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ORIGINAL PAPER

Condensation cascades and methylgroup transfer reactions during the formation of arsane, methyl- and dimethylarsane by aqueous borohydride and (methyl) arsenates

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Abstract The formation of volatile products during the reaction of As(III), As(V), $MeAsO(OH)_2$, and $Me_2AsO(OH)$ with aqueous $NaBH_4$ has been investigated, and the formation of arsanes, diarsanes, and triarsanes has been detected. The presence of triarsanes is reported here for the first time. Diarsanes and triarsanes are likely formed in condensation cascade reactions, whereas trimethylarsane arises via the transfer of a methyl group. The formation of volatile by-products is considerably reduced by increasing the acidity of the medium and the concentration of $NaBH_4$ or by the addition of thiols, such as cysteine. A reaction scheme is proposed which reconciles the evidence reported herein and elsewhere in the literature that is valid for both analytical (trace analysis) and non-analytical reaction conditions.

Keywords Arsenic · Monomethyarsonic acid · Dimethylarsinic acid · Tetrahydridoborate · Diarsanes · Triarsanes

Introduction

Chemical generation of volatile species (CGVS) of metallic or organometallic compounds by reactions with aqueous $NaBR_4$ (R=H, alkyl or phenyl group) or XBH_3 ($X=NH_3$, NR_3, CN^-) coupled with atomic or molecular spectroscopy or with mass spectrometry is among the most powerful analytical tools for trace element determination and speciation [1–3]. Despite the widespread analytical application of volatile hydride formation for the determination of trace amounts of elements such as arsenic, antimony, bismuth, germanium, tin, lead, selenium, tellurium, and mercury, the mechanism by which they are formed has been debated for many years. In particular, perpetuation of the notorious two-century-old incorrect hypothesis that free atomic (nascent) hydrogen is somehow involved in this reaction needs to be dispelled [4, 5].

Recent studies have shown that the aqueous phase reaction of $NaBH_4$ with oxoacid species of elements such as arsenic occurs through a concerted (direct) transfer of hydrogen atoms from boron to the element, thus forming the hydride, AsH_3 [6]. The generation of EH_n-type hydrides is an n-step process wherein each of the n hydrogen atoms in the hydride originates from different borane molecules [7]. In addition, acid hydrolysis of $NaBH_4$ is not necessary for the formation of hydrides [8, 9]. Analyte–borane intermediates have also been detected, as in the case of the reaction of $Me_2AsO(OH)$ with aqueous aminoboranes [7]. Certain aspects of the generation of the volatile hydrides, however, are not fully understood. An additional problem that arises from the incomplete understanding of this reaction is the assumption that the reaction of $NaBH_4$ with aqueous ions of the hydride-forming elements leads to the formation of a *unique* volatile hydride. It is well known,

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however, that with the increased concentration of the analytical substrate, many elements are partially converted to solid reaction products [10–12]. This diminishes the yield of volatile hydride and leads to a curvature in calibration plots at higher concentrations of analyte [11, 12]. At trace levels (sub-milligrams per liter), inorganic As (III) and As(V), $MeAsO(OH)_2$, and $Me_2AsO(OH)$ react with an excess of aqueous $NaBH_4$, forming AsH_3, $MeAsH_2$, and Me_2AsH, respectively [2]. As the concentration of the analytical substrate increases or the $NaBH_4$-to-analyte amount ratio decreases, various volatile by-products, such as diarsanes or Me_3As, are formed [7]. This phenomenon is of great importance to analytical chemists. For example, it casts doubt on whether diarsane and monomethyl diarsane are indeed present in the environment, as recently reported [13], or they only appear as artifacts of the analytical method, as will be demonstrated here.

This study is devoted to a clarification of the mechanism of arsane generation from inorganic and methyl arsenates under analytical and non-analytical conditions. A series of experiments was performed with deuterium-labeled reagents using gas chromatography coupled with mass spectrometry for the identification of the reaction products. The mass spectra of the hydrides were mathematically deconvoluted in order to obtain the amount fractions of isotopologues AsH_nD_{3-n} (n=0–3), $MeAsH_nD_{2-n}$ (n=0–2), and $Me_2AsH_nD_{1-n}$ (n=0–1) and the amount fraction of deuterium incorporated into the final hydrides [14].

Experimental section

Instrumentation

A Hewlett-Packard 6890 gas chromatograph (GC) operated in splitless mode and equipped with a Hewlett-Packard 5973 mass selective detector (MS) was fitted with a 30-m capillary GC column (Valcobond VB-1, 1-μm film thickness, 0.25-mm internal diameter) for the acquisition of the mass spectra of arsane and methylated arsane isotopologues. The GC was operated under the following conditions: injector temperature, 160 °C; oven temperature program, 35 °C; hold for 4 min; and heated to 200 °C at 15 °C min^{-1}. The initial transfer line temperature was 150 °C, heated at 30 °C min^{-1} to 250 °C. For the separation and identification of the less volatile arsenic species, a different GC capillary column was employed (DB-5; 30-m length, 5-μm film thickness, 0.25-mm internal diameter), and it was operated under the following conditions: injector temperature, 160 °C; oven temperature program, 35 °C; hold for 4 min; heated to 200 °C at 15 °C min^{-1}. The initial transfer line temperature was 150 °C, heated at 30 °C min^{-1} up to 250 °C. Gas-tight syringes (1 and 5 mL, Hamilton) were employed for sampling gases from the reaction vial headspace. Screw cap vials (4 mL) fitted with PTFE/silicone septa (borosilicate glass, Pierce Chemical Co.) were used. The carrier gas was He at 1.2 mL min^{-1}. Mass spectral deconvolution of the results was undertaken.

Chemicals

$NaBH_4$ pellets (Alfa Aesar, Word Hill, MA), $NaBD_4$ powder (isotopic purity, x_D=99%; Cambridge Isotope Laboratories, Cambridge, MA), 37% DCl in D_2O (x_D=99.5%; Aldrich), 30% NaOD in D_2O (x_D=99%; Aldrich), and D_2O (x_D=99.9%; Aldrich) were used. Arsenic standard solutions (2,000 μg As mL^{-1}) were prepared from K_3AsO_4 (>99.0% purity, Baker's Analyzed), $MeAsO(ONa)_2$ (99.0% purity, ChemService, PA, USA), and cacodylic acid, $Me_2AsO(OH)$ (99.3% purity, Sigma Aldrich). A 1 mol L^{-1} bromide/0.2 mol L^{-1} bromate solution was prepared from analytical grade solid reagents (Carlo Erba). L-Cysteine solution (γ=10 gL^{-1}) was prepared by dissolving the solid reagent (Fluka) in 0.1 MHCl. A hydrazine solution (w=250 mg g^{-1}, $NH_2NH_2 \cdot H_2O$; Fluka) was employed without further dilution. All other chemicals were reagent grade. Stock solutions of 1 M $NaBH_4$ or $NaBD_4$, prepared in H_2O, were stabilized with 0.5 M NaOH. A stock solution of 0.2 M $NaBD_4$ was prepared in D_2O and stabilized with 0.1 M NaOD. All $NaBH_4$ or $NaBD_4$ solutions were stored at 4 °C and were stable for a week. Working solutions for reactions were prepared by dilution of the stocks just before use.

Generation of arsanes

For the generation of different volatile arsanes, 1 mL of HCl solution (0.01–0.20 M) was placed into a 4-mL reaction vial and spiked with the required amount of the arsenic standard (5–400 μL of 2,000 μg As mL^{-1}). The vial was sealed, purged with nitrogen, and kept under magnetic stirring. An aliquot (0.1–1.0 mL) of 0.2 M $NaBH_4$ (or $NaBD_4$) in 0.1 M NaOH (or NaOD) was then added with a syringe. After the addition of the reducing agent, the headspace of the vial (approx. 0.25 mL) was sampled at different reaction times (from 5 s to 20 min) and analyzed by GC-MS.

For H/D exchange experiments, pure hydrogenated or deuterated arsanes were prepared shortly before their use from fully hydrogenated or deuterated media following the above procedure. After reaction, 5 mL of the headspace gas was sampled and then injected into another vial containing the exchange solution, H_2O or D_2O, at the required acidity. The vial was continuously shaken and the headspace (approx. 0.25 mL) was periodically sampled over an interval of 5 min.

Arsenic remaining in the liquid phase

Solutions resulting from the reaction of 10 mM As(III) or $MeAsO(OH)_2$ or $Me_2AsO(OH)$ in 1.4 mL 0.1 M HCl with 0.2 mL 0.2 M $NaBH_4$ in 0.1 M NaOH were analyzed following the same procedure described above for arsanes. During the reaction, several changes are observed for the different arsenic compounds; these are illustrated in Fig. 1. After 30 min, the headspace of the reaction vial was flushed with nitrogen in order to remove volatile products. The solution was analyzed for both the arsenic dissolved in the liquid phase and for the total arsenic (liquid phase + solid phase).

For the determination of arsenic dissolved in the liquid phase, 0.05 mL of the solution was diluted to 100 mL with 0.1 M HCl and 0.1 M cysteine solution. After 30 min, the solution was analyzed using arsane generation with detection by atomic absorption spectrometry (HG-AAS) [15]. For the determination of total arsenic, the solution containing the precipitate was acidified with 0.8 mL of 12 M HCl, and then bromine was developed in situ by the addition of 10 µL of a bromide/bromate solution. The solution was heated at 95 °C for 1 h in a heating block, and after cooling, the bromine was reduced with 10 µL of hydrazine solution. The determination of arsenic was achieved by HG-AAS, following the same procedure described for dissolved arsenic.

Amount fraction of arsane isotopologues

Separation of the arsane isotopologues AsH_nD_{3-n} (n=0–3), $MeAsH_nD_{2-n}$ (n=0–2), and $Me_2AsH_nD_{1-n}$ (n=0–1) cannot be accomplished using conventional capillary GC. Their separation, however, can be accurately performed in the mass domain since their mass spectra are different. For dimethylarsane, estimation of the Me_2AsH and Me_2AsD amount fractions can be performed from the fragments at m/z 106 and 107, respectively. Isotopologues of arsane and monomethyarsane, however, cannot be treated in a similar manner since the electron impact mass spectra of these hydrides overlap substantially. Additionally, there are no experimental strategies for obtaining pure AsH_2D, $AsHD_2$, or MeAsHD. In this case, relative abundances of the arsane and monomethylarsane isotopologues were estimated using mathematical deconvolution techniques previously developed for the quantitation of hydrides EH_2 (E=O, Se) [16], EH_3 (E=As, Sb, Bi), and EH_4 (E=Ge, Sn) [14]. The electron impact mass spectra of the pure arsane isotopologues are given below:

> AsH_nD_{3-n}, m/z=75–81: 0.145, 0.420, 0.105, 0.328, 0.000, 0.000, 0.000 (n=3); 0.139, 0.262, 0.177, 0.079, 0.343, 0.000, 0.000 (n=2); 0.135, 0.086, 0.324, 0.006, 0.103, 0.346, 0.000 (n=1) and 0.136, 0.000, 0.431, 0.000, 0.088, 0.000, 0.345 (n=0) [14]
> $MeAsH_nD_{2-n}$, m/z=90–94: 0.481, 0.079, 0.434, 0.006, 0.000 (n=2); 0.434, 0.151, 0.026, 0.389, 0.000 (n=1) and 0.350, 0.172, 0.068, 0.018, 0.392 (n=0)
> $Me_2AsH_nD_{1-n}$, m/z=106–107: 1.000, 0.000 (n=1) and 0.000, 1.000 (n=0)

Results and discussion

H/D exchange of hydridic hydrogen in methylarsanes

As reported recently, neither AsH_3 nor AsD_3 undergoes H/D exchange when in contact with acidic solutions (pH, or pD, in the range from 0 to 7) for several minutes [17]. In contrast, methylarsanes undergo fast H/D exchange in

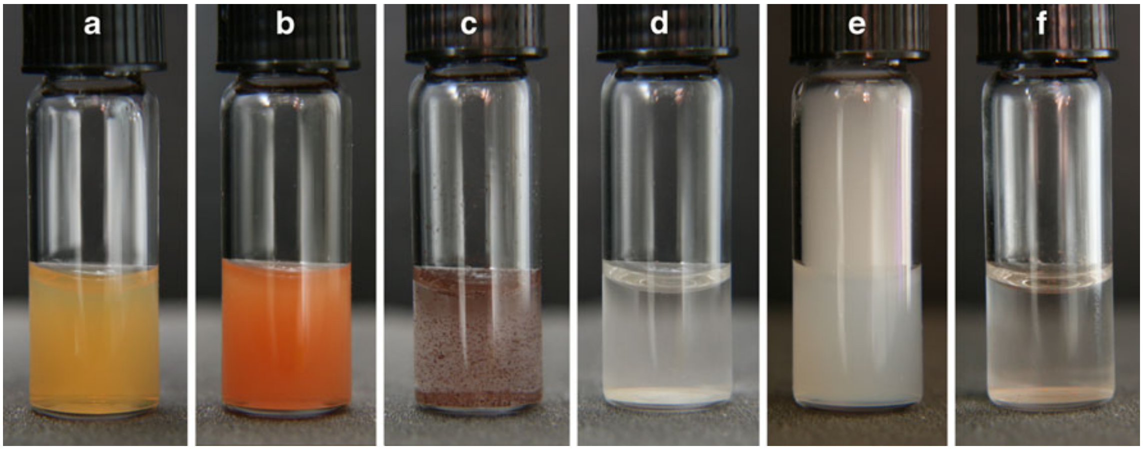


Fig. 1 Visual change occurring during the reduction of As(III) (**a**–**c**) and $Me_2AsO(OH)$ (**d**–**f**) with $NaBH_4$ (color change for As(III), As(V), and $MeAsO(OH)_2$ is similar). Images are taken approx. 1 s, 1 min, and 1 h after mixing the reagents, respectively. Experimental conditions: 1.4 mL of As solution (10 mM As in 0.1 MHCl) is reduced by 0.2 mL 0.2 M $NaBH_4$ in 0.1 M NaOH

acidic media [18]. Both $MeAsH_2$ and $MeAsD_2$ undergo a rapid H/D exchange in strongly acidic or alkaline conditions; however, no significant H/D exchange is observed in the interval of pH, or pD, from 6 to 10 for contact times with the liquid phase of up to 30 s, as evident from Fig. 2. The generation of $MeAsD_2$ at a final pH 9 results in a 95% isotopic purity of $MeAsD_2$ with only 4% of MeAsHD and 1% $MeAsH_2$. With the objective of evaluating the mechanism of hydrogen transfer, this was considered a tolerable level of H/D exchange. Both Me_2AsH and Me_2AsD undergo H/D exchange in strongly acidic media (pH, pD=1), yet are stable at pH, or pD, in the range from 6 to 13, where no significant exchange (<8%) takes place in the first 5 min. However, pure Me_2AsD could be obtained only in a strongly basic medium (pH>12), as shown in Fig. 3. In order to avoid any H/D exchange with the solvent, a final pH 13 was considered more appropriate, even though dimethylarsane is generated quite slowly under these conditions.

The identification of the pH regions where the arsanes are stable against H/D exchange with the media (HCl/H_2O) allowed the development of experimental designs in which the integrity of the isotopic composition of the generated volatile arsanes could be maintained. This, in turn, allowed probing the mechanism of hydride generation.

Mechanism of the hydrogen transfer from borohydride

Arsenic hydride generation experiments with pure $NaBD_4$ or from mixtures of $NaBD_4$ and $NaBH_4$ are useful for deciphering the origin of the hydrogen and, more importantly, the nature of the hydrogen transfer from the borohydride to arsenic. Most notably, it is among the simplest of means to dismiss the atomic hydrogen hypothesis of arsane generation [7]. Experiments with $NaBH_4$ and $NaBD_4$ mixtures can also differentiate between the single- and multistep transfer of hydrogen atoms from borohydride as these two scenarios result in different patterns of arsane isotopologues, as evident in Fig. 4.

In the multistep hydrogen transfer, the hydrogen atoms in the final hydride arise from different borane molecules, whereas in the case of a single-step hydrogen transfer, all hydrogen atoms in the final hydride derive from the same borane molecule. In the reaction of $MeAsO(OH)_2$ with a 1:1 mixture of $NaBH_4/NaBD_4$, the single-step hydrogen transfer would result in two hydrides, $MeAsH_2$ and $MeAsD_2$, both in equal amounts. In contrast, a two-step hydrogen transfer would result in a mixture of $MeAsH_2$, MeAsHD, and $MeAsD_2$ in a ratio of 1:2:1, as coefficients in the Pascal triangle. Comparison of the experimental and expected distributions of monomethylarsane isotopologues, shown in Fig. 4c, d, clearly favors the two-step transfer of hydrogen from boron to arsenic, analogous to the three-step transfer observed in the formation of AsH_3, SbH_3, or BiH_3 [7].

Isotope effects

The expected isotopologue distributions were calculated without considering the H/D isotope effect. Indeed, there is

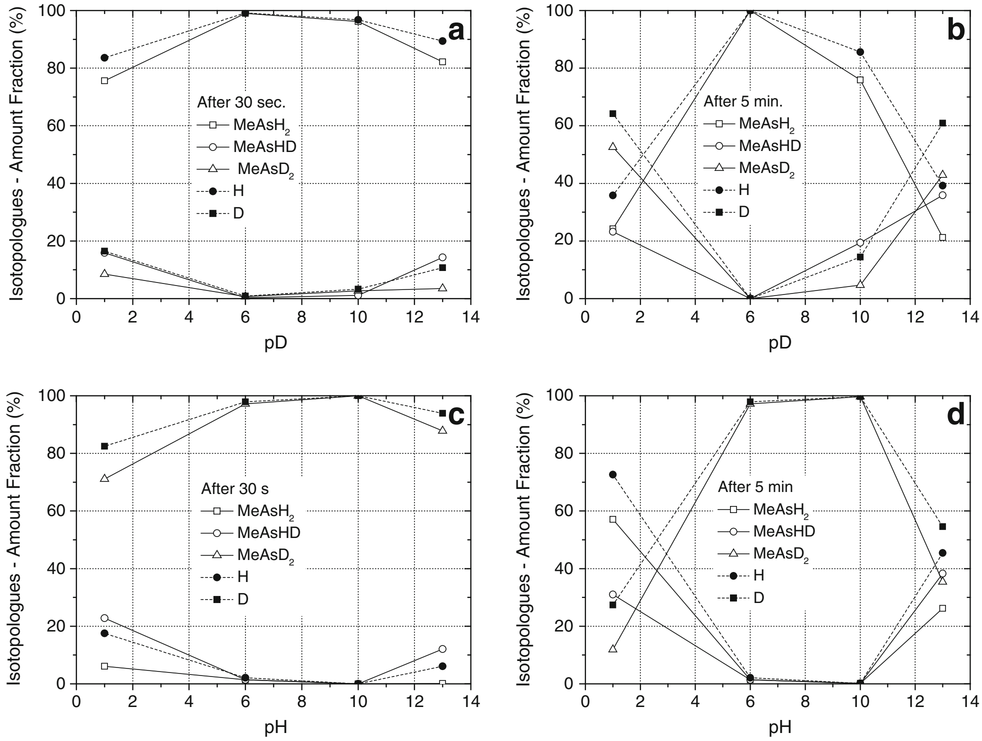


Fig. 2 H/D exchange of monomethylarsane. Pre-formed Me_2AsD (Me_2AsH) was placed in contact with the exchange media under various conditions. The amount fractions of $MeAsH_nD_{(2-n)}$ (n=0, 1, 2) detected in the headspace at different acidities are reported. **a** $MeAsH_2$ in D_2O at different pD values, 30-s contact time. **b** Same as (**a**), but with a 5-min contact time. **c** $MeAsD_2$ in H_2O at different pH values, 30-s contact time. **d** Same as (**c**), but with a 5-min contact time

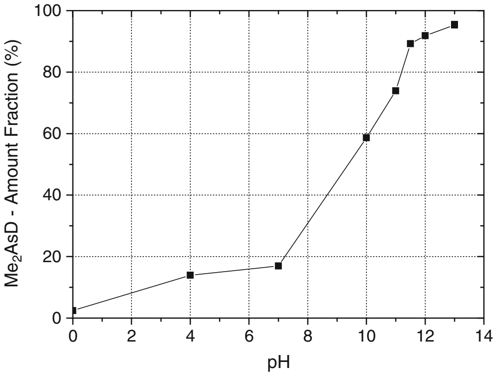


Fig. 3 Synthesis of dimethylarsane. 0.1 mM $Me_2AsO(OH)$ placed in a completely hydrogenated media was reduced with 0.2 M $NaBD_4$. The isotopic composition of dimethylarsane evolved has been followed against the acidity of the resulting solution. The amount fraction of Me_2AsD is reported at different pH values

no evidence of a significant isotope effect in the formation of dimethylarsane (Fig. 4a). In contrast to this, the isotopologue distributions of arsane (Fig. 4e) and monomethylarsane (Fig. 4c) are slightly skewed toward a more favorable incorporation of H over D, even if it appears of little relevance. Considering that no isotope effect is observed during the formation of dimethylarsane, this skew is likely due to a secondary isotope effect. This secondary isotope effect is reasonably due to the fact that the incorporation rate of an incoming H or D is dependent on the coordination sphere of arsenic, say to the presence of As–H or As–D bonds which are already formed in the preceding transfer step. In sum, the kinetic isotope effect, which has been observed by replacing H with D in $NaBH_4$, indicates that hydrogen transfer is not the rate-determining step in the formation of volatile arsanes.

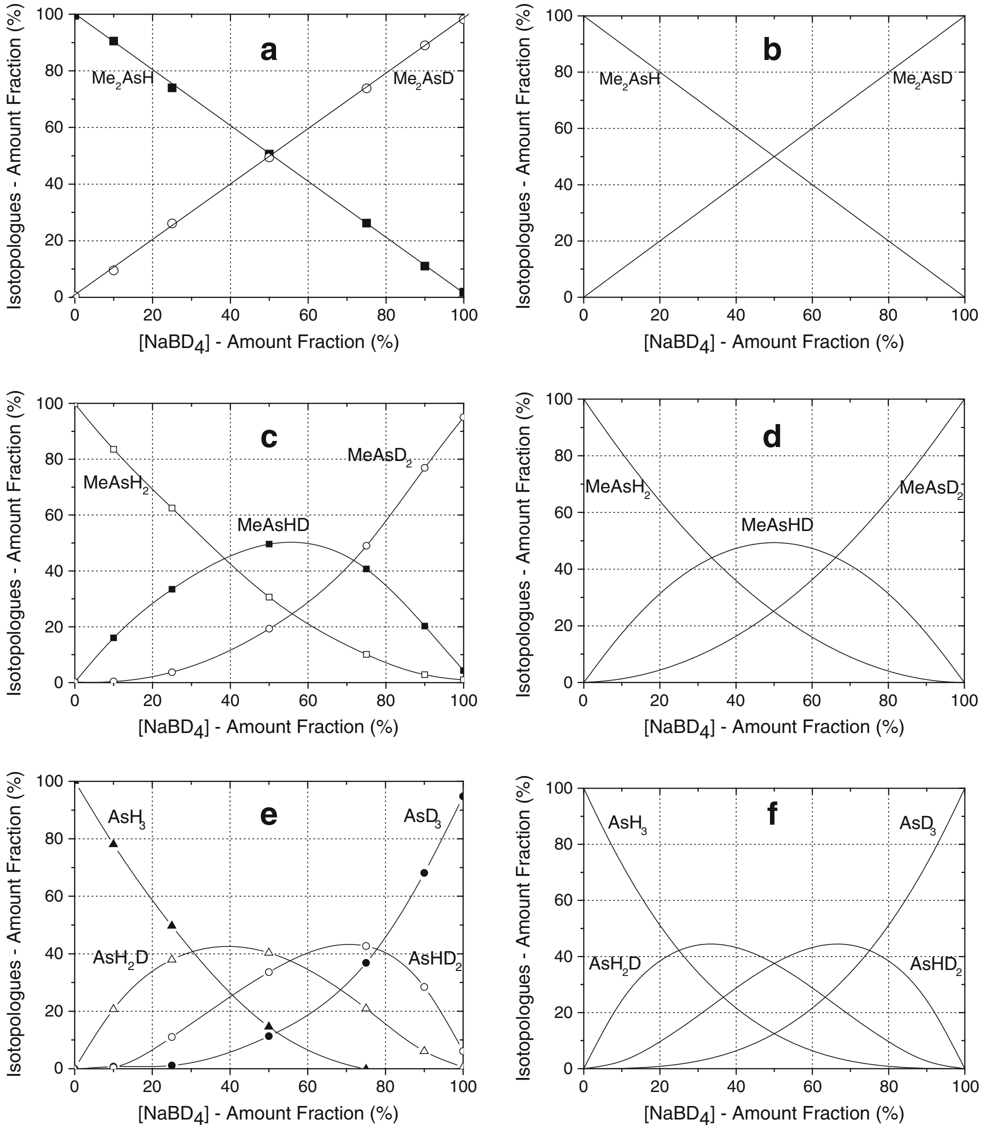


Fig. 4 Experimental (**a**, **c**, **e**) and predicted (**b**, **d**, **f**) distributions of arsane and methylated arsane isotopologues arising from the reduction of the corresponding pentavalent arsenic compounds. **a** Dimethylarsane. Conditions: 1 mL 60 μM $Me_2AsO(OH)$ in 1 mM HCl was reduced with 0.5 mL of 0.2 M ($NaBH_4$ + $NaBD_4$) in 0.1 M NaOH; all reagents were prepared in H_2O. **b** Predicted distribution of dimethylarsane isotopologues based on the direct hydrogen transfer from borohydride to arsenic. **c** Monomethylarsane. Conditions: 1 mL of 60 μM $MeAsO(OH)_2$ in 0.1 M HCl was reduced with 0.5 mL of 0.2 M ($NaBH_4$ + $NaBD_4$) in 0.1 M NaOH; all reagents were prepared in H_2O. **d** Predicted distribution of monomethylarsane isotopologues based on the direct hydrogen transfer from borohydride to As: two-step hydrogen transfer. **e** Arsane. Conditions: 1 mL of 60 μM $AsO(OH)_3$ in 1 M HCl was reduced with 0.5 mL of 0.2 M ($NaBH_4$ + $NaBD_4$) in 0.1 M NaOH; all reagents were prepared in H_2O. **f** Predicted distribution of arsane isotopologues based on the direct hydrogen transfer from borohydride to As: three-step hydrogen transfer

Volatile reaction by-products

Under analytical conditions and at ultra-trace levels of arsenic, hydride generation is commonly assumed to yield a single volatile product: AsH_3 from As(III) and As(V), $MeAsH_2$ from $MeAsO(OH)_2$, and Me_2AsH from $Me_2AsO(OH)$. To test this assumption, various experiments were conducted under analytical and non-analytical conditions wherein the concentration of the arsenic substrates was varied in the range from 10^{-2} to 10 mM (the typical analytical working range is from 1 nM to 1 μM of arsenic). While at the ultra-trace level the arsenic compounds are indeed converted to unique volatile arsanes, as mentioned above, the formation of other volatile arsanes is evident at a higher analyte concentration, as summarized in Tables 1 and 2. In certain cases, these by-products even become the major components of the headspace.

At arsenic concentrations up to 1 mM, the formation of a reddish suspended particulate matter is also evident for inorganic As and $MeAsO(OH)_2$, suggesting that they are not completely converted into volatile species (Fig. 1c). For $Me_2AsO(OH)$, no particulate matter is formed, but a white gas is generated upon the addition of $NaBH_4$, and it is clearly visible in the headspace of the reaction vial (Fig. 1e). At the highest concentration level of arsenic (10 mM), quantitative experiments indicate that a large fraction of arsenic remains in the vial after reaction with $NaBH_4$. For the inorganic arsenic compounds, about 65% of the total As remains in the condensed phase (45% in solution and 20% as solid precipitate). For both $MeAsO(OH)_2$ and $Me_2AsO(OH)$, the amount fraction of the total As remaining in solution as non-volatile compounds is >98%, but in the latter, no precipitate is visible. In spite of the small fraction amount of volatile species that are formed under these reaction conditions, their identification can give interesting information about the reactions which took place in the liquid phase.

For inorganic arsenic, the only observed volatile by-products are diarsane ($H_2As–AsH_2$) and triarsane ($H_2As–AsH–AsH_2$). A gamut of volatile compounds was produced during the reduction of methylated arsenic acids by $NaBH_4$, including dimeric and trimeric arsenic species. A summary of dimeric and trimeric arsenic species which have been detected in the headspace is reported in Table 4. The mass spectra of trimeric species are reported in Figs. 5, 6, 7, 8, and 9.

A rather interesting behavior is exhibited by the reaction of $Me_2AsO(OH)$ with $NaBH_4$/HCl, which, under certain conditions, can give Me_3As as the most abundant volatile product (Table 2). Experimental evidence indicates that Me_3As is formed simultaneously with the disappearance of Me_2AsH. In general, the formation of volatile by-products is more pronounced with increased reaction time, As/

Table 1 Volatile arsenic compounds detected during the reaction of inorganic As^{III}, As^{V}, or $MeAsO(OH)_2$ with $NaBH_4$

Compound	$As/NaBH_4$ (μmol/μmol)	Conditions[a]	Time (min)	Volatile arsenic species[b]							
				AsH_3	$MeAsH_2$	Me_2AsH	Me_3As	Me_2AsCl	As_2H_4	H_2As_2MeH	$As_2(HMe)_2$
$AsO(OH)_3$	2.7/20	pH 3	0.2	100	–	–	–	–	9.5	–	–
	2.7/100	pH 9	0.2	100	–	–	–	–	–	–	–
$As(OH)_3$	2.7/20	pH 3	0.2	100	–	–	–	–	1.4	–	–
	2.7/100	pH 9	0.2	100	–	–	–	–	0.2	–	–
$MeAsO(OH)_2$	10.8/8	pH 3–4	0.2	–	100	–	–	–	–	–	–
			30	–	100	–	–	–	–	–	–
	2.7/20	pH 3	0.2	2.1	100	0.2	–	0.1	–	0.1	4.9
			20	7.4	100	0.6	0.3	–	–	–	–
	1.3/100	pH 9	0.2	1.3	100	0.14	–	–	–	–	0.83
			0.2	2.4	100	0.18	–	–	–	–	3.5
	2.7/100	pH 9	0.2	0.16	100	0.14	–	–	–	–	0.6
		0.2 M Cys	20	0.14	100	0.37	–	–	–	–	0.27
		pH 6	0.2	0.17	100	0.14	–	–	–	–	0.35
		0.2 M Cys	20	0.21	100	0.35	–	–	–	–	–
	0.27/100	pH 9 0.2 M Cys	0.2	0.1	100	–	–	–	–	–	–

[a] $NaBH_4$ (0.5 mL) added to 1 mL sample solution. Final pH is given

[b] Relative signals are the integrated area of the TIC peaks. Relative signals <0.1 are not reported

$NaBH_4$ amount ratio, or acidity. It is interesting to note that the reaction of $Me_2AsO(OH)$ with metallic zinc in HCl generates the same volatile reaction products as with $NaBH_4$ (Table 3).

The addition of cysteine (R–SH) supressed the formation of unwanted by-products (Tables 1 and 2). In particular, it was rather effective for $Me_2AsO(OH)$ where the formation of Me_3As was completely eliminated (Table 2). It is well known that thiols reduce arsenic compounds to thiolates such as $As(SR)_3$, $MeAs(SR)_2$, and $Me_2As(SR)$ [19–22], which are quantitatively converted by $NaBH_4$ into the corresponding hydrides [23, 24]. Consequently, cold vapor generation by $NaBH_4$ in the presence of thiols presents an attractive way to estimate the purity of the methylarseno compounds.

Mechanism of volatile by-product formation: condensation reactions

The formation of volatile by-products is a result of the interaction between the reduction intermediates and the volatile arsanes. For example, pure Me_2AsH (prepared separately from $MeAsO(OH)_2/NaBH_4$ in the presence of cysteine), when injected into a vial containing aqueous $Me_2AsO(OH)$, does not result in the formation of Me_3As, nor diarsanes. According to the evidence collected herein, it can be assumed that the stepwise formation of arsanes proceeds through a series of intermediates, as summarized in reactions 1–4:

$$\mathbf{Me_2AsO(OH)} \rightarrow \mathbf{Me_2AsOH} \rightarrow \mathbf{Me_2AsH} \tag{1}$$

$$\mathbf{MeAsO(OH)_2} \rightarrow MeAs(OH)_2 \rightarrow MeAsH(OH) \rightarrow \mathbf{MeAsH_2} \tag{2}$$

$$\mathbf{AsO(OH)_3} \rightarrow As(OH)_3 \rightarrow AsH(OH)_2 \rightarrow AsH_2(OH) \rightarrow \mathbf{AsH_3} \tag{3}$$

$$\mathbf{As(OH)_3} \rightarrow AsH(OH)_2 \rightarrow AsH_2(OH) \rightarrow \mathbf{AsH_3} \tag{4}$$

Here, the reagents and all identified compounds are shown in bold. In each of the reaction sequences (1–4), arsenic becomes progressively less reactive toward the transfer of hydrogen from boron as a result of the decreasing number of oxygen atoms bound to it. The intermediates involved in the last hydrogen transfer step are, therefore, the least reactive toward the hydride attack in their relevant reaction sequences. Likewise, the reactivity toward the transfer of hydrogen from $NaBH_4$ is expected to decrease in the order $AsH_2(OH) < MeAsH(OH) < Me_2AsOH$.

Table 2 Volatile arsenic compounds detected during the reaction $Me_2AsO(OH)$ with $NaBH_4$

$As/NaBH_4$ (μmol/μmol)	Conditions[a]	Time (min)	Volatile arsenic species[b]								
			AsH_3	$MeAsH_2$	Me_2AsH	Me_3As	Me_3AsO	Me_2AsOH	Me_2AsCl	$As_2(O)Me_4$	As_2Me_4
0.27/100	pH 3	0.2	–	8.1	100	7.1	–	–	–	–	–
		20	–	15.1	6.9	100	–	–	–	–	–
0.13/100	pH 9	5	0.3	4.32	100	9.0	–	–	–	–	–
	pH 13	5	–	–	100	–	–	–	–	–	–
2.7/20	pH 3	4	0.1	0.1	1.5	100	–	0.2	2.1	0.13	0.2
		20	–	–	–	100	–	–	0.5	–	0.3
0.27/100	pH 9	0.2	–	4	100	2.9	–	–	–	–	0.9
		20	26	11	59	100	–	–	–	–	–
10.8/8	pH 2	0.2	–	1.3	–	100	0.7	1.1	0.9	5.6	5.0
		30	–	–	–	100	0.2	7.9	1.5	9.4	4.2
	pH 4	20	–	–	–	100	0.2	6.4	1.3	8.5	5.4
		20	–	–	16	100	0.6	2.2	0.9	9.8	7.0
0.27/100	pH 3	0.2	4	0.3	100	–	–	–	–	–	–
	0.2 M Cys	20	–	0.3	100	0.1	–	–	–	–	–
	pH 9	0.2	–	0.1	100	–	–	–	–	–	–
	0.2 M Cys	20	–	0.1	100	0.1	–	–	–	–	–
0.4/100	pH 9 0.2 M Cys	0.2	–	0.2	100	–	–	–	–	–	–

[a] $NaBH_4$ (0.05–0.5 mL) added to 1 mL sample solution. Final pH is given

[b] Relative signals are the integrated area of the TIC peaks. Relative signals <0.1 are not reported

Fig. 5 EI mass spectrum of As_3H_5. Molecular ion at *m/z*=230 Da $[As_3H_5]^+$. Fragment ions: *m/z* 225 $[As_3]^+$; *m/z* 152 $[As_2H_2]^+$; *m/z* 151 $[As_2H]^+$; *m/z* 150 $[As_2]^+$; *m/z* 75 $[As]^+$

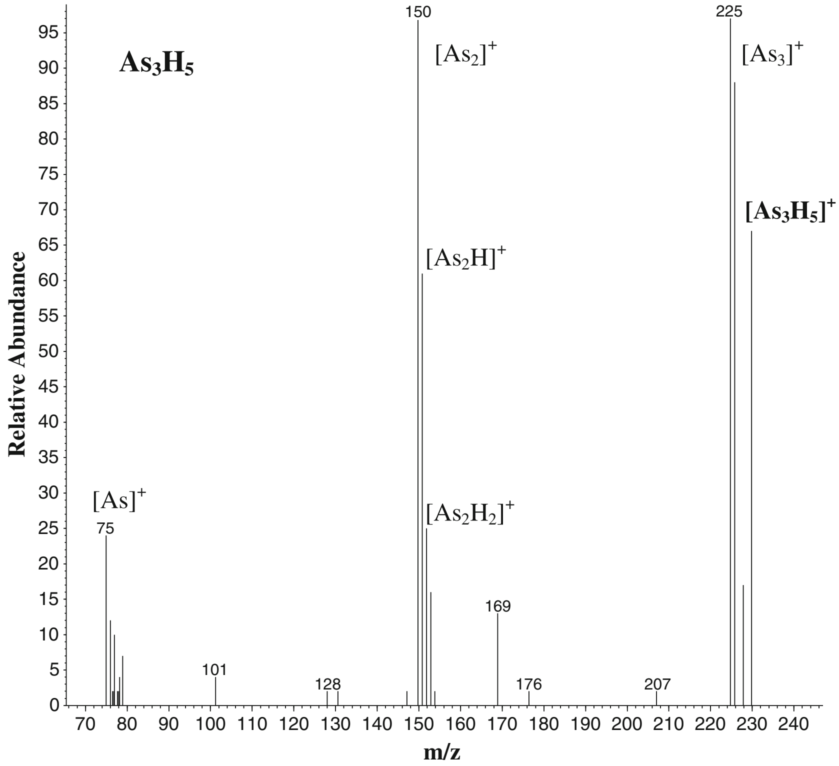


Fig. 6 EI mass spectrum of $MeAs_3H_4$. Molecular ion at *m/z*=244 Da $[MeAs_3H_4]^+$. Fragment ions: *m/z* 225 $[As_3]^+$; *m/z* 166 $[MeAs_2H]^+$; *m/z* 150 $[As_2]^+$; *m/z* 89 $[CH_2As]^+$; *m/z* 75 $[As]^+$

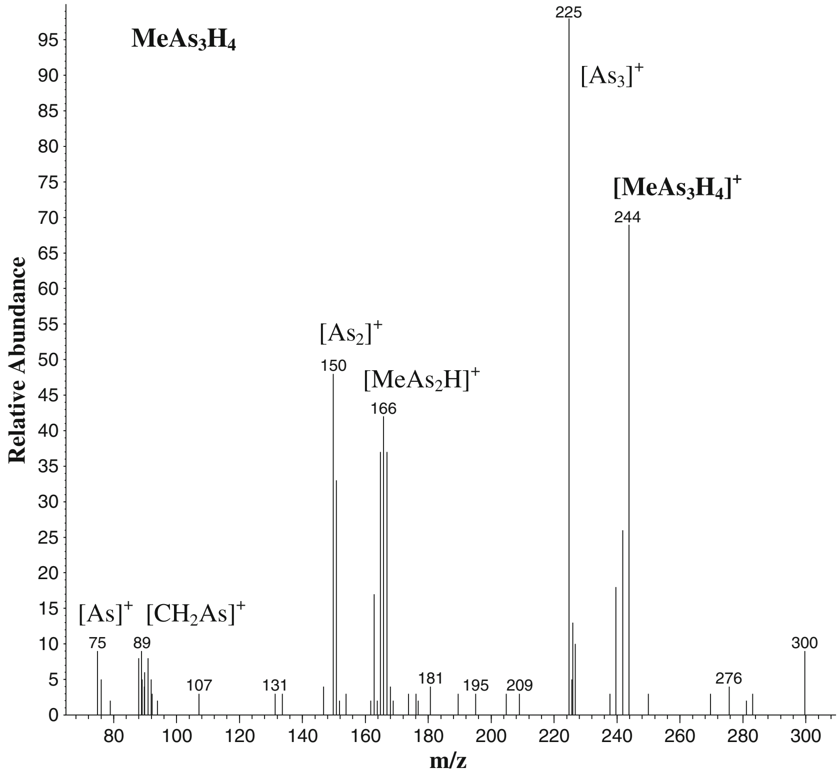


Fig. 7 EI mass spectrum of $Me_2As_3H_3$. Molecular ion at *m/z*=258 Da $[Me_2As_3H_3]^+$. Fragment ions: *m/z* 241 $[MeAs_3H]^+$; *m/z* 225 $[As_3]^+$; *m/z* 181 $[Me_2As_2H]^+$; *m/z* 165 $[MeAs_2]^+$; *m/z* 151 $[As_2H]^+$; *m/z* 105 $[Me_2As]^+$; *m/z* 90 $[MeAs]^+$; *m/z* 75 $[As]^+$

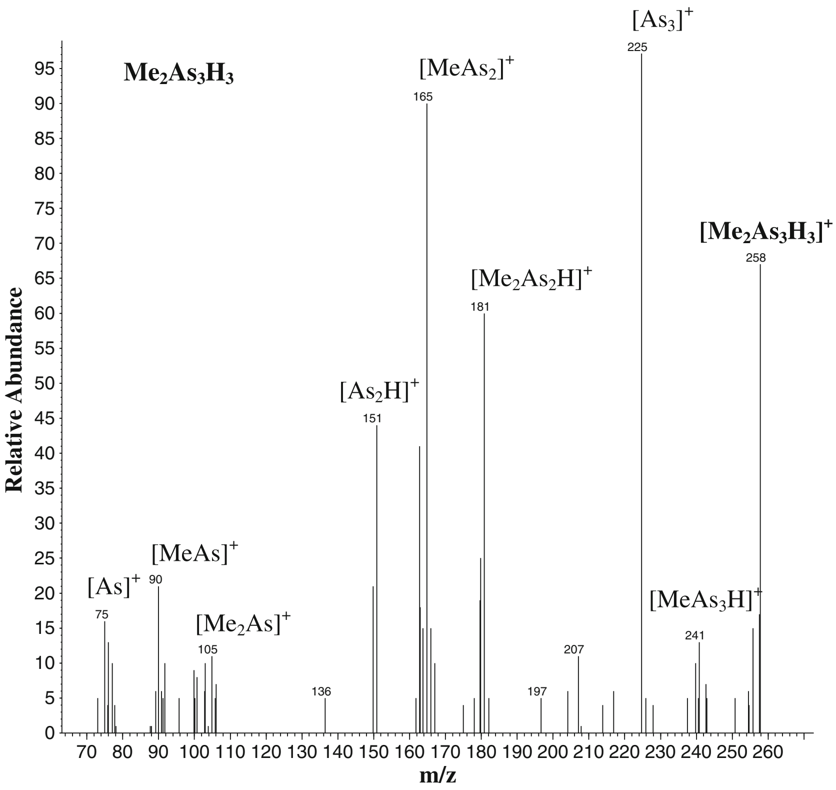
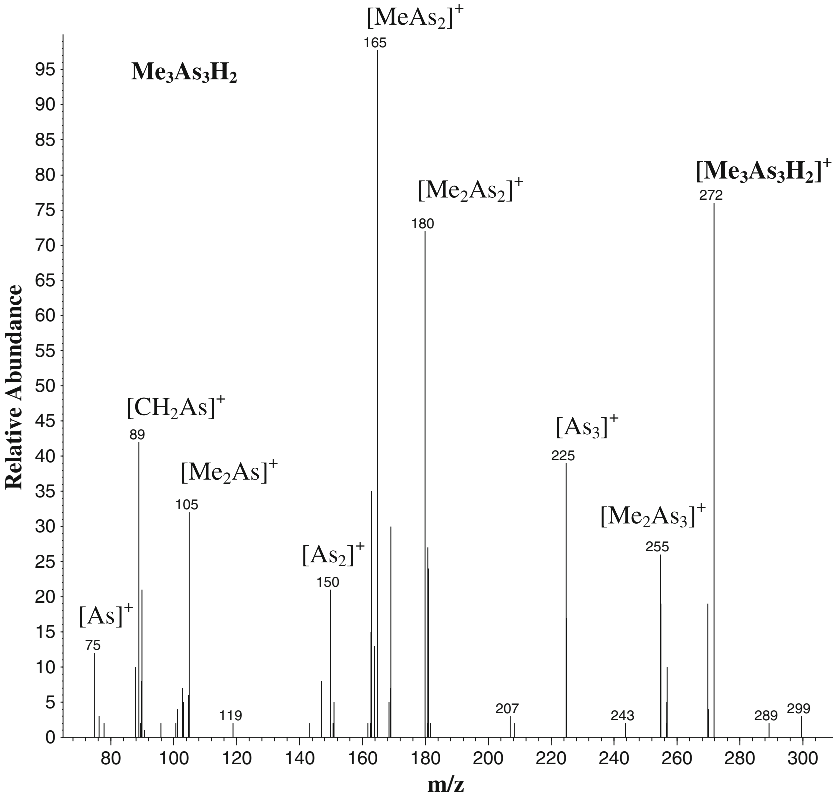


Fig. 8 EI mass spectrum of $Me_3As_3H_2$. Molecular ion at *m/z*=272 Da $[Me_3As_3H_2]^+$. Fragment ions: *m/z* 255 $[Me_2As_3]^+$; *m/z* 225 $[As_3]^+$; *m/z* 180 $[Me_2As_2]^+$; *m/z* 165 $[MeAs_2]^+$; *m/z* 150 $[As_2]^+$; *m/z* 105 $[Me_2As]^+$; *m/z* 89 $[CH_2As]^+$; *m/z* 75 $[As]^+$



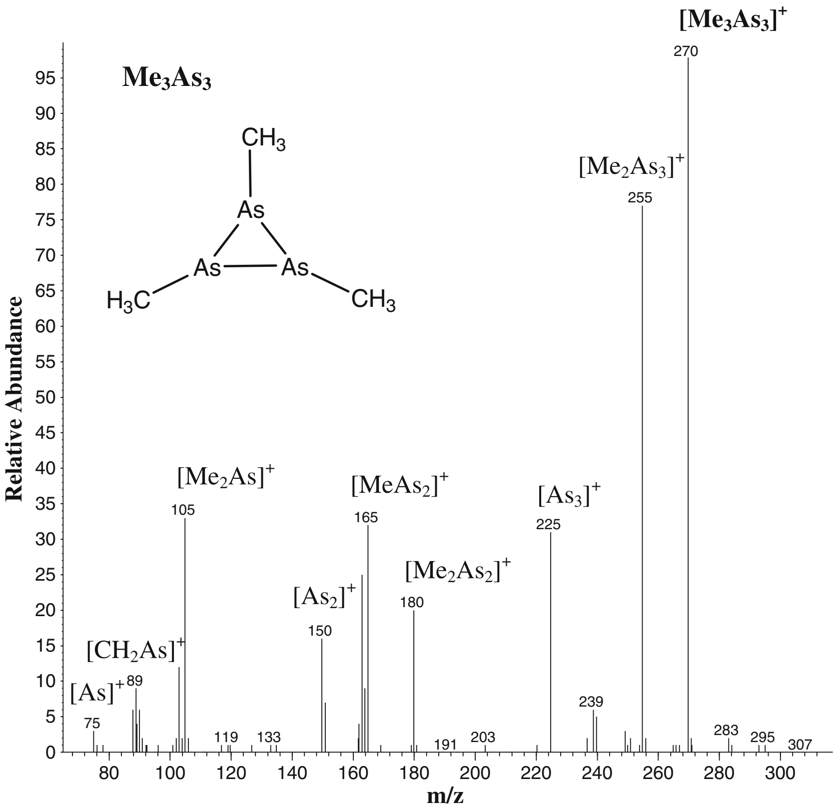


Fig. 9 EI mass spectrum of Me_3As_3. Molecular ion at *m/z*= 270 Da $[Me_3As_3]^+$. Fragment ions: *m/z* 255 $[Me_2As_3]^+$; *m/z* 225 $[As_3]^+$; *m/z* 180 $[Me_2As_2]^+$; *m/z* 165 $[MeAs_2]^+$; *m/z* 150 $[As_2]^+$; *m/z* 105 $[Me_2As]^+$; *m/z* 89 $[CH_2As]^+$; *m/z* 75 $[As]^+$

This is due to the replacement of the –OH groups by the methyl groups. The simultaneous presence of the reaction intermediates and the final hydrides leads to the formation of diarsanes via condensation reactions:

$$\mathbf{Me_2AsOH} + \mathbf{Me_2AsH} \rightleftarrows \mathbf{Me_2As{-}AsMe_2} + H_2O \qquad (5)$$

$$MeAsH(OH) + \mathbf{MeAsH_2} \rightleftarrows \mathbf{MeHAs{-}AsHMe} + H_2O \qquad (6)$$

$$AsH_2(OH) + \mathbf{AsH_3} \rightleftarrows \mathbf{H_2As{-}AsH_2} + H_2O \qquad (7)$$

The bidirectional reaction 5 is also supported by Rheingold et al. [25] who reported that tetramethyl diarsane was formed in a reaction of Me_2AsH with Me_2AsX (X=Cl, Br, I, or CN) in benzene:

$$Me_2AsX + Me_2AsH \rightleftarrows Me_2As{-}AsMe_2 + HX \qquad (8)$$

When aqueous As(III), $MeAsO(OH)_2$, or $Me_2AsO(OH)$, alone or in combination with each other, are treated with $NaBH_4$, all (six) possible structural isomers of diarsanes were detected in the headspace, i.e., $H_2As{-}AsH_2$, $MeHAs{-}AsH_2$, $Me_2As{-}AsH_2$, $MeHAs{-}AsHMe$, $Me_2As{-}AsHMe$, and $Me_2As{-}AsMe_2$, including the oxidation product ($Me_2As{-}As(O)Me_2$) of the latter and some triarsane species (Table 4). This clearly indicates that a condensation cascade took place among all possible intermediates which are

Table 3 Volatile arsenic compounds detected during $Me_2AsO(OH)$ reaction with metallic Zn powder

Conditions[a]	Time (min)	Volatile arsenic species[b]						
		AsH_3	$MeAsH_2$	Me_2AsH	Me_3As	Me_2AsOH	Me_2AsCl	As_2Me_4
1 M HCl	2	–	3.7	100	13.4	2.4	0.6	7.3
	25	3.9	3.5	100	38.5	0.1	–	0.4
0.1 M HCl	2	–	1.0	100	0.64	0.1	–	0.6
	25	12.5	5.4	76	100	–	–	0.3
	65	11.4	5.2	51	100	–	–	–

[a] $Me_2AsO(OH)$ (1.1 μmol) added into 1 mL sample solution reacted by 150 μmol zinc

[b] Relative signals are the integrated area of the TIC peaks. Relative signals <0.1 are not reported

Table 4 Volatile diarsanes and triarsanes detected in the headspace of reaction vials

As substrate	Arsanes[a]	t_R (min)[a]	Diarsanes	t_R (min)[b]	Triarsanes	t_R (min)[b]	Mass spectra
As(III)	AsH_3	1.35	$H_2As–AsH_2$	2.64	$H_2As–AsH–AsH_2$	9.08	Fig. 5
$MeAsO(OH)_2$	$MeAsH_2$	1.43	$MeHAs–AsH_2$	4.45	$Me_3As_3H_2$	11.60 (broad)	Fig. 8
			MeHAs–AsHMe	6.60	Me_3As_3	12.15	Fig. 9
			$Me_2As–AsHMe$	7.30			
$Me_2AsO(OH)$	Me_2AsH	1.65	$Me_2As–AsHMe$	7.30			
	Me_3As	1.84	Me_4As_2O	7.81			
			$Me_4As-AsMe_2$	8.06			
$MeAsO(OH)_2$ and As(III)	AsH_3	1.35	$H_2As–AsH_2$	2.64	$MeAs_3H_4$	9.40	Fig. 6
	Me_2AsH	1.65	$MeHAs–AsH_2$	4.45	$Me_2As_3H_3$	10.60	Fig. 7
			$Me_2As–AsH$	5.35			
			MeHAs–AsHMe	6.60			
$MeAsO(OH)_2$ and $Me_2AsO(OH)$	AsH_3	1.35	$Me_2As–AsH_2$	5.35	Me_3As_3	12.15	Fig. 9
	Me_2AsH	1.65	$Me_2As–AsHMe$	6.60			
	Me_3As	1.84	$Me_2As–AsMe_2$	8.06			

In all proofs, an acid solution (0.1 MHCl) containing the aforementioned As compounds (10 mM As content) was reduced by 0.2 $MNaBH_4$ in 0.1 MNaOH. A final pH 3–4 was measured

[a] The retention times of some detected mono-arsanes are given for comparison with the retention times of diarsanes and triarsanes. Other detected monoarsanes are reported in Table 2

[b] Retention times obtained with DB-5 column. See "Instrumentation" for details

formed in the reaction pathways of different arsenic substrates, including the final hydrides. The interaction between the proposed reaction intermediates is also confirmed in experiments where As(III) was reduced in the presence of Sb(III). In this case, the formation of the dimer $H_2As–SbH_2$ was observed (Fig. 10). The stibodiarsane could be formed only by the reaction of AsH_3 with SbH_2OH or AsH_2OH with SbH_3.

The formation of diarsanes and triarsanes also provides an explanation for the formation of precipitates in the case

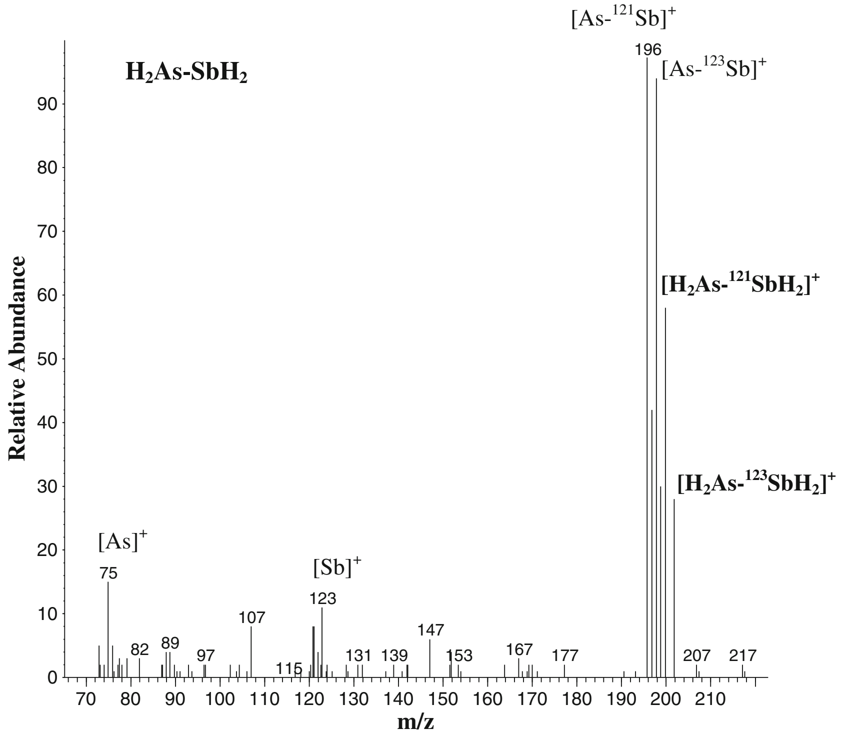


Fig. 10 EI mass spectrum of $H_2As–SbH_2$. Molecular ion at m/z=202 Da $[H_2{}^{75}As–{}^{123}SbH_2]^+$ and 200 Da $[H_2{}^{75}As–{}^{121}SbH_2]^+$. Fragment ions: m/z 198 $[{}^{75}As–{}^{123}Sb]^+$ and m/z 196 $[{}^{75}As–{}^{121}Sb]^+$

of As(III), As(V), and $MeAsO(OH)_2$. When mono-arsenic species contain either only one –H or –OH moiety, the condensation cascade terminates with the formation of a dimer (see reactions 5–7). Triarsanes, on the other hand, can be formed by condensation reactions of the following type:

$$\mathrm{H{-}(AsX)_2{-}OH + H{-}(AsX_2)} \rightarrow \qquad (9)$$

$$\mathrm{H{-}(AsX)_2{-}AsX_2 + H_2O} \qquad (\mathrm{X = Me, H})$$

In cases when the reaction intermediates contain arsenic bound to hydride and the hydroxo groups (H–AsX–OH, X=Me, H, or OH), the condensation reaction may proceed to the formation of linear or branched polymers,

$$2n\mathrm{H{-}(AsX){-}OH} \rightarrow \mathrm{H{-}(XAs{-}AsX)}_n\mathrm{{-}OH} + 2(n-1)\mathrm{H_2O} \qquad (10)$$

or cyclic As species,

$$n\mathrm{H{-}(AsX){-}OH} \rightarrow \mathrm{(AsX)}_n + n\,\mathrm{H_2O}, \qquad (11)$$

which remain in the solid phase.

The reaction schemes presented above are in agreement with observations reported elsewhere. Under conditions typically employed in analytical protocols for trace analysis, the main reaction products are the simple volatile arsanes (reactions 1–4). Approaching conditions for synthesis reactions, however, the occurrence of condensation reactions becomes more pronounced, which leads to the formation of non-volatile arsenic species that remain in the reaction solution in either soluble or insoluble form. For example, reddish solid arsenic hydrides, arising from the chemical reduction of inorganic As(III) in aqueous solution, are reported by Jolly et al. [26]. In the case of $MeAsO(OH)_2$, its reduction with H_3PO_2 resulted in the formation of linear or cyclic methyl polyarsanes [27, 28]. Under similar conditions, the reduction of $Me_2AsO(OH)$ with H_3PO_2 yields the water-soluble $Me_2As–AsMe_2$ [27]. The fully methylated diarsane cannot react further with other arsenic intermediates from reaction 1 and therefore is the terminus of the condensation cascade.

Formation of trimethylarsane

The observation that trimethylarsane, and not dimethylarsane, is the main volatile product of reduction of $Me_2AsO(OH)$ under non-analytical reaction conditions is puzzling. It appears, from the results reported in Table 2, that the formation of Me_3As coincides with the disappearence of Me_2AsH. This indicates that Me_3As is formed by the interaction of Me_2AsH with an arsenic intermediate capable of acting as a methylation agent. The presence of such species was confirmed in the reaction of $Me_2AsO(OH)$ and $NaBH_4$ in the presence of Sb(III). The formation of $MeSbH_2$ was confirmed. The formation of Me_3As during the reduction of $Me_2AsO(OH)$ by $NaBH_4$ is likely due to the known intermediate $Me_2As–AsMe_2$. Tetramethyl diarsane is also able to form Me_2AsH from $MeAsH_2$ [29]. As described above, the formation of diarsanes is supressed when the $NaBH_4$ reduction is performed in the presence of thiols. When this is conducted with the $Me_2AsO(OH)/NaBH_4$ reaction, Me_3As is not formed (Table 2).

Methyl transfer reactions take place also in the case of elevated concentrations of $MeAsO(OH)_2$, as is evident from the results reported in Table 1 (formation of AsH_3 and Me_2AsH) and in Table 4 (the formation of $MeHAs–AsH_2$ and $MeHAs–AsMe_2$ cannot be explained only by condensation reactions). The effects produced by methyl transfer reactions during the reaction of $MeAsO(OH)_2$ with $NaBH_4$/HCl are much less pronounced than those observed for $Me_2AsO(OH)$, and the main volatile product is still the expected $MeAsH_2$ (>92%).

Conclusions

The mechanism for the reaction of arsenates—$As(OH)_3$, $AsO(OH)_3$, $MeAsO(OH)_2$, $Me_2AsO(OH)$—with aqueous tetrahydroborate(III) has been proposed. It applies to a wide range of reaction conditions employed both in trace analysis and synthesis. Under analytical conditions, the action of $NaBH_4$ on the arsenic substrate promotes their conversion to the corresponding volatile hydrides AsH_3, $MeAsH_2$, and Me_2AsH. This process is the consequence of the direct stepwise hydrogen transfer from tetrahydroborate (III) to arsenic. The formation of volatile hydrides passes through arseno-intermediates wherein the –OH groups are sequentially replaced by hydrogen atoms. Under non-analytical (synthesis) conditions, reduction by $NaBH_4$ competes with two other processes: condensation between As–H and HO–As and the transfer of methyl group. The first effect arises from the condensation of intermediates and causes the formation of As–As bonds. Consequently, volatile diarsanes and triarsanes are formed along with a reddish precipitate of polymeric arsanes. The transfer of a methyl group between the reaction products and intermediates is peculiar to the reduction of $Me_2AsO(OH)$ with $NaBH_4$. Here, the identification of Me_3As as the main volatile reduction product is evidence that transfer of a methyl group has occurred. The likely alkylating agent seems to be the condensation cascade product, As_2Me_4, which has been detected in the headspace of the reaction medium.

The detected cross-reactions among intermediates belonging to different reaction pathways of the different arsenic compounds and arsenic and antimony compounds make the proposed reaction model also interesting for the interpretation and the comprehension of interference mechanisms in CGVS.

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