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Solubilization of Arsenic from Gallium Arsenide Using Aqueous Suspensions of Organic Halides

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The solubilization of arsenic in solid gallium arsenide by aqueous solutions/suspensions of organic halides is described. Although arsenic is removed from gallium arsenide surfaces, excess quantities of gallium are not found in the solution. The abilities of the organic halide to solubilize arsenic decreases as follows:

$$C_2H_5Br > CH_3I > 2\text{-}C_3H_7I > 1\text{-}C_3H_7I > 2\text{-}C_4H_9Br > CH_2{=}CHCH_2I > 2\text{-}C_3H_7Br \simeq 1\text{-}C_4H_9Br.$$

The results correlate with a combination of organic halide solubility, bond enthalpy and carbonium ion stability factors. Other parameters investigated using gallium arsenide and iodomethane include concentration, physical state of the arsenide, pH, role of oxygen and role of light.

Keywords: Gallium arsenide, organic halides, solubilization of arsenic, methylarsenic, ICP, GA AA, hydride generation

INTRODUCTION

A crucial stage in the fabrication of electronic devices from gallium arsenide (GaAs) semiconductor material is the etching process. The technique involves the progressive removal of surface material either selectively or non-selectively. Such a process can be used for surface polishing, to shape devices, and to reveal details of any surface defects. One of the more common etchants in use is a highly acidic H_2SO_4–H_2O_2 solution. One of the disadvantages of this mix is its deterioration with time (short shelf-life).

Alkyl halides, particularly iodomethane (methyl iodide, CH_3I) have been shown to be able to solubilize a range of elements and their simple compounds. The purpose of the present work was to examine the effect of aqueous alkyl halides on solid GaAs surfaces. As a potential etchant they are much milder and more time-stable than the acidic H_2SO_4–H_2O_2 mixture.

Iodomethane is a natural product produced globally by marine algae and fungi. Estimates of production rates annually vary up to 4 Mt.[1,2] Thayer *et al.* demonstrated that it would react with anoxic sediments to release metals into the surrounding water.[3] It was presumed that, under such conditions, the metals were present as sulphides, and that release was caused by reactions such as that shown in Eqn [1].

$$FeS(s) + 2CH_3I(aq) \rightarrow Fe^{2+}(aq) + 2I^-(aq) + (CH_3)_2S(g) \qquad [1]$$

It has also been shown that reaction of a suspension of tin(II) sulphide (SnS) and iodomethane in water at 60 °C over 24 h in darkness with shaking leads to solubilization of all of the tin sulphide and the production of CH_3SnI_3 in 33% yield.[4] The other product of interest was $(CH_3)_3SI$ (Eqn [2]).

$$SnS + 4CH_3I \rightarrow CH_3SnI_3 + (CH_3)_3SI \qquad [2]$$

Monomethyltin was the only organotin species observed (including headspace tests). No methyltins were detected in attempted reactions of iodomethane with SnS_2 or tin(0) powder (but see below). The mechanism proposed for the reaction in Eqn [2] was an initial methylation of sulphur in the $(\text{—Sn—S—})_n$ backbone chain so as to release slowly a tin-containing intermediate [such as $Sn(SCH_3)_2$] into solution. Methylation of the tin occurs following decomposition of $Sn(SCH_3)_2$ and oxidative addition to tin(II). It has also been observed that iodoethane reacts with tin(II) and that it also reacts with tin(II) sulphide to produce $C_2H_5SnI_3$ but at a much slower rate.[5]

Similar reactions of aqueous iodomethane with metal ores and metals have also been described.[6] Aqueous concentrations of the metals were enhanced above normal levels by extents ranging

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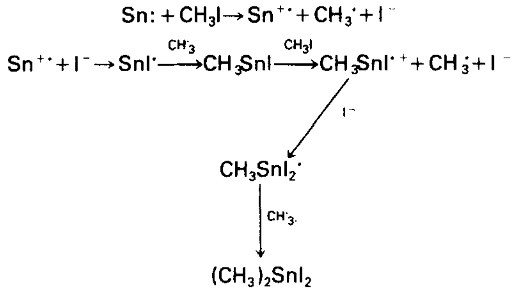


Scheme 1

from 3 to 242-fold. Species studied included iron(II) telluride (FeTe), lead(II) sulphide (PbS), iron(0), chalcopyrite ($FeCuS_2$), nickel(II) sulphide (NiS), copper(0), antimony(III) sulphide (As_2S_3) and (in a new system) iron(II) sulphide. The solubilization of the metals was demonstrated in a flow reactor, and solubilization could be increased or decreased at will by turning the iodomethane flow on or off.[6] The iodomethane solution in deionized water was saturated (approx. 100 mmol dm^{-3}).[7]

For the metal chalconides a similar mechanism to that proposed for the reaction with tin(II) sulphide was put forward, i.e. formation of the metallic iodide (soluble) and the methyl chalconide (gaseous).[6] For the metals themselves, a Grignard-type mechanism was proposed (Eqns [3]–[5]).

$$M(s) + CH_3I(aq) \rightarrow M \cdot CH_3I(s) \qquad [3]$$

$$M \cdot CH_3I(s) \rightarrow CH_3MI(aq) \qquad [4]$$

$$CH_3MI(aq) + H_2O(l) \rightarrow CH_4(g) + MI^+(aq) + OH^-(aq) \qquad [5]$$

Equation [4] is essentially an oxidative addition, well known in non-aqueous organometallic chemistry. This takes place on the surface of the metal lattice, removing the metal from the lattice into the solution as CH_3MI, where it is hydrolysed. Clearly, for metals, there results a layer-by-layer solubilization from the outer surface of the metal lattice inwards. For arsenic the As–C bond would be expected to be stable towards water, but with possible hydrolysis to methylarsenic acids.[8] The role of the surface(s) in Equation [3] is to facilitate electron transfer processes whereby M^+, $CH_3^{\cdot}$ and I^- exist transiently in the production of CH_3MI from adsorbed iodomethane.

Iodomethane has also been reacted with tin(0), lead(0) and tin(II) and lead(II) species under environmental conditions.[9] The reactants were placed in 50 cm^3 vials in distilled water and kept in darkness at 22–25 °C for 21 days. The headspace was analysed directly, and also the solvent layer following hydride generation. Small yields of mono- di, tri- and tetra-methylated species were observed (up to 1%). It was suggested that the reactions with tin occurred by a radical, one-equivalent, non-chain process to produce mono- and di-methyltin species (Scheme 1; Eqn [6]).[10, 11] Reaction with tin(II) is achieved by similar oxidative addition (Eqn [6]).[10, 11] Oxygen has been noted to be necessary in the reaction of methyl cobalamin (vitamin B_{12} with tin(II) species.[12]

$$CH_3I + SnY_2 \xrightarrow{\text{slow}} [CH_3SnY_2^{+}I^{-}] \xrightarrow{\text{fast}} CH_3SnY_2I \qquad [6]$$

Other methyltin products may be produced by disproportionation. Reactions with lead species occur in a similar manner, with monomethyl-lead compounds being very unstable, in particular, to disproportionation.

Other workers have also demonstrated the ability of alkyl halides to react directly with zero-valent or oxidized metallic species. This is of course the basis of the Grignard reaction with magnesium, the original Frankland preparation of $(C_2H_5)_2Zn$, the preparation of methylsilanes and the industrial preparation of alkyl-lead species. The present work extends these direct reactions with a view to improving etching processes for gallium arsenide semiconductor. The direct reaction general mechanism is shown in Scheme 2.[13, 14]

The direct reaction requires low-ionization-energy metals and efficient solvation of ionic intermediates. The reactions generally proceed at rates where RI > RBr > RCl, paralleling the increasing energy for bond cleavage in the rate-determining step (rds). Bond enthalpies (homolysis) in the above series are 2[illegible].0, 281.4 and

Direct reactions—general mechanism:

$$\mathrm{M + R{-}X \xrightarrow[\text{(surface)}]{\text{rds}} M^{+} + R^{\cdot}X^{-}}$$

or

$$\begin{cases} \mathrm{M + R{-}X \rightarrow M^{+} + RX^{\cdot -}} \\ \mathrm{RX^{\cdot -} \xrightarrow{\text{rds}} R^{\cdot} + X^{-}} \end{cases}$$

Then, for monovalent metals:

$$\mathrm{M^{+} + X^{-} \rightarrow MX}$$

$$\mathrm{R^{\cdot} + M \rightarrow RM}$$

For divalent metals:

$$\mathrm{M^{\cdot +} + X^{-} \rightarrow MX^{\cdot}}$$

$$\mathrm{R^{\cdot} + MX^{\cdot} \rightarrow RMX}$$

For tetravalent metals:

$$\mathrm{[RMX] + RX \rightarrow R_2MX_2}$$

Scheme 2 Abbreviation: rds, rate-determining step.

390 kJ mol^{-1} respectively.[15] Allyl and benzyl halides are very reactive, as stable radical intermediates occur. As can be seen in Scheme 2, the essential steps include a one-electron transfer from the metal to the organic halide and a heterolysis of the carbon–halogen bond as the rds, either simultaneously or subsequently. The breaking of the carbon–halogen bond appears to be a more important factor than the making of a (strong) metal–halogen bond, and the reactions are often kinetically controlled.

Recent work by Lin and Bent[16] has shown that the reaction of iodomethane with a clean copper-(III) surface proceeds by an oxidative addition of the iodide to the metal by atom-transfer or electron-transfer mechanisms analogous to those shown in Scheme 2. In this case an intermediate product has methyl and iodo moieties bound, separately, directly to the copper surface. The mechanism for this solid surface reaction suggests that (a) methyl radicals are evolved into the gas phase during the oxidative addition and (b) other methyl radicals are absorbed onto the copper metal surface. An activation energy of the carbon–iodide bond scission was calculated as 35.7 kJ mol^{-1}

EXPERIMENTAL

Materials

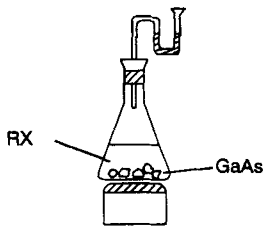


Figure 1 Apparatus for reaction of GaAs wafer with organic halides.

Gallium arsenide wafers were obtained from ICI Thin Wafers Technology plc. Following cleavage with a diamond-tipped cutter, a sample (or samples) of approximately 5.0 g of gallium arsenide was weighed out. To remove surface oxide, the wafer was washed using conc. hydrochloric acid and rinsed three times with excess of deionized water. These operations were carried out under nitrogen. Alkyl halides were purchased and used as obtained.

Reaction with iodomethane

Iodomethane (1 cm^3; 7 mmol) was pipetted into a 250 cm^3 Quickfit conical flask and made up to 100 cm^3 with deionized water. The suspension was continuously stirred magnetically during the experiment. Into the flask was placed a single sample of gallium arsenide (5.0 g; 34.5 mmol). A bubble trap containing ethanol was used to absorb any vapour (Fig. 1). This was placed on top of the conical flask. The experiment was carried out in daylight, at ambient temperature and in a normal atmosphere. To measure the reaction of the iodomethane suspension with the gallium arsenide, 5 cm^3 aliquots of the aqueous solution were pipetted from the reaction flask and elemental concentrations measured by inductively coupled plasma (ICP) emission spectrometry. Results for this reaction, shown in Fig. 2, represent the mean values of three experiments. No gallium was detected in this or in any of the similar experiments described below and the Discussion rests on the behaviour of the arsenic.

Analysis of reaction products

Total metal content was analysed using a Perkin–Elmer 40 ICP emission spectrometer. Wavelengths of 286.6 nm and 417.2 nm were used for arsenic and gallium respectively. Deionized water showed very small amounts of arsenic or gallium to be present and this is not the source of the arsenic levels shown in the Figures. The solutions from the experiments described below were aspirated directly into the ICP instrument, which had been previously calibrated from standard solutions. All analyses were carried out in triplicate. No gallium levels above those in the original deionized water were detected in any of the experiments described below.

Methylarsenic concentrations were detected using interfaced hydride generation followed by quartz furnace atomic absorption detection. The (presumed) methylarsenic species were reacted with sodium borohydride and sampled from a headspace. Arsenic was detected at 0.5 nm slit width and 286.6 nm. Hydride generation was achieved using 0.5 cm^3 of a 4% (w/v) solution of sodium borohydride in distilled water reacted with 10 cm^3 aliquots of the sample solution in a 20 cm^3 vial which had been brought to pH 7.2 with 2 cm^3 of aq. 2 M Tris–HCl. A volume of 10 μL of headspace vapour was injected into the GC AA systems. Similar methodology was used to obtain mass spectra (GC MS). General aspects of both sets of apparatus have been described in detail previously.[17-19]

Parameters investigated

The following separate parameters were also investigated in similar experiments. These include (a) concentration, (b) physical state of reactants, (c) pH, (d) oxygen, (e) light and (f) other halides. In each case 5 g of gallium arsenide [prepared as described above except for experiment (b)] was used and the apparatus was also as described. Apart from changing the parameter in question, all other parameters remained the same.

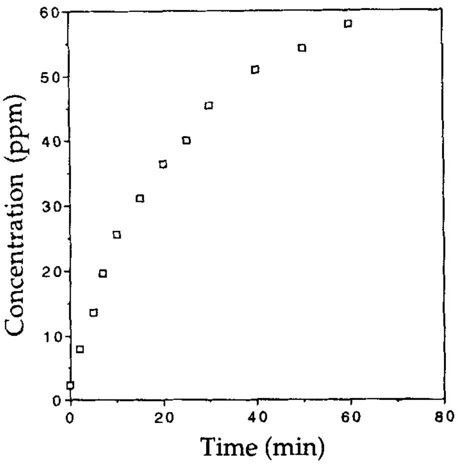


Figure 2 Variation with time of arsenic concentration in reaction products from treatment of GaAs with aqueous iodomethane.

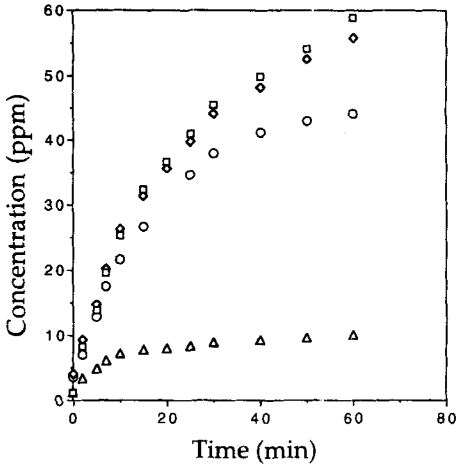


Figure 3 Effect of different concentrations of iodomethane on arsenic concentration: △, 0.1 cm^3/100 cm^3 water; ○, 0.5 cm^3/100 cm^3 water; □, 1 cm^3/100 cm^3 water; ◇, 2 cm^3/100 cm^3 water.

Concentration

This was varied using 0.1, 0.5, 1 and 2 cm^3 of iodomethane in 100 cm^3 of water, respectively. Results are shown in Fig. 3. This does not imply complete solubilization of iodomethane in water.

Reactants

In order to increase the surface area of gallium arsenide progressively, the experiment was carried out with (a) a *single* 5.0 g piece uncut, (b) 5.0 g in 0.5 cm^3 pieces and (c) 5.0 g crushed using a pestle and mortar. The results are shown in Fig. 4.

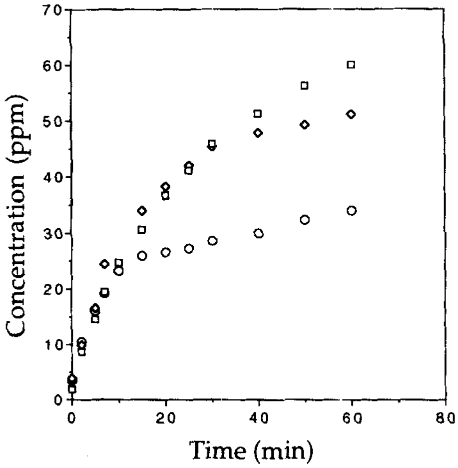


Figure 4 Effect of the physical state of the GaAs wafer on arsenic concentration: ○, single 5.0 g piece; ◇, 5.0 g in 0.5 cm^3 pieces; □, 5.0 g crushed with a pestle and mortar.

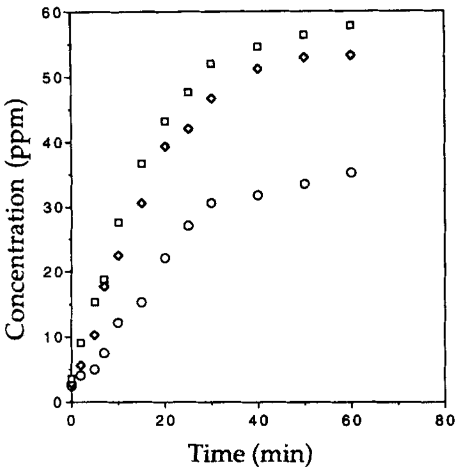


Figure 5 Effect of the pH of the reaction medium on arsenic concentration: ○, pH 4.0; ◇, pH 7.2; □, pH 12.3.

pH

Using a 5.0 g piece of gallium arsenide, the pH was varied by buffering to (a) 4.0, (b) 7.2 and (c) 12.3. The results are shown in Fig. 5. Buffering was carried out with acetate buffer, 2 M Tris–HCl and dihydrogenphosphate/hydroxide.

Oxygen

Using a 5.0 g piece of gallium arsenide, the oxygen effect was studied by (a) degassing the water with nitrogen for 1 h prior to the experiment and (b) carrying out the experiment in the normal way. The results are shown in Fig. 6

Light

Using a 5.0 g piece of gallium arsenide, one experiment was carried out in the normal way and a parallel experiment was carried out with the exclusion of light. The results are shown in Fig. 7.

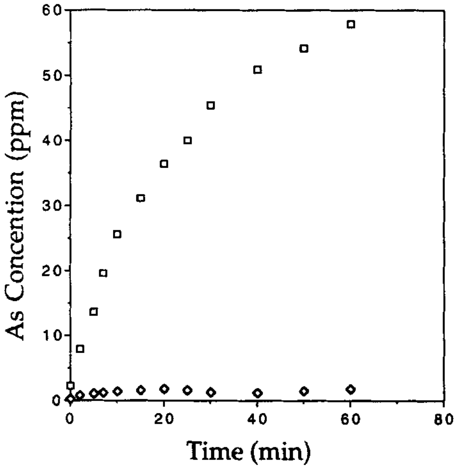


Figure 6 Effect of the environment on arsenic concentration: ◇, water degassed prior to experiment; □, normal conditions.

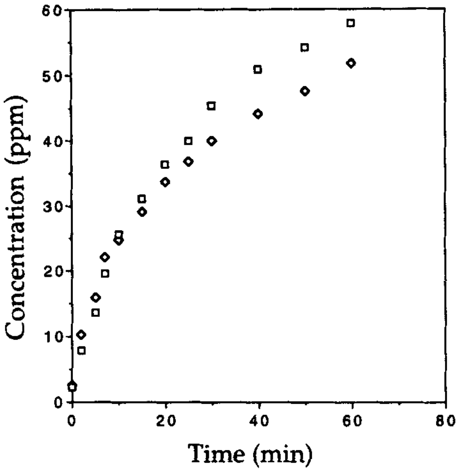


Figure 7 Effect of light conditions on arsenic concentration; ◇, light excluded; □, normal light conditions.

Other halides

Approximately 0.1 mol of each of the halogen species listed below was pipetted separately into the reaction vessel and the reaction carried out: (a) C_2H_5Br; (b) $CH_3CH_2CH_2Br$; (c) $CH_3CHBrCH_3$; (d) $CH_3CH_2CH_2CH_2Br$; (e) $CH_3CH_2CHBrCH_3$; (f) $CH_3CH_2CH_2I$; (g) CH_3CHICH_3; (h) $CH_2{=}CHCH_2I$. Results after 1 h are shown in Table 1.

RESULTS AND DISCUSSION

Reaction of the alkyl halides with gallium arsenide does not, under any of the circumstances examined by us, produce solutions containing

Table 1 Effect of different alkyl halides on concentrations of arsenic in solution after 1 h

Alkyl halide	Concn of As (ppm)	Relative rate[a]
CH_3I	58	11.6
C_2H_5Br	112	22.4
1-C_3H_7Br	5	1
2-C_3H_7Br	10	2
1-C_4H_9Br	5	1
2-C_4H_9Br	17	3.4
1-C_3H_7I	23	4.6
2-C_3H_7I	30	6
$CH_2{=}CH\,CH_2I$	13	2.6

Rate of appearance of arsenic in reaction products, [a] relative to 1-C_3H_7Br or 1-C_4H_9Br.

gallium. Only arsenic is mobilized from the lattice. The gallium arsenide wafers are produced from single crystals, which have the zinc blende structure and can be viewed as a layer structure AB· · ·AB· · ·AB· · · (A = Ga, B = As atoms). The bonding between the layers (B· · ·A) is relatively weak and hence can be readily cleaved in these directions. Almost all the major electronic and electro-optical devices are fabricated by cleaving along the (110) direction. The important consequence of this is the exposure of layers of excess arsenic atoms on one surface and excess gallium on the other, and so the dissolution of arsenic atoms can be envisaged to occur from the arsenic surface without necessarily simultaneous dissolution of gallium. Therefore, reaction of the halide with arsenic does *not* necessarily imply that gallium will also be liberated into the solution. In fact the appearance of arsenic but not gallium in solution in our experiments suggests that there is a reaction with available arsenic but not with gallium. If we consider the polarity of gallium arsenide (Ga—As) and the electronic structures involved (the arsenic possesses a lone electron pair, but the gallium does not), then these results follow. The profiles of the various reactions of gallium arsenide are shown in the Figures.

On the basis, therefore, of an oxidative addition of alkyl halide to arsenic, mobilization of arsenic appears to be reasonable, as arsenic but not gallium has the requisite lone electron pair essential for the addition. For both arsenic and gallium, three valence electrons are used for lattice bonding in GaAs; arsenic but not gallium has an electron pair remaining and available for the oxidation addition reaction (Eqn [7]).

$$\mathrm{RX'} + \mathrm{As^{III}X_3} \rightarrow \mathrm{RAs^{V}X_3X'} \qquad [7]$$

That less arsenic is solubilized at lower pH (Fig. 5) supports the basic oxidative addition methodology, in that the lone electron pair on arsenic may be more protonated at lower pH and hence less available for reaction with an incipient alkyl carbonium ion. Higher pH also increases the incipient carbonium ion character of iodomethane by increasing the leaving tendency of the iodide moiety. The near-essential role of oxygen (Fig. 6) is in accord with the free-radical mechanism discussed by Rapsomanikis and Craig[9] (Scheme 2).

As would be expected in these heterogeneous reactions, the rate of solubilization of arsenic is in proportion to increasing surface area (Fig. 4), but it is by no means in direct proportion. The surface area of the crushed gallium arsenide is many times greater than the surface area of a single piece of the material, but the solubilization increased by a factor of only about two.

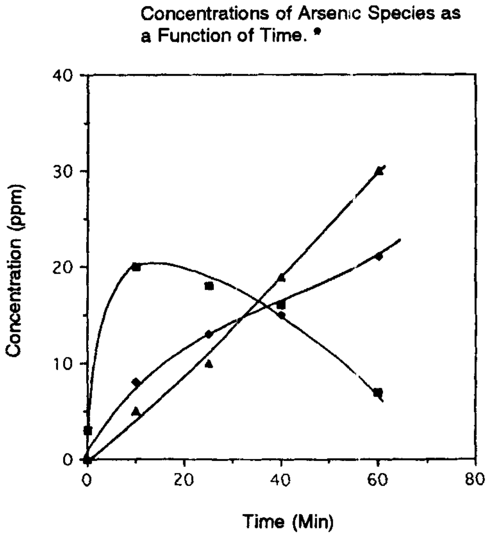
$$\mathrm{CH_3CoB_{12}} + \mathrm{Sn(II)} \rightarrow \mathrm{CH_3Sn(III)} + \mathrm{CoB_{12}} \xrightarrow{\mathrm{O_2}} \mathrm{CH_3Sn(IV)} + \mathrm{O_2^-}$$

Scheme 3

Removal of light appears to have little effect on the process (Fig. 7), suggesting that light-induced free-radical initiation does not occur. However, the role of oxygen has also been shown by Wood and co-workers to be important in the reaction of tin(II) compounds with methylcobalamin (vitamin B_{12}.[12] This is shown in Scheme 3. The electron-accepting role of oxygen here may be paralleled in a process analogous to that shown in Scheme 2.

Addition of organic halides to alkali metals usually occurs in the order RI > RBr > RCl. Thermodynamic considerations would suggest that the chlorides should react most readily as the driving force is a strongly bound alkali-metal halide. However, the reactions are normally kinetically controlled with the weaker carbon–iodine bond breaking in the rate-determining step. In the present case a combination of these factors appears to have placed a bromide species as the most reactive.

Finally, the speciation work shown in Figs 8–11



* ppm in the reaction solution

Figure 8 Concentrations of arsenic species as a function of time: ■, arsine; ◆, CH_3As^{2+}; ▲, $(CH_3)_2As^+$.

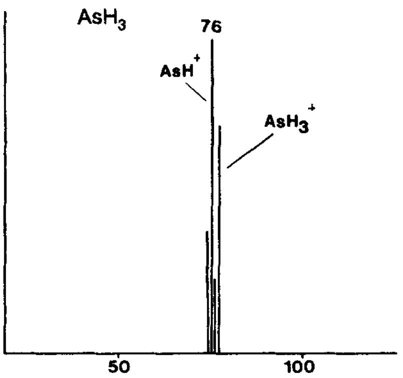


Figure 9 Mass spectrum showing arsine species in the reaction products.

shows that di- and monomethylarsenic species both increase with time, suggesting that further methylation of the monomethyl species is facile. The concentration of inorganic arsenic in the solution falls, either through methylation or hydrolysis to non-derivatizable species. We did not detect any trimethylarsenic species. It is worthy of note that at all times in Fig. 8 *total* arsenic corresponded quite well with total arsenic in Fig. 2. Rosner and Carter noted that hamsters fed gallium arsenide methylated arsenic to form methylarsenic species, including dimethylarsenic acid.[20]

CONCLUSIONS

Gallium arsenide has been shown to be selectively cleaved using iodomethane and other organic halide species. Some controlling parameters have been investigated, of which particle size, pH and oxygen content appear to be particularly important. Methylarsenic species have been identified in the products.

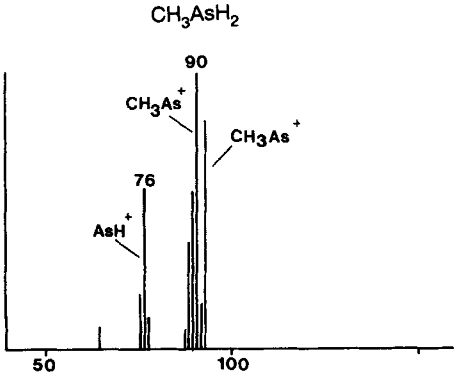


Figure 10 Mass spectrum showing monomethyl arsine species in the reaction products.

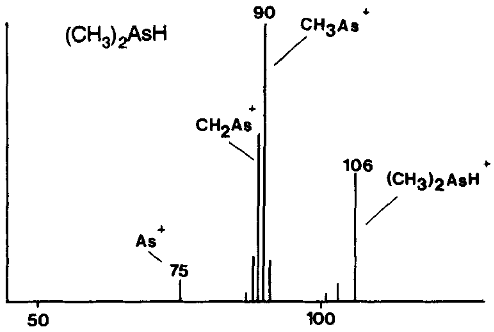


Figure 11 Mass spectrum showing dimethylarsine species in the reaction products.

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