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Behavior and kinetic of hydrolysis of amineboranes in chemical vapor generation at elevated acidities

Lucia D'Ulivo¹, Roberto Spiniello², Massimo Onor², Zoltan Mester¹, Alessandro D'Ulivo^{2*}

Abstract

Chemical vapor generation (CVG) of volatile derivatives is one of the most powerful sample introduction techniques for ultra-trace element determination in atomic and mass spectrometry. Tetrahydridoborate (THB) salts have been mostly employed as reagents for aqueous phase derivatization. On the other hand, amine-boranes found a few analytical applications in CVG. The limited use of amino-boranes is probably related to their kinetic constants for hydrolysis, which are 5-8 folds lower than those of THB. Consequently, a borane reagent which is characterized by a low reaction rate toward H_3O^+ would be also slow in the reaction with the analytical substrates.

Some recent evidences suggested that in strongly acidic aqueous solutions (5-10 M HClO_4 or HCl) borane ammonia may undergo hydrolysis by generating a first mole of hydrogen, before the displacement of the ligand.

This paper reports on a study for a better insight into the mechanism of hydrolysis of amine-boranes complexes, under conditions which are typically employed for trace element determination by CVG.

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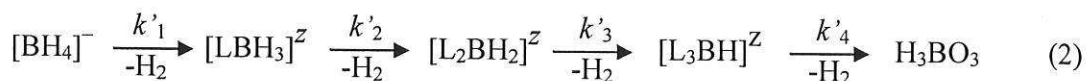
1. Introduction

Chemical vapor generation of volatile derivatives, hydrides and /or free atoms, of the heavier elements of the Groups 14-16 and of the elements of Group 12 is one of the most powerful sample introduction techniques for ultra-trace element determination in atomic and mass spectrometry [1,2]. Aqueous phase derivatization with tetrahydridoborate (-1) (THB) salts, MBH_4 ($\text{M}=\text{Na}, \text{K}$), have been employed as the reagents in almost all cases and their use have been expanded to the CVG of some transition and noble metals [2]. In spite of the relatively fast hydrolysis of THB in aqueous solution, which requires alkaline stabilization and cold storage, only few papers are devoted to the use alternative borane reagents in CVG which are more stable to hydrolysis as borane amine complexes, [3,4,5,6,7,8]. Both THB and amine-boranes undergo hydrolysis according a second order kinetic:

$$-\frac{d[\text{BH}_3\text{X}^z]}{dt} = k_{H^+} [\text{BH}_3\text{X}^z][\text{H}_3\text{O}^+] \quad (1)$$

($\text{X} = \text{H}$, $z = -1$ for THB; $\text{X} = \text{NH}_3$, *tert*butyl NH_2 , Me_2NH , $z = 0$ for amine-boranes;)

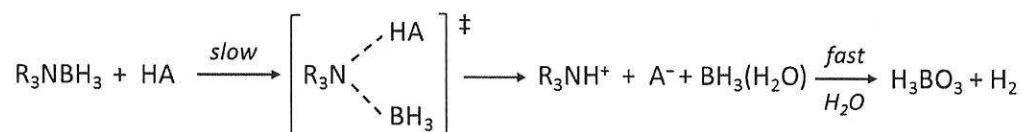
Due to their different rate of hydrolysis, which are about from 5 to 8 orders of magnitude lower than that of THB [9], amine-boranes found some useful applications in mechanistic study on CVG [3,5,6], whereas there are few analytical applications in CVG [4,7,8]. The limited usefulness of amine-boranes in CVG has been addressed to the correlation between the reaction efficiency and second order rate constant of hydrolysis, which has been verified for the most reactive substrates, Hg^{II} and Sb^{III} in 1M HCl reaction media [4]. It follows that a borane reagent which is characterized by a low reaction rate toward H_3O^+ would be also slow in the reaction with the analytical substrates. However, the use of kinetic data for the hydrolysis of boranes in aqueous media must be considered with some cautions because they are obtained under a limited range of acidities and solution composition, which are in most of cases very different from the condition employed in analytical CVG. In the case of THB strong deviations from kinetics and mechanism of hydrolysis are reported both in strongly alkaline and acidic media [9, 10,] and this can be addressed to the stepwise mechanism of hydrolysis of THB. In the hydrolysis of THB, the four moles of hydrogen are generated stepwise and with different rates and, simultaneously, $[\text{BH}_4]^-$ is converted to H_3BO_3 through hydridoboron intermediates of the type $[\text{L}_x\text{BH}_{4-x}]^z$ ($\text{L}=\text{H}_2\text{O}, \text{OH}^-$ etc, $x=1-3$ and $z = 0, +1, -1$) according to the sequence:



where k'_1 , k'_2 , k'_3 and k'_4 are the rate constants for each of the steps of hydrolysis. The stability of the hydridoboron intermediates toward hydrolysis increases with decreasing number of hydrogen atoms bound to boron, $k'_1 > k'_2 > k'_3 > k'_4$ [5]. In agreement with the kinetic laws reported for the different hydridoboron species involved in the hydrolysis of THB [6,11], only two species, $[\text{BH}_4]^-$ and, to a much lesser extent $\text{BH}_3(\text{H}_2\text{O})$, have a rate of hydrolysis which is dependent on acidity. For the Brønsted acid catalysed hydrolysis of amine-boranes:

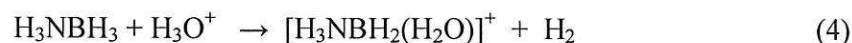


the accepted mechanism for hydrolysis is the displacement of the ligand following the protic attack [12,13,14] as better detailed in Scheme 1.



Scheme 1 – Brønsted acid-catalysed hydrolysis of amine-boranes. [14].

Some recent evidences suggested that in strongly acidic aqueous solutions (5-10 M HClO_4 or HCl) borane ammonia may undergo hydrolysis according a different reaction pathway from that reported in Scheme 1. In particular, the most interesting evidence is that in strongly acidic conditions a first mole of hydrogen is generated before the displacement of the ligand [5]:



It does not appear that further studies on the kinetic of acid-catalyzed hydrolysis of amine-boranes have been reported in the literature after those of Kelly and coworkers [12,14,**Error! Bookmark not defined.**,**Error! Bookmark not defined.**], and Ryschkewitsch [13], which brought to the presently accepted Brønsted acid-catalysed hydrolysis of borane amines (Scheme 1).

Moreover, the unexpected behavior of some amine-borane complexes in the CVG of hydrogen selenide at trace level, under strongly acidic conditions, stimulated more investigations. This paper reports on a study for a better insight into the mechanism of hydrolysis of amine-boranes complexes, under conditions which are typically employed for trace element determination by CVG.

2. Experimental

2.1. Reagents

Borane-ammonia (AB), borane *tert*-butylamine (TBAB) and borane dimethylamine (DMAB) complexes (assay 97%) and NaBH₄ (THB) (assay 98%) were from Sigma-Aldrich. NaOH (Pellets, 98%) was from Fluka Chemika, Sigma-Aldrich. Stock solution of 1000 mg L⁻¹ of selenite (H₂SeO₃ in HNO₃, AS standard solution), was from Fluka. Analytical grade inorganic acid, 37% HCl, 65% HClO₄ and 96% H₂SO₄ (RPE-for analysis) was from Carlo Erba. Stock solutions of 10 % NaBH₄ were prepared in 1 mol L⁻¹ NaOH and stored at 4 °C. NaBH₄ solutions were prepared daily by appropriate dilution of the stock solution. In all the working solutions of amine-boranes and NaBH₄, the final concentration of NaOH concentration was 0.05 M. 1M DMAB solution for DART experiments was prepared in ultrapure water. Ultrapure water was generated in house with a Barnstead™ Genpure purification system (Thermo Fisher Scientific, Canada).

2.2. Apparatus and measurements

2.2.1. CVG of hydrogen selenide

The efficiency of generation of hydrogen selenide was tested using a continuous flow reaction system coupled with atomic absorption spectrometry as reported elsewhere [5]. Sample and reductant solution flow rates are 4 and 2 mL min⁻¹, respectively, and the reaction loop is 3.9 mL (Teflon PFA, 1.5 mm i.d.). The absorbance, S₀, obtained by reduction of 0.2 mg L⁻¹ Se^{IV} in 4M HCl with 0.2 M THB was taken as reference signal, in consideration that ⁷⁵Se radiotracer studies indicated an almost quantitative conversion (>95%) of selenite to hydrogen selenide [15]. The absorbance ratio S/S₀ was taken as a measure of the generation efficiency of hydrogen selenide.

2.2.2. Rate of hydrogen gas evolution

The rate of hydrogen gas generated by the hydrolysis of amine-borane complexes was monitored using a modified version of the laboratory-made thermostated cell described previously [5]. The cell was realized in borosilicate glass (17.5 ml total volume) and was equipped with an injection port and pressure sensor (DS Europe, model LP625-1, 3.5 bar full scale). The measurements were performed by placing 2.0 mL of aqueous solution at different acidities and compositions (0.1, 0.5, 5.0 M HCl or HClO₄, 0.1M acid+0.1 M L-cysteine) in the cell. A 1 mL plastic syringe was loaded

with 0.5 mL of water followed by 0.5 mL of amine-borane solution (0.2 M for both AB and TBAB, 0.5 M for THB and 1M for DMAB, all prepared in 0.05 M NaOH). A schematic representation of the apparatus is showed in Figure 1. This particular loading sequence allows complete and reproducible injections, avoiding that an uncontrolled amount of amine-borane solution remains in the injection port. Then, the syringe was placed into the injection port, which comprised a check valve to avoid pressure losses. The solution was left under magnetic stirring for 5 min. After baseline stabilization, the pressure signal acquisition was started and the THB/amino-borane solution was injected, under constant stirring. The pressure signal was acquired for 30 min at 10 s^{-1} . The maximum pressure, P_{∞} , was reached in 5M strong acid solution at reaction times of about 150, 250 and 600 s for AB, TBAB and DMAB, respectively. P_{∞} remained constant until the end of the acquisition.

2.2.3. Mass spectrometric measurements

Mass spectrometric identification of reaction intermediates were performed by using DART (direct analysis in real time) ion source (IonSense, Saugus MA, USA) which was placed 17 mm away from the orifice of a LTQ linear ion trap-Orbitrap mass spectrometer working in positive ion mode (Thermo Fisher Scientific Inc., Bremen, Germany). The mass spectrometer was tuned and calibrated according to the manufacturer's operating instructions. The DART functioned using helium as carrier gas at 3.5 mL/min. Operating temperature was set at 200 °C and all other DART operating conditions were standard settings: needle current = 9990 mA; needle voltage = 2500 V; discharge electrode current = 7 mA; discharge electrode voltage = 149 V; grid electrode current = 10 mA; grid electrode voltage = 249 V. A DIP-it™ glass stick (IonSense Inc., USA) was dipped in 1M of DMAB solution to collect a DART scan of the unreacted compound. 0.5 mL of 1M DMAB was then placed into a 10 mL glass vial containing 2 mL of 5M, 0.5M or 0.1M HCl, under constant stirring. The solution was sampled with a glass stick and exposed to the DART ion current at time intervals ranging from 10 to 480s. Signal acquisition was performed with Xcalibur Thermo Tune Plus software (Thermo Fisher Scientific). The signal acquisition was started about 30 s before sample exposure and terminated about 30 s after sample removal from the ion source.

2.3. Kinetic calculations

Expected rates of hydrogen evolution were calculated only in those case in which the acidity of the solution can be considered almost constant during the early stage of hydrolysis, namely with 5M

acid and cysteine buffer, and the pseudo first order approximation applies to equation 1. The relation between the kinetic of hydrogen evolution and the kinetic of amine-borane hydrolysis is given by $x(t) = 1 - y(t)$, where $x(t)$ is the fraction amount of hydrogen evolved and $y(t)$ is the fraction amount of borane amine hydrolyzed at time t . It follows that $x(t) = 1 - e^{-k_H^+[H^+]t}$, where k_H^+ is the second order rate constant of hydrolysis. The values of k_H^+ employed, $6 \text{ L mol}^{-1} \text{ s}^{-1}$ for AB[16], $0.87 \text{ L mol}^{-1} \text{ s}^{-1}$ for TBAB [17] and $9.7 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ for DMAB, are available in the literature, [Error! Bookmark not defined.]. Assuming an ideal gas behavior for hydrogen $x(t) = P/P_\infty$, where P is the pressure measured at time t and P_∞ is the maximum pressure measured after complete hydrolysis of amine-borane (reaction 3), we obtained:

$$\frac{P}{P_\infty} = 1 - e^{-k_H^+[H^+]t} \quad (5)$$

which allows the comparison between experimental and calculated rate of hydrogen generated during the hydrolysis of the investigated amine-boranes.

Concentration of H^+ was considered equal to the stoichiometric concentration of the acid. The initial acid concentration after mixing of the reagents (2 mL acid + 1mL borane solution, section 2.2.2.) is 3.33M for experiments with 5M acid. For cysteine buffer, considering that the reported value of pK_{a3} span from about 1.7 to 2.4 at 25°C [18], the concentration of H^+ were calculated at two different values of pK_{a3} , 1.9 and 2.0.

3. Results and discussion

3.1. Reduction curves in CVG of hydrogen selenide

The reduction curves (absorbance signal vs borane concentration at a given acid concentration) reported in Figure 2 were obtained in the course of optimization studies on the CVG of H_2Se . Figure 2 illustrates the reaction of trace-level inorganic Se(IV) with aqueous solution of THB and amine-boranes, AB and TBAB, in strongly acidic conditions, . These reduction curves were found interesting both for the reactivity of CVG using aqueous boranes and from the analytical point of view.

The results reported in Figure 2 indicate an unexpected behavior in the reactivity of CVG. In the lower concentration range of borane reagent ($<0.005\text{M}$ borane for HCl media, $<0.05\text{M}$ borane for both $HClO_4$ and H_2SO_4 media) the reaction efficiency follows the trend $TBAB > AB > THB$. This is an opposite trend to that expected on the base of the evidences on the CVG of both inorganic Hg^{II} and Sb^{III} in 1M HCl media [5], where the reaction efficiencies increased with the second order rate

constant of boranes (THB = $1.0 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ [19], AB = $6 \text{ L mol}^{-1} \text{ s}^{-1}$ [Error! Bookmark not defined.], TBAB = $0.87 \text{ L mol}^{-1} \text{ s}^{-1}$ [Error! Bookmark not defined.]). The different trends of the reduction curves for HCl reaction medium, with respect to HClO_4 and H_2SO_4 , could be due to the complexity capacity of chloride, which can form complexes that modify the structure of both analytical substrate and borane. In this respect sulfate and, in particular, perchlorate can be considered non complexing anions.

From the analytical point of view the results obtained with HClO_4 and H_2SO_4 indicates the possibility to approach quantitative reaction efficiency of H_2Se (> 80%) with low concentrations of TBAB (0.02-0.05 M). This aspect will be not further considered in this paper and the attention will be focused on the reactivity of aqueous boranes.

3.2. Rate of hydrogen generation by hydrolysis of THB and amine-boranes

The behavior of aqueous boranes to acid hydrolysis was investigated by monitoring the rate of evolution of the hydrogen that is formed during the borane hydrolysis. The study was performed on THB, AB, TBAB and DMAB that were hydrolyzed in the acid media typically employed in CVG. The results are reported in Figure 3 for THB and in Figure 4 for AB, TBAB and DMAB.

3.2.1. Hydrolysis of THB

The experimental rates of hydrogen generated during THB hydrolysis are reported in Figure 3. As reported in previous studies [5], the rate of hydrogen evolution in 0.5 and 5M reaction media is much lower than expected. The same conclusion applies for cysteine buffered media ($\text{pH} \approx 2$). According to equation 5, at $\text{pH} \geq 4$ the hydrolysis of THB should be almost quantitative for the reaction time of 0.1 s, because the relative pressure of hydrogen evolved is $P/P_\infty \geq 99.9\%$. It follows that all THB should be hydrolyzed just during the mixing step (mixing time about 0.5 s) of the reagents. The formation of borane cations (e.g. $[\text{BH}_2(\text{H}_2\text{O})_2]^+$) which are more resistant to acid hydrolysis is considered the reason of this behavior [5, 10, 20].

The hydrolysis of THB in unbuffered 0.1 M reaction media represents a case in which the pH change dramatically during the reaction, starting at pH of about 1.2 and reaching $\text{pH} \approx 8$, within 2 s after reagent mixing, then approaching slowly toward the alkaline pH of borate buffer (9.2-9.8) [21]. The marked difference between HCl and HClO_4 media is probably due to the complexing capacity of chloride which could be able to modify the coordination sphere of boron during hydrolysis. The effect of complexing species could be even more evident in the case of cysteine

buffer. In this case the combined action of cysteine and chloride is able to slow significantly the rate of hydrogen evolution generated from the hydrolysis of THB in 0.1 M cysteine + 0.1M HCl media, with respect to 0.1 M HCl media. The opposite behavior is observed with 0.1 M cysteine + 0.1M HClO₄ reaction media, where only cysteine can modify the hydrolysis rate of THB.

The formation of a borane complex with donor species (i.e. thiols, HS⁻, carboxylate anions etc.) was demonstrated experimentally by ¹¹B-NMR experiments [9,10]. This evidence has been used to support that, also in analytical CVG reaction systems, the chemical additives can control the reactivity by interacting with both the analytical substrate and/or the borane reagent [9,10].

The results here obtained with or without cysteine at 0.1M HCl or HClO₄ initial acidity, are obtained under real analytical conditions. They represent a convincing evidence about the role that the chemical composition of a reaction matrix (type of acid, chemical additives) can play in the modification of the reactivity and, most probably, also the structure of the borane reagent and/or of its intermediate (reaction 2).

3.2.2. Hydrolysis of amine-boranes

The experimental rates of hydrogen evolved during the hydrolysis of amine-boranes are reported in Figure 4, whereas Figure 5 reports the rates of hydrogen evolution calculated according reaction 5 (see section 2.3.). The differences among the experimental and the calculated rates of hydrogen evolution are well evident, but some of them cannot be explained by the fact that in some case, i.e. 0.5 and 0.1 M acid concentration, the pH of solution change dramatically during the reaction.

With 5M acid, the concentration of H⁺ remains almost constant during reaction (from about 3.33 to 3.16 M), but it can be observed that hydrogen evolution takes place in two steps. In the first step, a significant fraction amount of hydrogen, from about $P/P_{\infty} = 0.20$ to about $P/P_{\infty} = 0.38$, is quickly generated, while the remaining fraction is released much slower. Considering that the maximum relative pressure of hydrogen, $P/P_{\infty} = 1$, corresponds to the release of three moles of hydrogen, at $P/P_{\infty} \cong 0.33$ we have the release of the first mole of hydrogen. The fact that the change of the slope reported for 5M reaction media takes place at $0.20 < P/P_{\infty} < 0.38$ is an evidence that about one mole of hydrogen is fast released at the beginning of the hydrolysis, similarly to the process described by reaction 4. The formed solvated borane cation $[R_2HNBH_2(H_2O)]^+$ (R=H or Alkyl) hydrolyses slowly, being these type of compounds remarkably resistant to hydrolysis and oxidation [22]. Similarly to the case of THB discussed above, the decreased rate of hydrolysis for amine-boranes can be addressed to the formation of borane cations. The above reported observations, valid

for the hydrolysis of AB [5], can also be extended to TBAB and DMAB, and, in general, to borane complexed with primary and secondary amines.

With both 5M acid and 0.1M cysteine buffer, the pseudo first order approximation is applied to the expected rate of hydrogen evolution (see section 2.3.) Experimental and theoretical rates are compared in Figure 6 for cysteine buffer, and in Figure 7 for 5M acid reaction media. With cysteine buffer, the expected kinetics of hydrogen evolution are in good agreement with the experimental results for TBAB and DMAB. For AB the observed discrepancies could be addressed to the formation of thiolate complexes of the borane substrate with cysteine, which undergo slower hydrolysis than AB. However, both experimental rates reported in Figure 6 for AB are almost perfectly fitted by assuming a $pK_{a3}=2.4$. In general, the results obtained with cysteine buffer confirm that, at moderate pH values, the kinetic data reported in the literature for amine-boranes are able to explain the experimental data, within the relatively high uncertainty of pK_{a3} values.

At extremely high concentration of H^+ (Figure 7) the dramatic discrepancies among expected and experimental kinetics indicated that the mechanism of hydrolysis of borane amines takes place at least in two steps and is different from the mechanism followed under moderate acidic conditions as depicted in Scheme 1.

3.3. Mass spectrometric evidences

Species detected in the Orbitrap are shown in Figure 8. The best S/N was obtained with 0.5M HCl, while more signal suppression was observed with 5M HCl. Detected species of analytical interest were:

- a) m/z 73.08 and 74.08 $[Me_2NHBH(OH)]^+$
- b) m/z 102.13 and 103.13 $[(Me_2NH)_2BH_2]^+$
- c) m/z 107.08 and 108.08 $[Me_2NHB(Cl)(OH)]^+$

m/z 73.08 and 74.08 were detectable in the unreacted DMAB and mostly through all kinetics at 5M, 0.5 and 0.1M, indicating the presence of incompletely hydrolyzed DMAB. On the other hand, m/z 107.08 and 108.08 was only detectable at 0.5 and 0.1M. This specie could be just an unreacted complex of DMAB with Cl^- and OH^- , which was not detectable at 5M because of the low S/N ratio. m/z 102.13 and 103.13 were detectable with 5M and 0.5M HCl only. These masses (b) case) might indicate the formation of the transition specie reported by Stephens *et al.* The b) masses suggest that the amine might remain bounded to the borane during hydrolysis, contrarily to what reported in

scheme (1). Structure b) is only obtainable from the reaction of cation $[\text{Me}_2\text{NHBH})_2]^+$ with amino-borane $\text{Me}_2\text{NH-BH}_3$.

4. Conclusions

In this paper, we investigated the behavior of amino-boranes at elevated acidities. Kinetic experiments, carried out in a pressure cell, demonstrated that hydrolysis proceeds in two steps, where a first mole of hydrogen is lost within the first 10s. Confirmation of the species involved into hydrolysis was obtained with a DART-Orbitrap mass spectrometer. The species characterized suggested a different reaction pathway for the hydrolysis of amino-boranes where the amine remains attached to the borane. This observation can open new perspectives for the applicability of amine-boranes in CVG.

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Figure 1

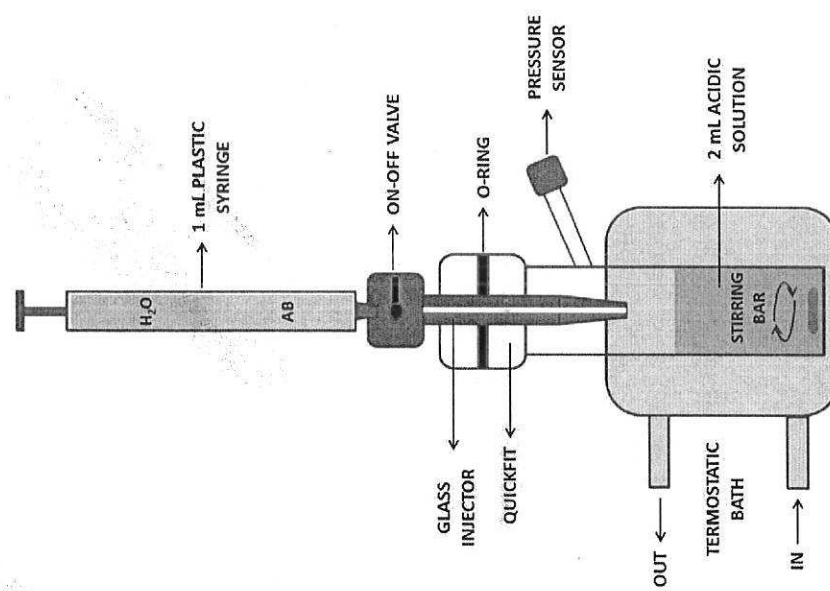


Figure 1 – Schematic representation of the pressure cell used to conduct hydrolysis experiments on amino boranes.

Figure 2

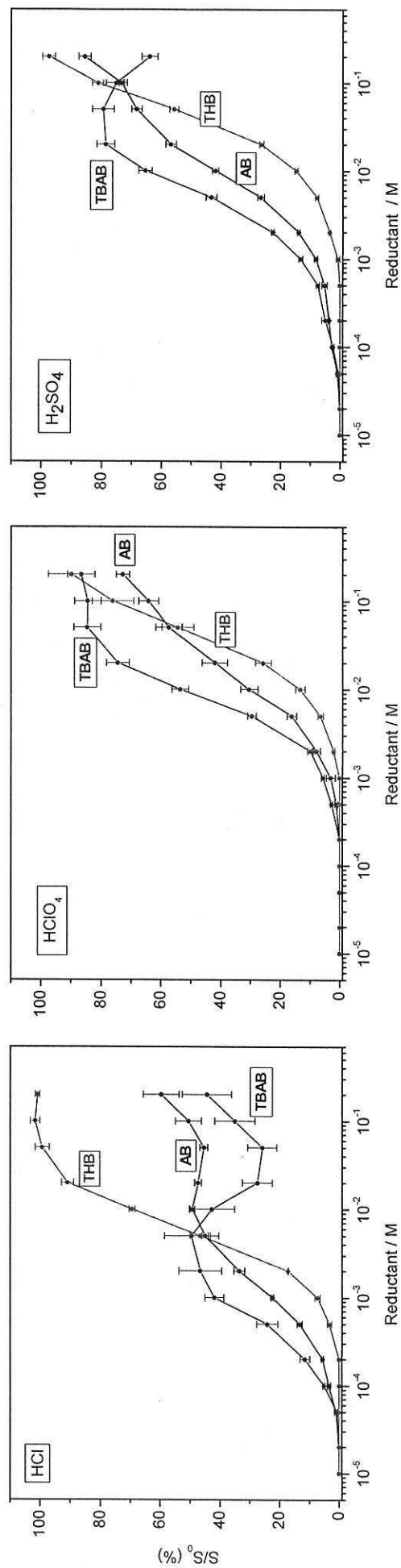


Figure 2 – Reduction curves of Se^{IV} (0.2 mg L⁻¹) to H₂Se by aqueous NaBH₄ (THB), borane ammonia (AB) and borane *tert*-butylamine (TBAB) using different inorganic acids ([H⁺] 5M) in a continuous flow reaction system. Borane concentration varied in the range from 10⁻⁵ to 0.2M.

Figure 3

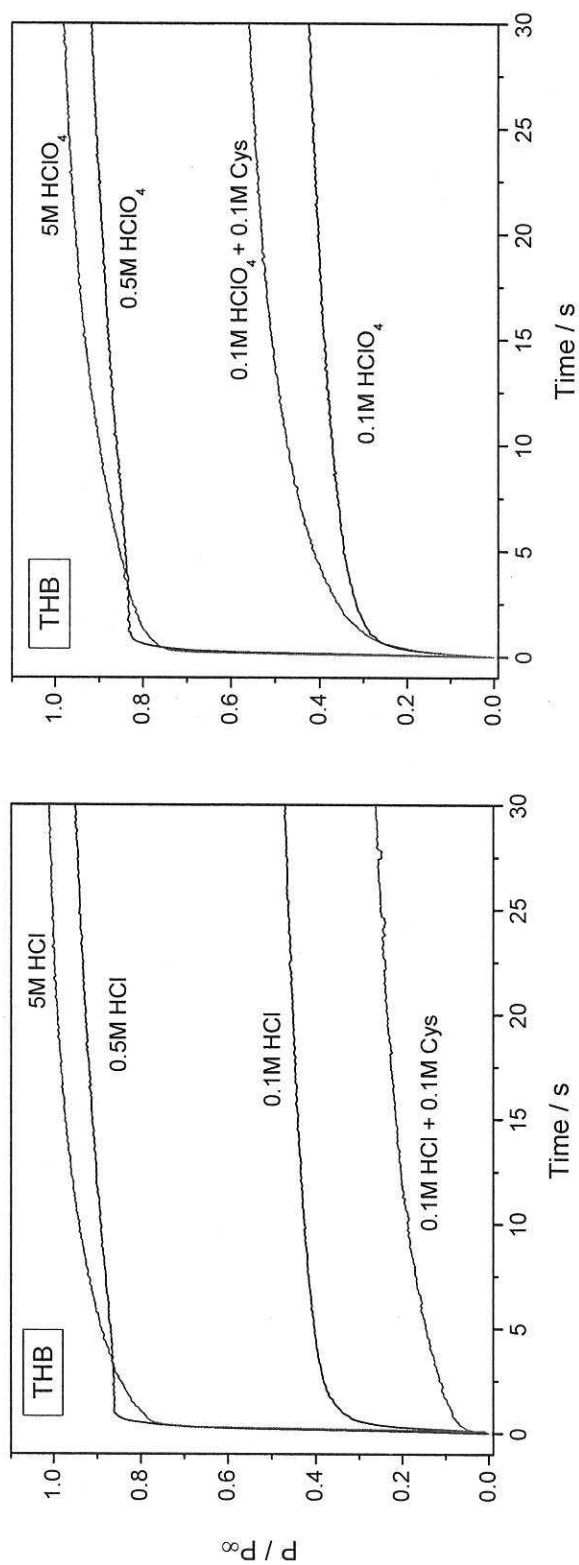


Figure 3 – Relative pressure increase monitored during acid hydrolysis of THB at +25 °C in HCl and HClO₄ media in various acid conditions. [Acid]/[THB] molar ratios are 0.8, 4 and 40 for acid concentration of 0.1, 0.5 and 5.0 M, respectively.

FIGURE 4

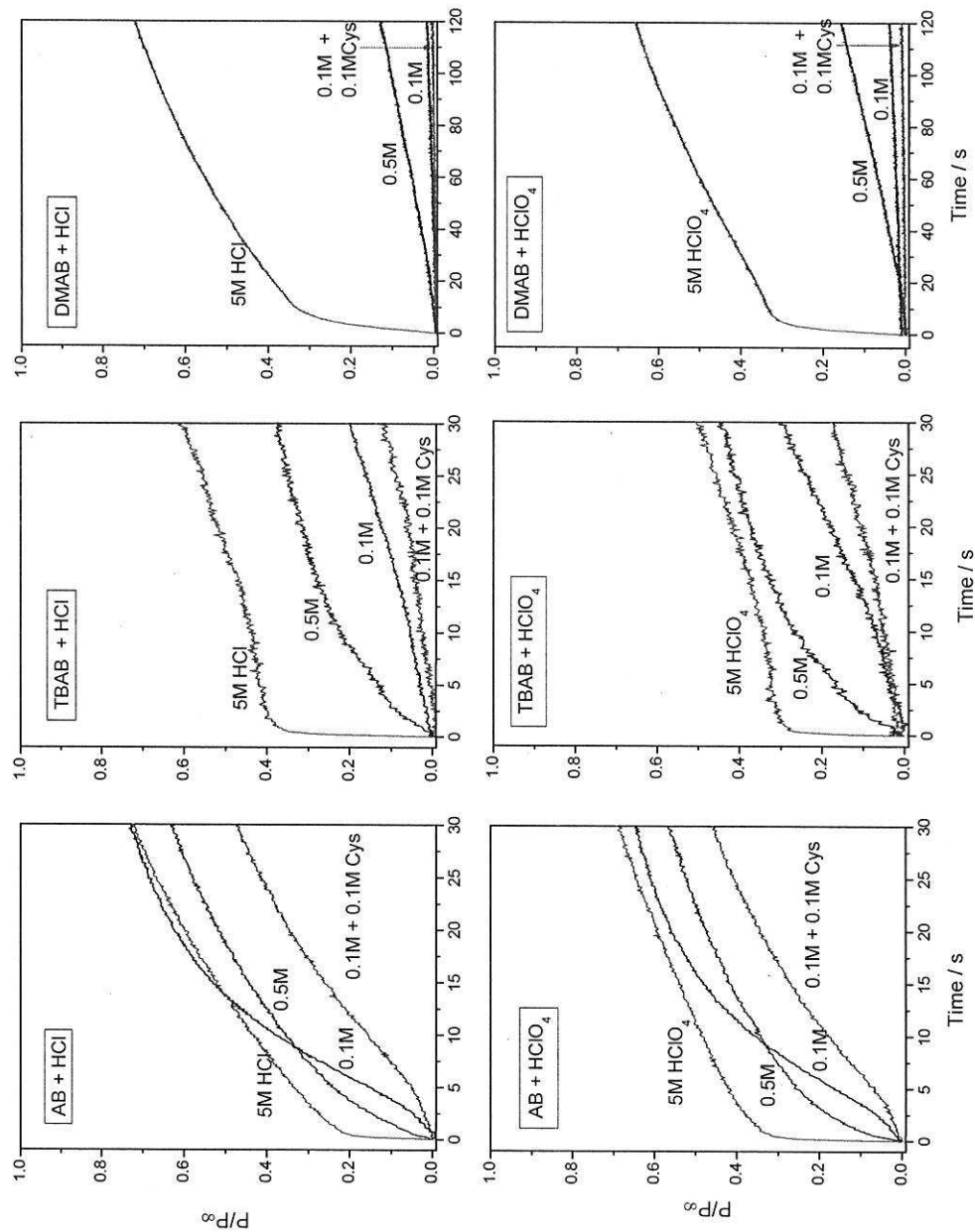


Figure 4 – Relative pressure increase monitored during acid hydrolysis of AB, TBAB and DMAB at +25 °C in HCl and HClO₄ media in various acid conditions.
For AB and TBAB the [Acid]/[Borane] molar ratios are 2, 10, 100 for acid concentration of 0.1, 0.5 and 5.0 M, respectively.
For DMAB the [Acid]/[Borane] molar ratios are 0.4, 2, 20 for acid concentration of 0.1, 0.5 and 5.0 M, respectively.

Figure 5

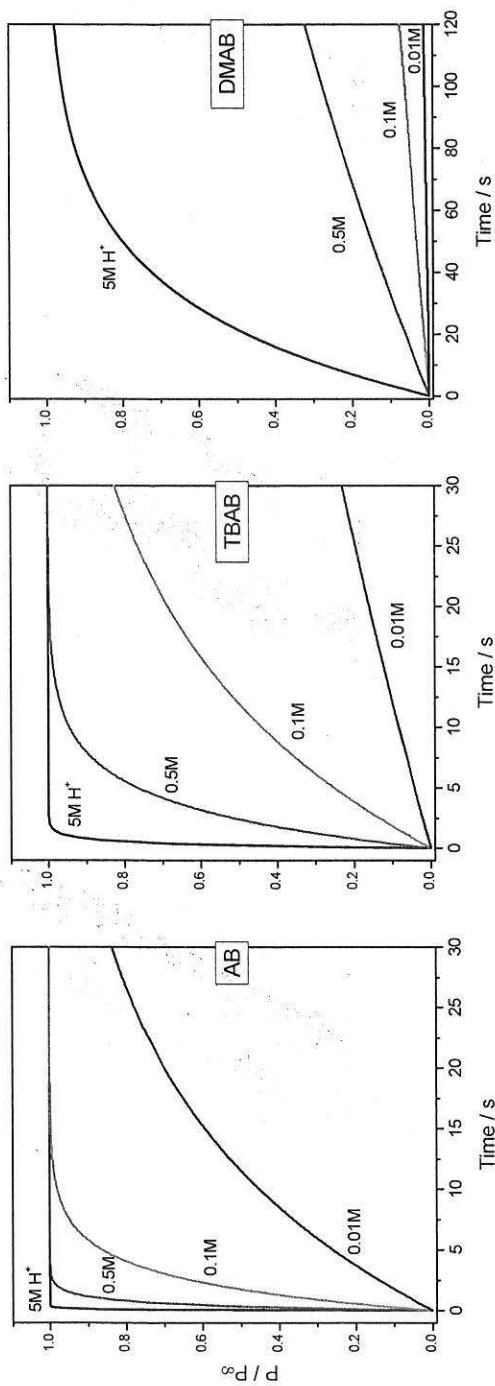


Figure 5 – Rates of hydrogen evolution calculated from equation 5 and rate constants reported in the literature for AB, TBAB and DMAB, at +25 °C. The initial H^+ concentrations used in the computation are 3.33, 0.33, 0.066 and 0.01 M for experiments 5, 0.5, 0.1 and 0.01 M acid concentration (2:3 dilution factor)

Figure 6

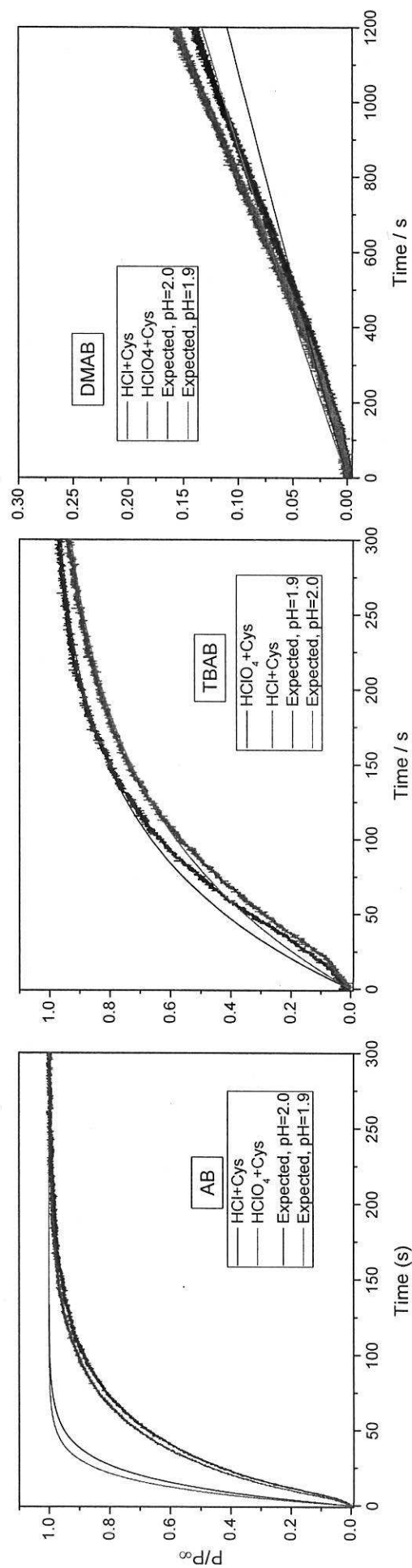


Figure 6 – Relative pressure increase due to hydrogen evolution arising from acid hydrolysis of AB, TBAB and DMAB at +25 °C in 0.1M HCl+0.1M Cys, and 0.1M HCO_4 + 0.1M Cys. Comparison of experimental data with the relative pressure calculated by equation 5 at pH=1.9 and 2.0 Cys buffer.

Figure 7

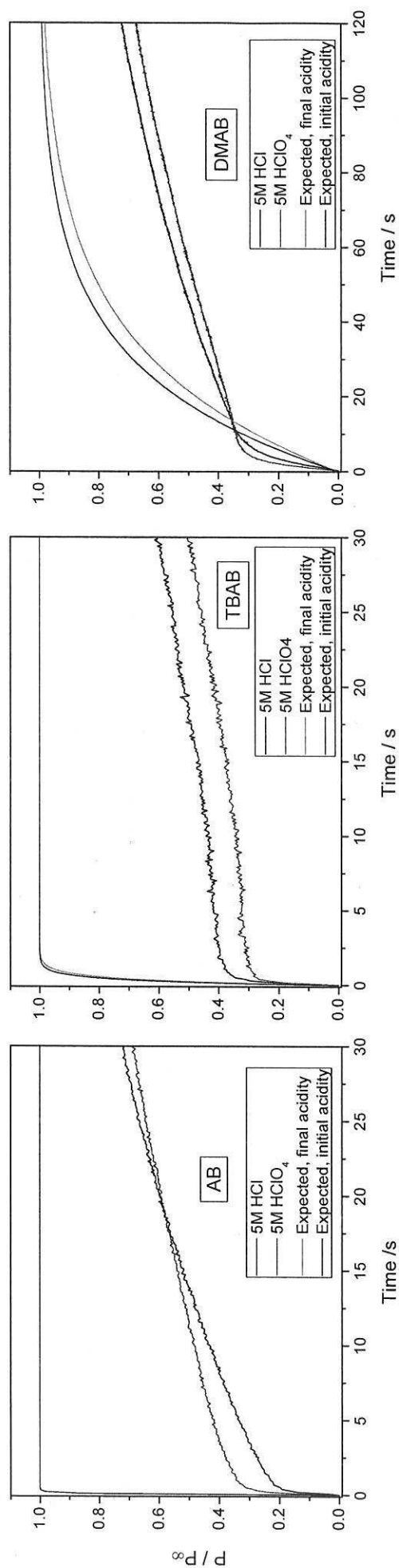


Figure 7 – Relative pressure increase due to hydrogen evolution arising from acid hydrolysis of AB, TBAB and DMAB at +25 °C in 5M HCl and 5M HClO₄. Comparison of experimental data with the pressure expected according to the kinetic law of hydrolysis at the calculated initial and final acidities.

Figure 8

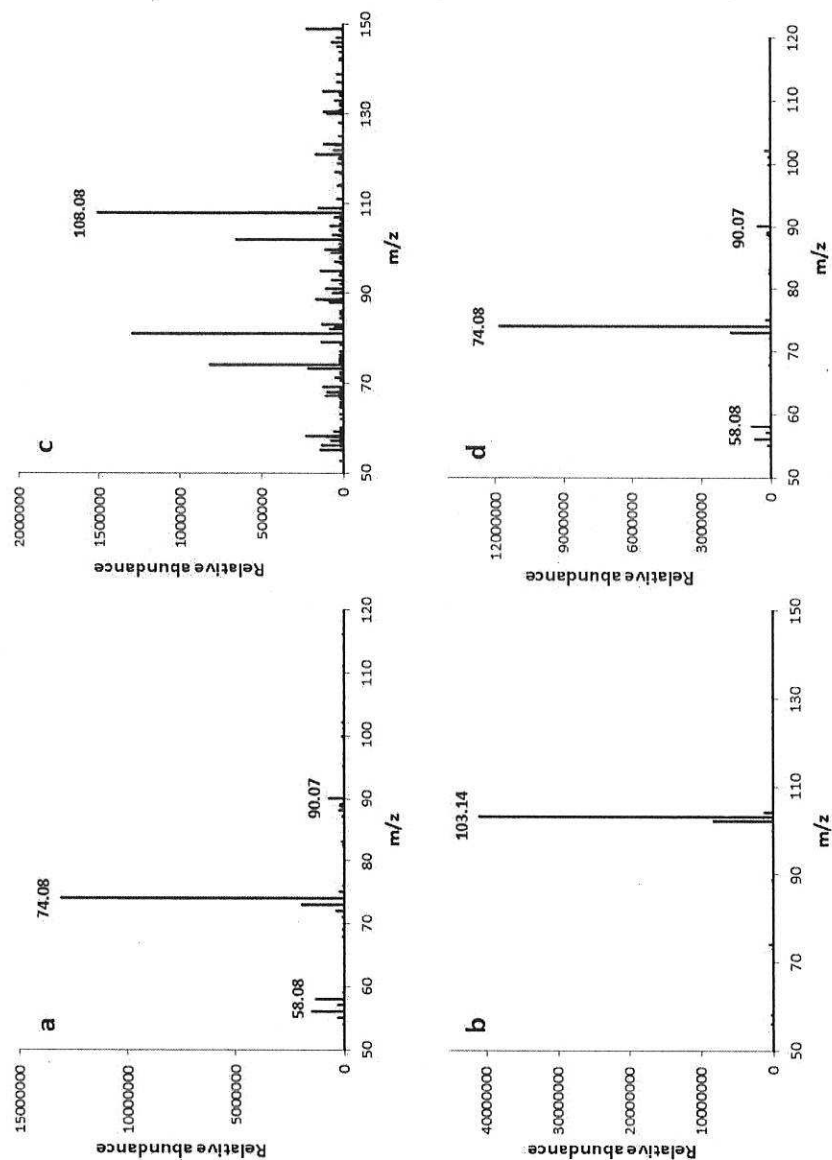


Figure 8 – DART-Orbitrap scans for unreacted DMAB (a), DMAB in 0.5M HCl at 60s, DMAB in 0.5M HCl at 300s, and DMAB in 0.5M HCl at 420s.