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REVIEW

Methylation: its role in the environmental mobility of heavy elements

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Formation of bonds between methyl groups and heavy elements (metals or metalloids) alters various physical properties such as solubility or volatility. This alteration enhances the mobility of the heavy metal and can play a major role in the environmental cycles for these elements. Environmental methylation has been established as a major factor in the environmental movement of mercury and arsenic, and very probably affects other elements similarly. Two methylating agents (methylcobalamin and methyl iodide) have been found to mobilize metals out of water-insoluble compounds and/or anoxic sediments. These two compounds react with quite different substrates, but the kinetics of the resulting dissolutions follow virtually identical patterns. These reactions proceed through formation of a methylated intermediate on the substrate surface, followed by movement of the heavy element out of the solid lattice into the surrounding solution.

Keywords: Methylation, metals, environment, mobility, cobalamin, methyl iodide

INTRODUCTION

If an inorganic ligand bonded to a metal or metalloid atom is replaced by a methyl group, the resulting compound usually differs markedly from its precursor in such physical properties as melting point, boiling point, solubility, etc. These changes arise primarily from the fact that methyl groups have neither empty orbitals nor non-bonding electrons available for intermolecular interactions. For example, although the methyl group is isoelectronic with the hydroxyl group, marked differences in the polarity of the C—H and O—H bonds, plus the two lone pairs of electrons on the oxygen, result in very substantial differences in the physical properties of nominally isoelectronic groups. Systematic replacement of covalently bonded inorganic groups by covalently bonded methyl groups can alter melting points (Table 1) or densities (Table 2) quite noticeably.

Replacement of a hydrophilic hydroxide group by a lipophilic methyl group would be expected to affect the solubility of the resulting compound in water and

Table 1 Methylation and melting points

Compound	Melting Point[a] (°C)	Compound	Melting Point[a] (°C)
$(HO)_2SO_2$	10.4	$OAs(OH)_3$	35.5
$HOSO_2CH_3$	20	$OAs(OH)_2CH_3$	159.8
$SO_2(CH_3)_2$	110	$OAs(OH)(CH_3)_2$	200
		$OAs(CH_3)_3$	195.2
		$As(CH_3)_3$	−87 (est)
SiO_2	1610	SnS_2	d600
$[CH_3SiO_{1.5}]_6$	210	$[CH_3SnS_{1.5}]_4$	200 (d)
$[(CH_3)_2SiO]_3$	64.5	$[(CH_3)_2SnS]_3$	149
$[(CH_3)_3SiO_{0.5}]_2$	−67	$[(CH_3)_3SnS_{0.5}]_2$	Oil
$(CH_3)_4Si$	−102	$(CH_3)_4Sn$	−55

[a] Abbreviations: est, estimated; d, decomposes.

Table 2 Methylation and other physical properties

	K (octanol/water), 25 °C[a]		Density (g cm^{-3})
$HgCl_2$	0.61[b]	$(HO)_2SO_2$	1.84
CH_3HgCl	2.54[b]	$HOSO_2CH_3$	1.48
$(CH_3)_2Hg$	191.3 [c]	$SO_2(CH_3)_2$	1.17

[a] *K*, octanol/water distribution coefficient. [b] Ref. 1. [c] Ref. 2.

in hydrocarbons. The octanol/water distribution coefficients (Table 2) for mercuric chloride, methylmercuric chloride (CH_3HgCl) and dimethylmercury [$(H_3)_2Hg$] show that the relative solubility in n-octanol increases with increasing number of methyl groups. Similarly, the 'permethyl' derivatives of metals [e.g. $(CH_3)_2Zn$, $(CH_3)_3In$, $(CH_3)_4Ge$, etc.] are all volatile substances having little solubility in oxygen-free water but quite soluble in hydrocarbons.

Binary metal oxides and sulfides show similar but even more drastic changes in physical properties when a methyl group is introduced (Table 1). In these compounds, the formation of a methyl–methyl linkage requires scission (or at least weakening) of a metal–oxygen (or sulfur) bond. If this is done repeatedly, the metal atom can be completely removed from the solid lattice. Note that the most drastic change in melting point comes when the first methyl group is introduced. Subsequent methyl groups cause less dramatic, albeit still substantial, changes.

Methylation can also increase the toxicity of metals and metalloids,[3a] probably at least partially because of the aforementioned changes in physical properties. Similarly, the enhancement of volatility and lipophilicity caused by methylation can enhance and expand the mobility of the metal or metalloid under environmental conditions.[3b,4] This latter aspect of methylation will be the focus of this review paper.

METHYLATION REACTIONS

Homogeneous systems

Methylation of metals and metalloids in homogeneous aqueous media has been extensively investigated (see Refs 3–5, and references therein). In terms of metal–methyl bond formation, these reactions fall into two broad categories: metathesis (Eqns [1] and [2]) and oxidation–reduction (Eqns [3] and [4]).

$$(CH_3)_3SnCl + HgCl_2 \longrightarrow CH_3HgCl + (CH_3)_2SnCl_2 \qquad [1]$$

$$PdCl^{2-}_{4(aq)} + CH_3B_{12(aq)} \longrightarrow [CH_3PdCl^{2-}_3]_{(aq)} + Cl^-_{(aq)} + B_{12(aq)}{}^+ \qquad [2a]$$

(CH_3B_{12} = methylcobalamin)

$$[CH_3PdCl^{2-}_3]_{(aq)} \longrightarrow CH_3Cl_{(g)} + Pd_{(s)} + 2Cl^-_{(aq)} \qquad [2b]$$

$$RR'\overset{+}{S}CH_3 + :As(OH)_3 \longrightarrow CH_3AsO_3H_2 + RR'S + H^+_{(aq)} \qquad [3]$$

$$Pb(NO)_3)_2 + CH_3I \longrightarrow (CH_3)_4Pb \qquad [4]$$

The reactions shown in Eqns [1] and [3] yield stable methylmetals, and are inorganic models or counterparts to the two major mechanisms of biological methylation.[3c,4,5] Equation [2] shows a reaction reported by Scovell[6] and by Russian workers.[7] Equation [4] shows a reaction studied by two groups investigating the possibility of the environmental methylation of lead.[8,9] These two reactions suggest an intriguing possibility: methylation of metals under environmental conditions, whether biotic or abiotic, could alter the mobility of metals even if the initially formed methylmetals are unstable. Reductive elimination of methyl halide from an intermediate species [e.g. $CH_3PdCl^{2-}_3$ proposed by Scovell[7]] may lead to compounds in lower oxidation states or to the free metals; this, in turn, may be useful in metal isolation, as discussed by Brinckman and Olson.[10] Alternatively, the methylmetals may undergo rearrangement reactions; this appears to be important for tin and lead, and possibly for other metals as well. Certainly these intriguing possibilities deserve more attention than they have heretofore received.

Heterogeneous systems

A metal substrate does not have to be dissolved in water to undergo methylation. At least two separate methylating agents will react with compounds whose solubility in water is very low; in both cases, the level of dissolved metal increases substantially.

Methylcobalamin (CH_3B_{12}) reacted with various metal oxides in dilute buffered acetic acid solution.[11,12] The methylcobalamin decomposed in a kinetic pattern consistent with two parallel first-order reactions, the faster of which was proposed as occurring on the oxide surface. Tetramethyllead[11] and methyltin compounds[12] could be detected directly when the corresponding dioxides reacted with methylcobalamin; in other systems, the methyl group was converted into various hydrocarbons (methane, methanol, etc.), presumably through decomposition of initially formed methylmetal compounds.[12] Similarly, aqueous solutions of methyl iodide reacted with metal sulfides or selenides, plus various binary or ternary ores involving metals combined with sulfur, selenium or tellurium,[13] as exemplified by Eqn [5]:

$$PbSe_{(s)} + 2CH_3I_{(aq)} \longrightarrow Pb^{2+}_{(aq)} + 2I^-_{(aq)} + (CH_3)_2Se_{(g)} \quad [5]$$

This reaction was also proposed as occurring on the surface of the solid.[13] In all these reactions, regardless of substrate, methylating agent or reaction conditions, methylation caused a substantial increase in the concentrations of dissolved metals, often 100-fold or higher.

Flow studies

The initial methylation studies were done by extraction, concentration being monitored by atomic absorption spectrometry.[11–13] Subsequently, we extended these investigations by using a technique in which distilled water or aqueous solutions of methylating agent could be passed at constant flow rate over a metal substrate.[14] In every methylation reaction investigated by this technique, we found a very sharp growth in the concentration of dissolved metal when the methylating agent came in contact with the substrate, as shown in Figs 1–3. This reaction could be extended to pure metals;[14] these showed an even greater enhancement of dissolution that is believed to occur according to Eqn [6]:

$$M_{(s)} + CH_3I_{(aq)} \longrightarrow [CH_3MI]_{(aq)} \quad [6a]$$

$$[CH_3MI]_{(aq)} + H_2O \longrightarrow MOH^+_{(aq)} + I^-_{(aq)} + CH_{4(g)} \quad [6b]$$

Flow technique also enabled us to carry out kinetic studies. The initial growth of dissolved metal concentration followed first-order kinetics,[15] although subsequently the rate of change slowed down. Also, as Table 3 shows, the solution became more acidic during the flow of methyl iodide over many different substrates, and this difference vanished when the methyl iodide flow ceased.

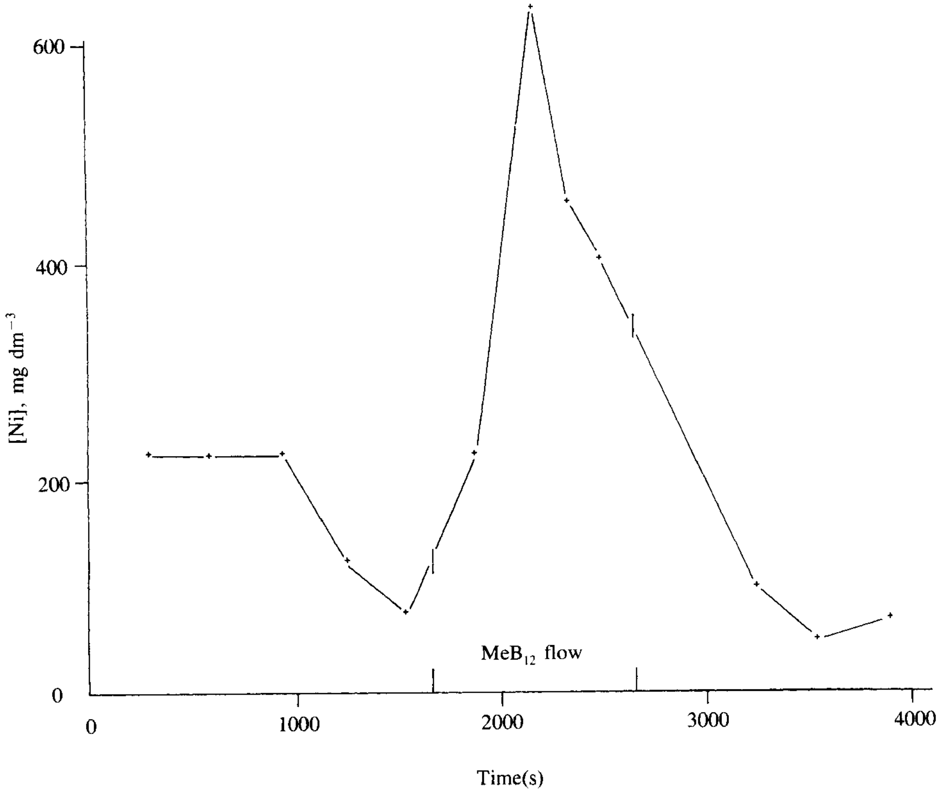

Figure 1 Dissolution of nickel dioxide by methylcobalamin solution.

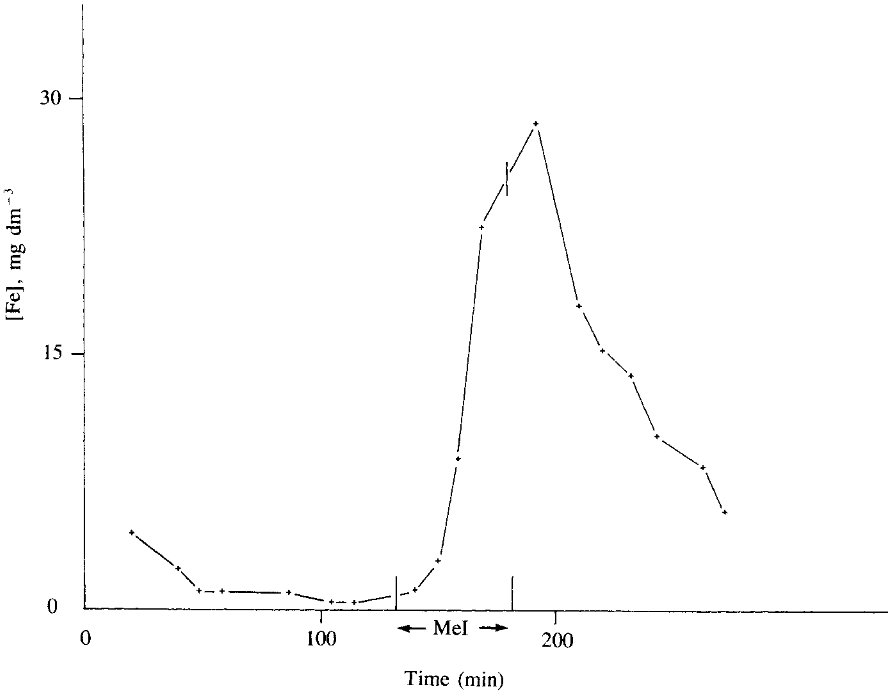

Figure 2 Dissolution of iron(II) sulfide by methyl iodide solution.

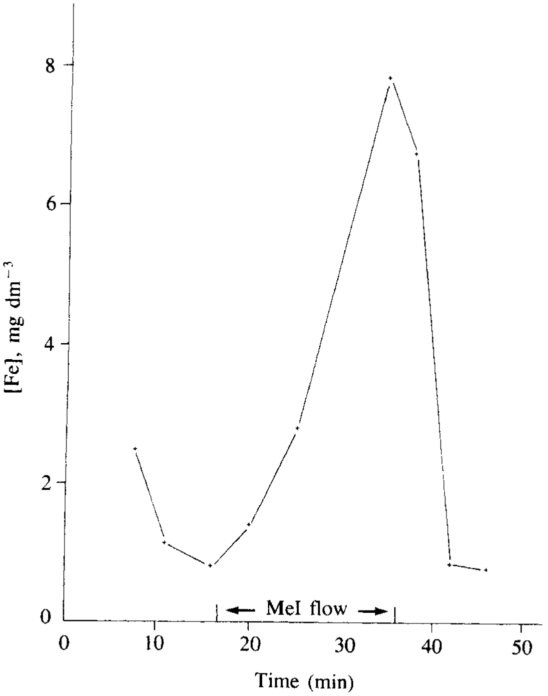

Figure 3 Dissolution of iron out of Baltimore Harbor sediments by methyl iodide flow.

Table 3 Change in pH during methyl iodide flow

Substrate		pH Before	pH During	pH After
Metals				
Al		7.46	7.16	7.39
Mg		7.49	6.97	7.45
Pb		—	6.46	7.53
Binary compounds				
AlN		5.50	4.15	5.56
NiP_2		6.42	5.70	6.47
Si_3N_4		7.55	7.00	—
WC		4.60	3.90	6.86
Standard Reference Materials (US NBS)				
330		7.21	6.89	7.43
365		7.53	7.32	7.56
875	(1)	7.22	7.02	7.42
	(2)	7.42	7.21	7.46
Specimen samples				
Chalcopyrite ($CuFeS_2$)		7.08	6.75	7.14
Ohio coal		4.85	4.50	5.13
Sediments (KP)[a]		7.51	7.21	7.30
Sediments (SR)[b]	(1)	7.43	7.36	7.39
	(2)	7.52	7.38	7.51

[a] Kent Point surface sample. [b] South River mouth: (1), surface sample; (2), 40-cm depth.

DISCUSSION

Both methylcobalamin[3–5] and methyl iodide[15] occur in nature; in fact, methyl iodide is but one of a large and steadily growing number of iodine-containing organic molecules that have been reported as exocellular metabolites in natural waters.[10] The role of methylation, especially biological methylation, in the natural cycles of the elements has been discussed at some length.[3b,4,5,16,17] The fact that methylation changes both the solubility and the volatility of the resulting species obviously affects the movement through water, through air, and/or through living organisms.

Almost all attention given to methylmetals, methylmetalloids and other organometals in the environment has concentrated on their detection and/or toxicity. In order for such compounds to be seen, they must be stable enough to reach the detector being used. Compounds not fulfilling this requirement are not observed, although their existence may be implied by indirect evidence. Our investigations suggest that exocellular methylating agents may react under natural conditions to form methylmetals. Even if such compounds are not sufficiently long-lived to be detected directly, they may well play an important and unrecognized part in the movement of metals through the biosphere.

The ability of organisms to methylate metals or metalloids may well have important potentialities in biotechnology – a point discussed by Brinckman and Olson.[10,18] One possibility is sequestration; marine algae have already been shown to accumulate substantial quantities of organoarsenicals[3b,4,5] and organoantimonials.[5] Another possibility is the use of biologically generated materials in metallurgy. Figure 4 shows how such a system might operate. Aqueous iodide ion is converted to methyl iodide by algae. This material is passed through a metal substrate, where it dissolves the metal. This dissolved metal is subsequently separated, reduced and isolated. The residual iodide is then either recycled through the algae or oxidized to triiodide ion. This in turn may react with methane (the product of the metal–methyl iodide reaction) under catalysis to generate more methyl iodide.

In any event, environmental methylation, whether biotic or abiotic, apparently exerts an important influence on movement of metals and metalloids through the environment. Much has already been learned, but considerably more seems to be awaiting discovery.

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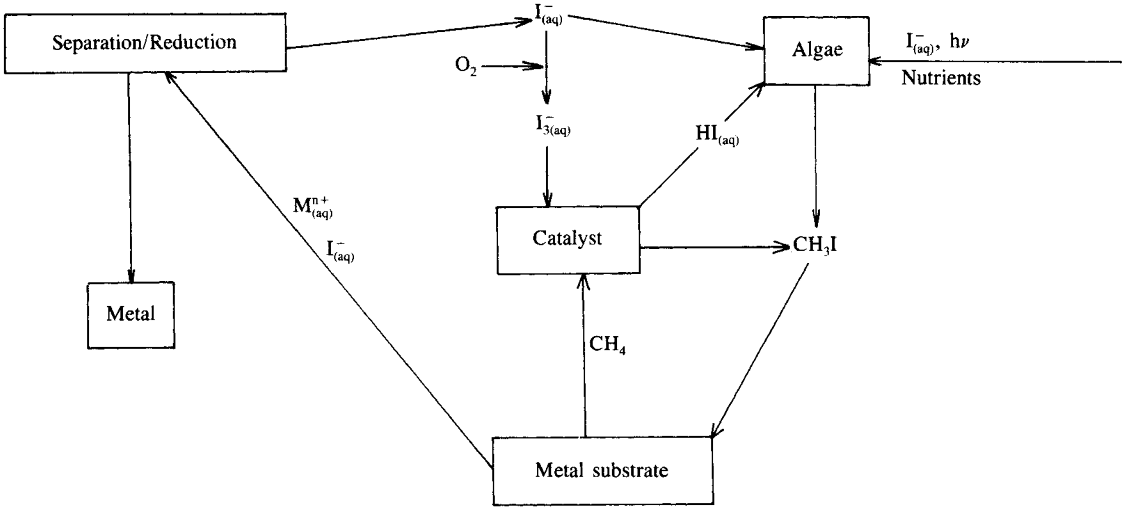

Figure 4 Proposed BROTH [Brinckman–Olson–Thayer] cycle for the application of biological methylation to metal isolation.

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