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Ethylation of methylarsenic(III) compounds by sodium tetraethylborate

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The compounds $MeAsBr_2$ and Me_2AsBr at concentrations of $(1–5)\times10^{-3}$ M in acetone solution are ethylated in high yield by $NaBEt_4$ to $MeEt_2As$ and Me_2EtAs, as shown by ^1H NMR spectroscopy. The extents of ethylation of $MeAs^{2+}$ and Me_2As^+ (expressed as ions, by convention) in aqueous acid solutions [at concentrations of $(5–20)\times10^{-6}$ M] were investigated using cold trap/AA and GC AA procedures. The species Me_2As^+ was ethylated (to give Me_2EtAs) in good yield (88%); in contrast, $MeAs^{2+}$ produced the volatile trialkylarsine, $MeEt_2As$, in poor yield (30%). No volatile trialkylarsine could be obtained on treating inorganic arsenic(III) (As^{3+}) solutions with $NaBEt_4$.

Keywords: Organoarsenic, sodium tetraethylborate, gas chromatography–atomic absorption spectrometry, cold trap–atomic absorption spectrometry

INTRODUCTION

Various types of arsenic compounds have been found in environmental samples.[1–3] These range from arsenic(III) to arsenic(V) compounds and from inorganic to organic derivatives. The organoarsenic species include the simple methylarsenic species $MeAs(O)(OH)_2$, $Me_2As(O)OH$, $Me_3As(O)$, Me_4As^+], arsenocholine, ($Me_3As^+CH_2CH_2OH$), arsenobetaine, ($Me_3As^+CH_2CO_2^-$), and arsenoribofuranosides.

As the toxicity of arsenic species varies widely, it is important to determine the amounts of individual compounds rather than just the total arsenic concentrations. So far, no general analytical method has been found which enables all arsenic species to be assayed. Several procedures have been devised which allow determination of some of the arsenic species, e.g. hydride generation using sodium tetrahydroborate ($NaBH_4$) for inorganic arsenic, $Me_2As(O)OH$ and $MeAs(O)(OH)_2$ (organic arsenic moiety only);[4–9] HPLC inductively coupled plasma (ICP) MS for $Me_3As^+CH_2CO_2^-$ and $Me_2As(O)OH$;[1] polarography for inorganic arsenic, $Me_2As(O)OH$ and $MeAs(O)(OH)_2$;[10] LC or ion chromatography/QF AA/ICP AE or ICP MS,[11] reduction by $HSCH_2CO_2Me$, followed by GC or HPLC/FAAS, flame atomic fluorescence (FAFS) or ICP AES for $Me_2As(O)(OH)_2$ and $MeAs(O)(OH)_2$;[12] HPLC/thermochemical hydrogenation/AAS for $Me_3As^+CH_2CO_2^-$, $Me_3As^+CH_2CH_2OH$ and Me_4As^+;[13] and ion-pair and ion-exchange HPLC/FAAS for inorganic arsenic, $Me_2As(O)OH$, $MeAs(O)(OH)_2$ and $Me_3As^+CH_2CO_2^-$.[14]

Sodium tetraethylborate ($NaBEt_4$) has been successfully used in speciation studies of tin,[15–17] mercury[18–20] and lead;[21] reactions lead to the formation of volatile peralkylated-metal derivatives. Sodium tetraethylborate has the major advantage over other alkylating reagents, e.g. Grignard reagents, in allowing use in aqueous media.

This study was designed to investigate the potential of $NaBEt_4$ in the speciation of organoarsenic compounds.

Note: we express the arsenic species as ions, as is conventional for this work; the compounds are likely to be present mainly as the covalent species added).

RESULTS

The NMR experiments showed that Me_2AsBr or $MeAsBr_2$ in acetone as well as in aqueous acetone [at concentrations of *ca* $(1–5)\times10^{-3}$ M were ethylated by $NaBEt_4$ to Me_2EtAs or $MeEt_2As$ in high yield. The NMR reactions were best monitored using the methylarsenic peaks. Only one ethyl group of each $NaBEt_4$ molecule was active. In reactions between $MeAsBr_2$ and more than one equivalent of $NaBEt_4$, the intermediate species, MeEtAsBr, was detected. Values of the chemical shift, δ^1 H(Me) for the various methylarsenic species are listed in Table 1.

Ethylation of arsenic(III) species was next attempted at lower concentration in purely aqueous media at different pH values. Aqueous

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Table 1 Values of δ^1H (Me) for methylarsenic species in CD_3COCD_3 solution

Compound	δ^1H (Me)[a]
Me_2AsBr	1.84
$MeAsBr_2$	2.70
Me_2EtAs	0.96
$MeEt_2As$	0.90
MeEtAsBr	1.80

[a] Relative to Me_4Si.

solutions of As^{3+}, $MeAs^{2+}$ or Me_2As^+ as bromides at different pH values were treated with aqueous $NaBEt_4$. The volatile arsenic species were determined by AA after stripping the solutions, using a stream of nitrogen, into a cold trap. As shown in the results given in Table 2, no volatile species were formed from As^{3+} at any pH. Both $MeAs^{2+}$ and Me_2As^+ are ethylated to different extents, to $MeEt_2As$ and Me_2EtAs respectively, depending on the pH value. At any of the pH regions investigated, little or no further alkylation was detected after 400 s from the start of the reaction, further addition of $NaBEt_4$ giving only a slight increase in the overall response. The shape of the responses (in particular the tailing) suggested that the ethylations were not immediate reactions. The better guide to the total amount of volatile trialkylarsine products was considered to be the total area of response in AA rather than the peak heights. From the results in Table 1, solutions at pH 1 give the best overall response and so all alkylations were subsequently carried out at pH 1; however, it should be noted that $NaBEt_4$ is sensitive to acids and that some decomposition occurs in these acid solutions.

Table 2 Determination of arsenic by derivatization using $NaBEt_4$–cold trap–AA[a]

	Arsenic reagent					
	As^{3+}		$MeAs^{2+}$		Me_2As^+	
pH	Peak height[b]	Peak area[b]	Peak height[b]	Peak area[b]	Peak height[b]	Peak area[b]
0	0	0	—	—	0.509	25.6
1	0	0	0.132	30.8	0.437	72.4
2	0	0	0.134	23.1	0.546	73.1
4.5	0	0	0.045	5.2	0.045	71.0

[a] Each solution contained the same mass of arsenic (80 μg).
[b] Relative values.

Table 3 shows that there is a linear correlation of the response obtained with the amount of arsenic species originally present. The response from Me_2As^+ was consistently greater than that from $MeAs^{2+}$ (by a factor of 2.8). Use of the ethylation/simple cold trap/AA combination did not result in any significant separation of the peaks arising from $MeEt_2As$ and Me_2EtAs from mixed derivatizations. It is likely that the boiling point of $MeEt_2As$ is too similar to that of Me_2EtAs (84 °C) for it to be separated simply by sequential release from the cold trap on warming. [This should be contrasted with the separation of AsH_3 (b.p. −55 °C), $MeAsH_2$ (b.p. 2 °C) and Me_2AsH (b.p. 36 °C) in the hydride generation/cold trap/AA approach; relative response times on removing the cold trap here were 27 s, 44 s and 58 s.]

Use of the ethylation/GC/AA approach does however allow separation of Me_2EtAs and $MeEt_2As$. Derivatization of Me_2As^+ or $MeAs^{2+}$ in aqueous hydrochloric acid (HCl) solution by $NaBEt_4$, followed by extraction into pentane, GC separation and AA analysis gave the following retention times (min): pentane/Me_2EtAs/$MeEt_2As$ = 1.04/2.26/3.79.

No volatile trialkylarsines remained in aqueous acid solution after the nitrogen purging. However, some non-volatile methylarsenic derivatives must still have been in the aqueous solution, due to the incomplete ethylations [viz. unreacted Me_2As^+ and $MeAs^{2+}$, as well as the partially ethylated $MeEtAs^+$]. The amounts of arsenic(III) species remaining in the aqueous solution after the $NaBEt_4$ treatments of $MeAs^{2+}$ and Me_2As^+ were determined by subjecting the nitrogen-purged solution to the hydride generation procedure (hydride generation/cold trapping/AA). It was established for the Me_2As^+ reactions that 12% of the arsenic remained in

Table 3 Response curves for determination of arsenic by ethylation–cold trapping–AA

	Peak area[a]	
Mass of arsenic (ng)	$MeAs^{2+}$	Me_2As^+
0	—	—
80	0.028	0.084
160	0.059	0.163
320	0.112	0.305

[a] Peak appeared at times between 160 and 180 s after removing the cold trap.

solution; whereas for reactions of $MeAs^{2+}$, 30% of the original arsenic content remained.

CONCLUSIONS

The results indicate that $NaBEt_4$ has a limited use in determining organoarsenic compounds directly in aqueous acidic solutions at concentrations found in environmental samples. Only Me_2As^+ was effectively ethylated (to *ca* 88%) under the conditions employed; in comparison only *ca* 30% of $MeAs^{2+}$ was diethylated.

Much higher levels of ethylation were detected by NMR spectroscopy using higher concentrations in acetone or aqueous acetone solutions.

EXPERIMENTAL

Reagents

$MeAsBr_2$ and Me_2AsBr were Johnson Matthey GmbH and Alfa products.

An arsenic(III) stock solution (As^{3+}) containing 50 μg As cm^{-3} was prepared by dissolving 21.7 mg of sodium arsenite in 250 cm^3 of 0.10 M HCl in water. Appropriate dilutions were made using 0.10 M HCl. Monomethylarsenic or dimethylarsenic stock solutions containing 40 μg As cm^{-3} were prepared by dissolving 33.3 mg of $MeAsBr_2$ or 24.8 mg of Me_2AsBr in 250 cm^3 water. Appropriate dilutions of the stock solutions were made using water. The stock solutions of As^{3+}, $MeAs^{2+}$ and $MeAs^+$ were stable at 6 °C for three weeks, three weeks and three days, respectively.

A 2% (w/v) solution of $NaBH_4$ (from Aldrich Chem. Co. Ltd) in 0.5% (w/v) NaOH solution in water was prepared daily. $NaBEt_4$ (from Stem Chemical Inc.) was stored under a nitrogen atmosphere and 0.4% (w/v) $NaBEt_4$ in water was prepared daily.

Apparatus

Hydride generation–cold trap–atomic absorption spectrometry system

This system comprised a discrete hydride generator and a cold trap with detection by AA. Solutions of the arsenic species (1 cm^3) and aqueous 0.10 M HCl (10 cm^3) were added to the generator. Volatile arsenic species were produced in the generator after injection of 2 cm^3 of the stock $NaBH_4$ solution and carried into a nitrogen flow. The gas stream was dried by passage through sodium hydroxide pellets and the arsenic species were trapped in a U-tube filled with broken Fenske helices and submerged in liquid nitrogen, at −190 °C. The arsines were collected in the cold trap for 100 s (a nitrogen carrier gas flow rate of 60 cm^3 min^{-1} was used); after removal of the liquid nitrogen, the trap was allowed to warm to room temperature, which resulted in the sequential elution of arsines in the order of their volatility into an air–acetylene-flame-heated quartz T-tube [*ca* 900 °C] in the lightpath of a Varian Spectra A.A-10 atomic absorption spectrometer (using the 193.7 mm wavelength). A hollow-cathode lamp was chosen as the arsenic line source, with a lamp current of 10 mA. A H_2–D_2 continuum source background correction system was used. The slit width was 0.5 mm. Relative times (s) found for $AsH_3/MeAsH_2/Me_2AsH$ were $27 \pm 1/44 \pm 1/58 \pm 2$; cf boiling points (°C) of $AsH_3/MeAsH_2/Me_2AsH$ were −55/2/36, respectively.

Ethylation–cold trap–AA

This system was similar to that used for the hydride generation–cold trap–AA system, with the following changes: (1) 2 cm^3 of the $NaBEt_4$ solution was used instead of 2 cm^3 of $NaBH_4$; and (2) the volatile alkylarsines were collected in the cold trap for 400 s.

Gas chromatography coupled with AA

A Perkin–Elmer E17 gas chromatograph was interfaced with a Perkin–Elmer 360 double-beam flame AA.[22] A Megabore DB-S capillary column was used. To the nitrogen flow used as carrier gas in the GC was added a supplementary nitrogen flow at the end of the column, in order to transport the separated compounds with greater efficiency. These were carried to the atomization cell, which consisted of a flame-heated quartz T-tube to which was added hydrogen and air flow for better atomization. The conditions used were as follows:

Injector temperature:	225 °C
Oven temperature:	60 °C
Interface temperature:	180 °C
H_2 flow rate:	100 cm^3 min^{-1}
Air flow rate:	50 cm^3 min^{-1}

Table 4 GC–AA data for ethylation of $MeAs^{2+}$ and Me_2As^+ (containing 80 μg of arsenic) by $NaBEt_4$

Original solution	Peak area (h)	Peak area[a]	Retention time (min)[b]	Assignment
Pentane	—	—	1.04	Pentane
Pentane + $MeAs^{2+}$	—	—	1.04	Pentane
	26 451	1	3.79	$MeEt_2AS$
Pentane + Me_2As^+	—	—	1.02	Pentane
	77 600	2.9	2.26	Me_2EtAs

[a] Relative values. [b] The cold trap was removed at time = 0.

Nitrogen flow rate: 1–5 psg for capillary GC and 125 cm^3 min^{-1} for additional flow to interface at the quartz cell.

Other instruments

For the NMR work a Bruker 250 MHz instrument was used.

Methods

Effect of pH on ethylation of As^+, $MeAs^{2+}$ and Me_2As^+ by aqueous $NaBEt_4$

To a solution of the arsenic compound [containing 80 μg As] in 20 cm^3 of acetate/HCl-buffered solution at pH 0, 1, 2 or 4.5 was added 2 cm^3 of 0.4% (w/v) $NaBEt_4$ solution in water. The volatile organoarsenic species were analysed by the cold trap–AA technique. Results are given in Table 2. As a result remaining determinations involving ethylation–cold trapping–AA reactions were performed at a pH of 1, for different concentrations of $MeAs^{2+}$ and Me_2As^+ (Table 3).

Determination of organoarsenic species remaining after ethylation of $MeAs^{2+}$ and Me_2As^+ by $NaBEt_4$

To a solution of $MeAs^{2+}$ or Me_2As^+ (containing 80 μg As) in 20 cm^3 of a 0.10 M HCl solution was added 2 cm^3 of the 0.4% solution of $NaBEt_4$ in water. This was purged for 400 s and then 100 μl of the remaining solution was subjected to the hydride generation technique. The remaining quantities generated by $NaBH_4$ were found to be 47 ng As from DMA In 100 μl (i.e. 10 μg overall) and 110 ng As from $MeAs^{2+}$ (i.e. 24 μg overall).

Determination of arsenic by ethylation–GC–AA

$MeAs^{2+}$ or Me_2As^+ (80 μg As) in 20 cm^3 of a 0.1 M HCl solution was derivatized with 2 cm^3 of 0.4% $NaBEt_4$ solution in water. After 7 min, the solution was extracted into pentane (5.0 cm^3); aliquots (2 μl) of the pentane solution were injected into the GC–AA (oven temperature 60 °C). Results are given in Table 4.

NMR study of reaction between methylarsenic(III) compounds and $NaBEt_4$ in CD_3COCD_3 and D_2O/CD_3COCD_3 ($D_2O/CD_3COCD_3 = 1:9$)

To a solution of a methylarsenic bromide (Me_2AsBr or $MeAsBr_2$) in CD_3COCD_3 solution (1 cm^3) was added a known quantity of $NaBEt_4$ under nitrogen. The reactions were monitored by ^1H NMR spectroscopy; the extent of the ethylation reactions was determined from integration of the singlet absorption for the methyl groups in the relevant methylarsenic species. Values of δ^1H (Me) for the methylarsenic reagents, products and intermediates are given in Table 1. The solutions used are listed in Table 5.

Table 5 Solutions used in ^1H NMR studies

	Methylarsenic bromide			$NaBEt_4$	
	Compd	(mg)	(μmol)	(mg)	(μmol)
1	Me_2AsBr	10.1	54.6	8.20	54.6
2	Me_2AsBr	10.1	54.6	16.40	109.2
3	Me_2AsBr	10.1	54.6	4.10	27.3
4	$MeAsBr_2$	13.0	52.0	7.81	52.0
5	$MeAsBr_2$	13.0	52.0	15.62	104.0
6	$MeAsBr_2$	13.0	52.0	23.43	156.0

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