Applied Organometallic Chemistry (1989) 3 115–120

0268–2605/89/031101 15/$03.50

A study of methylation of inorganic tin by iodomethane in an aquatic environment with ^{13}C carbon isotope tracer technique

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Received 8 July 1988 *Accepted 26 September 1988*

The methylation of tin(II) [Sn(II)] by iodomethane (CH_3I) under environmental conditions has been further demonstrated by a ^{13}C carbon isotope tracer method. Methylation products are mainly monomethyltin, and very small amounts of dimethyltin. The reaction of Sn(II) and CH_3I was investigated at pH 2, 4, 6, 8, 10 and salinity (S) 8, 15, 22, 28, 35% ; it has been found the reaction was affected by pH and salinity, the tin methylation activity being highest at about pH 6 and S = 28% . The methylation reaction is first-order for both CH_3I and Sn(II), and the rate equation has been obtained as follows:

$$\frac{d[CH_3Sn]}{dt} = (k' + k''[CH_3I])\,[SnY_2])$$

where $k' = 9.10 \times 10^{-7}$ **min**$^{-1}$,
$k'' = 1.11 \times 10^{-6}$ **mmol**$^{-1}$ **dm**^{3} **min**$^{-1}$,
Y = tin counterion.

Keywords: Environment, organotin, methylation, methyltin, iodomethane, isotope tracer technique, kinetic, ^{13}C carbon

INTRODUCTION

Methylation of inorganic tin or partially alkylated tin compounds in the environment would produce more toxic species, for example:

$$\text{Sn(II)/Sn(IV)} \xrightarrow{\text{methylation}} CH_3Sn^{3+} \xrightarrow{\text{methylation}} (CH_3)_2Sn^{2+} \xrightarrow{\text{methylation}} (CH_3)_3Sn^{+} \xrightarrow{\text{methylation}} (CH_3)_4Sn$$

Until now, methyltin compounds have been identified in various environmental samples at different conditions by workers in different countries; for instance, in fresh water, saline water, river water, tap water, and urine;[1] in Canadian waters,[2] in US and German river and estuarine water;[3] in various water, sediment and organism samples;[4] and in water, sediment and organism samples of Tianjin Harbor, People's Republic of China.[5]

Human production of methyltin compounds does not account for their ubiquitous presence in the environment. A number of reports have testified that the methylation of inorganic tin is the main source of methyltin in the environment. Chau *et al.*[6] studied tin methylation under environmental conditions with various tin compounds and lake sediments; Craig *et al.*[7] also did similar studies with electrophilic methylating agents (e.g. iodomethane, betaine), and Maguire[8] contributed to this conclusion by observing $(n\text{-}C_4H_9)_3CH_3Sn$ and $(n\text{-}C_4H_9)_2(CH_3)_2Sn$ moieties in freshwater sediments. These chemical species are unlikely to have an anthropogenic origin.

Methylation of tin in the environment has been studied widely; however, there are few reports concerning mechanistic investigations, or the demonstration was not conclusive,[9] so further study is necessary under both laboratory and environmental conditions. This paper describes a study of methylation of inorganotin by iodomethane with ^{13}C carbon isotope tracer technique under simulated harbor conditions; at the same time the reaction kinetics were also investigated. The mechanism of tin methylation has been further clarified by these methods.

EXPERIMENTAL

Materials and reagents

[^{13}C] methyl iodide (>90% in ^{13}C)

This was obtained from the Institute of Chemical Reagents of Shanghai, People's Republic of China.

Standard solution of Sn(II)

A 0.2 mol dm^{-3} standard solution of $SnCl_2 \cdot 2H_2O$ was prepared with 1 mol dm^{-3} hydrochloric acid.

Standard solution of Sn(IV)

A 0.42 mol dm^{-3} standard solution of $SnCl_4 \cdot 5H_2O$ was prepared with 10% hydrochloric acid.

Artificial seawater

Artificial seawater (S = 35%) was prepared according to Kester's formulation.

Instrumental conditions – gas chromatography, mass spectrometry and atomic absorption

GC MS and GC AA were used in this work, and the instrumental conditions were as follows.

GC MS

A Varian Model 3400 gas chromatograph, coupled with an Extrel ElQ-400-1 mass spectrometer, was used for the analysis. A GC elastic quartz capillary column was used with liquid-phase 007 series methylsilicone, film thickness 0.25 μm, and length 15 m × 0.25 mm i.d. Helium was used as carrier gas with an inlet pressure 0.2 kg cm^{-3} (3 psi). The column temperature was initially 50°C with a programme at the rate of 20°C min^{-1} to a final temperature of 200°C. The injection port temperature was 200°C and the transfer line temperature 225°C. For MS the mass range was 30–350 at a scanning rate of 500 amu s^{-1}; the ionic source temperature was 150°C.

GC AAS

GC conditions A glass column (2 m × 3 mm i.d.) was used with 3% OV-1 on Chromosorb W AW-DMCS (80–100 mesh) with nitrogen carrier gas with a pressure of 3.0 kg cm^{-2}. The injection port temperature was 170°C. The oven temperature programme was as follows: initially at 65°C, then at 35°C min^{-1}, finally 195°C.

AA conditions The wavelength was 224.6 nm, and the lamp current 8 mA. The transfer line temperature was 170°C, and the quartz furnace temperature 850°C. The flow rate of hydrogen was 118 cm^3 min^{-1}, and of air 56 cm^3 min^{-1}.

Experimental procedure

In general, 50 cm^3 test tubes were used for the incubations. Specific amounts of artificial seawater, $^{13}CH_3I$ and Sn(II) or Sn(IV) were added to the test tubes, which were sealed after addition of the required reagents. They were incubated at room temperature (20°C) for 15–30 days.

After incubation, the samples were analyzed according to the following method.[10,11] A 50 cm^3 sample was placed in a 125 cm^3 separating funnel, the pH adjusted to 5, 19 g of ultra-pure sodium chloride was added, and then 5 cm^3 of 0.5% tropolone-benzene was also added. The solution was allowed to stand for 12 h after being shaken for 300 times. The organic layer was separated and concentrated to one cm^3 using a stream of nitrogen gas; one cm^3 of BuMgBr was added. 15 min later the excess Grignard reagent was destroyed with 0.5 mol dm^3 sulfuric acid and the organic layer separated again. This was dried with anhydrous sodium sulfate and the sample was then injected into a GC AA system for analysis.

RESULTS AND DISCUSSION

Methylation of Sn(II) and Sn(IV) by iodomethane ($^{13}CH_3I$)

Artificial seawater (50 cm^3; S = 35%), $^{13}CH_3I$ (80 μmol), and Sn(II) or Sn(IV) (20 μmol) were added to the test tube, the solution adjusted to pH 7.5, and then incubated at room temperature for 30 days. A series of blank tests were performed in parallel in order

Table 1 Methyltin products from the methylation of tin(II) and tin(IV) by $^{13}CH_3I$

Inorganic tin	Sn(II)	Sn(IV)
CH_3Sn^{3+} (mg/50 cm^3)[a]	57.45 × 10^{-3}	0.19 × 10^{-3}
$(CH_3)_2Sn^{2+}$ (mg/50 cm^3)[a]	0.24 × 10^{-3}	n.d.[b]

[a]i.e. per 50 cm^3 of solution; [b]n.d., not determined.

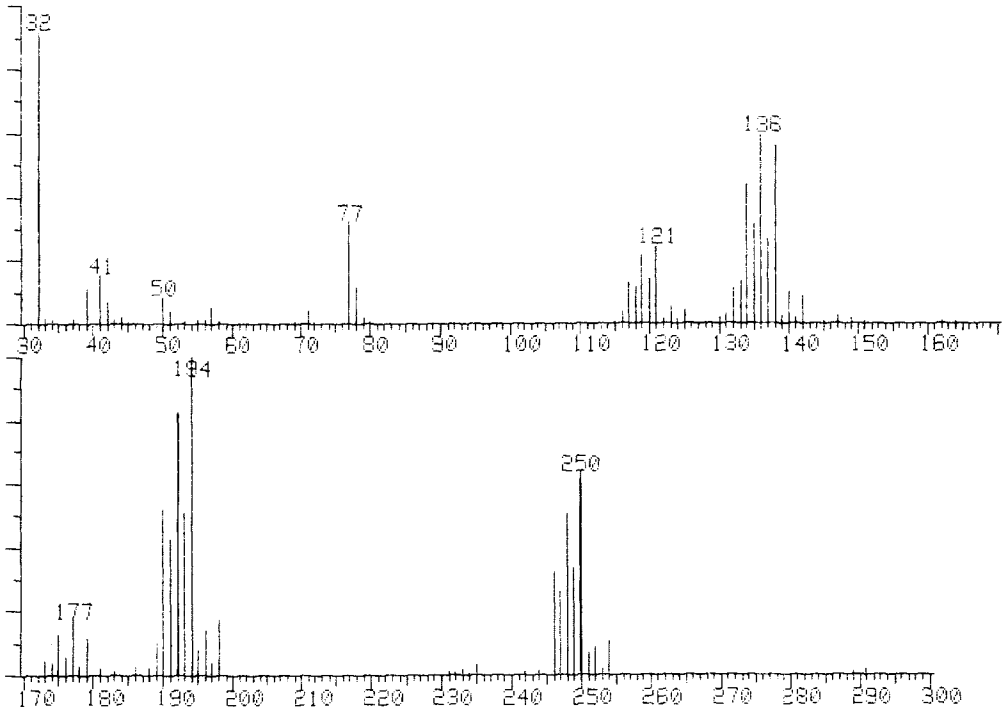

Figure 1 Mass spectrum of $(^{13}CH_3)_2Bu_2Sn$.

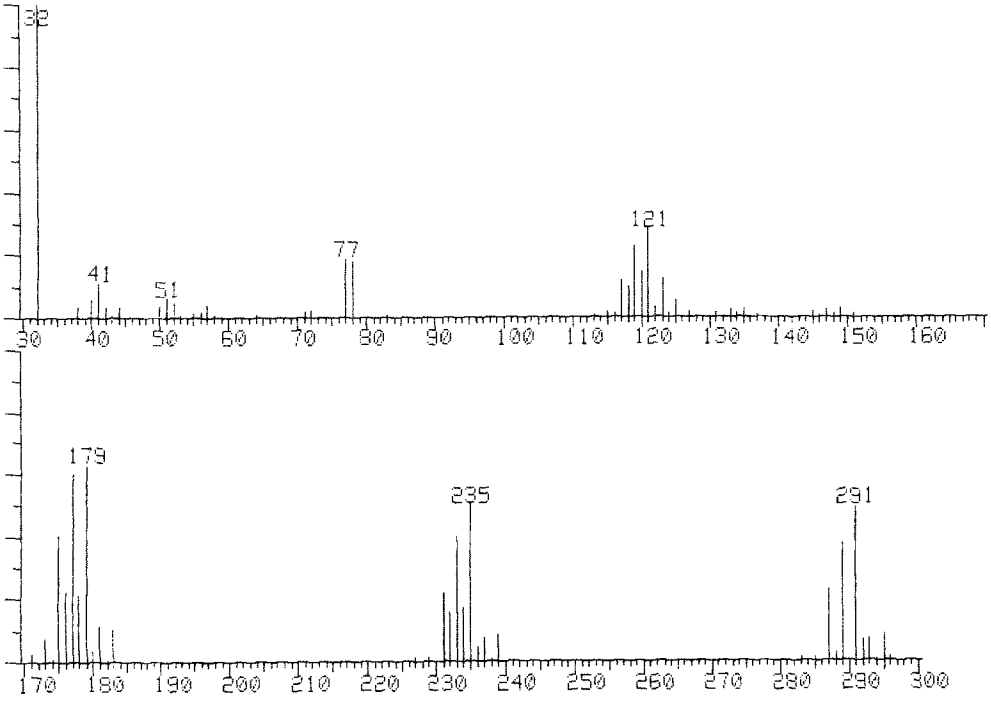

Figure 2 Mass spectrum of $^{13}CH_3Bu_3Sn$.

Table 2 Natural abundance of main isotopes of tin

Mass no.	Abundance (%)
116	14.30
117	7.61
118	24.03
119	8.95
120	32.85
122	4.72
124	5.94

to eliminate the possible artifacts. The experimental results are shown in Table 1.

From Table 1, it is indicated that Sn(II) could be methylated by CH_3I, and that the main product was monomethyltin. A very small amount of dimethyltin was also produced at the same time, but no trimethyltin was found. Compared with Sn(II), the reaction of Sn(IV) and CH_3I is very weak. In order to demonstrate this reaction, the samples were analyzed with the GC MS technique. The mass spectra are shown in Figs 1 and 2. Figure 1 shows the mass spectrum of $(^{13}CH_3)_2(n\text{-}C_4H_9)_2Sn$; different lines represent various fragment ions viz. m/z = 121 ($[^{120}SnH]$); 136 ($[^{13}CH_3{}^{120}Sn]^+$); 177 ($[Bu^{120}Sn]^+$); 194 ($[Bu^{13}CH_3H^{120}Sn]^+$); 250 ($[Bu_2{}^{13}CH_3{}^{120}Sn]^+$). Figure 2 shows the mass spectrum of $^{13}CH_3Bu_3Sn$, m/z = 121 ($[^{120}SnH]^+$); 179 ($[BuH_2{}^{120}Sn]^+$); 235 ($[Bu_2H^{120}Sn]^+$); 291 ($[Bu_3{}^{120}Sn]^+$). Table 2 shows the natural abundance of the main isotopes of tin.[11] Comparing with these data, it can be seen the proportion of isotopes of tin as shown in Figs 1 and 2 are quite reasonable.

So it could be concluded that CH_3I can methylate Sn(II) to form CH_3Sn^{3+} preferentially and the second-

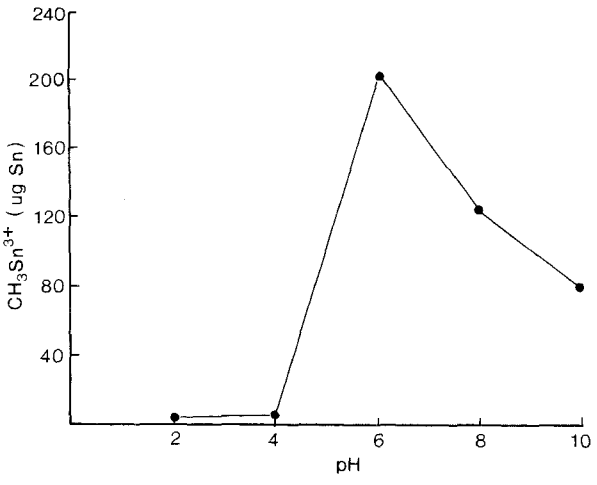

Figure 3 Monomethyltin production at various pH values.

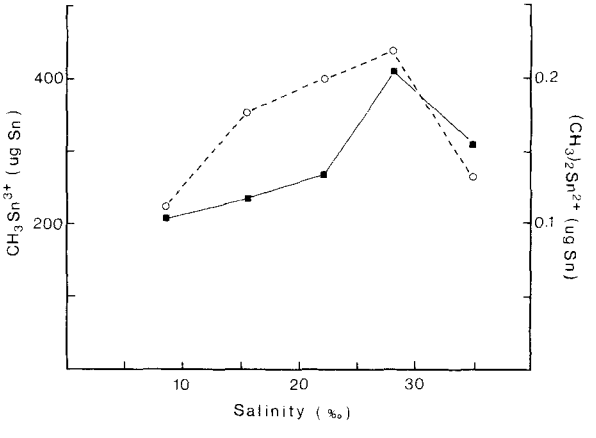

Figure 4 Methyltin production at various salinity values.

Table 3 Monomethyltin production at various pH values (S = 35%)

pH	2	4	6	8	10
CH_3Sn^{3+} ($\times 10^{-3}$ mg/50 cm^3)[a]	0.71	2.91	207.1	128.6	83.3

[a]i.e. per 50 cm^3 of solution

Table 4 Methyltin production at various salinity values (pH = 7.5)

S (%)	8	15	22	28	35
CH_3Sn^{3+} ($\times 10^{-3}$ mg/50 cm^3)[a]	209.5	238.1	266.7	416.7	314.3
$(CH_3)_2Sn^{2+}$ ($\times 10^{-3}$ mg/50 cm^3)[a]	0.112	0.178	0.202	0.225	0.135

[a]i.e. per 50 cm^3 of solution

ary methylated product $(CH_3)_2Sn^{2+}$ could be also formed to a much lesser extent.

Reaction of Sn(II) with $^{13}CH_3I$ under various pH and salinity conditions

The reaction of Sn(II) with $^{13}CH_3I$ at pH 2, 4, 6, 8, 10 and salinity 8, 15, 22, 28, 35% was investigated. The concentrations of $^{13}CH_3I$ and Sn(II) were 80 μmol/50 cm^3 and 20 μmol cm^{-3}, respectively. They were incubated at room temperature in the dark for 15 days. The results are shown in Tables 3 and 4 and Figs 3 and 4. In the experiments at various pH values, the methylated product was only monomethyltin; no dimethyltin was found.

It is indicated from Fig. 3 that pH can affect the methylation of Sn(II). The amount of CH_3Sn^{3+} was very small at pH <4, then CH_3Sn^{3+} production increased with pH. The tin methylation activity was found to be highest at pH 6. The effect of salinity on methylation of Sn(II) is also clearly significant. It is noticeable that methyltin production is most favourable at $S = 28\%$, which approximates to the salinity of Tianjin Harbour, People's Republic of China (27%).

Reaction kinetics of Sn(II) with $^{13}CH_3I$ in aquatic environments

Artificial seawater (500 cm^3; $S = 35\%$) was placed into each 1000 ml flask, followed by 0.1 cm^3 of 0.2 mol dm^{-3} $SnCl \cdot 2H_2O$ standard solution. Some *granular* tin (*ca* 0.12 g) was also added to each flask.

Table 5 Amounts of $^{13}CH_3I$ added[a]

	A	B	C	D
$^{13}CH_3I$ (mmol)	0.2	0.4	0.6	0.8

[a]0.02 mmol of soluble tin was present [Sn(II)]. Artificial seawater medium

Table 6 Concentrations of CH_3Sn^{3+} in reaction flasks at different times ($\times 10^{-5}$ mmol dm^{-3})

Time (min)	255	585	1695	3135	4575	6015	7455
A	6.4	9.1	15.5	25.1	31.5	38.9	42.1
B	10.5	17.5	21.6	38.4	49.0	58.1	62.5
C	14.8	19.2	29.3	43.0	53.0	74.0	76.7
D	19.5	22.6	36.4	55.3	60.8	82.7	94.2

The amount of $^{13}CH_3I$ added to the reaction flasks is recorded in Table 5. (That tin granules are not methylated by $^{13}CH_3I$ has also been demonstrated in another (control) experiment in this experimental series. The tin(0) was present to prevent oxidation of tin(II) to tin(IV) in the flask.) These solutions were adjusted to pH 7.5 and sealed under a nitrogen atmosphere; then the reaction kinetics for CH_3I and Sn(II) in artificial seawater were investigated at 20°C with the 10–40 fold excess of CH_3I. The results are shown in Table 6. Except for monomethyltin, other methyltin species were not observed.

Recently, the reaction of $^{13}CH_3I$ and Sn(II) has been discussed in certain reports (e.g. Craig *et al.*[9]). The suggested viewpoint was that the oxidative addition of iodomethane to tin(II) compounds produces CH_3SnY_2I, as shown in Eqn [1].

$$CH_3I + SnY_2 \longrightarrow CH_3SnY_2I \qquad [1]$$

Other methyltin species may be produced through rearrangement or by the reductive disproportionation reaction (Eqns [2]–[5]).

$$2CH_3SnY_2I \longrightarrow (CH_3)_2SnY_2 + SnY_2I_2 \qquad [2]$$

$$2(CH_3)_2SnY_2 \longrightarrow (CH_3)_3SnY + SnY_2 + CH_3Y \qquad [3]$$

$$4(CH_3)_3SnY \longrightarrow 2(CH_3)_4Sn + 2(CH_3)_2SnY_2 \qquad [4]$$

$$3(CH_3)_3SnY \longrightarrow 2(CH_3)_4Sn + SnY_2 + CH_3Y \qquad [5]$$

From our experimental results, it can be seen that the reaction product is mainly monomethyltin; other methylated products may be neglected. So it would not be determined whether or not reactions [2]–[5] could happen under environmental conditions; a further study might illustrate this point.

For Eqn [1], the rate equation may be expressed as

$$\frac{d[CH_3Sn]}{dt} = k[CH_3I]^n[SnY_2]^m \qquad [6]$$

Because CH_3I is in large excess, the rate equation [7] may be obtained from [6].

$$\frac{d[CH_3Sn]}{dt} = k_{obs}[SnY_2]^m \qquad [7]$$

where k_{obs} is the observed rate constant. If $m = 1$, the methylation reaction is pseudo-first-order for Sn(II), i.e. Eqn [8] applies.

Table 7 Kinetic results for CH_3I and Sn(II) reaction in artificial seawater

	A	B	C	D
k_{obs} ($\times 10^{-6}$ min^{-1})	1.29	1.88	2.28	2.64
r	0.992	0.990	0.992	0.994

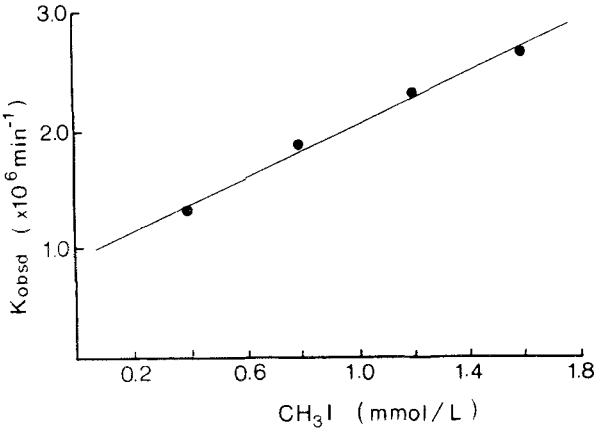

Figure 5 Plot of k_{obs} vs $[CH_3I]$.

$$\ln \frac{[SnY_2]_0}{[SnY_2]_0 - [CH_3Sn]_t} = k_{obs}t \qquad [8]$$

$[SnY_2]_0$, the initial concentration of Sn(II), is 0.04 mmol dm^{-3} in this experiment. According to the results of A, B, C and D in Table 6, a good linear plot of $\ln[SnY_2]_0/([SnY_2]_0 - [CH_3Sn]_t)$ vs time was gained. The results are shown in Table 7. It has been demonstrated that the reaction is really first-order for Sn(II) ($m = 1$). By the same method, under pseudo-first-order conditions with varying initial concentrations of CH_3I (Table 5), a good linear plot of k_{obs} vs $[CH_3I]$ was also obtained in Fig. 5. The plot of k_{obs} vs $[CH_3I]$ gives a straight line of slope k'' and intercept k'. The relation is:

$$k_{obs} = k' + k''[CH_3I] \qquad [9]$$

where $k' = 9.10 \times 10^{-7}$ min^{-1} (intercept)

$k'' = 1.11 \times 10^{-6}$ mmol^{-1} dm^{-3} min^{-1} (slope)

The correlation coefficient r is 0.993. So it can be seen that the reaction is also first-order for CH_3I ($n = 1$).

If we substitute Eqn [9] into equation [6], then we get

$$\frac{d[CH_3Sn]}{dt} = (k' + k''[CH_3I])[SnY_2] \qquad [10]$$

Hence, the rate equation indicates that the reaction of Sn(II) and CH_3I possesses a competitive process mechanism, i.e. one is iodomethane-dependent and the other is independent of iodomethane.

CONCLUSION

The methylation of tin(II) by iodomethane under environmental conditions has been further demonstrated by a ^{13}C carbon method. The methylated species are mainly monomethyltin, and very small amounts of dimethyltin. The reaction is affected by pH and salinity; the tin methylation activity is highest at *ca* pH 6 and $S = 28\%$. The methylation reaction is first-order for both CH_3I and Sn(II), and the rate equation can be expressed overall as:

$$\frac{d[CH_3Sn]}{dt} = (k' + k''[CH_3I])[SnY_2]$$

Acknowledgement This project was supported by the National Natural Science Foundation of China.

The GC MS analysis was accomplished by Mr Wang Liansheng of The Tianjin Municipal Institute for Environmental Protection Research, Tianjin, People's Republic of China.

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