APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 12, 237–241 (1998)

Extent and Rate of Solubilization of Tin by Iodomethane–Water Mixtures

Peter J. Craig, Stuart H. Laurie* and Reman McDonagh
Department of Chemistry, De Montfort University, The Gateway, Leicester, LE1 9BH, UK

The dissolution of tin metal by iodomethane–water mixtures has been studied and the influence of several parameters on both the extent and rate of reaction investigated. The rate-determining step shows a pseudo-first-order dependence on iodomethane (CH_3I). The reaction is strongly dependent upon both water and oxygen. The activation energy of only 16 kJ mol^{-1} is interpreted in terms of a facile bond-breaking and making process at the metal surface, generating methyltin species. Analysis by hydride generation and GC–AA confirmed the formation of methylated species ranging from monomethyl- to tetramethyl-tin; inorganic tin (from hydrolysis) was the major form, however. These findings are similar to those made earlier by us on the solubilization of arsenic from GaAs by alkyl halide-water mixtures, and a similar multi-step scheme is proposed. © 1998 John Wiley & Sons, Ltd.

Appl. Organometal. Chem. **12**, 237–241 (1998)

Keywords: tin; iodomethane; solubilization; methyltin species

Received 28 April 1997; accepted 8 September 1997

INTRODUCTION

We recently reported results on the solubilization of the semiconductor GaAs with aqueous organic halide mixtures.[1] Only arsenic was found to be mobilized, in keeping with an oxidative addition of alkyl halide to surface As atoms. It had earlier been shown[2] that CH_3I could react with Sn(0), Pb(0), Sn(II) and Pb(II) under environmental conditions; small amounts of methylated metal species were identified. These results contrasted with those of Manders *et al.*,[3] who could not detect any methylated tin species.

The ability of alkyl halides to react with metals in their elemental forms to form soluble organometallic compounds has long been known, being the basis of the classic Frankland and Grignard reactions. CH_3I also occurs naturally in the environment and, in contrast to the Frankland and Grignard reactions, has been shown to methylate metals, metalloids and metal compounds by oxidative addition under aqueous conditions.[4,5] A more detailed discussion of these environmentally important reactions can be found in our earlier report.[1] A comprehensive review by Thayer[6] on the mechanistic and practical aspects of the reactions of organic halides with metal surfaces has recently been published.

In this paper we report results from experiments on the dissolution of tin metal with aqueous CH_3I mixtures and the factors influencing both rates and amounts of metal dissolved.

EXPERIMENTAL

Materials

Tin foil (99.99% purity) and powder (*ca* 100-mesh, 149 μm 99.5% purity) and iodomethane (99.5% purity) were purchased from the Aldrich Chemical Company and were used without further purification. The tin standard for inductively coupled plasma (ICP) spectrometry calibration was of commercial AAS grade and was diluted to 10–100 ppm concentrations with deionized water.

Analyses

Total tin concentrations were determined by ICP spectrometry (wavelength 286.6 nm) using a Perkin-Elmer 40 Spectrometer. Filtered solutions from the kinetic runs were aspirated directly into the spectrometer. Methyltin concentrations were determined by hydride generation with sodium boro-

---

* Correspondence to: Stuart H. Laurie, Department of Chemistry, De Montfort University, The Gateway, Leicester, LE1 9BH, UK.

CCC 0268–2605/98/040237–05 $17.50

hydride (4%, w/v) solution; 2 cm^3 of 2 M Tris–HCl buffer was added to stabilize the solutions. A portion (0.5 cm^3) of the borohydride solution was added to 10 cm^3 of the tin solution in a sealed vial, then 10 μl of gas from the headspace was injected into a GC–AA interfaced instrument. This has been described previously.[7] The AA spectrometer was fitted with a quartz furnace and tin lamp. The interfaced instrument was calibrated with mono-, di-, and tri-methyltin hydrides derivatized from their respective chlorides; linearity was observed over a solution concentration range of 10–100 ppm. The retention times were 1.4, 2.5 and 3.9 min respectively. For stannane, SnH_4 and tetramethyltin, respective retention times were 1.1 and 5.0 min. All analyses were carried out in triplicate.

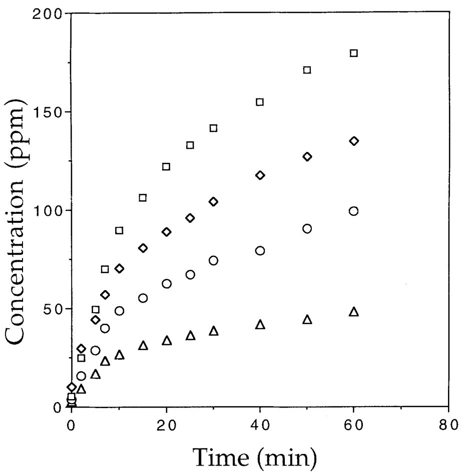


Figure 1 Solubilization of tin as a function of time (ppm = mg Sn/dm^3 H_2O): △, 0.25 cm^3 CH_3I–100 cm^3 H_2O; ○, 0.50 cm^3 CH_3I–100 cm^3 H_2O; ◇, 0.75 cm^3 CH_3I–100 cm^3 H_2O; □, 1.0 cm^3 CH_3I–100 cm^3 H_2O.

Kinetic runs

In a typical kinetic run 5 g of tin metal (foil or powder) was initially washed three times with conc. HCl and deionized water. To this was added the CH_3I–water mixture (CH_3I has a limited solubility in water) and the two-phase mixture was stirred vigorously over the course of the reaction. At specific times, 5 cm^3 aliquots of the aqueous layer were removed using a pipette filled with a glass-wool plug at its tip. Each analysis was carried out in triplicate and the results reported are the mean of the three measurements. The reaction mixtures were thermostated at 20 °C unless otherwise stated.

RESULTS

The parameters chosen for investigation were (a) the 'concentration' of MeI, (b) the influence of water, (c) the physical state of the tin metal, (d) the temperature, (e) oxygen and (f) light. Each of these was studied singly, keeping all other factors constant.

Iodomethane 'concentration'

A range from 0.25 to 1.0 cm^3 (0.004 to 0.0161 mol) of CH_3I with 100 cm^3 H_2O was used. Because of the limited solubility of CH_3I in water (literature sources give a value of approx. 1 g/100 cm^3; our experience is that it is considerably less than this but we have not quantified the value), two-phase solutions were always obtained: a saturated aqueous CH_3I phase and 'free' CH_3I (i.e. CH_3I saturated with H_2O). The results given in Fig. 1 show that both the rates and amount of tin dissolved increased as the total amount of CH_3I increased. Furthermore, a plot of the initial rates of reaction versus total CH_3I gave a linear plot, showing the dissolution reaction to be first order with respect to *total* MeI present. This vigorous stirring of the CH_3I/H_2O

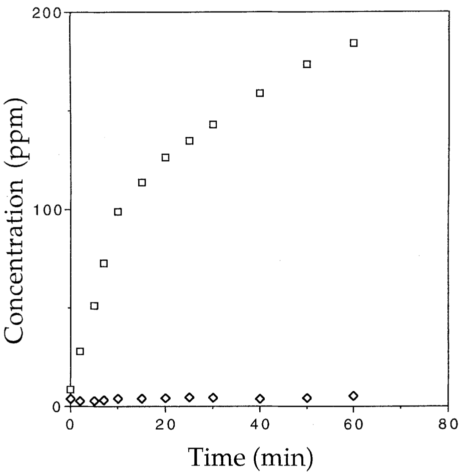


Figure 2 Effect of change of solvent on tin dissolution rate (ppm = mg Sn/dm^3 H_2O): □, 1.0 cm^3 CH_3I/100 cm^3 H_2O; ◇, 1.0 cm^3 CH_3I/100 cm^3 white spirit (hydrocarbons).

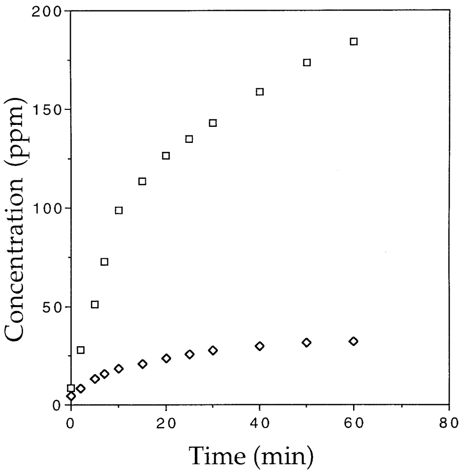


Figure 3 Effect of the physical state of tin on dissolution rate in water (ppm = mg Sn/dm^3 H_2O): □, tin powder, ◇, tin metal; 0.5 g Sn, 1.0 cm^3 CH_3I/100 cm^3 H_2O were used in both cases.

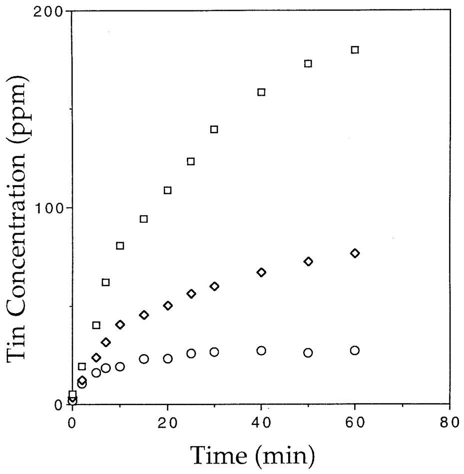


Figure 4 Effect of temperature on tin dissolution rate in water (ppm = mg Sn/dm^3 H_2O): O, 0 °C; ◇, 10 °C; □, 20 °C; 1.0 cm^3 CH_3I/100 cm^3 H_2O was used in all cases.

mixture was assumed to present a ‘uniform’ exposure of CH_3I to the tin metal.

Influence of water

Using CH_3I dissolved in a non-polar solvent (white spirit: a mixture of saturated hydrocarbons) to give a homogeneous solution, with no H_2O present, resulted in a dramatic decrease in tin solubilization. Typical results are shown in Fig. 2.

Physical state of the tin metal

As the results in Fig. 3 show, increasing the surface area of the tin metal by using a powder form led to an increase in reaction. Such an increase was as expected for a heterogeneous reaction occurring at a metal surface.

Unfortunately, it was not possible to obtain any meaningful value for the relative surface areas of the two forms of the metal. (Johnson *et al.*,[8] in a survey of the kinetics of organic halide decomposition at iron surfaces, could not relate the increase in rate of the reaction simply to increased surface area; the nature of the surface also appeared to be involved).

Temperature variation

The dissolution reaction was studied at 0, 10 and 20 °C. Increasing the temperature increased the rate of reaction, as shown in Fig. 4. A log plot of initial rate constants versus inverse temperature (K) gave a straight line and an activation energy of *ca* 16 kJ mol^{-1}.

Others factors

As with the solubilization of GaAs,[1] the reaction was found to be totally suppressed when nitrogen-saturated systems were used, consistent with a requirement for oxygen. Also, as with the GaAs studies, there was found to be no requirement for light, which ruled out a photo-activation process.

Formulation of methyltin species

All the above reactions (Figs 1–4) involved the determination only of *total* dissolved tin by AA spectrometry. The same reactions were repeated, but in these cases samples were withdrawn and treated with sodium borohydride. The volatile hydrides produced, Me_x SnH_{4-x} ($x = 0$–4) were determined quantitatively by GC–AA analysis,[7] with the exception of Me_4Sn, for which quantitative determination was not possible due to its volatility.

In all cases inorganic tin was the major species. Over the initial phase of the dissolution the order of concentrations of the methylated species was monomethyl > dimethyl > trimethyl. Tetramethyltin was not detected until after *ca* 25 min of reaction. After an extensive reaction time (*ca* 60 min) the concentrations of the various methyl-

Table 1 Concentrations of derivatized hydride species from reaction of tin (powder) with iodomethane[a]

Time/ mins	Concentrations (ppm)				
	SnH_4	CH_3SnH_3	$(CH_3)_2SnH_2$	$(CH_3)_3SnH$	$(CH_3)_4Sn$
0	7	0	0	0	0
10	63	20	16	10	0
25	80	35	26	15	i[b]
40	97	40	33	26	ii[b]
60	100	49	43	37	iii[b]

[a] Conditions: 5 g tin powder + 0.10 cm^3 CH_3I/100 cm^3 H_2O at 20 °C. b Peak heights (iii) > (ii) > (i), but not quantifiable (see text).

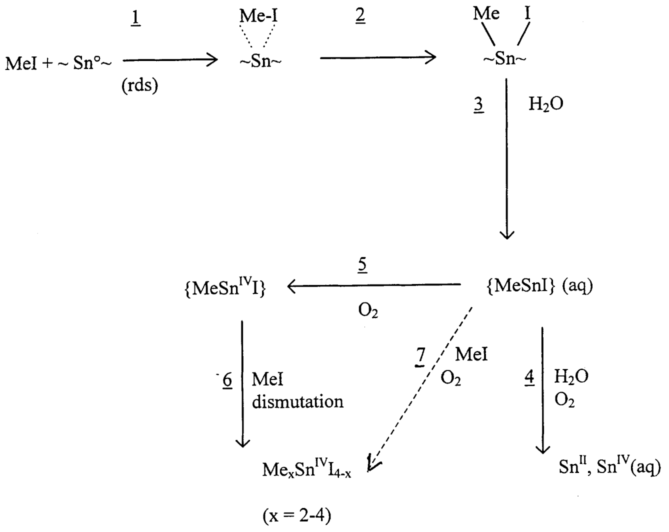
ated species were similar. Typical results are shown in Table 1.

CONCLUSIONS

As expected for a heterogeneous reaction, an increased surface area increased the dissolution rate, showing the importance of adsorption of the reactant at the metal surface. This phenomenon has been well researched with respect to the related Grignard reaction and has recently been reviewed.[9] The first-order dependence on CH_3I concentration supports a rate-determining step of unimolecular adsorption (step 1, Scheme 1) with subsequent covalent bond-breaking and-making to give CH_3–Sn bonding (step 2). There is now overwhelming evidence for steps 1 and 2 in the decomposition of a range of alkyl halides at different metal surfaces.[5,8,10] The observed low activation energy of *ca* 16 kJ mol^{-1} suggests that this bonding rearrangement is facile—in keeping with observations by Jenks *et al.*[11] that iodopropane adsorbed at a copper metal surface at 100 K undergoes decomposition at just 110 K to form surface-bound propyl groups, and by Tjandra and Zaera[12] that the energy required to break a C–I bond at a Ni(100) surface was no more than *ca* 20 kJ mol^{-1}.

The strong dependence on water can be attributed to solvation enhancing dissolution (step 3) providing a strong thermodynamic driving force, and to rapid hydrolysis of intermediate Sn species (step 4). This latter step is supported by the speciation experiments showing that inorganic tin is the major product at all stages. The influence of solution speciation on dissolution rates has been studied recently by Ludwig *et al.*[13] in relation to natural mineral dissolution. These authors showed that a direct correlation existed between dissolution rates and the nature of the species in solution.

The speciation analysis lends further support to the initial formation of a monomethyltin species followed by oxidative addition (O_2 requirement) leading to the Sn(IV) species Me_xSnI_{4-x} (steps 5, 6 and possibly 7). The formation of the higher methylated species from monomethyltin(II) can proceed via a series of dismutation reactions as established earlier.[14] These observations are con-



Scheme 1

sistent with those made by Craig and Rapsomanakis[2] on the environmental methylation of tin and lead in which sequential methylation was observed, and with those made by Fanchiang and Wood[15] on the requirement of oxygen in the reaction of Sn(II) compounds with methylcobalamin. In this latter case, molecular O_2 was postulated as oxidizing an intermediate Sn(III) species to the final Sn(IV) product.

Finally, the influence of the various parameters studied here parallel those reported earlier by us[1] on the dissolution of arsenic from GaAs by alkyl halides and suggests that the mechanism in Scheme 1 is a common one for the (environmental) dissolution of a range of inorganic species by alkyl halides.

REFERENCES

1. P. J. Craig, S. H. Laurie and R. McDonagh, *Appl. Organometal. Chem.* **8,** 183 (1994).
2. P. J. Craig and S. Rapsomanakis, *Environ. Sci. Technol.* **19,** 726 (1985).
3. W. F. Manders, G. J. Olsen, F. E. Brinckman and J. M. Bellama, *J. Chem. Soc., Chem. Commun.* 538 (1984).
4. J. S. Thayer, G. J. Olson and F. E. Brinckman, *Environ. Sci. Technol.* **18,** 726 (1984).
5. J. S. Thayer, G. J. Olson and F. E. Brinckman, *Appl. Organometal. Chem.* **1,** 73 (1987).
6. J. S. Thayer, *Adv. Organometal. Chem.* **38,** 59 (1995)
7. S. Clark and P. J. Craig, *Appl. Organometal. Chem.* **2,** 33 (1988).
8. T. L. Johnson, M. M. Scherer and P. G. Tratnyek, *Environ. Sci. Technol.* **30,** 2634 (1996)
9. H. M. Walborksy, *Acc. Chem. Res.* **23,** 286 (1993).
10. F. Zaera, *Acc. Chem. Res.* **25,** 260 (1992).
11. C. J. Jenks, B. E. Bent, N. Bernstein and F. Zaera, *J. Am. Chem. Soc.* **115,** 308 (1993).
12. S. J. Tjandra and F. Zaera, *J. Vac. Sci. Technol.* **10,** 404 (1992).
13. C. Ludwig, W. H. Casey and P. A. Rock, *Nature (London)* **375,** 44 (1995).
14. P. J. Craig, *Organometallic Compounds in the Environment,* Longman, London, 1986, p. 126.
15. Y. T. Fanchiang and J. M. Wood, *J. Am. Chem Soc.* **103,** 5100 (1981).