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Photochemical alkylation of inorganic arsenic

Part 1. Identification of volatile arsenic species†

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Volatile arsenic species generated by UV irradiation of aqueous solutions of arsenite in low molecular weight (LMW) carboxylic acid media (formic, acetic, propionic and butyric) were identified using ICP-TOF-MS and GC-MS. Cryogenic trapping-GC-MS reveals that inorganic arsenite can be alkylated to yield AsH_3 in the presence of formic acid, trimethylarsine in acetic acid, triethylarsine in propionic acid and tripropylarsine in butyric acid solutions. Mixed ligand arsenic species such as methylarsine, dimethylarsine, dimethylethylarsine and diethylmethylarsine are also formed when a mixture of acids is used. Using $0.05 \text{ mg l}^{-1} \text{ As(III)}$ as the test solution in 3.1 M acetic acid, a methylation efficiency of approximately 75% was achieved.

Introduction

Biological methylation of arsenic has been of interest for more than a century, the milestone discovery being the elucidation of the source of toxic “Gosio Gas” emanating from damp wall-papers laden with arsenic containing pigments. Trimethylarsine $[(\text{CH}_3)_3\text{As}]$ was identified by Challenger and co-workers^{1,2} as a product of mould metabolism. Subsequent studies demonstrated that the ability to produce trimethylarsine was widespread amongst yeasts and fungi and that biological methylation of arsenic was a general phenomenon.^{3–6} Environmental conditions present in sediments, wetlands and hydrothermal springs,⁷ wastewater treatment plants and waste deposits are responsible for the occurrence of diverse methylated species. Many microorganisms (bacteria, fungi and yeasts), plants, algae, animals and even humans biomethylate arsenic, forming both volatile (e.g., methylarsines) and non-volatile (e.g., methylarsonic acid and dimethylarsinic acid) compounds. All such studies have shown that microbes are particularly proficient biomethylating organisms. Apart from As, sewage sludge, bacteria and fungi are also able to biomethylate Hg, Se and Te.⁸ Cox and Alexander⁹ have shown that microbes in soil organisms produce trimethylarsine; McBride and Wolfe¹⁰ demonstrated that anaerobic methane bacteria synthesize dimethylarsine; Reimer¹¹ showed that microorganisms present in both natural marine sediments and those contaminated with mine tailings are capable of methylating arsenic under aerobic and anaerobic conditions. Incubation of sediments with culture media produced several volatile arsines $[\text{AsH}_3, (\text{CH}_3)\text{AsH}_2, (\text{CH}_3)_2\text{AsH}$ and $(\text{CH}_3)_3\text{As}]$ ($n = 1, 2, 3$). In addition to trimethylarsine, dimethyl- and monomethylarsine have been detected in sewage gas. Arsenic oxide reportedly interacts with fungi from sewage (*C. humicola* and *S. brevicaulis*) to yield trimethylarsine and small amounts of monomethylarsine.¹² A mixture of glucose and soils enriched with sodium arsenate released arsine (AsH_3). Marine plants and algae methylate arsenic to yield non-volatile methylarsonic and dimethylarsinic acids in sea-water. In biological matrices, more complex organic arsenic forms such as arsenocholine (AsC) and arsenobetaine (AsB) can occur.¹³ In algae, arsenic is also present as arsenosugars, resulting from the biotransformation of simpler arsenic compounds.¹⁴ Braman

and Foreback¹⁵ reported the occurrence of arsenite, arsenate, methylarsonate and dimethylarsonate (cacodylate) in many environmental samples, including sea-shells, egg shells, natural waters and human urine. Methylation and ethylation were established not only under anaerobic conditions in recent sediments, but also within macroscopically aerobic milieus and in fossil substances such as natural gas and crude oil.^{16,17} It is generally accepted that the key to biological methylation of arsenic lies in methyl transfer to arsenic from the major natural methyl donors such as methionine or S-adenosylmethionine (SAM),¹⁸ methyltetrahydrofolic acid (THF), methylcobalamin ($\text{CH}_3\text{CoB}_{12}$)¹⁹ and methyl iodide produced by macro algae,¹⁹ which is widely present in coastal air and sea-water.^{20–22} The various methyl sources can lead to different products, i.e., fungi use SAM as the methyl donor yielding quite different products from those derived from bacteria, which commonly reduce methylarsenic species to arsines $[\text{Me}_x\text{AsH}_{3-x} \text{ (} x = 0–2 \text{)}]$.

Although much is understood of the biomethylation of arsenic in natural environments and progress has been made in understanding methyl transfer reactions, the major transformation pathways involved in methylation of arsenic remain largely unknown. Thus, additional intensive research in this field is needed. For example, it is unclear at the molecular level which factors are responsible for producing different products by the same organism under different conditions and why biomethylation by bacteria is always accompanied by production of methane, carbon dioxide and hydrogen.^{10,23} It is assumed that methyl transfer reagents appear periodically in nature and are mainly responsible for arsenic methylation, but the detailed pathway is vague and the function played by such reagents, rather than their metabolic intermediates such as formate, acetate and methanol, is not obvious. Such methylating reagents are not able to account for the formation of other alkylated products^{16,17} and it is clear that other possible methylation (or alkylation) pathways and potential methyl donors remain to be discovered.

Apart from biomethylation, many studies have implied that photochemical alkylation of inorganic elements exists as a parallel process in nature. Akagi *et al.*^{24,25} demonstrated that methylmercury could be produced in the natural environment solely through chemical reaction of acetic acid, propionic acid, methanol or ethanol with mercuric chloride in water under the influence of sunlight. Similarly, a methylchromium bond was

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shown to be formed during the photolysis of tertiary-butoxy radicals and chromium(II) in aqueous solution.²⁶ Results from our laboratory have earlier shown that selenium hydride, selenium carbonyl, dimethylselenide, and diethylselenide can be generated by exposure of solutions of inorganic selenium(IV) to UV irradiation in the presence of low molecular weight (LMW) organic acids.^{27,28} Volatile nickel tetracarbonyl can be produced from aqueous solutions of Ni(II) under similar conditions.²⁹ In general, in the presence of LMW acids, photochemical processes appear to be a common phenomenon, capable of converting almost 30% of the elements in the Periodic Table to volatile species.³⁰ Unfortunately, little is known of this area in clarifying the photochemical alkylation of arsenic and in this study it is shown that ultraviolet radiation induces synthesis of volatile arsenic species wherein LMW acids serve as alkyl donors in a new pathway for the transformation of inorganic arsenic. These findings could have profound environmental consequences and should provide a new approach to vapor generation for analytical chemical use.

Experimental

Instrumentation

Measurements were made in a continuous mode to characterize the yield of the reaction products using ICP-MS detection and in an off-line mode to cryogenically trap them for subsequent characterization using GC-MS techniques. Photo-reduction was accomplished using a 100 ml septum-sealed glass batch reactor (20 cm diameter $\times$ 30 cm depth) reported earlier.^{28,30} Sample solutions containing the analytes were irradiated with a UVC pen lamp (Analamp, Claremont, CA, 79 $\mu\text{W cm}^{-2}$, λ_{max} 253.7 nm) inserted into a quartz finger (12 mm od, 10 mm id, 11.5 cm depth) positioned at the center of the reactor such that it was effectively immersed in the analyte solutions but isolated from direct contact with the liquid medium. A simple scanning monochromator was used to record the spectral output and relative energy distribution of the UV light source before and after passage through the quartz finger used in the photoreactor. Most output occurs at 253.7 nm or longer (296.6 nm, 313.0 nm and 365.1 nm), these being the primary emission lines of mercury. The photoreactor was wrapped with aluminium metal foil for safety of operation. An Optimass 8000 ICP-TOF-MS instrument (GBC Scientific Equipment Pty. Ltd.) was used for detection of all volatile forms of ⁷⁵As transported from the photoreactor; operating parameters are given in Table 1. Argon carrier gas was used to mechanically sparge gaseous products from the reactor and to help maintain the solution at 30 ± 5 °C. Optimum flow rates for sample sparging were between 20 and 100 mL min⁻¹ and were selected based on maximum response. An additional flow of 1 L min⁻¹ Ar was introduced into the system *via* a T joint to maintain the plasma.

Table 1 ICP-TOF-MS operating conditions

ICP-TOF-MS	
Rf power (27.12 MHz)	1200 W
Plasma gas flow rate	10 l min ⁻¹
Auxiliary gas flow rate	0.60 l min ⁻¹
Nebulizer gas flow rate	0.65 l min ⁻¹
GC-MS	
Column	30 m $\times$ 0.25 mm id $\times$ 1.00 μm film (VICI) VB-1 capillary column
Injector temp	40 °C
Carrier gas	High-purity He, 0.8 mL min ⁻¹
Column temperature	40 °C to 100 °C, 5 min; 100 °C min ⁻¹ to 250 °C, 1.5 min
Transfer line	80 °C

Identification of the various alkylated arsenic species was accomplished after their cryogenic collection, for which a series of cooled U-tube traps (0.8 cm od $\times$ 0.6 cm id $\times$ 13 cm deep $\times$ 4 cm across) inserted between the photoreactor and the detection system condensed the analyte species. The first trap removed water using a dry ice-acetone bath (-78 °C); the second, packed with glass wool and immersed in liquid nitrogen (-196 °C), was used to sequester the volatile species swept from the dry ice bath. Helium was chosen as the carrier gas because it was not condensed in the U-tube at liquid nitrogen temperatures and did not give rise to any mass spectral interferences in the subsequent identification of trapped species by GC-MS. No volatile arsenic containing species were detected in the first trap.

A Hewlett-Packard (HP) Model 6890 gas chromatograph was interfaced to an HP5973 mass selective detector (mass range 60–270 Da). Arsenic compounds were separated on a 30 m $\times$ 0.25 mm id $\times$ 1.00 μm film (VICI) VB-1 capillary column using UHP helium carrier gas and detected following electron impact ionization (70 eV).

Reagents and samples

All solutions were prepared using 18 M Ω cm deionized, reverse osmosis water (DIW) obtained from a mixed bed ion-exchange system (NanoPure, Model D4744, Barnstead/Thermoline, Dubuque, IA). Working solutions were prepared daily by diluting 1000 mg l⁻¹ stock solutions prepared from arsenite (Na₃AsO₃ 99%, Aldrich, Milwaukee, USA) and arsenate (Na₃AsO₄ 99%, Aldrich). Sodium tetrahydroborate(III) reagent, obtained by dissolving sodium tetrahydroborate(III) powder (Fluka, Buchs, Switzerland) in 0.5% m/v NaOH, was prepared fresh each day and passed through a 0.45 μm membrane filter before use. Solutions of LMW acids were prepared from analytical reagent grade materials: formic acid (23 M, Anachemica, Canada), acetic acid (6.3 M, BDH, Canada), propionic acid (13 M, BDH) and butyric acid (10.3 M, BDH). High purity HNO₃ and HCl (Fisher Scientific) were used, except where indicated otherwise.

Procedure

Volatile arsenic compounds were generated by UV photolysis of arsenic solutions containing various LMW acids at different concentrations. The gaseous products were flushed into the ICP torch for TOF-MS measurements so as to find optimal detection conditions (note that optimal generation conditions were not rigorously pursued as quantitative analysis was not the objective of this study). Every irradiation step was preceded by at least a 20 s purge with Ar to ensure that constant response was obtained and that subsequent reactions occurred under oxygen-free conditions. A blank was measured before every analytical run using solutions containing only the LMW acids. No detectable analyte was found. "Dark" experiments were performed using an aluminium foil-wrapped lamp, wherein the test solutions received no UV radiation, in order to confirm that no volatile species were generated as a consequence of thermal effects.

Prior to commencing trapping experiments, the U-tubes were flushed with He for 10 min at room temperature in order to remove any air entrained in the system and eliminate memory effects. Following cryo-condensation, the second U-tube was closed at both ends by rubber septa and removed from the liquid nitrogen bath to equilibrate to room temperature for about 15 min. A 250 μL volume of the volatile As species was sampled through the septum of the U-tube using a gas-tight syringe and injected into the GC-MS for species identification.

Working standard solutions (20 mL of 0.05 mg l⁻¹ As(III) or As(V)), acidified to contain 0.5 M HCl, were added to a 40-mL glass reaction vessel which was then sealed with a septum. The

solutions were vigorously stirred on a stirring plate by means of a Teflon-coated stir bar. Sodium tetrahydroborate solution (0.5% m/v, 2 mL) was injected through the septum into the closed vial by means of a plastic syringe. The septum was also fitted with a 22-gauge syringe needle which served as a “de-compression vent” for excess hydrogen. Volatile arsenic species were sampled from the headspace of the vial with a syringe and transferred to the GC-MS for subsequent identification of the contents. Measurements with the borohydride system were undertaken solely for the purposes of providing benchmark GC-MS spectra with which to compare those obtained following photoalkylation.

Results and discussion

The detection of volatile arsenic species was undertaken using a 40 mL sample volume at a concentration of 0.05 mg l^{-1} of As(III) in the presence of the various LMW acids. The on-line ICP-TOF-MS response was monitored. The gaseous arsenic containing products were flushed to the torch using an optimized flow of Ar purge gas. As it had the simplest structure among the organic acids used, formic acid was selected for initial investigation of its effects on the photochemical formation of volatile arsenic species. Volatile forms were readily detected when samples were exposed to UV light; typical results are reported in Fig. 1. In the case of formic acid (Fig. 1a I), a very sharp signal (although much weaker in intensity in comparison with that arising from use of other acids) could be obtained with irradiation times as short as 20 s and the entire reaction could, apparently, be completed within 40 s. Acetic acid (Fig. 1a II) was comparatively much more efficient for the generation of volatile arsenic compounds; the signal intensity obtained was about 30-fold greater in peak height and 1000-fold larger in peak area than that obtained using formic acid. A 60 s irradiation “induction” period was needed before detection of any volatile arsenic species was achieved, and more than 40 min was required for completion of the reaction. A similar situation was observed when using propionic acid (Fig. 1a III). Clearly, the UV irradiation time for release of volatile species varies with the acid used, suggesting that the resultant molecular species are different and the species produced with formic acid is more volatile, or less water soluble, than those formed using the other LMW acids. Part of the induction period is related to the time required to de-gas the solution with the argon purge stream so as to remove oxygen, a well-known radical scavenger. Additionally, the relatively small integrated response from the formic acid system suggests that only a small fraction of the As(III) is converted to a volatile form, the rest remaining as some ionic water soluble species yet to be identified. Generation efficiency was found to be markedly dependent on the acidity under which the reaction was performed (*cf.* Fig. 1b); the higher the acid concentration used, the more quickly the volatile arsenic species was observed. In a 3.1 M acetic acid solution the signal appeared immediately after UV irradiation commenced, thereafter decreasing rapidly. In 0.3 M acetic acid, formation of volatile species could be delayed for up to 3 hours. The signal intensity arising from an 0.05 mg l^{-1} solution of As(III) increased 10-fold in peak height and 70-fold in area when the concentration of acetic acid was increased from 0.3 M to 3.1 M. The noisy signal traces may reflect the poor efficiency of formation of the arsenic species at low concentrations of acetic acid.

Interesting results were obtained when a mixture of LMW acids was used, as illustrated in Fig. 1c. In a solution containing 1.9 M acetic and 1.7 M formic acids, the evolution of two arsenic peaks is readily discerned. The first peak appeared very quickly (after 10 s UV irradiation) and lasted for 1 min. It had the same characteristics as the species evolved when only formic acid was used, but its intensity was enhanced 8-fold in peak height and 6-fold in peak area. The second peak appeared

Fig. 1 ICP-TOF-MS transient response obtained for photochemical production of volatile arsenic species from solutions containing 0.05 mg l^{-1} of As(III) and LMW organic acids. (a) I: 4.6 M formic; II: 3.1 M acetic; III: 6.5 M propionic. (b) Effect of acetic acid concentration: IV: 0.3 M; V: 0.6 M; VI: 3.1 M. (c) Effect of a mixture of LMW organic acids: VII: 1.7 M formic acid; VIII: 1.7 M formic + 1.9 M acetic acid; IX: 1.7 M formic + 4 M propionic acid; X: 4 M propionic + 0.5 M acetic acid.

slowly after 10 min UV irradiation and persisted for more than an hour. Large amounts of gaseous arsenic products were easily produced from mixtures of formic and propionic acids and from acetic and propionic acids. However, only one of these arsenic containing peaks had the same temporal characteristics as that arising from use of propionic acid alone.

Apart from arsenite, generation of volatile forms of arsenic from arsenate also occurred but the signal intensity was low and persisted longer, suggesting that reaction kinetics were quite slow and that it apparently proceeded *via* a different mechanism. As generation of volatile species arsenic was relatively inefficient for arsenate in acetic acid solutions, further studies/identification were not pursued. With extended irradiation time, the overall generation efficiency (under potentially non-optimized conditions) was approximately 75% for As(III), with the batch reactor using a 0.05 mg l^{-1} As(III) in 3.1 M acetic acid.

Production of volatile species was dependent on the presence of both UV light and LMW acids. No measurable signals arose when reagent blanks were processed, nor was there any response during photolysis in the absence of LMW organic acids. Additionally, response immediately ceased when the UV lamp was turned off and significantly increased again in its presence, consistent with the results of the “dark test” noted above.

In an effort to identify the arsenic containing compounds, the volatile species arising from the processing of up to 0.5 l sample volumes of a 50 mg l^{-1} solution of As(III) and various LMW acids were swept from the gas-liquid separator and subsequently cryogenically trapped, as described earlier. Figs. 2 and 3 show the typical total ion GC-MS chromatograms of

Fig. 2 GC-MS total ion chromatograms characterizing cryogenically trapped volatile As compounds produced by UV irradiation of 50 mg l^{-1} As(III) solutions in: (a) 0.46 M HCOOH ; (b) 3.1 M CH_3COOH ; (c) 5.2 M $\text{CH}_3\text{CH}_2\text{COOH}$; (d) hexane extracted As containing compounds produced by UV irradiation of 50 mg l^{-1} As(III) solutions in 4 M $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$.

the volatile As species liberated from the UV irradiation of various acid mixtures. Fig. 4 presents the mass spectra of these species and the second column of Table 2 relates them to the appropriate figure panel. GC-MS results for a 0.46 M HCOOH solution are presented in Fig. 2a. The peak at 1.4 min (Fig. 2a) was clearly identified as arsine. The mass spectrum is presented in Fig. 4a and is consistent with that reported earlier.^{31–35} Arsine is the only product arising from the irradiation of As(III) in a solution of formic acid.

Compared with formic, use of acetic acid produced more complex results. Three arsenic containing peaks are shown in Fig. 2b, with retention times of 3.2 min, 5.8 min and 11.0 min. These correspond to trimethylarsine (Fig. 4b), dimethylethylarsine (Fig. 4c) and triethylarsine (Fig. 4e), respectively. Trimethylarsine has been reported earlier as arising from bacterial cultures,^{31–36} Dimethylethylarsine has been detected in landfill and sewage gas,³⁷ natural gas³⁸ as well as river and harbor sediments.³⁹ Triethylarsine has been detected under conditions similar to those which give rise to dimethylethylarsine.^{37–39} Both peak height and area response for each species suggest that the major product formed from irradiation of inorganic As(III) in the acetic acid solution is trimethylarsine, estimated to be about 95% (by area count) of all volatile arsenic containing species. The dimethylethylarsine and triethylarsine account for only 3.4% and 1.6%, respectively.

Fig. 3 GC-MS total ion chromatograms characterizing cryogenically trapped volatile As compounds produced by UV irradiation of 50 mg l^{-1} As(III) solutions in the mixture of LMW organic acids: (a) 0.46 M HCOOH + 3.1 M CH_3COOH ; (b) 1.2 M HCOOH + 5.1 M $\text{CH}_3\text{CH}_2\text{COOH}$; (c) 1.2 M CH_3COOH + 2.6 M $\text{CH}_3\text{CH}_2\text{COOH}$.

UV irradiation of a solution of propionic acid containing As(III) resulted in generation of four volatile arsenic compounds having retention times of 3.2, 5.8, 8.6 and 11.0 min (cf. Fig. 2c). The compounds were identified as trimethylarsine, dimethylethylarsine, diethylmethylarsine and triethylarsine, respectively, and their mass spectra are presented in Fig. 4 b–e, respectively. Diethylmethylarsine has been reported to occur only in river and harbor sediments.³⁹ In contrast to the acetic acid solution, the major product formed from irradiation of As(III) in the propionic acid was triethylarsine (52.3%). However, trimethylarsine was relatively abundant (35%) while dimethylethylarsine and diethylmethylarsine comprised about 4 and 8% of the total, respectively.

Photo-generated arsenic species arising from solutions containing mixtures of acids were also characterized. As noted earlier, in the presence of 1.9 M acetic and 1.7 M formic acid, two arsenic containing peaks were detected using ICP-TOF-MS. The first peak quickly appeared and its intensity was 8-fold larger than that arising from use of formic acid alone (cf. Fig. 1cII). The second peak appeared more slowly but persisted longer. It is possible that more than two arsenic species are produced and, in an effort to explain this phenomenon, the volatile species produced by subjecting a 0.5 l volume of sample containing 50 mg l^{-1} As(III) and 0.46 M formic + 3.1 M acetic acid were cryogenically trapped. Surprisingly, four species, having retention times of 1.8, 2.5, 3.2, and 8.6 min, were detected, corresponding to methylarsine, dimethylarsine, trimethylarsine, and diethylmethylarsine (cf. Fig. 3a). Further investigations showed that the products were dependent on the LMW acid composition under which the reactions were performed. For example, when the solution composition was changed to 4.6 M formic + 1.3 M acetic acid (as opposed to

Fig. 4 GC-MS mass spectrum of: (a) arsine; (b) trimethylarsine; (c) dimethylethylarsine; (d) diethylmethylarsine; (e) triethylarsine; and (f) tripropylarsine. The arsenic species were generated by UV irradiation of solutions containing $50 \text{ mg l}^{-1} \text{ As(III)}$ and LMW organic acids. The volatile compounds arising from the reaction were cryogenically trapped and later dissolved in hexane and analyzed by GC-MS.

the earlier 0.46 M formic acid + 3.1 M acetic acid) only arsine was found, the same species as was generated with formic acid alone. When a solution of 0.23 M formic + 3.1 M acetic acid was used, the products were trimethylarsine, dimethylethylarsine and triethylarsine, the same species as were generated when using acetic acid alone.

A similar situation arises with solutions containing both formic and propionic acids. Addition of 0.46 M formic acid to

5.1 M propionic acid produced no change in the composition of the photochemical products (*i.e.*, triethylarsine, trimethylarsine remained abundant but dimethylethylarsine and diethylmethylarsine were also present). These are the same species as those generated in 5.1 M propionic acid alone. However, as the concentration of formic acid increases from 0.46 to 1.2 M, the products become quite different. Three chromatographic peaks containing arsenic and having

Table 2 Photochemical alkylation products of inorganic arsenic (H_3AsO_3)

LMW acid	Peak identity	Alkylation products	Retention time/min
Formic acid HCOOH	Fig. 2a	Arsine, AsH_3 (bp -55°C)	1.4
Acetic acid CH_3COOH	Fig. 2b	Trimethylarsine, $\text{As}(\text{CH}_3)_3$ (bp 52°C) Dimethylethylarsine, $(\text{CH}_3)_2\text{AsCH}_2\text{CH}_3^a$ Triethylarsine, $(\text{CH}_3\text{CH}_2)_3\text{As}^a$ (bp $138\text{--}139^\circ\text{C}$)	3.2 5.8 11
Propionic acid $\text{CH}_3\text{CH}_2\text{COOH}$	Fig. 2c	Triethylarsine Trimethylarsine Dimethylethylarsine ^a Diethylmethylarsine, $(\text{CH}_3\text{CH}_2)_2\text{AsCH}_3^a$ Tripropylarsine, $\text{As}(\text{CH}_3\text{CH}_2\text{CH}_2)_3$	11 3.2 5.8 8.6 17.7
Butyric acid $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	Fig. 2d		
Formic + Acetic acid	Fig. 3a	Methylarsine, CH_3AsH_2 (bp 2°C) Dimethylarsine, $(\text{CH}_3)_2\text{AsH}$ (bp 36°C) Trimethylarsine Diethylmethylarsine	1.8 2.5 3.2 8.6
Formic + Propionic acid	Fig. 3b	Arsine Trimethylarsine Dimethylarsine or ethylarsine, $\text{CH}_3\text{CH}_2\text{AsH}_2$	1.4 3.2 2.5
Acetic + Propionic acid	Fig. 3c	Trimethylarsine Dimethylethylarsine Diethylmethylarsine Triethylarsine	3.2 5.8 8.6 11

^a Minor products. ^b bp: boiling point.

retention times of 1.4, 2.5 and 3.2 min were obtained (*cf.* Fig. 3b). The fragmentation patterns of the first and third peaks correspond to arsine and trimethylarsine, respectively. The second peak may correspond to dimethylarsine but this remains speculative as ethylarsine (bp 36 °C) may also be a product.³⁶

Large amounts of dimethylethylarsine (retention time 5.8 min), diethylmethylarsine (retention time 8.6 min), as well as trimethylarsine (retention time 3.2 min) and triethylarsine (retention time 11.0 min) were readily produced from solutions containing both acetic and propionic acids, as shown in Fig. 3c. All four compounds appear to be major products with relative abundances of 29%, 27%, 35% and 9% as trimethylarsine, dimethylethylarsine, diethylmethylarsine and triethylarsine, respectively. For clarity, all photochemically formed products in the various LMW acids are summarized in Table 2.

The irradiation of 0.5 l volumes of 4 M butyric acid containing 50 mg l⁻¹ of As(III) initially failed to yield any product in the cryogenic traps. However, if the irradiated solution was subsequently extracted with 5 ml hexane and 2 µl of this organic phase injected into the GC, one chromatographic peak containing arsenic having a retention time of 17.7 min was obtained, as shown in Fig. 2d. The mass spectrum for this analyte, shown in Fig. 4f, clearly indicates generation of tripropylarsine.

Aliphatic organic acids may follow one of several pathways during anaerobic photolytic decomposition,^{27–29} which usually produces hydrocarbon radicals, hydrocarbons and CO₂, *i.e.*:

(R = C_nH_{2n+1}, n = 0, 1, 2).

As(III) may serve as a radical scavenger, recombining with the hydrocarbon radicals to form stable methylation products:

In the mixed acid systems, more than one type of hydrocarbon radical may be formed through reaction (1), leading to the following possible pathway:

(R' = C_nH_{2n+1}, n = 0, 1, 2; R'' = C_{n'}H_{2n'+1}, n' = 0, 1, 2; m = 0, 1, 2, 3).

It remains to account for the clear difference in the products of photolysis obtained using pure acetic or propionic acids with what is predicted by eqn. (2). For example, when an acetic acid solution is used, trimethylarsine is the only product, in agreement with the prediction of eqn. (2). In the propionic acid system, although triethylarsine is the only product expected, small amounts of dimethylethylarsine and trimethylarsine are also produced and trimethylarsine, dimethylethylarsine and diethylmethylarsine appear as unexpected by-products. In order to understand this, the gaseous products formed in the headspace of the photoreactor during UV irradiation were sampled using an SPME fiber. After a five minute sampling period, the product was desorbed from the fiber into the GC-MS. It was found that when acetic acid was used, a small quantity of propionic acid was also synthesized. Similarly, some acetic acid was produced when only propionic acid was used for photochemical alkylation, arising from the loss of one methyl radical. Clearly, the photochemical alkylation pathway remains consistent with eqn. (3) because it was occurring in an essentially mixed acid medium, thereby explaining why these by-products were formed even though a single organic acid was used as the starting reagent.

Conclusions

These studies have demonstrated that inorganic arsenic(III) can be easily converted into various organometallic compounds by the action of UV light in the presence of LMW acids. Using GC-MS and ICP-TOF-MS, several volatile alkyl arsenic species have been identified. Evidence is provided that LMW acids serve as alkyl donors and photochemical alkylation may provide a new pathway for the transformation of inorganic arsenic to its volatile hydride and alkylated analogues. Although significant concentrations of LMW organic acids were used in this study, in an effort to promote the rate of generation and produce sufficient quantities of the volatile products for analytical characterization, such reactions can proceed at the mM level of LMW in nature, at correspondingly lower rates. Analytical application of this alkylation reaction is currently underway in an effort to enhance detection power for arsenic by atomic spectroscopy.

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