

## NRC Publications Archive Archives des publications du CNRC

### **Mechanism of generation of volatile hydrides of trace elements by aqueous tetrahydroborate(III). Mass spectrometric studies on reaction products and intermediates**

D'Ulivo, A.; Mester, Z.; Meija, J.; Sturgeon, R.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

#### **Publisher's version / Version de l'éditeur:**

<https://doi.org/10.1021/ac061962c>

*Analytical Chemistry*, 79, 7, pp. 3008-3015, 2007-03-06

#### **NRC Publications Archive Record / Notice des Archives des publications du CNRC :**

<https://nrc-publications.canada.ca/eng/view/object/?id=4986e512-0abc-4d87-93ba-a939bf8bdf06>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=4986e512-0abc-4d87-93ba-a939bf8bdf06>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

**Questions?** Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

**Vous avez des questions?** Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

# Mechanism of Generation of Volatile Hydrides of Trace Elements by Aqueous Tetrahydroborate(III). Mass Spectrometric Studies on Reaction Products and Intermediates

Alessandro D'Ulivo,\*† Zoltán Mester,‡ Juris Meija,‡ and Ralph E. Sturgeon‡

Institute of Chemical-Physical Processes, National Research Council of Italy, Research Area, Via G. Moruzzi, 1, 56124 Pisa, Italy, and Institute for National Measurement Standards, National Research Council Canada, Ottawa, Canada K1A 0R9

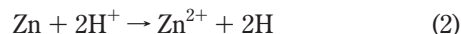
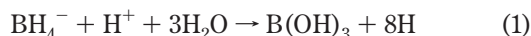
The mechanism of generation of volatile metal/metalloid hydrides by derivatization with borane complexes is presented. This reaction has been employed for ultratrace element analysis since 1972 and has been the source of much controversy in regard to the reaction mechanism. Here we investigated this derivatization by using As(III), Sb(III), Bi(III), MeAsO(OH)<sub>2</sub>, and Me<sub>2</sub>AsO(OH) as model analytes and NaBH<sub>4</sub>, NaBD<sub>4</sub>, *tert*-BuNH<sub>2</sub>BH<sub>3</sub>, and Me<sub>2</sub>NHBH<sub>3</sub> as borane reagents. The identification of reaction products and intermediates observed under various reaction conditions was performed by gas chromatography/mass spectrometry and electrospray ionization mass spectrometry. An alternative reaction model, based on the formation of analyte–borane complex (ABC) intermediates, is able to reconcile all the experimental evidence reported in the literature. In this study, we provide definitive evidence of the ABC hydride generation mechanism, which shows that the generation of volatile hydrides occurs via formation of ABC intermediates between hydroboron species and the analyte substrate followed by the direct transfer of hydrogen from boron to the analyte atom, and fast hydrolysis leading to the final product.

Aqueous-phase chemical generation of volatile hydrides (HG) coupled with various detection techniques, mainly atomic (AS) and mass (MS) spectrometry, provides one of the most powerful tools used in analytical chemistry for determination and speciation of group IVA, VA, and VIA elements at sub-part per billion levels.<sup>1</sup>

The generation of volatile hydrides for synthetic purposes by using aqueous tetrahydroborate(III) (THB) was first reported in 1954 for stannane by Schaeffer and Emilius,<sup>2</sup> just 1 year after the first publication reporting the synthesis of NaBH<sub>4</sub> by Schlesinger et al.<sup>3</sup> Then, in 1960, Berka et al.<sup>4</sup> reported the preparation of SbH<sub>3</sub> and Jolly<sup>5</sup> reported the preparation of SbH<sub>3</sub>, AsH<sub>3</sub>, SnH<sub>4</sub>, and GeH<sub>4</sub>

together with some dimerization products (As<sub>2</sub>H<sub>4</sub>, Ge<sub>2</sub>H<sub>6</sub>, Sn<sub>2</sub>H<sub>6</sub>). Following these first publications, the topic appears to have disappeared from the fundamental chemistry literature to find a new interest in the analytical field. This was evidenced by Holak's work in 1969<sup>6</sup> using a Zn–acid reaction system to generate AsH<sub>3</sub>, demonstrating the great advantage arising from the introduction of gaseous hydrides in AS. The Zn–acid system for HG was progressively replaced by the more convenient THB–acid reaction system following the first applications reported by Braman and co-workers who determined trace mercury,<sup>7</sup> arsenic, and antimony<sup>8</sup> by atomic spectrometry. Thousands of research papers and many regulated analytical methods are based on HG. However, the mechanism of this commonly employed derivatization reaction remains virtually unknown despite passage of 35 years since its first application in analytical chemistry.

Under conventional analytical reaction conditions, borane is present at concentrations several orders of magnitude in molar excess over that of the analyte and the only observed reaction products are the volatile metal hydride and molecular hydrogen. As such, the analyte is quantitatively transformed to the volatile metal hydride, making this reaction ideal for analytical applications. However, the mechanism of HG has received little attention in the analytical chemistry community, where applications continue to present the main challenge. The first authors proposing a reaction mechanism for HG were Robbins and Caruso<sup>9</sup> (in an A page review article), who postulated a simple reaction scheme for both the Zn–acid and THB–acid systems:



The resultant atomic hydrogen reacts with aqueous ions of the

\* Corresponding author. E-mail: dulivo@cnr.ipcf.it.

† Institute of Chemical and Physical Processes.

‡ Institute for National Measurement Standards.

(1) Dédina, J.; Tsalev, D. L. *Hydride Generation Atomic Spectrometry*; Wiley: Chichester, 1995; Chapter 2.

(2) Shaeffer, G. W.; Emilius, E. *J. Am. Chem. Soc.* **1954**, *76*, 1203–1204.

(3) Schlesinger, H. I.; Brown, H. C.; Hoekstra, H. R.; Rapp, L. R. *J. Am. Chem. Soc.* **1953**, *75*, 199–204.

(4) Berka, L.; Briggs, T.; Millard, M.; Jolly, W. *J. Inorg. Nucl. Chem.* **1960**, *14*, 190–194.

(5) Jolly, W. *J. Am. Chem. Soc.* **1960**, *83*, 335–337.

(6) Holak, W. *Anal. Chem.* **1969**, *41*, 1712–1713.

(7) Braman, R. S. *Anal. Chem.* **1971**, *43*, 1462–1467.

(8) Braman, R. S.; Justen, L. L.; Foreback, C. C. *Anal. Chem.* **1972**, *44*, 2195–2199.

(9) Robbins, W. B.; Caruso, J. A. *Anal. Chem.* **1979**, *51*, 889A–899A.

element forming the volatile metal hydride:



Over the following years, this reaction scheme was subsequently adopted by many authors<sup>1,10,11</sup> in the analytical literature, where it became known as the “nascent hydrogen” mechanism. It became a convenient explanation for hydrogen-transfer reactions in HG techniques (the nascent hydrogen concept was proposed in the 1800s<sup>12</sup>). This mechanism has been the subject of criticism. It is evident from a thermodynamic point of view that both reactions 1 and 2 cannot generate atomic (nascent) hydrogen,<sup>13</sup> and deuterium-labeled experiments on hydrolysis of THB clearly indicate that atomic hydrogen cannot be the intermediate giving rise to the formation of molecular hydrogen as the final product of hydrolysis of THB.<sup>14</sup> However, the HG reaction has only recently been investigated in an effort to detail the mechanism of this process.<sup>15–17</sup> On the basis of deuterium-labeled experiments and the properties of the borane complex,<sup>15,17</sup> a general reaction model was proposed based on the direct transfer of hydrogen through a concerted mechanism taking place via “analyte–borane complex” (ABC) intermediates.

Definitive evidence is reported here that clarifies the complex mechanism of HG using THB derivatization based on a simple experimental system that examines the formation of stable arsenic and antimony compounds present in both the aqueous and gas phases.

## EXPERIMENTAL SECTION

**Chemicals.** The following reagents were used: NaBH<sub>4</sub> pellets (Alfa Aesar, Word Hill, MA); NaBD<sub>4</sub> pellets (99% D, Cambridge Isotope Laboratories, MA); borane-*tert*-butylamine complex (Aldrich, pellets, assay 97%); borane–dimethylamine complex (Aldrich, assay 97%). The 1 M stock solutions of NaBH<sub>4</sub> and NaBD<sub>4</sub> were prepared in H<sub>2</sub>O and stabilized with 0.5 M NaOH and were used for preparation of mixed NaBH<sub>4</sub> + NaBD<sub>4</sub> (0.2 M total concentration). Working solutions, prepared by dilution of appropriate volumes of stock solutions, contained molar fractions of NaBD<sub>4</sub> of 0, 10, 25, 50, 75, 90, and 100% and 0.1 M NaOH.

Stock solutions of As(III) and Bi(III) (1000 mg L<sup>-1</sup>) were prepared from As<sub>2</sub>O<sub>3</sub> and Bi metal, respectively. Monomethylarsonic acid, disodium salt was obtained from Chem Service (PA, assay 99.0%). Dimethylarsinic acid was obtained from Sigma-Aldrich (assay 99.3%). To study the generation of antimony hydride, enriched isotopic standard solutions (300 μg mL<sup>-1</sup>) of <sup>123</sup>Sb(III) (Oak Ridge National Laboratory, Oak Ridge, TN) were used to spike the reaction media in septum-sealed vials to produce the corresponding hydride.

The impurity level of arsenic compounds in arsenic standards was checked by gas chromatography/mass spectrometry (GC/MS) after HG (0.1 M HCl + 0.2 M L-cysteine, 0.2 M NaBH<sub>4</sub> in 0.1 M NaOH; pH at the end of reaction was 8).

Reactions were conducted in screw-capped reaction vials fitted with PTFE/silicone septa (4 and 12 mL, Pierce Chemical Co.). Acidity or pH adjustments were made with dilute HCl or HClO<sub>4</sub> and NaOH solution. The headspace of reaction vials was flushed with nitrogen gas before the reactions were initiated.

**Instrumentation.** A Hewlett-Packard 6890 gas chromatograph operated in the splitless mode and equipped with a Hewlett-Packard 5973 mass-selective detector (MS) was fitted with a 30 m × 0.25 mm i.d. capillary GC column (1-μm Valcobond VB-1). A gastight Hamilton syringe (5 mL) was employed for sampling headspace gases from reaction vial headspace. The GC was operated under the following conditions: injector temperature, 150 °C; oven temperature program, 35 °C, hold for 10 min, heated to 150 °C at 30 °C min<sup>-1</sup>; transfer line temperature, 150 °C. The carrier gas was He at 1.2 mL min<sup>-1</sup>.

Electrospray ionization mass spectrometry (ESI-MS) experiments were performed using a Finnigan LCQ Deca mass spectrometer (Thermo Finnigan, San Jose, CA) equipped with a commercial ESI source. For ESI-MS experiments, nitrogen was used as sheath gas (100 psi) at a flow rate of 20 arbitrary units. An electrospray voltage of 4.5 kV and a capillary temperature of 150 °C were used. The infusion rate was 3 μL/min. The ESI interface and mass spectrometer parameters were optimized to obtain maximum sensitivity. For MS<sup>n</sup> experiments, the ion isolation window was set at 1 Da and the collision energies were set at 20–35%. Ultrahigh purity helium was used as the buffer gas.

## RESULTS AND DISCUSSION

**Generation of Deuterated Hydrides.** In the reaction of trivalent As, Sb, or Bi in H<sub>2</sub>O/H<sub>3</sub>O<sup>+</sup> with mixed NaBD<sub>4</sub>/NaBH<sub>4</sub> (TDB/THB) reagent (wherein the molar fraction of NaBD<sub>4</sub> in this reagent,  $x(\text{TDB})$ , varied from 0 to 100%) and under analytical conditions (wherein As(III), Sb(III), or Bi(III) is present at concentrations in the range of 10<sup>-6</sup>–10<sup>-5</sup> M in 1 M HCl, NaBD<sub>4</sub> + NaBH<sub>4</sub> = 0.2 M, final pH = 0), the formation of different isotopologues, EH<sub>m</sub>D<sub>3-m</sub>, takes place. The relative abundance distribution of each isotopologue,  $x(\text{EH}_m\text{D}_{3-m})$ , in the synthesized hydride as a function of  $x(\text{BD}_4^-)$  can be predicted on the basis of a postulated mechanism, assuming an absence of any isotope effects. In addition to the mechanism outlined in reactions 1 and 3 (nascent hydrogen mechanism, hypothesis A), two reaction mechanisms are postulated based on direct transfer of H/D from boron to the element following the formation of an ABC intermediate: the three H/D in the final hydride come from different borane molecules (hypothesis B), and all three H/D in the final hydride arise from the same borane molecule (hypothesis C). The experimental distribution of  $x(\text{EH}_m\text{D}_{3-m})$  versus  $x(\text{BD}_4^-)$  for As, Sb, and Bi can be obtained by analyzing the gaseous reaction products generated using varying molar fractions of TDB in the mixed THB + TDB reagent (i.e.,  $x(\text{BD}_4^-) = 0, 10, 25, 50, 75, 100\%$ ). The analysis of the gaseous products was performed by GC/MS, and the results were interpreted following mass spectral deconvolution.<sup>18,19</sup> The predicted, “theoretical”, and experimental distributions  $x(\text{EH}_m\text{D}_{3-m})$  versus  $x(\text{TDB})$  are compared in Figure 1.

(10) Nakahara, T. *Prog. Anal. At. Spectrosc.* **1983**, *6*, 163–223.

(11) Pohl, P. *Trends Anal. Chem.* **2004**, *23*, 87–101.

(12) Tommasi, D. *Rendiconti dell' Istituto Lombardo di Milano 1877*; pp 797–798.

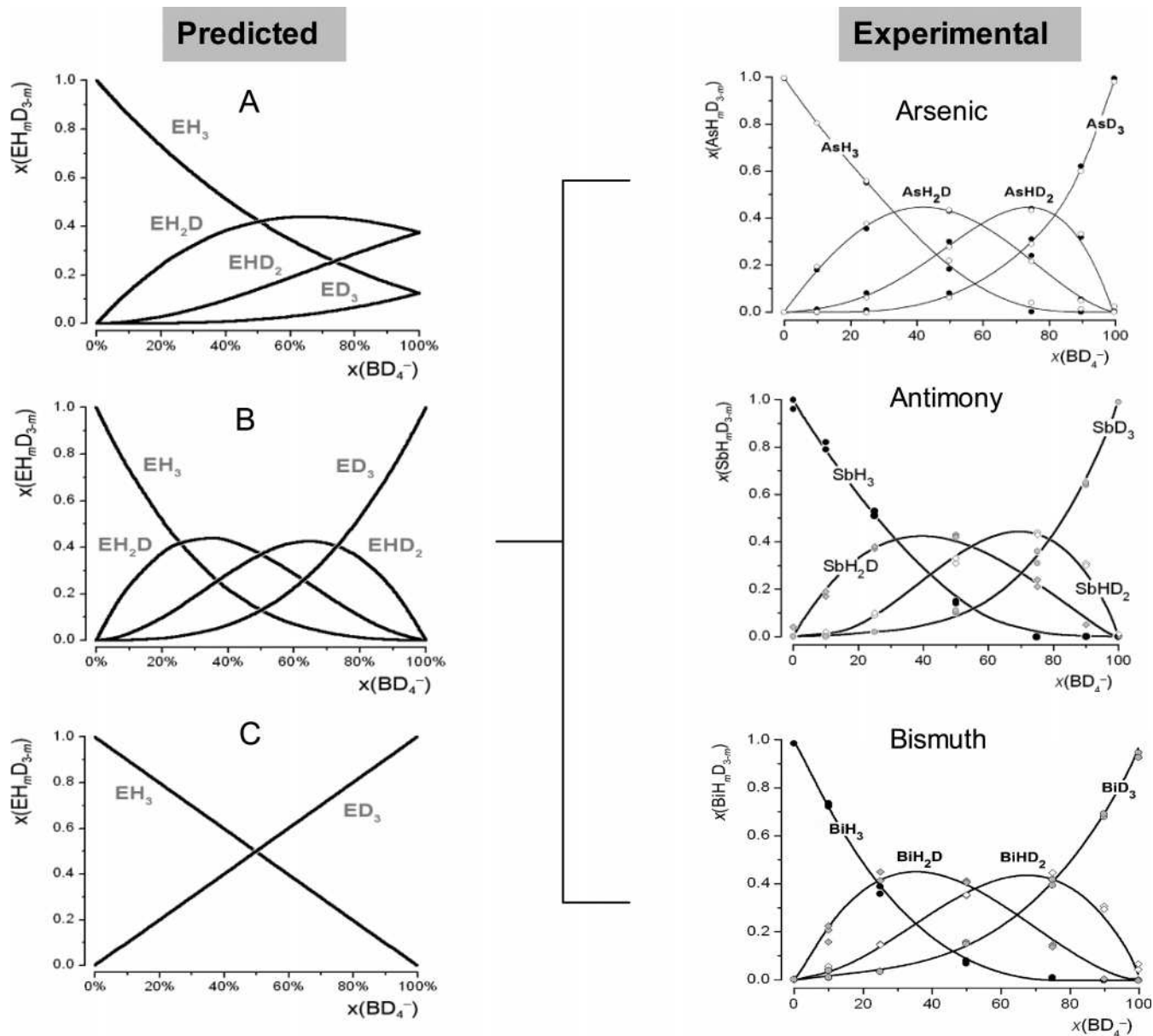
(13) Laborda, F.; Bolea, E.; Baranguan, M. T.; Castillo, J. R. *Spectrochim. Acta, Part B* **2002**, *57*, 797–802.

(14) D'Ulivo, A. *Spectrochim. Acta, Part B* **2004**, *59*, 793–825.

(15) D'Ulivo, A.; Onor, M.; Pitzalis, E. *Anal. Chem.* **2004**, *76*, 6342–6352.

(16) D'Ulivo, A.; Baiocchi, C.; Pitzalis, E.; Onor, M.; Zamboni, R. *Spectrochim. Acta, Part B* **2004**, *59*, 471–486.

(17) D'Ulivo, A.; Mester, Z.; Sturgeon, R. E. *Spectrochim. Acta, Part B* **2005**, *60*, 423–428.



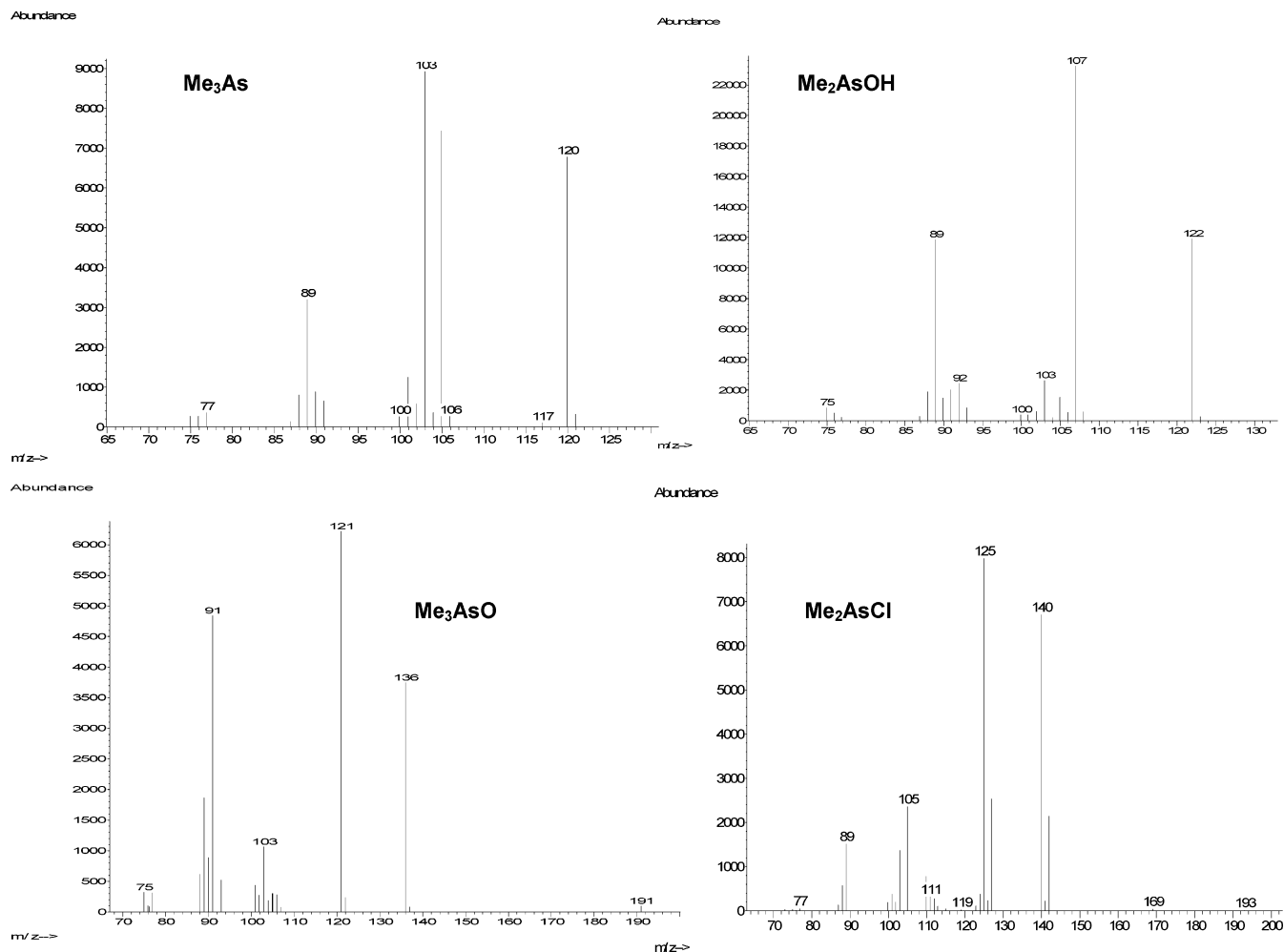
**Figure 1.** Comparison of predicted (first column) and experimental (second column) distribution of metal hydride isotopologues,  $x(\text{EH}_m\text{D}_{3-m})$ , generated by reaction of As(III), Sb(III) ( $10^{-5}$  M), and Bi(III) ( $3 \times 10^{-6}$  M) with 0.2 M mixed  $\text{NaBD}_4/\text{NaBH}_4$  reagent (wherein the molar fraction of  $\text{NaBD}_4$  in this reagent is denoted  $x(\text{BD}_4^-)$ ) in 1 M HCl reaction media (final pH = 0). In the first column, graph A corresponds to the nascent hydrogen mechanism; (B) corresponds to mechanisms based on direct transfer of H/D from boron to the element where the three H/D in the final hydride come from different borane molecules; (C) corresponds to mechanisms based on direct transfer of H/D from boron to the element, and the three H/D in the final hydride come from the same borane molecule. The second column depicts the observed distribution of As, Sb, and Bi hydride isotopologues. The experimental data are in good agreement with mechanism B.

The identification of the mechanism thus becomes quite straightforward as a consequence of the different “fingerprints” arising for the relative abundance distributions of the isotopologues depending on which reaction mechanism is considered. The experimental “fingerprint” distributions for arsenic, antimony, and bismuth are in perfect agreement with those predicted based on the mechanism outlined in hypothesis B, the direct transfer of H/D from boron to the element with H/D coming from different borane molecules. This result provides definitive proof against the “nascent hydrogen” mechanism outlined in reactions 1 and

3. The experimental distributions are not perfectly symmetric, as predicted, and the degree of asymmetry decreases from As to Sb with Bi being almost identical to the predicted statistical distribution. The asymmetry is due to the more pronounced incorporation of H with respect to D, and it is a consequence of kinetic isotope effects, the magnitude of which cannot be estimated a priori because of the potential superimposition of primary and secondary kinetic isotope effects. Consequently, it was not accounted for in calculating the theoretically expected distributions.

(18) Meija, J.; Mester, Z.; D’Ulivo, A. J. *Am. Soc. Mass Spectrom.* **2006**, *17*, 1028–1036.

(19) Meija, J.; Mester, Z.; D’Ulivo, A. J. *Am. Soc. Mass Spectrom.* **2007**, *18*, 337–345.



**Figure 2.** Mass spectra of volatile compounds containing one arsenic atom produced during reaction of As(III), MMAA and DMAA with different borane complexes under stoichiometric reaction conditions ( $c(\text{As}) = 0.01 \text{ M}$ ,  $3 \leq \text{pH} \leq 6$ ).

**Table 1. Identification by GC/MS of Volatile Arsenic Species Produced by Reaction of Borane Complexes with As(III), MMAA, and DMAA.**

As reagent	volatile arsenic reaction product <sup>a</sup>
As(OH) <sub>3</sub>	AsH <sub>3</sub> ; H <sub>2</sub> AsAsH <sub>2</sub>
MeAsO(OH) <sub>2</sub>	MeAsH <sub>2</sub> ; Me <sub>2</sub> AsH; Me <sub>3</sub> As; MeHAsAsHMe
Me <sub>2</sub> AsO(OH)	Me <sub>2</sub> AsH; Me <sub>3</sub> As; Me <sub>3</sub> AsO; Me <sub>2</sub> AsOH; Me <sub>2</sub> AsCl; Me <sub>2</sub> AsAsMe <sub>2</sub> ; Me <sub>2</sub> AsAs(O)Me <sub>2</sub>

<sup>a</sup>  $c(\text{As}) = 0.01 \text{ M}$ , stoichiometric reaction conditions,  $3 \leq \text{pH} \leq 6$ . Reaction with NaBH<sub>4</sub>, H<sub>3</sub>B/NH<sub>2</sub>C(Me)<sub>3</sub>, or H<sub>3</sub>B/NH(Me)<sub>2</sub> gave similar results

**Table 2. Retention Times of Volatile Arsenic Compounds Identified by GC/MS**

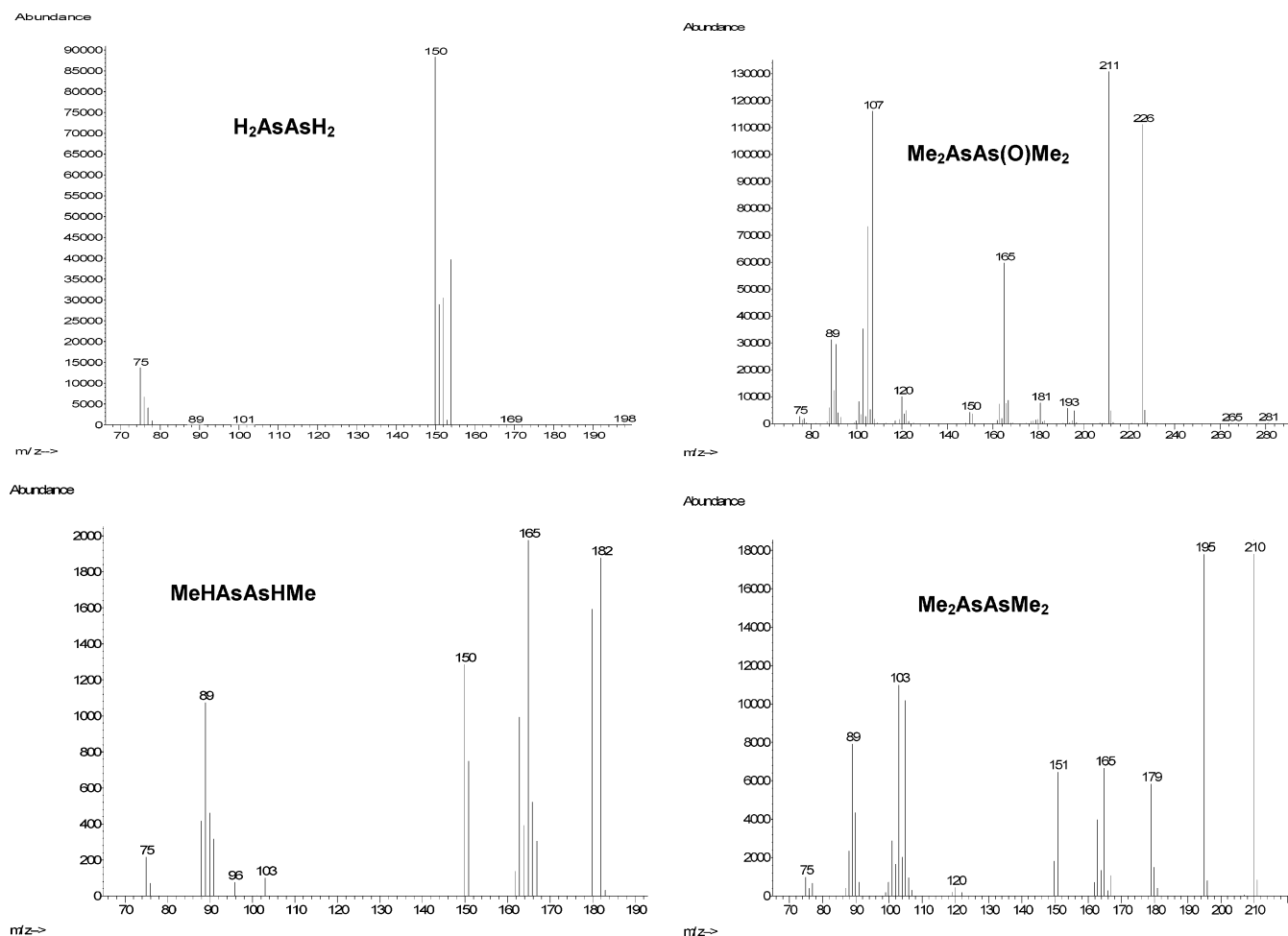
arsenic compound	ret time (min)	mass spectra
AsH <sub>3</sub>	1.45	
MeAsH <sub>2</sub>	1.82	
Me <sub>2</sub> AsH	2.69	
Me <sub>3</sub> As	3.49	Figure 2
H <sub>2</sub> As-AsH <sub>2</sub>	5.26	Figure 3
Me <sub>3</sub> AsO	5.46	Figure 2
Me <sub>2</sub> AsOH	5.66	Figure 2
Me <sub>2</sub> AsCl	6.10	Figure 2
MeHAs-AsHMe	7.77	Figure 3
Me <sub>2</sub> As-As(O)Me <sub>2</sub>	8.30	Figure 3
Me <sub>2</sub> As-AsMe <sub>2</sub>	8.51	Figure 3

**Identification of Volatile Arsenic Species by GC/MS.** A second piece of experimental evidence is based on the idea that HG of simple inorganic or organometallic substrates by derivatization with borane complexes (THB or amine boranes<sup>20</sup>) passes through reaction intermediates that can evolve to various products, depending on the reaction conditions. This concept arises from the well-known chemistry of borane in organic reactions where there is a high degree of complexity of hydroboration/reduction of organic substrates (i.e., concerted reactions through multicentered intermediates). Under optimized analytical conditions for

trace element analysis/speciation (substrate  $< 10^{-5} \text{ M}$ , borane complex  $> 0.1 \text{ M}$ , acidic or strongly acidic conditions,  $-1 < \text{pH} < 1$ ), it is reasonable to assume that the intermediates are forced to evolve toward the rapid formation of the simple hydride derivatives,  $\text{EH}_m$ , because of the extremely high borane/substrate ratio and the acidic reaction media, which favor rapid hydrolysis of intermediates to the final products.

Careful choice of the substrates [inorganic As(III), monomethylarsonic acid (MMAA), and dimethylarsinic acid (DMAA)] and of the borane reagents [THB, *tert*BuNH<sub>2</sub>BH<sub>3</sub> (TBAB) and

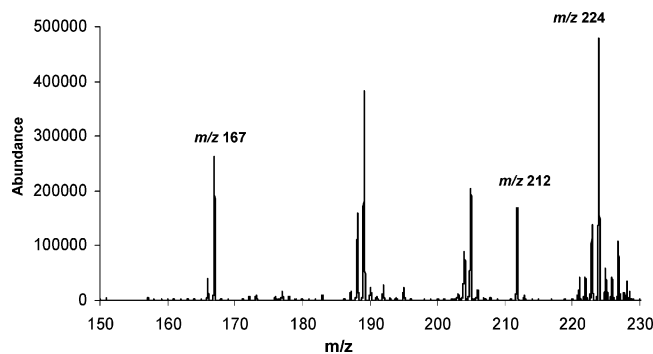
(20) D'Ulivo, A.; Loreti, V.; Onor, M.; Pitzalis, E.; Zamboni, R. *Anal. Chem.* **2003**, *75*, 2591–2600.



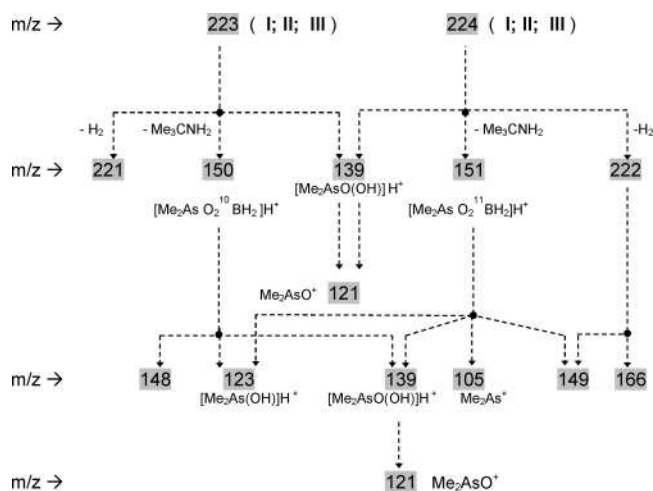
**Figure 3.** Mass spectra of volatile compounds containing two arsenic atoms produced during reaction of As(III), MMAA, and DMAA with different borane complexes under stoichiometric reaction conditions ( $c(\text{As}) = 0.01 \text{ M}$ ,  $3 \leq \text{pH} \leq 6$ ).

( $\text{CH}_3$ )<sub>2</sub>NHBH<sub>3</sub> (DMAB)], as well as adoption of nonanalytical reaction conditions ( $c(\text{As}) = 0.01 \text{ M}$ , borane/substrate  $\sim 1 \text{ mol/mol}$ ,  $3 < \text{pH} < 6$ ) allows such identification using GC/MS. In the course of the reaction, formation of suspended reddish particulates, which were assumed to be elemental arsenic, occurred. Under such conditions, many other volatile arsenic species have been detected in the headspace of the reaction vial and are reported in Table 1. Identification of these arsenic products is accomplished using the known retention times of standards (see Table 2) as well as from a consideration of their fragmentation mass spectra (see Figures 2 and 3). Some of the identified arsenic species can be the final products whereas others may only be intermediate products of the reaction under nonanalytical conditions. Rearrangements of these intermediate products or further reactions between different intermediate products very likely take place. Some of them could be responsible for methyl transfer, leading to formation of  $\text{Me}_3\text{As}$  species or to the formation of the As–As bond in diarsane species. In the case of DMAA, it is evident that species such as  $\text{Me}_2\text{AsOH}$  serve as the reaction intermediate wherein the arsenic has been converted to the trivalent oxidation state by reduction of  $\text{As}=\text{O}$ ; this represents the first step of the analytically expected reaction leading to the formation of  $\text{Me}_2\text{AsH}$ . With respect to the formation of trimethylated species, the most interesting is  $\text{Me}_3\text{As}$ . At the beginning of the reaction, the most abundant species in the headspace volume among those

reported in Table 1 were  $\text{Me}_2\text{AsH}$  and  $\text{Me}_3\text{As}$ . However, within 1–2 h,  $\text{Me}_2\text{AsH}$  disappeared almost completely and  $\text{Me}_3\text{As}$  simultaneously became the dominant species. This means that  $\text{Me}_2\text{AsH}$  reacts with other intermediate products formed during the reaction. A reaction of the type,  $\text{Me}_2\text{AsH} + \text{Me}_2\text{AsOH} \rightarrow \text{Me}_2\text{AsAsMe}_2 + \text{H}_2\text{O}$ , could account for the origin of dimers, not only for DMAA but also for As(III) and MMAA. Considering that formation of the hydride is a stepwise process, it is possible that, for As(III), reaction intermediates of the type  $\text{H}_2\text{AsOH}$  further react with  $\text{AsH}_3$  producing  $\text{H}_2\text{AsAsH}_2$ . In an analogous manner for MMAA, a reaction intermediate of the type  $\text{MeHAsOH}$  reacts with  $\text{MeAsH}_2$  to yield the possible isomers  $\text{MeHAsAsHMe}$  or  $\text{Me}_2\text{AsAsH}_2$ . However, the fragmentation pattern (Figure 3) indicates that it is  $\text{MeHAsAsHMe}$  because of the presence of  $\text{MeHAs}^+$  and the absence of  $\text{Me}_2\text{As}^+$  in the mass spectra. The formation of dimers could also follow different pathways as, for example, through ABC intermediates in which more than one As species could be bound to the same borane molecule at any given time. This event is unlikely to occur under analytical reaction conditions wherein the B/As ratio is several orders of magnitude higher than with stoichiometric reaction conditions. The latter hypothesis supports reaction pathways in which the borane species attack the arsenic substrates forming ABC intermediates that further evolve to yield different reaction products, depending on the ambient reaction conditions.



**Figure 4.** ESI-MS spectra of liquid-phase species observed during the reaction of DMAA with TBAB under stoichiometric reaction conditions ( $c(\text{As}) = 0.01 \text{ M}$ ,  $\text{pH} = 6$ ). DMAA and TBAB reaction products are identified at  $m/z$  167, 212, and 224. Identification and proposed structure for these compounds are presented in Figures 5–7. Note:  $m/z$  range 220–230 magnified 20-fold.

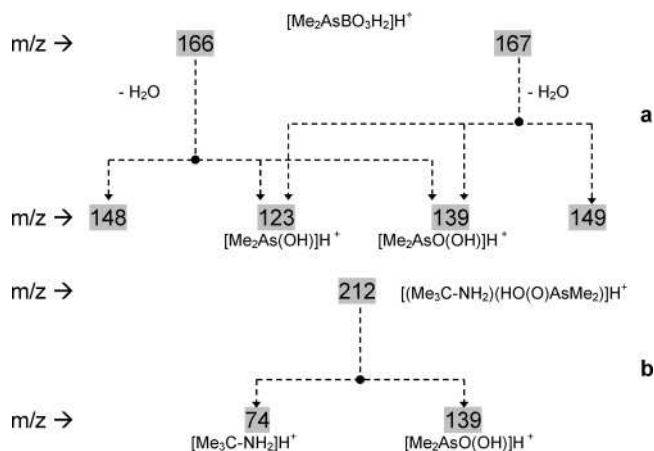
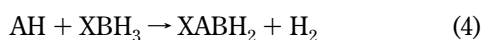


**Figure 5.** MS/MS fragmentation of species detected by ESI-MS at  $m/z$  223, 224 (see Figure 4) during the reaction of DMAA with TBAB and under stoichiometric reaction conditions ( $c(\text{As}) = 0.01 \text{ M}$ ,  $\text{pH} = 6$ ). Structures I, II, and III are detailed in Figure 7.

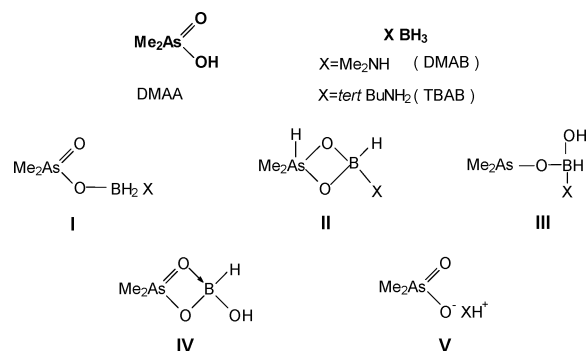
### Identification of Aqueous-Phase Arsenic Species by ESI-MS.

Analysis of the bulk aqueous solution during the reaction was performed by ESI-MS. The same nonanalytical reaction conditions used for gas-phase analysis were employed. No complex species could be detected in the aqueous reaction media, with the exception of the DMAA reaction at  $\text{pH} 6$  with both TBAB and DBAB. In this case, the species presented in Figures 7 and 8 were identified based on molecular mass and mass spectral fragmentation patterns employing up to  $\text{MS}^3$ . An example of the ESI-MS results is reported in Figure 4 for reaction of DMAA with TBAB. Fragmentation patterns for some of the detected species are presented in Figures 5 and 6.

The information generated from the reaction of DMAA with TBAB or DMAB indicates the formation of complex species in the condensed phase, the structure of which is in agreement with the general acid-catalyzed hydrolysis of borane complexes,  $\text{XBH}_3$  ( $\text{X} = \text{H}^-, \text{NR}_3$ ) with proton-containing species ( $\text{AH}^{21,22}$ ) leading to formation of a new borane complex and elimination of  $\text{H}_2$ :

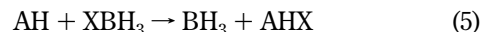


**Figure 6.** MS/MS fragmentation of species detected by ESI-MS (see Figure 4) at  $m/z$  166, 167 (a) and 1212 (b) during the reaction of DMAA with TBAB and under stoichiometric reaction conditions ( $c(\text{As}) = 0.01 \text{ M}$ ,  $\text{pH} = 6$ ). Structures I, II, and III are detailed in Figure 7.



**Figure 7.** Proposed reaction intermediates observed under stoichiometric reaction conditions for DMAA (0.01 M,  $\text{pH} = 6$ ) and amineboranes with ESI-MS.

Or, alternatively, the proton can also attack the ligand, as in the case of amine boranes:<sup>23</sup>

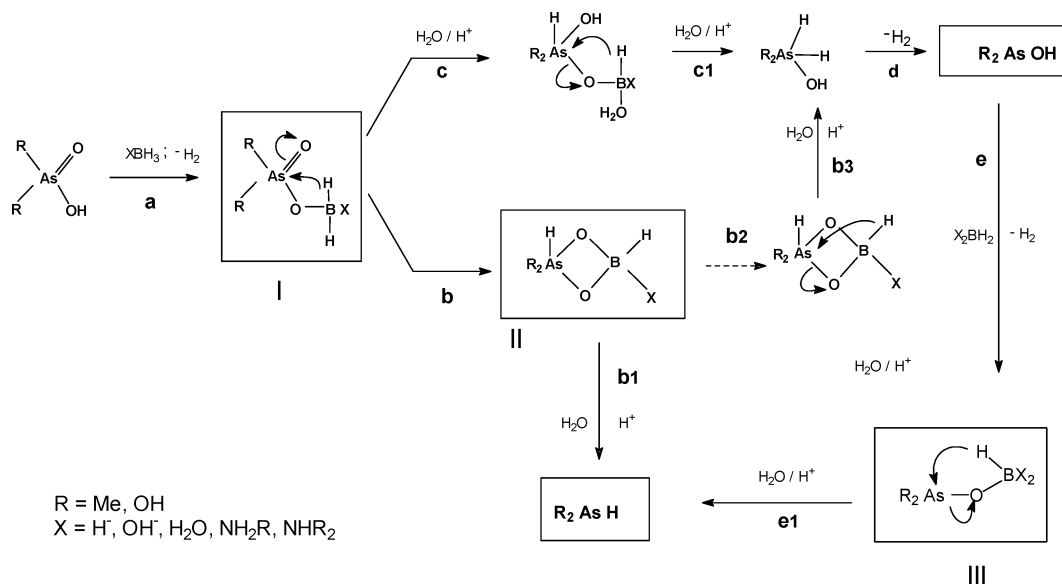


For the case when  $\text{AH} = \text{H}_2\text{O}$  or  $\text{H}_3\text{O}^+$ , this represents the initial hydrolysis reactions of tetrahydroborate(III) (reaction 4) and amine borane (reactions 4 and 5) in aqueous solution.

Compounds I, II, and III shown in Figure 7 represent some of the possible isomers fitting the experimental evidence for reaction of DMAA with both TBAB ( $m/z = 223, 224$  for protonated species, boron isotopic envelope, both containing DMAA residue; see Figure 5) and DMAB ( $m/z = 195, 196$  for protonated species, boron isotopic envelope and both containing DMAA residue).

Structure I in Figure 7 corresponds to an ABC formed by reaction 4, where  $\text{AH}$  is  $\text{Me}_2\text{As}(\text{O})\text{OH}$ , while  $\text{XBH}_3 = \text{TBAB}$  or  $\text{DMAB}$ . Structure II is an ABC arising from rearrangement of structure I following hydrogen transfer from boron to arsenic with the formation of a new intramolecular B–O bond, which leads to the four-membered ring structure. Structure III corresponds to an ABC formed by the reaction of  $\text{MeAsOH}$  with  $\text{XBH}_3$  (TBAB

(21) Davis, R. E.; Swain, C. G. *J. Am. Chem. Soc.* **1960**, *82*, 5949–5950.  
 (22) Gardiner, J. A.; Collat, J. W. *J. Am. Chem. Soc.* **1965**, *87*, 1692–1695.  
 (23) Kelly, H. C.; Marchelli, F. R.; Giusto, M. R. *Inorg. Chem.* **1964**, *3*, 431–437.



**Figure 8.** General reaction scheme of  $\text{R}_2\text{As}(\text{O})\text{OH}$  and  $\text{R}_2\text{AsOH}$  ( $\text{R} = \text{OH, alkyl}$ ) with borane complexes under analytical conditions. Chemical species in boxed frames have been identified in the liquid phase (structures I, II, and III) and in the gas phase.

or DMAB) followed by the replacement of the hydride with a hydroxyl group due to partial hydrolysis with  $\text{H}_2\text{O}$  or vice versa. Both steps take place according to reaction 4, and in this case, two molecules of  $\text{H}_2$  are eliminated.

The compound corresponding to structure IV ( $m/z$  166, 167 for protonated species, boron isotopic envelope and both containing DMAA residue) is the same for reaction of DMAA with both TBAB and DMAB. Here, only one of the possible structures is reported because this compound could be an artifact, generated during the ES-MS measurement process because fragments of similar structure ( $\text{Me}_2\text{AsO}_2\text{BH}_2$ ,  $m/z$  150, 151, Figure 5) are detected during MS/MS fragmentation of species at  $m/z$  223, 224 and 195, 196 (structures I, II, and III, Figure 7). The other possible structures fitting the species at  $m/z$  166, 167 are  $\text{Me}_2\text{AsH}(\text{O})_2\text{BOH}$ , containing two oxygen bridges, and  $\text{Me}_2\text{As}-\text{O}-\text{B}(\text{OH})_2$ , containing only one oxygen bridge. These latter two structures seem not very likely due to the presence of electrophilic trivalent boron, which is not complexed by any ligand.

Structure V represents salts resulting from acid–base reaction of DMMA with the amines, which are displaced from boron by hydrolysis reaction 5 (*tert*- $\text{BuNH}_2$  in the case TBAB or  $\text{Me}_2\text{NH}$  in the case of DMAB).

**Reaction Mechanism.** Among the different reaction pathways identified above, it is possible to recognize the most likely analytical path based on the species identified in the gas phase ( $\text{Me}_2\text{AsH}$  and  $\text{Me}_2\text{AsOH}$ ; Table 1) and in solution (structures I, II, and III; Figure 7). It is possible to propose a reaction scheme taking into consideration only those reactions which are most likely under analytical conditions (that is, analyte at trace level, high borane-to-analyte ratio), which excludes reactions among arsenic intermediates and formation of ABC containing more than one arsenic atom. The analytical reaction scheme is presented in Figure 8 and is of general validity for the reduction of both As(V) species,  $\text{R}_2\text{As}(\text{O})\text{OH}$  ( $\text{R} = \text{Me, OH}$ ) and As(III) species  $\text{R}_2\text{AsOH}$  ( $\text{R} = \text{Me, OH}$ ). In this reaction scheme, the species that have been experimentally identified are reported inside frames.

The first step is the formation of ABC-I (structure I, Figure 8), which takes place by hydrolysis of a borane complex with an acid, AH (reaction 4). The ABC-I can then evolve by intramolecular transfer of hydrogen from boron to arsenic according to reaction b or c. Reaction pathway b passes through a rearrangement to yield ABC-II (structure II, Figure 8). In this case, tetracoordinate boron is achieved through the formation of a second As–O–B bridge, rather than the formation of a complex with water,  $\text{BOH}_2$ , as in the case of reaction c. The hydrolysis of ABC-II, in the case when both R ligands are Me, yields the final expected products  $\text{Me}_2\text{AsH}$  (reaction b1). In the other cases, reaction b1 will give  $\text{MeHAsOH}$  or  $\text{HAs}(\text{OH})_2$ , and the replacement of OH by H would take place according to reaction e–e1. Alternatively, ABC-II undergoes internal hydrogen transfer to As (reaction b2) and hydrolysis (reaction b3) to yield unstable  $\text{R}_2\text{AsH}_2\text{OH}$ , which eliminates  $\text{H}_2$  (reaction d) giving  $\text{R}_2\text{AsOH}$ . The production of  $\text{R}_2\text{AsH}_2\text{OH}$  intermediate can also be achieved via a different pathway, as described by reaction c–c1.

Pathways a–c–d and a–b–d represent reduction of As(V) to As(III). The As(III) compound,  $\text{R}_2\text{AsOH}$ , is converted to the hydride via formation of ABC-III (structure III, Figure 8, reactions e and e1). Pathway e–e1 represents hydride formation starting with As(III) compounds. In the case when both R ligands are OH ( $\text{R} = \text{OH}$ ), this is the path for hydride generation of  $\text{AsH}_3$  from inorganic As(III); after the first step, the intermediate  $(\text{OH})_2\text{AsH}$  undergoes a reiteration of reaction e–e1 to give  $(\text{OH})\text{AsH}_2$  and the final product  $\text{AsH}_3$ . The reiteration of reaction pathway e is in perfect agreement with the experimental results obtained by THB + TDB reduction of As(III) reported above, indicating that the three hydrogens present in  $\text{AsH}_3$  come from different borane molecules.

## CONCLUSION

The mechanism of HG by aqueous-phase derivatization of simple inorganic and organometallic species with THB and

amine–boranes passes through a series of reactions, starting with the formation of ABC intermediates between the borane and the analyte substrate. These ABC intermediates evolve to intermediate metal compounds and to the final products through different reaction pathways characterized by rearrangements, hydride transfer, and hydrolysis. Under stoichiometric, mild reaction conditions, at least three different reaction pathways can be identified leading to formation of (i) fully hydrogenated hydrides, (ii) dimers containing a metal–metal bond, and (iii) metal derivatives arising from a methyl-transfer reaction. Under strict analytical reaction conditions (high borane-to-substrate ratio and strongly acidic aqueous media), ABC intermediates will prefer-

entially evolve toward the fully hydrogenated volatile hydrides due to the fast hydrogen-transfer reactions followed by quick hydrolysis of the intermediates.

#### **ACKNOWLEDGMENT**

A.D. is grateful to NRC Canada for the financial support in the form of Visting Fellowship.

Received for review October 18, 2006. Accepted February 19, 2007.

AC061962C