Spectroscopic Study on Photolysis of Aqueous Solution of Zinc Pyrithione

Yoshitaka YAMAGUCHI¹⁾, Ryuji KOJIMA¹⁾, Akira KUMAKURA²⁾,
Yasuhiro YAMADA²⁾, Kiyoshi SHIBATA³⁾ and Tetsuya SENDA¹⁾

¹⁾National Maritime Research Institute

(6–38–1 Shinkawa, Mitaka, Tokyo 181–0004 Japan)

²⁾Faculty of Science, Tokyo University of Science

(1–3 Kagurazaka, Shinjuku, Tokyo 162–8601 Japan)

³⁾Faculty of Social Systems Science, Chiba Institute of Technology

(2–17–1 Tsudanuma, Narashino, Chiba 275–0016 Japan)

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Summary

Photodegradation process of zinc pyrithione (Zn(PT)_2) in aqueous solution was investigated using a photo spectroscopic technique. Three characteristic peaks were observed in ultraviolet and visible light absorption spectrum of Zn(PT)_2 . By xenon lamp irradiation, the spectrum rapidly changes to that of 2-pyridinsulfonic acid (PSA) and finally exhibits nearly flat with several very weak unknown peaks. Rate constants, obtained on a basis of the first order kinetics, do not depend on either the concentration between 0.03 and 3 mg/ ℓ or the temperature from 283 to 303 K, but are proportional to the intensity of irradiation light. The half life of Zn(PT)_2 in water is estimated to be approximately 25 minutes under an average natural sun light intensity (188 W/ m^2) on the ocean surface.

Key words: Zinc Pyrithione, Photolysis, Antifouling Paints, Booster Biocide

Introduction

Zinc pyrithione (Zn(PT)_2), a chelate compound of Zn^{2+} ion with pyrithione (1-hydroxy-2-pyridinethione) as shown in Fig. 1(a), is white powder and has a crystal structure of dimmer with pentacoordinated zinc¹⁾. It is employed as bactericide and fungicide, and has been widely used in several hair care and cosmetic products as antidandruff. Another application of Zn(PT)_2 is a booster biocide in antifouling paints for ships' hull since early 1990's. A treaty banning the use of organotin compounds, such as tributyltin (TBT) and triphenyltin (TPT) compounds, as anti-fouling agent has been adopted by the International Maritime Organization (IMO). As an alternative for organotin compounds, Zn(PT)_2 also exhibits a broad action against

marine fouling organisms and thus finds appreciation as a booster biocide in anti-fouling paints. It has been considered that Zn(PT)_2 could be a non-persistent antifouling biocide and rapidly degrade into less toxic compounds by natural sunlight. However, Zn(PT)_2 has been found to exhibit highly toxic effects to some aquatic organisms including urchins²⁾ even at an extremely low concentration. It is necessary to investigate the degradation behavior of Zn(PT)_2 in water environment in detail in order to carry out the environmental risk assessment for the use as a booster biocide in antifouling paints.

Analytical methods of Zn(PT)_2 concentration, which are necessary for environmental monitoring and laboratory tests, have been developed using chelate change³⁾, polarography⁴⁾, thin-layer chromatography⁵⁾, stripping

voltammetry⁶⁾ and high performance liquid chromatography (HPLC). In particular, chromatographic techniques including HPLC coupled with proper detectors such as single wave ultraviolet absorption detector⁷⁾, photodiode array detector^{8,9)} and mass spectrometer¹⁰⁻¹²⁾, have been developed for analysis of Zn(PT)₂, where the pretreatment has been carried out to control transchelation to copper pyrithione (Cu(PT)₂)^{7,10)}. Chromatographic analyses essentially need a number of pretreatment procedures, such as extraction, enrichment and derivatization¹⁰⁻¹³⁾. In case of the presence of thin metallic and metal cationic contaminations, transchelation from Zn(PT)₂ to another pyrithione metal, mainly Cu(PT)₂, may occur during pretreatment. Those analytical methods, including pretreatment from environmental and laboratory scale test samples to injection, were not well sophisticated enough to detect Zn(PT)₂ of such low concentrations as in environmental samples. Thus, only a few have been reported on monitoring the concentrations of Zn(PT)₂ and related chemicals in seawater and in sediment¹⁴⁻¹⁷⁾.

In this study, the behavior of Zn(PT)₂ in aqueous solution under light irradiation has been investigated. Since transchelation of Zn(PT)₂ readily occurs even in laboratory solution by small amount of contamination, we have applied a direct analysis technique by using spectroscopic method without any pretreatment to detect Zn(PT)₂ of low concentrations in aqueous solution. Change in ultraviolet and visible light absorption spectra are measured for Zn(PT)₂ solutions during the irradiation by air mass filtered xenon lamp. Degraded products were identified and photolysis kinetics were calculated from the obtained spectra.

Experimental

Materials

Chemical grade zinc pyrithione (Zn(PT)₂) with purity above 90% was obtained from Wako Pure Chemical Industries, Ltd., Japan. Several pyridine compounds shown in Fig. 1 (b)-(g) have been proposed as degradation products of Zn(PT)₂^{5,12,18,19)}. Pyridine-N-oxide (PO) and 2-mercaptopyridine N-oxide (HPT) were purchased from Aldrich Chemical Company, U.S.A.; 2-mercaptopyridine (HPS) and 2,2'-dithio-bis-pyridine ((PS)₂) from Tokyo Kasei, Japan; 2,2'-dithio-bis-pyridine-N-oxide ((PT)₂) from Chem Service and 2-pyridinesulfonic acid (PSA) from Synchem, U.S.A. Ultrapure water was prepared by a water purifying apparatus, Elix(UV-5, Millipore)

and Milli-Q(Gradient A10, Millipore).

Preparation of solutions

Solutions for photolysis experiments were prepared by stirring Zn(PT)₂ powder in ultrapure water for approximately 10 hours. Unresolved Zn(PT)₂ particles were then separated from the solutions by 0.45 μm membrane filter (25A chromato disk, GL Science, Japan). The concentration of Zn(PT)₂ solution was determined from zinc concentration measured by inductively coupled plasma mass spectrometry (Agilent 7500i Series). Solutions of lower concentrations, 1/10, 1/20, 1/50 and 1/100, were prepared by diluting the original solution with ultrapure water.

Fig. 1 Structures of zinc pyrithione and reaction product candidates. (a) zinc pyrithione (Zn(PT)₂), (b) pyridine-N-oxide (PO), (c) 2-mercaptopyridine N-oxide (HPT), (d) 2-mercaptopyridine (HPS), (e) 2,2'-dithio-bis-pyridine ((PS)₂), (f) 2,2'-dithio-bis-pyridine-N-oxide ((PT)₂), (g) 2-pyridinesulfonic acid (PSA)

Photolysis experiments

Light source consists of xenon arc lamp (500W, Ushio SX-UI501XQ) and air mass filter 1.5 (Ushio) to simulate average natural sun light received at a latitude of 37 degrees N following the ASTM G173-03. A glass beaker of 1 ℓ in volume was used as a reactor, the temperature of which was controlled in a bath (Eyela NCB-1200) filled with water kept at a constant temperature. Light from filtered xenon lamp was irradiated perpendicularly to the surface of a solution. The irradiation intensity of light was determined by the average intensity of the surface area. Under the light irradiation of the maximum power of 297 W/m², the temperature fluctuation of the reactor was kept within 1 degree.

Eight hundred mL of Zn(PT)₂ solutions in glass beaker were irradiated with filtered xenon lamp under continuous stirring. To collect samples, solutions are average concentration of chemicals in the reactor for stirring. The depth of the solution in this reactor is about 10 cm. Irradiation intensity was measured by photo power meter (Spectra-physics 407A TC) at the surface of water. Light intensities of 163, 213 and 297 W/m² were employed at temperatures of 283, 293 and 303 K, respectively. A control sample was prepared under a dark condition at each temperature.

Spectroscopic measurements

Spectra of Zn(PT)₂ solutions were measured by ultraviolet and visible light absorption spectrometer (Shimadzu UV-2500PC, Japan). Quartz faced cells of 1 cm and 10 cm in thickness (GL science, Japan) were used to obtain spectra for Zn(PT)₂ and related substance in solutions. Full scan acquisitions were made over a wavelength range of 190~800 nm.

Results and Discussion

Photolysis of Zn(PT)₂

Characteristic peaks were obtained for the initial Zn(PT)₂ solution and solutions after irradiation at various irradiation periods of time from 1 to 7,530 minutes. A spectrum of the initial Zn(PT)₂ solution, at the time of zero, exhibits characteristic peaks at 240, 270, and 328 nm. Spectra for a photolysis series of Zn(PT)₂ for the light intensity of 297 W/m² on the reactor surface are shown in Fig. 2. In the spectra irradiated for longer than 210 minutes, the characteristic peaks of Zn(PT)₂ found at 240, 270 and 328 nm disappeared, instead a broad peak accompanied by a fine structure

near 260 nm was observed. By further irradiation for longer than 7530 minutes, the peak of 260 nm also disappeared.

A calculation using a semi-empirical molecular orbital method ZINDO/S, suggests that characteristic peaks observed at 240 and 270 nm are assigned to $\pi-\pi^*$ and $\pi-n^*$ transitions, respectively¹⁸⁾. Absorption peak near 260 nm was consistently observed both in Zn(PT)₂ and the first reaction product. Since Zn(PT)₂ has pyridine structure, it is reasonable to assume that the degradation product obtained from chelate of

Fig. 2 Ultraviolet and visible light absorption spectra of Zn(PT)₂ solution under photolysis. ① Zn(PT)₂ solution (irradiation time: 0 min.), ② irradiation time of 20 min., ③ 40 min., ④ 210 min., ⑤ 570 min. and ⑥ 7530 min. (Irradiation intensity: 297 W/m², temperature: 298 K and concentration: 3 mg/ ℓ). Peaks of Zn(PT)₂ and PSA were indicated by black and white arrows, respectively

$\text{Zn}(\text{PT})_2$ at the first stage has also a pyridine ring. Six compounds shown in Fig.1 were chosen as candidates for the reaction product. Ultraviolet and visible light absorption spectra of the substances were measured and are shown in Fig. 3. Comparing the spectra of reaction product with those of candidates, the reaction product is assigned as PSA because the fine structures observed in both spectra around 260 nm are resem-

blance. It has been reported that PSA is the main product of termination from $\text{Zn}(\text{PT})_2$ in photolysis¹⁹⁾. However, the present series of spectra changing by further irradiation implies that the photolysis is not terminated at PSA, which is further decomposed by extended irradiation to another compound which shows no particular peaks within the range of ultraviolet and visible light absorption spectra.

Fig. 3 Ultraviolet and visible light absorption spectra of reaction product candidates and irradiation time of 210 min. (a) PO, (b) HPT, (c) HPS, (d) $(\text{PS})_2$, (e) $(\text{PT})_2$, (f) PSA and (g) spectrum of solution after irradiation for 210 min.

Rate constants

Rate constants for photolysis of Zn(PT)_2 are estimated for various temperatures, concentrations and intensity of irradiation. The Photolysis of Zn(PT)_2 is assumed to follow the first order kinetics expressed as:

$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (1)$$

where C is the concentration of Zn(PT)_2 at a time t , C_0 is the initial concentration of Zn(PT)_2 and k is the rate constant.

Rate constant for Zn(PT)_2 the first stage of degradation process was estimated by the time claimed for the decrease in characteristic peak intensities of 240 nm by 20 % from the initial spectrum using equation (1). In case of the same condition of Fig. 2 (irradiated intensity: 297 W/m^2 , temperature: 298 K and concentra-

Fig. 4 Relationship between Zn(PT)_2 concentration and irradiation time. (Irradiation intensity: 297 W/m^2 , temperature: 298 K and concentration: 3 mg/l , this test was repeated 3 times, each plots were shown in different marks.)

Fig. 5 Relationship between the rate constant of Zn(PT)_2 photolysis and temperature

tion of Zn(PT)_2 : 3 mg/l), obtained result was shown in Fig. 4. Assuming that the degradation of Zn(PT)_2 yields the first-order kinetic reaction, rate constants of photolysis can be obtained from equation (1). Fig. 5 shows the effect of temperature on the rate constant for the average irradiation intensity of 297 W/m^2 on the surface at approximately 3 mg/l Zn(PT)_2 solutions. The rate constants between 283 and 303 K are nearly constant, suggesting that the degradation is independent on temperature and follows the same kinetics. The rate constants of Zn(PT)_2 solutions of various concentrations between 0.03 and 3 mg/l at an average irradiation intensity of 297 W/m^2 on the surface are shown in Fig. 6, where the temperature were kept at 293 K during irradiation. The rate constants do not depend on these concentrations in this range. The rate constant in low concentration solution as ppt level like samples of ports and harbors is estimated by extrapolation to same degradation kinetics at these experimental conditions.

Rate constants for the average irradiation intensities of 163 , 213 and 297 W/m^2 are shown in Fig. 7. The temperature and the concentration were 293 K and 3 mg/l , respectively. In case of first order kinetics the rate constant should be proportional to irradiation intensity and can be expressed as

$$k = 1.4 \times 10^{-4} I \quad (2)$$

where I is the irradiation intensity on surface (W/m^2). The half life $t_{1/2}$ is calculated by the following equation:

$$t_{1/2} = \frac{\ln 2}{k} \quad (3)$$

Using these equations, the half life of Zn(PT)_2 in aque-

Fig. 6 Relationship between the rate constant of Zn(PT)_2 photolysis and initial concentrations

Fig. 7 Relationship between the rate constant of Zn(PT)₂ photolysis and the irradiated intensity

ous solution is estimated to be 25 minutes for irradiation intensity of 188 W/m² which has been reported for an average irradiation intensity at ocean surface²⁰.

Previous studies on photodegradation of Zn(PT)₂ have reported half life values of 17.5 minutes¹⁹ and 8.3±0.9 minutes²¹. However, experimental details such as light source and intensity as well as the depth of solutions have not been shown in these reports. The results obtained in the present study show a good agreement with those reported by Turley¹⁹ and Maraldo²¹. They have employed more complicated analytical methods such as HPLC using radioisotope and bioassay. The spectroscopic method employed in the present study demonstrates that degradation process of biocide like Zn(PT)₂ in solutions is more readily analyzed without complicated pretreatment.

Conclusions

Photolysis of Zn(PT)₂ in the aqueous solution was investigated using a spectroscopic technique. Zn(PT)₂ solutions irradiated with filtered xenon lamp was analyzed with ultraviolet and visible light absorption spectroscopy. Zn(PT)₂ was found to be decomposed initially to PSA and to further unidentified products. The rate constant, obtained assuming the first order kinetics, is proportional to the light irradiation intensity. It suggests that the photodegradation rate is drastically changed with time, geographical location and water depth. The half life of Zn(PT)₂ in aqueous solution was estimated as approximately 25 minutes under an average sun light on the surface of ocean. It has been demonstrated that the spectroscopic method can readily analyze the photolysis of Zn(PT)₂.

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