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Stimulation of Elemental Mercury Oxidation by SH Compounds

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Anthropogenic mercury pollution has been a serious environmental problem. The presence of mercury in the environment has received a great deal of attention due to its highly toxic nature and translocation through the food chain. Elemental mercury released into the Amazon River basin due to gold mining activities is roughly estimated at 130 tons per year (Pfeiffer and Lacerda 1988). In fact, high levels of total mercury, mostly in the form of methylmercury, in fish collected from around the gold mining areas and high levels of methylmercury in the hair of humans living in fishing villages downstream of these areas have recently been documented (Martinelli et al. 1988; Malm et al. 1990; Nriagu et al. 1992). These results suggest that the reaction which converts the discharged elemental mercury into mercuric mercury is present in nature before the methylation of the generated mercuric mercury. Methylation and reduction of mercuric mercury and decomposition of organomercury have been extensively studied (Nriagu 1979). However, little information is available concerning the conversion of elemental mercury in aquatic ecosystems.

The purpose of this study was to clarify the mechanism of oxidation of elemental mercury to mercuric mercury in the aquatic environment.

MATERIALS AND METHODS

Analytical grade reagents and distilled water were used in this experiment. The following chemicals were obtained from the indicated sources: mercury (purity: > 99.9 %), dilute H_2SO_4 and L-cysteine (L-cys) (Kanto Chemical co, Inc.); glutathione and L- ascorbic acid (AsA) (Wako Pure Chemical Industries, Ltd.); D-penicillamine (Aldrich Chemical Co, Inc.); and NaOH and $SnCl_2 \cdot 2H_2O$ (Merck Co, Inc.).

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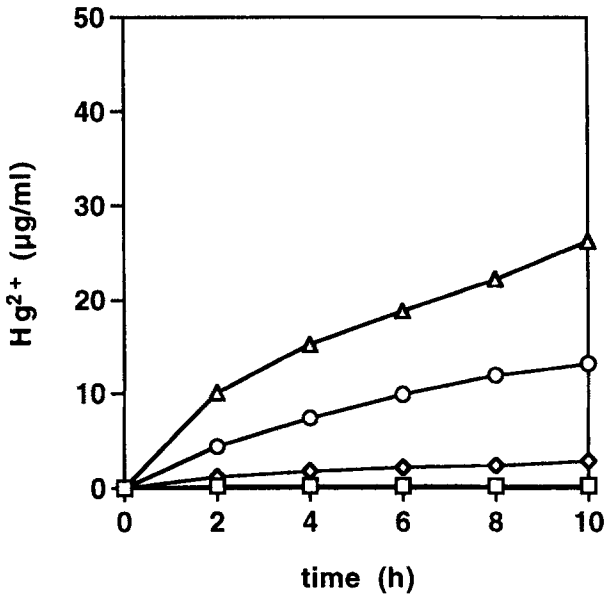

Figure 1. Effect of SH compounds on the oxidation of elemental mercury in distilled water: □, none; ○, 1 mM L-cysteine; △, 1 mM Glutathione; ◇, 1 mM D-penicillamine.

The reaction was carried out in 10 ml of a reaction mixture containing 0.1 M KH_2PO_4-NaOH buffer (pH 6.5), 10 μl of elemental mercury (130 mg as mercury) and varying concentrations of the compounds to be tested. SH compounds and $SnCl_2$ solution were made up fresh each time. After incubation in a 50-ml glass vial with a Teflon-lined screw cap and shaking at 100 rpm by rotary shaker in the dark at 25℃, the sample (10 μl) was added to 5 ml of 10 mM L- cysteine and Hg^0 remaining in the sample was removed by bubbling with N_2 gas. The flow rate of N_2 gas was constant at 0.7 L/min. The ionized mercuric mercury in the sample was then measured by the reduction vaporization method (Magos and Clarkson 1972). Chiefly, ionized mercuric mercury in the sample was reduced by the addition of 0.5 ml of 10 % (w/v) $SnCl_2$ dissolved in 1.8 N H_2SO_4 and 5 ml of 3.6 N H_2SO_4. After 5 ml of 10 N NaOH were added, the absorption of mercury vapor was measured at 253.7 nm. The detection of mercury was carried out using a flameless atomic adsorption mercury analyzer MV-253R (Sugiyamagen Environmental Science Co. Ltd. Japan).

RESULTS AND DISCUSSION

The amounts of mercuric mercury produced in the reaction mixture increased along with incubation time in the presence of 1 mM L-cysteine in distilled water, whereas there was no increase in the absence of L-cysteine (Fig. 1).

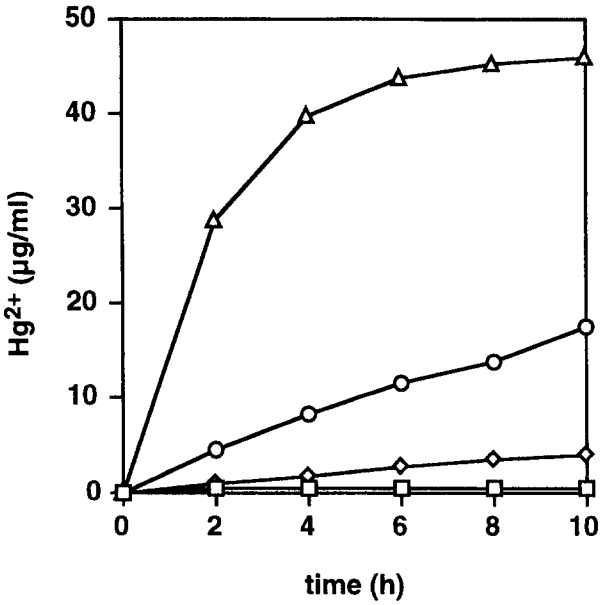

Figure 2. Effect of SH compounds on the oxidation of elemental mercury in 0.1 M phosphate buffer (pH 6.5) : □, none; ○, 1 mM L-cysteine; △, 1 mM Glutathione; ◇, 1 mM D-penicillamine.

The effect of sulfhydryl compounds on the formation of mercuric mercury from elemental mercury was further examined. Glutathione was more effective, but D-penicillamine was less effective than L-cysteine. An almost similar result was found in the buffer solution (Fig. 2).

The oxidation of elemental mercury was shown to be roughly constant in the range of 1 to 10 mM of L-cysteine (Fig. 3). Sulfhydryl compounds are known to have a high affinity for mercuric ion. The conversion of elemental mercury to ionized mercuric mercury, therefore, may be due to the result of the shift of equilibrium between Hg^0 and Hg^{2+} induced by the added L-cysteine by virtue of its reactivity to mercuric ion.

The oxidation of elemental mercury to mercuric mercury by L-cysteine in distilled water was accelerated by the addition of L-ascorbic acid which is known to be a reductant (Fig. 4). As a result of further examination, the acceleration of elemental mercury oxidation by L-cysteine was also found in the acidified solution, and no such effect was found in the neutral buffer solution. These results suggest that the pH in the reaction might have been essential for the oxidation of elemental mercury by L-cysteine.

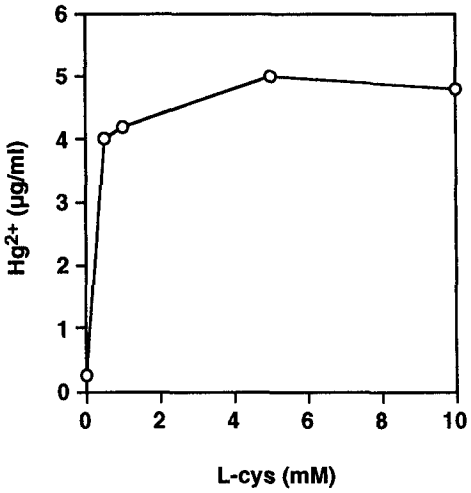

Figure 3. The concentration dependence of L-cysteine on the oxidation of elemental mercury. Ionized mercuric mercury was measured after 2 hours.

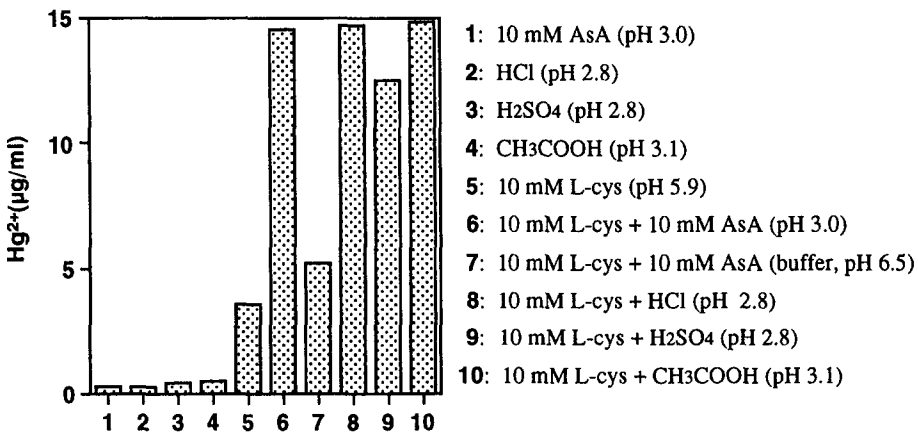

Figure 4. Effect of acid on the oxidation of elemental mercury by L-cysteine. Ionized mercuric mercury was measured after 2 hours.

The methylation of mercury has received a great deal of attention since the discovery that methylmercury is present at relatively high levels in aquatic organisms in the Amazon River despite a lack of methylmercury input into the river basin. Methylmercury is a neurotoxin and may be accumulated in the food chain, making it a potential health problem. Although it is well known that elemental mercury in vivo is oxidized by catalase or peroxidase, relatively little attention has been paid to the transformation of this metal to ionized mercuric mercury in the environment (Kudsk 1969; Magos et al. 1974; Eide and Syversen 1983; Ogata and Aikoh 1984; Wigfield and Tse 1986).

This paper reports a preliminary survey of the conversion of elemental mercury to mercuric mercury in the presence of SH compounds which are widespread in organisms. The mechanism of oxidation of elemental mercury by L-cysteine or glutathione, which is generally believed to be one of the potential reductants, remains obscure. Further investigations are now in progress in our laboratory.

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