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TRANSMETHYLATION OF METALS IN AQUATIC SYSTEMS

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• Environment Canada

EXECUTIVE SUMMARY

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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 sediments were investigated. It was found that alkyllead compounds can transfer their methyl 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 lead(II).

Methylarsenic acids transfer their methyl groups to Sn(II) and Sn(IV) in an abiotic system, but not in biotic systems 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 transmethyrate lead(II).

Other alkyllead compounds such as ethyllead, and butyllead were also able to transfer their alkyl groups to tin.

The findings of this study suggest that alkyllead compounds, when present in the environment, could be potential methylating agents for the formation of other methyl-metals, such as methyltins. Methyltin has been documented to methylate mercury in aqueous solutions. 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.

RÉSUMÉ A L'INTENTION DE LA DIRECTION

TRANSMÉTHYLATION DES MÉTAUX DANS LES MILIEUX AQUATIQUES

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On a étudié les réactions de transméthylation entre des organométalliques et des ions métalliques en solution aqueuse dans des systèmes biotiques et abiotiques et en présence ou non de sédiments. On a observé que les dérivés alcoylés de plomb peuvent transférer leurs groupements méthyles aux ions Sn (II) et Sn (IV) pour former divers dérivés méthylés de l'étain dans des systèmes biotiques et abiotiques. La présence de sédiments augmente les réactions de transméthylation. Les dérivés méthylés de l'étain ne transfèrent pas leurs groupements méthyles au plomb (II).

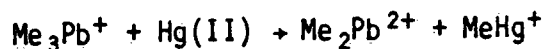
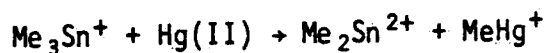
Les acides méthylarseniques transfèrent leurs groupements méthyles au Sn (II) et au Sn (IV) dans un système abiotique mais non dans des systèmes biotiques renfermant des sédiments. Les ions étain ne peuvent pas être méthylés en raison de la forte adsorption de l'étain sur les sédiments. Les acides méthylarseniques ne

transméthylent pas le plomb (II). D'autres dérivés alcoylés du plomb comme les dérivés éthylés et les dérivés butylés peuvent également ⁰trnsfé^rer leurs groupements alcoyles à l'étain.

Cette étude indique que les dérivés alcoylés du plomb dans le milieu peuvent agir comme agents méthylants et donner naissance à d'autres composés métalliques méthylés, comme les dérivés méthylés de l'étain. On sait que les composés méthylés de l'étain peuvent méthyler le mercure en solution aqueuse. L'étude des réactions de transméthylation donne donc lieu à de nouvelles recherches essentielles pour prédire le sort des organométalliques dans l'environnement.

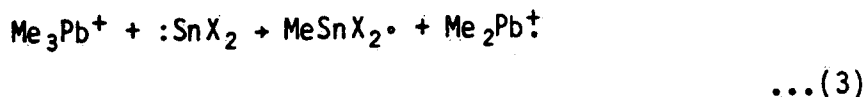
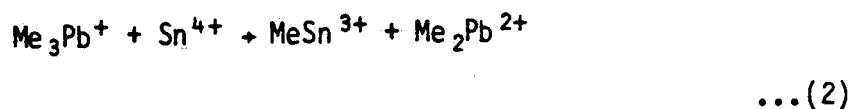
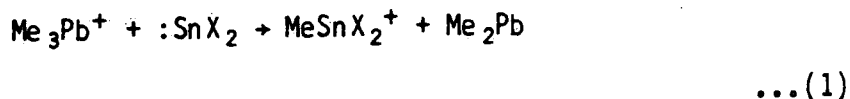
Transmethylation between organometallic species and aquatic metal ions has been reported to occur in water between Me_3Sn^+ and Hg(II) , with Hg(II) as the end acceptor for the methyl group. Such reactions may have significant consequences for the environmental formation and distribution of organometals.

Abiotic transmethylation reactions of environmental importance in aqueous solutions are: (Jewett and Brinkman 1975)



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 $\text{Cl}^-/\text{Hg(II)}$. 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.

In principle such reactions might involve transfer of a carbonium ion from Me_3Pb^+ to Sn(II) (eqn 1), alkylation of Sn(IV) by CH_3^- affording MeSn^{3+} (eqn 2) or a radical reaction (eqn 3)



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).

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 ml of water containing 1 μ mole of metal ions. One hundred μ mole of 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 (Chau et al. 1982) and methylated lead species (Chau et al. 1983) resulting from the transfer of methyl groups from the added methyl metals.

Results indicated that trimethyllead and dimethyllead transferred their methyl groups to Sn(II) and Sn(IV), forming methylated derivatives of Sn 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 methyltin 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) are involved in transmethylation. However more methyltin was

produced in both distilled water and sediment systems from Sn(II) than from Sn(IV) salt. When the concentrations of methyllead were increased two-fold (200 ppm), 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 methyllead. A possible explanation for this phenomenon is the toxic effect of alkyllead compounds which may suppress biological methylation.

It is also evident from Table I that methyl derivatives of lead(IV) compounds are able to transfer their methyl groups to Sn(II) and Sn(IV). However methylmercury MeHg^+ does not donate its methyl group to either Sn(II) or Pb(II). Methylarsenic acids transfer their methyl groups to Sn(II) and Sn(IV) in aqueous chemical systems but such behaviour was inhibited in the presence of sediment. Such a retardation is likely due to adsorption of tin and arsenic species by the sediment, a phenomenon well known to inorganic chemists. The loss of tin ions due to sediment adsorption was substantiated by the results of control experiments; 5 ppm of Sn(II) and Sn(IV) added to the system are lost from solution (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) in solution.

In order to provide further insights into transmethylation between methyllead species and Sn(II) and Sn(IV) in solution, experiments were carried out with other alkyllead derivatives, including triethyllead, tributyllead, and simultaneous additions of both trimethyl- and triethyllead to solutions containing Sn(II) or Sn(IV). 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_4 , Et_3 , Et_2) were found to transfer their ethyl groups to Sn(II) in solution in various degrees as indicated in Table 3. While the transmethylation reactions were unmistakably observed with Sn(II), reactions with Sn(IV) were only sporadic and quantities of alkylated products produced 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 effort was made to design experimental conditions to 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 $\text{BuSn}(3+)$ 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 and Sn, the production of butyltins was higher in the distilled water system than in the presence of sediments. It is of interest to note that, although both trimethyllead and triethyllead were present in the same solution, only the individual mono-alkyl tin species were formed in both the Sn(II) and Sn(IV) solutions. No mixed alkyltin was produced. The high concentrations of Me_4Sn and Et_4Sn produced in the reaction mixture of Me_3Pb and Et_3Pb and Sn(II) was probably due to chemical disproportionation of Me_3Pb^+ and Et_4Pb 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 were formed with Sn(II) than with Sn(IV); greater quantities 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 di-alkyl 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 systems containing trimethyl-, triethyllead and Sn(II). Monomethyl diethyltin (MeEt_2Sn) was formed, which was butylated to MeEt_2BuSn on analysis. Although it was not the intention of the present study to investigate the reaction mechanisms of alkyllead and mixed alkyllead trans-alkylation, we have however demonstrated that transmethylation is possible between methyllead and Sn(II) under certain environmental conditions.

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

System	Sn(IV)				Sn(IV)
	Me4-	Me3-	Me2-	Me-	
Distilled water system					
Sn(II) + Me3Pb	1.47	2.83	1.43	-	1.95
Sn(II) + Me2Pb	-	0.50	14.80	4.40	16.88
Sn(IV) + Me3Pb	-	-	-	-	34.50
Sn(IV) + Me2Pb	-	-	0.83	2.30	19.95
Sediment system					
Sn(II) + Me3Pb + S + N	257.35	21.85	28.35	11.68	1.38
Sn(II) + Me2Pb + S + N	155.95	40.40	18.93	2.95	-
Sn(IV) + Me3Pb + S + N	97.82	5.83	4.10	2.20	-
Sn(IV) + Me2Pb + 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 ppm as Sn; Me₄Pb⁽⁴⁻⁾ = 100ppm as Pb; sediment, 50g; water, 100ml; nutrient broth, 0.5%; yeast extract, 0.1%; dextrose, 0.1%; incubation time, 10 days. Me₄Sn (as ng Sn) was analyzed in total headspace, other tin derivatives in culture solution in ng/ml as Sn. S+N, sediment and nutrients. (-) not detectable.

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

System	-----Sn(IV)-----				Sn(IV)
	Me4-	Me3-	Me2-	Me-	
Distilled water system					
Sn(II) + MeAs(OH)2O + H2O	-	-	-	-	83.28
Sn(II) + Me2As(OH)O + H2O	-	33.60	-	-	44.23
Sn(IV) + MeAs(OH)2O + H2O	-	26.33	-	-	12.78
Sn(IV) + Me2As(OH)O + H2O	-	7.52	-	-	53.85
Sediment system					
Sn(II) + MeAs(OH)2O + S + N	-	-	-	-	12.89
Sn(II) + Me2As(OH)O + S + N	-	-	-	-	1.28
Sn(IV) + MeAs(OH)2O + S + N	-	-	-	-	2.18
Sn(IV) + Me2As(OH)O + S + N	-	-	-	-	-
Control S + N	-	-	-	-	-
Control Sn(II) + S + N	-	-	-	-	-
Control Sn(IV) + S + N	-	-	-	-	-
	Me4Pb	Me3Pb	Me2Pb		Pb(II)
Pb(II) + MeAs(OH)2O + H2O	-	-	-		1647.0
Pb(II) + Me2As(OH)O + H2O	-	-	-		1287.0
Pb(II) + MeAs(OH)2O + S + N	-	-	-		369.6
Pb(II) + Me2As(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 = 5ppm as Sn or Pb; Methylarsenic acids, 100ppm; sediment 50 g; water, 100ml; nutrient broth, 0.5%; yeast extract, 0.1%; dextrose, 0.1%; incubation time, 10 days. Me4Sn (ng Sn) and Me4Pb (ng Pb) were analyzed in total headspace, other Sn and Pb derivatives in culture solutions in ng/ml as Sn or Pb. S+N, sediment and nutrients. (-) not detectable.

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

System	Sn(IV)				Sn(IV)
	Et4-	Et3-	Et2-	Et-	
Distilled water system					
Et4Pb + Sn(II) + H2O	4.09	0.83	-	-	4.68
Et4Pb + Sn(IV) + H2O	3.28	0.75	-	-	9.06
Et3Pb + Sn(II) + H2O	-	0.37	0.56	4.14	18.81
Et3Pb + Sn(IV) + H2O	-	-	-	-	8.00
Et2Pb + Sn(II) + H2O	2.78	-	0.58	-	17.44
Et2Pb + Sn(IV) + H2O	0.86	-	-	-	10.22
Sediment system					
Et4Pb + Sn(II) + S + N	2.34	-	-	-	25.46
Et4Pb + Sn(IV) + S + N	1.75	-	-	0.58	9.39
Et3Pb + Sn(II) + S + N	2.50	0.52	-	3.09	78.61
Et3Pb + Sn(IV) + S + N	2.08	-	-	-	58.44
Et2Pb + Sn(II) + S + N	-	-	-	-	1.14
Et2Pb + 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 = 5ppm as Sn; $Et_nPb^{(4-n)+}$ = 100ppm as Pb; sediment 50 g; water, 100 ml; other conditions as in Table 1. Concentrations of ethyltin derivatives and Sn(IV) in ng/ml as Sn. (-) not detectable.

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

System	*Me4Sn	Me3EtSn	Me3BuSn	Me2Bu2Sn	MeBu3Sn	Et4Sn	Et3BuSn	Et2Bu2Sn	EtBu3Sn	MeEtBu2Sn	MeEt2BuSn	Bu4Sn
Me3Pb+Et3Pb+SnII+N+S	46.80	6.21	nd	2.38	6.56	8.44	1.52	1.19	5.90	nd	nd	16.40
Me3Pb+Et3Pb+SnIV+N+S	17.9	0.80	nd	0.37	0.30	nd	nd	nd	nd	nd	nd	1.40
Me3Pb+Et3Pb+SnII+H2O	7.70	nd	nd	nd	0.81	nd	nd	3.72	0.36	nd	2.65	8.30
Me3Pb+Et3Pb+SnIV+H2O	nd	nd	nd	nd	nd	nd	nd	2.51	nd	nd	nd	10.10
Bu3Pb+SnII+N+S	nd	nd	10.50	nd	nd	0.35	nd	nd	nd	0.73	nd	1.32
Bu3Pb+SnIV+N+S	nd	nd	1.60	nd	nd	0.28	nd	nd	nd	nd	nd	nd
Bu3Pb+SnII+H2O	nd	nd	12.60	nd	nd	nd	nd	nd	nd	0.55	nd	3.32
Bu3Pb+SnIV+H2O	nd	nd	17.10	nd	nd	nd	nd	nd	nd	1.20	nd	4.00
N + S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SnII +N+S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.76
SnIV +N+S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.95

Alkyllead 100ppm Pb; Sn(II), Sn(IV), 5 ppm Sn; N - nutrients, 0.5% nutrient broth, 0.1% yeast extract; 0.1% dextrose. S - 50g Hamilton Harbour sediment.

* - Me4Sn, ng Sn in total headspace.
 Concentrations in ng/ml as Sn in 100 ml culture solution. nd- not detectable.
 Butyl groups in the compounds are derived from butylation of the species for analysis.