0.11	0.0050	NH_4^+	100	$NH_4^+(NH_3)_{1-3}$

[a] See text; k_c is the calculated collision rate coefficient.

Reactions (1), (2) and (3) describe the various types of primary reactions that were observed.

$$M^+ + NH_3 \rightarrow M(NH_3)^+ \quad (1)$$

$$M^+ + NH_3 \rightarrow MNH_2^+ + H \quad (2)$$

$$M^+ + 2NH_3 \rightarrow NH_4^+ + MNH_2 \quad (3)$$

N–H bond activation in the form of H-atom elimination becomes obvious in reaction (2). Reaction (1) corresponds to ammonia addition. Addition reactions are expected to occur in a termolecular fashion under our experimental operating conditions with helium atoms acting as the stabilizing third body. No attempt was made to measure the pressure dependence of this channel since a large range in pressure was not experimentally accessible. Reaction (3) is second-order in ammonia and can occur if the first ammonia adduct (or an isomer of it) transfers a proton to a second ammonia molecule before being stabilized by collisions with the He bath gas atoms.

The primary chemistry observed with the main-group atomic cations varies significantly across the periodic Table and is different for each of the four atomic ions investigated. Ga^+ only adds ammonia and is collisionally stabilized according to reaction (1). Ge^+ exhibits mainly N–H bond activation resulting in the loss of atomic hydrogen, reaction (2), with only minor contributions from reactions (1) and (3). As^+ exhibits only reaction (2), while Se^+ proceeds exclusively by reaction (3).

In addition to primary reactions, secondary and higher-order NH_3 clustering was observed, according to reactions (4), (5) and (6). The observed product clusters are included in Table 1.

$$M^+(NH_3)_{0-3} + NH_3 \rightarrow M^+(NH_3)_{1-4} \qquad (4)$$

$$MNH_2^+(NH_3)_{0,1,2} + NH_3 \rightarrow MNH_2^+(NH_3)_{1,2,3} \qquad (5)$$

$$NH_4^+(NH_3)_{0,1} + NH_3 \rightarrow NH_4^+(NH_3)_{1,2} \qquad (6)$$

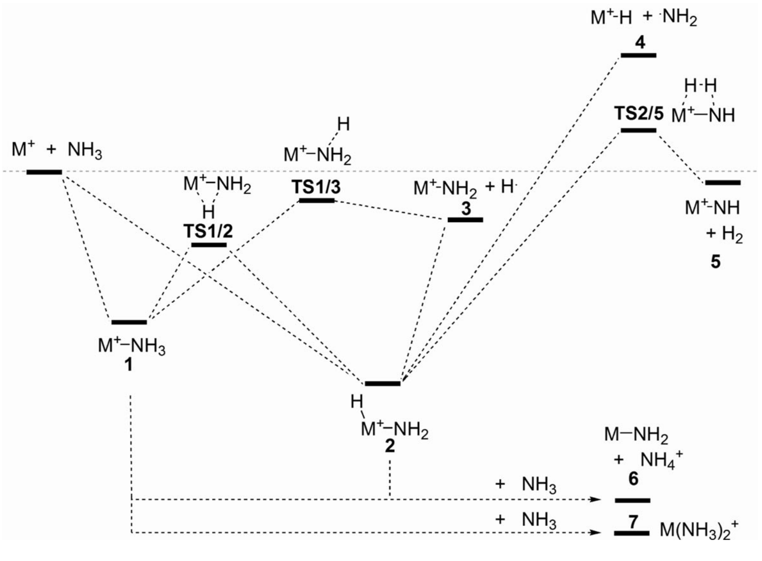
Theoretical Results: Computations have been performed for M^+ = Ga, Ge, As and Se to address the following processes in their thermal reactions with NH_3 (Scheme 1): Formation of the association complexes **1** and **7**, oxidative insertion of M^+ into an N–H bond to generate **2**, elimination of atomic hydrogen to produce $M(NH_2)^+$ (**3**), metal hydride MH^+ (**4**) formation, dehydrogenation of ammonia to produce $M(NH)^+$ (**5**), and cation-mediated proton transfer to form NH_4^+ and neutral MNH_2, Equation (3). A generalized schematic energy diagram is given in Scheme 1, the computed relative energies and Gibbs free energies are listed in Table 2, and geometrical parameters are given in Table 3.

Several structural features should be noted from Table 3. (1) In general, the bond lengths correlate with the atomic radius. (2) Ga–N bond lengths are much longer than those of other elements in **1**, **3** and **5**. This is because the bonding character between the $4s^24p^0$ Ga^+ and the N moieties, i.e. NH_3, doublet NH_2 and triplet NH, is less covalent than those of the other elements. The weak interaction between group III elements with NH_n is consistent with that reported in the literature.[17] (3) Due to electronegativity, the positive charge is mainly localized on M^+. N atoms are saturated with three single bonds in most of the cases. According to the Wiberg bond index, an M–N double bond was

Table 2. Relative energies (kcal·mol^{-1}) and Gibbs free energies (kcal·mol^{-1}, in parentheses) of the species shown in Scheme 1. Only the energies of electronic ground states (2S+1 values are given in square brackets) are listed.

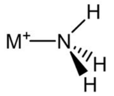
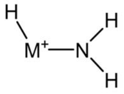
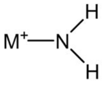
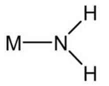
	Ga^+	Ge^+	As^+	Se^+
M^+ + NH_3	0.0 (0.0) [1]	0.0 (0.0) [2]	0.0 (0.0) [3]	0.0 (0.0) [4]
1	**–30.2 (–24.9)** [1]	**–50.8 (–45.3)** [2]	–74.5 (–68.8) [3]	–61.5 (–55.3) [2]
TS1/2	57.1 (62.8) [1]	–7.4 (–1.8) [2]	–25.2 (–19.5) [3]	–13.7 (–7.5) [2]
2	10.4 (16.2) [1]	–28.5 (–22.8) [2]	–80.3 (–73.8) [1][a]	–59.1 (–53.0) [2]
TS1/3	–	3.6 (9.1) [2]	–8.5 (–3.1) [3]	–
3	78.5 (76.9) [1 or 3][b]	**–2.5 (–2.7)** [2]	**–10.4 (–10.7)** [1 or 3][b]	13.8 (14.2) [2]
4	93.5 (90.8) [1 or 3][b]	34.8 (33.0) [2]	32.4 (30.5) [1 or 3][b]	27.7 (25.7) [2 or 4][c]
TS2/5	–	–	–4.8 (1.6) [1]	–
5	76.1 (78.6) [3]	10.9 (14.7) [2]	–47.4 (–42.7) [1]	13.8 (14.2) [2]
6	–5.2 (1.2) [1]	**–48.5 (–42.0)** [2]	–71.0 (–64.5) [3]	**–75.0 (–68.3)** [2]
7	**–50.6 (–37.2)** [1]	**–84.6 (–71.1)** [2]	–90.4 (–76.4) [1]	–89.3 (–76.3) [2]

[a] The relative energy and Gibbs' free energy of the triplet state [3] are –39.6 and –33.9 kcal mol^{-1}, respectively. [b] This corresponds to a combination of a doublet M moiety with the doublet hydrogen atom or the doublet NH_2. [c] This corresponds to a combination of triplet M moiety with the doublet of NH_2.



Scheme 1. Generalized potential energy surface for the reaction of main-group atomic ions with ammonia. Computed relative energies and Gibbs free energies are provided in Table 2.

Table 3. Geometrical parameters of optimized ground state structures of **1** – **6**. Bond lengths and bond angles are given in Ångströms and degrees, respectively.

			Ga^+	Ge^+	As^+	Se^+
	1	r(M–N)	2.326	2.160	2.051	1.970
		∠M–N–H	112.4	111.5	111.1	111.0
	2	r(M–N)	1.747	1.752	1.857	1.771
		r(M–H)	1.508	1.567	1.544	1.481
		∠M–N–H	123.6	122.7	121.8	123.1
		∠H–M–N	180.0	116.1	94.4	94.3
	3	r(M–N)	2.372	1.770	1.736	1.706
		∠M–N–H	126.6	124.5	123.2	122.0
$M^+–H$	4	r(M–H)	1.687	1.591	1.539	1.495
$M^+—N—H$	5	r(M–N)	2.495	1.772	1.586	1.626
		∠M–N–H	180.0	180.0	180.0	180.0
	6	r(M–N)	1.887	1.829	1.777	1.793
		∠M–N–H	125.5	124.2	123.3	120.8

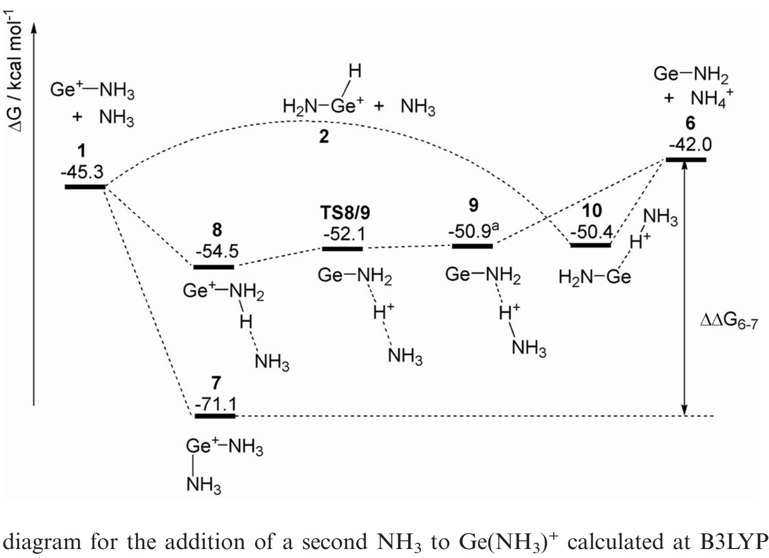
only found in **5** for As and Se. (4) The bond strength of M–N is not as strong as that of their counterparts of the 3rd row because of a less efficient orbital overlap.[8f,8g,8j]

Inspection of Table 2, in which those reactions that are observed experimentally are indicated in bold, reveals a good, if not excellent agreement between the experimental and computational findings.

For the Ga^+/NH_3 couple, only the formation of an association complex **1** is both exothermic and exergonic. The low efficiency of this process is not really anomalous given the rather weak binding energy and the small number of effective degrees of freedom that shorten the lifetime of the intermediate for collisional stabilization. Insertion of Ga^+ into the N–H bond to produce isomeric $(H)Ga(NH_2)^+$ (**2**) can be ruled out given the huge **TS1/2** barrier height and the endothermicity of this process. Since there is no other reaction channel accessible for $Ga(NH_3)^+$, further coordination of NH_3 to produce $Ga(NH_3)_2^+$ (**7**), which is calculated to be exergonic, was observed experimentally.

Our computations find that the formations of products **1**, **3**, **6** and **7** are accessible, from a thermochemical point of view, in the reaction of Ge^+ with NH_3. All four are observed experimentally. Furthermore, based on the computational findings of the barrier heights as well as the thermochemistry, one cannot rule out that, in addition to the association complex **1**, also the insertion intermediates **2** are cogenerated for M^+ = Ge, As, Se. This dichotomy has also been noted earlier for M^+ = Co.[5c] In fact, for Ge^+, product **3** is unlikely to be formed via **TS1/3** because of the high barrier to break the N–H bond directly from **1**. Scheme 2 shows the addition of a second NH_3 to **1** in detail for Ge, as a prototype. At high flows of NH_3, an additional NH_3 can either coordinate directly with Ge^+ in **1**, forming **7**, or produce **8** via hydrogen-bonding. Although **8** is less stable, it can easily undergo a low barrier H-transfer followed by irreversible dissociation to give rise to **6**. It is also possible that the additional NH_3 abstracts H from the Ge–H bond of **2**, forming complex **10** in a barrier-free process. Nevertheless, the critical factor is the relative energy of **6**, the exit channel for NH_4^+. This channel is calculated to be slightly endoergonic in the case of Ge^+ and so is observed to be minor; the clustering channel to produce **7** is preferred due to the large $\Delta\Delta G_{6-7}$.

All processes are thermochemically feasible for the As^+/NH_3 couple, except for the generation of AsH^+/NH_2. However, dehydrogenation of NH_3 to generate $As(NH)^+$ according to reaction (7) is prohibited by the energetic requirement of **TS2/5**, in contrast to the entropically favored loss



Scheme 2. Gibbs free energy diagram for the addition of a second NH_3 to $Ge(NH_3)^+$ calculated at B3LYP/aug-cc-pVTZ.[a] Due to the free energy correction, intermediate **9** is slightly higher in free energy than the transition state **TS8/9**.

of atomic H$^{\cdot}$ from either **1** or **2**. Unlike $Ga(NH_2)^+$, the unpaired electron occupies the p orbital of As in the doublet product $As(NH_2)^+$.

$$As^+ + NH_3 \rightarrow As(NH)^+ + H_2 \tag{7}$$

For atomic Se^+, all N–H bond activation processes resulting in the formation of products such as $Se(NH_2)^+$, $Se(NH)^+$ or $Se(H)^+$ are endothermic and, in line with the experiments, not accessible under thermal conditions. Only the termolecular reaction, Equation (3), to generate NH_4^+ is very exothermic and the most obvious pathway involves deprotonation of the initially formed association complex $Se(NH_3)^+$ (**1**) or its insertion intermediate $(H)Se(NH_2)^+$ (**2**) by a second molecule of NH_3. Unlike the case with Ge^+, **7** was not observed for Se^+ because $\Delta\Delta G_{6-7}$ is not large enough.

Conclusion

As for the activation of methane,[10,11] we now have provided a rather complete understanding of the room-temperature activation of ammonia with the main-group cations Ga^+, Ge^+, As^+ and Se^+. Both room-temperature reaction measurements and energy calculations have been performed with good accuracy and these provide a clear picture of the substantial variation in the ammonia chemistry across the periodic Table. Dehydrogenation by loss of molecular hydrogen such as that observed with methane[10] is not a feature of the chemistry observed with ammonia. This difference in chemistry is clearly explained by theory;[11] the study reported here predicts a substantial kinetic barrier to the elimination of molecular hydrogen from ammonia with all of the four main-group atomic cations.

Experimental Section

General: The experimental results reported here were obtained with the ICP/SIFT tandem mass spectrometer in the Ion Chemistry Laboratory at York University and has been described in detail previously.[18] The atomic ions were generated within an atmospheric-pressure argon plasma at 5500 K fed peristaltically via a nebulizer with a solution containing the main-group metal salt with concentrations of ca. 5 µg l^{-1}. The plasma gas flow was adjusted to maximize the ion signal detected downstream of the SIFT. The ions emerging from the ICP were injected through a differentially pumped sampling interface into a quadrupole mass filter and, after mass analysis, introduced through an aspirator-like interface into flowing helium carrier gas at 0.35 ± 0.01 Torr and 295 ± 2 K. After experiencing about 10^5 collisions with He atoms, the ions were allowed to react at room temperature with NH_3 added into the flow tube.

The main-group atomic ions emerging from the plasma initially have a Boltzmann internal energy distribution characteristic of the plasma temperature. However, these emerging populations are expected to be down-graded during the approximately 20 ms duration before entry into the reaction region in the flow tube. Energy degradation can occur by radiative decay as well as by collisions with argon atoms and the 10^5 collisions with He before entry into the reaction region. The observed semi-logarithmic decays of the reacting atomic cations are linear and are indicative of single-state populations (or multiple-state populations with equal reactivities). The many collisions with Ar and He between the source and the reaction region should ensure that the atomic ions reach a translational temperature equal to the tube temperature of 295 ± 2 K prior to entering the reaction region.

Reactant and product ions were sampled at the end of the flow tube with a second quadrupole mass filter and their signals were measured as a function of added reactant. The resulting profiles provide information about reaction rate coefficients and product-ion distributions. Rate coefficients for primary reactions were determined using pseudo first-order kinetics from the semi-logarithmic decay of the reactant ion intensity as a function of added reactant with an uncertainty estimated to be less than ± 30%. Pure NH_3 gas was obtained commercially (Semiconductor Grade 99.999%, Matheson/Linde, Canada), and introduced into the reaction region of the flow tube as a dilute (15%) mixture in helium.

Theoretical Section: The calculations were performed using the Gaussian03 package.[19] Geometries of all stationary points were optimized at the unrestricted UB3LYP level of theory[20] using the aug-cc-pVTZ basis set.[21] As already mentioned and shown previously,[11] the role of relativistic effects in the description of the ion-molecule reactions of these main group elements is negligible; therefore, they were not included in the present study. Frequency calculations were carried out for all optimized structures with the same method to verify the nature of the stationary points on the potential energy surface (PES) and to obtain the zero-point energies (ZPEs) and to calculate the Gibbs' free energies (at 298 K). Intrinsic reaction coordinate (IRC) calculations were performed to confirm the links between intermediates and transition structures.[22] The Wiberg bond indices (WBIs)[23] were calculated at the same level of theory using the NBO version 3.1.[24] Finally, all relative energies (corrected for ZPE contributions) and Gibbs free energies (at 298 K) are reported in kcal·mol^{-1}.

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