APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 161–167
Speciation Analysis and Environment **AOC**
DOI:10.1002/aoc.1032

Methylation of tin(II) by methyl iodide: influences of different environmental factors on the efficiency and reaction kinetics

Chen Baowei, Jiang Guibin*, Yang Ruiqiang and Liu Jiyan

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center of Eco-Environmental Sciences, Chinese Academy of Sciences, PO Box 2871, Beijing 100085, People's Republic of China

Received 10 October 2005; Accepted 25 November 2005

The methylation reaction of Sn(II) with methyl iodide (MeI) in water has been studied using sensitive GC-QSIL-FPD technology. The pH value, amount of MeI and salinity (S) are the three important factors that influence the methylation reaction in an aquatic environment. In all experiments, monomethyltin (MMT) is the only methylation product of the tin(II) reacting with MeI observed. At the 95% confidence level, the pH, MeI and S are significant for the MMT yield. The concentration of MMT in the reactor increases with increase in pH within the selected pH range of 4–9 because four different species of Sn(II)–Sn^{2+}, $SnOH^{+}$, $Sn(OH)_2{}^0$ and $Sn(OH)_3{}^-$–have different reaction activities with MeI. The methylation activity of Sn(II) was found to be highest at a salinity of 0.1 M at three different pH levels: 5, 7 and 9. Higher concentration of Cl^- (as a relatively weak nucleophilic ion) will obstruct nucleophilic attack of Sn(II) on MeI. MMT production also increases with rising volume of MeI. Moreover, first-order reaction rates have been calculated at different pH, salinity and MeI, and found to be in the range 0.0018–0.0199 h^{-1}. The reaction rate also varies largely under different reaction conditions. One probable mechanism for the methylation reaction of Sn(II) with MeI is a S_N2 nucleophilic attack on the methyl group of MeI by Sn(II), via a process of oxidative methyl-transfer.

KEYWORDS: methylation; methyltin; reaction kinetic; divalent tin; methyl iodide

INTRODUCTION

Organotin compounds have been used extensively as antifouling paints, biocides and stabilizers for polyvinyl chloride in agriculture and industry.[1,2] Pollution by organotin is of concern because of their threat to the ecosystem and humans. Although there are only some limited and localized uses of methyltin compounds, a wide presence of methyltin in open seawater or unpolluted river and estuaries has been found.[3,4] Therefore various chemical and biological reactions must be found to convert other tin compounds to methyltin compounds in the environment. Butyltin compounds can be degraded to inorganic tin by debutylation and inorganic tin can be methylated in the environment.[5,6] Moreover, the mechanism of methylation of tin has been of considerable interest since the toxicity to animals and humans increases from inorganic tin to methyltin.[7]

Many scientists have carried out research to elucidate the methylation mechanisms of tin in the environment. Dizikes clearly showed that inorganic tin could be methylated by methylcobalamin, which is a co-enzyme of vitamin B_{12}.[8] Hallas found that microorganisms in the estuarine samples could produce mono-, di- and trimethyltin from $SnCl_4$.[9] Guard also proved that it is possible for trimethyltin compounds to be further methylated by estuarine sediments.[10] These studies validated the possibility of methylation of tin in the environment by two routes: chemical and biological.

Methylation reagents exist widely in the aquatic environment. For example, methyl iodide is easily produced by macro algae and kelp which grow in the seawater.[11,12] This means

---

*Correspondence to: Jiang Guibin, State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center of Eco-Environmental Sciences, Chinese Academy of Sciences, PO Box 2871, Beijing 100085, People's Republic of China.
E-mail: gbjiang@mail.rcees.ac.cn
Contract/grant sponsor: National Natural Science Foundation of China; Contract/grant number: 20477053.
Contract/grant sponsor: National Basic Research Program of China; Contract/grant number: 2003CB415001.

that MeI may be an important methyl provider of methylation reactions in the environment. There have been some reports concerning methylation of tin by MeI.[13–15] However, they have not explained why environmental factors affect methylation reactions of tin. The concentration of inorganic tin is often very low in aquatic environments. Therefore it is important environmentally to study reaction kinetics of methylation at lower concentrations.

The aim of this work is to study the influences of some factors on the chemical methylation reaction of Sn(II) under possible environmental conditions using a sensitive GC-QSIL-FPD system and to put forward reasonable explanations for the methylation mechanism of Sn(II) with MeI. The methylation kinetics of tin at lower concentrations and the corresponding factors are also studied. The pH range and salinity range was selected as 5–9, 0–1.0 M, respectively, which are of great interest for natural fluids.

EXPERIMENTAL SECTION

Materials

All reagents were obtained commercially and used without further purification unless otherwise stated. The standards of trimethyltin chloride (TMT, 98%), dimethyltin (DMT, 97%) and monomethyltin (MMT, 97%) were obtained from Aldrich Chemical Co. (USA). Iodomethane (99.5%) was purchased from Phentex Corp. (USA). Stannous chloride (98%) was obtained from Beijing Yili Company of Chemical Reagents (China).

Reaction design

In general, methylation reactions took place in darkness at about 30 °C using 50 ml aqueous solutions in 100 ml vials sealed with septa. For all experiments, 10 µl of 0.2 M $SnCl_2$ stock solution in 2 M HCl were used as the Sn(II) source. Oxidation was prevented by adding tin granules to the flask of stock solution and sealing it under nitrogen. The factors and factor levels of factorial experiments are shown in Table 1. The pH value of the reaction system was adjusted using 0.1 M NaOH and determined with a pH meter (Hanna Instruments pH211C and HI 1200B glass-body combination pH electrode). Solutions were adjusted for chloride ion concentration with 5 M NaCl. The dark condition was achieved by covering the reactor with aluminum foil. Reaction vials were always sealed under nitrogen atmosphere after adding the required reagents. For factorial experiments, the vials were placed in a thermostatic bath for 22 h. Kinetic experiments were performed by analyzing the water solution sampled from the 100 ml vials at different times.

Table 1. Factors and factor levels of factorial experiments[a,b]

Factors	Level +1	0	−1
S	1	0.5	0.1
PH	9	7	5
I[c]	6	4	2

[a] The source of each experiment is 2.0 µmol of $SnCl_2$.
[b] S, salinity (NaCl/M); I, volume of MeI used in the experiment (µl).
[c] 1 µl MeI = 16.06 µmol.

Instruments

A GC-9A gas chromatograph (Shimadzu, Japan) equipped with an HP-1 capillary column (25 m × 0.32 mm i.d. ×0.17 µm) was used for quantitative analysis throughout the experiment. The GC temperature was programmed from 50 °C (held for 2 min) to final temperature of 200 °C at 10 °C/min rate, and then held for 5 min. The injector temperature was 220 °C. High-purity nitrogen was used as the carrier gas and the column head pressure was kept at 260 kPa. A laboratory-made flame photometric detector using quartz surface-induced tin emission (QSIL-FPD) was used to differentiate methyltin compounds; its configuration and application were reported previously.[16,17] The detector temperature was set at 160 °C. Hydrogen and air were controlled at 260 and 90 ml/min. The measurement was carried out by using a 394 nm interference filter. Furthermore, an Agilent 5793N GC-MS with a HP-5MS capillary column (30 m × 0.25 mm i.d. ×0.25 µm) was used for qualitative analysis of methyltin. Temperature program was from 50 °C (held for 3 min) to a final temperature of 280 °C (held for 10 min) at 20 °C/min rate. The injector temperature was 220 °C. High-purity nitrogen was used as the carrier gas and the flow rate was kept at 1.0 ml/min.

Analytical method

For the sample preparation, 1–2 ml of water samples were taken out from the reaction system and placed in a centrifugation tube together with 5 ml citric acid–NaH_2PO_4 buffer solution (pH = 5). A 50 µl aliquot of the internal standard ($MeSnPr_3$, 2 µg/ml), and 2.5 ml of 0.1% tropolone–cyclohexane were added in sequence. The mixture was extracted for 25 min in an ultrasonic bath. After 5 min centrifugation at 3000 rpm and removal of supernatant, the residue was re-extracted once again with another 2.5 ml of the same extraction solution. Then the combined organic phases were dried on anhydrous Na_2SO_4. Each extract reacted with 1 ml of 2.3 M *n*-PeMgBr for 25 min in an ultrasonic bath. Excess Grignard reagent was eliminated by the addition of about 5 ml of 0.5 M H_2SO_4. The organic phase was purified by a glass pipette packed with 1.5 g Na_2SO_4 and 0.5 g Florisil. Another 5 ml of cyclohexane were used to elute the pentylated derivatives. Lastly, the eluted organic phase was concentrated to 2 ml under a stream of nitrogen.

RESULTS AND DISCUSSION

Qualitative analysis of reaction product

In order to identify the reaction product, its GC-QSIL-FPD chromatogram was compared with that of standard substances (Fig. 1). It can be seen that the reaction product has the same retention time as MMT standard in the GC-QSIL-FPD chromatogram. The MMT production was further confirmed by mass spectrum. Figures 2 and 3 show the mass spectrums of $SnMePe_3$, the derivatives of MMT from the standard and the reaction product, respectively. Various fragment ions are represented as follows: m/z 277 ($SnMePe_2^+$), 207 ($SnMePe^+$) and 135 ($SnMe^+$). It was shown that the reaction product has the same characteristic fragment ions as standard MMT. As a result, MMT was the only detectable methylation product of Sn(II) reacting with CH_3I. No other methyltins were detected in all experiments.

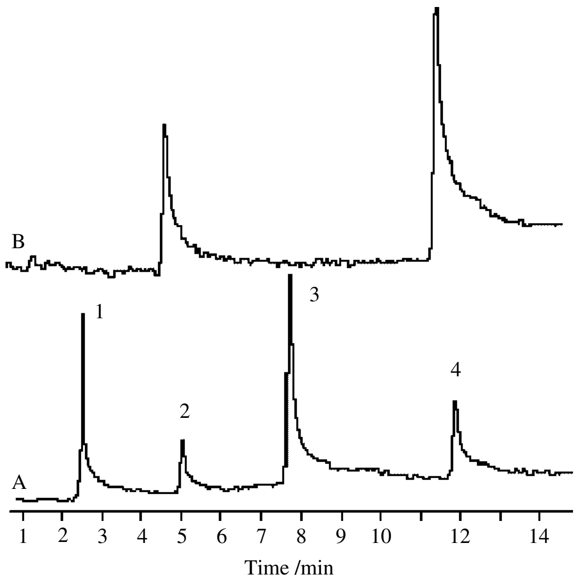

Figure 1. GC-QSIL-FPD chromatogram of standard substances and reaction product. A, standard substances; B, reaction product; 1, trimethyltin; 2, internal standard; 3, dimethyltin; 4, monomethyltin.

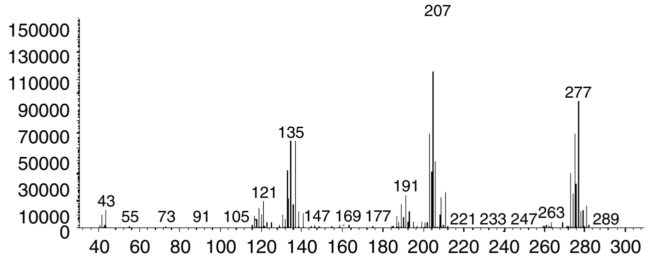

Figure 3. Mass spectrum of pentyl-derivatives of reaction product.

Factorial experiments

A $2^3 + 1$ factorial experiment of the methylation of $SnCl_2$ by MeI was carried out to evaluate the effects of some factors on methylation efficiency, including salinity, amount of MeI and pH. The results of the orthogonal experiment are shown in Table 2. The concentration of MMT obtained in the reaction system varied in the range 82.8–1164.3 ng/ml according to the different reaction conditions. Centerpoint experiments had an RSD of 10.35%.

The results of variance analysis of factorial experiment, listed in Table 3, showed that S, pH, MeI and their interactions

Table 2. Experimental result

No.	pH	S	I	Yield of MMT (%)	Concentration (ng/ml)
1	+1	+1	+1	18.1	859.3
2	+1	+1	−1	6.3	298.9
3	+1	−1	+1	24.5	1164.3
4	+1	−1	−1	6.5	310.4
5	−1	+1	+1	3.6	169.7
6	−1	+1	−1	1.7	82.8
7	−1	−1	+1	3.5	167.8
8	−1	−1	−1	2.2	103.8
9[a]	0	0	0	4.0	191.9
10[a]	0	0	0	3.6	169.8
11[a]	0	0	0	3.7	175.8
12[a]	0	0	0	4.5	213.2

[a] %RSD for experiments 9–12 is 10.3%.

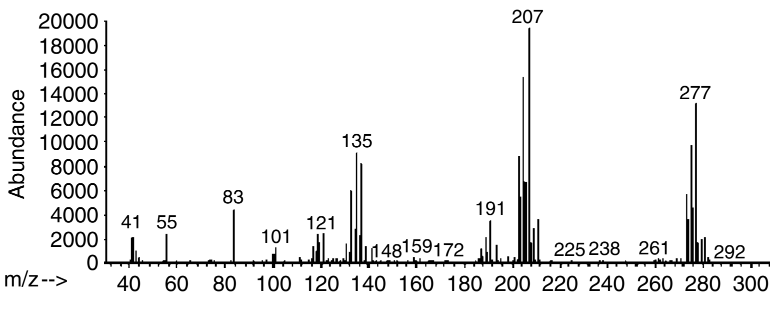

Figure 2. Mass spectrum of pentyl-derivatives of standard MMT.

Table 3. Analysis of variance (ANOVA) (95% confidence)

Factors	Variance	Free-dom	F	Critical value	Significance
pH	470 970.5	1	1247.5	10.1	*
S	31 684.9	1	83.9	10.1	*
pH & S	2099.3	1	5.6	10.1	—
I	375 396.8	1	994.4	10.1	*
pH & I	150 035	1	397.4	10.1	*
S–I	24 029.5	1	63.6	10.1	*
pH–S–I	2756.3	1	7.3	10.1	—
Error	377.5	3	—	—	—

* F-value has significance at 95% confidence level.

of pH–I and S–I were all significant for the production of MMT at a 95% confidence level. In particular, the very high F-value for MeI, pH and interaction of pH and MeI showed overwhelming significance for the methylation reaction.

Based on the results of factorial experiments, more detailed experiments about the influence of these environment factors on methylation reaction were performed.

Effect of pH

Figure 4 shows the effect of pH on the production of MMT. It can be seen clearly that the concentration of MMT in the reactor increases with pH increasing from 4 to 9. This is probably due to different species of Sn(II) in the water at different pH, which have different reaction activities with MeI.

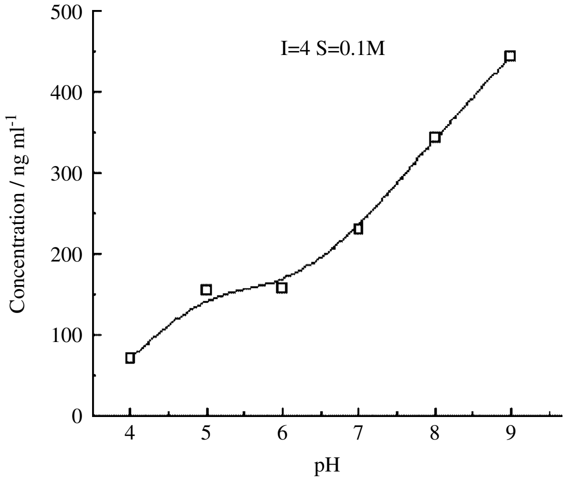

Figure 4. The effect of pH on MMT production.

Table 4. Stability constant of Sn^{2+} complexing with OH^-

Equilibrium reaction	β^a	β^b
$Sn^{2+} + OH = SnOH^-$	11.86	10.06
$Sn^{2+} + 2OH = SnOH_2{}^-$	20.64	19.89
$Sn^{2+} + 3OH = SnOH_3{}^-$	25.13	23.94

[a] Stability constant from reference 18. Ionic strength = 0.

[b] Stability constant from website jess.murdoch.edu.au. Ionic strength = 0.5 in NaCl.

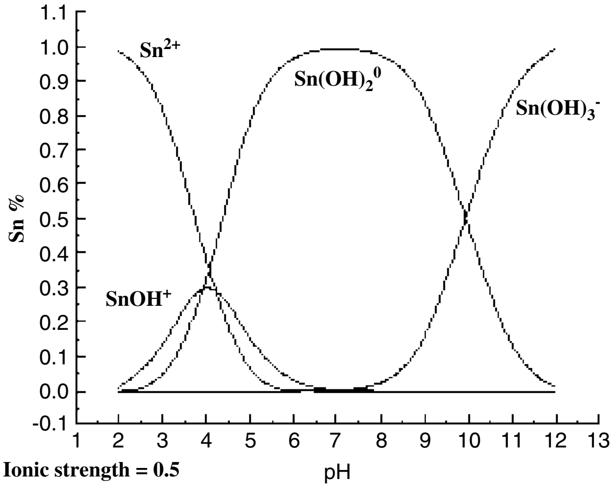

Figure 5. Distribution diagram of Sn(II) hydrolytic species vs pH in NaCl.

According to the stability constants of Sn^{2+} complexing with OH^- (Table 4), the percentages of different species of tin(II) in the water at different pH can be obtained from Fig. 5. There are four species of tin(II), Sn^{2+}, $SnOH^+$, $Sn(OH)_2{}^0$ and $Sn(OH)_3{}^-$, in the pH range from 2 to 12. In strong acidic conditions, Sn^{2+} is the main species of Sn(II). With pH increasing, part of the Sn^{2+} is converted to $SnOH^+$. When pH is equal to 7, Sn^{2+} and $SnOH^+$ disappear and $Sn(OH)_2{}^0$ is the main species of Sn(II). However, the ratio of $Sn(OH)_2{}^0$ decreases and $Sn(OH)_3{}^-$ occurs with higher pH. Eventually, all Sn(II) is converted to $Sn(OH)_3{}^-$ in strong basic solution. Methylation of Sn(II) by MeI is reported as a reaction of oxidative addition. Tin(II) is a strong nucleophilic reagent because of its lone-pair electrons, so it is easy for Sn(II) to perform a nucleophilic attack on the carbonium methyl groups of MeI while itself being oxidized from divalence to quadrivalence. However, different Sn(II) species in the water have different nucleophilicities. The electron cloud density of Sn(II) will be intensified with increasing amount of OH^- complexation with Sn(II) because OH^- is a good electron provider. The increase in electron cloud density will ease the nucleophilic attack in methylation reactions.

On the other hand, the standard redox potential may also demonstrate the nucleophilicity of metal ions in water. In acidic conditions, the standard redox potential of Sn^{4+} (IV)/Sn^{2+} (II) is 0.154 V. Nevertheless, the standard redox potential of $Sn(OH)_6{}^{2-}$ (IV)/$Sn(OH)_3{}^-$ (II) is −0.93 V in basic conditions. From standard redox potentials, it was judged that $Sn(OH)_3{}^-$ is more easily subject to oxidative methylation than Sn^{2+}, which is in agreement with our experimental results, showing that the methylation efficiency of tin(II) increases with the increase in pH.

Effect of salinity and MeI

Besides considering the effect of pH on methylation efficiency, the effects of salinity and the volume of MeI were also studied. The results were depicted in Figs 6 and 7. The reactions were carried out at MeI volumes of 2, 4 and 6 μl and salinities of 0, 0.1, 0.5 and 1 M. In particular, a salinity of 0.5 M is close to the salinity of seawater, which is of great interest to the environment.

In single-factor experiments on salinity, MMT production did not always decrease with increase in the salinity of water. The methylation yield of Sn(II) was found to be highest at salinity 0.1 M. The same conclusion about the influence of salinity on production of MMT can be drawn from three different pH levels: 5, 7 and 9. At the beginning, a slight increase in Cl^- ions was beneficial to methylation, but more Cl^- would be a large barrier to the methylation reaction of Sn(II) and MeI. In this reaction system, there are several kinds of nucleophilic ion: Cl^-, I^-, OH^- and Sn^{2+}. The order of nucleophilic capability of the anion is $I^- > OH^- > Cl^-$ in protic solvents.[19] By comparing standard redox potentials, the nucleophilicity of Sn^{2+} is judged to be higher than that of I^-, so the order of nucleophilicity is: $Sn^{2+} > I^- > OH^- > Cl^-$. Although Cl^- is a relatively weak nucleophilic ion, high concentrations of Cl^- will obstruct the nucleophilic attack of Sn(II) on MeI. Moreover, it is also true that the volume of MeI has a great influence on the reaction. It is indicated in Fig. 7 that methyltin production rises with the volume of MeI increasing under two reaction conditions: pH = 7, S = 0.5 and pH = 9, S = 1.0.

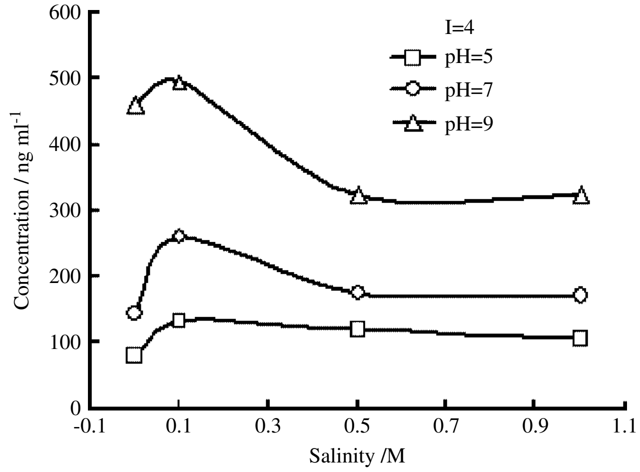

Figure 6. The effect of salinity on monomethyltin production.

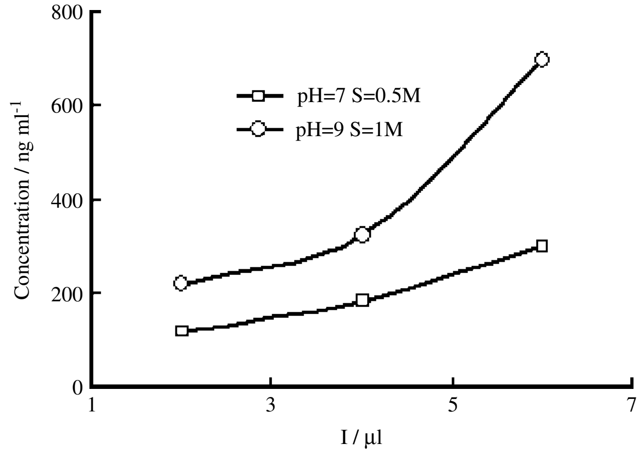

Figure 7. The effect of the amount of MeI on monomethyltin production.

Reaction kinetics of Sn(II) and MeI in aquatic environment

Experiments to study the kinetics of the methylation reaction under different environmental conditions were performed. The effects of pH, volume of MeI and salinity on reaction kinetics are presented in Figs 8–10, respectively. In all kinetics experiments, MMT was produced very quickly in the first 10 h after the methylation reaction began. During this period, the concentration of MMT can reach up to 70% of its final concentration. However, the methylation rate slowed down subsequently. Lastly, methylation reactions reached equilibrium after almost 40 h. All of salinity, pH and the volume of MeI have a strong influence on the kinetics of the methylation reaction.

The first-order kinetics of the methylation reaction under different reaction conditions was confirmed by plotting $-\ln[(C_0 - C)/C_0]$ vs reaction time to yield a straight line. The results for first-order fit appear in Figs 11–13. The r^2 of the first-order fit of all kinetic curves was in the range 0.8573–0.991, which demonstrates that methylation reactions have a good correlation with first-order reaction kinetics. First-order reaction rates, whose range was from 0.0018 to

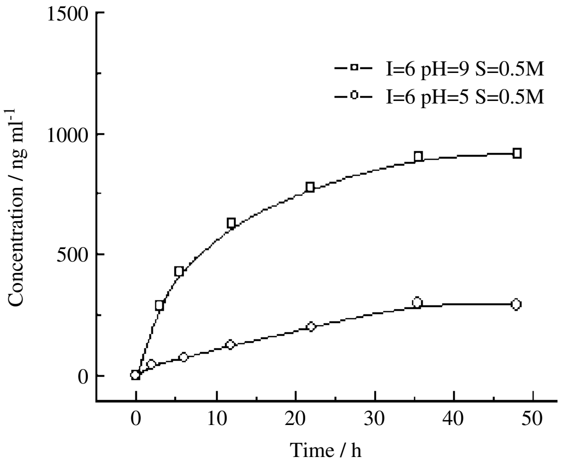

Figure 8. Kinetic curves at different pH.

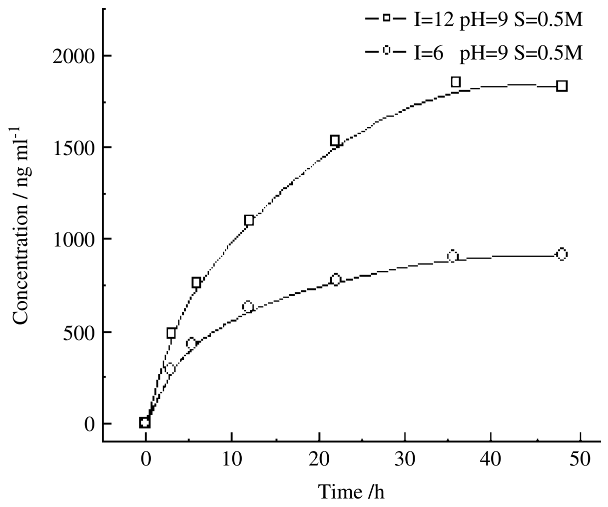

Figure 9. Kinetic curves at different volume of MeI.

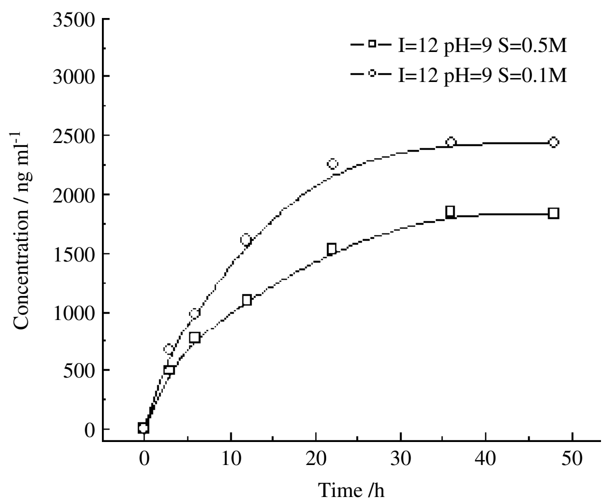

Figure 10. Kinetic curves at different salinity.

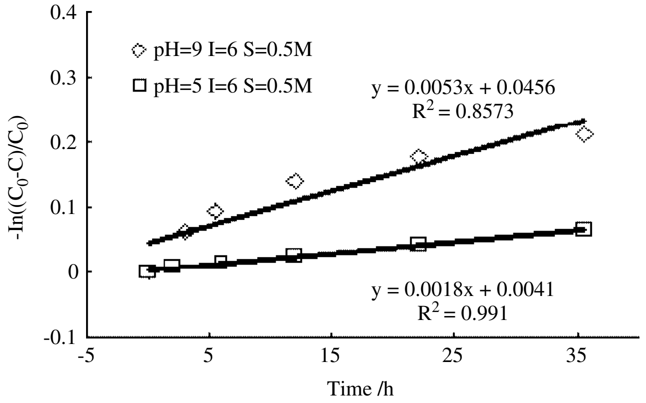

Figure 11. First-order rate plots at different pH [C_0, initial concentration of Sn(II) C, concentration of MMT].

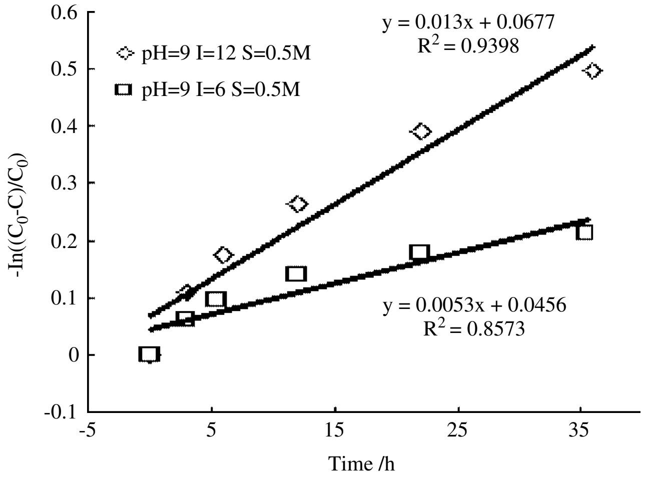

Figure 12. First-order rate plots at different volume of MeI.

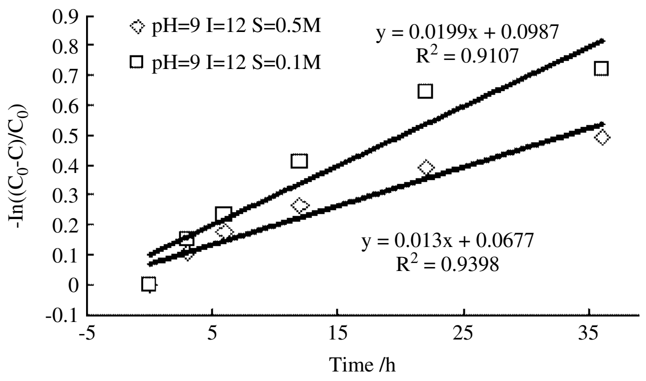

Figure 13. First-order rate plots at different salinity.

0.0199 h^{-1}, varied greatly in different reaction conditions. Reaction rates increased from 0.0018 h^{-1} at pH = 5 to 0.0053 h^{-1} at pH = 9 with S = 0.5 M and I = 6 μl. Under the conditions of pH = 9 and S = 0.5 M, the first-order reaction rate increased from 0.0053 to 0.013 h^{-1} when the volume of MeI increased from 6 to 12 μl. Moreover, the reaction rate rose from 0.013 to 0.0199 h^{-1} when salinity decreased from 0.5 to 0.1 M at pH = 9 and I = 12 μl. From this trend, an interesting conclusion can be drawn that the methylation reaction of Sn(II) with MeI in freshwater is faster than that in seawater, i.e. different environment conditions have a strong influence on the methylation reaction in water.

Under nitrogen, inorganic tin will not be oxidized from Sn(II) to Sn(IV) by other compounds except for MeI in this reaction system. Thus the methylation reaction of Sn(II) with MeI should be a process of oxidative methyl-transfer. It is unlikely that MeI reacts with a nucleophile according to an S_N1 mechanism.[19] One probable mechanism for this methyl-transfer is a S_N2 nucleophilic attack on the methyl group of MeI by Sn(II), which results in the formation of $(CH_3)Sn(II)$, as shown in Eqn. (1).

$$Sn^{2+}(II) + CH_3^{+} - I^{-} \longrightarrow [Sn^{2+}(II)\cdots\cdots CH_3^{+\cdots\cdots}I^{-}] \longrightarrow [CH_3Sn(IV)]^{3+}I^{-} \quad (1)$$

In the S_N2 reaction, the nucleophilicity of the reagent is an important factor that influences the reaction rate. Therefore, the effect of pH on the reaction rate was due to the four species of Sn(II) having different nucleophilicities in water. In addition, large amounts of Cl^{-} decrease methylation reaction rates because they hinder nucleophilic attack of Sn(II) on MeI.

$$2MeSn(II) \longrightarrow Me_2Sn(II) + Sn(0) \quad (2)$$

$$2Me_2Sn(II) \longrightarrow Me_3Sn(IV) + MeSn(II) \quad (3)$$

$$2Me_3Sn(II) \longrightarrow Me_4Sn(IV) + Me_2Sn(II) \quad (4)$$

Equations (2)–(4) show the possible pathways that di-, tri- and tetra-methyltin species may be yielded by dismutation or disproportionation reactions. In our experiments, MMT was the only methylation product in the reaction of Sn(II) with MeI; no other methyltin species were found. This experimental result was consistent with Ring and Weber.[13] However, further study is necessary to validate whether or not these reactions could happen in the water under environment conditions.

CONCLUSION

The methylation reactions of Sn(II) with MeI in different aquatic environments were studied using a sensitive GC-QSIL-FPD system. In factorial experiments, at 95% confidence level, we found that the pH and the amounts of MeI and salinity are significant for MMT yield.

Production of MMT and reaction rates rose with increase of pH in the range 4–9 because four different species of Sn(II), Sn^{2+}, $SnOH^{+}$, $Sn(OH)_2^{0}$ and $Sn(OH)_3^{-}$, have different methylation activities with MeI, which is related to their nucleophilicity. When pH is below 7, Sn(II) takes part in the reaction in the form of Sn^{2+}, $SnOH^{+}$ and $Sn(OH)_2^{0}$. However, $Sn(OH)_2^{0}$ and $Sn(OH)_3^{-}$ are the main species which react with MeI in basic solution. More MMT is produced in the methylation reaction when the amount of MeI increased. As a relatively weak nucleophilic ion, the Cl^{-} ion at relatively high concentrations would obstruct the nucleophilic attack of Sn(II) on MeI.

The methylation reaction of Sn(II) with MeI correlated well with first-order reaction kinetics. The reaction rate varied largely under different environment conditions. A first-order rate was found in the range 0.0018–0.0199 h^{-1} in our experiments.

The methylation reaction of Sn(II) with MeI is presumed to be a process of oxidative methyl-transfer. One probable mechanism for this methylation reaction is an S_N2 nucleophilic attack on the methyl group of MeI by Sn(II).

Acknowledgements

This work was jointly supported by the National Natural Science Foundation of China (20477053) and the National Basic Research Program of China (2003CB415001).

REFERENCES

1. Clark EA, Sterritt RM, Lster JN. *Environ. Sci. Technol.* 1988; **22**: 600. DOI: 10.1021/es00171a001.
2. Hugget RJ, Unger MA, Seligman PF, Valkirs AO. *Environ. Sci. Technol.* 1992; **26**: 232. DOI: 10.1021/es00026a001.
3. Braman RS, Tompkins MA. *Anal. Chem.* 1979; **51**: 12. DOI: 10.1021/ac50037a011.
4. Donard OFX, Rapsomanikis S, Weber JH. *Anal. Chem.* 1986; **58**: 772. DOI: 10.1021/ac00295a027.
5. Adelman D, Hinga KR, Pilson MEQ. *Environ. Sci. Technol.* 1990; **24**: 1027. DOI: 10.1021/es00077a012.
6. Navio JA, Marchena FJ, Cerrilos C, Pablos F. *J. Photochem. Photobiol. A. Chem.* 1993; **71**: 97. DOI: 10.1016/1010-6030(93)87014-E.
7. Boyer IJ. *Toxicology* 1989; **55**: 253. DOI: 10.1016/0300-483X(89)90018-8.
8. Dizikes LJ, Ridely WP, Wood JM. *J. Am. Chem. Soc.* 1978; **100**: 1010.
9. Hallas LE, Mreans JC, Cooney JJ. *Science* 1982; **215**: 1505.
10. Guard HE, Cobet AB, Coleman WM. *Science* 1981; **213**: 770.
11. Gschwend PM, MacFarlane JK, Newman KA. *Science* 1985; **227**: 1033.
12. Lovelock JE. *Nature* 1975; **256**: 193. DOI: 10.1038/256193a0.
13. Ring RM, Weber JH. *Sci. Total Environ.* 1988; **68**: 225. DOI: 10.1016/0048-9697(88)90374-9.
14. Shugi D, Guolan H, Yong C. *Appl. Organomet. Chem.* 1989; **3**: 115. DOI: 10.1002/aoc.590030112.
15. Craig PJ, Rapsomanikis S. *Environ. Sci. Technol.* 1985; **19**: 726. DOI: 10.1021/es00138a012.
16. Jiang GB, Xu FZ. *Appl. Organomet. Chem.* 1996; **10**: 77. DOI: 10.1002/(SICI)1099-0739(199603)10 : 2<77::AID-AOC482>3.0.CO;2-7.
17. Jiang GB, Ceulemans M, Adams FC. *J. Chromatogr. A* 1996; **727**: 119. DOI: 10.1016/0021-9673(95)01099-8.
18. Xu ML, Lai XX, Fan J, Zheng PL. *Handbook of Analytical Chemistry*. Science Press: Beijing, 1982; 621.
19. Xing QY, Xu RQ, Zhou ZH, Pei WW. *Organic Chemistry*. Higher Education Press: Beijing 1992; 137–144.