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Mechanisms of chemical generation of volatile hydrides for trace element determination (IUPAC Technical Report)*

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Abstract: Aqueous-phase chemical generation of volatile hydrides (CHG) by derivatization with borane complexes is one of the most powerful and widely employed methods for determination and speciation analysis of trace and ultratrace elements (viz. Ge, Sn, Pb, As, Sb, Bi, Se, Te, Hg, Cd, and, more recently, several transition and noble metals) when coupled with atomic and mass spectrometric detection techniques. Analytical CHG is still dominated by erroneous concepts, which have been disseminated and consolidated within the analytical scientific community over the course of many years. The overall approach to CHG has thus remained completely empirical, which hinders possibilities for further development. This report is focused on the rationalization and clarification of fundamental aspects related to CHG: (i) mechanism of hydrolysis of borane complexes; (ii) mechanism of hydrogen transfer from the borane complex to the analytical substrate; (iii) mechanisms through which the different chemical reaction conditions control the CHG process; and (iv) mechanism of action of chemical additives and foreign species. Enhanced comprehension of these different mechanisms and their mutual influence can be achieved in light of the present state of knowledge. This provides the tools to explain the reactivity of a CHG system and contributes to the clarification of several controversial aspects and the elimination of erroneous concepts in CHG.

Keywords: borane complexes; chemical generation of volatile hydrides (CHG); IUPAC Analytical Chemistry Division; speciation; tetrahydridoborate(1–); trace analysis; ultratrace analysis; volatile hydrides.

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CONTENTS

1. INTRODUCTORY NOTES ON CHEMICAL GENERATION OF VOLATILE HYDRIDES (CHG)

The generation of volatile species is one of the most powerful and widely employed methods for trace and ultratrace element determination and speciation in analytical chemistry. The most popular techniques for the generation of volatile species deal with the elements forming volatile hydrides and mercury, which can be achieved by using different derivatization strategies such as chemical generation [1], electrochemical generation [2], photochemical generation [3], and sonochemical generation [4]. This report is focused on aqueous-phase chemical generation of volatile hydrides (CHG) by derivatization with tetrahydridoborate(1–) (THB) salts (mainly, $NaBH_4$ and KBH_4) and other borane complexes. This method is the most widely employed for determination and speciation analysis of trace and ultratrace concentration of Ge, Sn, Pb, As, Sb, Bi, Se, Te, Hg, Cd, and, more recently, several transition and noble metals when coupled with atomic and mass spectrometric detection techniques. Thousands of research papers and many regulated analytical methods are based on CHG. However, since its inception more than 35 years ago, the application and validation of CHG to many different analytical targets has been the prevailing focus of "research", whereas only limited efforts have been dedicated to clarification of mechanistic aspects of the reactions. Analytical CHG is still dominated by erroneous concepts which have been disseminated and consolidated within the analytical scientific community over the course of many years. The overall approach to CHG has thus remained completely empirical, which has hindered possibilities for further development.

A rationalization of the field based on a more rigorous scientific approach appears to be necessary. The aspects requiring rationalization, the clarification of which represents the objective of the present project, can be classified as follows: mechanism of hydrolysis of borane complexes, mechanism of hydrogen transfer from the borane complex to the analytical substrate, and mechanism of action of additives commonly employed in analytical applications of CHG. Enhanced comprehension of these three different mechanisms and their mutual influence will provide the tools to explain the reactivity of a CHG system.

At present, there are essentially two main sources of information useful for comprehension of the mechanistic aspects of CHG. The first is represented by the fundamental data and experimental evidence relating to the chemistry of borane complexes that has been collected and reported in the literature in past years (1950–1980); regrettably, the analytical community has disregarded most of this fundamental literature. The second source is represented by the most recent experimental evidence specifically devoted to clarification of the mechanism of CHG (the past 10 years of work). The combination of these two major sources of information should make possible rationalization of the mechanistic aspects of CHG, and will hopefully provide the impetus for further development in the field.

1.1 Notes on the nomenclature of hydrides

Concerning reagents and reaction products which are most frequently involved in CHG techniques, systematic IUPAC nomenclature for inorganic compounds [5] provides recommended names which may differ from those that have been reported or that are still currently reported in papers and other publications. The names of the most common chemical species are listed in Table 1.

Table 1 Nomenclature of some hydrides typically encountered in CHG techniques.

	Most frequent names	IUPAC names [5]
GeH_4	germanium hydride, germane	germane (parent hydride name), tetrahydridogermanium
SnH_4	tin hydride, stannane	stannane (parent hydride name), tetrahydridotin, tin tetrahydride
PbH_4	lead hydride, plumbane	plumbane (parent hydride name), tetrahydridolead, lead tetrahydride
AsH_3	arsenic hydride, arsine	arsane (parent hydride name), trihydridoarsenic, arsenic trihydride
SbH_3	antimony hydride, stibine	stibane (parent hydride name), trihydridoantimony,antimony trihydride
BiH_3	bismuth hydride, bismuthine	bismuthane (parent hydride name), trihydridobismuth, bismuth trihydride
H_2Se	selenium hydride, hydrogen selenide	selane (parent hydride name), dihydridoselenium, dihydrogenselenide
H_2Te	tellurium hydride, hydrogen telluride	tellane (parent hydride name), dihydridotellurium, dihydrogentelluride
BH_3	borane	borane (parent hydride name), trihydridoboron, boron trihydride
$[BH_4]^-$	tetrahydroborate(III), tetrahydroborate, borohydride	boranuide, tetrahydridoborate(1–)
$[BH_3CN]^-$	cyanotrihydroborate(III), cyanotrihydroborate, cyanoborohydride	cyanoboranuide, cyanidotrihydridoborate(1–)

1.2 Briefs on the historical development of aqueous-phase CHG

The generation of volatile hydrides for synthetic purposes using aqueous THB was first reported in 1954 for stannane by Schaeffer and Emilius [6], just one year after the first publication reporting the synthesis of $NaBH_4$ by Schlesinger et al. [7]. Then, in 1960, Berka et al. [8] reported the preparation of SbH_3 and Jolly [9], in 1961, reported the preparation of SbH_3, AsH_3, SnH_4, and GeH_4 together with some dimerization products, diarsane ($H_2As–AsH_2$), digermane ($H_3Ge–GeH_3$) and distannane ($H_3Sn–SnH_3$). The generation of bismuthane and plumbane was not feasible by this synthetic route [9].

Following these first publications, the topic appears to have disappeared from the fundamental chemistry literature to find a new interest in the analytical field, where Holak's work in 1969 [10] evidenced the great advantage arising from the introduction of gaseous hydrides in the determination of arsenic by atomic spectrometry. In practice, Holak interfaced a Zn-acid apparatus for the generation of AsH_3, similar to that employed in the "Marsh test" (see Brindle review for more information on the genesis and early developments of CHG [11]), to an atomic absorption spectrometer. Subsequently, the Zn-acid reaction system coupled with atomic spectrometry was applied to the determination of trace Sb, Se, and Te [1]. The Zn-acid system for hydride generation was progressively replaced by the more convenient $NaBH_4$-acid reaction system following the first applications reported by Braman and co-workers who determined trace mercury [12], arsenic, and antimony [13] by atomic spectrometry.

Subsequently, the $NaBH_4$-acid reaction system was successfully extended to all the other classical hydride-forming elements, Bi, Ge, Sn, Pb, Se, and Te [14], at trace level. The efficiency of CHG, defined as the fraction of analyte present in the sample, which is converted to hydride and released from the reaction mixture, can be generally considered to be close to unity at trace level and under optimized experimental conditions [1].

CHG coupled with various detection techniques, mainly atomic and mass spectrometry, provides one of the most powerful tools used in analytical chemistry for determination and speciation analysis of mercury and the elements of Groups 14, 15, and 16 at mass concentration much below 1 $\mu g\ L^{-1}$ level [1]. The almost unique employed reagent in CHG remains THB as the sodium salt or, less frequently, potassium salt. Other borane complexes such as $NaBH_3CN$ [15], borane ammonia, and different amine boranes have been employed [16]. Their effectiveness in terms of analytical performance has not been fully exploited, but they have found useful applications in diagnostic and mechanistic studies of CHG [16–19].

More recently, the aim of CHG has been expanded to an increasing number of elements, including In [20], Tl [21,22], Cd [23], Cu [24], Zn [25,26], and many other transition metals such as Ni, Co, Cr, Fe, Ti, and the noble metals Au, Ag, Pd, Pt, Ir, Os, Ru, and Rh [27,28]. The nature of the volatile reaction products obtained from CHG of transition and noble metals has not been yet identified; as well, CHG of these elements has found limited analytical applications [24,29] in comparison with the classical hydride-forming elements. The efficiency of CHG of these elements is generally much lower than that for the classical hydride forming elements [30].

Most of the papers published on CHG deal with analytical method development and applications, while fundamental aspects related to the mechanisms taking place in CHG have received relatively poor attention. The first authors proposing a reaction mechanism for HG were Robbins and Caruso [31], who postulated a simple reaction scheme for both the $NaBH_4$-acid and Zn-acid systems

$$[BH_4]^- + H^+ + 3H_2O \rightarrow H_3BO_3 + 8H^\cdot \qquad (1)^1$$

$$Zn + 2H^+ \rightarrow Zn^{2+} + 2H^\cdot \qquad (2)$$

The resultant atomic hydrogen reacts with aqueous ions of the element, $E^{(m+)}$, forming the volatile hydride

$$E^{(m+)} + (m + n)\, H^\cdot \rightarrow EH_n + m\, H^+ \qquad (3)$$

Over the following years, this reaction scheme was subsequently adopted by many authors [1,32,33] in the analytical literature where it became known as the "nascent hydrogen" mechanism and provided a convenient explanation for hydrogen-transfer reactions in CHG techniques.

The concept of nascent hydrogen is not new but it is as old as the discovery of hydrogen. It all started in the 18th century when English theologian and natural philosopher Joseph Priestley was among the first to put forward the concept of inflammable air in the nascent state or nascent hydrogen as we know it now. The "nascent state" was born, and the idea that elements are more "available" at the time of formation found wide acceptance among virtually all chemists and, surprisingly, still persists in the minds of modern chemists. While no substantial evidence, however, was ever presented to support or deny this claim, by the end of the 19th century it was well accepted that the newly formed or "nascent hydrogen" has superior reducing power over the hydrogen gas. Otto Wallach (1910), Paul Sabatier (1912), and Frederic Joliot (1935) all use the term "nascent hydrogen" in their Nobel lectures. James Marsh was among the first to introduce such a method for separation and determination of small quantities of arsenic in the form of its hydride in 1836, citing the reaction of arsenic with nascent hydrogen as the mechanism of arsane formation.

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[1] It is worth noting the difference between $[BH_4]^-$, which is the THB ion, whereas $[BH_4^-]$ is the amount concentration of the THB ion.

The hypothesis that CHG takes place in accordance with the "nascent hydrogen" pathway described by reactions 1 and 3 has been a matter of debate inside the analytical community since the first proposal of this mechanism [31]. An excellent synthesis of this debate was reported by Dědina in 1999 [34] who concluded that, at that time, there was no convincing evidence supporting or refuting the "nascent hydrogen" hypothesis.

In 2002, Laborda et al. [35] strongly criticized the possibility that atomic hydrogen could be formed during hydrolysis of $NaBH_4$, based on thermodynamic considerations. Considering that the estimated standard reduction potential for the H^+/H couple is $E°(H^+/H) = –2.016$ V, neither THB [$E°(H_3BO_3/[BH_4]^-) = –0.482$ V], nor zinc [$E°(Zn^{2+}/Zn) = –0.763$ V], would be able to perform the reduction of protons to atomic hydrogen.

More recently, a careful survey of the chemistry literature of borane complexes together with some dedicated experiments and the use of deuterium-labeled reagents contributed to the clarification of some controversial points concerning the mechanisms of CHG, as the definitive rejection of the "nascent hydrogen" hypothesis, and the adoption of a reaction model based on the direct transfer of hydrogen from boron to the element through analyte-borane complex intermediates [17–19,36–38].

1.3 CHG reaction products

Analytical application of CHG is performed under specific chemical reaction conditions which are far from those employed for synthetic purposes. In CHG, the analytical species are present at mass concentrations below 1 mg L^{-1} level or amount concentration below 10^{-5} mol L^{-1}, while the concentration of borane reagents is typically in the range of (0.05–0.50) mol L^{-1}. Under optimized reaction conditions, in terms of pH, type of acid, and other reaction parameters (chemical additives, CHG reactor design, reaction time), the almost pure hydrides are obtained from reaction of some inorganic and organo-element analytical substrates. The nature of the reaction products may change dramatically by increasing the analyte concentration above the linear dynamic range measured under optimized analytical conditions. Another point that is not sufficiently clarified is the reactivity of some organo-element species which were considered for a long time to be nonreactive toward CHG, or there could be different analytical organo-metal substrates of the same elements, giving the same volatile reaction products in the GHG procedure. In many cases, a check of the chemical identity can be performed by mass spectrometry [39,40] or by gas chromatography-mass spectrometry (GC-MS) [36,41], at least for most stable and volatile reaction products. The exceptions to this rule, which could be a source of inaccuracy in CHG, summarized in Table 2, are discussed below.

Inorganic arsenic species [As^{III}, As^V] yield AsH_3 with different reaction yields [1], while methylated As^V species, $CH_3AsO(OH)_2$, $(CH_3)_2AsO(OH)$, and $(CH_3)_3AsO$ yield CH_3AsH_2, $(CH_3)_2AsH$, and $(CH_3)_3As$, respectively [42–44]. However, sulfur analogues of methylated As^V species, $CH_3AsS(OH)_2$, and $(CH_3)_2AsS(OH)$ are also active in CHG techniques giving, although with relatively low yields, CH_3AsH_2 and $(CH_3)_2AsH$, respectively [45], but in a broader range of pH with respect to $CH_3AsO(OH)_2$ and $(CH_3)_2AsO(OH)$. Other organoarsenic compounds, such as arsenosugars and those containing the arsonium moiety (e.g., tetramethylarsonium, arsenocholine, arsenobetaine) are reported to be CHG inactive due to the inability of $NaBH_4$ to cleave the As–C bond. Francesconi's group first reported that arsenosugars are not completely inactive in CHG, and they can generate significant amounts of volatile arsenic species upon reaction with THB [46]. This evidence has been recently confirmed by Feldmann's group, who demonstrated that arsenosugars are able to generate volatile arsenic species such as $(CH_3)_2AsH$ with reaction yields around 5–9 % [45]. By increasing the analyte concentration above the trace level, formation of significant amount fractions of other products can be detected in the head space volume of the reaction cell. Inorganic As^{III} yields AsH_3 together with a significant fraction of diarsane, while $(CH_3)_2AsO(OH)$ gives $(CH_3)_3As$ as the main reaction product, and Me_2AsH, Me_3AsO, Me_2AsOH, Me_2AsCl, $Me_2AsAsMe_2$, $Me_2AsAs(O)Me_2$ [19].

Table 2 Reaction products obtained during CHG by THB derivatization[a].

Element	Analytical species	Reaction products		
		Analytical conditions		Nonanalytical conditions
		Low conc.	High conc.	
As	Inorganic As	AsH_3		AsH_3, As_2H_4
	$MeAsO(OH)_2$	$MeAsH_2$		$MeAsH_2$; Me_2AsH; Me_3As; MeHAsAsHMe
	$Me_2AsO(OH)$	Me_2AsH		Me_2AsH; Me_3As; Me_3AsO; Me_2AsOH; Me_2AsCl; $Me_2AsAsMe_2$; $Me_2AsAs(O)Me_2$
	$MeAsS(OH)_2$	$MeAsH_2$ (low yield)		
	$Me_2AsS(OH)$	Me_2AsH (low yield)		
	Arsenosugars	Me_2AsH (low yield)		
Sb	Inorganic Sb	SbH_3		
	Me_3SbX_2 (X = OH, Cl)	Me_3Sb (may rearrange to Me_2SbH, $MeSbH_2$, and SbH_3)		
Bi	Inorganic Bi^{III}	BiH_3	Bi^0	
Ge	Inorganic Ge^{IV}	GeH_4		GeH_4, Ge_2H_6
	$R_nGe^{(4-n)+}$	$R_nGeH_{(4-n)}$		
Sn	Inorganic Sn	SnH_4		SnH_4, Sn_2H_6
	$R_nSn^{(4-n)+}$	$R_nSnH_{(4-n)}$		
Pb	Inorganic Pb	PbH_4		
	$R_nPb^{(4-n)+}$	$R_nPbH_{(4-n)}$		
Se	Inorganic Se^{IV}	H_2Se		Se^0
	Inorganic Se^{VI}	No reaction		
	RSeSeR	RSeH		RSeH
	R_2SeO, R_2SeO_2	R_2Se		
	R_3Se^+	R_2Se		
	Se-methionine	Me_2Se_2		
	Se-ethionine	Et_2Se_2, EtSeH		
Te	Inorganic Te^{IV}	H_2Te	Te^0	
	Inorganic Te^{VI}	No reaction		

[a] See Section 1.3 for discussion.

At trace level, inorganic Sb^{III} and Sb^V species form SbH_3 with different reaction yield [1], and methylated Sb^V species behave similarly to arsenic species [47]. However, the behavior of trimethylated Sb^V species in the CHG technique is prone to molecular rearrangements even at the trace level [48,49]. This might invalidate the relationship among the detected volatile methylstibanes and the parent Sb compounds. The careful removal of trace oxygen from CHG apparatus is reported to remove the problem [50].

For inorganic selenium species, Se^{IV} produces H_2Se whereas Se^{VI} is nonreactive. Organic selenium species have been considered CHG inactive for a long time but recent evidence has demonstrated that selenonium species, R_3Se^+, can be dealkylated by THB under CHG conditions, giving R_2Se as the main product [51,52]. Other organoselenium species can be reduced during CHG; R_2SeO is reduced to

R_2Se and RSeSeR is reduced to RSeH [51]. Selenoethionine produces CH_3CH_2SeH and $CH_3CH_2SeSeCH_2CH_3$, and selenomethionine generates $CH_3SeSeCH_3$ [52].

With regard to reaction products remaining in the liquid phase, it is well documented that many analytes are reduced to the elements and form finely dispersed solid precipitates when the analyte concentration is increased; this phenomenon is readily observed for Se [53], Te [54], and Bi [55,56], sometimes at mass concentrations of a few mg L^{-1} or less. This effect can cause curvature and rollover of analytical calibration graphs, as demonstrated for Te [54] and Bi [56]. The nature of such solid precipitates has been assumed to be the element in the zerovalent oxidation state. In the case of As, it has been reported that it can also form solid hydrides, AsH_x, where $x \le 0.59$ [57]. Diarsane decomposes to solid As_2H [9,58].

1.4 CHG reaction mechanisms

In a classical analytical CHG experiment, the aqueous sample solution is mixed with aqueous THB solution (or another borane complex) in a suitable chemical reactor and under optimized conditions in order to achieve fast and quantitative conversion of analytical species to their volatile species. Upon mixing of sample and reagent solutions, several processes start simultaneously:

(i) decomposition of borane reagent by acid-catalyzed hydrolysis reactions (discussed in Section 2);
(ii) reaction of the analytical substrate(s) with borane(s), to form the volatile species of interest (discussed in Section 3); and
(iii) reactions of borane reagent with other components present in the reaction matrix, to form by-products which can interact with process (i) and/or (ii) (discussed in Section 5).

Some of the factors controlling reactivity in CHG are discussed in Section 4. The effects of the composition of the reaction medium on the reactivity of CHG are discussed in Section 5.

2. MECHANISM OF HYDROLYSIS OF BORANE COMPLEXES

2.1 Hydrolysis of borane complexes in aqueous solution

In pure aqueous solution, the THB and borane complexes decompose to give both dihydrogen and boric acid as the principal final products. This is a hydrolysis reaction formally consisting of two processes: (i) a hydroxyl group replaces the hydride in the coordination sphere of boron, giving boric acid and (ii) a disproportion reaction between hydride and proton yields dihydrogen.

The hydrolysis is acid-catalyzed [59–62] and takes place according to the general reaction schemes

$$[BH_3X]^z + H_3O^+ + 2H_2O = H_3BO_3 + 3H_2 + [HX]^{z+1} \tag{4}$$

or in aqueous solution, where the acid is H_2O itself

$$[BH_3X]^z + 4H_2O = H_3BO_3 + 3H_2 + [HX]^{z+1} + OH^- \tag{4a}$$

where X = H^-, CN^-, OH^-, RS^-, NR_3, etc., and the charge of the complex is z, the same as the ligand, X.

The pH during hydrolysis will be controlled by the equilibrium between the acidic and basic species which are present during the evolution of reactions 4 and 4a. In one of the simplest cases, the hydrolysis of THB in water, reaction 4a becomes

$$[BH_4]^- + 4H_2O = H_3BO_3 + 4H_2 + OH^- \tag{5}$$

and the formation of borate buffer (H_3BO_3 and OH^-) controls the final pH of reaction, which is around 9.2 [63].

Reactions 4 and 4a are not descriptive of the mechanisms which are involved in the hydrolysis of borane complexes in aqueous solution, and these will be discussed in detail in the following sections.

Concerning the kinetics of reaction 4, there is general agreement that, over a wide range of acidity (see Table 3), hydrolysis of borane complexes is an acid-catalyzed, second-order reaction

$$-\frac{\mathrm{d}[\mathrm{BH_3X}^z]}{\mathrm{d}t} = k_{\mathrm{H}^+}[\mathrm{BH_3X}^z][\mathrm{H_3O^+}] \tag{6}$$

where k_{H^+} is the second-order rate constant for H_3O^+-catalyzed hydrolysis of the borane complex, and z is the charge. The values of k_{H^+} for different borane complexes are reported in Table 3, and they can vary to a dramatic extent as a function of the nature of the ligand.

Table 3 Second-order rate constants[a] for acid-catalyzed hydrolysis of some borane complexes and in water at 25 °C

	k_{H^+}/(L mol^{-1} s^{-1})	pH range	I_c/(mol L^{-1})	Reference
Anionic complexes				
$[BH_3OH]^-$	$(8 \pm 3) \times 10^6$	$9.1 < pH < 10.2$	0.5	[70]
$[BH_4]^-$	$(9.9 \pm 0.3) \times 10^5$	Alkaline, pH <12	0	[65]
	1.6×10^6	$3.8 < pH < 12$	1.0	[60
	$(1.00 \pm 0.04) \times 10^6$	$7.4 < pH < 14.7$	0.1	[69]
	$(2.30 \pm 0.04) \times 10^6$	$7.4 < pH < 14.7$	0	[69]
	$(6.0 \pm 0.3) \times 10^5$	$9.1 < pH < 10.2$	0.5	[70]
$[N{\equiv}C{-}S{-}BH_3]^-$	≈ 50[b]	pH 5	–	[165]
$[N{\equiv}C{-}BH_3]^-$	1.7×10^{-2}	$[HCl] \approx 0.1$ mol L^{-1}	–	[61]
Amineboranes				
$BH_3(NH_3)$	6	$4.3 < pH < 6.1$	0.3	[68]
$BH_3(MeNH_2)$	0.45	$0.5 < pH < 5$	0.5	[62]
$BH_3(EtNH_2)$	0.58	$0.5 < pH < 5$	0.5	[62]
BH_3(*i*-PropylNH_2)	0.67	$0.5 < pH < 5$	0.5	[62]
BH_3(*tert*-ButylNH_2)	0.87	$0.5 < pH < 5$	0.5	[62]
$BH_3(Me_2NH)$	9.7×10^{-3}	$0.5 < pH < 5$	0.08	[62]
BH_3(Morpholine)	7.2×10^{-4}	$0.5 < pH < 5$	0.5	[62]
$BH_3(Me_3N)$	1.2×10^{-4}	$[H_2SO_4] = 0.29$ mol L^{-1} at 27.5 °C		[68]

[a] $-\mathrm{d}[BH_3X]/\mathrm{d}t = k_{\mathrm{H}^+}[BH_3X][H_3O^+]$.

[b] Estimated from reported observation of about 50 % hydrolysis in 10 min. (Adapted from *Spectrochim. Acta, Part B*, Vol. 59, A. D'Ulivo, Chemical vapor generation by tetrahydroborate(III) and other borane complexes in aqueous media A critical discussion of fundamental processes and mechanisms involved in reagent decomposition and hydride formation, pp. 793–825, Copyright © 2004, with permission from Elsevier, ref. [37]).

Large deviations of the experimental rates of hydrolysis from those predicted by the effective kinetic law described by eq. 6 are reported for $[BH_4]^-$ under strongly acidic [17,64] and strongly alkaline [64] conditions and for $BH_3(NH_3)$ under strongly acidic conditions [17] (see Sections 2.3.1 and 2.3.2).

2.2 Acid-catalyzed hydrolysis of borane complexes

The aqueous-phase hydrolysis of a borane complex of general formula $[BH_3Y]^z$ (Y is a neutral or anionic ligand, and z is the charge) is catalyzed by acids, and it starts with the protonation of the borane complex (this can performed by H_3O^+ or H_2O, or by generic acid HA) according to the equilibrium reaction:

$$[BH_3Y]^z + HA \leftrightarrows \underset{\mathbf{I}}{[(BH_3Y)H]^{z+1}} + A^- \tag{7}$$

which is essentially an acid–base reaction. The equilibrium constant for reaction 7 has been estimated to be around 10^{-10} for $[BH_3CN]^-$ when HA indicates water, H_2O [66].

The fate of the intermediate **I** depends on the nature of the ligand bound to the borane unit, resulting in different types of intermediates and reaction pathways. A convenient schematization can be made by assuming that the proton can attack the borane complex either at the hydride or at the ligand moiety. $[BH_4]^-$ represents an exception in consideration of the fact that boron is coordinated by four chemically indistinguishable hydridic hydrogen atoms and the proton can attack only at one of the four hydrides.

2.2.1 Proton attack of the hydride

This represents the pathways through which the borane complex decomposes giving molecular hydrogen. It starts with the proton attacking the hydride

$$[BH_3Y]^z + HA \leftrightarrows \underset{\mathbf{Ia}}{[BH_4Y]^{z+1}} + A^- \tag{7a}$$

The structure of intermediate **Ia** is quite peculiar because the hydrogens bound to boron are not equivalent [37,61,65]. The more correct formulation for **Ia** is $[BH_2Y(H_2)]^{z+1}$, where only two hydrides are bound to boron while the other two hydrogens are in the form of molecular hydrogen complexed to the borane BH_2Y. Intermediates similar to **Ia** are involved in the hydrolysis of $[BH_3CN]^-$ [61] and $[BH_4]^-$ [65]. Equilibrium 7a and intermediate **Ia** are the basis of hydrogen–deuterium (H–D) exchange in borane complexes, which has been observed when borane complexes are dissolved in D_2O under appropriate conditions [61,65,67] (see Section 2.7).

Intermediate **Ia** can evolve producing either the starting reagents, the borane complex and HA according to equilibrium 7a, or decomposing to yield dihydrogen

$$[BH_4Y]^{z+1} \rightarrow [BH_2Y]^{z+1} + H_2 \tag{7b}$$

The resulting electron-deficient species $[BH_2Y]^{z+1}$ will be complexed with the solvent

$$[BH_2Y]^{z+1} + H_2O \rightarrow [BH_2(H_2O)Y]^{z+1} \tag{7c}$$

The reiteration of reactions from 7a to 7c on $[BH_2(H_2O)Y]^{z+1}$ will result in complete hydrolysis of the borane complex to give the final products delineated by reactions from 4 to 5.

2.2.2 Proton attack of the ligand

$$[BH_3Y]^z + HA \leftrightarrows \underset{\mathbf{Ib}}{[HA\cdots BH_3Y]^z} \tag{8}$$

Depending on the ligand, the intermediate **Ib**, which has the characteristics of an activated complex, evolution toward either the formation of a fairly stable protonated borane complex

$$[HA\cdots BH_3Y]^z \leftrightarrows [HY{-}BH_3]^{z+1} + A^- \tag{8a}$$

or toward the cleavage of the ligand from the borane may occur

$$[HA\cdots BH_3Y]^z \rightarrow BH_3 + HY^{z+1} + A^- \tag{8b}$$

$$BH_3 + H_2O \rightarrow BH_3(H_2O) \tag{8c}$$

Reaction 8a is typically followed by ligands containing oxygen [64], while reaction 8b is followed by amine boranes [62,68] and can represent an important step in their hydrolysis reaction.

2.3 Hydrolysis of $[BH_4]^-$

Most kinetic studies are dedicated to THB hydrolysis catalyzed by H_3O^+. Davis and Swain [59] and Davis et al. [69] concluded, on the basis of their experiments, that THB undergoes general acid catalysis rather than specific H_3O^+ ion catalysis. They proposed a more accurate rate expression, taking into account the contributions of a general acid HA (HA = H_3O^+, H_2O, H_3BO_3, NH_4^+, etc.), each of them contributing with a specific rate constant k_{HA}:

$$-\frac{d[BH_4^-]}{dt} = [BH_4^-]\cdot\left(\sum_{HA} k_{HA}[HA]\right) = [BH_4^-]\cdot k' \qquad (9)$$

where k' represents the pseudo-first-order rate constant (in s^{-1}) for THB hydrolysis. Deviations from the kinetic law described by eq. 9 take place under both strongly acidic [17,37] and strongly alkaline conditions [65].

Equation 9 reduces to eq. 6 for the case where the only significant contribution to hydrolysis is given by $[H_3O]^+$. Several rate constants specific for a given acid (HA) can be found in the literature. Table 3 reports a summary of k_{H^+} values from the literature for borane complexes. Gardiner and Collat [70] applied general acid catalysis to the hydrolysis of both $[BH_4]^-$ and its hydrolysis product, $[BH_3(OH)]^-$, in the pH range of 9.1 to 10.2 using different buffer solutions. They estimated the specific rate constants k_{H^+}, $k_{NH_4^+}$, k_{H_2O}, and $k_{HCO_3^-}$ for both $[BH_4]^-$ and $[BH_3(OH)]^-$. The values of these specific rate constants, k_{HA}, are reported in Table 4.

Table 4 Specific rate constants, k_{HA}, for the acid-catalyzed hydrolysis of $[BH_4]^-$ and $[BH_3OH]^-$ by different weak acids, HA.

HA	$[BH_4]^-$ k_{HA}/(L mol $^{-1}$ s^{-1})	I_c/(mol L^{-1})	$[BH_3OH]^-$ k_{HA}/(L mol $^{-1}$ s^{-1})	I_c/(mol L^{-1})	Reference
H_2O	6×10^{-8}	0.2	2×10^{-5}	0.2	[70]
	4×10^{-9}	1.0	4×10^{-5}	1.0	[70]
	$(2 \pm 1) \times 10^{-9}$	0.1; 0.5	–	–	[69]
	$(4.0 \pm 0.3) \times 10^{-9}$	0	–	–	[65]
	1.2×10^{-9}	1.0	–	–	[60]
$[NH_4]^+$	$(5 \pm 2) \times 10^{-4}$	0.2	$(8.7 \pm 0.1) \times 10^{-2}$	0.2	[70]
	$(2.4 \pm 0.2) \times 10^{-4}$	1.0	$(4.1 \pm 0.1) \times 10^{-2}$	1.0	[70]
	$(1.5 \pm 0.4) \times 10^{-3}$	0.16	–	–	[72]
$[HCO_3]^-$	$(1.1 \pm 0.2) \times 10^{-3}$	0.2	$(2.4 \pm 0.5) \times 10^{-1}$	0.2	[70]
	$(9 \pm 4) \times 10^{-5}$	0.10	–	–	[59]
$[H_2PO_4]^-$	$(1 \pm 4) \times 10^{-2}$	0.10	–	–	[59]
H_3BO_3	$(8 \pm 4) \times 10^{-4}$	0.2	–		[69]
	$(2.0 \pm 0.3) \times 10^{-3}$	0.16	–	–	[72]

(Adapted from *Spectrochim. Acta, Part B*, Vol. 59, A. D'Ulivo, Chemical vapor generation by tetrahydroborate (III) and other borane complexes in aqueous media A critical discussion of fundamental processes and mechanisms involved in reagent decomposition and hydride formation, pp. 793–825, copyright © 2004, with permission from Elsevier, ref. [64]).

The contribution of weak acids to the entire process of hydrolysis of $[BH_4]^-$ cannot be neglected *a priori*, and must be verified through eq. 9. For example, in the case of hydrolysis of $[BH_4]^-$ in an ammonia buffer, the contribution of single species, such as H_3O^+, NH_4^+, and H_2O, should be taken into consideration: $k' = k_{H^+}[H_3O^+] + k_{NH_4^+}[NH_4^+] + k_{H_2O}[H_2O]$. In the case reported above, the main contributor to hydrolysis of $[BH_4]^-$ is H_3O^+, while neglecting the contribution of ammonium ion introduces underestimation of k', the magnitude of which is dependent on the value of specific rate constants chosen from among those reported in Tables 3 and 4. The degree of uncertainty in estimating k' could, in some cases, be relatively high. This uncertainty is due both to the contributions of the single experimental uncertainties for the specific rate constants and to discrepancies reported by several authors for the same specific rate constant.

Considering the fast hydrolysis of $[BH_4]^-$ in acid aqueous media, most kinetic studies were performed under alkaline conditions [69–72]. The only exceptions are the studies by Jolly and coworkers [60,64]. They performed kinetic studies of THB hydrolysis in aqueous solutions in the pH range 3.8–14 and for different temperatures in the range of (10–50) °C [60]; furthermore, they performed additional kinetic studies at elevated acidities (in the range of 0.1 to 1.1 mol L^{-1} HCl reaction media) but at low temperatures (down to –78 °C) in methanol–water solutions [64].

The study at low temperatures [64] demonstrated that the hydrolysis of THB in strongly acidic conditions takes place stepwise. The $[BH_4]^-$ ion is not converted to boric acid in a single step, but its hydrolysis passes through borane complex intermediates containing from three to one hydrides bound to boron. As a consequence, the four moles of hydrogen are evolved sequentially and with different rates. The kinetic constants for the hydrolysis of the hydridoboron intermediates in water–methanol solution are reported in Table 5. According to the kinetic studies of Wang and Jolly [64], and the mechanistic details discussed in Section 2.2, the mechanism of hydrolysis of $[BH_4]^-$ ion can be described as follows [37]. The first step is the hydronium attack on the hydride, forming the $BH_3(H_2)$ intermediate, which then decomposes to give the first mole of dihydrogen:

$$[BH_4]^- + H_3O^+ \leftrightarrows BH_3(H_2) + H_2O \rightarrow BH_3(H_2O) + H_2 \tag{10}$$

$$[BH_4]^- + H_2O \leftrightarrows BH_3(H_2) + OH^- \rightarrow [BH_3(OH)]^- + H_2 \tag{10a}$$

where the intermediate species containing BH_3 moiety can be interconverted into each other by acid–base equilibria involving protonation or deprotonation of the ligand (see also Section 2.2.2).

Table 5 Rate constants for hydrolysis of intermediate species formed during hydrolysis of $NaBH_4$ in methanol 88 %–water 12 % solution [64].

Species	Rate constant, k_{hydr} /s$^{-1\S}$	θ /°C	Conditions
$[BH_4]^-$	Too fast to be measured	–78	$[H^+] = (0.1–1.1)$ mol L^{-1}
tri-hydridoboron			
$BH_3(H_2O)$	$1.5 \times 10^{-3} + 1.6 \times 10^{-3}\,[H^+]$	–78	$[H^+] = (0.1–1.1)$ mol L^{-1}
$[BH_3OH]^-$	1.8×10^{-4}	+20	NaOH; pH(12.5–13.5)
di-hydridoboron			
$[BH_2(H_2O)_2]^+$	≈0		
	fairly stable intermediate	–36	$[H^+] = (0.1–1.1)$ mol L^{-1}
$BH_2OH(H_2O)$	1.7×10^{-2}	–36	$[H^+] = (0.1–1.1)$ mol L^{-1}
$[BH_2(OH)_2]^-$	2.2×10^{-5}	0	NaOH; pH(12.5–13.5)
mono-hydridoboron			
$BH(OH)_2(H_2O)$	3.3×10^{-4}	–36	$[H^+] = (0.1–1.1)$ mol L^{-1}
	4.4×10^{-3}	0	$[H^+] = (0.1–1.1)$ mol L^{-1}
$[BH(OH)_3]^-$	1.1×10^{-3}	0	NaOH, pH(12.5–13.5)

$$^{\S}k_{\mathrm{hydr}} = -\frac{\mathrm{d}\ln\left[BH_nX_{4-n}\right]}{\mathrm{d}t}$$

(Adapted from *Spectrochim. Acta, Part B*, Vol. 59, A. D'Ulivo, Chemical vapor generation by tetrahydroborate(III) and other borane complexes in aqueous media A critical discussion of fundamental processes and mechanisms involved in reagent decomposition and hydride formation, pp. 793–825, copyright © 2004, with permission from Elsevier, ref. [37]).

The next steps will generate intermediates containing two B–H bonds, $[BH_2(OH)_2]^-$, $BH_2OH(H_2O)$, $[BH_2(H_2O)_2]^+$, and dihydrogen according to a scheme similar to that of reactions 10 and 10a. Also in this case, the intermediate species can be interconverted into each other by acid–base equilibria. Under strongly acidic conditions (greater than 0.5 mol L^{-1} HCl) the borane cation [73,74] is the prevalent species

$$BH_3(H_2O) + H_3O^+ \rightarrow [BH_2(H_2O)_2]^+ + H_2 \tag{11}$$

and, under such conditions, it is pretty much resistant to hydrolysis (see Table 5). At lower acidities, because of the equilibrium

$$H_3O^+ + BH_2OH(H_2O) \rightleftharpoons [BH_2(H_2O)_2]^+ + H_2O \ (K_{eq} = 6.4 \text{ at } -36\ ^\circ C) \tag{12}$$

it is converted into $BH_2OH(H_2O)$, which hydrolyzes quite fast (see Table 5).

The third step is the hydrolysis of $BH_2OH(H_2O)$, or $[BH_2(HO)_2]^-$ to give, depending on pH conditions, the intermediate species $BH(OH)_2(H_2O)$ and $[BH(OH)_3]^-$ (see Table 5) and dihydrogen. Finally, the intermediates species containing one B–H bond hydrolyze to boric acid and dihydrogen.

Recent investigations performed in aqueous solution and under strongly acidic conditions confirm the stepwise hydrolysis of THB and ammonia–borane [17]. The stability of the intermediates toward hydrolysis (k_1, k_2, k_3, and k_4 are the second-order rate constants), which are reported in the following simplified reaction scheme:

$$[BH_4]^- \xrightarrow{k_1} [BH_3X]^z \xrightarrow{k_2} [BH_2X_2]^z \xrightarrow{k_3} [BHX_3]^z \xrightarrow{k_4} H_3BO_3 \tag{13}$$

($X = H_2O$, OH^- and $z = 0, +1, -1$ is the charge)

increase with decreasing number of hydrogens bound to boron, $k_1 > k_2 > k_3 > k_4$. This is in agreement with the findings reported in Table 5, where it is evident that only two species, $[BH_4]^-$ and, to a lesser extent, $BH_3(H_2O)$, have a rate of hydrolysis which is dependent on acidity. According to the evidence discussed above, a simplified reaction scheme, representative of most analytical applications of CHG, for the hydrolysis of THB in strongly acidic to almost neutral solution is

$$[BH_4]^- + H_3O^+ \rightarrow BH_3(H_2O) + H_2 \tag{14}$$

$$BH_3(H_2O) + H_2O \rightarrow BH_2OH(H_2O) + H_2 \tag{15}$$

$$BH_2OH(H_2O) + H_3O^+ \rightleftharpoons [BH_2(H_2O)_2]^+ + H_2O \tag{15a}$$

$$BH_2OH(H_2O) + H_2O \rightarrow BH(OH)_2(H_2O) + H_2 \tag{16}$$

$$BH(OH)_2(H_2O) + H_2O \rightarrow H_3BO_3 + H_2 \tag{17}$$

2.3.1 Deviations from second-order kinetics under strongly acidic conditions

The rates of hydrolysis of THB are several orders of magnitude lower than those predicted by eq. 9 at pH lower than 1, which are the most frequently used conditions in many CHG systems. This large deviation is due to the fact that the rate constant for the first step, k_1 (see reaction 13), is taken as the overall rate constant k_{H^+} of hydrolysis for THB (eq. 6). Under strongly acidic conditions, the stepwise hydrolysis mechanism and the different kinetics laws for $[BH_4]^-$ of the hydridoboron intermediates are the reasons for the large deviation from the rate of hydrolysis expected on the basis of general acid catalysis described by eq. 9.

The confusion that is present in the analytical literature concerning the rate of hydrolysis of $[BH_4]^-$ arises from considering k_1 (see reaction 13) as representative of the overall hydrolysis process for $[BH_4]^-$ to H_3BO_3, whereas in reality it only refers to the rate of loss of the first molecular hydrogen to give $BH_3(H_2O)$ (reaction 14), which is first order in both $[BH_4^-]$ and $[H_3O^+]$. Therefore, $k_1 \times [H_3O^+]$ identifies with the rate of hydrolysis for low $[H_3O^+]$ values, such as those realized at pH > 3.8 [60].

Under strongly acidic conditions, $k_1 \times [H_3O^+]$ becomes much higher than the relatively pH independent k_2, k_3, and k_4 (see reaction 13), and the overall rate of hydrolysis of THB is controlled by decomposition of one of the intermediates. This behavior has important consequences in analytical CHG. Considering that for $[H_3O^+] = 1$ mol L^{-1}, 99 % of the first hydrogen of $[BH_4]^-$ is lost in less than 3 μs (much less than the typical 20 to 30 ms mixing times of reagents in any CHG apparatus [18]), it casts doubt on the probability that $[BH_4]^-$ species can play an active role in most derivatization reactions conducted under strongly acidic conditions. Under these conditions, other intermediates, containing at least a B–H bond, can survive for a long time; they are still able to perform the analytical derivatization reactions after a relatively long time (up to 5 s) after mixing the sample with the $[BH_4]^-$ solution [17].

2.3.2 Deviations from second-order kinetics under strongly alkaline conditions

Deviations from eq. 9 have also been reported under strongly alkaline conditions [65]. This effect has less relevance for analytical CHG than that discussed for strongly acidic conditions, but it has a remarkable relevance for the clarification of the mechanism of hydrolysis of $[BH_4]^-$. The existence of the $BH_3(H_2)$ intermediate, proposed by several workers, was supported by indirect experimental evidence by Kreevoy and Hutchins [65]. They found that kinetic models based on general acid catalysis failed to correlate the measured rate of hydrolysis of $[BH_4]^-$ under strongly basic solutions ($0.1 < [NaOH] < 2.3$ mol L^{-1}). In particular, at pH > 13, the experimental rates of hydrolysis of $[BH_4]^-$ were much slower than those predicted by eq. 9. Among other evidence, the observation of the kinetics of H–D exchange of $[BH_4]^-$ with the solvent (NaOD in D_2O), measured by ^{11}B NMR under appropriate conditions, was employed to support the existence of a reaction intermediate. This reaction intermediate, which can react with the base OH^- to regenerate $[BH_4]^-$, should have the formula BH_5, but with the added proton equivalent to only one of the original four. The proposed structure is similar to the isoelectronic $[CH_5]^+$.

Kreevoy and Hutchins developed a kinetic model based on the following reaction scheme:

$$[BH_4]^- + H^+ \xrightleftharpoons[k_{-H^+}]{k_{H^+}} BH_3(H_2) \tag{18}$$

$$[BH_4]^- + H_2O \xrightleftharpoons[k_{-H_2O}]{k_{H_2O}} BH_3(H_2) + OH^- \tag{19}$$

$$BH_3(H_2) \xrightarrow{k_2} H_2 + BH_3 \tag{20}$$

$$BH_3 + 3H_2O \xrightarrow{\text{very fast}} 3H_2 + H_3BO_3 \tag{21}$$

$$OH^- + H_3BO_3 \rightleftharpoons [B(OH)_4]^- \tag{22}$$

wherein the equilibrium represented by reaction 22 is reached very quickly.

The rate of hydrolysis of THB, can be predicted with good accuracy by using the following equation for k':

$$k' = \frac{\eta k_{H^+} + k'_{H_2O}}{1 + \dfrac{K'_W\, k_{-H_2O}}{\eta k_2}} \tag{23}$$

where $\eta = K'_W/[OH^-]$ and $K'_W = [OH^-]\,[H_3O^+]$. The numerator in eq. 23, where $\eta\, k_{H^+} = k'_{H^+} = k_{H^+}\,[H_3O^+]$ and $k'_{H_2O} = k_{H_2O}\,[H_2O]$, corresponds to k' defined by eq. 9.

The values of specific rate constants for THB hydrolysis, estimated at 25 °C by Kreevoy and Hutchins [65], were $k_{H^+} = (9.9 \pm 0.3) \times 10^5$ L mol^{-1} s^{-1} and $k'_{H_2O} = (2.2 \pm 0.2) \times 10^{-7}$ s^{-1}. The values for k_{H^+} reported by other authors (most of them can be found in reference [70] and in Tables 3 and 4) are in the range $(2.5 \times 10^5 - 2.3 \times 10^6)$ L mol^{-1} s^{-1}. These discrepancies among the values reported for

k_{H^+} by other authors were considered by Kreevoy and Hutchins to be more apparent than real, arising from the use of different ionic strengths and different methods of treating the electrolyte effects. Other authors reported k_{H_2O}, values (listed in Table 4) to which correspond k'_{H_2O} values in the range ($6 \times 10^{-6} - 10^{-7}$) s^{-1}. The value for k'_{H_2O} of $(2.2 \pm 0.2) \times 10^{-7}$ s^{-1} was considered in this case more accurate by the authors [65] because they took into account the nonlinear behavior at elevated pH values with the term $k_{-H_2O}/k_2 = (2.3 \pm 0.3)$ L mol^{-1} (at 25 °C). This term represents the contribution of the two reactions causing the disappearance of $BH_3(H_2)$, the regeneration of $[BH_4]^-$ from $BH_3(H_2)$ (reaction 19), and the irreversible decomposition of the intermediate (reaction 20).

It can be verified [37,65] that eq. 23 gives results comparable to that of eq. 9 at pH < 13. Even only the numerator of eq. 23, which corresponds to eq. 9, gives values in fairly good agreement with the experimental results at pH < 13. However, at pH > 13, only eq. 23 gives an accurate description of the experimental behavior of k'.

Reaction 21 is not a single-step reaction but includes several intermediates, the nature of which depend on solution acidity. In alkaline aqueous media, anionic intermediates of the type $[BH_{4-n}(OH)_n]^-$ are involved, as discussed in Section 2.3. The intermediate, $[BH_3(OH)]^-$, has been identified by ^{11}B NMR [75]. Other studies give strong support to the existence of other intermediate anions, $[BH_2(OH)]^-$ and $[BH(OH)_3]^-$, which are involved in reaction 21 [64,65,76]. Molecular hydrogen (not atomic hydrogen, see Section 2.6 and ref. [38]) is then released stepwise from all the intermediates, the first evolution from $BH_3(H_2)$ being the slowest, and it determines the rate of the whole process.

The studies of Kreevoy and Hutchins [65] stimulated research for many years devoted to the identification of the $BH_3(H_2)$ species. The existence of this remarkable molecule has been demonstrated recently, even if only in gaseous state, by both theoretical [76] and experimental investigations [77]. This molecule can be regarded as a borane complex consisting of molecular hydrogen bound to an almost unperturbed borane molecule [76].

2.4 Hydrolysis of $[BH_3CN]^-$

Little, sometimes controversial, information is available on the kinetics and the mechanism of hydrolysis of $[BH_3CN]^-$ (CBH) which is known to be much more resistant to acid hydrolysis than $[BH_4]^-$ [61,66,78] (see Table 3). The initial step of the hydrolysis of CBH follows the same reaction pattern as that for $[BH_4]^-$, i.e., reversible protonation of $[N{\equiv}C{-}BH_3]^-$ to form the intermediate $[(N{\equiv}C{-}BH_3)H]$, according to reaction 7. Available information about the structure and fate of this intermediate is quite controversial. Kreevoy and Hutchins [61] proposed protonation of boron to give an intermediate, $BH_2CN(H_2)$, the structure of which has been predicted to be similar to that of $BH_3(H_2)$ [79]. In this case, the following reactions have been proposed for the loss of the first hydrogen [61,79]:

$$[N{\equiv}C{-}BH_3]^- + H^+ \leftrightarrows BH_2CN(H_2) \qquad \text{fast} \qquad (23a)$$

$$BH_2CN(H_2) \rightarrow BH_2CN + H_2 \qquad \text{slow} \qquad (23b)$$

In the case of CBH, the rate-limiting step is the loss of molecular hydrogen (reaction 23b), while in the case of THB, the rate-limiting step is the protonation of $[BH_4]^-$ leading to formation of $BH_3(H_2)$ (reactions 10 and 10a). This reaction scheme easily explains the experimental evidence on the H–D exchange, cited above.

The other hypothesis involves protonation of the ligand on the nitrogen atom (reaction 8a) to give the intermediate $HNC{-}BH_3$ [66], which undergoes decomposition by losing HCN. Das et al. [78] reported that, during aqueous hydrolysis at pH 5.3, the evolution of H_2 was observed for about 15 min but HCN was completely lost after dissolution. In this second case, a reaction could be proposed:

$$[NC{-}BH_3]^- + H^+ \rightleftharpoons HNC{-}BH_3 \qquad (24)$$

$$HNC{-}BH_3 \rightarrow BH_3 + HCN \qquad (24a)$$

In this case, Custelcean [79] proposed HNC–BH_3 as a possible intermediate because of its higher stability with respect to $BH_2CN(H_2)$, but concluded that the process of proton exchange should be much less probable since it should involve a highly energetic allene-type intermediate, $H_2B{=}C{=}NH$. The existence of the HNC–BH_3 intermediate seems, therefore, not to be compatible with the experimental evidence on H–D exchange.

2.5 Hydrolysis of amine boranes

The rate law for hydrolysis of amine boranes in aqueous solution can be described by the equation [62]

$$\frac{-\mathrm{d}\left[\mathrm{BH_3X}\right]}{\mathrm{d}t} = \left[\mathrm{BH_3X}\right]\cdot\left(k_{\mathrm{H^+}}\left[\mathrm{H_3O^+}\right] + k_0\right) \qquad (25)$$

where BH_3X is the amine borane, k_{H^+} is the acid-catalyzed rate constant (see Table 3) and k_0 is the acid-independent rate constant. In the case of hydrolysis of amine boranes an acid-independent pathway has been recognized but it can be neglected in aqueous solutions and in the pH range typically employed in CHG considering that k_0 is much smaller than k_{H^+} $[H_3O^+]$ [68].

Several kinetic studies reported on amine boranes demonstrated that these borane complexes are much more resistant to hydrolysis in acidic media than $[BH_4]^-$. In general, the second-order rate constants for acid hydrolysis are several orders of magnitude smaller than that of $[BH_4]^-$ and are dramatically dependent on the number and nature of alkyl groups bound to nitrogen; for example, for $BH_3(NH_3)$, BH_3 (*tert*-ButylNH_2), $BH_3(Me_2NH)$, and $BH_3(NMe_3)$ they are 6.0, 0.87, 9.7×10^{-3} and 1.2×10^{-4} L mol^{-1} s^{-1}, respectively [62,68,80] (see Table 3 for pH conditions and other amine boranes). For alkylamine boranes, $BH_3(NR_3)$ (R = alkyl, H), the most likely mechanism for acid hydrolysis differs from both those proposed for $[BH_4]^-$, and it is the attack of protic species on nitrogen, followed by the displacement of BH_3:

$$\mathrm{BH_3(NR_3) + H_3O^+ \rightleftharpoons [H_2O\cdots H\cdots N(R_3)\cdots BH_3]^+} \qquad (25a)$$

$$\mathrm{[H_2O\cdots H\cdots N(R_3)\cdots BH_3]^+ \rightarrow R_3NH^+ + BH_3(H_2O)} \qquad \text{slow} \qquad (25b)$$

The $BH_3(H_2O)$ is hydrolyzed following the same stepwise reaction schemes proposed for $[BH_4]^-$ [62,68,80], as discussed in Section 2.3. In this reaction scheme, the rate-determining step is represented by the displacement of the amino group.

However, for $BH_3(NH_3)$ ($k_{H^+} = 6$ L mol^{-1} s^{-1} at 25 °C, $4.3 < pH < 6.1$) recent investigations [17] indicated that the hydrolysis rate for this amina borane is much lower in strongly acidic media ($-1 < pH < 2$, in HCl or $HClO_4$ media). As well, different reactivity during CHG was observed with respect to $[BH_4]^-$ under strongly acidic conditions. This suggested that the hydrolysis of ammonia borane (AB) under strongly acidic conditions follows a mechanism similar to that described by reactions 24 and 24a for $[BH_3CN]^-$, in which the proton attack is on the hydride, and it gives an alternative reaction pathway [68]:

$$\mathrm{BH_3(NH_3) + H_3O^+ \rightleftharpoons [H\cdots HBH_2(NH_3)]^+ + H_2O \rightarrow [BH_2(NH_3)(H_2O)]^+ + H_2} \qquad (26)$$

The borane cations follow a stepwise hydrolysis, which is different from that of $BH_3(H_2O)$.

2.6 H–D exchange in borane complexes

H–D exchange in borane complexes (or deuterated borane complexes), which can be observed when they are dissolved in D_2O/D_3O^+ (or in H_2O/H_3O^+), is strictly related to the mechanism of their hydrolysis according to reactions 7 and 7a.

$$\mathrm{[BH_3Y]^z + D_3O^+ \rightleftharpoons [(BH_2(HD)Y]^{z+1} + D_2O} \qquad (27)$$

$$[BH_3Y]^z + D_2O \rightleftharpoons [(BH_2(HD)Y]^{z+1} + DO^- \qquad (27a)$$

The intermediate $[(BH_2(HD)\ Y]^{z+1}$ can evolve in different directions, giving the original borane complex according to equilibrium reactions 27–27a or through H–D exchange

$$[(BH_2(HD)Y]^{z+1} + D_2O \rightleftharpoons [BH_2DY]^z + [HD_2O]^+ \qquad (28)$$

$$[(BH_2(HD)Y]^{z+1} + DO^- \rightleftharpoons [BH_2DY]^z + HDO \qquad (28a)$$

or by eliminating HD

$$[(BH_2(HD)Y]^{z+1} + D_2O \rightarrow BH_2(D_2O)Y + HD \qquad (29)$$

The reiteration of reactions 27–27a–28–28a on $[BH_2DY]^z$ can lead to complete H–D exchange in the borane complex. The same reactions are valid for deuterated borane complexes in H_2O/H_3O^+ solution.

The possibility of obtaining a specific degree of H–D exchange in a borane complex depends on the relative rates of the H–D and hydrogen elimination reactions. For $[BH_4]^-$ (see also Section 2.3.2), the rate of the H–D exchange reaction is much lower than the rate of hydrogen elimination. This is demonstrated by the experimental evidence that complete hydrolysis in strongly acidic media of $[BH_4]^-$ or $[BD_4]^-$ (TDB) in D_2O or H_2O, respectively, forms HD as the main hydrogen isotopologue (≥95 % [81,82] and ≥98 % [83] have been reported) with minimum fractions of H_2 and D_2. In order to observe H–D exchange in $[BH_4]^-$, the rate of hydrolysis was minimized by increasing the alkalinity in the presence of 1–4.4 mol L^{-1} NaOD [65]; significant exchange was observed after 1 month up to 2 years reaction times due to the low rate involved in the protonation step.

The experimental evidences reported above are a convincing proof that the hydrolysis of $[BH_4]^-$ cannot take place according to reaction 1. In such a case, considering that the reaction should be written as

$$[BH_4]^- + D^+ + 3D_2O \rightarrow D_3BO_3 + 4H^{\cdot} + 4D^{\cdot} \qquad (30)$$

The recombination of H and D radicals, to produce four moles of hydrogen gas, should generate H_2, D_2, and HD in the ratio 1:1:2, which is in contrast with the experimental evidence reporting HD ≥ 95 %. A detailed discussion on the generation of dihydrogen in the chemical reaction system is reported in ref. [38].

In other borane complexes, the exchange reaction is much faster than hydrolysis. This is the case of $[BH_3CN]^-$ and $BH_3(Me_3N)$, the rate of hydrolysis of which is about 8 and 10 orders of magnitude lower than $[BH_4]^-$ (Table 3). The rate of hydrolysis of $[BH_3CN]^-$ is about 15 times slower than the H–D exchange, which allows preparation of $[BD_3CN]^-$ in a simple way by dissolving CBH in a D_2O/D^+ solution for a controlled time [61]. Similarly, $BD_3(Me_3N)$ can be prepared by simple dissolution in 5 mol L^{-1} DCl for a controlled time [67]. In the case of complete hydrolysis of $[BH_3CN]^-$ and $BH_3(NH_3)$ in D_2O/D^+, the main hydrogen isotopologue is D_2, confirming that in these cases the hydrogen elimination reaction is much slower than the H–D exchange process [61,67].

2.7 Metal-catalyzed hydrolysis of $[BH_4]^-$

The presence of finely dispersed metals (colloidal platinum, Raney nickel, copper-chromic oxide, etc.) [7] was found to accelerate the hydrolysis of THB. Transition-metal ions, in neutral-alkaline solutions, reacted rapidly with THB giving dark suspensions or precipitates, which have a marked catalytic action in the hydrolysis of THB [7,84]. The dried precipitates can be added to THB solutions giving the same catalytic effect as the metal ions as it can be observed that all the metal ion is transformed in the dark material long before the catalyzed generation of hydrogen is complete [7,84]. The most active catalysts were the platinum group metals whose effects were investigated in more detail by adding metal chloride solution (OsO_4 for osmium) to aqueous THB [84]. There are marked differences in the catalytic activity of different metals (to final concentration of 2×10^{-4} mol L^{-1} in metal ion and 0.5 mol L^{-1} THB) and the time (in min) required for the evolution of 50 % available hydrogen gas was Ru^{III}, Rh^{III} (0.3 min), Pt^{IV} (1 min), Co^{II} (9 min), Ni^{II} (18 min), Os^{VIII} (18.5 min), Ir^{IV} (28 min), Fe^{II} (38 min), and Pd^{II} (180 min) [84]. Catalytic activity for Mn^{II} and Cu^{II} was reported to be comparable to that of Fe^{II} [7].

The nature of reaction products was investigated for Co and Pt, and it was reported to be a cobalt boride, Co_2B [7] and platinum metal, Pt^0 [84].

Davis et al. [83] studied the isotopic composition of hydrogen evolved during the hydrolysis of about 10 mg of $NaBH_4$ in 5 mL 0.1 mol L^{-1} Na_2CO_3 in D_2O, in the presence of preformed Co_2B 0.001–30 mg, or 5 % Pd supported on carbon 0.10–5.0 mg or 5 % Pt supported on carbon 0.37–16.0 mg. In all cases, the fraction of D_2 evolved was considerably higher (16 to 92 %) than those obtained in the absence of metal catalyst where the main product was HD > 98 %. In the presence of 1.6 mg Pt/C the final product was almost pure D_2 (92.2 %). Furthermore, the fraction of $[BH_4]^-$ remaining in solution at different reaction times was pure $[BH_4]^-$ containing only 2 % D, and the evolved H_2 did not undergo H–D exchange in the presence of the catalyst. This experimental evidence, among the other mechanistic information, clearly indicates that trace metal impurities in the reagents must be carefully checked in order to avoid erroneous results in deuterium-labeled experiments.

It is worth emphasizing that metal-catalyzed hydrolysis of THB, which can be performed by different metallic catalysts, represents one of the most important methods in the hydrogen generation technology [85]. The mechanism of metal-catalyzed hydrolysis of THB has been investigated by several authors, namely, Kaufman and Sen [86] and Guella et al. [87], and the topic has been reviewed recently by Liu et al. [85].

3. MECHANISM OF CHG OF VOLATILE HYDRIDES

3.1 Use of deuterium-labeled reagents

This section deals mainly with the mechanisms by which the hydrogen has transferred from the borane or, more generally, from the reaction environment to the analytical substrate $[EY_n]^z$ containing the element (E = As, Sb, Bi, Ge, Sn, etc.; Y = H_2O, OH^-, Cl^-, etc., and z is the charge) to be converted into its volatile hydrides, EH_m. The most informative experiments on the mechanisms are those involving deuterium-labeled reagents, deuterated boranes in H_2O/H_3O^+, or hydrogenated boranes in D_2O/D_3O^+, coupled with GC-MS [36,41,88–90]. In general, those reactions led to formation of a mixture of isotopologues, $EH_{m-x}D_x$, which result from the different processes through which H and D can be incorporated into the final hydrides.

The first is the process leading to formation of the final hydride

$$[EY_n]^z + XBD_3 \xrightarrow{H_2O/H_3O^+} \text{Reaction intermediates} \longrightarrow EH_xD_{m-x} \quad (31)$$

The others are the interactions of the borane complex with the solvent

$$BD_3X \xrightarrow{H_2O/H_3O^+} BH_{3\text{-}x}D_xX \quad (32)$$

which can lead to H–D exchange on the borane before reaction 31, and the interactions of the solvent with the already formed hydride, for example, ED_m

$$ED_m \xrightarrow{H_2O/H_3O^+} EH_xD_{m-x} \quad (33)$$

The reactions contributing to eqs. 32 and 33 interfere with the investigation of the mechanism, which is determined by the complex of reactions contributing to reaction 31.

The interference arising from reaction 32 can be minimized by the use of $[BD_4]^-$ (or $[BH_4]^-$ in deuterated media) which does not undergo H–D exchange over a wide range of pH conditions, from strongly acidic to neutral or slightly alkaline (see Section 2.7).

The interferences arising from H–D exchange on the already formed hydrides can be minimized by conducting the derivatization reaction under appropriate pH conditions. In dedicated studies on H–D exchange using pure hydrogenated and deuterated hydrides [89], it was reported that no significant H–D exchange was detected within the following pH intervals that can be considered free from interference: arsane pH range from 0 to 7, stibane pH range from 0 to 7, bismuthane, germane, and stannane pH range from 0 to 13. Dihydrogen selenide, due to its acidic character, exchanges quickly in solution and precludes the use of deuterium-labeled reagents in mechanistic studies [36]. The same could be said for the even more acidic dihydrogen telluride. Monomethylarsane and dimethylarsane are reported to undergo H–D exchange in acidic solutions [41], which poses severe limitations to the use of deuterium-labeled reagents for the investigation of mechanism of their formation.

3.1.1 Results of experiments with deuterium-labeled reagents

In 1961, Freund [88] prepared stibane by slowly dropping an alkaline solution of 0.5 mol L^{-1} Sb^{III} containing 0.4 mol L^{-1} KBH_4 into a D_2O solution containing 2 mol L^{-1} D_2SO_4. The volatile reaction products were continuously stripped from reaction solution by nitrogen, trapped, and purified. Although the total exchangeable hydrogen was 97 % deuterium, the main products were SbH_3 (>93 %) and SbD_3 (≈7 %) while none of the other possible stibanes (SbH_2D and $SbHD_2$) was found.

Craig et al. [90] reported that CH_3Hg^+ has been derivatized at pH of 4 in aqueous solution to CH_3HgH by reaction with $NaBH_4$ and to CH_3HgD by reaction with $NaBD_4$.

Pergantis et al. [41], in their studies on arsane generation using deuterated reagents and mass spectrometry, found that the reaction of both As^{III} and As^V with $NaBD_4$ in HCl (about 3 mol L^{-1}) and H_2O produces AsD_3 as the main product. When the reaction was performed using $NaBH_4$ and arsenic species in DCl and D_2O the main product was AsH_3. All the evidence presented above clearly indicated that the main reaction product of reaction 31 is ED_m with minor amounts of hydrogenated isotopologues EH_xD_{m-x}. This supports all the mechanisms based on the direct transfer of hydrogen from boron to analyte atom.

D'Ulivo et al. [36] investigated the generation of arsane, stibane, bismuthane, germane, and stannane using $NaBD_4$ in H_2O reaction media and under various reaction conditions. In strongly acidic solutions ($0 < pH < 1$), almost pure AsD_3 (>93 %), SbD_3 (>98 %), and BiD_3 (>98 %) were obtained. For tin and germanium, pure GeD_4 and SnD_4 could never be obtained. The anomalous fraction of hydrogen that was incorporated into the final hydride could not be explained through H–D exchange on $NaBD_4$ nor with H–D exchange with the already formed hydrides in consideration of the experimental evidence that both mechanisms are not significant under the reaction conditions employed. This led to the conclusion that H–D exchange takes place in accord with reaction 31 and, in particular, that the identity of the reaction intermediate is that of a borane complex formed by interaction between the analytical substrate and $[BH_4]^-$ or one of its hydridoboron intermediates. The intermediate complex, possessing different characteristics from tetrahydridoborate(1–), can undergo H–D exchange before formation of the final hydride. A general reaction model was proposed, which is in agreement with the properties and reactivity of boranes for reduction and hydroboration reactions. Several intermediate complexes were proposed, depending on the element and the nature of analytical substrate [36].

The reaction model, based on the formation of reaction intermediates between the analyte substrate and the hydridoboron species, has been the subject of more detailed investigations [19] that were based on the verification of three different hypotheses:

- the hydrides are formed according to "nascent hydrogen" mechanism, taking place through reactions 1 and 3 (hypothesis A);

and the second model based on direct transfer of H–D from boron to the element following the formation of an analyte–borane intermediate complex (ABC):

- 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).

In order to isolate the correct hypothesis, trivalent As or Sb or Bi in H_2O/H_3O^+ were reduced with mixed $NaBD_4/NaBH_4$ reagent [wherein the mole fraction of $NaBD_4$ in this reagent, $x(BD_4^-)$, varied from 0 to 1)] under normal analytical conditions in 1 mol L^{-1} HCl. Under these conditions, formation of different isotopologues, EH_mD_{3-m}, occurs. The relative abundance of each isotopologue, $x(EH_mD_{3-m})$ in the synthesized hydride as a function of $x(BD_4^-)$ can be predicted on the basis of the postulated mechanism (hypotheses A, B, and C), assuming an absence of any isotope effects. The experimental distribution of $x(EH_mD_{3-m})$ vs. $x(BD_4^-)$ for As, Sb, and Bi can be obtained by analyzing the gaseous reaction products generated using varying mole fractions of TDB in the mixed THB and TDB reagent [i.e., (x values) = 0.0, 0.1, 0.25, 0.50, 0.75, 1.0]. The analysis of the gaseous products was performed by GC-MS and results interpreted applying mass spectral deconvolution [91,92]. The predicted "theoretical" and experimental distributions of $x(EH_mD_{3-m})$ vs. $x(BD_4^-)$ are compared in Fig. 1. 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 As, Sb, and Bi are in perfect agreement with those predicted for the mechanism outlined in hypothesis B, direct transfer of H–D from boron to the element with H–D coming from different borane molecules. This result provides definitive proof refuting 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 in the order As, Sb, with Bi being almost identical to the predicted distribution. The asymmetric effect is due to the more pronounced incorporation of H with respect to D, and 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.

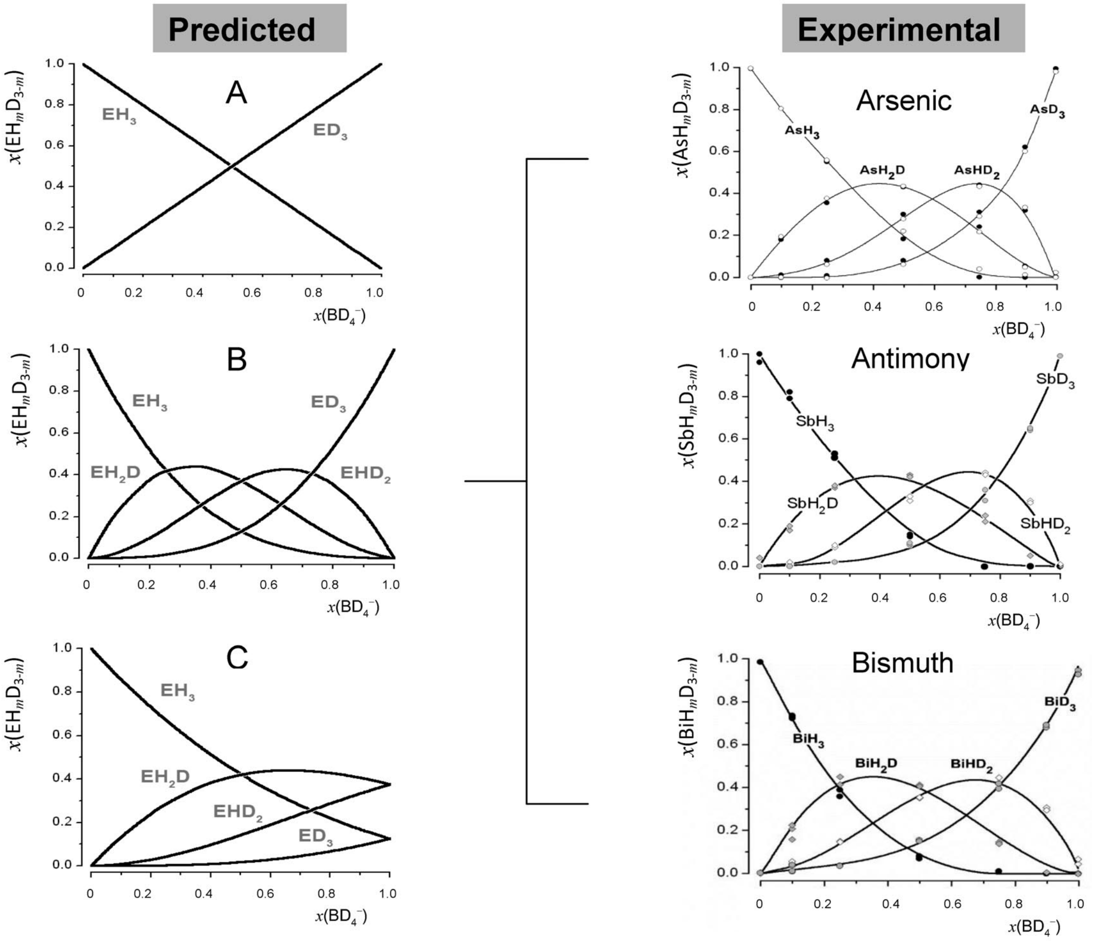


Fig. 1 Reduction of As^{III}, Sb^{III}, and Bi^{III} with a mixture of $NaBH_4$ and $NaBD_4$ in 1 mol L^{-1} reaction media. Predicted and experimental distributions of the relative abundances of the isotopologues of arsane, stibane, and bismuthane as a function of the mole fraction, x, of $NaBD_4$. (Adapted with permission from A. D'Ulivo, Z. Mester, J. Meija, R. E. Sturgeon. *Anal. Chem.* **79**, 3008 (2007). Copyright © 2007 American Chemical Society, ref. [19]).

3.2 Experimental evidence for ABC intermediates

The experimental evidence summarized in Table 2 that the CHG reaction products depend on reaction conditions (analyte-to-borane amount ratio, pH, etc.) suggest that CHG of simple inorganic or organometallic substrates by derivatization with borane complexes ($NaBH_4$ or amine boranes [16]) 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 wherein there is a high degree of complexity of hydroboration/reduction of organic substrates (i.e., concerted reactions through multi-centered intermediates). Under optimized analytical conditions for trace element analysis/speciation (substrate < 10^{-5} mol L^{-1}, borane complex > 0.1 mol L^{-1}, acidic or strongly acidic conditions, $-1 < pH < 1$), it is reasonable to assume that the intermediates are forced to evolve toward the rapid formation of the simple hydride, 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)], of the borane reagents [$NaBH_4$, BH_3(*tert*-ButylNH_2) (TBAB) and $BH_3(Me_2NH)$ (DMAB)] as well as adoption of non-analytical reaction conditions ($[As^{III}]$ = 0.01 mol L^{-1}, borane/substrate ≈1 mol/mol, $3 < pH < 6$) allows such identification using both GC-MS, for volatile products, and electrospray ionization-mass spectrometry (ESI-MS) for the products in the reaction solutions. During the course of the reaction, formation of suspended reddish particulates was evident, which was assumed to be elemental As, and no attempt was made to confirm this hypothesis.

Arsenic compounds in the gas phase [19]. Under the same conditions reported above, many volatile arsenic species have been identified within the headspace of the reaction vial and are reported in Table 2 under non-analytical conditions. Some of the identified As species can be the final reaction products, whereas others can be only intermediate products under non-analytical conditions. Rearrangements of these intermediate products and/or further reactions between different intermediate products very likely take place. Some of them could be responsible for methyl transfer, leading to formation of Me_3As species or to the formation of the As–As bond in diarsane species. In the case of dimethylarsinic acid, it is evident that species such as Me_2AsOH serve as the reaction intermediate in which the arsenic has been converted to the trivalent oxidation state by reduction of the As=O bond; this represents the first step of the analytically expected reaction, leading to the formation of Me_2AsH. With regard to the formation of trimethylated species, the most interesting is Me_3As. At the beginning of the reaction, the most abundant species in the headspace volume among those reported in Table 2 were Me_2AsH and Me_3As. However, within 1 to 2 h, Me_2AsH disappeared almost completely and Me_3As simultaneously became the dominant species. This means that Me_2AsH reacts with some of the other intermediate products which are formed during the reaction. A reaction of the type: $Me_2AsH + Me_2AsOH \rightarrow Me_2AsAsMe_2 + H_2O$ could account for the origin of dimers, not only for dimethylarsinic acid, but also for As^{III} and MMAA. Considering that formation of the hydride is a stepwise process (see Section 3.1.1), it is possible that for As^{III}, reaction intermediates of the type H_2AsOH further react with AsH_3 producing H_2AsAsH_2. In an analogous manner for MMAA, a reaction intermediate of the type MeHAsOH reacts with $MeAsH_2$ to yield the possible isomers MeHAsAsHMe or Me_2AsAsH_2. However, fragmentation patterns indicate that it is MeHAsAsHMe, because of the presence of $MeHAs^+$ and the absence of Me_2As^+ in the mass spectra. However, the formation of dimers could also follow a different pathway 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 also supports reaction pathways in which the borane species attack the As substrates, forming ABC intermediates that further evolve to yield different reaction products, depending on the ambient reaction conditions.

Arsenic compounds in reaction solution [19]. Analysis of the bulk aqueous solution during the reaction was performed by ESI-MS. The same non-analytical 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 dimethylarsinic acid reaction at pH = 6 with both TBAB and DBAB. The species are reported in Fig. 2 and were identified on the basis of molecular mass and mass spectral fragmentation patterns employing up to MS^3. The information generated in the reaction of DMAA with TBAB or DMAB indicates the formation of complex species in the condensed phase, the structures of which are in agreement with the general acid-catalyzed hydrolysis of borane complexes, BH_3X ($X = H^-, NR_3$) with proton-containing species HA (see Section 1) leading to formation of a new borane complex and elimination of H_2

$$HA + BH_3X \rightarrow BH_2AX + H_2 \tag{34}$$

Or, alternatively, the proton can also attack the ligand, as in the case of amine boranes [93]

$$HA + BH_3X \rightarrow BH_3 + HXA \tag{34a}$$

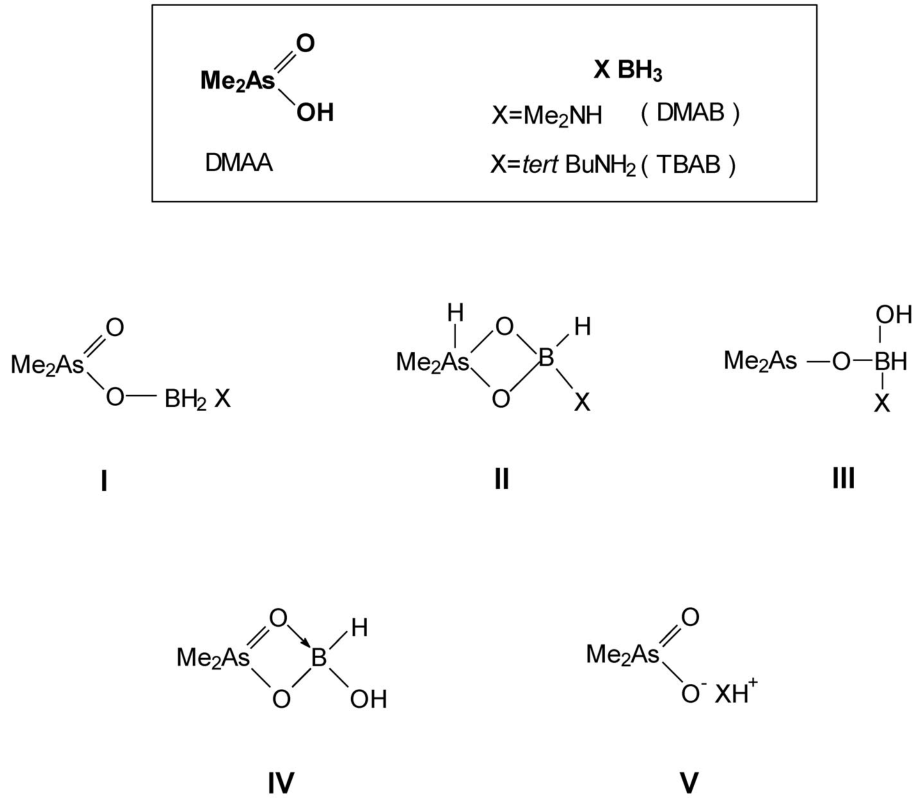


Fig. 2 Reaction products identified in the reaction of 0.01 mol L^{-1} dimethylarsinic acid with amine boranes at pH 6 under stoichiometric reaction conditions. (Reprinted with permission from A. D'Ulivo, Z. Mester, J. Meija, R. E. Sturgeon. *Anal. Chem.* **79**, 3008 (2007). Copyright © 2007 American Chemical Society, ref. [19]).

In the case when HA is either H_2O or H_3O^+, this represents the initial hydrolysis reaction of THB (reaction 34) and amine borane (reactions 34 and 34a) in aqueous solutions.

Compounds **I**, **II**, and **III** shown in Fig. 2 represent some of the possible isomers fitting the experimental evidence for reaction of DMAA with both TBAB. Structure **I** in Fig. 3 corresponds to an ABC formed by reaction 34, where HA is $Me_2As(O)OH$, while BH_3X is TBAB or DMAB. Structure **II** is an ABC arising from rearrangement of structure **I** following hydrogen transfer from B to As 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 MeAsOH with BH_3X (TBAB or DMAB) followed by the replacement of the hydride with a hydroxyl group due to partial hydrolysis with H_2O or vice versa. Both steps take place according to reaction 35 and, in this case, two molecules of H_2 are eliminated. The compound corresponding to structure **IV** 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 most probably be an artifact, generated during the ESI-MS measurement process as fragments of similar structure, $Me_2AsO_2BH_2$, are detected during MS/MS fragmentation of species corresponding to structures **I**, **II**, and **III** (Fig. 2). Structure **V** represents salts resulting from acid–base reaction of DMMA with the amines, which are displaced from B by hydrolysis reaction 34a (*tert*-$BuNH_2$ in the case of TBAB or Me_2NH in the case of DMAB).

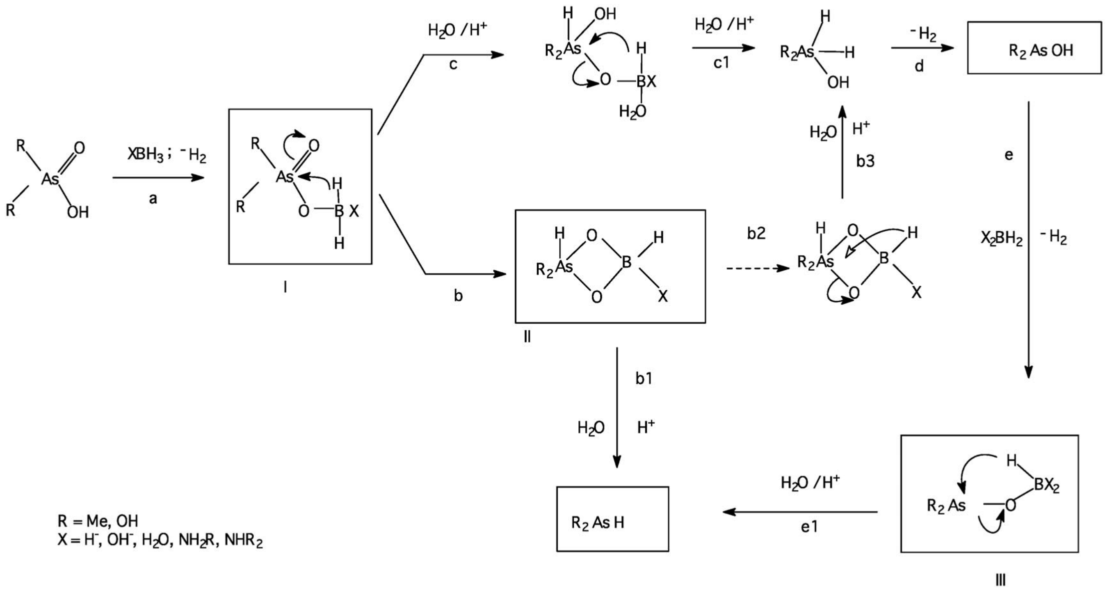


Fig. 3 Reaction mechanism for the formation of arsanes proposed on the base of reaction products identified in the liquid phase and gaseous phase. Reaction products I, II, and III, and R_2AsOH, R_2AsH are identified when R is methyl. (Reprinted with permission from A. D'Ulivo, Z. Mester, J. Meija, R. E. Sturgeon. *Anal. Chem.* **79**, 3008 (2007). Copyright © 2007 American Chemical Societ, ref. [19]).

3.3 Mechanism of CHG through ABC intermediates

Among the different reaction pathways identified in Section 3.2, it is possible to recognize the most likely analytical path based on the species identified in the gas phase, Me_2AsH and Me_2AsOH (Table 1), and in solution, structures **I**, **II**, and **III** (Fig. 2). It is possible to propose a scheme taking into consideration only those reactions which are more likely under analytical conditions for trace element determination (that is, analyte at amount concentration below 10^{-5} mol L^{-1}, high borane-to-analyte ratio), which excludes both reactions among As intermediates and formation of any ABC containing more than one As atom. The analytical reaction scheme is presented in Fig. 3 and it is of general validity for the reduction of both As^{V} species, $R_2As(O)OH$ (R = Me, OH) and As^{III} species R_2AsOH (R = 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**, Fig. 3), which takes place according to hydrolysis of a borane complex with an acid, HA (reaction 34). ABC-I can evolve following either of two different pathways, starting with the intramolecular transfer of hydrogen from B to As according reaction **b** or **c**.

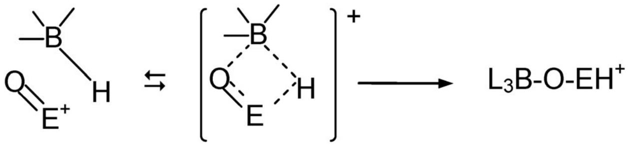
The pathway starting with reaction **b** passes through a rearrangement to yield the ABC-II (structure **II**, Fig. 3). In this case, the tetracoordinate boron is achieved through the formation of a second As-O-B bridge, rather than the formation of a complex with water, $-BOH_2$, as in the case of reaction **c**. The hydrolysis of ABC-II, in the case when both R ligands are Me, gives the final expected products, Me_2AsH (reaction **b1**). In the other cases, reaction **b1** will give MeHAsOH or $HAs(OH)_2$, and the replacement of OH by H would take place according to reactions **e–e1**. Alternatively, ABC-II may follow internal hydrogen transfer to As (reaction **b2**) and hydrolysis (reaction **b3**), to give the unstable R_2AsH_2OH which eliminates H_2 (reaction **d**) giving R_2AsOH. The formation of $ReAsH_2OH$ intermediate can also be achieved following the different pathway described by reactions **c–c1**.

Pathways **a–c–d** and **a–b–d** represent reduction of As^{V} to As^{III}. The As^{III} compound, R_2AsOH, is converted to the hydride via formation of ABC-III (structure **III**, Fig. 3, reaction **e**) followed by the hydrolysis of ABC-III (reaction **e1**). Pathway **e–e1** represents hydride formation starting with As^{III} compounds. In the case when both R ligands are OH (R = OH), this is the path for hydride generation of AsH_3 from inorganic As^{III}; after the first step, the intermediate $(OH)_2AsH$ undergoes a reiteration of reactions **e–e1** to give $(OH)AsH_2$ and the final product AsH_3. The reiteration of reaction pathway **e** is in perfect agreement with the experimental results obtained for $[BH_4]^-$ and $[BD_4]^-$ reduction of As^{III} reported in Section 3.1.1, indicating that the three hydrogens present in AsH_3 come from different borane molecules.

3.4 Some conclusions regarding the mechanism of CHG of hydrides

The experimental evidence on the existence of ABC intermediates is derived from reaction conditions that make reaction rates slow enough to allow the detection of intermediate compounds. Therefore, many other reaction pathways can be followed under analytical conditions where the rate of formation of the final hydride can be comparable to the rate of mixing of the reagents. Reaction 34 represents a case in which the intermediate is formed by hydrolysis of the borane complex with the analytical acid substrate, HA; it could be valid for the case of As^{III}, Ge^{IV}, and Se^{IV}, which form oxyacids of the type As(O)OH, $As(OH)_3$, $GeO(OH)_2$, and $SeO(OH)_2$ [36]. Some other possible ABC intermediates are proposed, and probably they are operative under conditions in which the analytical substrate is strongly activated toward the borane complex.

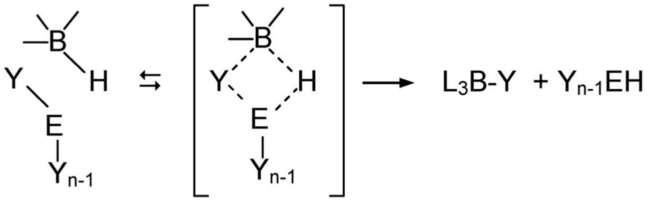
In the case of Sb^{III} and Bi^{III}, the most likely analyte complexes reacting with the reagent in an acidic medium are species of the type EO^+ (see Section 4.3), which should be strongly activated toward hydrogen transfer from boron



(35)

Further reactions of $L_3B–O–EH^+$ (one or more L can be H^-) cannot include intramolecular hydrogen transfer from B to E because, for As, Sb, and Bi, there is the experimental evidence that the hydrogen atoms in the final hydride come from three different borane units [19] (see Section 3.1.1). The intermediate $L_3B–O–EH^+$ and/or its hydrolysis products (i.e., $HO–EH^+$, OEH) will then react with more BHL_3, giving the final hydride ($EO^+ \rightarrow HOEH^+ \rightarrow HOEH_2 \rightarrow EH_3$).

In general, reaction 35 can be operative in the case in which the element is bound or complexed with ligand, EY_n, different from oxygen or hydroxyl



(35a)

Ligands, being then able to form complexes with both analyte and borane, can strongly influence the coordination sphere of both the analytical substrate and the borane forming the ABC intermediate. The role of ligands in CHG is discussed in Section 5.

In general, the structure of ABC intermediates and their fate will be dependent on CHG conditions (pH, matrix composition). The ABC intermediates arising from simple inorganic or organo-metallic analytical substrates evolve to intermediate metal(loid) 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 compounds arising from methyl transfer reactions. Under strictly analytical conditions (high borane-to-substrate ratio and strongly acidic aqueous media), ABC intermediates and intermediate metal(loid) compounds will preferentially evolve toward the fully hydrogenated volatile hydrides due to the fast hydrogen-transfer reactions followed by quick hydrolysis of intermediates.

3.5 Mechanism of CHG of transition and noble metals

The mechanism of formation of volatile species by CHG of transition and noble metals is almost unknown, and the main reason is the instability of these volatile metal derivatives, the nature of which remains to be identified. Many hypotheses have been proposed for the nature of volatile products formed by reaction of THB with different metal ions, such as hydrides [94,95], free atoms [23], nanoparticles [96], and hydridometal complexes [97]. The only paper that gives a contribution in this direction has been recently published, and it concerns the CHG of silver [98]. For this element, experimental proofs confirm that Ag-containing nanoparticles are the species present in the gaseous phase, or at least they are the species at the output of the gas–liquid separator of CHG apparatus. If those nanoparticles consist of metallic Ag or species containing also hydrogen and/or boron it is yet to be proven [98]. Other studies reported that free Pd, Ag, and Cu atoms are formed in solution [99,100] following the reduction of corresponding transition-metal ions with THB. In the case of Pd it has been proven that gas-phase atoms could exist at room temperature "in solution" if the atoms were trapped in very small bubbles [100].

However, volatile metallic species can be observed mainly when the reaction products are quickly separated from reaction solution and delivered to atomizers as fast as possible [24,25,95]. In many CHG set-ups, where the gas–liquid phase separation is relatively slow, the reaction of metal ions with THB results in formation of the reduced element, M^0 (in some cases, borides) in the form of nanoparticles, colloids, or macroprecipitates, depending on reaction conditions, which can cause severe interference effects in CHG analysis [1]. For some elements, mainly Ni and Co, there could be formation of borides or boride-like compounds; in the case of Ni^{II}, Lugowska and Brindle [101] reported the formation of compounds of the type $(NiH_2)\cdot(Ni_2B)\cdot 2H_2O$ and $B(NiH_2)(ONiH)_2$. This indicates the presence of Ni–H, Ni–B, and B–O–Ni–H bonds that can be formed by reaction paths not dissimilar from those discussed for the hydride-forming elements (Sections 3.2, 3.3, and 3.4), in which the hydrogen is transferred from boron to the metal. The evidence discussed above, brings to the conclusion that the reduction of metal ions to the element passes through the formation of M–H bonds

$$M^{n+} \xrightarrow{L_nBH_{4-n}} MH_n \xrightarrow{-\,n/_2\,H_2} M^0 \tag{36}$$

For Hg^{2+}, the well-known reaction giving Hg^0 can be written as

$$Hg^{2+} \xrightarrow{L_nBH_{4-n}} HgH_2 \xrightarrow{-H_2} Hg^0 \tag{37}$$

Similar reactions can be written for Cd^{2+} and Zn^{2+}.

Reactions 36 and 37 are supported by the evidence that gaseous compounds of HgH_2, HgD_2, CdH_2, CD_2, ZnH_2, and ZnD_2 have recently been synthesized and characterized in the gas phase by Shayesteh et al. [102–104]. The same authors [102] concluded that the relative stability of gaseous HgH_2, CdH_2, and ZnH_2 molecules supports the hypothesis that these species are formed during the reduction of aqueous Hg, Cd, and Zn ions in the "hydride generation" technique. However, simple binary metal hydrides are solid. For example, CuH is a solid with wurtzite structure, and it could be prepared in aqueous solution by reduction of copper sulfate with THB or H_3PO_2 [105]. ZnH_2 and CdH_2, prepared in diethyl ether solution, are solid and ZnH_2 decomposes slowly in water [106]. The possible existence of more transition-metal hydrides has been demonstrated, for example for Cu, Ag, Au [107], Rh [108], and Cr [109], by trapping the synthesized species (free atoms + H_2 or D_2) in solid argon or neon matrices and recording IR spectra at low temperatures. In this case, several hydrides corresponding to many different structures have been identified, such as MH and $MH(H_2)$ (M = Cu, Ag, Au, Rh), MH_2 (M = Cu, Au, Cr, Rh) and $MH_3(H_2)$ (Au, Rh). It is worth noting that the trihydride complex with dihydrogen, $MH_3(H_2)$, is similar to the $BH_3(H_2)$ intermediate arising from protonation of $[BH_4]^-$ (see Section 2.3.2).

In the absence of direct evidence of the nature of volatile metal species, a reaction scheme for the CHG of volatile transition-metal species can still be drawn, similar to those proposed by Feng et al. [97] (see Fig. 4). In the scheme reported in Fig. 4, it has been considered that the possibility that nanoparticles could be formed also by the aggregation of simple, solid binary metallic hydrides. The reaction scheme of Fig. 4 assumes that hydrogen atoms are transferred stepwise to the metal, by analogy to the route evidenced for volatile hydrides (Section 3.1.1), through ABC intermediates (not reported in Fig. 4).

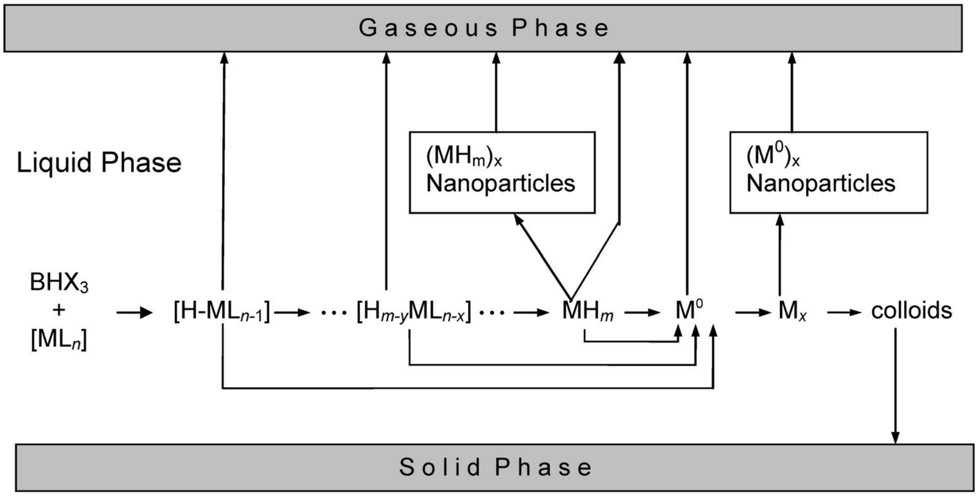


Fig. 4 General reaction pathway proposed for the formation of volatile species of metal and semimetal following aqueous reaction of THB with metallic and semimetallic aqueous species.

The structure of such ABC complexes for transition metals can differ from that of hydride-forming elements. Berschied and Purcell [66] suggested that the reaction between $[BH_3CN]^-$ and Hg^{2+}, Ag^+, and Cu^{2+} to give the reduced metal, M^0, starts with the coordination of the metal to form MBH_3CN, which evolves to yield M^0. Synthesis of hydridometal complexes can be achieved by hydrolysis of metal tetrahydridoborate(1–) complexes, $M(BH_4)_n$; as well, they can be obtained by reaction of metal complexes, ML_n, with THB [159]. The stability of the hydridometal complexes is strongly related to the nature of the ligands complexing the metal, and few hydrido metal complexes are known in which the ancillary ligands are nitrogen, oxygen, sulfur, or halogen donors, as, for example, $[RhH(NH_3)_5]^{2+}$ and $[CrH(H_2O)_5]^{2+}$ [110]. An example of hydridometal complexes, which have been observed in aqueous solution, is reported in ref. [38].

In CHG, the ABC intermediates are formed by interaction between the complex containing the metal, ML_n, (L = OH^-, H_2O, Cl^-, etc.) and one of the BHX_3 intermediates (X can be one among H^-, OH^-, and H_2O) formed during hydrolysis of THB. The charges of both analyte and borane complex have been omitted for the sake of simplicity (Fig. 4). Stepwise hydrogen transfer generates hydridometal complexes, $H_{m-x}ML_{n-y}$ (in general, $m \neq n$, and $x \leq m$ and $y \leq n$) in which the hydride is added to the metal complex or replaces one of the ligands. At the end of the process, the metal hydride, MH_m, will be obtained. Depending on the stability of any intermediate hydridometal complexes and the final metal hydride, and on their volatility, they might have the chance to be partially transferred into the gas phase. The other possibility is that the reaction can stop at any step because of instability of one of the hydridometal complexes or the final hydride. The decomposition product is assumed to be the metal atom in consideration of the experimental evidence that free atoms are formed in aqueous solution after the reaction of tetrahydridoborate with aqueous ions of Ag, Pd, and Cu [99]. The free atoms, following coalescence processes, will form metallic aggregates whose size increases with time: nanoparticles, M_x, then colloids, and finally, macroprecipitates.

The scheme reported in Fig. 4 is of general validity for analytical reaction conditions, and it can also be applied to classic hydride-forming elements [38]. In such a case, all the intermediate hydridometal complexes and the final hydride are stable and the reaction ends with the formation of the volatile, stable hydride (e.g., for As^{III} reaction: $As(OH)_3 \rightarrow AsH(OH)_2 \rightarrow AsH_2OH \rightarrow AsH_3$).

3.6 Some comparison with organic substrates

Some of the mechanisms and reaction pathways presented in the previous section for CHG of hydrides using borane reagents found some significant analogies and similarities with those concerning the reaction of borane complexes with organic substrates.

Concerning the possible mechanisms playing a role in the reaction of amine boranes with some organic substrates (ketones, alkenes) Brown[2] and Murray [111] considered the following reaction pathways:

A) *Direct attack.* The BH_3 complex reacts directly with the reactive group

$RCH{=}X + BH_3(R_3N) \rightarrow RCH_2{-}X{-}BH_2(R_3N)_3 \quad X = CH_2, O$

B) *Prior dissociation.* The borane complex undergoes an initial dissociation to the free BH_3 followed by reaction of the borane with the reactive group:

$BH_3(R_3N) \rightleftharpoons BH_3 + R_3N$

$RCH{=}X + BH_3 \rightarrow RCH_2{-}X{-}BH_2 \quad X = CH_2, O$

This reaction pathways is not operative in protic or aqueous solvent where the mechanism of hydrolysis of amine boranes follows different routes (see Section 2.5).

C) *Prior dissociation in the presence of acidic solvents or media.* Dissociation of the borane complex would be facilitated by reaction of liberated amine with acids

$BH_3(R_3N) \rightleftharpoons BH_3 + R_3N$

$R_3N + H^+ \rightleftharpoons [R_3NH]^+$

The BH_3 reacts with the substrate as in the pathway B.

D) *Activation of reducible group by protonation.* The carbonyl group can be activated by coordination with protonic acids or Lewis acids

---

[2] Herbert Charles Brown and Georg Wittig received the Nobel Prize in Chemistry on December 1979 "for their development of the use of boron- and phosphorus-containing compounds, respectively, into important reagents in organic synthesis".

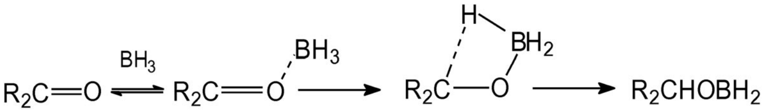
$R_2C{=}O + H^+ \rightleftharpoons R_2C{=}OH^+ \leftrightarrow R_2C^+{-}OH$

making it more active toward attack by hydride reagents.

E) *Activation of the borane complex by protonation or association with Lewis acids*. The attack of the proton on amine boranes (already discussed in Sections 2.2 and 2.5)

$BH_3(R_3N) + H^+ \rightleftharpoons [(BH_3(R_3N)H]^+$

In this case, a greater reactivity of the borane moiety is postulated.



The mechanism of reduction of ketones to alcohols was investigated by Fehlner [112] who proposed the formation of substrate-borane complex, as the reaction intermediates.

Also in this case, as for CHG of hydrides, the intermediate step is the formation of a complex between the borane and the substrate, followed by hydrogen transfer from boron to the activated atom of the substrate through a four-center transition state. Also the hydroboration of alkenes takes place following a similar route passing through a four-center transition state [113,114]. Similar reaction pathways are proposed in previous sections for the reduction of inorganic species BiO^+ and the reduction of As=O moiety in inorganic and methylated species of As^V. More examples can be found in Section 5.2 concerning the role and the mechanism of action of additives.

4. FACTORS CONTROLLING REACTIVITY IN CHG

In general, reactivity in CHG is controlled by all parameters that can exert an effect on the activation of the analytical substrate for the attack of the borane complex. In this section, some of these parameters will be discussed, while the effect of additives and foreign elements will be discussed in Section 5.

4.1 Accessibility of the analyte atom to hydride

The interesting discussion reported by Jolly (see [9] and refs. therein) in his pioneering work on the synthesis of volatile hydrides of As, Sb, Sn, and Ge by means of aqueous $[BH_4]^-$ stressed the concept of accessibility of the hydride-forming element to the hydridic hydrogen of $[BH_4]^-$. For example, the fact that Ge^{IV}, not Si^{IV}, and As^{III}, not P^{III}, are reduced by $[BH_4]^-$ could be explained both by the greater strength of Si–O and P–O bonds, and by the greater size of the Ge and As central atoms, which are then more accessible to hydride. The number of oxygens bound to the analyte could also have a strong influence on the accessibility of the central atom to hydride. Sulfite and sulfurous acid are readily reduced to H_2S by THB while the sulfate ion is inert to THB. The same consideration applies to the homologous species, Se^{IV} and Se^{VI}, and also to Te^{IV} and Te^{VI}. In the case of Te^{VI}, the corresponding telluric acid is $Te(OH)_6$, and the central atom appears even less accessible than in sulfuric and selenic acids. Nitrous acid, HNO_2, is readily reduced by aqueous THB to ammonium ion, while the three oxygens of nitrate appear to be sufficient to prevent the hydride attack on nitrogen, considering that nitrate is inert to THB in aqueous solution. The different accessibility of the central atom could also be one of the factors determining the higher reactivity of As^{III} and Sb^{III} species with regard to their respective pentavalent species.

4.2 Dependence of reactivity on the nature of the borane complex

As demonstrated by the numerous studies and investigation of Herbert C. Brown (see footnote in Section 3.6), a remarkable difference exists between the reactivity of $[BH_4]^-$ anion and the neutral borane complexes $[(H_2O)$, amine boranes, etc.] or diborane. The first is a nucleophile that seeks out an electron-poor center for reaction, whereas the second are electrophilic species that seek out an electron-rich center for reaction [115].

The nature and the number of ligands present in the coordination sphere of boron strongly affect the general reactivity of borane complexes because they strongly influence the hydridic character of the hydrogen atoms bound to boron. In Section 2, it has been reported that the $[BH_4]^-$ and the borane complexes or hydridoborate species arising from its hydrolysis present large differences in their relative rates of hydrolysis (Tables 3 and 5). Limiting the attention to $[BH_3X]^z$ complexes, it is clear that replacement of one of the four hydrogens of $[BH_4]^-$ by a cyanide or amine group reduces the hydridic character of the remaining hydrogens of $[BH_3CN]^-$ and $BH_3(R_3N)$ with respect to $[BH_4]^-$. It is evident from this data reported in Table 3 that it is possible to modulate the rate constants for hydrolysis of the borane complexes over a range of about 12 orders of magnitude by simply changing the complexing group. Therefore, knowledge of the reaction rates of borane complexes with H_3O^+ (rate constant, k_{H^+}, see Table 3) provides a first, although rough, indication of their reactivity because they reflect the hydridic character of hydrogen bound to boron.

The highest rate constant among those reported in Table 3 is connected with the hydroxytrihydridoborate(1–) anion, $[BH_3OH]^-$, which hydrolyzes about one order of magnitude faster than $[BH_4]^-$. Therefore, $[BH_3OH]^-$ should be a powerful derivatizing agent compared to $[BH_4]^-$. Jolly and co-workers [116] synthesized aqueous $[BH_3OH]^-$ by acid decomposition of $[BH_4]^-$ in a flowing reaction system (θ from 0 to 6 °C). The decomposition reaction, which produces $BH_3(H_2O)$ as the first intermediate (reaction 14), was stopped with on line addition of NaOH after a reaction time of 16 ms. In this manner, the intermediate $BH_3(H_2O)$ was converted to its conjugate base, $[BH_3OH]^-$ (94 % yield). The reactivity of $[BH_3OH]^-$, in terms of reducing power toward organic substrates (esters, ketones, nitrobenzene, benzonitrile) is intermediate between that of the rather powerful $LiAlH_4$ and the rather mild and selective $NaBH_4$ [117], which is in agreement with the prediction made using k_{H^+} as a reactivity parameter.

The correlation between rate constants for hydrolysis and reaction rates of borane complexes has recently been confirmed for CHG of mercury and hydride-forming elements as well, using $NaBH_4$, $NaBH_3CN$, and amine borane reagents [16]. The results relative to Hg and Sb are reported in Fig. 5. There is a good linear correlation between c_R (the concentration of the reagent giving 50 % of maximum yield) and the rate constant, k_{H^+}, for acid hydrolysis of amine boranes and $NaBH_3CN$. The exception is represented by $NaBH_4$, which appears not to belong to the family of the borane complexes investigated. This discrepancy has been attributed to the fact that both the decomposition rate of $NaBH_4$ and its reaction rate with the element are much faster than the rate of mixing of the solutions in the T-junction (Figs. 6 and 7), which has been subsequently measured to be around 20 ms [18]. In this case, the reactions are not controlled by their respective kinetic constants but rather by the mixing rate of the solutions. By graphic extrapolation of the data shown in Fig. 5 it is easy to verify that $NaBH_4$ apparently behaves as a borane complex with $k_{H^+} \approx 16$ L mol^{-1} s^{-1} in the case of Sb and $k_{H^+} \approx 21$ L mol^{-1} s^{-1} in the case of Hg. Therefore, the hypothesis that the kinetics of hydride formation may be controlled by the rate of mixing of the solutions, and not by the reaction rate of the analytes with $NaBH_4$, represents one of the possible explanations for the anomalous behavior of $NaBH_4$, which is consistent with experimental evidence.

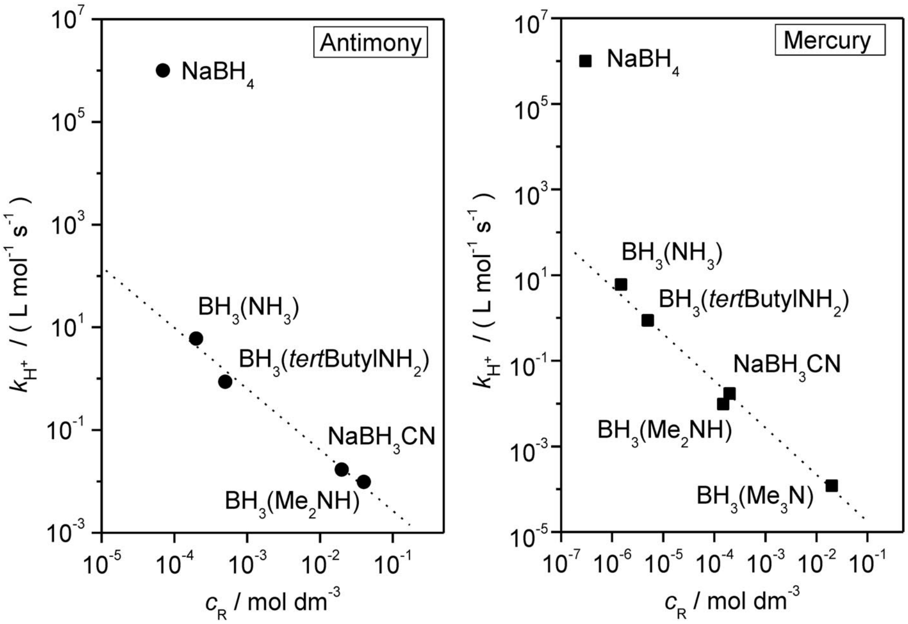


Fig. 5 Correlation between the second-order rate constant of hydrolysis of borane complexes (k_{H^+}) and the concentration of of borane complex giving 50 % reaction yield (c_R), in the GHG of stibane and Hg^0. Conditions: 8×10^{-7} mol L^{-1} Sb^{III}, 5×10^{-7} mol L^{-1} Hg^{II}, in 1 mol L^{-1} HCl reaction media. (Adapted with permission from A. D'Ulivo, V. Loreti, M. Onor, E. Pitzalis, R. Zamboni. *Anal. Chem.* **75**, 2591 (2003). Copyright © 2003 American Chemical Society, ref. [16]).

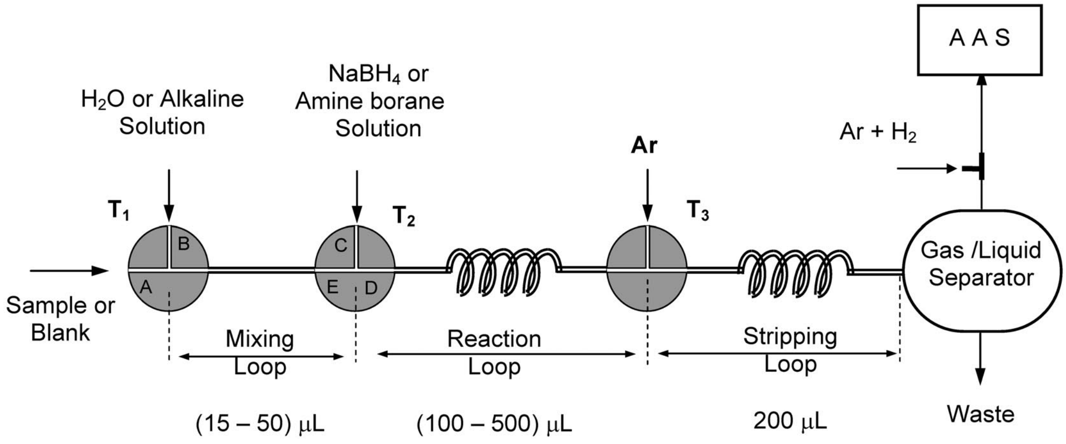


Fig. 6 Schematic representation of flow system employed to investigate the role played by acidity and matrix composition in determining the efficiency of generation of stannane, stibane, and bismuthane, using THB and other borane complexes. (Reprinted from A. D'Ulivo, C. Baiocchi, E. Pitzalis, M. Onor, R. Zamboni. *Spectrochim. Acta, Part B* **59**, 471 (2004). Copyright © 2004, with permission from Elsevier. ref. [18]).

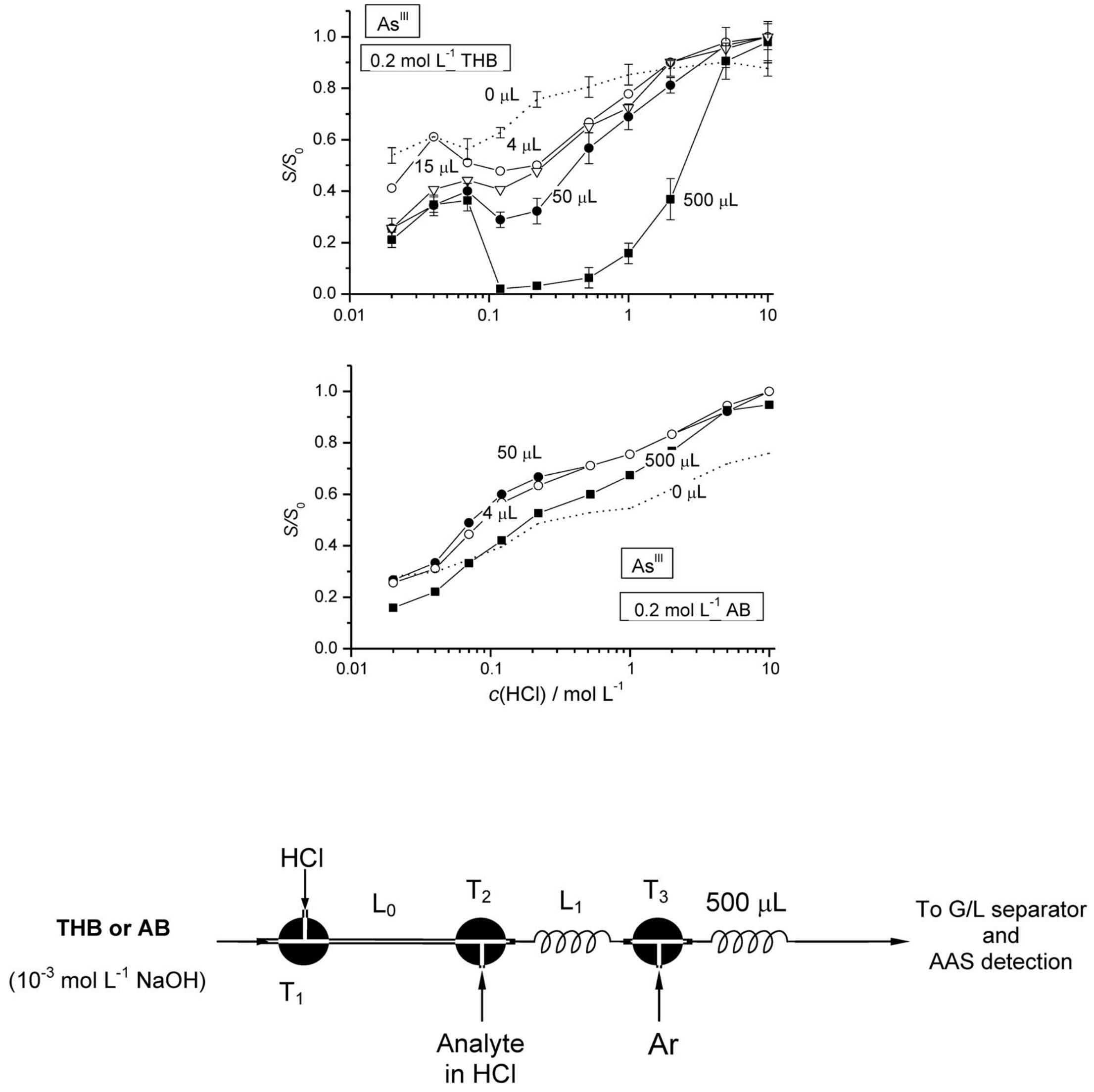


Fig. 7 GHG of AsH_3 from As^{III}. Effect of delayed addition of the analyte solution (in T_2) to the solution of THB or amine borane (AB), after that hydrolysis of THB or AB has started in T_1. The effect is reported as a function of L_0 (0–500) μL and acidity of reaction medium (HCl). S is the absorbance signal and S_0 is the absorbance signal measured under optimized analytical reaction conditions. (Adapted with permission from A. D'Ulivo, M. Onor, E. Pitzalis. *Anal. Chem.* **76**, 6342 (2004). Copyright © 2004 American Chemical Society, ref. [17]).

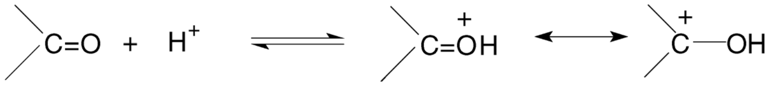
The second explanation of the anomalous behavior of $NaBH_4$ reported in Fig. 5 could also be explained by taking into account evidence on the mechanism of hydrolysis of $NaBH_4$ in strongly acidic solution (Section 2). In this case, at $[H_3O^+] = 1$ mol L^{-1}, the $[BH_4]^-$ species should be quickly and completely lost but its intermediates are much more stable toward acid hydrolysis and could have greater opportunity to react with the analyte. Therefore, the anomalous position of $NaBH_4$ in the plots of Fig. 5 could be due to the fact that k_{H^+} for $[BH_4]^-$ ($\approx 10^6$ L mol^{-1} s^{-1}) has been reported instead of the rate constant for the intermediate {e.g., $BH_3(H_2O)$, $BH_2OH(H_2O)$, $[BH_2(H_2O)_2]^+$, $BH(OH)_2(H_2O)$, etc.}, which could act as the effective derivatizing agent in the CHG process.

4.3 The role of pH

In a CHG reaction system, the role played by pH can be identified mainly in the control that it exerts (i) on the activation of the analyte substrate and (ii) on the formation of intermediate borane complexes which are active toward those analyte substrates that are formed under the same pH conditions. Under optimal conditions, the analyte substrate and borane complex will quickly form an ABC intermediate which rapidly evolves toward the final product according to the mechanisms discussed in Section 3. The optimal pH giving the best "tuning" between the analyte substrate and the borane complex must be determined experimentally.

4.3.1 Activation of the analyte substrate

The pH can act on the analyte substrate by modifying its structure, which could exert control on both the accessibility of the analyte atom and on the activation of the central atom toward hydride attack. Protonation of organic or inorganic substrates dramatically enhances the rate of reduction. A representative example is the reduction of ketones by very weak reducing agents, such as $BH_3(Me_3N)$ and BH_3(morpholine). In this case, the protonation of the carbonyl group



(38)

results in an increased rate of reduction, which has been estimated to be ≈10^{11} times faster than for the non-protonated carbonyl group [118]. The activation of the reducible group by protonation was one of the possible reaction pathways considered by Brown and Murray [111] (Section 3.6).

An interesting example concerning inorganic substrates is the study by Bell and Kelly [119] on acid-catalyzed reduction of nitrite to N_2O by a weak reducing agent, $BH_3(Me_3N)$ ($k_{H^+} = 1.2 \times 10^{-4}$ L mol^{-1} s^{-1}). They found that the rate of formation of N_2O increased ≈10^9 times by decreasing the pH from 5.85 to 0.3. They also concluded that the rate-limiting step is hydride attack to protonated nitrous acid, H_2ONO^+ or to free NO^+:

$$\mathrm{HONO + H^+ \rightleftharpoons [H_2ONO]^+ \rightleftharpoons [NO]^+ + H_2O} \qquad (39)$$

giving the nitrosyl hydride HNO which rapidly evolves to N_2O (2 HNO → $N_2O + H_2O$, fast step). Considering that HNO_2 is a weak inorganic acid ($K_a = 5 \times 10^{-4}$), it is likely that a similar mechanism also takes place for the weak inorganic oxoacids of those metalloids which are the precursors of volatile hydrides with the CHG technique. For example, for Sb^{III} and Bi^{III}, the species $[BiO]^+$ and $[SbO]^+$ should be, by analogy with $[NO]^+$, suitable precursors for hydride attack. In the case of Sb^{III}, by increasing the pH, the substrate would evolve in the sequence $Sb^{3+} \rightarrow [SbO]^+ \rightarrow [Sb(OH)_2]^+ \rightarrow Sb(O)OH \rightarrow [SbO_2]^-$. Whereas Sb(O)OH is insoluble, the antimonite, $[SbO_2]^-$, which is formed in alkaline solution, is not reactive toward aqueous $NaBH_4$ [9]. The work of Bell and Kelly [119] indicates that one of the roles of pH in CHG could also be the formation of suitable precursors of the analyte as opposed to the decomposition of the borane complex.

4.3.2 Formation of suitable hydridoboron species

The effect of pH on the hydrolysis of $NaBH_4$ and other borane complexes, and its role in determining the structure of hydridoboron intermediates has already been discussed in Section 2. In pure aqueous solution, depending on the pH conditions, one or more of these species would be the effective derivatization agent. Under alkaline conditions, it has been found that the $[BH_4]^-$ and $BH_3(R_3N)$ species are the effective derivatization agents for the formation of stannane, stibane, and bismuthane [18] when $NaBH_4$ and amine boranes have been employed, respectively.

In acidic and strongly acidic media, the lifetime of some amine boranes is high enough (see Table 3) to ensure that a significant fraction of the initial reagent is not decomposed at the completion of the mixing process. For example, in accord with second-order kinetics ($k_{H^+} = 6$ L mol^{-1} s^{-1}), 11 and

70 % decomposition of $BH_3(NH_3)$ at $[H_3O^+] = 1$ mol L^{-1}, occurs after 20 and 200 ms, respectively. A significant fraction of undecomposed amineboranes can also be found after 0.6–3 s reaction time, which is typically employed in CHG continuous flow reaction systems. Recent studies on $BH_3(NH_3)$ [17] show that it decomposes more slowly in strongly acidic media (HCl or $HClO_4$ with concentrations larger than 0.2 mol L^{-1}) than the above prediction due to the formation of intermediates different from BH_3, for example, $H_3N–BH_2X$ ($X = H_2O$, OH^-, Cl^-). These intermediates, in addition to $BH_3(NH_3)$, and/or the mono-hydridoboron intermediate arising from its decomposition, are the effective derivatizing species in CHG using the ammonia–borane complex. However, the first hydrogen of $BH_3(NH_3)$ is lost rapidly under strongly acidic conditions, which suggests its marginal role in derivatization reactions at elevated acidity. Similar considerations raise the conclusion that, with more reasons, the $[BH_4]^-$ species could not be able to act as the derivatizing species in acidic conditions, which are typical of most analytical determinations ($-1 < pH < 1$), since it should be hydrolyzed, at least to $BH_3(H_2O)$, at the end of the mixing process.

The uncertainty over the possible role of $[BH_4]^-$ under strongly acidic conditions is mainly due to the lack of kinetic data for the formation of the volatile hydrides, as discussed in Sections 3.1 and 4.2. A plausible explanation could be that in strongly acidic media the rate of formation of hydrides by reaction with THB is controlled by the action of the hydridoboron species, which are more resistant to acid hydrolysis than $[BH_4]^-$. These species would be less reactive than $[BH_4]^-$ in forming the hydrides, considering the correlation between the rate constants for hydrolysis and hydride formation. Under acidic or strongly acidic conditions, the lower reactivity of the derivatizing species can probably be counterbalanced by the formation of analyte substrates which are more active toward hydride attack, as discussed in Section 5.2.1.

4.3.3 Protonation or deprotonation of the final hydrides

After the generation of the hydrides within the reaction solution, they must preserve a neutral molecular structure, EH_m, in order to undergo liquid–gas phase separation. In the case that the hydrides present an acid or a basic behavior, they could be either deprotonated or protonated to form $[EH_{m-1}]^-$ or $[EH_{m+1}]^+$, respectively, depending on pH conditions.

Volatile hydrides such as H_2Se and H_2Te possess a pronounced acid behavior ($H_2E + H_2O = HE^- + H_3O^+$; $pK = 3.8$ when E is Se and $pK = 2.3$ when E is Te) [120], which implies that a large fraction of these hydrides can be present in a nonvolatile form, $[HE]^-$, even under mild acidic conditions [121]. This is one of the reasons why the CHG involving H_2Se and H_2Te is typically performed under strongly acidic condition ($[H_3O]^+ > 1$ mol L^{-1}) [1].

Arsane and stibane undergo deprotonation in alkaline media (pH > 7) as has been demonstrated by H–D exchange experiments, but the equilibrium concentration of deprotonated species $[EH_2]^-$ (when E is As or Sb) is negligible [89]. Arsane, in addition, can be protonated to give AsH_4^+ under extreme acidic conditions (when $[H_3O^+]$ is between 3 and 6 mol L^{-1}) [89]. Also in this case, the equilibrium concentration of the arsonium ion is negligible. The formation of arsonium controls only the H–D exchange, it does not affect the liquid–gas phase distribution of AsH_3. On the contrary, the protonation of methylated arsanes, $MeAsH_2$ and Me_2AsH, can affect their liquid–gas phase distribution as has been demonstrated by batch experiments [41], where a significant fraction of gas-phase $MeAsH_2$ and Me_2AsH, can be captured by an acid solution (about 6 mol L^{-1} HCl) after 4 min equilibration. The protonation of methylated arsanes to give the corresponding nonvolatile arsonium cations, was assumed to be the reason for the low-generation efficiencies observed in CHG of MMAA and DMAA at high acidities [41]. This hypothesis was not confirmed by CHG experiments in a continuous flow system [122]. The acidic reaction mixture obtained after reaction of THB with either MMAA and DMAA, which should contain the protonated, nonvolatile methylated arsanes, was neutralized on-line with NaOH. The neutralization of acidity did not liberate the volatile methylarsanes, which casts doubt on the possibility that methylarsonium species are present in a continuous-flow CHG system and supports the hypothesis that methylarsanes are not generated at high acidities for lack of reactivitiy between analytical substrates and $[BH_4]^-$/hydridoboron species (Sections 4.3.1, 4.3.2, 4.4.2).

Similarly to methyl arsanes, also stannane cannot be generated from highly acidic media ($[H_3O^+] > 0.5$ mol L^{-1} [1]). The ionization of stannane to give the stannonium ion $SnH_4 + H_3O^+ \rightarrow SnH_3^+ + H_2O$ under strong acidic conditions [123] was proposed as the explanation for the low-generation efficiency achieved for inorganic tin by CHG [124]. Recently, dedicated experiments demonstrated that stannane is not captured by strongly acidic solution when the concentration of HCl or $HClO_4$ is 10 mol L^{-1} in a continuous-flow CHG system [125]. This ruled out any hypothesis based on the formation of stannonium ion and indicates that the failure of stannane generation at high acidity has to be addressed by a lack of reactivity between analytical substrates and $[BH_4]^-$/hydridoboron species (Sections 4.3.1, 4.3.2, 4.4.2).

4.4 Experimental evidence of the role of pH in CHG

Let us consider the three processes involved in CHG, which start simultaneously upon solution mixing

$$H_3O^+ + OH^- \rightarrow 2H_2O \tag{40}$$

$$\text{THB} + H_3O^+ + 2H_2O \rightarrow \text{Intermediates} \rightarrow H_3BO_3 + H_2 \tag{41}$$

$$\text{THB/Intermediates} + \text{Analyte} \rightarrow \text{Hydride} \tag{42}$$

The neutralization reaction 40 is fast (diffusion-limited reaction), with $k >> 10^9$ L mol^{-1} s^{-1} much greater than hydrolysis of THB ($k_{H^+} \approx 10^6$ L mol^{-1} s^{-1}), see Tables 3 and 4. Concerning reaction 42, the kinetics of formation of volatile hydrides is unknown. Any assumption about the rate of hydride formation could be reasonable and logical, but arbitrary in nature. Finally, it must be remembered that whatever the magnitude of the specific rate constants of the above reactions, the observed reaction rate cannot be faster than the rate of mixing of the solutions.

4.4.1 Alkaline conditions

There is a quite widespread concept that CHG occurs mostly under acidic conditions, and that acid decomposition of the borane reagent is necessary in order to generate the active species which are able to perform the derivatization. At the base of the nascent hydrogen concept there is the conviction that the borane complex must be decomposed in acidic media to be active, with a reaction pattern similar to that followed in the metal/acid reduction system (e.g., Zn/HCl). Just from a thermodynamic point of view, alkaline reaction with THB presents a much higher standard reduction potential $[E°(BO_2^-/BH_4^-) = -1.24\ V]$ with respect to both acid THB $[E°(H_3BO_3/BH_4^-) = -0.482\ V]$ and Zn/acid $[E°(Zn^{2+}/Zn) = -0.763\ V]$ [126].

Therefore, generation of volatile hydrides under alkaline conditions could provide additional evidence supporting the mechanism of CHG.

The determination of several hydride-forming elements in alkaline media reported in the literature [127,128] cannot be considered proof because, as noted by Dědina [34], the reduction with THB is performed in alkaline media followed by acidification of the reaction mixture, which might still be compatible with a mechanism involving nascent hydrogen. The generation of stannane in alkaline media was first reported by Qiu et al. [129]. They mixed an acidified Sn^{IV} solution with an alkaline solution of THB and observed stannane formation up to pH 12, the latter being measured after complete mixing of the reacting solutions. This evidence cannot be considered as convincing proof mainly because the hydrolysis of THB can take place, to some extent, during the mixing time of the solutions, perhaps before the pH is constant [37].

In order to investigate the role played by acidity and matrix composition in determining the efficiency of generation of stannane, stibane, and bismuthane, a flow system which allowed on-line pre-equilibration of pH before the derivatization reaction [$NaBH_4$, $BH_3(NH_3)$ and BH_3(*tert*-ButylNH_2)

were employed] was used by D'Ulivo et al. [18]. The reaction system (see Fig. 6) allowed the mixing of a 0.1 mol L^{-1} HCl analyte solution (channel A), with H_2O or alkaline solution (channel B) in a first mixing block T_1, followed by the reaction of the analyte solution with the borane complex in T_2 (channel C). The contact time of the solutions could be controlled using different mixing loop volumes of 4 μL (realized in a single mixing block [18]), 15 and 50 μL. Mixing times were experimentally investigated and concluded to be around 20 ms, which was less than the residence times (30, 113, and 375 ms) of solution in the mixing volume between T_1 and T_2 (4, 15, and 50 μL). Therefore, considering that pH equilibration is a very fast reaction (diffusion-limited reaction, $k >> 10^9$ L mol^{-1} s^{-1}), any change in the hydride generation efficiency correlated with reaction loop volume could not be ascribed to pH variation, but must be related to variation in the structure of the molecular species containing the analyte. The subsequent reaction step occurring in T_2 using different reaction times (0.6 and 3 s, obtained with 100 and 500 μL reaction loops, respectively), provides information about the reactivity of the analyte substrate toward the different borane complex employed. The results demonstrated that for Sb, Bi, and Sn, volatile hydrides can be generated under strongly alkaline conditions. The pronounced dependence of reaction efficiency on mixing loop volume clearly indicates that over the investigated range of pH from 1.38 to 12.70 both pH and acid identity, HA, can play a decisive role through the formation of substrates which are more or less active in the derivatization process. Unsuccessful hydride generation in alkaline media mostly results from the loss of reactive species of the analyte rather than from an insufficient degree of decomposition of the borane complex, in agreement with the conclusions reported by Jolly in early studies on the preparation of hydrides of Sb, Bi, Sn, As, and Ge using $NaBH_4$ in acidic media [9].

The data collected during the above study [18] also allowed calculation of the fractional amount of borane complex that has been hydrolyzed and the relevant fractional amount of hydrogen evolved at the end of reaction loop (Fig. 6). The results indicate that, in some cases, the concentration of hydrolyzed borane and that of evolved hydrogen are much lower than the stoichiometric levels necessary for hydride generation. Nevertheless, hydrides of Sb, Bi, and Sn are evolved, demonstrating that the nonhydrolized borane complex is the effective species. Simultaneously, by calculating the virtual concentration of H atoms, it was also possible to demonstrate that "nascent hydrogen" (reactions 1 and 3) is not involved in the derivatization.

One more example is given by Hg, which can be determined by reduction of Hg^{II} by $NaBH_4$ in alkaline media (pH = 13) [130]. For this reaction

$$[BH_4]^- + 8OH^- + 4Hg^{2+} = BO_2^- + 6H_2O + 4Hg^0 \tag{43}$$

it has been verified that a chemical amount ratio for THB/Hg is 0.25 ± 0.02 for Hg in the concentration range (10^{-10}–10^{-6}) mol L^{-1} Hg^{II} [130]. The experimental results confirmed the stoichiometry of reaction 43. In consideration of the fact that the fraction of $[BH_4]^-$ hydrolyzed at pH = 13 in a continuous-flow system (reaction times smaller than 5 s) is less than 5×10^{-7}, it can be concluded that under strongly alkaline conditions inorganic Hg^{II} is reduced to Hg^0 by $[BH_4]^-$, which is the effective derivatization species. In this case, the sample contains about 0.05 mol L^{-1} Cl^-, which prevents precipitation of mercury hydroxide by formation of mercury chloro-complexes, $[HgCl_4]^{2-}$, which are the analyte substrates reacting with $[BH_4]^-$.

4.4.2 Acidic conditions

These are the most widely employed conditions in CHG. Under acidic or strongly acidic conditions, an important role is played by the $[BH_4]^-$ intermediates, tri-, di-, and mono-hydridoboron species (see Table 5), which appear to be much more resistant to acid hydrolysis. This holds also for $NH_3(BH_3)$ [17]. Recent experiments [17] using $NaBH_4$ or $NH_3(BH_3)$ as reagents confirmed the above hypothesis. CHG of mercury, arsane, stibane, bismuthane, stannane, didihydrogen selenide, and dihydrogen telluride can occur using a continuous flow apparatus similar to that described in Fig. 7. Borane reagent solution THB or AB and HCl (0.01–10) mol L^{-1} solution were mixed in T_1 and allowed to react for (0.02–5) s in the mixing loop (4–500) µL. In this manner, simultaneous variation of acidity and reaction times in the mixing loop allowed hydrolysis of the borane reagent to a different degree, even if unknown, of mono-, di- and tri-hydridoboron intermediates. These hydridoboron intermediates merge with the analyte solution (0.01–10) mol L^{-1} in HCl in T_2. The fraction of reagent decomposed in the mixing loop is estimated in separated batch experiments in which the kinetics of hydrogen evolution were measured. The results indicate that Hg^{II} and Sb^{III} species react unselectively with all the hydridoboron intermediates, which are formed in reaction loop. The other analytes As^{III}, Se^{IV}, Te^{IV}, and Sn^{IV}, show a different degree of selectivity toward the different hydridoboron species as evidenced from the results reported in Figs. 7–10. In particular, Te^{IV} (Fig. 10) and Sn^{IV} (Fig. 11) exhibit almost opposite behavior: dihydrogen telluride is preferentially formed by those hydridoboron species which are stable under strongly acidic conditions, while the same species are nonreactive toward generation of stannane.

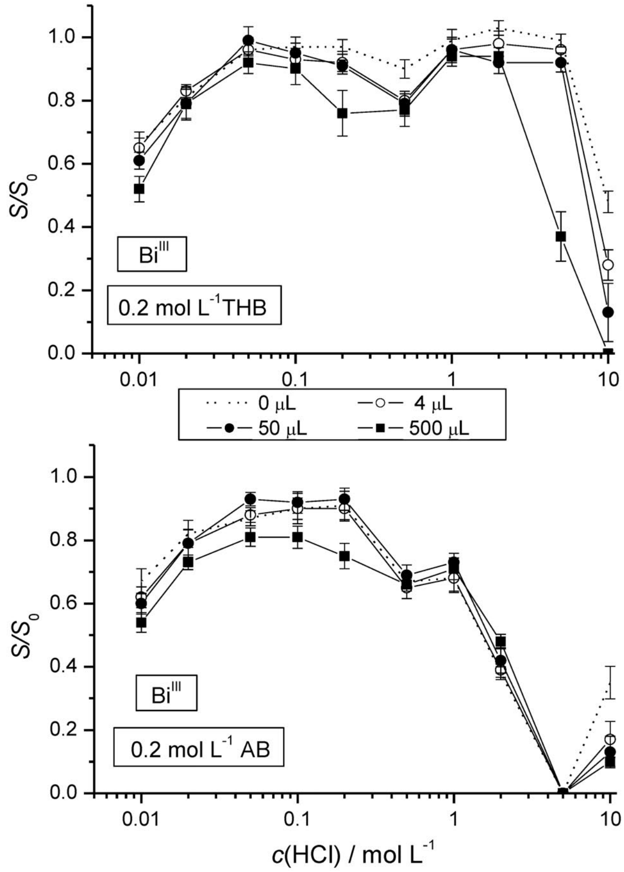


Fig. 8 GHG of BiH_3 from Bi^{III}. Effect of delayed addition of the analyte solution (in T_2) to the solution of THB or amine borane (AB), after that hydrolysis of THB or AB has started in T_1. The effect is reported as a function of L_0 (0–500) µL and acidity of reaction medium (HCl). S is the absorbance signal and S_0 is the absorbance signal measured under optimized analytical reaction conditions. The reaction scheme is the same reported in Fig. 7. (Reprinted with permission from A. D'Ulivo, M. Onor, E. Pitzalis. *Anal. Chem.* **76**, 6342 (2004). Copyright © 2004 American Chemical Society, ref. [17]).

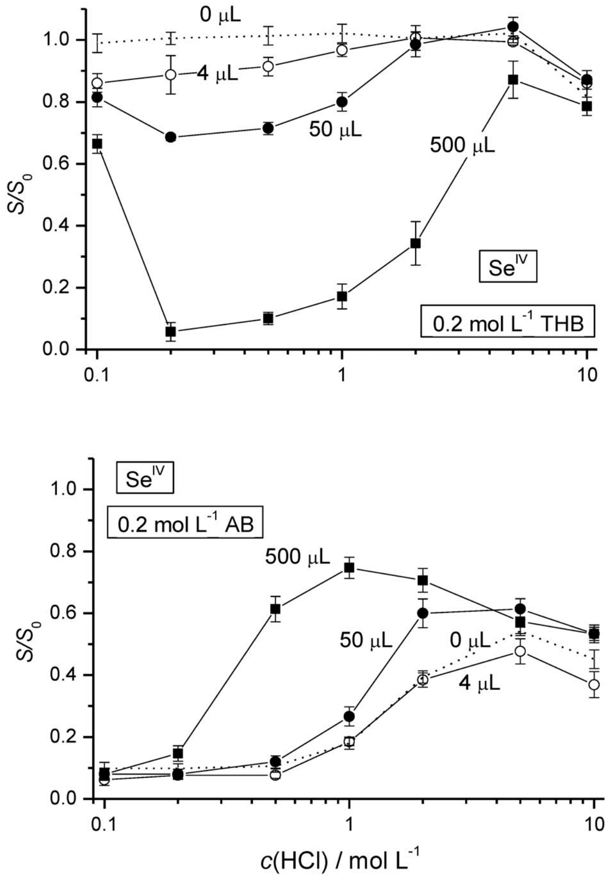


Fig. 9 GHG of H_2Se from Se^{IV}. Effect of delayed addition of the analyte solution (in T_2) to the solution of THB or ammonia borane (AB), after that hydrolysis of THB or AB has started in T_1. The effect is reported as a function of L_0 (0–500) μL and acidity of reaction medium (HCl). S is the absorbance signal and S_0 is the absorbance signal measured under optimized analytical reaction conditions. The reaction scheme is the same reported in Fig. 7. (Reprinted with permission from A. D'Ulivo, M. Onor, E. Pitzalis. *Anal. Chem.* **76**, 6342 (2004). Copyright © 2004 American Chemical Society, ref. [17]).

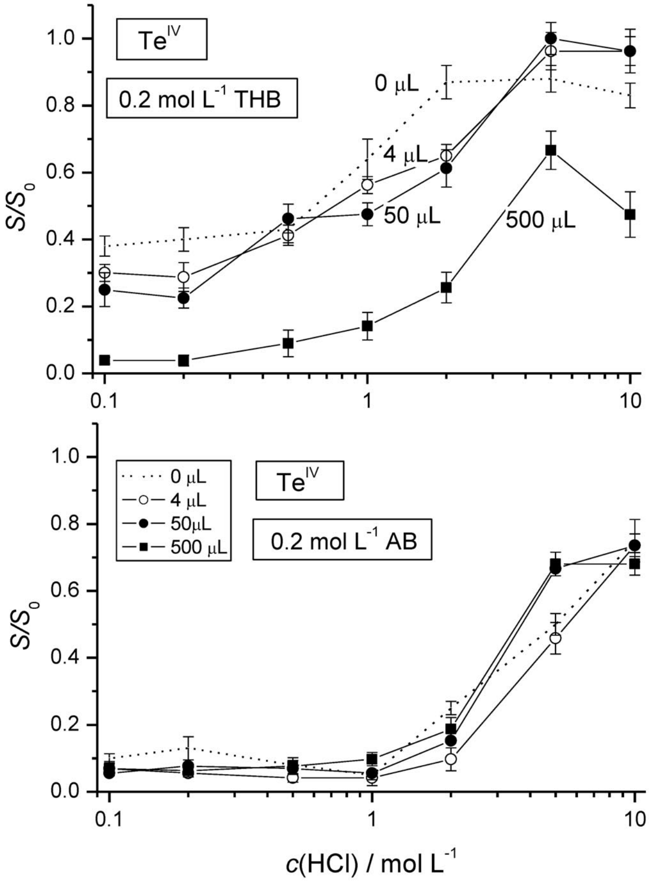


Fig. 10 GHG of H_2Te from Te^{IV}. Effect of delayed addition of the analyte solution (in T_2) to the solution of THB or ammonia borane (AB), after that hydrolysis of THB or AB has started in T_1. The effect is reported as a function of L_0 (0–500) μL and acidity of reaction medium (HCl). *S* is the absorbance signal and S_0 is the absorbance signal measured under optimized analytical reaction conditions. The reaction scheme is the same reported in Fig. 7. (Reprinted with permission from A. D'Ulivo, M. Onor, E. Pitzalis. *Anal. Chem.* **76**, 6342 (2004). Copyright © 2004 American Chemical Society, ref. [17]).

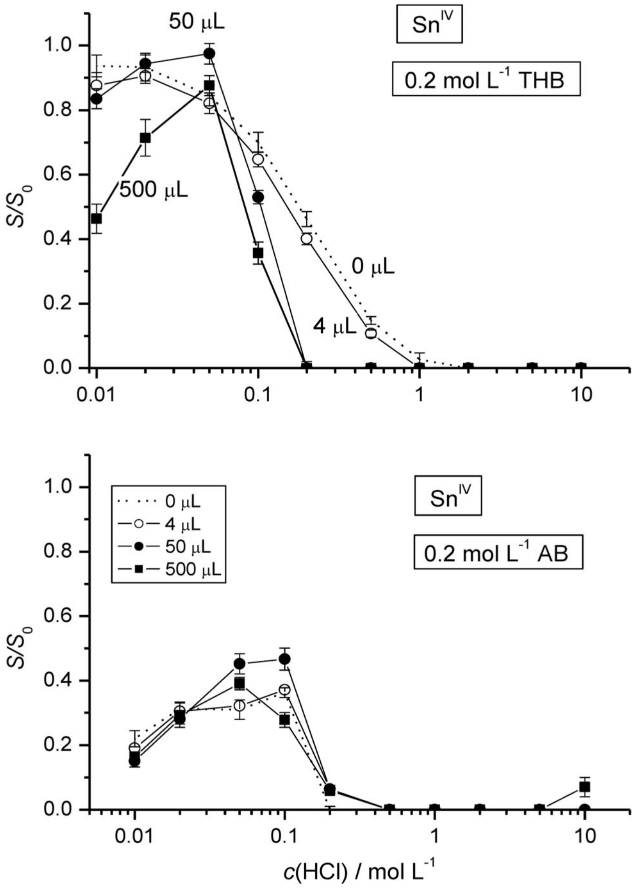


Fig. 11 GHG of SnH_4 from Sn^{IV}. Effect of delayed addition of the analyte solution (in T_2) to the solution of THB or ammonia borane (AB), after that hydrolysis of THB or AB has started in T_1. The effect is reported as a function of L_0 (0–500) μL and acidity of reaction medium (HCl). S is the absorbance signal and S_0 is the absorbance signal measured under optimized analytical reaction conditions. The reaction scheme is the same reported in Fig. 7. (Reprinted with permission from A. D'Ulivo, M. Onor, E. Pitzalis. *Anal. Chem.* **76**, 6342 (2004). Copyright © 2004 American Chemical Society, ref. [17]).

5. EFFECTS OF MATRIX COMPOSITION IN CHG

In this section, the mechanisms through which the components of the sample can modify reactivity in CHG will be discussed. The components can be foreign species, which are already present in the sample, or they can be purposely introduced as *additives* to the reaction system in order to obtain modification of reactivity. The effect of foreign species is of great interest because it is associated with interferences that represent the most severe problem in CHG. The use of additives is employed to improve the characteristics of CHG in terms of reaction efficiency, selectivity, and control of interferences.

5.1 Effects of foreign elements: Interferences

According to the classification of non-spectral interferences given by Dědina [131], these can be divided into liquid- and gas-phase interferences. Herein will be discussed liquid-phase interferences which are strictly related to the mechanism of CHG with borane complexes. Species responsible for the interferences are usually present in great excess over the analyte.

The most severe interference effects taking place in the liquid phase are typically associated with transition metals, in particular, noble metals, followed by the interference from the hydride-forming elements [1]. These interferences are extremely variable and unpredictable, being dependent on the specific analyte-interferent couple, and on many experimental parameters such as reaction conditions (acid and THB concentration, type of acid, and additives) and the type and design of the CHG apparatus (continuous-flow, flow-injection, batch). Furthermore, it has been almost unanimously recognized that the separation of volatile analytical species from the reaction matrix should be realized as fast as possible in an effort to minimize such effects.

The mechanism of interferences have been investigated by several authors during a time when the mechanisms involved in CHG of hydrides, including THB hydrolysis, were not clear enough to the analytical community. The categorization of interferences made by Dědina and Tsalev [1], schematically represented in Fig. 12, suffers from such a limitation, but it still maintains some validity and represents a good base for discussion. This categorization considers some of the possible binary interactions between the reagents (analyte, interferent, THB) and reaction products (hydride, reduced products of interfering species):

- *Ion–ion interference*. The analyte (ionic form) reacts with the interferent (ionic form) in the sample solution, prior to THB, and it is converted to a compound that is not reactive or less reactive than the analyte ion.
- *Ion–product interference.* Analyte (ionic form) is captured (or bound) by species (product) formed by the reaction between the interferent and THB such that the release of the hydride is less efficient.
- *Hydride–ion interferences.* The generated hydride is bound by the dissolved interferent (present in ionic form).
- *Hydride–product interferent.* Hydride is captured by species (product) formed by the reaction of interferent with THB.
- *THB depletion interference.* The reagent (THB) is preferentially consumed by the interferent.

Most of the above mechanisms have been proven to be effective in CHG [132,133]. However, the most severe effects, which are produced by low concentrations of interferent, belong to the category of *hydride-product*s: the interfering metal ions are converted to the element or borides and the coalescence process forms nanoparticles and colloids which are able to capture the hydride on their large, reactive surface. Colloids can then remain bound in the CHG apparatus, producing memory interference.

The *hydride-ion* and the *THB depletion* mechanisms do play a role in CHG but in general, as demonstrated by experimental evidence, they take place at concentration levels much higher than those operating for the *hydride-product* mechanism [132,133]. The effect of the *hydride-ion* mechanism is typically enhanced in batch reaction apparatuses where the residence time of hydrides in the liquid phase is much higher than in continuous-flow systems [1].

Subsequent studies modeling the interference process of Cu, Ag, Au, on the H_2Se generation confirmed the hydride-product mechanism. The shape of interference plots, reporting the signal suppression against the concentration of interferents, corresponded to an interference model based on the capture of the dihydrogen selenide on the surface of particles supposedly grown in solution and possessing a highly folded surface that is fractal in nature [134]. The shape of analytical signal and its modification during the interference were also modeled in the CHG of H_2Se in the presence of Cu [135]. Signal deconvolution allowed the conclusion that the interference does not alter the generation efficiency of dihydrogen selenide, but it influences the kinetics of stripping of the hydride from the reaction solution.

The limitation of the categorization scheme of Fig. 12 is that it considered the three reaction pathways as independent and that they are described by single-step reactions instead of multi-step reactions. This categorization, for example, is not able to explain the experimental evidence reported by Aggett

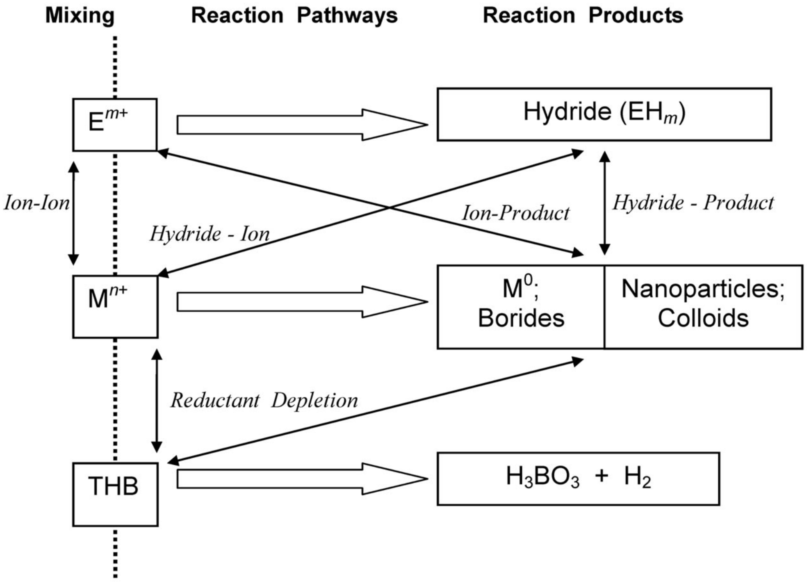


Fig. 12 Schematic representation of categorization of interferences according to Dědina and Tsalev, ref. [1].

and Hayashi [136]. They found that Ni^{II} and Co^{II} interfere in CHG of arsane without any apparent formation of precipitates. On the contrary, Cu^{II}, which forms a finely dispersed precipitate, did not produce remarkable interference effects. In this case, the mechanism of interference was considered to take place through formation of soluble species between the analyte and the interferent in lower than normal oxidation state. This explanation is in agreement with the possibility that the interference can also play a role in the modification of reaction pathways between the reagents and the final products. On the other hand, being that the reaction pathways for hydride-forming elements and for transition and noble metals are very similar, the distinction between analytes, i.e., the hydride-forming elements, and the interfering element, is at present just a matter of formalism. Aqueous ions, ionic Cu^{II}, Ag^{I}, Ni^{II}, Au^{III}, etc., are the species which generate the most serious interferences in CHG of hydride-forming elements; nevertheless, they cannot be considered at present only interfering species because they can also be converted into volatile species during CHG. On the other hand, when a transition metal is the analyte, interference from other concomitants, transition and noble metal ions, and hydride-forming element ions remains a severe problem [28]. A noticeable exception was the determination of Cu by CHG, which was markedly free from interference effects [24].

In light of the discussion developed in the previous section, a more general scheme should take into account that the reaction pathways overlap, and this includes the formation of all possible ABC intermediates among the components, including the ABC intermediates formed by binary interactions THB/E, THB/M (E is a classical hydride-forming element, M is a transition metal), and the ABC intermediates formed by ternary E/THB/M interactions. The possible interactions among the reaction matrix components would be even more complicated in the case of introduction of an additive, L, which can interact with all the other species, E, M, and THB. This makes the rationalization of interferences and the comprehension of their mechanism of action extremely difficult.

5.1.1 Selectivity of borane complexes toward analyte and interfering species

Depending on their structure, borane complexes can present a different degree of selectivity with respect to analytical substrates and interfering species. The milder amine boranes, $BH_3(NH_3)$, BH_3(*tert*-ButylNH_2), $BH_3(Me_2NH)$, and $NaBH_3CN$, are demonstrated to generate much less interference than THB in the determination of Hg^{II}, As^{III}, Sb^{III}, and Bi^{III} in the presence of Fe^{III}, Co^{II}, Ni^{II}, and Cu^{II} [16]. In the determination of inorganic As^{III} in the presence of interfering ions Cu^{II}, Fe^{III}, Ni^{II}, Co^{II}, Ag^{I}, Pd^{II}, Pt^{IV}, and Au^{III}, the preformation of a cysteine–borane complex was found to be a decisive factor in controlling the interferent effects arising from metal ions. Preformation of a complex with cysteine and Au^{III} was found to be the best way to control this interference [157]. This behavior is in agreement with the study of Brindle and Le, where the thiol–borane complex was considered to react selectively with the analyte (inorganic Ge^{IV}), avoiding formation of interfering species with metal ions [147].

In the absence of additives, an important role can be played by the intermediate hydridoboron species, in addition to $[BH_4]^-$, which are formed during the hydrolysis of $[BH_4]^-$ in pure aqueous solutions (reactions 14 to 17). All of them can react, in addition to the analytical substrate (Section 4.2.2), with ionic metal interfering species to form ABC intermediates (Section 3.3) which can evolve to give reaction intermediates and final products (Section 3.4). At high acidity, the species that are more likely to be involved in the derivatization process are those hydridoboron species $BH_2OH(H_2O)$, $[BH_2(H_2O)_2]^+$, $BH(OH)_2(H_2O)$ (see Table 5) which are more resistant to acid hydrolysis. Similarly to amine boranes, they should present a certain degree of selectivity toward analyte and interfering species. The better control of interferences which can be achieved in CHG by increasing the acid concentration (up to 5–7.5 mol L^{-1} HCl) has been ascribed to formation of chloride complexes of the metal and to the re-dissolution of reduced metals [1,137–141]; the possibility that acid-resistant hydridoboron intermediates, in the presence of transition-metal ions, react selectively with analytical substrates could be one factor contributing to the control of interferences.

5.1.2 Effect of interferent on reaction intermediates

The interfering species can interact with the borane complex by forming new borane species which may or may not contain the interfering species. The new borane species so formed will possess different reactivity with respect to the analytical species, forming ABC intermediates of a different nature, the fate of which is to evolve toward the formation of species different from the expected hydride.

This type of mechanism can be identified in the particular case in which the analytical species and the interfering species are the same, for example, when the concentrations of the analytical species are much higher than those commonly used in analytical studies. In this case, as reported and discussed in Section 2.1 (see also Table 2), the products of CHG can be different from those expected under analytical conditions.

CHG of Te [54] and Bi [56] using a continuous-flow reaction system produced curvature and rollover of calibration curves, ascribed to the formation of the analyte in an elemental state (no investigations were performed to assess the composition of particulate matter). When the concentration of particulate reaches a critical threshold, the particles can start to adsorb the hydride onto their surface. This also introduces modification of the shape of analytical signals, with the formation of double peaks [54,56], a clear indication of the occurrence of heterogeneous-phase reactions in CHG [142]. The effect was studied in detail for Bi, and it can be eliminated by the presence of millimolar concentrations of Fe^{III}, K_3FeCN_6, Mo^{VI}, $KMnO_4$, and NaSCN [56]. The re-oxidation pathways, $Bi^0 \rightarrow Bi^{III} \rightarrow BiH_3$, can be excluded for NaSCN and it can be excluded also for many of the other oxidants employed as additives. The other alternative mechanism is that both BiH_3 and Bi^0 are directly formed from reaction intermediates or from ABC intermediates, which can evolve in different directions depending on the analyte/borane ratio. The role of the additive is the formation of suitable intermediates that evolve preferentially to the hydride.

A similar mechanism could be operative in some cases where the analyte and the interferent are not the same species and the ratio analyte/borane is low (analytical conditions) but the ratio interferent/borane is much higher. In this proposed mechanism, the analyte and interference are interchangeable, and they can be hydride-forming element-transition metal, hydride-forming element-hydride forming element or transition metal-transition metal.

The reaction pathways passing through ABC intermediates also serve to unify the discussion of the role and the mechanism played by additives both in the control of interference and in the enhancement of generation efficiency in CHG; the enhancement effect of an additive, similar to its masking capacity, can be considered as the removal of those conditions which interfere with the efficient generation of the hydride.

5.2 The effect of additives on the reactivity of $[BH_4]^-$

The most commonly used additives are ligand/donor species (A^-, X) which are able to form complexes; as a consequence, different types of acid (HA) and buffers (HA/A^- or XH^+/X) can also be considered additives unless they do not present any significant complexation capacity (e.g., ClO_4^-, NO_3^-). Oxidizing or reducing species added to the reaction system are also in widespread use in CHG.

In general, the additives can interact with all the components of the reaction matrix: analyte, interferent, borane reagent, and their reaction products at any step of the reaction pathways. This makes it difficult to recognize the role played by the different interactions among the components of the reaction matrix, giving rise to the observed modification of the reactivity of the CHG system. The possible effects ligand/donors and other additives could have in modifying the structure of borane complexes used in CHG have been disregarded to a considerable extent in the analytical chemistry literature. Considering that the aspect that requires most clarification is the interaction of additives with borane complexes, in the following sections particular attention will be dedicated to the possible formation of borane complexes in the presence of different ligand/donor species.

The use of additives that modify the reactivity and selectivity of THB under various reaction conditions is well known in organic chemistry and has reached some degree of rationalization. From a review by Flores-Parra and Contreras [143], it is possible to obtain an appreciation of the vast number of reactions that a borane complex BH_3X (typically X is tetrahydrofuran or Me_2S) undergoes with many bifunctional ligands to give boranes of complex structure. In another review, Periasamy and Thirumalaikumar [144] discussed the methods employed in organic synthesis to enhance reactivity and selectivity of THB. From this review, it clearly emerges that THB is employed as a *convenient precursor* for the in situ preparation of borane species that present the desired degree of reactivity and selectivity toward a selected class of targeted compounds.

The effect that some additives could play in the modification of THB in CHG is not easy to predict on the basis of our present knowledge, taking also into consideration that the information reported in the following sections is taken from the organic and synthetic chemistry literature.

In general, a modified borane complex can be achieved by hydrolysis in the presence of the ligand/donor species

$$[BH_4]^- + H_3O^+ + A^- \rightarrow [BH_3A]^- + H_2O + H_2 \tag{44}$$

$$[BH_4]^- + HA \rightarrow [BH_3A]^- + H_2 \tag{44a}$$

$$[BH_4]^- + H_3O^+ + X \rightarrow BH_3X + H_2O + H_2 \tag{44b}$$

$$[BH_4]^- + XH^+ \rightarrow BH_3X + H_2 \tag{44c}$$

The reiteration of reactions 44 and 44a can give a variety of borane complexes in which the hydride is replaced by the donor/ligand or OH^-/H_2O. The competition between the complexation capacity of the donor/ligand with respect to H_2O/OH^- is important for the formation of the modified borane complex in aqueous solution.

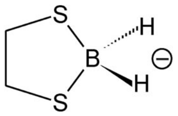
5.3 Additives containing sulfur donors

Thiols (RSH) and other additives containing sulfur donors (e.g., thiourea, tetramethylthiourea, thiosemicarbazide, etc.) are widely employed in CHG using THB derivatization. The low affinity of sulfur for protons in comparison to other heteroatoms, nitrogen and oxygen, preserved the donor capacities of functional groups containing sulfur even at elevated acidities, where they are available to interact, in principle, with all the components of the reaction matrix, analyte, borane complex, foreign elements, and reaction products. Tsalev et al. [145] discussed how L-cysteine can serve as a pre-reductant for the analytical species, as a complexing agent for both analyte and borane, and as a buffer for the CHG reaction.

The peculiar behavior of thiols in modifying the characteristics of many CHG reaction systems was demonstrated by Brindle's group for the generation of arsane [146], germanium [147,148], and tin [149]. One of the common characteristics of thiols observed by Brindle and co-workers is that they change the pH at which the maximum sensitivity (efficiency) is obtained. Thiols can act as a suitable pre-reducing agent, as for example in the case of As^V and Sb^V which are converted to the trivalent state [146,150]. Signal enhancement was also reported, mainly using batch CHG systems, and for tin using a flow-injection CHG system. The signal enhancement effect was not observed by other authors using different apparatus [122,151].

Brindle and Le [147] found that in aqueous solution, L-cysteine, penicillamine, and thioglycerol produce a thiolate–borane complex according to reaction: $[BH_4]^- + RSH = [RS–BH_3]^- + H_2$. The formation of $[RS–BH_3]^-$ was confirmed by ^{11}B NMR at a ratio of chemical amount of thiol and THB in the range of 0.66 to 0.83. Brindle and Le [147] proposed that the thiol ligand competes with the solvent for the formation of the complex with BH_3. The possible formation of complexes containing more thiolic groups was not verified by increasing the molar thiol/THB ratio.

Formation of both $[HS–BH_3]^-$ and $[(HS)_2BH_2]^-$ was observed by ^{11}B NMR in the reaction of $LiBH_4$ with H_2S in tetrahydrofuran in a temperature range of –22–0 °C [152]. The formation of a particular dihydridoborate was observed by ^{11}B NMR during reaction of THB with ethanedithiol, $HS–CH_2–CH_2–SH$ in dry diglyme ($CH_3OCH_2CH_2OCH_3$), giving a compound with the structure [153]:



The above reducing system was found to be more powerful than THB itself in the reduction of esters and other carboxylates, but it is also selective because it is sensitive to the steric environment of the carbonyl group. The enhanced reactivity of thioloborane complexes with respect to THB is probably due to electron release from the sulfur group, by analogy with alkoxy-boranes (e.g., $[RO–BH_3]^-$) and hydroxy-boranes (e.g., $[BH_3OH]^-$). At the same time, they should be hydrolyzed faster than THB according to the relation between the rates of formation of hydrides and the hydrolysis rates of borane complexes (see Fig. 5 and Section 4.2).

5.3.1 Effects on generation of arsanes

The optimum acidity conditions for the generation of arsane and methylarsanes from As^{III}, As^V, monomethylarsonic (V) acid [MMAA(V)], dimethylarsinic (V) acid [DMAA (V)] are quite different and it is not possible to find acceptable acidity conditions under which all the arsanes are generated with similar efficiency [122,154,155]. (The origin for the different responses remains controversial.) After sample pretreatment with a thiolic compound [122,154,155] for a suitable time period, the reactivity of the arsenic species are drastically changed. In particular, the range(s) of optimal acidity at which arsanes are efficiently produced is dramatically changed, and it is possible to find conditions at which the response of arsanes is almost the same. Thioglycolic acid is much faster than cysteine in reducing the oxidation state (V) to (III) for both inorganic and methylated arsenic species and it can be used for on-line pre-reduction [156], while cysteine works well also for the speciation analysis of methylated As^{III} and As^{V} species [42,44]. On the contrary, the presence of thiourea did not affect the optimum acidity conditions for CHG of arsane [151].

One of the possible mechanisms of action of thiols influencing the generation of arsane and methylarsanes is the formation of arsenic thiol complexes [155]

$$H_3AsO_4 + 5RSH = As(SR)_3 + RSSR + 4H_2O \tag{45}$$

$$H_3AsO_3 + 3RSH = As(SR)_3 + 3H_2O \tag{45a}$$

$$MeAsO(OH)_2 + 4RSH = MeAs(SR)_2 + RSSR + 3H_2O \tag{45b}$$

$$Me_2AsO(OH) + 3RSH = Me_2As(SR) + RSSR + 2H_2O \tag{45c}$$

This can dramatically change the nature of the analyte substrate. In this case, replacement of As=O and As–OH bonds by As–SR bonds remarkably changes the nature of the ABC intermediates through which the hydrogen has transferred from boron to arsenic.

The role played by the formation of thiolate–borane complexes has been recently investigated in the case of As^{III} [157]. It was found that thiolate–borane complexes are formed much faster than As^{III}–thiol complexes, and that the formation of thiolate–borane complexes is responsible for the sensitivity enhancement observed at low acidities (HCl, $HClO_4$, H_2SO_4, and acetic acid). In the intermediate range of sample acidity (0.2–2) mol L^{-1}, the efficiency of arsane formation depends on the identity of the acid. The strongest depressing effect is observed for $HClO_4$ and H_2SO_4, followed in order by HCl and acetic acid, which exhibits little or no depressive effect. The observed effect can be addressed by a low reaction rate of cysteine-THB or hydridoboron intermediates with the As^{III} substrates, which are formed under the same reaction conditions. At higher H_3O^+ concentration, achievable in 5–10 mol L^{-1} strong acids, arsane is efficiently formed only in the presence of chloride ions. The formation of cysteine-THB complexes seems to be a decisive factor in the achievement of sensitivity enhancement and in the control of interference from transition-metal ions for determination of As^{III}. Pretreatment of As^{III} with cysteine to generate As^{III}-thiol complexes was found to be unnecessary in order to achieve most of the beneficial effects produced by cysteine. This was also a good approach to an analytical method based on highly selective, interference-free determination of inorganic As^{III} in the presence of inorganic As^{V}.

5.3.2 Effect on stibane and bismuthane generation

The optimum generation conditions for stibane and bismuthane, in terms of both acidity and THB concentration, appear to be little affected by the presence of both thiols and thiourea. L-cysteine did not alter the optimum conditions for stibane generation in a continuous-flow CHG system, which are mainly controlled by THB concentration in the acid range of 0.01–3 mol L^{-1} [158]. The same observation was reported for bismuth in a continuous flow CHG system, both in the presence of L-cysteine and thiourea [151]. The reason why the thiol-modified reaction system does not produce any detectable effect on the CHG of stibane and bismuthane cannot necessarily be ascribed to the lack of interaction between analyte and thiols. On the other hand, Sb^{III} and Bi^{III} present a more pronounced cationic character compared to As^{III}, and it is likely that their analyte substrates, as, for example, SbO^+, $Sb(OH)_2{}^+$, BiO^+, etc. (see Chapter 11 of ref. [159]) already present a suitable reactivity toward hydride attack of unmodified hydridoboron species.

The thiol-modified reaction system may be able to modify the reaction rates of both stibane and bismuthane, but it is not stated that this is detectable because the CHG systems typically work with fixed reaction times, the shortest of which is limited by the mixing rate of the solutions. For As^{III}, the $As(OH)_3$ species are probably not reactive enough for the hydride attack and the modification of the systems by thiols improves the reaction rate for arsane formation.

At present, there is no information available to discriminate the effects that the interaction of thiols with the analyte and THB produce on the final results of a given CHG experiment.

5.3.3 Effect on stannane generation

The optimum acidity for stannane generation is typically over a narrow range of sample acidity of (0.1–0.2) mol L^{-1} HCl (others strong acids behave similarly). This effect is not due to the ionization of stannane to stannonium, as discussed in Section 4.3.3. In the presence of L-cysteine [149,151], the dependance on sample acidity is less critical (0.1–0.5 mol L^{-1} acidity) and in some cases signal enhancement is also observed [149]. Most recent dedicated investigation indicated that, in the presence of L-cysteine, the shift of stannane generation to higher acidities is only partly due to the buffering effect of L-cysteine, whereas a significant role in determining this effect is played by the formation of Sn–Cys complexes [125].

By analogy with arsane, stibane, and bismuthane generation, the presence of thiourea did not significantly alter the optimum generation conditions for stannane, which remain mainly controlled by the THB concentration in the same range of acidity considered above [151].

5.3.4 Effect on selenium and tellurium hydride generation

Thiols present a negative influence on the generation of H_2Se and H_2Te with THB, and must be considered in some cases as interfering species [160]. The seleno- and telluro-trisulfides, RS–Se–SR, and RS–Te–SR, which are formed in the presence of thiols [160], are probably much less reactive substrates toward hydride attack than Se^{IV} and Te^{IV} oxyacids. The less pronounced depressing effect was found by on-line addition of DL-penicillamine to Se^{IV}, but it increases the concentration of THB necessary for the achievement of maximum sensitivity, even at low thiol mass concentration smaller than 0.1 g L^{-1}. In conclusion, it appears that thiols are not able to create suitable couples, thiol-modified substrate/THB or thiol-modified substrate/thiol-modified THB, to provide positive modification of the reaction system.

Thiourea [53,160] and tetramethylthiourea [53] interact moderately with the Se^{IV}-THB and Te^{IV}-THB reaction systems and produce only moderate depression in the efficiency of hydride generation, providing that some precautions are taken regarding the mode of addition of these reagents. The on-line addition of a neutral solution of thiourea (TU) to the sample prevents the degradation of thiourea in acid media and reduction of Se^{IV} to Se^0. Fewer problems were found with Te^{IV}, which forms Te^{II} complexes of the type $[Te(TU)_4]^{2+}$ [160].

Sulfur-containing additives find application in the control of interferences (Fe, Cu, Ni, Co, Pt, Pd, Ag, Au) for selenium determination by continuous-flow CHG apparatus in which they were added either before (thiourea, tetramethylthiourea in batch to sample solution) or after (cysteine, thiourea, tetramethylthiourea) the generation of dihydrogen selenide [53]. In any case, the generation of H_2Se was achieved by THB containing KI. Some interferences, Ag and Cu, were much better controlled by the addition of the additives after the CHG step. This result was addressed by the formation of insoluble species of the interfering metal, which changes the nature of the metal colloid interfering with the hydride generation. In the case of Cu^{II}, the nature of the precipitate formed by reaction of THB and KI could be a combination of Cu^0, CuI, and I_2. In this case, the colloid could be able to adsorb the hydride but not to decompose it. The subsequent addition of the masking agent is able to reverse the process by desorbing the hydride through a mechanism based on the competition between the additive and the hydride for the adsorption sites on the surface of finely dispersed colloid.

The protecting activity of sulfur-containing additives from interference of THB-reduced Cu, deposited on the wall of CHG apparatus, has been reported by Welz and Šuchmanova and [161] Narsito and Agterdenbos [162] in the determination of Sb. In particular, thiourea was also able to recover, presumably as stibane, part of the Sb captured by THB-reduced Cu deposited in previous experiments. In this case, the THB-reduced Cu could be able to adsorb stibane but not to decompose it, and the additive can act through a mechanism based on the competitive adsorption for the active sites on the surface of THB-reduced Cu deposited in the CHG apparatus.

5.4 Effect of halogen ions and thiocyanate

Agterdenbos et al. [163] found that halide ions, Cl^-, Br^-, and I^-, have a beneficial effect on the generation of H_2Se by THB derivatization in a continuous-flow reaction system. More recently, the effect of halides and thiocyanate, SCN^- was studied and systematically compared for the determination of H_2Se [53] (iodide caused the formation of Se^0 and therefore it must be added to the THB solution). In the presence of these species in the reaction medium, the amount of THB necessary to achieve optimum sensitivity decreases dramatically, about 3 orders of magnitude in the presence of iodide. The effect takes place under strongly acidic conditions ($pH \leq 0$) typically employed for dihydrogen selenide evolution, and decreases in the order iodide > thiocyanate > bromide > chloride.

This effect was also arbitrarily termed a "catalytic effect" by Agterdenbos et al. [163] because it clearly influenced the rate of formation of dihydrogen selenide. At present, this effect can be more correctly interpreted in the light of the CHG mechanisms discussed in this paper. However, due to the lack of specific experimental evidence on CHG of H_2Se, it is not possible to state if the increase in the reaction rate is due to additive–borane interaction or additive–analyte interaction. The existence of stable complexes of the type $[BH_3F]^-$ [164] and $[NCS–BH_3]^-$ [165] have been reported, but nothing is known about similar complexes with Cl^-, Br^- and I^-. The other possibility that could account for this effect is the additive–analyte which interaction leads to formation of halogenated species. The formation of halogen complex of Se^{IV} is well known in the literature. Halogen anions play a role in the reduction of Se^{VI} to Se^{IV} by formation of $[SeCl_6]^{2-}$ [101,166]. Formation of volatile species of Se^{IV}, $SeOCl_2$, and $SeCl_4$ accounts for losses in open digestion system [167] or their volatility can be used for quantitative separation of Se^{IV} by distillation of $SeOBr_2$ and $SeBr_4$ (see [168] and refs. therein). The formation of additive–analyte substrates such as $SeOX_2$, SeX_4, and $[SeX_6]^{2-}$ (X = Cl, Br, I), in which the analyte substrate could be more active toward hydride attack than $Se(O)(OH)_2$ [37], is at present the most reasonable hypothesis for the role played by halogen anions in the enhancement of the rate of generation of H_2Se in CHG.

The presence of iodide in the sample solution is also beneficial in the case of generation of H_2Te by THB reduction. It prevents the formation of Te^0 at low THB concentration, probably because of formation of iodotellurite complexes, TeI_4, $[TeI_5]^-$, $[TeI_6]^{2-}$, which are more quickly reduced to the hydride as compared to $Te(O)(OH)_2$, and minimizes the reaction producing Te^0, which takes place at relatively low concentration and is responsible for curvature of calibration graphs [54].

5.5 Effect of alcohols

THB is readily soluble in methyl and ethyl alcohol but possesses a modest solubility in propan-2-ol. The reaction with these solvents is slow with the exception of methyl alcohol where it decomposes quite fast [169].

The kinetics of decomposition THB in methanol have been investigated by Davis and Gottbrath [170]. At 25 °C, the rate of decomposition of THB in methanol was found to be about one order of magnitude faster than in water, with a rate constant of $(1.6 \pm 0.3) \times 10^7$ L mol^{-1} s^{-1}. The data could be explained by reactions of the type:

$$2\,CH_3OH \rightleftharpoons [CH_3OH_2]^+ + [CH_3O]^- \text{ (autoprotolysis of methanol)} \tag{46}$$

$$[CH_3OH_2]^+ + [BH_4]^- \rightarrow \text{products} \tag{47}$$

$$CH_3OH + [BH_4]^- \rightarrow \text{products} \tag{48}$$

which are completely equivalent to those reported for hydrolysis of THB in water according to general acid catalysis (Section 2.3, eq. 9). By analogy, intermediates with similar structures to those produced in aqueous media are postulated as $BH_3(CH_3OH)$, $[BH_3(CH_3O)]^-$, $[BH_2(CH_3O)_2]^-$, $[BH(CH_3O)_3]^-$, and $[B(CH_3O)_4]^-$. The alkoxyhydridoborates are considered to be more reactive than THB because the electron release from the oxygen group increases the hydridic character of the hydrogen [170]. A similar conclusion, supported by experimental evidence, has already been made for a similar species, $[BH_3OH]^-$ (Section 4.2).

5.6 Effect of carboxylic acids

These compounds are often used in CHG, alone or mixed with other additives. In some particular cases, for example, tin and germanium, the generation of the hydrides is better realized by sample acidification with carboxylic acid. The most common is acetic acid, or acetate buffers [1].

According to the organic chemistry literature [144], the reactivity of THB can be readily modified through its reaction with acetic acid:

$$[BH_4]^- + CH_3COOH \rightarrow [BH_3(CH_3COO)]^- + H_2 \tag{49}$$

$$[BH_3(CH_3COO)]^- + CH_3COOH \rightarrow [BH_2(CH_3COO)_2]^- + H_2 \tag{49a}$$

$$[BH_2(CH_3COO)_2]^- + CH_3COOH \rightarrow [BH(CH_3COO)_3]^- + H_2 \tag{49b}$$

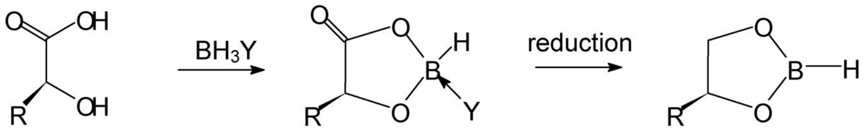
$$[BH(CH_3COO)_3]^- + CH_3COOH \rightarrow [B(CH_3COO)_4]^- + H_2 \tag{49c}$$

By proper choice of the molar ratio between acetic acid and THB, it is possible to produce a specific acetyloxyhydridoborate, among those reported in reactions 49 to 49c. Acetyloxytrihydridoborate(1–) (see reaction 49) has been employed for the hydroboration of alkenes [144], while triacetyloxymonohydridoborate(1–) (see reaction 49b) has been employed as a reductant for certain classes of organic compounds or for chemoselective or stereoselective reduction of aldehydes and ketones [144]. Kreevoy et al. [171] reported the formation of acetoxytrihydridoborate(1–), $[BH_3(CH_3COO)]^-$, identified by ^{11}B NMR, following the reaction of THB with acetic acid (reaction 49).

5.7 Effect of α-hydroxyacids

These compounds have been used alone or together with other additives in the CHG of many hydrides, including stibane, arsane, germane, stannane, plumbane, and also dihydrogen selenide [1]. Those most often used are lactic, malic, citric, and tartaric acids.

The reaction with α-hydroxyacids with the borane complex BH_3Y, (Y is tetrahydrofuran or Me_2S) could, according to the literature [143], give the cyclic intermediate (III)

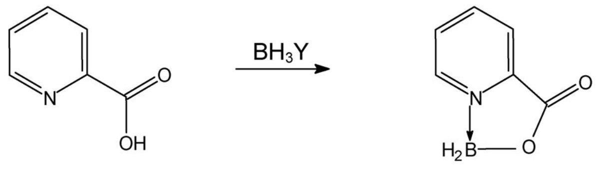


(II) (III) (IV)

in which the carbonyl can be reduced to give (IV) by excess BH_3. A similar reaction could also occur in aqueous solutions between the α-hydroxyacids and the nascent borane, or its complex $BH_3(H_2O)$.

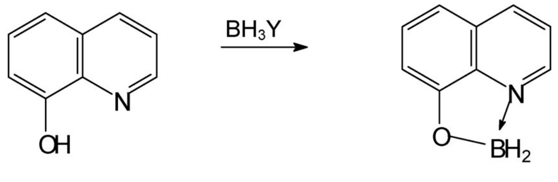
5.8 Some bifunctional donors

Campos et al. [172] used picolinic acid (which contains both pyridine and carboxylic functions, see structure **V**) to mask interferences by Ni^{II} and Cu^{II} in the determination of Sb using CHG with THB. Apart form interaction of picolinic acid with both analyte and interfering species, another possible interaction is with THB and its decomposition products, e.g., the nascent borane or its aquated complex, $BH_3(H_2O)$, and, according to literature [143], it could yield the cyclic dihydrides (**VI**):



(V) (VI)

Deng et al. [173] used 8-hydroxyquinoline (which contains both the pyridinic and phenolic function) for the selective generation of stibane from Sb^{III} by THB and to mask interferences from many foreign elements. Also in this case, apart from the interactions proposed by the authors with both analyte and foreign elements, 8-hydroxyquinoline (structure **VII**) could also interact with borane or its aqueous complex to give a cyclic dihydride phenolborinic ester [143] (structure **VIII**).



(VII) (VIII)

Formation of dihydroboron complex **VIII** could also play a role in the enhancement of generation efficiency of volatile species of some transition metals by reaction of THB in nitric acid + 8-hydroxyquinoline + Co^{II} reaction media [174].

Histidine was successfully employed to mask Ni^{II} interference in the determination of germanium by CHG [147]. In this case, the addition of histidine to THB reagent (0.4 mol L^{-1} histidine and 0.6 mol L^{-1} THB) did not show any interaction with THB detectable by ^{11}B NMR, as it did for L-cysteine. UV–vis spectrophotometry indicated the formation of a histidine-Ni^{II} complex, which has already been considered as the mechanism removing the interference.

5.9 Oxidizing agents

Several beneficial applications of oxidizing agents have been reported in CHG of Ge [175], Bi [56], and Pb (Chapter 12 in ref. [1]) and will be discussed in the next sections. Concerning oxidants, it is interesting to report that for some of them, kinetic and mechanistic studies are reported for their reaction with THB, while no kinetic data are reported for hydride-forming elements.

5.9.1 Studies on reaction of $[BH_4]^-$ *with oxidizing agents*

The reaction of MnO_4^- with THB was studied in alkaline solution and produces Mn^{IV} and hydrogen. It was found to be kinetically first order in both THB and MnO_4^-, independent of pH and with a rate constant of 2×10^3 L mol^{-1} s^{-1} at 20 °C [176]. The complexity of this reaction, which includes the formation of a hypomanganate intermediate, is demonstrated by the experimental evidence obtained in a D_2O reaction medium. In this medium, the evolved hydrogen is only H_2, in contrast to the acid hydrolysis of THB, where the evolved hydrogen is mainly HD (Section 2.6). In the presence of permanganate ion, the evolved hydrogen gas arose only from THB [176], indicating the formation of hydridoboron intermediates different from those reported in the case of THB hydrolysis in pure aqueous solvent.

Another reaction presenting a certain degree of complexity is that of THB with IO_3^-, which has been investigated under alkaline conditions [177]. The rate of disappearance of iodate was found to be $d[(IO_3)^-]/dt = k[IO_3^-][BH_4^-][H^+]$, with $k = 7.4 \times 10^7$ L^2 mol^{-2} s^{-1} at 25 °C. In this case, the mechanism of reaction also appears quite complex and includes various iodine intermediates, such as IO^+ or IO^-.

Freund [178] investigated the mechanism and kinetics of reduction of hexacyanoferrate(III) by THB in the pH range from 9 to 13, which produces boric acid and ferrocyanide as the final products. For this reaction, the rate of disappearance of ferricyanide was found to be $d[Fe(CN)_6^{3-}]/dt = k\,[BH_4^-][H^+]$ with $k = 5.1 \times 10^6$ L mol^{-1} s^{-1} at 25 °C, and independent of ferricyanide concentration. The reduction rate of ferricyanide is even faster than that of THB hydrolysis ($\approx 10^6$ L mol^{-1} s^{-1}). As such, both species could be active as donors during THB hydrolysis and they can also act as chelating species for lead during plumbane formation. Another possibility which emerges from the studies of Freund [178] is that ferricyanide could oxidize the intermediates of THB hydrolysis through alternative one- and two-electron reactions. For example, the intermediate BH_2OH (the water or hydroxyl complexing group are omitted here) can be oxidized as follows:

$$BH_2OH + [Fe(CN)_6]^{3-} + H_2O \rightarrow [BH(OH)_2]^- + [Fe(CN)_6]^{4-} + 2\ H^+ \qquad (50)$$

$$BH_2OH + 2\ [Fe(CN)_6]^{3-} + H_2O \rightarrow BH(OH)_2 + 2\ [Fe(CN)_6]^{4-} + 2\ H^+ \qquad (51)$$

Intermediates, such as $[BH(OH)_2]^-$, cannot be obtained through the reaction scheme reported in Fig. 3. Indeed, each step in which one hydride is lost by reaction with H^+ represents a two-electron process and species such as $[BH_2(OH)]^-$ and $[BH(OH)_2]^-$ cannot be formed. These hydridoborate intermediates could play a role in determining the efficiency of generation of plumbane.

5.9.2 Plumbane generation

The efficient generation of plumbane can be achieved only in the presence of suitable additives and, most often, in a restricted interval of sample pH between 1 and 2. The most common are strong oxidizing agents, $[S_2O_8]^{2-}$, H_2O_2, $[MnO_4]^-$, Ce^{IV}, and $[Cr_2O_7]^{2-}$, combined with inorganic (HCl, HNO_3, $HClO_4$, H_2SO_4) or with some suitable organic acids (lactic, tartaric, malic, oxalic, citric) or with suitable buffers (citrate, acetate) (Chapter 12 in ref. [1]). The most common explanation of this behavior is that Pb^{IV} is the most suitable species from which to generate plumbane. An attempt to synthesize plumbane from Pb^{II} gave Pb^0 as the main product, as reported in the pioneering work of Jolly [9]. Therefore, the most accepted conclusion is that Pb^{II} must be oxidized to Pb^{IV}, which is difficult to maintain in solution, and the presence of complexing agents (chloride, bromide, organic acid) may be helpful in this respect. The possible role of the oxidant should be revised on the basis of evidence reported by Nerin et al. [179]. They found that the presence of the oxidant is necessary for the efficient generation of plumbane, independent of the oxidation state of lead. The efficient generation of plumbane from Pb^{IV} compounds [PbO_2, $Pb(CH_3COO)_4$] required the presence of an oxidant (H_2O_2). In the absence of the oxidant, the sensitivities were lower by a factor of 20 to 30, and similar to those obtained using Pb^{II} compounds in the absence of the oxidant. The presence of the oxidant is not necessary when using additives such as nitroso-R salt (disodium 3-hydroxy-4-nitrosonaphthalene-2,7-disulfonate) [180], PAN-S {5-hydroxy-6-[(pyridine-2-yl)azo]naphthalene-2-sulfonic acid} [181] and $K_3Fe(CN)_6$ [182]. In particular, the relatively low reduction potential of ferricyanide ($E° = 0.36$ V), and the absence of suitable oxidizing properties of PAN-S indicates that only oxidation of Pb^{II} to Pb^{IV} cannot explain the role of additives in the generation of plumbane.

A recent study on the role of $K_3Fe(CN)_6$ in plumbane generation [63] was conducted using a chemifold similar to that reported in Fig. 6: THB and $K_3Fe(CN)_6$ were mixed in T_1, allowed to react in the mixing loop, then Pb^{II} solution was merged with the reaction solution in T_2. Taking into account the kinetics of reduction of hexacyanoferrate(III), the pH and the effective residence time in the mixing loop, it has been possible to estimate the concentration of $K_3Fe(CN)_6$ remaining at the end of the mixing loop, before it merged with Pb^{II}.

In many cases, it has been possible to observe strong signal enhancement due to an improved plumbane generation when the hexacyanoferrate(III) was completely reduced at the end of the mixing loop. Experiments conducted in the absence of $K_3Fe(CN)_6$ with the same mixing sequence did not result in any signal enhancement; as well, $K_4Fe(CN)_6$ did not produce any signal enhancements. The conclusions are that the strong enhancement produced by $K_4Fe(CN)_6$ in the generation efficiency of plumbane by reaction of aqueous THB with Pb^{II} is due to the formation of particular hydridoboron intermediates. These intermediates are formed by reaction of $K_3Fe(CN)_6$ with THB and cannot be obtained by simple hydrolysis of THB in pure aqueous solution. The other hypotheses considering Pb^{II} oxidation to Pb^{IV} or formation of lead complexes with $K_4Fe(CN)_6$ or $K_3Fe(CN)_6$ can be ruled out in the light of experimental evidence that has been collected [63].

5.9.3 Germane and bismuthane generation

Brindle and Ceccarelli Ponzoni [175] found that $(NH_4)_2S_2O_8$ produced enhancement of generation efficiency and good control of interferences during the generation of germane by reaction of inorganic Ge^{IV} with THB. Both the effects were explained by the oxidizing action of the additive. For generation of germane, it has been proposed that the germanium-containing polymers $(GeH_x)_n$, which can be formed by reaction with THB, can be rapidly oxidized by $(NH_4)_2 S_2O_8$ back to Ge^{IV}, which is converted to GeH_4 by THB. A similar interpretation was given for the control of interference, wherein $(NH_4)_2S_2O_8$ was considered to act by maintaining interfering elements in their higher oxidation states.

For generation of bismuthane by reaction of Bi^{III} with THB (1 mol L^{-1}, HCl or HNO_3), the effect of 10^{-3} mol L^{-1} concentrations of $K_3[Fe(CN)_6]$, Fe^{III}, Mo^{VI}, KSCN, and $KMnO_4$ was to eliminate the formation of black particulate (assumed to be elemental Bi) which is responsible for the severe curvature and rollover of calibration curves [56]. GC-MS experiments with $NaBD_4$ in H_2O solutions indicated that the presence of additives did not affect the direct transfer of H from boron to bismuth. Atomic absorption spectrometry using a continuous-flow reaction system (CF-CHG-AAS) and different mixing sequences and reagent reaction times suggest that additives act by preventing the formation of Bi^0 through the formation of reaction intermediates which evolve toward the formation of BiH_3 at elevated concentration ratios of Bi^{III} and $NaBH_4$.

6. CHG: FUTURE PERSPECTIVES

At least two considerations can be made in the light of the fundamental aspects of CHG discussed in the previous sections.

The first concerns the use borane complexes alternative to THB. As reported in Fig. 5 and discussed in Section 4.2, the effectiveness of THB in strongly acidic media is much lower than expected based on the value of the rate constant for acid hydrolysis. This is because the first of the four hydrides is lost very quickly and cannot play an effective role in CHG. In this condition the resulting BH_3 complexes and their decomposition products are the effective derivatization species. Therefore, some of the more reactive amine boranes, mainly the primary amine complexes, could be a useful alternative to THB. The reactivity of borane complexes toward the analytical substrate should be modulated properly. The use of borane complexes possessing an exceeding reactivity toward a given analytical substrate can favor the occurrence of unwanted side reactions, which can generate interference effects. The modulation of reactivity can be made by an appropriate choice of the borane complex and/or by controlling the reaction with suitable additives.

The second concerns the use of mixing sequences between the sample and the other reagents necessary to achieve an efficient CHG (acid, borane complex, additives). In this case, the use of continuous-flow apparatus is mandatory for the control of reaction sequences and reaction times. In most of the analytical applications of CHG, the almost unique mixing sequence is the mixing of the sample solution (containing the acid and the additives, if any) with the borane reagent. The numerous studies using different mixing sequences and reaction times for diagnostic purposes indicate that the CHG process could be optimized by using a much better control of the mixing sequences and reaction times. A premixing of borane reagents with the acid or additives for a controlled time can generate borane complexes that react selectively with the analyte, minimizing side reactions and interferent effects. The same can be said for those additives that can present favorable masking features toward interference but cannot be used because they form complexes with the analytical species which are not efficiently converted to hydride following reaction with the borane. Many other examples could be reported but, in light of the evidences reported on the complexity of the mechanisms governing CHG, it is worth trying and optimzing any mixing sequences among reagents. The final ideal results are the achievement of experimental conditions under which the selective generation of analytical species is achieved in complex, real sample matrices.

7. LIST OF ABBREVIATIONS AND SYMBOLS

It is worth noting the difference between $[BH_4]^-$, which is the THB ion, whereas $[BH_4^-]$ is the amount concentration of the THB ion.

AAS	atomic absorption spectrometry
AB	ammonia borane, $BH_3(NH_3)$
ABC	analyte borane complex
CBH	cyanotrihydridoborate(1–), $[BH_3CN]^-$
CF	continuous flow
CHG	chemical generation of volatile hydrides
DMAA	dimethylarsinic acid, $(CH_3)_2As(O)(OH)$
DMAB	dimethylamine borane, $BH_3(Me_2NH)$
E	semimetal or non metal atom
E°	standard reduction potential
ESI-MS	electrospray ionization-mass spectrometry
GC-MS	gas chromatography-mass spectrometry
HA	generic acid
k	rate constant
K	equilibrium constant
L	neutral or anionic ligand
M	metal atom
MS	mass spectrometry
MS^n	multiple-stage mass spectrometry experiment recording n^{th} generation product ions
MMAA	monomethylarsonic acid, $CH_3As(O)(OH)_2$
NMR	nuclear magnetic resonance
R	alkyl group
TBAB	*tert*-butylamine borane, BH_3(*tert*-butylNH_2)
TDB	tetradeuteridoborate(1–), $[BD_4]^-$
THB	tetrahydridoborate(1–), $[BH_4]^-$
TU	thiourea
UV	ultraviolet
VIS	visible
X, Y	neutral or anionic ligands

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