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The Behaviour of Different Organometallic Compounds in the Presence of Inorganic Mercury(II): Transalkylation of Mercury Species and their Analysis by the GC–MIP–PED System

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It is shown that four different mercury species are formed by the abiotic reaction of inorganic mercury with different, ecologically relevant, organolead and organoarsenic compounds. Therefore solutions of tetraethyl-lead, trimethyl-lead chloride and dimethylarsonic acid were prepared and mixed with stock solutions of inorganic mercury at different concentrations. The final solutions were analyzed for their content of newly synthesized mercury species. The analysis was carried out by using a system of solid-phase microextraction (SPME): capillary gas chromatography (GC), microwave-induced plasma (MIP) and a plasma-emission detector (PED). We found that transfer of one or two alkyl groups to the inorganic mercury is possible under the conditions mentioned below. The transalkylation rate depends on the kind of organometallic compound and on the pH. The results were confirmed by the reaction with inorganic mercury and analysis of a soil sample, containing tetraethyl-lead and trimethyl-lead, in which not only the monoalkyl compound, but also the dialkylated compound of the relevant inorganic metal, were found.

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INTRODUCTION

Speciation of trace elements has become an important and challenging issue during the past decade because of its impact on some key disciplines, including environmental chemistry, toxicology and fertilizing and energy-related industry. Information on speciation is vital in ecotoxicological studies of the natural production of organic forms of elements in the environment, of the fate of organometallic anthropogenic pollutants (degradation, partition in biota, long-range transport) and of transformation of organoelements via biotic processes in biogeochemical cycles. Decay of species usually takes place by dealkylation. Methylmercury, for example, may be decomposed by numerous bacteria, in the first step to methane and mercury(II)and then to mercury(0); photodegradation is also known for this compound.[1] However, the question remains, of whether there is chemical decay of various species independently of bacterial activities. There are several very well-known species in different environmental samples, such as methylmercury in fish, tributyltin in anti-fouling paints or chromium species at the workplace.[2–4] For all these examples special techniques have been established. What is not so commonly understood as the analysis of these substances is their behaviour with one another.[5] The formation of organometallic compounds in the environment is partly explained by biomethylation, which is known for many heavy metals such as mercury, selenium and others.[6, 7] Another reason for the existence of those organometallic compounds is direct entry by men.

But there is another possibility for the formation of some species in combination with other heavy metals. A partial clarification of this situation is the aim of our experiments. Therefore solutions of the antiknock compound tetraethyl-

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lead, trimethyl-lead chloride and of the sodium salt of dimethylarsonic acid were mixed with stock solutions of inorganic mercury(II). The final solutions were analyzed for the nature and quantity of the organometallic compounds present in terms of concentration and pH. To complete these series, a sample containing polluted (with antiknock compounds) soil was spiked with inorganic mercury to find out whether there were similar reactions in real samples. The analyis of these organometallic compounds was realized by a system containing a microwave-induced plasma (MIP) and a plasma-emission detector (PED) developed by Cammann, which was described previously.[8, 9] The extraction of the analyte is performed by solid-phase micro-extraction (SPME). This method has been tried and tested for the analysis of other organometallic compounds, e.g. lead species.[10]

EXPERIMENTAL

Instrumentation

The principle experimental set-up is based on the work of Bettmer *et al.* and is described elsewhere.[11] The measurements were carried out with the following instruments: gas chromatograph (Hewlett-Packard HP 5890A with split/splitless injector), GC–MIP interface (AHF, Tübingen, Germany), resonator (TM_{010} Resonator, Model HMW 25-471 N-W, AHF), microwave generator (GMW 24-301 DR, AHF) and integrator (C/R6A Chromatopac, Shimadzu, Duisburg, Germany) and solid-phase micro-extraction (Supelco, Deisenhofen, Germany).

The gas-chromatographic parameters are given in Table 1.

Reagents, standard solutions and extraction procedure

Mercury stock solution ($1000\ \text{mg l}^{-1}$ as Hg), 100% acetic acid p.a., methanol p.a., sodium hydroxide p.a. and dimethylmercury p.a. were obtained from Merck (Darmstadt, Germany); sodium tetraphenylborate and the sodium salt of dimethylarsonic acid trihydrate p.a. were obtained from Fluka (Germany); methylmercury chloride p.a., diethylmercury p.a., trimethyl-lead chloride p.a. and phenylmercury chloride p.a. were obtained from Alfa Ventron (Karlsruhe, Germany); sodium tetraethylborate was from Strem Chemicals (Newburyport, USA).

For the soil sample treatment, methanolic NaOH (15% w/w methanol, in 10% v/v NaOH) was used. Clean water was produced with the Seralpur PRO 90 CN system.

Extraction

The extraction technique used in this experiment was solid-phase micro-extraction (SPME). This method has been applied to the separation of hydrophobic substances such as BTX but also for the extraction of organometallic compounds.[12] The extraction parameters optimized for maximum sensitivity for mercury species detection are given in Table 2. This method was used for the stock solutions of mercury and in the same way for the extraction of the analytes from the soil sample. While doing this the coated fiber was exposed to the sample and the target analytes were extracted from the sample matrix into the coating. The fiber with the concentrated analytes was then transferred to the injection port of the GC for thermal desorption.[13]

Table 1 Gas-chromatographic conditions for the separation of the mercury compounds

Gas parameters	
Column	Ultra-1
Dimensions	25 m × 0.32 mm i.d. × 52 μm film thickness
Column head pressure	100 kPa helium
Injection port temperature	250 °C
Injection	Split/Splitless
Purge time: off/on	0–2 min/2–7 min
Oven program	
Initial temperature	60 °C
Initial time	1 min
Ramp rate	35 °C min^{-1}
Final temperature	245 °C
Final time	2 min
Interface parameters	
Transfer line	Ultra-1
Transfer temperature	250 °C
Detection parameters	
MIP	Beenaker TM_{010} cavity
Microwave power	75 W (reflected power 3W)
Helium flow rate	135 ml min^{-1}
Oscillation angle	4.4°
Oscillation frequency	20 Hz
Interference filter	HWB 0.75 nm; max. transmission 254 nm 13%

Table 2 Parameters for solid-phase micro-extraction (SPME)

Extractor coating	Dimethylsiloxan
Thickness	100 μm
Extraction time	20 min
Extraction temperature	45 °C
Extraction conditions	Solution stirred

Formation of solutions

In the case of the sodium salt of dimethylarsonic acid, four different solutions were made with different concentrations of inorganic mercury: $0.5\ \mathrm{ml}^{-1}$, $1\ \mathrm{mg\ l}^{-1}$, $5\ \mathrm{mg\ l}^{-1}$ and $10\ \mathrm{mg\ l}^{-1}$. These four solutions were also designed with two different pH values: $\mathrm{pH}_1 = 4.75$ and $\mathrm{pH}_2 = 7$. In the case of tetraethyl-lead and trimethyl-lead chloride there was an additional solution with a concentration of $0.1\ \mathrm{mg\ l}^{-1}$ of mercury(II). The solubility in water of tetraethyl-lead is extremely small, so it was necessary to add methanol (15% v/v) in this case.

All these solutions were stored for four days at room temperature.

Pretreatment

An aliqot of 1 ml of the original solution and 8 ml of clean water was treated with 1 ml of an aqueous solution of tetraphenylborate (10% w/w) to convert the monoalkyl compounds to the appropriate phenyl derivate (pH = 5, acetate buffer, 0.5 ml of acetic acid), which was necessary for the extraction by SPME and also for the separation in the gas chromatograph. The real sample (weighed amount: 2.83 g) was treated with 1 ml of a solution of sodium hydroxide (15% w/w) to remove the species from the soil. The alkylation of the monoalkyl compounds was carried out by a reaction with an aqueous methanolic solution (8% v/v methanol) of sodium tetraphenylborate (2 mL, 10% w/w) at a pH of 5 (acetate buffer). In the same way the aqueous solutions for the standard addition method were pretreated.

RESULTS AND DISCUSSION

Dimethylarsonic acid

The results of transalkylation with dimethylarsonic aid are shown in Fig. 1. It is clear that a transfer of one or two methyl groups from the dimethylarsonic acid is possible and happens under the conditions mentioned above. The rate of transfer depends firstly on the pH. Further experiments for the clarification of this context are in progress. But it is also shown that the transfer of two methyl groups, yielding dimethylmercury, seems to be more common than the transformation of one methyl group, yielding monomethylmercury (analyzed as phenyl methylmercury). The absolute transformation rates (a maximum of 1.3% under these conditions) are quite small, as shown in Fig. 1, compared with the transalkylation of tetraethyl-lead (Fig. 2) below.

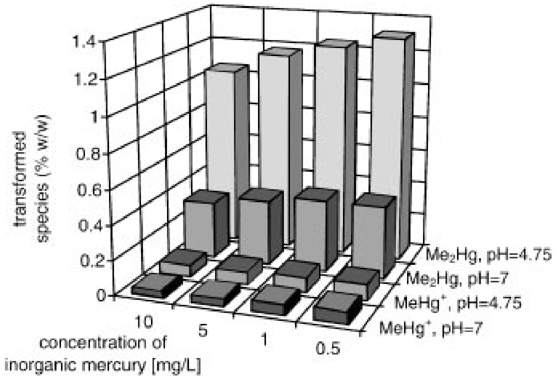

Figure 1 Transformation of methyl groups from dimethylarsonic acid to inorganic mercury (the relative standard deviation, RSD, is not shown but was approximately 5–9%).

Tetraethyl-lead/trimethyl-lead chloride

Qualitatively comparable results were obtained in transalkylation experiments for ethyl and

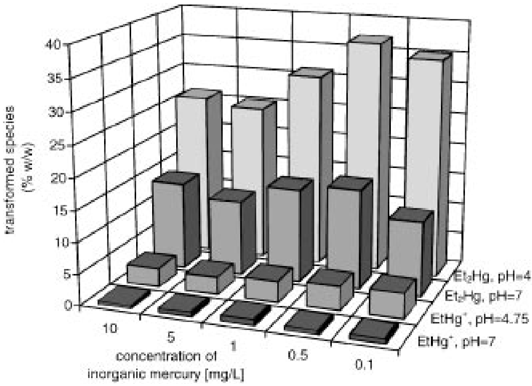

Figure 2 Transformation of ethyl groups from tetraethyl-lead to inorganic mercury (the RSD is not shown but was 8–11%).

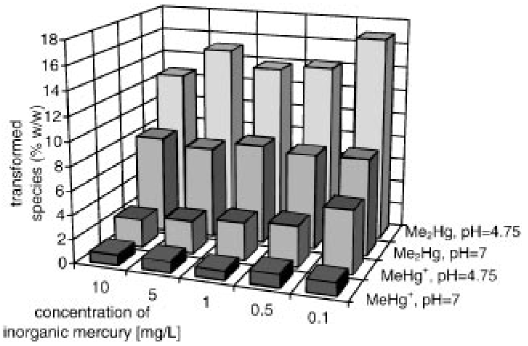

Figure 3 Transformation of methyl groups from trimethyl-lead chloride to inorganic mercury (the RSD is not shown but was 4–10%).

methyl groups from tetraethyl-lead/trimethyl-lead chloride (Figs 2 and 3). The main difference in this case is the enormous increase in the rate and the explicit dependence on the pH and the amount of the dialkylmercury formed. An average of nearly 28% of the possible ethyl groups (relative to inorganic mercury) were transformed to produce diethylmercury from tetraethyl-lead, as Fig. 2 demonstrates. Concerning the dependence of the reaction on the pH, this is the same as mentioned in the reaction of dimethylarsonic acid. Furthermore we started experiments to clarify the reason for the higher yields of the dialkyl compounds. The first results seem to confirm the assumption that the final oxidation state of lead is responsible for this. Lead(II) is the most stable form of lead in aqueous solutions, which indicates that the loss of two alkyl groups leads to the more stable lead(II) state, via the formation of an intermediate $Et_3Pb\bullet$ radical.[14] Further experiments are in progress to understand the mechanism.

Analysis of a contaminated soil sample

To ensure that the results of the aqueous solutions are of fundamental interest, a soil sample from the site of a former factory producing antiknock additives was taken. These soil samples contain both tetraethyl-lead and trimethyl-lead (0.123 ± 0.009 mg kg^{-1} total organic lead). One part of this sample was spiked with a stock solution of inorganic mercury ($c = 100$ mg l^{-1}, in 10 ml aqueous solution). The samples were stored for four days at room temperature and then prepared for analysis. In Fig. 4 two comparative chromatograms are shown, one of the spiked and one of the natural soil sample. The predominant species in the sample were dimethylmercury (0.54 ± 0.03 mg kg^{-1} as Hg) and inorganic mercury (0.75 ± 0.01 mg kg^{-1} as Hg), but methyl- and ethyl-mercury could also be detected. The presence of ethylmercury could be a result of transalkylation from ethyl-lead species, because there is no evidence given in the literature for a bioethylation process. It is clear that the transformation rate of the alkyl groups increases with the concentration of inorganic mercury and takes place in the same way as was discussed for the aqueous solution. Experiments to clarify the functional relationship between the amount of transformation and the time of reaction are also in progress.

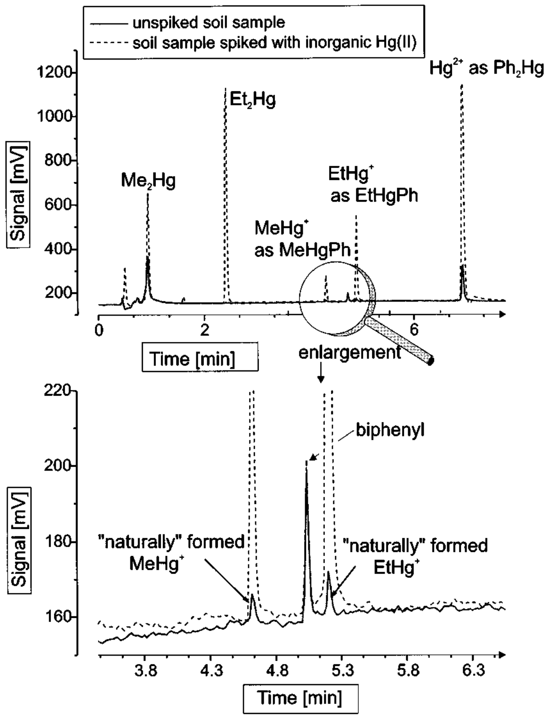

Figure 4 Comparative chromatograms of the spiked and unspiked soil samples.

CONCLUSIONS

This series of experiments have shown that the transformation of alkyl groups from one species to the other is possible for those species used in our experiments. Under laboratory conditions the main factor influencing this transformation is the resulting form of the alkylated species first, and also the pH. It should be noted that the formation of dialkylated species from inorganic mercury was favored over the transformation of only one alkyl group. The possible reasons for this are discussed above. The amount of the transformation may depend on conditions such as temperature or light intensity, but there seems to be no functional relationship to the concentration of the relevant species. As a demonstration, a soil sample with organolead contamination was analyzed to verify whether a transalkylation could occur or not. The results obtained were similar to those with the aqueous standards, which indicates a possible transalkylation under natural conditions.

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