Photochemical reaction of Tl in aqueous solution and its environmental significance

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(Received January 23, 2004; Accepted June 30, 2004)

The valence state of thallium determines its toxicity, distribution and mobility. Tl(I) can be oxidized to Tl(III) under photoirradiation of the high-pressure mercury arc lamp and solar light. A photooxidation experiment of thallium showed that the photooxidation rate could be affected by the pH of the solution, and the intensity and wavelength of the light source. Lowering the pH and increasing the light intensity have the effect of increasing the photooxidation rate. UV radiation (UVB and UVC regions) plays an important role in the photooxidation of Tl(I). However, the microbial effect is not obvious in comparison with photooxidation effect in this experiment. The study can provide important scientific groundwork for handling of thallium pollution.

Keywords: photooxidation, Tl, light intensity, pH, Hg arc light

INTRODUCTION

Thallium is a toxic heavy metal, its toxicity being higher than that of Hg, Cd, Pb, Zn and Cu, and only inferior to that of methyl mercury. The symptoms of thallium poisoning in human body are hair-loss, body-ache, reduction of eyesight, insomnia, blindness and even death. Thallium concentrations in natural waters are very low, with 1–550 ng/L in groundwater, 1–410 ng/L in lakes, 13–1350 ng/L in rivers and 10–20 ng/L in seawater (Lin and Nriagu, 1999), all of which are lower than the maximum permitted concentrations in drinking water stipulated by some countries (for example, no greater than 1 μg/L in China, and 0.1 μg/L in Canada (Anna et al., 1999)). But anthropogenic activity can lead to the enhancement of thallium concentrations in natural waters. For example, the average thallium concentration in a mine water of SW Guizhou Province, China, is 340 μg/L, 4 orders of magnitude higher than the background level (0.005 μg/L). Tl contents range from 13 to 1100 μg/L in deep mine groundwater in the area where intensive Tl mineralization is developed (Xiao et al., 2003). Due to the long-term exploiting of thallium-bearing resources, chronic Tl poisoning is very common and very severe in this region. Locally about 1000 people were affected by endemic Tl poisoning during the 1960s–1970s (Zhou and Lin, 1985). The release of thallium into the environment in the case of smelting of lead, copper and zinc ores, the combustion of fossil fuels, oil refining, and other industrial activities, has become one of the major subjects of study in China (Xie et al., 2000, 2001). But no detailed and systematic study has been conducted on the change of thallium’s valence state in surface water, which thus has aroused our interest in this aspect.

Thallium usually exists in two oxidation states in nature: Tl(I) and Tl(III). Thallous compounds are quite similar to the compounds of alkali metals, are highly soluble, and can be easily absorbed by plants. Studies on the concentrations of Tl in soils and vegetables in the Lanmuchang area of China (Xiao et al., 2004) indicated that thallium contents range from 40 to 124 mg/kg in soil in the mining area, from 20 to 28 mg/kg in slope wash materials, from 14 to 62 mg/kg in alluvial deposits downstream, and from several times to several hundreds times higher than the background level (0.2–0.5 mg/kg). The Tl concentrations of vegetables are very high in response to the high concentrations of Tl in the soil, and Tl in green cabbage can be as much as 500 mg/kg in dry weight. The average daily uptake of Tl by the local inhabitants of the Lanmuchang area via locally planted crops has been estimated to be 1.9 mg/person, which is 50 times the daily ingestion by individuals from Tl background areas. The weathering/degradation of thallium-bearing ores is a major factor leading to the incorporation of thallium into soil and water, and the increase of Tl concentration. Thallium can be absorbed by plants and uptaken by domestic ani-
mals, and is readily transferred into human body through the food chain. However, Tl(III) usually exists in aqueous solution in the form of Tl(OH)₃, with a solubility product $K_{sp} = 10^{-45.2}$, among the least soluble metal hydroxides (Lin and Nriagu, 1998), so Tl(III) is easy to be deposited or be adsorbed. It is commonly considered that thallium contamination in the environment is controlled mainly by soluble Tl(I). An additional study (Twining et al., 2003) indicated that the toxicity of Tl(III) in the isolated (free) state is 50000 times that of Tl(I). Therefore it is of great importance to study the change of thallium’s valence state in natural waters.

The standard redox potential of Tl³⁺/Tl⁺ is 1.28 V, so Tl(I) can only be oxidized to Tl(III) by a strong oxidant, such as bromic water or MnO₂. Since there is no strong oxidant in natural waters, Tl(I) is thought to be the predominant form of Tl in natural waters. However, Batley and Florence (1975) found that up to 80% of soluble thallium in seawater was present as anionic Tl(III) complexes, as revealed by cation resin separation techniques. Recently, Lin and Nriagu (1999) found that Tl(III) in the total dissolved thallium ranges from 43% to 73% in the Great Lakes of the United States and their inflow steams by Chelex-100 resin separating techniques, with an average of 66% in the analyzed water samples. In addition, a significant proportion of Tl(III) may exist in the colloidal state. This result has challenged traditional viewpoints and aroused a great debate in academic circles. Cheam (2000) considered that the proportion of trivalent thallium may be overestimated as a result of oxidation by nitric acid. But Lin and Nriagu (2000) argued that nitric acid is not powerful enough to oxidize Tl(I) to Tl(III).

The experiment made by Savenko (2001) showed that Tl(III) exists in the form of Tl(OH)₃ complexes in 3.5% NaCl solution and 0.01 mol/L sodium perchlorates solutions, with an average solubility of $0.8 \times 10^{-6}$ mol/L. Oxidation of Tl(I) may be the most important source of Tl(III) in natural waters, with minor amounts of Tl(III) brought about directly from the outside. Some studies (e.g., Paul et al., 2001) indicated that the species in the water column can be oxidized, or oxidative species such as OH⁻ and H₂O₂ can be produced by way of photoirradiation. Therefore we hypothesized that Tl(I) photooxidation may be one of the most important sources of Tl(III). The aim of our experiment is to study the photooxidation of Tl(I) in the aquatic environment, and provide important groundwork for handling thallium contamination.

**EXPERIMENT METHODS**

**Instrumentation and reagent**

Shimazhu RF-540 spectrofluorimeter; Orion 868 pH meter; 125 W high-pressure mercury arc light with a cylinder vent; magnetic stirrer.

Stock solution: $0.5 \times 10^{-3}$ mol/L Tl(I) stock solution was prepared by dissolving an appropriate amount of thallium nitrate (analytical grade) and thallium chloride (analytical grade) and wrapped with aluminum foil to avoid light. Tl(I) solutions of varying concentrations were prepared by diluting the stock solutions in Milli-Q water. To avoid interference, thallium nitrate was adopted as the standard solution in most of the experiments, but thallium chloride was used in sodium chloride media.

**Procedure**

The tested solution was irradiated by the high-pressure mercury arc light and solar light, respectively. The concentrations of the solution were kept at $1 \times 10^{-5}$ mol/L by adding thallous nitrate or thallous chloride. The solution placed in a broad beaker was irradiated by Hg arc light, and stirred. Sampling was done at a fixed time interval and kept in dark conditions for later measurements. The vertical distance between Hg arc light and solution surface was kept at 40 cm in most cases with the exception of the experiment on the effect of light intensity (Fig. 1). The experiment of temperature was 25–27°C, the solution was not treated for oxygen removal, and the temperature variation was less than 1°C during the entire procedure. The experiment with sunlight as the irradiation source was similar to that with Hg arc light, and the working time was usually between 11:00 A.M.–16:00 P.M. The same experiment was done on water samples taken from Hongfeng Lake near Guiyang City, China.
Analysis

So far, there are many methods available to determine thallium, such as the Chelex-100 resin separating method (Lin and Nriagu, 1999b), and the electrochemical method (Pizeta et al., 1996; Hassanien et al., 2003). Tl(I) is one of the few inorganic ions which fluoresces under UV light, but Tl(III) in contrast is not fluorescent, therefore, Tl(I) can be determined directly by fluorospetrophotometry (Ensafi and Rezaei, 1998; Tomás et al., 1996). Its exciting wavelength is 227 nm, and the emission wavelength is 419 nm. The fluorescence intensity of Tl(I) shows a good linear relationship with Tl(I) concentration (Fig. 2). However, the Tl(I) fluorescence intensity would be affected by the pH of the solution, the concentrations of Cl– and other factors, and also varies in different solution media; hence the relative fluorescence intensity is adopted in this experiment, that is to say, the ratio of fluorescence values for the tested solution is adopted before and after irradiation. The fluorescence value is very low in thallium-free solution and is deduced as blank. To confirm the increase of Tl(III) concentrations and concomitant decrease of Tl(I) concentrations, the reaction products were confirmed by Rodamine B (Ma et al., 2001) and Ethyl violet tests (Lin and Wang, 1999).

Experiment Results

Confirmation of irradiation products

Highly concentrated TlNO₃ solution (0.5 × 10⁻³ mol/L) was used in the experiment. The colorless solution turned to a yellow-brown suspension after one hour of continuing irradiation by Hg-arc light and the suspension tended to increase further over time. Yellow-brown precipitate was seen after standing. Tl(III) can be extracted by benzene and isoamyl acetate, but this is not the case for Tl(I). The precipitate was dissolved with hydrochloric acid, extracted using benzene (Ma et al., 2001), and color-developed with rodamine B. The organic phase turned pink in color, and if extracted by isoamyl acetate (Lin and Wang, 1999) and color-developed by ethyl violet, the organic phase would turn blue, indicating the production of Tl(III). The TlCl solution with the same concentration of thallium yielded the same results after radiation by Hg-arc light. However, the TlCl solution did not produce the suspension or deposition after radiation, and this could be attributed to the formation of a Tl(III)chloride complex (Oldenburg et al., 1997), which is not sensitive to hydrolysis. But the thallium solution did not give the same results without the treatment by photoirradiation. Therefore, it can be concluded that Tl(III) had resulted from photoirradiation.

Effects of pH on Tl(I) photooxidation

Tl(III) was firstly discovered in seawater (Batley and Florence, 1975). 3.5% NaCl solution was prepared to simulate the salinity of seawater, The concentrations of thallium were adjusted to 1 × 10⁻⁶ mol/L by adding TlCl. Using solutions of differing pH (adjusted by HCl and NaOH solutions) irradiated by Hg-arc light, the results showed (Fig. 3) that the Tl(I) oxidation rate increased while the solution pH decreased. In the case of pH = 2, nearly all Tl(I) in the solution was oxidized to Tl(III) within 10 minutes; if pH = 5, 21.2% Tl(I) still remained in the solution after 1 hour; at pH = 9, the reaction rate was much slower, with about 83% Tl(I) in the solution after 1 hour. The solar radiation experiment gave similar results: we chose a spot in Guiyang City (N26°34′25″, E106°43′26″) to carry out the experiments. The Tl(I)-contained solution was exposed directly to sunlight for 5 hours at temperature of 28–30°C. Two different media—water and 3.5% NaCl solution with the same thallium concentration—were adopted in the experiment. For each medium, two samples were prepared as two solutions dif-
ferring in pH: one is acidic (pH = 2) and the other is neutral. Then the sunlight irradiation experiment was done for the solar irradiation experiment (Fig. 4) after 5 hours, it was found that the Tl(I) concentrations in the irradiated acid solution are reduced rapidly with about 2.8% Tl(I) in the solution, while 72.3% Tl(I) remained in the neutral solution. In the 3.5% NaCl acidic solution, the Tl(I) was reduced more rapidly: only less than 1% Tl(I) remained in the solution after 5 hours. Therefore, the solution pH can affect the photooxidation rate of Tl(I) in the solution, and low pH promotes the photooxidation of Tl(I).

Effects of light intensity on Tl(I) photooxidation

The light intensity can be controlled by adjusting the vertical distance between the light source and the surface of the solution. The experiment on light intensity showed (Fig. 5) that there was only 4% Tl(I) in the pH = 3, 3.5% NaCl solution after 5 minutes of irradiation during the strong light intensity (20 cm vertical distance) experiment, but during the weak light intensity experiment (36 cm vertical distance), there was still 5% Tl(I) after 15 minutes of irradiation. This indicated that strong light intensity benefits the oxidation of Tl(I).

Effects of Wavelength of the light source on Tl(I) photooxidation

Using a piece of 3 mm-thick window plate glass as a light filter, the contrast experiment was done under filtered light and non-filtered light, and with the pH = 2, 3.5% NaCl-containing Tl(I) solution. The results showed (Fig. 6) that there was 90% Tl(I) in the solution after 5 minutes of irradiation under filtered light, while less than 1% under non-filtered light. The Hg-arc light source has the strongest peak at 366 nm in the UV A region and 313 nm in the UVB region, but the light transmittance of plate glass was high in UVA region, while very low in UVB and UVC regions Fig. 7). This may indicate that the light of UVB and UVC bands plays an important role in the Tl(I) photooxidation in this experiment.
Effects of microbial activities on Tl(I) photooxidation

In order to get a better understanding the effects of microbial activities on Tl(I) photooxidation, water samples were collected from the Hongfeng Lake near Guiyang City (water type: Ca2+-Mg2+-HCO3, TDS 245 mg/L, DOC 2.6 mg/L) and treated three separate ways to exclude the effects of microbial activities: (i) filtered by 0.7-μm filter membrane; (ii) filtered by 0.22-μm filter membrane; (iii) sterilize-filtered (i.e., the solution was filtered after boiling) by 0.22-μm filter membrane. The solution is neutral in this experiment. The standard 1 × 10^{-6} mol/L TlNO_3 solution was added to the above three groups of samples, which then were irradiated immediately by Hg arc light and sunlight, respectively. The results showed (Fig. 8) that photoirradiation can oxidize Tl(I) to Tl(III) in the treated solutions at approximately the same rate. However, the Tl(I) photooxidation rate was raised, as observed in the Hg arc light photoirradiation experiment. This result showed that Tl(I) can be oxidized to Tl(III) in the same manner for the samples dealt in three different ways, but the microbial effect is not obvious in comparison with photooxidation effect in this experiment.

DISCUSSION

(a) At present there are scant literature data on the photooxidation mechanism of thallium. Oldenburg and Horváth (Oldenburg et al., 1997; Horváth et al., 1999) studied the photochemical reaction mechanism of thallium in strongly alkaline solution, by irradiating 1 × 10^{-3} mol/L TiClO_4 in 1 mol/L NaOH solution using UV light. The overall reaction in the presence of oxygen is: 2TlOH + 2O_2 + H_2O → Tl_2O_3 + 2H_2O_2. The irradiated solution yielded a yellow-brown suspension, identical to our observations on our neutral solution experiment. It is assumed that the same reaction mechanism may be involved in neutral solution, but this requires further study.

(b) It is of significance that Tl(I) can be oxidized to Tl(III) by photolysis. The concentrations of thallium are very low in natural waters, but higher than 10^{-6} mol/L in a contaminated area. In view of the high toxicity of thallium, it is generally taken as a matter of priority to clean the water polluted by this toxic material. It is feasible to clean thallium-contaminated water by precipitating any insoluble or barely soluble thallium compound. The Eh-pH diagram (Nriagu, 1998) shows that the monovalent thallium ionic species Tl(I) occupies almost all Eh-pH space. Only under very alkaline and oxidizing conditions will thallium oxides be produced (Tl_2O_3 and Tl_2O_4), and under very alkaline and reducing conditions, it is expected to form the simple sulfide Tl_2S. As it is considered as an active element, thallium should be extremely mobile under virtually all natural surface and subsurface conditions. One may try to create a strongly alkaline environment by the adding certain chemicals, followed by the addition of a strongly oxidizing agent in order to attempt to make Tl(I) ion precipitate as Tl_2O_3 and/or Tl_2O_4.

Thallous chloride is a rather insoluble compound with a suitable low solubility product (K_s = 10^{-7.26}), so one would try to create a high-Cl^- environment in order to make the Tl(I) ion precipitate as TlCl_2. The thermodynamics data indicates that one needs a concentration of 10 × 10^{-6} mol/L thallium in wastewater in order to precipitate as thallium chloride, provided the Cl^- ions concentration is 6.166 mol/L. Addition of the chloride ionic species could be done by adding hydrochloric acid or sodium chloride. But this may result in a temporarily strong increase in both acidity and salinity, and the Cl^- concentration required is unpractical in pollution treatment. Whatever chemicals are added, they will enter into the environment and create new pollution problems. Tl(I) can be oxidized to Tl(III) by photolysis without the involvement of any chemical, and precipitated ultimately as Tl(OH)_3 in water. This can reduce thallium mobility and effects on the aquatic environment. Of course, our study on the photochemistry reaction of thallium is only at a preliminary stage, and a lot of problems need to be solved and a lot of work still needs to be done.

(c) The role of microorganisms in Tl(I) photooxidation experiment. Twining and his colleagues (Twining et al., 2003) conducted lab and field incubations for the Great Lakes (Lake Ontario, the pH of the Lake is about 8.0). The cultivatable solution was placed on the ship deck under direct sunlight for 60 hours, where Tl(III) comprised 74% of the total dissolved thallium. But no Tl(I) oxidation was observed in the solution sterile-filtered by 0.2-μm filter to exclude microorganisms. So Twining assumed
that solar radiation alone can not make Tl(I) oxidize to Tl(III). Microorganism are indispensable during Tl(I) photooxidation. Twining used the 204 Tl tracing method, that solar radiation alone can not make Tl(I) oxidize to Tl(III). Microorganism are indispensable during Tl(I) photooxidation. Twining used the 204 Tl tracing method, and the concentrations of thallium spiked in the sample were just (1.3–2.2) × 10^{-9} mol/L, about 500 times lower than that in our experiments. Thallium can inhibit the growth of microorganisms. A study on the uptake of thallium by cyanobacteria indicates (Ritchle and Larkum, 1998) that the inhibitory effects of Tl on cyanobacteria growth were remarkable when its concentrations reached 10^{-6} mol/L, even still more remarkable when its concentrations reached 10 × 10^{-6} mol/L, as evidenced by the fact the cell turned yellow. Thus, it can be seen that microbial activities are dissimilar in solutions of different Tl concentrations. Microorganisms are active under low Tl concentration and direct sunlight, and probably can affect the photooxidation of Tl(I). But the microorganism growth is inhibited in highly Tl concentrated solution. In addition, the solution was continuously radiated by the high-pressure Hg-arc light, whereas microbial activities were reduced rapidly. For this experiment we did, we can see photoirradiation still plays an important role in the photooxidation of Tl(I), but the microbial effect is not obvious in comparison with photooxidation effect in this experiment. Thus the microbial effect requires further investigation.

Some auto-oxidation on precipitated particle surfaces might be occurring to facilitate the photoreaction. From the experiment confirming the irradiation products, we can see the highly concentrated TlNO₃ solution (0.5 × 10^{-3} mol/L) was turn to a yellow-brown suspension after irradiation, while the same concentrated TlCl solution did not produce the suspension or deposition after radiation, but still led to the production of Tl(III).

CONCLUSIONS

(a) Our experiment showed that photoirradiation can promote the oxidation of Tl(I) to Tl(III) in aqueous solution by both sunlight and high-pressure Hg arc light. The lower the pH and the higher the light intensity, the greater the photooxidation rate will be. UV radiation (UVB and UVC regions) plays an important role in the photooxidation, but the microbial effect is not obvious in comparison with photooxidation effect in this experiment.

(b) The photooxidation process of Tl(I) is of important practical value. It is well known that the solubility of Tl(OH)₃ is very low, and the compound is easily deposited and adsorbed. As a result the mobility of thallium can be reduced and thus thallium contamination in the aquatic environment can be diminished. This study offers an important piece of scientific evidence for environmental handling of thallium contamination.

Acknowledgments—This work was financially supported by the National Natural Science Foundation of China (Grant No. 40373041).

REFERENCES


