Mechanisms of chemical vapor generation by aqueous boranes for trace element analysis—A rather long and unfinished story

1. Introduction

In analytical chemistry, the term Vapor Generation (VG) encompasses a variety of derivatization techniques that play an important role in the determination and speciation of trace elements by means of atomic optical and mass spectrometry.

Chemical vapor generation (CVG) was the first of these applied in the late 1960s, and in 1971 a decisive impulse to CVG arose from the introduction of $NaBH_4$ (THB) as a derivatization reagent. The tetrahydridoborate ion is able to convert many elements at trace concentrations, such as Ge, Sn, Pb, As, Sb, Bi, Se, Te, to their corresponding volatile hydrides, and mercury to Hg^0. CVG by aqueous $[BH_4]^-$ became very popular and found many applications to trace element determinations and speciation, including methods used by regulatory agencies. Much later, in the early 2000s, the scope of CVG by $[BH_4]^-$ derivatization would extend to several transition metals.

At the time of publication of the first monograph on CVG by Dědina and Tsalev, in 1995, it was evident that, after more than twenty years since its introduction, the analytical chemistry community had disregarded the fundamental aspects of CVG. Studies reporting method development and optimization were carried out empirically, and the field was dominated by erroneous concepts and controversial aspects.

Dedicated studies on fundamental aspects of CVG began around 2003 and stimulated the launch of an IUPAC 4-year-long project in 2007 which contributed to the clarification of erroneous concepts and controversial aspects. CVG mechanistic studies further continued after 2011. The IUPAC project also stimulated studies on fundamental aspects of other emerging vapor generation techniques, such as photochemical VG, in order to avoid the empirical approach that plagued CVG for many years.

This article briefly illustrates the course of studies that have contributed to the understanding of some fundamental aspects of CVG, and the current state of knowledge.

2. Erroneous concepts in CVG

In 1979, Robbins and Caruso postulated the following mechanism for the CVG of volatile hydrides:

$$BH_4^- + H^+ + 3H_2O \rightarrow B(OH)_3 + 8H^\bullet \quad (1)$$

$$E^{m+} + (m+n)H^\bullet \rightarrow EH_n + mH^+ \quad (2)$$

Where E is the analyte element (Ge, Sn, Pb, As, Sb, Bi, Se, Te, Hg, *etc.*). Even if not explicitly mentioned by the authors, it could be assumed that the molecular hydrogen, which is evolved by $[BH_4]^-$ hydrolysis, is formed by recombination of hydrogen radicals:

$$H^\bullet + H^\bullet \rightarrow H_2 \quad (3)$$

This reaction pathway was later named the "nascent hydrogen mechanism," because the active species generating the volatile hydrides were believed to be transient species of hydrogen (*i.e.* hydrogen radicals, H^*), which were considered to be hydrogen in its nascent form. Reactions 1-3 reported the observed final products of CVG, *i.e.,* $B(OH)_3$, EH_n and H_2.

This mechanism contains some erroneous concepts: (i) the hydrolysis of THB is not a single step reaction and (ii) atomic hydrogen H cannot be formed by hydrolysis of THB. Despite no evidence supporting or refuting the theory, the nascent hydrogen mechanism was reported for many years, becoming very popular and accepted by a large part of the analytical community.

3. Clarification of controversial aspects and removal of erroneous concepts of CVG

3.1 Initial studies on hydrolysis of THB

Initial experiments, from 2003 to 2004, demonstrated that volatile hydrides can be generated by replacing THB with milder amine borane (AB) reagents (BH_3NR_3, R=H, alkyl). Further dedicated experiments demonstrated that hydrides can be generated by the direct action of AB on the analytical substrate without the need to generate any hydrogen (H^* or H_2) by hydrolysis of the borane reagent (reactions 1, 2).

Soon after, attention was dedicated to the mechanism of hydrolysis of THB. Analytical chemists had unfortunately ignored the studies on the mechanisms of THB hydrolysis reported in the early seventies. Reaction (1) is largely incomplete, because it considers only the final products. In fact, as it was reported in the fundamental chemistry literature, it takes place stepwise:

$$[BH_4]^- \xrightarrow[-H_2]{k_1^*} [BH_3X]^z \xrightarrow[-H_2]{k_2^*} [BH_2X_2]^z \xrightarrow[-H_2]{k_3^*} [BHX_3]^z \xrightarrow[-H_2]{k_4^*} B(OH)_3 \quad (4)$$

The hydrolysis of THB passes though hydrido-boron intermediates $[BH_{4-n}X_n]^z$ (where X = H_2O, OH, etc., n = 1-3, z = 0, ±1 is the charge; for n = 0 $[BH_{4-n}X_n]^z = [BH_4]^-$). Also, molecular hydrogen (*not* atomic hydrogen as for reaction 1) is formed stepwise with different kinetics. The degree of complexity of reaction 4 is better illustrated in a reaction scheme reported recently (Figure 1).

Dedicated studies—reported in 2004—were in agreement with reaction (4), particularly that $[BH_4]^-$ and hydrido-boron intermediates (B–H) are able to generate volatile hydrides by direct interaction with analytical substrates. Each of the B–H species of reaction 4 can be active in the generation of hydrides, as demonstrated by dedicated experiments.

3.2. Mechanism of hydrogen transfer in the generation of volatile hydrides

From 2005 to 2007, dedicated experiments using deuterium labelled reagents were carried out with the aim of clarifying the mechanism of hydrogen transfer in the generation of volatile hydrides from As^{III}, As^{V}, Sb^{III}, Bi^{III}, Ge^{IV} and Sn^{IV} substrates. The most informative results were achieved by using gravimetric mixtures of $[BH_4]^-$ and $[BD_4]^-$ in H_2O, and under ideal analytical conditions, *i.e.,* analyte at trace level, high borane/analyte molar ratios (> 10^4), absence of chemical additives and interfering species. They revealed that the formation of volatile hydrides (i) takes place stepwise, by the direct transfer of hydrogen atoms from boron ($[BH_4]^-$ and/or B–H species) to the analyte atom of the substrate, and (ii) the hydrogen atoms incorporated into the final hydrides come from different borane molecules. These evidences led to the conclusion that, similar to the mechanism of hydrolysis, hydride formation also takes place stepwise:

$$EY_n \xrightarrow[ABC^1]{B\text{-}H} HEY_{(n-1)} \xrightarrow[ABC^2]{B\text{-}H} \dots H_xEY_{(n-x)} \dots \xrightarrow[ABC^{(n-1)}]{B\text{-}H} H_{(n-1)}EY \xrightarrow[ABC^n]{B\text{-}H} EH_n \quad (5)$$

Where EY_n is the analyte substrate (E = element, such as As, Sb, Bi etc, Y = ligand, such as OH, Cl etc), B–H is a hydridoboron species, ABC is the analyte-borane complex, and $H_xEY_{(n-x)}$ is a hydrido-metal(loid) complex (HMC, $1 \le x \le n$-1). The ABC complexes are intermediate compounds through which the hydrogen transfer takes place, and their existence was confirmed by MS. The hydrogen transfer leads to the formation of intermediate hydrido-metal(oid) complexes $H_xEY_{(n-x)}$ (HMC, $1 \le x \le n$-1).

The reaction scheme 5 was considered to also be valid for transition and noble metals. The only difference is represented by the stability of intermediates and final products, which can evolve to species different from those that are formed in CVG of classical hydrides.

It is interesting to note that some applications of CVG

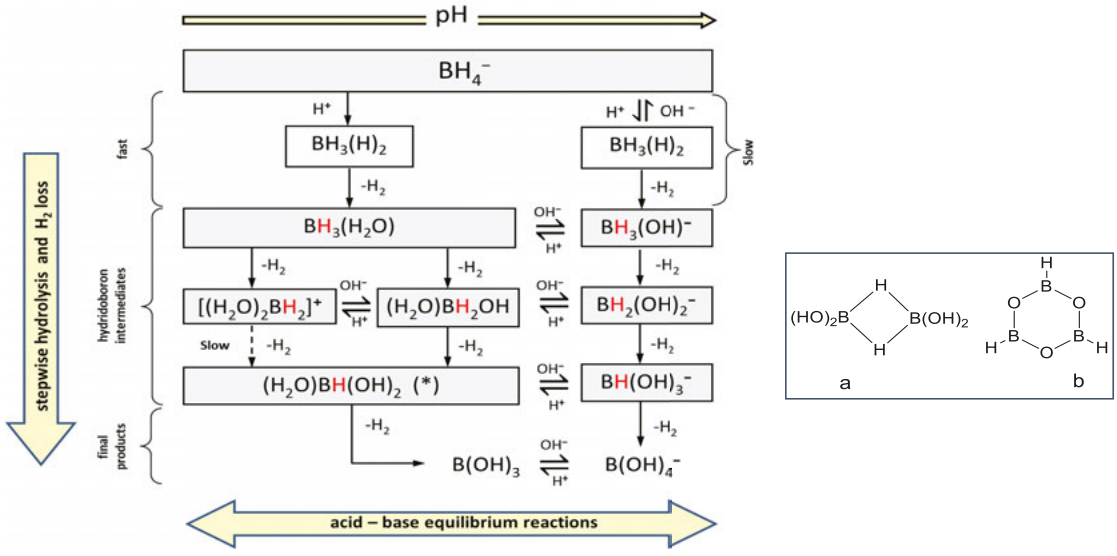

Figure 1. Qualitative representation of reaction pathways involved in the aqueous hydrolysis of THB. (*) a and b are conceivable structures of neutral monohydridoboron species. Reproduced from A. D'Ulivo, The contribution of chemical vapor generation coupled with atomic or mass spectrometry to the comprehension of the chemistry of aqueous boranes, J. Anal. At. Spectrom. 34 (2019) 823_827 [19], with permission of The Royal Society of Chemistry.

generation, performed much later from 2016 to 2018, confirmed that ABC intermediates are involved in the generation of methylated arsanes following the reaction of As-sugar with THB. Also, it was demonstrated that the extent of demethylation during methylarsane generation [$Me_nAsO(OH)_{3-n}$ – Me_nAsH_{3-n} (n=1-3)] depends on the nature of the hydridoboron species (see reaction 4) and it increases in the order: $[BHX_3]^z$, $[BH_2X_2]^z$, $[BH_3X]^z$, BH_4^-.

3.3. The IUPAC project

The newly collected evidence seemed quite convincing and stimulated in 2007 the launch of an IUPAC project (#2007-041-1-500), which focused on the clarification of the fundamental mechanisms governing CVG of volatile hydrides by aqueous boranes. The completion of the project, in 2011, brought a suitable degree of rationalization to the mechanisms governing CVG, reconciled the collected evidence with that previously reported in the chemistry literature, and toadied in the removal of erroneous concepts.

Nevertheless, the analytical model (reactions 4, 5) cannot explain several observations such as the mechanism of action of some interferences and additives, as well as the formation of oligomers at high analyte concentrations. Therefore, after 2011, studies continued to better understand the processes controlling CVG. A summary of these studies is reported in Table 1. Among these, those which led to the definition of more general reaction models are illustrated in the next section 3.3.1.

3.3.1 More general reaction models. When the concentration of analyte increases and/or the borane/analyte ratio decreases (non-analytical conditions), the formation of hydride oligomers, nanoparticles and precipitates is observed. The analytical reaction model cannot explain this evidence.

Just to give an example, arsane formation can be schematized as follows:

$$As(OH)_3 \xrightarrow[ABC^1]{BH} AsH(OH)_2 \xrightarrow[ABC^2]{BH} AsH_2(OH) \xrightarrow[ABC^3]{BH} AsH_3 \quad (6)$$

Where $AsH(OH)_2$, $AsH_2(OH)$ are HMC intermediates. Deuterium labelled experiments on arsanes in non-analytical conditions generate evidence supporting a reaction model wherein the hydrogen transfer competes with condensation reactions. A simplified reaction scheme is reported in Figure 2 for a generic HMC intermediate, RAs(OH)H. Among the possible condensation reactions, those leading to formation of easily identifiable volatile polymeric arsanes represent evidence of HMCs intermediates. For example, for HMC=H_2AsOH a condensation cascade reaction can be suggested:

$$H_2AsOH + AsH_3 \xrightarrow{-H_2O} AsH_2AsH_2 \xrightarrow[-H_2O]{-H_2AsOH} AsH_2AsHAsH_2 \xrightarrow[-H_2O]{-H_2AsOH} \ldots As_nH_{n+2} \quad (7)$$

Where di- and tri-arsane can be easily identified. Competition between hydrogen transfer and condensation reactions can also be confirmed for methylarsane formation. Increasing the analyte concentration up to the millimolar level led to formation of high molecular weight polyarsanes, nanoparticles and precipitates.

The condensation among HMC intermediates, final product and analytical substrate contribute to a redrawn a non-analytical reaction model, which is valid both in non-analytical and analytical conditions.

The non-analytical reaction model can be employed to also explain some types of interferences. It introduces a different view of the mechanisms of interferences in CVG, where they can also originated by the interaction among the intermediates that are formed during

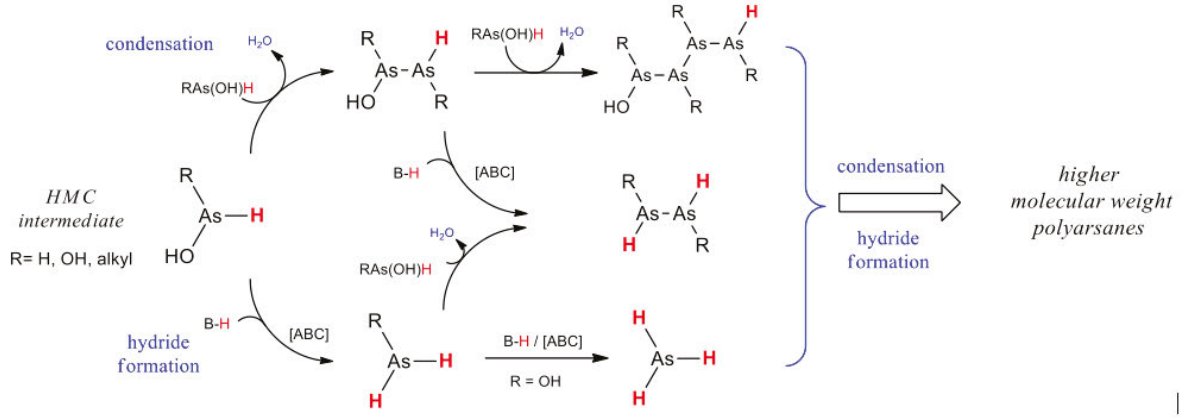

Figure 2. Competition between hydride formation and condensation reactions involving an HMC intermediate. Reproduced from A. D'Ulivo, The contribution of chemical vapor generation coupled with atomic or mass spectrometry to the comprehension of the chemistry of aqueous boranes, *J. Anal. At. Spectrom.* 34 (2019) 823_827 [19], with permission of The Royal Society of Chemistry.

reaction of both the analyte and the interferent with the borane/B-H species.

4. Fundamental aspects of VG techniques

Since 2003, almost simultaneously with the beginning of studies on the mechanisms governing CVG (section 3), numerous alternative techniques have been developed and established that have provided further impetus to renew the interest and use of these techniques. In CVG, derivatization reactions have been extended to the generation of alkyl derivatives and volatile chelates. Furthermore, new 'greener' techniques, which allow the elimination of most reagents, such as photochemical, thermochemical, sonochemical and

Year	Description and comments	Reference*
2011	Deuterium labelled experiments disclose the occurrence of a "*mechanistic interference*" generated by Au^{III}, Rh^{III}, Pt^{II} and Pd^{II} aqueous ions, which interfere with the process of hydrogen transfer from boron to analyte. These metal ions can promote the incorporation of large amount fraction of hydrogen from the aqueous reaction environment to final hydride.	[1, 2]
2012 2014	The direct, stepwise mechanism of hydrogen transfer was confirmed also for pentavalent As species, $Me_nAs^{V}O(OH)_{3-n}$ (n=0,1,2) under analytical conditions. Studies under non-analytical reaction conditions discloses the formation of polyarsanes due to condensation reactions. Definition of a more general reaction model for CVG based on the competition between hydrogen transfer and condensation reactions.	[2,3] [4]
2014	Application of the acquired knowledge on the mechanisms of CVG to the speciation analysis of As. Studies on reactivity modification using ammonia borane and L-cysteine in different reaction media.	[5]
2016	Critical evaluation of the state of knowledge on mechanisms and fundamental aspects of GCV. Definition of more general reaction models.	[6]
2016	Application of the acquired knowledge on the mechanisms of CVG to the speciation analysis of As. Evidence of demethylation of As species during THB derivatization. The extent of demethylation decrease passing from BH_4^- to its hydrolysis products: $BH_3L < BH_2L_2 < BHL_3$ (L=OH, H_2O etc; charge omitted).	[7]
2018	Determination of As-sugars by THB derivatization and investigation of related mechanism. The generation of methylated arsanes from As-sugars passes through the reversible formation of analyte-borane complex intermediates (ABC).	[8]
2018	Application of the acquired knowledge on the mechanisms of CVG to study of the mechanisms controlling the generation of volatile Cd species. Use of THB and its hydrolysis intermediate BH_3OH^-.	[9]
2018	Study of the mechanism of action of additives in CVG. The role of iodide and thiocyanate in the generation of H_2Se by THB and ammonia borane.	[10]
2018 2019	Study of the mechanisms of CVG of hydrogen selenide by THB and amine boranes. The anomalous behavior of amine boranes during hydrolysis in strongly acidic media. Identification of hydrolysis products of amine boranes and revision of the mechanism of hydrolysis which is commonly accepted in the literature	[11] [13]
2019	Critical evaluation of the state of knowledge on mechanisms and fundamental aspects of GCV.	[13]
2022	A book reports and discusses fundamental aspects of VG techniques including: • chemical-, electrochemical-, photochemical-, sonochemical-, thermochemical- and plasma induced-vapor generation; • atomization devices for VG techniques.	[14]

(*) see: https://iupac.org/project/2007-041-1-500/

Table 1. Summary of studies related to the mechanisms of CVG by aqueous boranes after 2011.

plasma mediated VG techniques have been added to the already existing techniques of chemical and electrochemical derivatization. The VGTs which are until now available, allow the derivatization to volatile species of a significant number of elements:

Be, N, F, Si, P, S, Cl, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Y, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Lanthanoids (except Pm), W, Os, Ir, Pt, Au, Hg, Tl, Pb and Bi.

In spite of numerous applications, very few efforts have focused on understanding the fundamental processes governing the derivatization reactions associated with the various VGTs. Sources of information unfortunately remain mostly fragmented in many papers published across a spectrum of scientific journals.

From these considerations the stimulus was born to bring together in a single work the existing information on the fundamental aspects of VGTs. The results of this effort are reported in a new book, *Vapor Generation Techniques for Trace Element Analysis: Fundamental Aspects*. (Elsevier, 2022)

The book is devoted to a comprehensive coverage of the fundamental aspects of VGTs, encompassing methodologies ranging from the classical chemical approaches to the most recent frontiers and presents a thorough overview and critical discussion of the state-of-the-art of knowledge of the mechanisms that control the generation of volatile derivatives and their atomization/detection by atomic spectrometry.

Recently, the use of CVG techniques, in particular those using aqueous boranes, is being increasingly replaced with other greener techniques, in particular photochemical VG. This is due to the lower use of reactants, fewer interfering effects, and the possibility of derivatizing new elements that are inactive or difficult to derivatize by CVG techniques. Nevertheless, the fundamental studies on CVG with aqueous boranes have contributed not only to improve the applicative aspects of CVG but they also represent a contribution to the understanding of the chemistry of aqueous boranes.

Some aspects of CVG still remain controversial, for example the role played by some additives and interferents. As well, greater efforts must be directed to the identification of many volatile derivatives of noble and transition metals, which hinders further advances in the understanding of the mechanisms governing CVG and in general that of VGTs.

https://iupac.org/project/2007-041-1-500/

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IUPAC Provisional Recommendations

Provisional Recommendations are preliminary drafts of IUPAC recommendations. These drafts encompass topics including terminology, nomenclature, and symbols. Following approval, the final recommendations are published in IUPAC's journal *Pure and Applied Chemistry* (PAC) or in IUPAC books. During the commentary period for Provisional Recommendations, interested parties are encouraged to suggest revisions to the recommendation's author. https://iupac.org/recommendations/under-review-by-the-public/

Definition of the Pnictogen Bond

This recommendation proposes a definition for the term "pnictogen bond": the term pnictogen bond designates a subset of the attractive interactions between an electrophilic region on a pnictogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity.

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Comments by 31 May 2023