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Application of direct analysis in real time to a multiphase chemical system: Identification of polymeric arsanes generated by reduction of monomethylarsenate with sodium tetrahydroborate

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ABSTRACT

Direct analysis in real time (DART) has been applied in conjunction with high-resolution Orbitrap mass spectrometry to characterize the aqueous reduction of monomethylarsenate by tetrahydroborate (B/As molar ratio $\approx$ 4 mol/mol). Under these conditions, the reaction gives rise to a complex mixture of arsenic compounds which result in the formation of a reddish precipitate. The use of the DART revealed the presence of a number of polymeric arsanes – up to eight arsenic atoms – associated with the liquid/solid phase of this reaction system. From a reactivity point-of-view, these polymers exhibit an uncommon ionization pathway. In fact, similar to the alkanes, the action of the DART results in the generation of $[M-H]^+$ ions. Furthermore, for each oligomer MeHAs–$(AsMe)_n$–AsHMe ($n = 0$–8), a series of oxidation products $[(M+nO)-H]^+$ were also identified and their formation has been discussed.

1. Introduction

In the field of mass spectrometry, direct analysis in real time (DART) is regarded as the most significant invention since the introduction of electrospray (ESI) and matrix assisted laser desorption ionization (MALDI) [1]. DART is a non-destructive ambient ion source able to yield desorption/ionization – directly in open air – of low molecular weight analytes present on the surface of liquid/solid materials or in gas-phase [1,2]. Relative to the fundamentals of its ionization mechanism, DART is among the best understood ambient ionization technique. In fact, alike other atmospheric pressure ionization techniques [3], the action of the DART on a molecule (M) results in the production of $M^{+\bullet}$ and $[M+H]^+$ positive ions and $[M-H]^-$ negative ions [1]. Since its introduction in 2005 [2], DART has witnessed an increasing number of applications in many fields of analytical science [1–4], including analysis of pharmaceuticals [5], warfare agents [6], drug discovery monitoring [7] and food testing [8–10].

In this study, we present use of the DART source interfaced with an Orbitrap high resolution mass spectrometer for monitoring the constituents of a complex-multiphase chemical system. The reaction under study is the aqueous reduction of a solution of monomethylarsenate with sodium tetrahydroborate. This chemistry – hydride generation – has been utilized in analytical chemistry for many years [11,12] and applied to the determination and speciation of trace levels of arsenic compounds [13]. Under analytical conditions (i.e., trace and ultratrace levels of As), borohydride converts simple arsenic oxoacids into their corresponding arsanes through a concerted reduction [14]. However, when the concentration of arsenic increases, a complex scenario of side reactions takes place, resulting in the formation of condensation byproducts which can result in the precipitation of compounds containing arsenic [15]. Most of the analytical work to date on the characterization of this chemical system has been performed by GC/MS analysis of the reaction headspace [14,16]. No direct confirmation of compounds associated with the liquid/solid phase of this reaction system has been achieved. Considering the complex nature of this chemistry, direct chromatographic investigation of the liquid/solid phase is unfeasible. Here, we propose use of DART for the identification

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of the compounds associated with the condensed phase of this aqueous system.

2. Materials and methods

2.1. Reagents and materials

An aqueous standard solution of monomethylarsenate was prepared from its sodium salt [$w(\mathrm{MeAsO(ONa)_2}) = 0.99$ g/g, ChemService, PA, USA] in 0.1 M HCl at a mass fraction of 1000 μg/g of As. A reducing solution of sodium tetrahydroborate (1% w/w) was prepared by dissolving the solid salt ($w(\mathrm{NaBH_4}) \geq 0.98$ g/g, Alfa Aesar, Word Hill, MA, USA) in aqueous 0.1 M NaOH.

2.2. Instrumentation

A DART (direct analysis in real time) ion source (IonSence, Saugus MA, USA) 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 100 °C and all other DART operating conditions were standard settings: needle current = 9990 μA; needle voltage = 3500 V; discharge electrode current = 7 μA; discharge electrode voltage = 150 V; grid electrode current = 10 μA; grid electrode voltage = 250 V.

2.3. Hydride generation

A 1 mL volume of 1000 μg/g As as monomethylarsenate in 0.1 M HCl was introduced into a 4 mL borosilicate vial. The vial was then closed with a holed screw cap equipped with a teflon/silicone septum. A 200 μL volume of borohydride solution (1% w/w $\mathrm{NaBH_4}$ in 0.1 M NaOH) was then injected with a plastic syringe into the solution of the monomethylarsenate.

2.4. Safety considerations

Because of the high toxicity and volatility of the arsenic compounds generated, all experiments were conducted in a vented lab, using adequate PPE.

3. Results and discussion

When a dilute aqueous solution of monomethylarsenate ($w(\mathrm{As}) < 1$ μg/g) is mixed with an excess of tetrahydroborate (B/As molar ratio > 10^3 mol/mol), complete conversion of the arsenic oxoacid into monomethylarsane is normally expected [11,14]:

$$\mathrm{MeAsO(OH)_2} + [\mathrm{BH_4}]^- \rightarrow \mathrm{MeAsH_2(g)} \qquad (1)$$

However, when the same reaction is conducted at high concentration of arsenic (e.g., 1000 μg/g As), the reaction medium immediately becomes yellowish following injection of the reducing agent, and the subsequent formation of a reddish precipitate reveals a peculiar chemistry unexplained by Reaction (1) alone (see Fig. 1). Obviously this is an unwanted phenomenon from an analytical point of view.

An interpretation of this observation was recently advanced based on GC/MS analysis of the reaction headspace [15]. The identification of polymeric arsenic compounds yields the conclusion that under non-analytical conditions, hydride generation of $\mathrm{MeAsH_2}$(1) becomes competitive with that of condensation between arsanes and arsenic oxoacids not yet reduced, which are simultaneously present in the reaction medium:

$$\mathrm{MeXAs(OH)} + \mathrm{HAsYMe} \rightarrow \mathrm{MeXAs{-}AsYMe}\ (\mathrm{dimer}) + \mathrm{H_2O}$$

$$\mathrm{MeYAs{-}AsMe(H)} + \mathrm{(OH)AsXMe} \rightarrow \mathrm{MeYAs{-}AsMe{-}AsXMe}\ (\mathrm{trimer}) + \mathrm{H_2O}$$

$$\mathrm{X, Y} = -\mathrm{H}\ \text{or}\ -\mathrm{OH} \qquad (2)$$

Using GC/MS, it was possible to identify only arsane dimers (As–As) and trimers (As–As–As) which are sufficiently volatile to be sampled via the headspace [17]; unfortunately, it was not possible to achieve identification of heavier compounds. Furthermore, due to the complex multiphase nature of the reaction medium, the implementation of other chromatographic techniques was precluded. A DART–Orbitrap setup was thus investigated as a means to identify any higher molecular weight byproducts that may be produced during this hydride generation chemistry.

3.1. Positive ion DART mass spectrum of $Me_2As_2H_2$

The reduction of monomethylarsenate by tetrahydroborate under non-analytical conditions was achieved as described in Section 2.3. The headspace of the reaction vessel was sampled with a

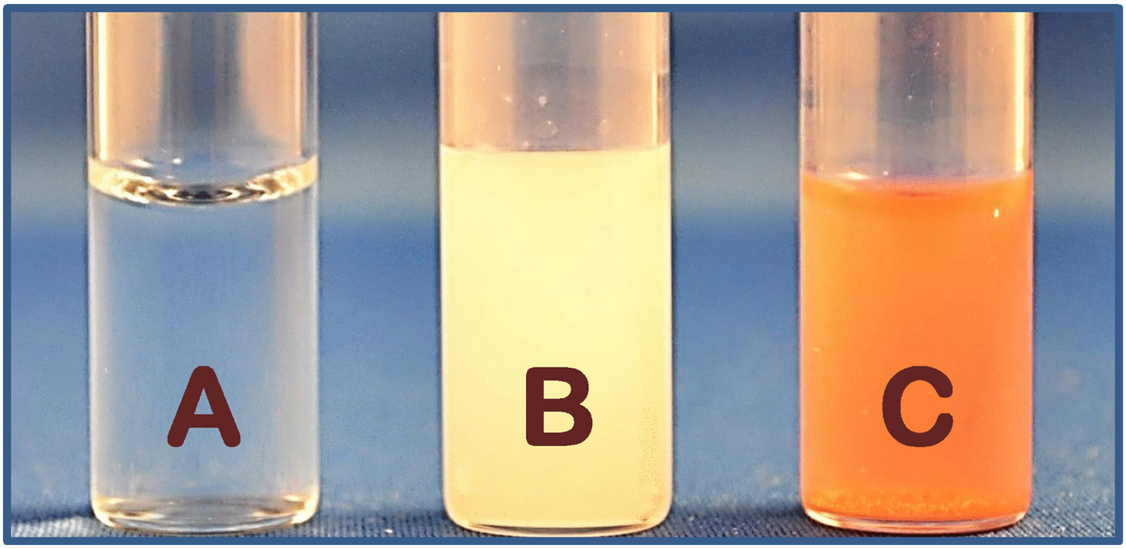

Fig. 1. An aqueous solution of monomethylarsenate ($w(\mathrm{As}) = 1000$ μg/g) in 0.1 M HCl (A) is reacted with $[\mathrm{BH_4}]^-$. After 30 s, the solution becomes yellowish (B) and after 30 min a precipitate appears (C).