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Transmethylation of metals in aquatic systems

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Transmethylation reactions between organometals and metal ions in aqueous solutions in biotic and abiotic systems, with and without the presence of sediment, were investigated. It was found that alkyllead compounds can transfer their alkyl groups to Sn(II) and Sn(IV) ions to form various methyltin compounds in biotic and abiotic systems. The presence of sediment enhanced the transmethylation reactions. Methyltin compounds do not transfer their methyl groups to Pb(II). Methylarsenic acids transfer their methyl groups to Sn(II) and Sn(IV) in an abiotic system, but not in a biotic system containing sediment. The strong adsorption of tin onto sediment was the reason for the non-availability of tin ions for methylation. Methylarsenic acids do not transmethylate Pb(II). Other alkyllead compounds, such as ethyllead and butyllead species were also able to transfer their alkyl groups to tin. When both trimethyllead and triethyllead species are present in the same system, only the individual monoalkyl tin species were formed in both the Sn(II) and Sn(IV) solutions. No mixed alkyltin was produced. The findings of this study suggest that alkyllead compounds, if present in the environment, could be potential methylating agents for the formation of other methylmetals, such as methyltins. Methyltin compounds have already been documented to methylate mercuric ions in aqueous solution. Thus the study of transmethylation reactions opens up a new area of research that is essential in predicting the fate of organometals in the environment.

Keywords: Environment, transmethylation, alkyllead, alkyltin, methylarsenic compounds

INTRODUCTION

Transmethylation between organometallic species and aquatic metal ions has been reported to occur in water between Me_3Sn^+ and Hg(II), with Hg(II) as the end acceptor for the methyl group. Such reactions may have significant consequences for the environmental formation and distribution of organometals.

Abiotic transmethylation reactions of environmental importance in aqueous solutions are shown in Eqns 1 and 2:[1,2]

$$Me_3Sn^+ + Hg^{2+} \rightarrow Me_2Sn^{2+} + MeHg^+ \quad [1]$$

$$Me_3Pb^+ + Hg^{2+} \rightarrow Me_2Pb^{2+} + MeHg^+ \quad [2]$$

When chloride is the counter ion it has been observed that the extent of the transmethylation reaction is affected by the ratio of total chloride ion concentration to total mercury ion concentration ($Cl^-/Hg(II)$). Chloride ion is a strong coordinating ligand, forming a number of complex species with mercuric ion in aqueous solution. The chlorohydroxy complexes implicated in the transmethylation sequence have been identified. Other transmethylation reactions such as the transfer of methyl groups to tin ions from methyllead compounds, may also have significant consequences for the environment but such reactions have not to our knowledge been investigated.[3]

In principle such reactions might involve transfer of a carbonium ion from Me_3Pb^+ to Sn(II) (Eqn. 3), alkylation of Sn(IV) by a carbanion affording $MeSn^{3+}$ (Eqn. 4), or a radical reaction (Eqn. 5)

$$Me_3Pb^+ + :SnX_2 \rightarrow MeSnX_2{}^+ + Me_2Pb \quad [3]$$

$$Me_3Pb^+ + Sn^{4+} \rightarrow MeSn^{3+} + Me_2Pb^{2+} \quad [4]$$

$$Me_3Pb^+ + :SnX_2 \rightarrow MeSnX_2\cdot + Me_2Pb^+ \quad [5]$$

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In an attempt to probe the pathways and fate of organometals in the environment we have examined the feasibility of methyl group transfer from methyl derivatives of arsenic, mercury and lead to Sn(II), Sn(IV) and Pb(II) species.

METHODS, RESULTS AND DISCUSSION

Studies were conducted in abiotic chemical systems using distilled water and in biological systems containing sediment. Experiments were carried out with $50\,cm^3$ of water containing $1\,\mu$mole of substrate ions. One hundred μmoles of the different methylated lead compounds were added and the mixtures were incubated for 7–10 days at 20°C in an Erlenmeyer flask in light. The headspace gases and the solution were analyzed by GC-AAS methods for the presence of methylated tin species[4] and methylated lead species[5] resulting from the transfer of methyl groups from the added methyl lead compounds.

Results indicated that trimethyllead and dimethyllead species transferred their methyl groups to Sn(II) and Sn(IV), forming methylated derivatives of tin with different degrees of methyl substitution in water with and without sediment. In the presence of sediment there is an enhancement in the formation of transmethylated products, as seen in Table 1.

Significant amounts of methyltin compounds are formed as a result of transmethylation by methyllead. It is clear that the production of methyltins is considerably enhanced in the presence of sediments. Since the initial sediment contained no detectable quantities of methyltin compounds, such an enhancement could be due to microbial mediation, surface catalytic effects or both. There is no evidence as yet to distinguish between these two possibilities. The results (vide infra) also indicate that both Sn(II) and Sn(IV) species are involved in transmethylation. However more methyltin was produced in both distilled water and sediment systems from a Sn(II) than from a Sn(IV) salt. When the concentrations of the methyllead compound were increased two-fold ($200\,\mu g\,cm^{-3}$), the formation of methyltin in the pure chemical system was not proportionately increased. In the sediment system, the production of methyltin derivatives was actually lower in the presence of higher concentrations of the methyllead. A possible explanation for this phenomenon is the toxic effect of alkyllead compounds which may suppress a biological methylation component.

It is also evident from Table 1 that methyl derivatives of lead(IV) compounds are able to transfer their methyl groups to Sn(II) and Sn(IV)

Table 1 Transmethylation of Sn(II) and Sn(IV) ions by various methyllead compounds in aqueous systems

	Products Sn(IV)				
System	Me_4Sn	Me_3Sn^+	Me_2Sn^{2+}	$MeSn^{3+}$	Sn(IV)
Distilled water system					
$Sn(II) + Me_3Pb^+$	1.47	2.83	1.43	—	1.95
$Sn(II) + Me_2Pb^{2+}$	—	0.50	14.80	4.40	16.88
$Sn(IV) + Me_3Pb^+$	—	—	—	—	34.50
$Sn(IV) + Me_2Pb^{2+}$	—	—	0.83	2.30	19.95
Sediment system					
$Sn(II) + Me_3Pb^+ + S + N$	257.35	21.85	28.35	11.68	1.38
$Sn(II) + Me_2Pb^{2+} + S + N$	155.95	40.40	18.93	2.95	—
$Sn(IV) + Me_3Pb^+ + S + N$	97.82	5.83	4.10	2.20	—
$Sn(IV) + Me_2Pb^{2+} + S + N$	102.41	6.60	8.68	2.05	—
Blank (S + N)	—	—	—	—	—
Control Sn(II) + S + N	—	—	—	—	—
Control Sn(IV) + S + N	—	—	—	—	—

Concentrations: Sn(II) or Sn(IV) salt $= 5\,\mu g\,cm^{-3}$ as Sn; $Me_nPb^{(4-n)+} = 100\,\mu g\,cm^{-3}$ as Pb; sediment = 50 g; water = $100\,cm^3$; nutrient broth, 0.5%; yeast extract, 0.1%; dextrose, 0.1%; incubation time = 10 d. Me_4Sn (as ng Sn) was analyzed and given above for total headspace ($100\,cm^3$), other tin derivatives in culture solution are given as $ng\,cm^{-3}$ as tin. S + N = sediment and nutrients. (–) = not detectable.

salts. However methylmercury($MeHg^+$) does not donate its methyl group to either Sn(II) or Pb(II) salts. Methylarsenic acids transfer their methyl groups to Sn(II) and Sn(IV) salts in aqueous chemical systems but such behaviour was inhibited in the presence of sediment (Table 2). Such a retardation is likely due to adsorption of tin and arsenic species by the sediment. The loss of tin ions due to sediment adsorption was substantiated by the results of control experiments; $5\,\mu g\,cm^{-3}$ of Sn(II) and Sn(IV) salts in water added to the system are completely lost from solution in 10 days (Table 2). In the case of transmethylation by the potent methylating agent Me_3Pb^+, methyl transfer to tin competes favourably with removal of tin ions by sediment adsorption. None of the methylarsenic acids were able to transfer their methyl groups to Pb(II) salts in solution (Table 2).

In order to provide further insights into transmethylation between methyllead species and Sn(II) and Sn(IV) species in solution, experiments were carried out with other alkyllead derivatives, including triethyllead (Table 3), tributyllead compounds and simultaneous additions of both trimethyl- and triethyllead compounds to solutions containing Sn(II) or Sn(IV) species (Table 4). In systems with tributyllead, methylation was used in derivatization for analysis. For systems with trimethyllead and triethyllead, butylation was adopted for derivatization so that the transalkylation of methyl- and ethyl-groups could be recognized. All ethyllead compounds (Et_4Pb, Et_3Pb^+, Et_2Pb^{2+}) were found to transfer their ethyl groups to Sn(II) salts in solution in various degrees as indicated in Table 3. While the transmethylation reactions were unmistakably observed with Sn(II), reactions with Sn(IV) compounds were only sporadic and quantities of alkylated products were less significant. It seems likely that kinetic factors influence reaction rates such that monoethyl, diethyl, triethyl and tetraethyllead are sequentially formed. However in the present study no attempt was made to design experi-

Table 2 Transmethylation of Sn(II), Sn(IV) and Pb(II) ions by methylarsenic acids

	Products Sn(IV)				
System	Me_4Sn	Me_3Sn^+	Me_2Sn^{2+}	$MeSn^{3+}$	Sn(IV)
Distilled water system					
$Sn(II) + MeAs(OH)_2O + H_2O$	—	—	—	—	83.28
$Sn(II) + Me_2As(OH)O + H_2O$	—	33.60	—	—	44.23
$Sn(IV) + MeAs(OH)_2O + H_2O$	—	26.33			12.78
$Sn(IV) + Me_2As(OH)O + H_2O$	—	7.52	—	—	53.85
Sediment system					
$Sn(II) + MeAs(OH)_2O + S + N$	—	—	—	—	12.89
$Sn(II) + Me_2As(OH)O + S + N$	—	—	—	—	1.28
$Sn(IV) + MeAs(OH)_2O + S + N$	—	—	—	—	2.18
$Sn(IV) + Me_2As(OH)O + S + N$		—	—	—	—
Control S + N	—		—	—	—
Control Sn(II) + S + N†	—	—		—	—
Control Sn(IV) + S + N†	—	—	—	—	—
	Me_4Pb	Me_3Pb^+	Me_2Pb^{2+}		Pb(II)
$Pb(II) + MeAs(OH)_2O + H_2O$	—	—	—		1647.0
$Pb(II) + Me_2As(OH)O + H_2O$	—	—	—		1287.0
$Pb(II) + MeAs(OH)_2O + S + N$	—	—	—		369.6
$Pb(II) + Me_2As(OH)O + S + N$	—	—	—		176.6
Control S + N	—	—	—		18.7
Pb(II) + S + N	—	—	—		347.7

Concentrations: Sn(II), Sn(IV) or Pb(II) salt = $5\,\mu g\,cm^{-3}$ as Sn or Pb; Methylarsenic acids = $100\,\mu g\,cm^{-3}$; sediment = 50 g; water = $100\,cm^3$; nutrient broth, 0.5%; yeast extract, 0.1%; dextrose, 0.1%; incubation time = 10 d. Me_4Sn (ng Sn) and Me_4Pb (ng Pb) were analyzed in total headspace ($100\,cm^3$), other tin and lead derivatives in culture solutions in $ng\,cm^{-3}$ as tin or lead. S + N = sediment and nutrients. (—) = not detectable. † These results demonstrate loss of metal ions from solution.

Table 3 Transethylation of Sn(II) and Sn(IV) ions by Ethyllead species.

System	Products Sn(IV)				
	Et_4Sn	Et_3Sn^+	Et_2Sn^{2+}	$EtSn^{3+}$	Sn(IV)
Distilled water system					
$Et_4Pb+Sn(II)+H_2O$	4.09	0.83	—	—	4.68
$Et_4Pb+Sn(IV)+H_2O$	3.28	0.75	—	—	9.06
$Et_3Pb^++Sn(II)+H_2O$	—	0.37	0.56	4.14	18.81
$Et_3Pb^++Sn(IV)+H_2O$	—	—	—	—	8.00
$Et_2Pb^{2+}+Sn(II)+H_2O$	2.78	—	0.58	—	17.44
$Et_2Pb^{2+}+Sn(IV)+H_2O$	0.86	—	—	—	10.22
Sediment system					
$Et_4Pb+Sn(II)+S+N$	2.34	—	—	—	25.46
$Et_4Pb+Sn(IV)+S+N$	1.75	—	—	0.58	9.39
$Et_3Pb^++Sn(II)+S+N$	2.50	0.52	—	3.09	78.61
$Et_3Pb^++Sn(IV)+S+N$	2.08	—	—	—	58.44
$Et_2Pb^{2+}+Sn(II)+S+N$	—	—	—	—	1.14
$Et_2Pb^{2+}+Sn(IV)+S+N$	2.80	—	—	—	7.94
Control S+N	—	—	—	—	—
Control Sn(II)+S+N	—	—	—	—	—
Control Sn(IV)+S+N	—	—	—	—	—

Concentrations: Sn(II) or Sn(IV) salt = 5 $\mu g\,g^{-1}$ as Sn; $Et_nPb^{(4-n)+}$ = 100 $\mu g\,g^{-1}$ as lead; sediment = 50 g; water = 100 cm^3; other conditions as in Table 1. Concentrations of ethyltin derivatives and Sn(IV) are given as tin. Et_4Sn (as ngSn) was analyzed and given above per total headspace (100 cm^3). (—) = not detectable.

Table 4 Transalkylation of Sn(II) and Sn(IV) by alkyllead doners

System	Products											
	*Me_4-Sn	Me_3-EtSn	Me_3-BuSn	Me_2-Bu_2Sn	Me-Bu_3Sn	Et_4-Sn	Et_3-BuSn	Et_2-Bu_2Sn	Et-Bu_3Sn	MeEt-Bu_2Sn	$MeEt_2$-BuSn	Bu_4-Sn
$Me_3Pb^++Et_3Pb^+$ $+Sn(II)+N+S$	46.80	6.21	—	2.38	6.56	8.44	1.52	1.19	5.90	—	—	16.40
$Me_3Pb^++Et_3Pb^+$ $+Sn(IV)+N+S$	17.9	0.80	—	0.37	0.30	—	—	—	—	—	—	1.40
$Me_3Pb^++Et_3Pb^+$ $+Sn(II)+H_2O$	7.70	—	—	—	0.81	—	-	3.72	0.36	—	2.65	8.30
$Me_3Pb^++Et_3Pb^+$ $+Sn(IV)+H_2O$	—	—	—	—	—	—	—	2.51	—	—	—	10.10
$Bu_3Pb^++Sn(II)+N+S$	—	—	10.50	—	—	0.35	—	—	—	0.73	—	1.32
$Bu_3Pb^++Sn(IV)+N+S$	—	—	1.60	—	—	0.28	—	—	—	—	—	—
$Bu_3Pb^++Sn(II)+H_2O$	—	—	12.60	—	—	—	—	—	—	0.55	—	3.32
$Bu_3Pb^++Sn(IV)+H_2O$	—	—	17.10	—	—	—	—	—	—	1.20	—	4.00
N+S	—	—	—	—	—	—	—	—	—	—	—	—
Sn(II)+N+S	—	—	—	—	—	—	—	—	—	—	—	0.76
Sn(IV)+N+S	—	—	—	—	—	—		--	—	—	—	1.95

Alkyllead 100 $\mu g\,g^{-1}$ Pb; Sn(II), Sn(IV), 5 ppm Sn; N = nutrients, 0.5% nutrient broth, 0.1% yeast extract; 0.1% dextrose. S = 50 g Hamilton Harbour sediment. * Me_4Sn, ng Sn in total headspace (100 cm^3). Concentrations in ng/cm^3 as Sn in 100 cm^3 culture solution. (—) = not detectable. Butyl groups in the compounds are derived from butylation of the species for analysis.

mental conditions to mechanistically follow these successive transformations. For the ethyl systems no distinct enhancement of transalkylation was observed in the presence of sediment.

With tributyllead as the alkyl donor, only $BuSn^{3+}$ was produced in almost equal quantities in both Sn(II) and Sn(IV) solutions (Table 4). There was no enhancement of transalkylation in the presence of sediment. Contrary to the reaction of methyllead donors and tin compounds, the production of butyltins was higher in the distilled water system than in the presence of sediments. It is of interest to note that, where both trimethyllead and triethyllead were present in the same solution (Table 4) only the individual monoalkyl tin species were formed in both the Sn(II) and Sn(IV) solutions. No mixed alkyltin was produced. The high concentration of Me_4Sn and Et_4Sn produced in the reaction mixture of Me_3Pb^+ and Et_3Pb^+ donors and Sn(II) was probably due to chemical disproportionation of Me_3Pb^+ and Et_3Pb^+ respectively. The difference in quantities of Me_4Sn and Et_4Sn produced follow the difference in disproportionation rates of the methyl and ethyl moieties. Results further indicated that more methyltin and ethyltin species were formed with Sn(II) than with Sn(IV); greater quantities of methyl were formed than the ethyl derivatives, suggesting a significantly greater activity of the methyl moiety in transalkylation reactions. In both cases, more monomethyltin and monoethyltin were formed than the dialkyl species. Formation of the mixed alkyltin (Me, Et) species as a result of simultaneous transalkylation of both of methyl- and ethyl-groups to Sn in the same reaction mixture was probably not a spontaneous reaction. This reaction was only observed on one occasion in a system containing trimethyl-triethyllead and a Sn(II) substrate. Monomethyl diethyltin ($MeEt_2Sn^+$) was formed here and this was butylated to $MeEt_2BuSn$ for analysis. Although it was not the intention of the present study to investigate the reaction mechanisms of alkyllead and mixed alkyllead transalkylation, we have however demonstrated that transmethylation is possible between methyllead and Sn(II) under certain environmental conditions.

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