Formation of argon–boron bonds in the reactions of BF$_n^+$/2+ cations with neutral argon

Lauren Leveea, Catherine Calogeroa, Edward Barbieria, Steven Byrnea, Courtney Donahuea,
Michael Eisenbergb, Sean Hattenbachc, Julie Lea, Joseph F. Capitanib, Jana Roithováb, Detlef Schröderea,*

a Department of Chemistry and Biochemistry, Manhattan College, Riverdale, NY 10471, USA
b Department of Chemical Engineering, Manhattan College, Riverdale, NY, 10471, USA
c Department of Organic Chemistry, Charles University in Prague, Hlavova 8, 12843 Prague 2, Czech Republic
d Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo náměstí 2, 16610 Prague 6, Czech Republic

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ABSTRACT

Experimental data on the reactions of argon with BF$_n^+$ monocations ($n$ = 0–3) and BF$_2^+$/2 dications ($n$ = 1, 2) and dications reveal the formation of the new argon species ArBF$_2^+$ and ArBF$_2^+$. Theoretical calculations on the stability of these ions using density functional theory confirm the formation of the rare-gas compounds, but their formation is only exothermic for the reaction Ar + BF$_2^+$ → ArBF$_2^+$ + F. According to theory, the corresponding neon compounds all involve endothermic pathways and could hence only be formed via involvement of excited states.

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1. Introduction

Recently, we have found that several small gaseous dications can act as sufficiently superelectrophilic reagents [1] to promote the formation of bonds between rare gases and other elements than fluorine, which is the most common bonding partner in rare-gas compounds [2]. For example, by the use of gaseous dications [3,4] the organo-rare-gas compounds ArCH$_2^+$ [5], ArCF$_2^+$ [6], and ArCCH$_2^+$ [7] could have been generated, thereby verifying a prediction made earlier for halocarbenes [8]. Recently, several other hydrocarbon-rare gas adducts have also been generated via ion/molecule reactions of gaseous dications [9–11]. In a deliberate strategy attempting to maximize the yield of rare-gas compounds, the silicon derivatives NeSiF$_2^+$ and ArSiF$_2^+$ were generated in the reaction of mass-selected SiF$_2^+$ with neon and argon, respectively [12,13]. Likewise, gas-phase ion chemistry has recently been successfully applied to generate novel rare-gas species such as XeNF$_2^+$ [14] and XeGeF$_3^+$ [15]. Accordingly, similar approaches might enable the formation of species having bonds between boron and rare gases [16]; for the related synthesis of FXBf$_2$, see Refs. [17,18],

and for a theoretical prediction of anionic boron compounds of rare gases, see Refs. [19,20]. In this context we note that the ArBF$_2^+$ cation has been observed in the chemical ionization of Ar/BF$_3$ mixtures [21], and that this and the related species KrBF$_2^+$ and XeBF$_2^+$ as well as the isomeric structures FrgBF$_4^+$ have recently been studied in high-level ab initio calculations parallel to our work [22].

Inspired by results from a teaching course held at the Manhattan College in early 2010, here we report a combined experimental and theoretical study of the reactions of argon with some superelectrophilic BF$_2^+$/2 mono- and dications. As documented below, several of the reactions observed in the highly diluted gas phase do indeed lead to the formation of Ar–B bonds and the molecular species reported here may thus inspire research on new rare-gas compounds in condensed media.

2. Experimental and theoretical methods

The experiments were performed with a TSQ Classic mass spectrometer [23,24] equipped with an ion source for electron ionization (EI) and an analyzer of QOQ configuration (Q stands for quadrupole and O for octopole), which permits a variety of MS/MS experiments. The octopole serving as a collision cell has a separate housing which limits the penetration of gases admitted to the octopole to the vacuum of the manifold. The kinetic energy
of the ions entering the octopole can be varied between 0 and 200 eV, which allows the investigation of ion/molecule reactions at quasi-thermal conditions or collision-induced dissociation (CID) at elevated kinetic energies. The BF$_3$$^{12+}$/Ar mono- and dication reactions were generated by EI of BF$_3$ gas (Sigma–Aldrich), mass-selected with the first quadrupole (Q1) at a mass resolution fully sufficient to resolve mono- and dications, then reacted with argon admitted to the octopole at a pressure of typically 3 × 10$^{-4}$ mbar. The bimolecular reactions reported below were recorded at an ion kinetic energy which corresponds to the point of inflection of the curve obtained by retarding-potential analysis. We have shown previously that quasi-thermal reactivity can be monitored under these conditions [25–28]; here, the term quasi-thermal appreciates the fact that the ions’ average kinetic energy is indeed close to thermal conditions, while the width of the ions’ kinetic energy distribution is not. Note that within the limits of our instrumentation, we could not further cool the cations investigated in this work [4,10]. The mass-selected dications were then reacted with neutral rare gases admitted to the octopole at a typical pressure of 10$^{-4}$ mbar. In some cases, the pressure of the neutral gases was deliberately raised above the single-collision regime [29] in order to investigate consecutive reactions as well as termolecular processes [30]; for a recent detailed study of the dynamics of collisional stabilization, see [31]. Unless otherwise specified, the collision energy was set by changing the offset between the first quadrupole and the octopole, while the offset of Q2 was locked to the sum of the offsets of Q1 and O. The zero-point of the kinetic energy scale as well as the width of the kinetic energy distribution were determined by means of retarding-potential analysis; for the dications reported here, the beam width at half maximum was about (5 ± 1) eV in the laboratory frame. Ionic products emerging from the octopole were then mass-analyzed by scanning Q2 operated at unit mass resolution. Typically, about hundred scans were accumulated resulting in an average scan time of 5 min per spectrum.

Due to its corrosive properties, boron trifluoride is harmful for the experimental set-up and significant instabilities of the pressure in the ion source as well as a loss of performance of the filaments in the ion source and in the pressure gauges were observed during the measurements. To keep the damage to the instrumentation at a tolerable level, we hence refrained from extensive kinetic studies of the ion/molecule reactions observed, for which a multipole arrangement anyhow is not ideally suited [30]. Accordingly, we neither convert the relative reactivities found in the experiments into absolute rate constants nor make corrections for the differences in the transmission of the light and heavy product ions to the detector [32,33].

Note of caution: While being obvious to chemists routinely working with corrosive gases, we wish to point out an important safety aspect of which mass spectrometers are not always aware. Thus, prior to any venting or disconnection of a line which contains or has contained a corrosive gas (e.g., BF$_3$, but the same applies for Cl$_2$, HCl, NO$_2$, etc.), complete evacuation and subsequent purging of the line is essential. While this operation also helps to avoid unintended contact with the gas, the major purpose is the protection of the gas bottle itself. If this pumping step is omitted, rests of the gases in the line react with the humidity in the laboratory air to yield strong acids as droplets of fluid, which often collect right at the seat of the main valve of the reservoir gas tank, where they cause serious corrosion and frequently blockage of the main valve. Such clogged gas tanks with high pressures of hazardous gases present serious safety and disposal issues. The simple pump/purge step mentioned above should thus never be forgotten.

For the theoretical work, a 2006 version of the Spartan computer program was used to determine the stability of Argon and Neon complexes with BF$_3$$^{2+}$. We used a cc-pVTZ basis set with the B3LYP density functional [34–37] in order to calculate the equilibrium geometry at the ground state. The charge and multiplicity (doublet for an odd number of electrons and singlet for an even number) had to be adjusted to suit the characteristics of each compound in the reaction. The computed energetics are given in terms of electron volts (eV) and refer to total energies at 0 K. A test calculation for the dication ArBF$_3$$^{2+}$ indicated that the basis set superposition error at our level of theory is in the order of 0.02 eV. This number is at the border of the precision of the method, therefore in the following the possible basis set superposition error is not accounted for. Frequency analysis at the same level of theory was performed for all optimized structures, in order to assign stationary points on the potential-energy surface as genuine minima or transition structures, as well as to calculate zero-point vibrational energies (ZPVEs). All results were further checked by an independent optimization at the same level of theory (B3LYP/cc-pVTZ) using the Gaussian 09 program [38] and the results listed below refer to these values.

**Scholarly implementation.** The theoretical part of this work was performed within an undergraduate course in theoretical chemistry at the Manhattan College under the supervision of JFC in spring 2010. This course is a senior level requirement for all Chemistry and Biochemistry majors, and is a popular elective with Chemical Engineering majors. Our task is to cover chemical bonding by doing calculations on new materials and molecular systems as presented in the current literature. We stress molecular mechanics, semi-empirical, and ab initio methods with a strong emphasis on density functional theory, through hands on use of standard quantum chemistry programs such as Gaussian, Orca, and Spartan. Past class projects have included calculating UV–Vis spectra for photogray optical lenses, predicting the spectra of blue dyes of archeological interest, a mechanism of DNA intercalation, and the structure and bonding of proposed novel organic compounds recently detected in deep space. After being taught basics in quantum chemistry and ab initio computations, the students received different parts of the BF$_3^{-}$+Ne/Ar) systems as tasks for performing independent ab initio calculations, including the detailed analysis of the results. The complete set of results was then compiled by the entire course, discussed in detail, and summarized in a first draft of the paper.

The results of the students were carefully controlled by JFC and afterwards JR checked all data by fully independent calculations at the same level of theory.

### 3. Results and discussion

The experiments on the BF$_3$$^{12+}$/Ar system were initiated by a suggestion of the supervisor of the theoretical course (JFC), who coordinated the theoretical study executed in parallel to the experiments. In the following, we first describe the experimental findings, followed by a summary of the results of the computational studies.

#### 3.1. Experimental results

Not unexpectedly, the experiments with boron trifluoride are harmful to the inlet system and the mass spectrometer instrumentation. Thus, even with traces of moisture BF$_3$ liberates corrosive hydrogen fluoride, but even more so BF$_3$ itself is a strong Lewis acid and thus highly corrosive. In practice, this manifest in pale, hygroscopic deposits in all parts of the inlet system of the mass spectrometer and the transfer lines, which are to be treated with caution because of the possible generation of gaseous HF. Likewise, the components of high vacuum manifold suffer in the presence of BF$_3$ as manifested by a continuous decrease of the performance of the filament used in electron ionization as well as an unstable
response of the high-vacuum ion gauge for pressure measurement. These harmful effects could be reduced by a parallel purging of the source manifold with nitrogen, which is in turn associated with some diffusion of nitrogen gas from the source region to the interaction region used to study ion/molecule reactions. Hence, the reactions with argon reported below also include reactions with molecular nitrogen. Further, due to the obviously harmful effect of BF3 on the instrumentation, the overall measuring time was restricted to a few hours, and hence more sophisticated experiments possible in our set-up (e.g., calibrated rate constants, detailed energy dependences, etc.) [12,23,30,33] were omitted for the sake of the equipment [39].

Electron ionization of BF2 in the positive ion mode provides the cations BF2+* (n = 0–3) [40–45] and ~about two orders of magnitude less abundant ~the dications BF2+* (n = 0–2) [46]. Using MS/MS techniques in our multipole device [23,24], these species were probed with respect to their quasi-thermal reactivity with argon. Due to the use of nitrogen as a purging gas in the ion source, the reactions with N2 were studied in parallel. Note that argon and nitrogen are quite similar reactants in several respects [12,13]. For example, the ionization energy IE(Ar) = 15.759 eV almost matches IE(N2) = 15.581 eV, and also the proton affinities PA(Ar) = 3.83 eV and PA(N2) = 5.12 eV do not differ too largely [47]. Therefore, the parallel information about the reactivity of the BF2+* cations with Ar as well as N2 can in fact be regarded as a useful complement.

As an example for the reactivity of the dicaticonic species, Fig. 1 shows the mass spectrum obtained for the BF2+ dication, where the experiments shown in the insets (a) and (b) verify the assignments made below. The major ionic products with argon can be summarized in Eqs. (1)–(3) and similarly, the reactions (4)–(6) occur with nitrogen; minor reactions due to residual water are discussed further below.

\[
\text{BF}_2^{2+} + \text{Ar} \rightarrow \text{BF}_2^{+} + \text{Ar}^+ \quad (\text{SET}) \tag{1}
\]

\[
\text{BF}_2^{2+} + \text{Ar} \rightarrow \text{BF}^{+} + \text{F}^+ + \text{Ar}^+ \quad (\text{DET}) \tag{2}
\]

\[
\text{BF}_2^{2+} + \text{Ar} \rightarrow \text{ArBF}_2^{2+} + \text{F} \quad (\text{BFR}) \tag{3}
\]

\[
\text{BF}_2^{2+} + \text{N}_2 \rightarrow \text{BF}_2^{+} + \text{N}_2^+ \quad (\text{SET}) \tag{4}
\]

\[
\text{BF}_2^{2+} + \text{N}_2 \rightarrow \text{BF}^{+} + \text{F} + \text{N}_2^+ \quad (\text{DET}) \tag{5}
\]

\[
\text{BF}_2^{2+} + \text{N}_2 \rightarrow \text{N}_2\text{BF}_2^{2+} + \text{F} \quad (\text{BFR}) \tag{6}
\]

\[
\text{BF}_2^{2+} \rightarrow \text{BF}^{2+} + \text{F} \quad (\text{CID/MI}) \tag{7}
\]

Reactions (1)–(4) can be ascribed to (i) single electron transfer (SET) between the highly electrophilic dicaticon and the neutral reagent (reactions (1) and (4)), likewise (ii) dissociative electron transfer (DET) can occur due to the large exothermicities of most charge-separation reactions [48] (reactions (2) and (5)), and (iii) bond-forming reactions (BFR) affording new gaseous dications with maintenance of the two-fold charge [3,4,49] (reactions (3) and (6)). In addition, a small amount of collision-induced dissociation (CID) and/or metastable ion decay (MI) is observed (reaction (7)). Observation of the latter process highlights the excess energy deposited in the cations formed upon electron ionization, because the fragmentation of BF2+ via loss of fluorine is an endothermic process [40].

Much weaker in abundance, but still significant were bond-forming reactions of the BF+ monocation, monitored in a separate experiment, which lead to the species BN2+ and Arb+ in conjunction with loss of a fluorine atom (Fig. 2). In 1999, Koskinen and Cooks reported the formation of Brg+ monocations (Rg = Ar, Kr, Xe) in collisions of BBr+ with rare gases as a very similar process [16]. Further, the corresponding reactivity is observed for the nitrogen gas present in the collision region and leads to BN2+ cation as one of the major products. Note, however, that the overall reaction efficiency is low as demonstrated by reference to the abundance scale in which the sum of the product ions comprises less than 1% of the total ion signal.

Although with a low efficiency, another bond-forming reaction was found in the reaction of argon with the molecular ion BF3+ which leads to an ion with m/z 89 which corresponds to ArBF2+ (Fig. 3); for the 10B isotope of BF3 this product shifts to m/z 88, as expected. The major product ion corresponds to BF2+ as the product of the dissociation of metastable BF3+ ions as well as some amount of collisional activation of BF2+ to afford BF2+ in the presence of the neutral collision partners. Further, small amounts of electron transfer are observed, which is consistent with IE(BF3) = (15.7 ± 0.3) eV [47] compared to IE(Ar) = 15.759 eV and IE(N2) = 15.581 eV. Again,
nitrogen undergoes the analogous reaction to afford a N₂BF₂⁺ cation.

\[ \text{BF}_n^{m+} + \text{Ar} \rightarrow \text{ArBF}_{n-1}^{m+} + \text{F} \quad (n = \text{1, 3 for } m = \text{1; n = 2 for } m = \text{2}) \quad (8) \]

\[ \text{BF}_n^{m+} + \text{N}_2 \rightarrow \text{N}_2\text{BF}_{n-1}^{m+} + \text{F} \quad (n = \text{1, 3 for } m = \text{1; n = 2 for } m = \text{2}) \quad (9) \]

The results obtained for the other BF⁺/BF₂⁺ cations are summarized in Table 1, where the abundances of the product ions are given relative to the precursor ion. Although less efficient, bond-forming reactions with argon are observed for the monocations BF⁺ and BF₂⁺ and the dication BF₂⁺, and in all cases these reactions can be described as a displacement of a fluorine atom by argon (reaction (8)). These results are complemented by the same type of reactivity observed with dinitrogen (reaction (9)). In the case of the BF⁺ monocation, the low reactivity suggest that the bond-forming product might also be due to an electronically excited state of this diatomic cation.

While the B–F bond in general is rather strong chemical bond, consideration of the electronic structure of the precursor ions involved provides a straightforward rationale for the facile loss of atomic fluorine. Thus, the molecular ion BF₃⁺ is an open-shell compound for which the loss of atomic fluorine leads to the closed-shell species BF₂⁺ which is a linear molecule isoelectronic to CO₂. Similarly, the BF₂⁺ dication is an open-shell species from which loss of atomic fluorine leads to the closed-shell compound BF⁺, which is a diatomic dication with an extraordinary deep potential-energy well [46]. Likewise, BF⁺ is a radical cation, whereas all other, non-reactive species are formal closed-shell species.

### 3.2. Theoretical calculations

With respect to the experimental results, the theoretical survey focused on the reactions of argon with the BF₃⁺ monocation and the BF₂⁺ dication (Table 2). Fully consistent with the measurement, reaction (8) is found to be 1.61 eV exothermic for BF₂⁺ as a precursor (Fig. 4). Notable is also the binding energy of argon in the intermediate ArBF₂⁺ which amounts to 3.16 eV and hence reaches the strength of typical covalent bonds. In comparison, the B–F bond in ArBF₂⁺ is much weaker (1.55 eV), hence accounting for the formation of ArBF₂⁺ as theionic product. In the ArBF₂⁺ intermediate, one B–F bond is slightly shortened with respect to the BF₂⁺ reactant (see Fig. 4), whereas the other B–F bond is significantly elongated to 1.51 Å. The bond distance between boron and argon is 1.81 Å. A qualitative assessment of the bonding situation can be obtained from the Mulliken bonding analysis. It suggest that the Ar–B bond is associated with 0.35 shared electrons, whereas the B–F bonds share 0.52 and 0.26 electrons, respectively. The latter value corresponds to the longer bond and on the corresponding fluoride atom is also mostly localized the unpaired electron (0.87 e). The subsequent elimination of the fluoride atom leads to a shortening of both remaining bonds, hence the argon–boron bond length amounts to 1.72 Å and the boron–fluorine distance shrink to 1.20 Å. The bonding analysis leads to the values of 0.40 and 0.57 shared electron in these bonds, respectively.

The reaction between BF₂⁺ monocation and argon leading to the second observed argon-containing ion, ArBF₃⁺, is predicted to be endothermic by 0.46 eV. This finding is consistent with the low yield of the bond-forming product and the prevalence of the competing fragmentation of BF₂⁺ into BF₂⁺ + F (Figs. 2 and 5). The occurrence of the endothermic process Ar + BF₂⁺ → ArBF₃⁺ + F is attributed to the excess energy deposited in the precursor ions upon electron ionization. The [ArBF₃⁺] intermediate does not contain an Ar–B bond as it was found in the previous case, but it can also be considered as a van der Waals complex, in which argon interacts with fluorine atoms (Fig. 5). Nevertheless, in the
computed bond-formation products in the reaction of $\text{BF}_2^+$ with argon is fully supported by theory, which predicts the formation of the corresponding $\text{ArBF}_2^+$ cation to be endothermic by almost 7 eV.

For comparison, we have also studied computationally the corresponding reactions of neon (Table 3); for some isomeric FRgBF$^+$ ions, also see Ref. [22]. For this lighter rare gas, all bond-forming processes are clearly endothermic, such that any reactivity possibly observed could only arise from contributions of electronically excited states of the precursor ions formed upon electron ionization.

In comparison, the bond-forming channels with the superelectrophilic $\text{BF}_n^{+2+}$ cations are much more pronounced for argon than for neon. However, both rare gases share a trend in that the first half of the reaction involves a transient adduct from which ‘cooling’ by loss of atomic fluorine eventually leads to the substitution products.

4. Conclusions

Among the $\text{BF}_n^{+2+}$ cations accessible by electron ionization of neutral $\text{BF}_3$, the dication $\text{BF}_2^{2+}$ is able to promote the formation of a rare-gas compound $\text{ArBF}_2^{2+}$ in the reaction with argon. Theory predicts this process to start with the formation of an $\text{ArBF}_2^{2+}$ complex having a binding energy of 3.16 eV, which is in the order of magnitude of typical covalent bonds. The reaction is completed by loss of a neutral fluorine atom resulting in a net exchange for fluorine by argon with an overall exothermicity of 1.61 eV. These observations suggest $\text{BF}_2^{2+}$ as one of the strongest and most reactive electrophiles in the gas phase. Similar processes with $\text{Ar}−\text{B}$ bond formation, though less efficiently, occur for the monocations $\text{BF}^+$ and $\text{BF}_2^+$, which are both open-shell species, whereas the closed-shell ions like $\text{BF}_3^+$, $\text{BF}_2^+$ are unreactive towards argon. While nitrogen reacts in a manner very similar to argon, theory predicts that rare-gas species are not likely to be formed with neon as a reagent.

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[47] Data taken from the NIST Chemistry Webbook, National Institute of Standards, Gaithersburg, USA, see: http://webbook.nist.gov/chemistry/.