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The binomial distribution of hydrogen and deuterium in arsanes, diarsanes, and triarsanes generated from As(III)/$[BH_nD_{4-n}]^-$ and the effect of trace amounts of Rh(III) ions

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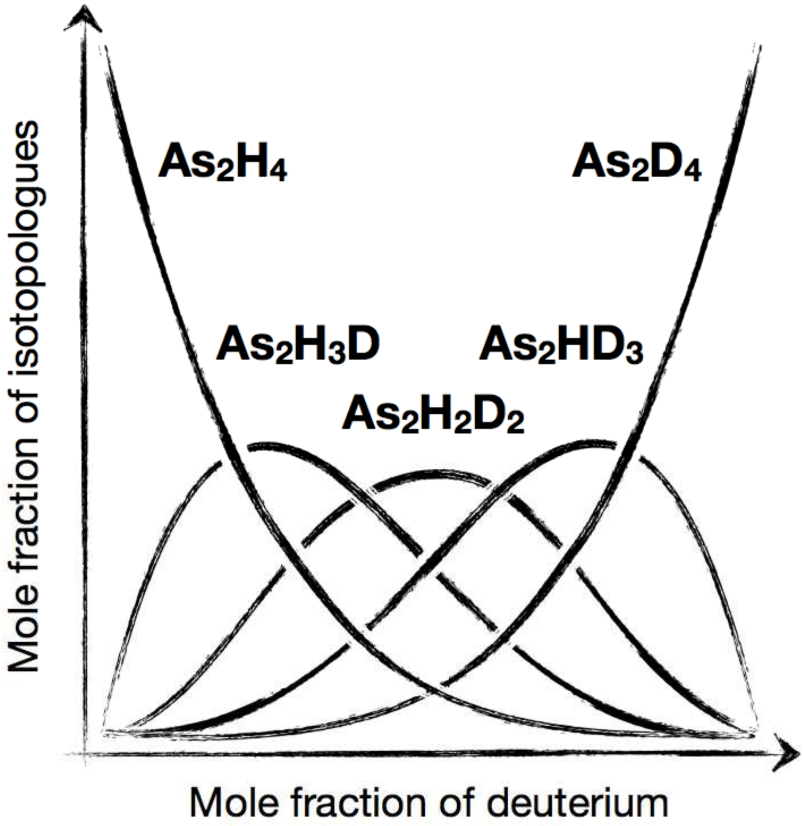
ABSTRACT

Recent studies of the formation of arsane in the borohydride/arsenate reaction demonstrate the occurrence of condensation cascades whereby small quantities of di- and triarsanes are formed. In this study, the isotopic composition of these di- and triarsanes was examined using deuterium labelled borohydrides. A statistical model was employed to construct the mass spectra of all diarsane and triarsane isotopologues ($As_2H_nD_{4-n}$ and $As_3H_nD_{5-n}$) from the mass spectra of isotopically pure compounds (As_2H_4, As_2D_4, As_3H_5, and As_3D_5). Subsequent deconvolution of the experimental mixed spectra shows that incorporation of hydrogen closely follows the binomial distribution, in accord with arsane formation. The H/D distribution in arsane, diarsane and triarsane isotopologues is binomial in the absence of any interference. However, this is significantly altered by the presence of some transition metals and presented here, for the first time, are the effects of Rh(III). The presence of Rh(III) in the As(III)/$[BD_4]^-$ system entails the incorporation of hydrogen into the arsanes arising from the solvent, altering the expected binomial H/D distribution.

Graphic Abstract



INTRODUCTION

Generation of volatile compounds is regarded as one of the most robust analytical tools for determination (and speciation) of trace and ultra-trace levels of numerous elements [1–2]. The main advantage of this technique lies with the possibility of separating the analyte from its matrix in the form of a vapour, thus allowing for better sensitivity, detection power and fewer interferences [2]. Chemical vapor generation using $NaBH_4$ is common practice in analytical chemistry and it finds routine application for the determination of many elements [3]. Furthermore, other boranes, such as $NaBEt_4$ and, more recently, triethyloxonium tetrafluoroborate, have been successfully applied for speciation of organometallic compounds [4] and vapor generation of anionic substrates such as Br^-, NO_3^-, and NO_2^- [5–6]. Despite widespread analytical application of hydride generation, attention to mechanistic aspects of this derivatization reaction has only recently arisen [7–10].

Reaction of inorganic As(III) with $NaBH_4$ occurs *via* a concerted multistep process wherein all hydrogen atoms in AsH_3 arise from different $[BH_4]^-$ molecules [11]. This mechanism, however, is strongly altered in the presence of noble metals such as Au(III), Pd(II), and Pt(II) – their action on hydride generation cannot be completely explained as causing a decrease in the amount of hydride generated *(yield interference)* [12]; they play an active role in the transfer of hydrogen from $[BH_4]^-$ to the arsenic *(mechanistic interference)* [13]. Furthermore, another source of complexity in the formation of arsane arises due to condensation reactions that occur at high substrate concentration; the formation of polyarsanes, such as diarsane (As_2H_4) and triarsane (As_3H_5), is due to a reaction of the form [14]:

$$R_1R_2{-}As{-}OH + H{-}As{-}R_3R_4 \rightarrow R_1R_2{-}As{-}As{-}R_3R_4 + H_2O.$$

Herein we investigate the formation of these polyarsanes generated under non-analytical conditions in the absence and presence of Rh(III) ions. In particular, this work illustrates how complex mass spectra can be deconstructed and interpreted with the aid of simple mathematical models based on molecular symmetry considerations [15–16] so as to infer valuable information about the mechanisms of arsane condensation.

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EXPERIMENTAL

Reagents and Materials

Sodium tetrahydroborate pellets (Alfa Aesar, Ward Hill, MA) and sodium tetradeuteroborate (Cambridge Isotope Laboratories, Andover, MA; $x(\mathrm{D}) = 0.99$) were employed to prepare stock solutions of 0.2 M $NaBH_4$ and 0.2 M $NaBD_4$ in 0.1 M NaOH. In order to vary the deuterium mole fraction in the reducing agent, different mixtures of the above solutions were also prepared. Arsane generation was performed in septum-sealed vials using inorganic As(III) from Oak Ridge National Laboratory (Oak Ridge, TN). Rhodium(III) (1000 mg/L in 10% HCl) was purchased from SCP Science (Baie D'Urfé, Québec) and used for the interference experiments. All other reagents were analytical grade.

GC/MS method

A Hewlett-Packard gas chromatograph (Wilmington, DE) equipped with a Hewlett-Packard 5973 mass spectrometer was operated in splitless mode and fitted with a DB-5 capillary column (30 m × 0.25 mm i.d. × 5 μm). The GC was operated under the following conditions: injector temperature: 160 °C; oven: isothermal at 35 °C for 4 min, 15 °C/min up to 200 °C; transfer line program: initial temperature 150 °C, 30 °C/min up to 250 °C; He gas flow of 1.2 mL/min was chosen. MS detector was working in positive EI at 70 eV (full-scan mode). The pressure of the source was 2 mPa.

Generation of arsane and polyarsanes

For generating arsane and polyarsanes, the following non-analytical procedure was adopted: 1 mL 800 mg/L As(III) in 1 M HCl was transferred to a screw capped vial (4 mL; Pierce Chemical Co., Rockford, IL) fitted with a PTFE/silicone septum. The vial was closed and the headspace flushed with nitrogen. Hydride generation was subsequently performed by injecting 0.2 mL of 0.2 M $[BH_4]^-/[BD_4]^-$ through the septum. GC/MS analysis was achieved by sampling a 0.5 mL volume of the vial headspace.

Interference of rhodium(III) on arsane generation

To test the mechanistic interference of Rh(III) on arsane generation, the following procedure was adopted: 2 mL 1 mg/L As(III) in 1 M HCl + 20 µL 1000 mg/L Rh(III) in 10% HCl were placed into a 4 mL vial. After flushing the headspace with nitrogen, 0.2 mL of 0.2 M $[BD_4]^-$ in 0.1 M NaOH was injected into the solution using a plastic syringe fitted with a stainless steel needle to pierce the septum. A 0.4 mL volume of vial headspace was taken for analysis by GC/MS and the mass spectrum of the generated arsanes was monitored. The same procedure, omitting the spike of the interfering metal, was followed for reference purposes. Four independent replicates of this experiment were performed in order to assess the difference between the mass spectrum of the arsanes generated in the presence and absence of Rh(III).

Health and safety considerations

Due to the toxicity of the gaseous arsanes generated, all experiments should be conducted in a fume hood, and extreme care should be taken to avoid any exposure to these substances.

RESULTS AND DISCUSSION

Mass spectra of arsenic hydride isotopologues show significant overlap, *e.g.*, AsD^+ and AsH_2^+, etc. Moreover, it is not feasible to synthesize pure partially deuterated isotopologues or separate them by conventional gas chromatography. Nevertheless, the determination of the mole fraction of each isotopologue in a mixture can be achieved mathematically by applying a statistical mass balance model [15–16]. Using this method, it was possible to delineate the mechanism of formation of diarsane and triarsane in the As(III)/$[BH_4]^-$ system and to discover a strong perturbation to the mechanism of arsane generation due to the presence of Rh(III).

Statistical model for the mass spectra of $As_2H_nD_{4-n}$ *and* $As_3H_nD_{5-n}$

Statistical reconstruction of partially deuterated hydride has been reported previously for deuterated homologues of diborane [17], methane [18], ethane [19], water, selane [15], arsane, stibane, bismuthane, stannane, and germane [16]. Here, a model proposed by Meija et al. [16] was used for this purpose. For the application of this model to diarsane ($H_2As–AsH_2$) and triarsane ($H_2As–AsH–AsH_2$) it was assumed that the arsenic backbone (As–As; As–As–As) behaves as a virtual super-atom; in this way it is possible to consider diarsane and triarsane as tetra- and penta- hydrides (EH_4 and EH_5). A statistical mass balance method bases the reconstruction of EH_nD_m mass spectra on experimental EH_{n+m} and ED_{n+m} mass spectra. All possible EH_nD_m fragmentation pathways can be written as combinations of events, such as loss of H ($k_{H,i}$), loss of D ($k_{D,i}$), loss of HD ($k_{HD,i}$), loss of H_2 ($k_{H2,i}$), and loss of D_2 ($k_{D2,i}$). For each reaction, a probability coefficient k is assigned (see Fig. 1).

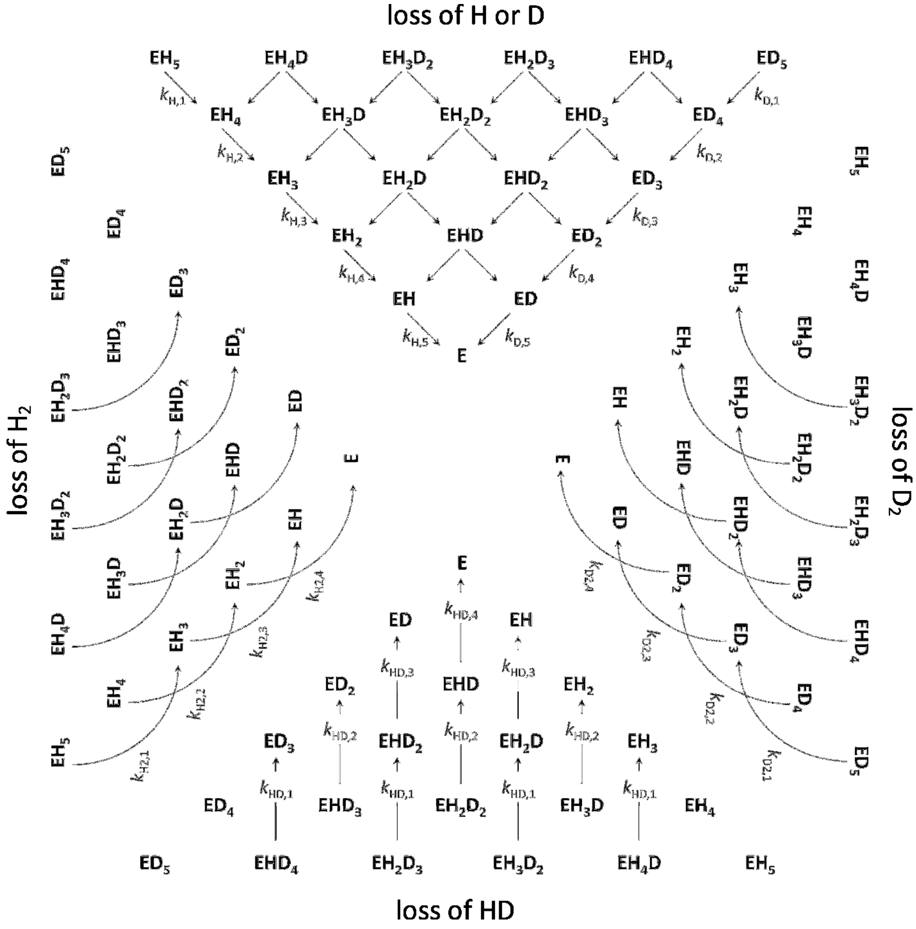

Fig. 1 Deconstruction of the EH_nD_{5-n} mass spectrum. The symbol "E" represents the atom or group of atoms which constitute the backbone of the hydride. In this case E = As_3 and the diagram provides an atlas of all fragmentation pathways for the statistical model for $As_3H_nD_{5-n}$: loss of H or D (top); loss of HD (bottom); loss of H_2 (left); and loss of D_2 (right).

The abundance of a particular molecular ion/fragment ion with composition EH_nD_m can be written as follows:

$$I(\mathrm{EH}_n\mathrm{D}_m) = \left[1 - \sum f_-(\mathrm{EH}_n\mathrm{D}_m)\right] \cdot f_+(\mathrm{EH}_n\mathrm{D}_m) \cdot \tag{1}$$

where $\Sigma f_-(\mathrm{EH}_n\mathrm{D}_m)$ is the sum of all events comprising the fragmentation of $\mathrm{EH}_n\mathrm{D}_m$:

$$\sum f_- = f_{-\mathrm{H}} + f_{-\mathrm{D}} + f_{-\mathrm{HD}} + f_{-\mathrm{H}_2} + f_{-\mathrm{D}_2} \tag{2}$$

$$\sum f_- = \frac{{}_nC_1}{{}_{n+m}C_1}k_{\mathrm{H},i} + \frac{{}_mC_1}{{}_{n+m}C_1}k_{\mathrm{D},i} + \frac{{}_nC_1 \cdot {}_mC_1}{{}_{n+m}C_2}k_{\mathrm{HD},i} + \frac{{}_nC_2}{{}_{n+m}C_2}k_{\mathrm{H2},i} + \frac{{}_mC_2}{{}_{n+m}C_2}k_{\mathrm{D2},i} \tag{3}$$

and $f_+(\mathrm{EH}_n\mathrm{D}_m)$ is the sum of all events comprising the formation of $\mathrm{EH}_n\mathrm{D}_m$ from other ions. For the molecular ion $f_+ = 1$ by definition, whereas for the fragment ions with formula $\mathrm{EH}_n\mathrm{D}_m$ the following can be written:

$$\begin{aligned} f_+(\mathrm{EH}_n\mathrm{D}_m) = {} & f_{-\mathrm{H}}(\mathrm{EH}_{n+1}\mathrm{D}_m)\cdot f_+(\mathrm{EH}_{n+1}\mathrm{D}_m) + \\ & f_{-\mathrm{D}}(\mathrm{EH}_n\mathrm{D}_{m+1})\cdot f_+(\mathrm{EH}_n\mathrm{D}_{m+1}) + \\ & f_{-\mathrm{HD}}(\mathrm{EH}_{n+1}\mathrm{D}_{m+1})\cdot f_+(\mathrm{EH}_{n+1}\mathrm{D}_{m+1}) + \\ & f_{-\mathrm{H}_2}(\mathrm{EH}_{n+2}\mathrm{D}_m)\cdot f_+(\mathrm{EH}_{n+2}\mathrm{D}_m) + \\ & f_{-\mathrm{D}_2}(\mathrm{EH}_n\mathrm{D}_{m+2})\cdot f_+(\mathrm{EH}_n\mathrm{D}_{m+2}). \end{aligned} \tag{4}$$

Therefore, $f_+(\mathrm{EH}_n\mathrm{D}_m)$ is obtained from all precursor fragments, $\mathrm{EH}_{n+\alpha}\mathrm{D}_{m+\beta}$. Using the above recursive equations, it is possible to express the observed abundance of each fragment ion in terms of the probability coefficients k_i. Fig. 1 shows the pictorial representation of all of these events for compounds $\mathrm{EH}_n\mathrm{D}_m$ with $n + m \leq 5$. The numerical values for coefficients k_i are obtained from the mass spectra of the EH_{n+m} and ED_{n+m} compounds. As an example, from the mass spectrum of EH_{n+m}, one can write the following:

$$\begin{aligned} I(\mathrm{EH}_{n+m}) &= 1 - k_{\mathrm{H},1} - k_{\mathrm{H2},1}, \\ I(\mathrm{EH}_{n+m-1}) &= \left(1 - k_{\mathrm{H},2} - k_{\mathrm{H2},2}\right)\cdot\left[k_{\mathrm{H},1}\cdot f_+(\mathrm{EH}_{n+m})\right], \\ \text{where } f_+(\mathrm{EH}_{n+m}) &= 1, \\ I(\mathrm{EH}_{n+m-2}) &= \left(1 - k_{\mathrm{H},3} - k_{\mathrm{H2},3}\right)\cdot\left[k_{\mathrm{H},2}\cdot f_+(\mathrm{EH}_{n+m-1}) + k_{\mathrm{H2},1}\cdot f_+(\mathrm{EH}_{n+m})\right], \\ \text{where } f_+(\mathrm{EH}_{n+m-1}) &= k_{\mathrm{H},1}\cdot f_+(\mathrm{EH}_{n+m}), \\ &\vdots \\ I(\mathrm{E}) &= f_+(\mathrm{E}). \end{aligned} \tag{5}$$

From Eq. (5) it is possible to obtain coefficients $k_{\mathrm{H}i}$ as a function of the observed ion intensities I_i. Unfortunately, considering also the equations arising from ED_{n+m} (for the coefficients $k_{\mathrm{D}i}$), this is always an undetermined system of $2(n + m)$ equations in $2(2n + 2m - 1)$ unknown variables. However, one can assign all the possible combinations in $k_i \in [0; 1]$ to an arbitrary set of $2(n + m - 1)$ values for k_i, and then

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calculate the remaining reaction probabilities from Eq. (5). To estimate the probability of HD elimination, the following formula is used [16]:

$$k_{\mathrm{HD},i} = \frac{k_{\mathrm{H2},i} + k_{\mathrm{D2},i}}{2} \qquad (6)$$

The choice of the arithmetic to estimate the loss of HD is conventional, and no difference in the results is observed if the geometric mean is utilized instead. In addition, all sets of k_i with negative values were discarded in order to obtain physically meaningful results. All sets that satisfy the above condition are then used to reconstruct the mass spectra of the isotopologues. Mass spectra obtained from the various sets of k present no substantial differences and the average results of the constructed mass spectra of $As_2H_nD_{4-n}$ and $As_3H_nD_{5-n}$ isotopologues are given in Tables 1 and 2. As a consequence of the statistical model, the individual k-set values do not reflect any physical properties of the fragmentation. Rather, they represent a mathematical fit consistent with the input data. However, it is possible to select only k-sets which satisfy certain physical properties of the system. For example, one can discard sets with k_H and k_D values differing by more than 50%; This condition is in agreement with the isotopic effect observed in the mass spectra of AsH_3 and AsD_3 and has previously been used for arsanes [16]. The data reported in Tables 1 and 2 were calculated by omitting this condition, which does not alter the resulting mass spectra of di- and triarsanes. However, larger uncertainties are obtained (corresponding to the "worst-case scenario").

Although the statistical model suffers limitations when applied to small molecules (it fails to predict the mass spectrum of HOD with great accuracy [15]), it has proven to be effective for heavier molecules such as selane [15], arsane, stibane, bismuthane, stannane, and germane [16].

In practice it is difficult to obtain a mass spectrum of pure ED_{n+m} from $NaBD_4$ in D_2O and NaOD or DCl. The omnipresence of H_2O in the ambient air inevitably leads to a mixture of ED_{n+m} with traces of EHD_{n+m-1}. For example, a typical mass spectrum of As_2D_4 is

$$\begin{pmatrix} m/z \\ I \end{pmatrix} = \begin{pmatrix} 150 & 151 & 152 & 153 & 154 & 155 & 156 & 157 & 158 \\ 0.425 & \mathbf{0.002} & 0.119 & \mathbf{0.008} & 0.200 & \mathbf{0.000} & 0.004 & \mathbf{0.020} & 0.223 \end{pmatrix},$$

where the presence of signals at odd nominal mass values is indicative of the presence of protium-containing isotopologues. In the first iteration of the calculations, the spectrum of As_2D_4 is taken by simply ignoring the odd-mass signals. Then, the spectrum of As_2HD_3 is obtained using the statistical model. At this point it is feasible to subtract the obtained spectrum of As_2HD_3 from the experimental spectrum of "crude" As_2D_4 (shown above). This calculation loop is repeated until all odd-mass signals vanish. After three iterations this procedure converged to the following mass spectrum of "pure" As_2D_4:

$$\begin{pmatrix} m/z \\ I \end{pmatrix} = \begin{pmatrix} 150 & 151 & 152 & 153 & 154 & 155 & 156 & 157 & 158 \\ 0.425 & \mathbf{0.000} & 0.120 & \mathbf{0.000} & 0.208 & \mathbf{0.000} & 0.004 & \mathbf{0.000} & 0.243 \end{pmatrix}.$$

The mass spectra of all isotopologues of diarsane and triarsane are shown in Tables 1 and 2. Contributions of $As_2H_2D_2$ and As_2H_3D are omitted in this iteration procedure due to the extremely low levels of these isotopologues in the "crude" As_2D_4.

Table 1. Reconstructed mass spectra of $As_2H_nD_{4-n}$ isotopologues

(m/z)/Da	$\mathbf{As_2H_4}^{(a)}$	$\mathbf{As_2H_3D}^{(b)}$	$\mathbf{As_2H_2D_2}^{(b)}$	$\mathbf{As_2HD_3}^{(b)}$	$\mathbf{As_2D_4}^{(a)}$
150	0.478±0.003	0.449±0.022	0.431±0.029	0.423±0.023	0.425±0.003
151	0.146±0.002	0.109±0.025	0.072±0.029	0.036±0.020	0.000
152	0.158±0.002	0.121±0.037	0.101±0.037	0.100±0.027	0.120±0.003
153	0.003±0.001	0.096±0.022	0.125±0.018	0.094±0.018	0.000
154	0.215±0.003	0.003±0.001	0.039±0.015	0.106±0.026	0.208±0.002
155	0.000	0.222±0.003	0.003±0.002	0.003±0.001	0.000
156	0.000	0.000	0.229±0.003	0.002±0.001	0.004±0.001
157	0.000	0.000	0.000	0.236±0.004	0.000
158	0.000	0.000	0.000	0.000	0.243±0.004

(a) Experimental mass spectrum. Each experimental set of data represents the mean of three independent determinations. Standard deviation of the results is reported in parentheses.

(b) Statistical model. Each set of data represents the mean of 5×10^7 simulations. Standard deviation of the results is reported in parentheses.

Table 2. Reconstructed mass spectra of $As_3H_nD_{5-n}$ isotopologues

(m/z)/Da	As_3H_5[(a)]	As_3H_4D[(b)]	$As_3H_3D_2$[(b)]	$As_3H_2D_3$[(b)]	As_3HD_4[(b)]	As_3D_5[(a)]
225	0.360±0.008	0.333±0.017	0.310±0.025	0.288±0.024	0.269±0.016	0.250±0.006
226	0.327±0.009	0.250±0.024	0.183±0.029	0.120±0.025	0.060±0.015	0.000
227	0.002±0.002	0.078±0.019	0.144±0.027	0.206±0.028	0.267±0.021	0.330±0.014
228	0.062±0.004	0.028±0.009	0.011±0.005	0.004±0.002	0.002±0.001	0.000
229	0.000±0.000	0.043±0.008	0.040±0.008	0.022±0.008	0.007±0.003	0.009±0.003
230	0.250±0.003	0.002±0.001	0.022±0.008	0.040±0.008	0.037±0.006	0.000
231	0.000	0.269±0.005	0.003±0.001	0.009±0.004	0.027±0.009	0.061±0.009
232	0.000	0.000	0.288±0.006	0.003±0.001	0.003±0.001	0.000
233	0.000	0.000	0.000	0.307±0.008	0.002±0.001	0.005±0.001
234	0.000	0.000	0.000	0.000	0.326±0.011	0.000
235	0.000	0.000	0.000	0.000	0.000	0.345±0.015

[(a)] Experimental mass spectrum. Each experimental set of data represents the mean of three independent determinations. Standard deviation of the results is reported in parentheses.
[(b)] Statistical model. Each set of data represents the mean of 8×10^7 simulations. Standard deviation of the results is reported in parentheses.

Application

The statistical model allows the calculation of the mass spectra of the isotopologues, as presented in Tables 1 and 2. The model has been validated by comparing generated results to the weighted two-band target entropy minimization model [15–16] which produced consistent mass spectra of isotopologues of arsane, stibane, and selane.

From the reconstructed spectra in Tables 1 and 2, it is possible to determine the quantity of the various isotopologues from their mixtures. This is achieved using the relationship:

$$Y = FA, \tag{7}$$

where Y is the mass spectrum (vector) of the mixture of isotopologues, F is the matrix reporting the mass spectra of the pure isotopomers (Tables 1 and 2) and A is the vector reporting the mole fraction of each component in the mixture. In this work, Eq. (7) was solved for A with a least squares method using the

LINEST function in Microsoft *Excel*. Moreover, agreement between the gravimetric mole fraction of deuterium in the reducing agent ($NaBH_4$ + $NaBD_4$) and the net mole fraction of deuterium in the generated isotopologue mixtures as calculated from the statistical model ($R^2 > 0.98$) is obtained.

Mechanism of formation of polyarsanes

Reduction of arsenates and methylarsenates with boranes is a concerted multistep reaction wherein all −OH groups from the As-substrate are replaced by −H groups originating from different borane molecules [11]:

$$As(OH)_3 + 3[BX_3H]^- \rightarrow AsH_3 + 3[BX_3OH]^- \text{ (X = H, OH)}.$$

The incorporation of hydrogen into the final hydride can be monitored using tetrahydroborate enriched in deuterium *via* plots of the mole fraction of each isotopologue generated versus the mole fraction of deuterium in the tetrahydroborate reductant [8]. The stoichiometry of the above reaction is respected only when arsenic compounds are present at trace levels in an excess of boranes (*i.e.*, under analytical conditions). When the concentration of arsenic rises above the millimolar level, however, a complex set of side reactions takes place [14] with formation of condensation products:

$$X_2As{-}OH + H{-}AsX_2 \rightarrow X_2As{-}AsX_2 + H_2O,$$

$$X_2As{-}OH + H{-}AsX{-}AsX_2 \rightarrow X_2As{-}AsX{-}AsX_2 + H_2O,$$

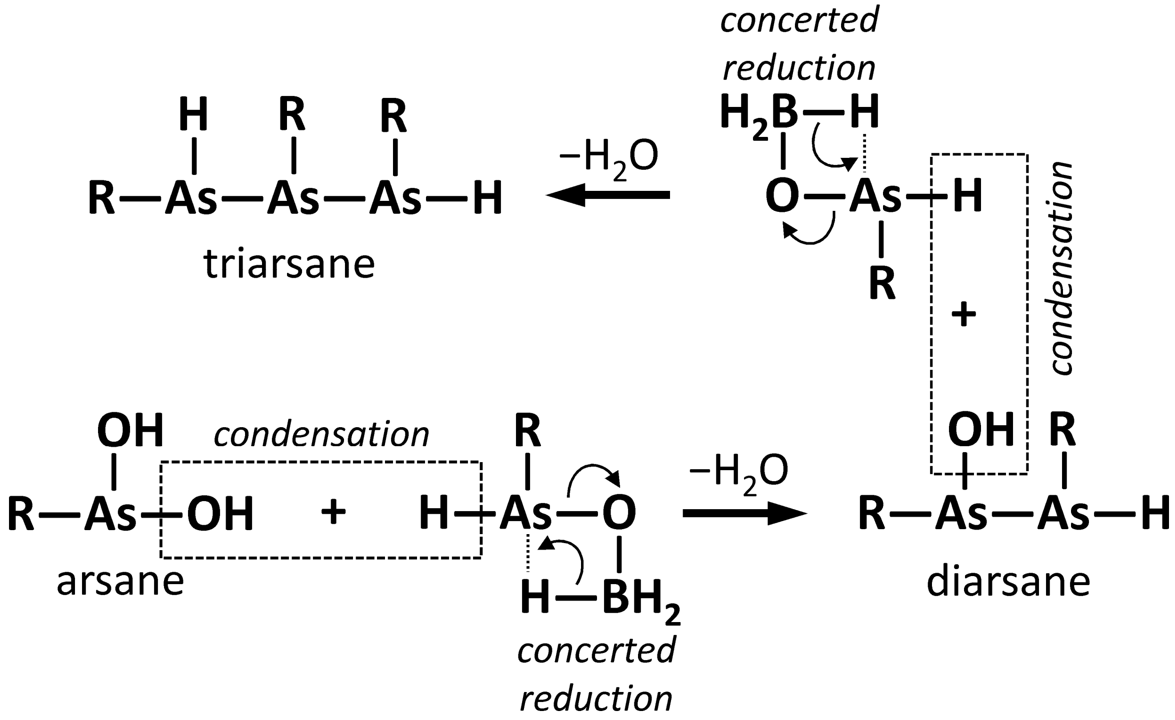
$$X_2As{-}AsX_2,\ X_2As{-}AsX{-}AsX_2 + [BH_4]^- \rightarrow As_2H_4,\ As_3H_5 \qquad \text{(X = H, OH)}.$$

In this work, we have investigated for the first time the mechanism of incorporation of hydrogen into the di- and triarsanes arising from these condensation cascades. Experimental conditions are chosen to avoid any unwanted H/D exchange with the solvent (H_2O) [20].The mole fraction of deuterium in the $NaBH_4$ and $NaBD_4$ mixtures was obtained gravimetrically and the mass spectra of the resultant di- and triarsanes were deconvoluted to obtain the mole fraction of each isotopologue. Results are shown in Figs. 2 and 3. It is evident that the incorporation of protium and deuterium in di- and triarsanes closely follows the binomial distribution, i.e.,

$$x_{\mathrm{As_2H}_n\mathrm{D}_{4-n}} = \frac{4!}{n!(4-n)!} \cdot x_{\mathrm{D}}^{4-n} \cdot \left(1 - x_{\mathrm{D}}\right)^n \tag{8}$$

$$x_{\mathrm{As_3H}_n\mathrm{D}_{5-n}} = \frac{5!}{n!(5-n)!} \cdot x_{\mathrm{D}}^{5-n} \cdot \left(1 - x_{\mathrm{D}}\right)^n \tag{9}$$

as illustrated by the continuous line in Figs. 2 and 3. The binomial distribution originates from the multistep hydrogen transfer, as outlined for diarsane in Fig. 4. The trends observed in the composition of diarsane and triarsane follow the hypothesis of a concerted multistep formation of arsane in a fashion already demonstrated for AsH_3 [11], and they further validate the proposed condensation cascade mechanism [14]. Therefore, the formation of di- and triarsanes can be described as a combination of two independent events: *condensation* of two hydroxoarsanes and their *reduction* by borohydrides via the concerted transfer of hydrogen to the arsenic substrate, as summarized in Scheme 1.



Scheme 1. Formation of di- and triarsanes in a concerted reduction and condensation cascade (R = H or OH).

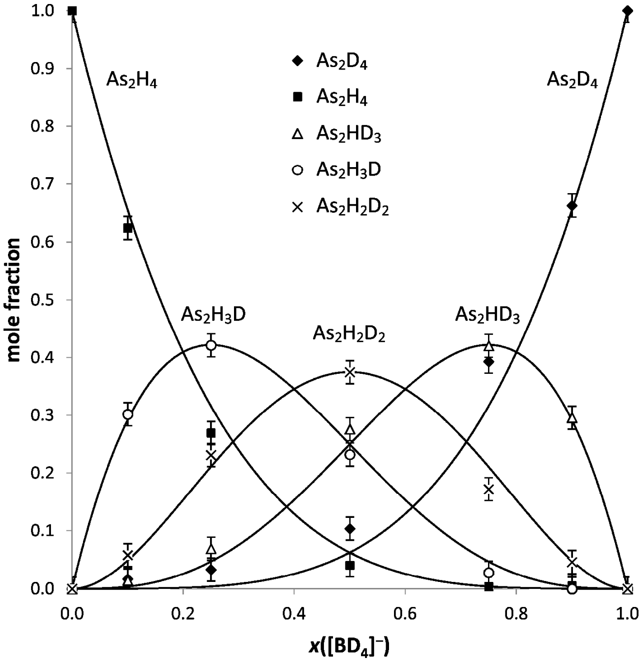


Fig. 2 Mole fraction of diarsane isotopologues, $x(As_2H_nD_{4-n})$, generated using mixtures of $NaBH_4$ and $NaBD_4$. The continuous lines portray the theoretical trend based on a multistep direct hydrogen transfer from tetrahydroborate to the As-substrate.

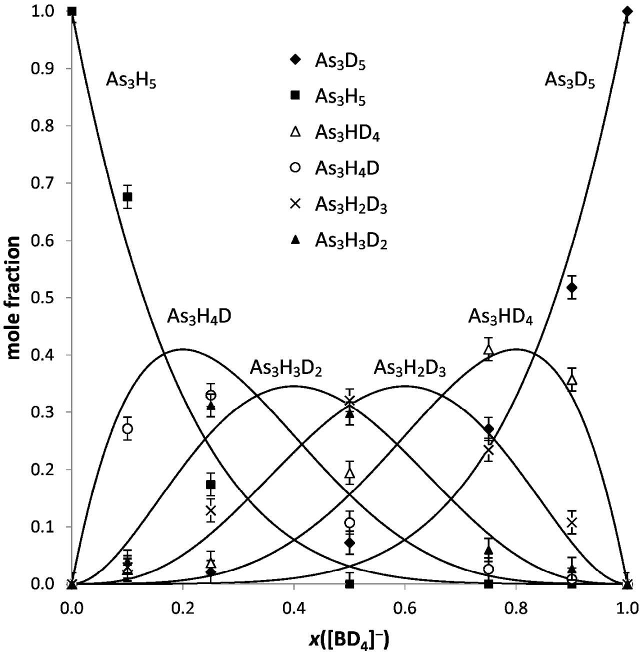


Fig. 3 Mole fraction of triarsane isotopologues, $x(As_3H_nD_{5-n})$, generated using mixtures of $NaBH_4$ and $NaBD_4$. The continuous lines portray the theoretical trend based on a concerted multistep hydrogen transfer from tetrahydroborate to the As-substrate.

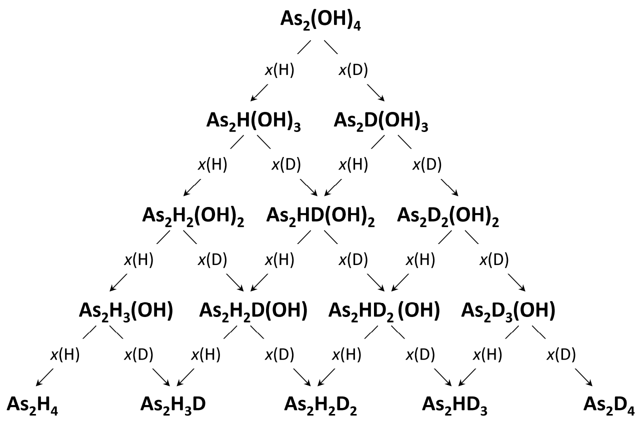


Fig. 4 Pascal triangle used to predict the isotopic composition of diarsane generated using various mixtures of $NaBH_4$ and $NaBD_4$

Mechanistic interference from rhodium(III)

The interaction between transition elements and tetrahydroborate is of great importance in chemistry, not just in analytical chemistry. Tetrahydroborate is of interest due to its capability to store hydrogen and its hydrolysis is catalyzed by noble and transition elements [21–22]. Reaction of transition elements with tetrahydroborate is also employed in the synthesis of nanoparticles [23–24] and to generate volatile derivatives suitable for analytical purposes [10]. Noteworthy is also the possibility of using transition elements, such as Co(II), Ni(II) [25], and Rh(III) [26], to modify the reducing power of the tetrahydroborate. For example, $[BH_4]^-$ cannot reduce nitriles, amides, and olefins, but it can do so in combination with transition element halides [27–28]. Recent observations of the effects of Au(III), Pd(II), and Pt(II) on generation of arsane [13] confirm a peculiar chemistry in this system, and in this study we report a similar behaviour with Rh(III). The first macroscopic observation regarding the interference of Rh(III) within the As(III)/$[BD_4]^-$ system is the increased incorporation of hydrogen from the solvent into the arsanes. Indeed, when As(III) is derivatized to arsane by $[BD_4]^-$ in aqueous media, AsD_3 is the major isotopologue formed, 86%, while trace (< 1%) AsH_3 is observed. The presence of rhodium alters this composition to 63% AsD_3 and 13% AsH_3.

Although this phenomenon could be interpreted as an H/D exchange of the arsane catalyzed by the presence of rhodium, it would be inconsistent with the observation that the injection of preformed AsD_3 into a vial containing Rh(III)/$[BD_4]^-$ does not alter the integrity of AsD_3. This evidence suggests that this H/D exchange occurs during the generation of arsane.

Therefore, the presence of Rh(III) causes a strong perturbation to the mechanism of hydrogen transfer from tetrahydroborate to arsenic, creating a "loss" in the typical binomial character (Table 3), *i.e.*, the amount of AsH_3 (among the other isotopologues) increases significantly in the presence of Rh(III). A possible interpretation of the results shown in Table 3 can be achieved by considering the reductive process as the sum of two competing events: the reduction by $[BD_4]^-$ which is binomial, and the reduction by a hydride-borane-Rh intermediate, present in the early stages of the reaction, and able to exchange hydrogen with the solvent. The postulation of the formation of a "new" reducing agent, with differing reductive power with respect to $[BD_4]^-$, is also supported by observations reported in the organic chemistry literature, as noted earlier.

It was not possible to study how the mechanistic interference of rhodium ions propagates from arsane to di- and triarsane generated *via* the condensation cascades under non-analytical conditions. This was due to the fact that the large concentration of As(III) necessary to produce polyarsanes creates prohibitive conditions for Rh(III), leading to significant precipitation and significant reduction in the yield of the volatile arsanes.

Table 3. Composite mass spectra of arsanes generated in the reaction of As(III) with $[BD_4]^-$ in the presence and absence of Rh(III) ions (**A**) and the corresponding isotopologue distribution (**B**).

A		**B**		
(m/z)/Da	Intensity[a]	$\mathrm{As(III)} + [\mathrm{BD_4}]^- + \mathrm{Rh(III)} \rightarrow \mathrm{AsH}_n\mathrm{D}_{3-n}$		
75	0.146±0.004	*Isotopologue*	*Experimental*	*Binomial*[b]
76	0.092±0.013	AsH_3	0.133±0.046	0.013
77	0.342±0.012	AsH_2D	0.058±0.013	0.127
78	0.062±0.014	$AsHD_2$	0.175±0.057	0.413
79	0.082±0.003	AsD_3	0.629±0.048	0.448
80	0.060±0.019			
81	0.216±0.016	x(D)	0.765±0.035	0.765
		$\mathrm{As(III)} + [\mathrm{BD_4}]^- \rightarrow \mathrm{AsH}_n\mathrm{D}_{3-n}$		
75	0.149±0.002	*Isotopologue*	*Experimental*	*Binomial*[b]
76	0.003±0.003	AsH_3	0.000±0.006	0.000
77	0.411±0.005	AsH_2D	0.021±0.006	0.005
78	0.011±0.006	$AsHD_2$	0.145±0.011	0.111
79	0.089±0.004	AsD_3	0.856±0.018	0.885
80	0.047±0.005			
81	0.289±0.006	x(D)	0.960±0.010	0.960

(*a*) Each set of experimental data reflects the mean of four independent determinations. Standard deviation is reported in the parentheses.

(*b*) The experimental isotopologue distribution is compared with the calculated binomial distribution corresponding to the same level of deuterium incorporation, x(D).

References

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[1] Dědina, J.; Tsalev, D. L. Hydride generation atomic absorption spectroscopy; Wiley: Chichester, 1995.

[2] Sturgeon, R. E.; Guo, X; Mester, Z. Chemical vapor generation: are further advances yet possible? *Anal. Bioanal. Chem.* **2005**, *382*, 881-883.

[3] Luna, A. S.; Sturgeon, R. E.; de Campos, R. C. Chemical vapor generation: atomic absorption by Ag, Au, Cu, and Zn following reduction of aquo ions with sodium tetrahydroborate(III). *Anal. Chem.* **2000**, *72*, 3523-3531.

[4] Rapsomanikis, S. Derivatization by ethylation with sodium tetraethylborate for the speciation of metals and organometallics in environmental samples. A review. *Analyst* **1994**, *119*, 1429-1439.

[5] D'Ulivo, A.; Pagliano, E.; Onor, M.; Pitzalis, E.; Zamboni, R. Vapor generation of inorganic anionic species after aqueous phase alkylation with trialkyloxonium tetrafluoroborates. *Anal. Chem.* **2009**, *81*, 6399-6406.

[6] Pagliano, E.; Meija, J.; Sturgeon, R. E.; Mester, Z.; D'Ulivo, A. Negative chemical ionization GC/MS determination of nitrite and nitrate in seawater using exact matching double spike isotope dilution and derivatization with triethyloxonium tetrafluoroborate. *Anal. Chem.* **2012**, *84*, 2592-2596.

[7] D'Ulivo, A. 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. *Spectrochim. Acta Part B* **2004**, *59*, 793-825.

[8] D'Ulivo, A. Mechanism of generation of volatile species by aqueous boranes: towards the clarification of most controversial aspects. *Spectrochim. Acta Part B* **2010**, *65*, 360-375.

[9] D'Ulivo, A.; Dědina, J.; Mester, Z.; Sturgeon, R. E.; Wang, Q.; Welz, B. Mechanisms of chemical generation of volatile hydrides for trace element determination. *Pure Appl. Chem.* **2011**, *83*, 1283-1340.

[10] Feng Y.-L.; Sturgeon, R. E.; Lam, J. W.; D'Ulivo, A. Insights into the mechanism of chemical vapor generation of transition and noble metals. *J. Anal. At. Spectrom.* **2005**, *20*, 255-265.

[11] D'Ulivo, A.; Mester, Z.; Sturgeon, R. E. The mechanism of formation of volatile hydrides by tetrahydroborate(III) derivatization: a mass spectrometric study performed with deuterium labeled reagents. *Spectrochim. Acta Part B* **2005**, *60*, 423-438.

[12] Bax, D.; Agterdenbos, J.; Worrell, E.; Beneken Kolmer, J. The mechanism of transition metal interference in hydride generation atomic absorption spectrometry. *Spectrochim. Acta Part B* **1988**, *43*, 1349-1354.

[13] Pagliano, E.; Onor, M.; Meija, J.; Mester, Z.; Sturgeon, R. E.; D'Ulivo, A. Mechanism of hydrogen transfer in arsane generation by aqueous tetrahydridoborate: interference effects of Au^{III} and other noble metals. *Spectrochim. Acta Part B* **2011**, *66*, 740–747.

[14] D'Ulivo, A.; Meija, J.; Mester, Z.; Pagliano, E.; Sturgeon R. E. Condensation cascades and methylgroup transfer reactions during the formation of arsane, methyl- and dimethylarsane by aqueous borohydride and (methyl) arsenates. *Anal. Bioanal. Chem.* **2012**, *402*, 921-933.

[15] Meija, J.; Mester, Z.; D'Ulivo, A. Mass spectrometric separation and quantitation of overlapping isotopologues. H_2O/HOD/D_2O and H_2Se/HDSe/D_2Se mixtures. *J. Am. Soc. Mass Spectrom.* **2006**, *17* 1028-1036.

[16] Meija, J.; Mester, Z.; D'Ulivo, A. Mass spectrometric separation and quantitation of overlapping isotopologues. Deuterium containing hydrides of As, Sb, Bi, Sn, and Ge. *J. Am. Soc. Mass Spectrom.* **2007**, *18*, 337-345.

[17] Ditter, J. F.; Klusmann, E. B.; Perrine, J. C.; Shapiro, I. Mass spectra of deuterated diboranes. *J. Phys. Chem.* **1960**, *64*, 1682-1685.

[18] Schoofs, B.; Martens, J. A.; Jacobs, P. A.; Schoonheydt, R. A. Kinetic of hydrogen-deuterium exchange reactions of methane and deuterated acid FAU- and MFI-type zeolites. *J. Catal.* **1999**, *183*, 355-367.

[19] Amenomiya, Y.; Pottie, R. F. Mass spectra of some deuterated ethanes. II. An empirical method of calculation of the spectra. *Can. J. Chem.* **1968**, *46*, 1741-1746.

[20] D'Ulivo, A.; Mester, Z.; Meija, J.; Sturgeon, R. E. Gas chromatography–mass spectrometry study of hydrogen–deuterium exchange reactions of volatile hydrides of As, Sb, Bi, Ge and Sn in aqueous media. *Spectrochim. Acta Part B* **2006**, *61*, 778-787.

[21] Muir, S. S.; Yao, X. Progress in sodium borohydride as a hydrogen storage material: development of hydrolysis catalysts and reaction systems. *Int. J. Hydrogen Energy* **2011**, *36*, 5983-5997.

[22] Guella, G.; Zanchetta, C.; Patton, B.; Miotello, A. New insights on the mechanism of palladium-catalyzed hydrolysis of sodium borohydride from ^{11}B NMR measurements. *J. Phys. Chem. B* **2006**, *110*, 17024-17033.

[23] Dragieva, I. D.; Stoynov, Z. B.; Klabunde, K. J. Synthesis of nanoparticles by borohydride reduction and their applications. *Scripta mater.* **2001**, *44*, 2187-2191.

[24] Van Hyning, D. L.; Zukoski, C. F. Formation mechanisms and aggregation behavior of borohydride reduced silver particles. *Lagmuir* **1998**, *14*, 7034-7046.

[25] Satoh, T.; Suzuki, S.; Suzuki, Y.; Miyaji, Y.; Imai, Z. Reduction of organic compounds with sodium borohydride-transition metal salt systems: reduction of organic nitrile, nitro and amide compounds to primary amines. *Tetrahedron Lett.* **1969**, *10*, 4555-4558.

[26] Nishiki, M.; Miyataka, H.; Niino, Y.; Mitsuo, N.; Satoh, T. Facile hydrogenation of aromatic nuclei with sodium borohydride-rhodium chloride in hydroxylic solvents. *Tetrahedron Lett.* **1982**, *23*, 193-196.

[27] Heinzman, S. W.; Ganem, B. Mechanism of sodium borohydride-cobaltous chloride reductions. *J. Am. Chem. Soc.* **1982**, *104*, 6801-6802.

[28] Osby, J. O.; Heinzman, S. W.; Ganem, B. Studies on the mechanism of transition-metal-assisted sodium borohydride and lithium aluminum hydride reductions. *J. Am. Chem. Soc.* **1986**, *108*, 67-72.