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Enhanced Degradation of Halogenated Hydrocarbons in a Water-Photolysis System

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The catalyzed water-photolysis system has recently drawn considerable attention for the production of hydrogen (Gratzel et al 1982; Gratzel 1983). Excitation of the photosystem with visible light will induce hydrogen generation from water. The hydrogen generated in situ can be used as a reducing agent for hydrogenation of unsaturated organic compounds and hydrogenolysis of benzyl chloride to ethyl benzene (Tan et al 1987). This study is to report the results of reduction of trichloroethylene (TCE) and trihalomethane (THM)in the water-photolysis system. TCE and THM are chosen for this study because these compounds have posed a potentially serious environmental problem in both natural and drinking waters (Symons et al 1975), these carcinogenic suspected chemicals are also classified as 'priority pollutants' by the U.S. Environmental Protection Agency (US EPA 1979).

MATERIALS AND METHODS

Colloidal platinum catalyst was prepared by reducing chloroplatinic acid with excess potassium citrate and 1% of poly(vinyl alcohol) was then added and dissolved in this solution. This suspension was then centrifuged at $1.2\text{x}10^{3}$ rpm for 1.5 hours (Brugger et al 1981).

The reactions were carried out in a 125 ml erlenmeyer flask equipped with a screw cap and a teflon/silicon septum. Platinum-colloid (125 ml), Ru(bipy)_3^{2+} ($4.0\text{x}10^{-5}$ mole), methyl viologen (MV^{2+}, $2.0\text{x}10^{-3}$ mole or $8.0\text{x}10^{-3}$ mole), and disodium ethylenediamine tetraacetic acid ($3.0\text{x}10^{-3}$ mole) were added into the flask. This mixture was then evacuated for 5 minutes and a desired amount of THM was injected into the system. The resulting suspension was stirred vigorously while irradiated with a 450-watts Hanovia Hg lamp, which was placed in a pyrex immersion well with cool water. Samples were taken from both headspace and liquid phases at different time intervals for analysis. A Perkin Elmer 900 gas chromatograph equipped with a FID and a Carbosive G column was used to analyze the gas samples. The liquid samples were analyzed with a Hewlett Packard 5702A gas

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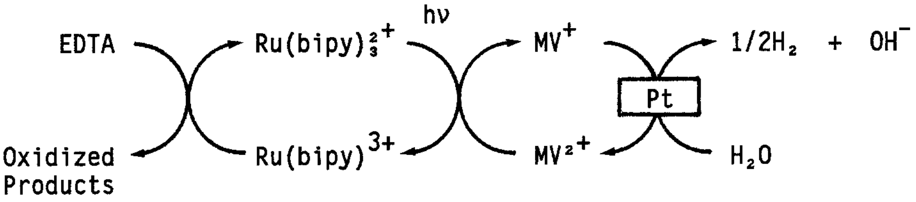
chromatograph equipped with an ECD and a Carbopak B column for measuring halogenated methane concentrations (Wang et al 1985).

RESULTS AND DISCUSSION

In this photosystem, the chromophore, Ru(bipy)$_3^{2+}$, acts as a photosensitizer and absorbs a photon. The excited state Ru(bipy)$_3^{2+}$ reacts with an electron relay, methyl viologen (MV^{2+}), and transfer an electron to methyl viologen. The platinum catalyzes the reaction of reduced methyl viologen (MV^{+}) with water and thus produces hydrogen. This sacrificial photoredox process was performed as shown in Scheme 1:



Scheme 1.

In this water-photolysis system, the hydrogen atoms generated can be an active species for hydrogenation and hydrogenolysis reactions (Tan 1987). With the presence of halogenated methane compounds (CHX_3), consecutive displacement of halides (X) by metal-bonded hydrogen atoms could lead to the formation of methane.

$$\mathrm{CHCl_3} \xrightarrow{\dot{H}} \mathrm{CH_2Cl_2} \xrightarrow{\dot{H}} \mathrm{CH_3Cl} \xrightarrow{\dot{H}} \mathrm{CH_4} \qquad (1)$$

Figure 1 indicates that the reduction of chloroform from 300 ηg/μl to 10 ηg/μl required 15 hours. A blue color of MV^+ was noticed during the irradiation process. In order to enhance the degradation rate of halogenated compounds, active metal, zinc, was added to the system. The standard potential of redox system with $Zn^{2+}/Zn = -0.7628V$ and $MV^+ = -0.45V$ induces an electron transfer reaction such as

$$\mathrm{Zn} + 2\mathrm{MV^{2+}}(\text{colorless}) \longrightarrow \mathrm{Zn^{2+}} + 2\mathrm{MV^{+}}(\text{blue}) \qquad (2)$$

This spontaneous reaction together with the photoreduction of MV^{2+} by photoexcited Ru(bipy)$^{2+}$ increase the amount of MV^+ in the aqueous system. As a result, hydrogen molecules and reactive atoms could be greatly produced and thus enhanced the degradation of the substrate in the system. Figure 1 shows 0.1g of Zn added to the system, 300ηg/μl of chloroform was reduced to 10 ηg/μl in two hours and a yield of 210 ηg/μl of methane was obtained. The total degradation time of chloroform at 300 ηg/μl with the presence of zinc in the system was 7.5 times faster than the identical system without zinc added.

Bromoform at an initial 2000 ηg/μl was approximately 50% degraded after 20 hours of irradiation. However, with 3000 ηg/μl of initial concentration of bromoform was prepared in the photosystem with the presence of 0.1g of zinc, only trace quantity of the substrate (0.1 ηg/μl) was detected after 14 hours of reaction. The results of this experiment is shown in Figure 2.

Chlorodibromomethane with an initial concentration of 2000 ηg/μl was degraded to 80 ηg/μl of bromochloromethane, 22 ηg/μl of methyl chloride, and 1050 ηg/μl of methane in 20 hours of irradiation. Under the identical conditions with 1g of zinc added, the total degradation time required for the reduction of 2000 ηg/μl of $CHClBr_2$, was approximately 1 hour as shown in Figure 3. The degradation rate was increased by a factor of 20.

Other than trihalomethane compounds, trichloroethylene (TCE) could also be reduced in the system. Figure 4 shows that 300 ηg/μl of TCE after 12 hours of irradiation was reduced to 7.4 ηg/μl and 223.9 ηg/μl of ethane was detected. When 1g of zinc added to the system, the degradation of TCE was enhanced. Ethane at 259.9 ηg/μl was formed and TCE was not detected after 5 hours.

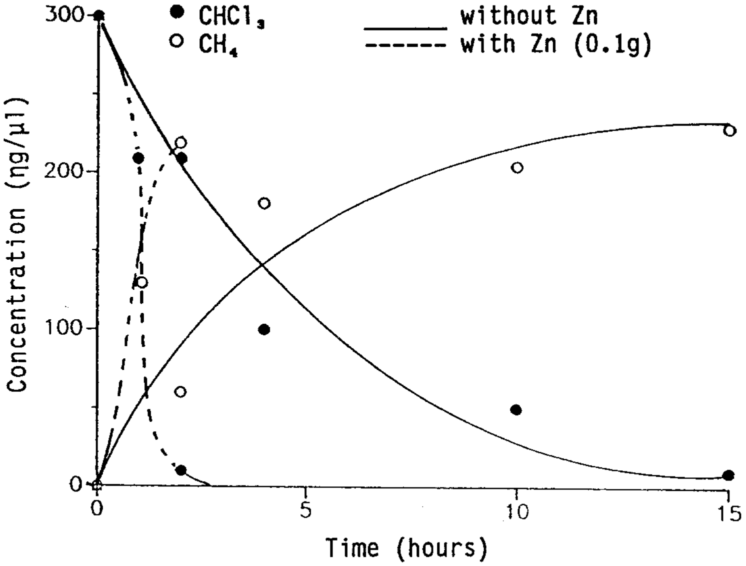


Figure 1. Photodegradation of $CHCl_3$-300 ηg/μl in the-photolysis system.

Visible light irradiation of the water-photolysis system (Pt-colloi/$Ru(bipy)_3^{2+}$/MV^{2+}/EDTA) induces considerable cleavage of water to hydrogen. The excitation wavelength of $Ru(bipy)_3^{2+}$ (λ=452 nm) is covered in the solar spectrum. The sucess of mercury lamp irradiation could lead us to explore natural sunlight as an irradiation source. Furthermore, this photolysis system can be used for reduction of halogenated compounds with the presence of the finely dispersed platinum particles. Addition of zinc to the photolysis system increases the degradation rate of these substrates and the oxidized hydroxide, $Zn(OH)_2$, can be reclaimed as a chemical feedstock. Other active metals such as magnesium and aluminum with higher electrode potential could also be used as a reducing agent to enhance the degradation.

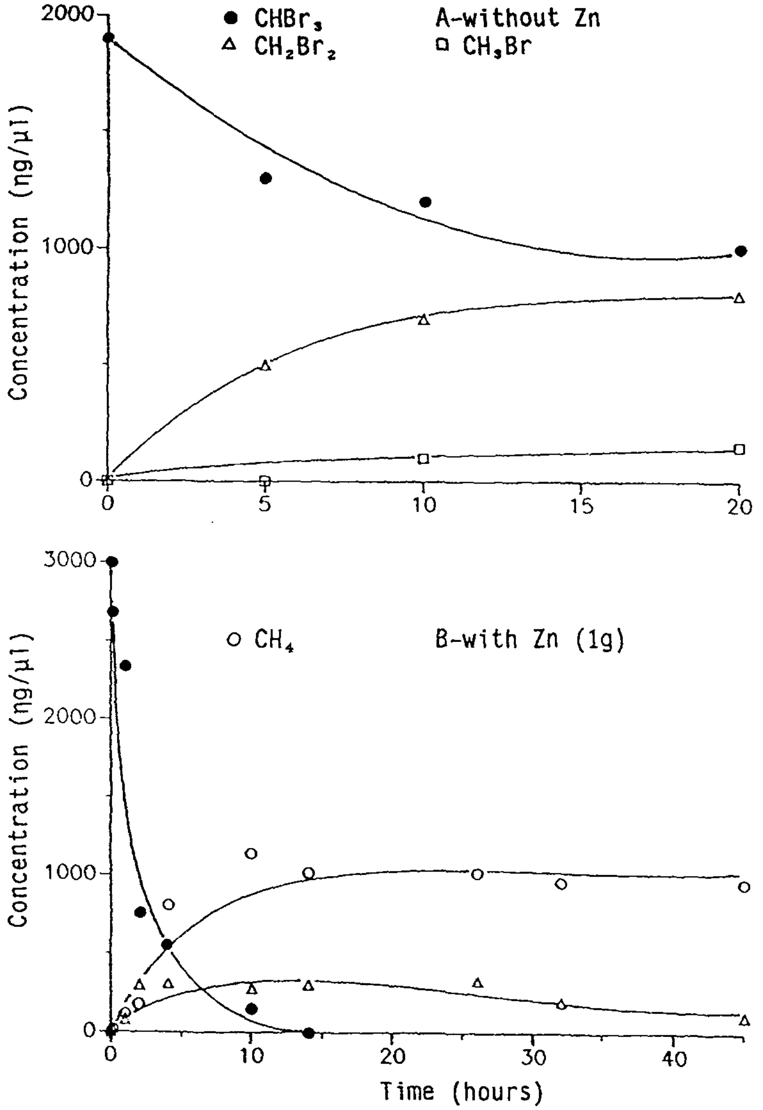


Figure 2. Photodegradation of $CHBr_3$-2000 and 3000 ηg/μl in the photolysis system.

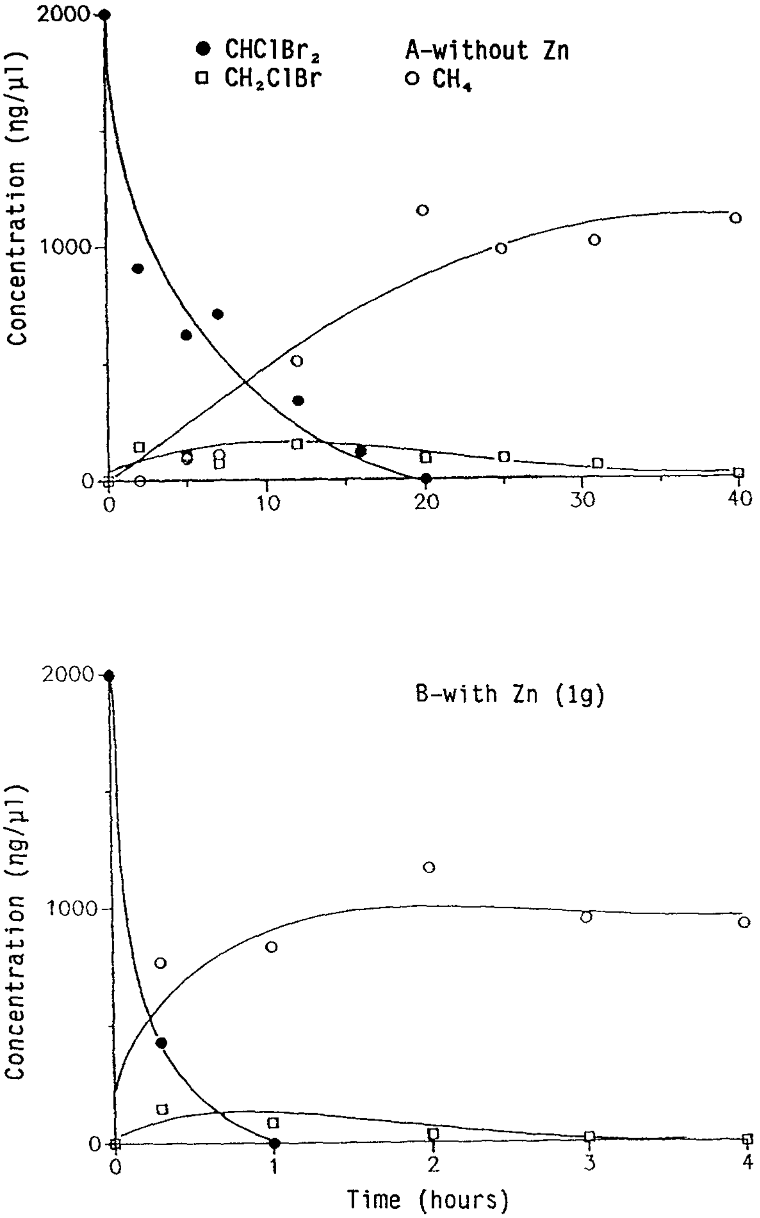


Figure 3. Photodegradation of $CHClBr_2$-2000 ng/µl in the photolysis system.

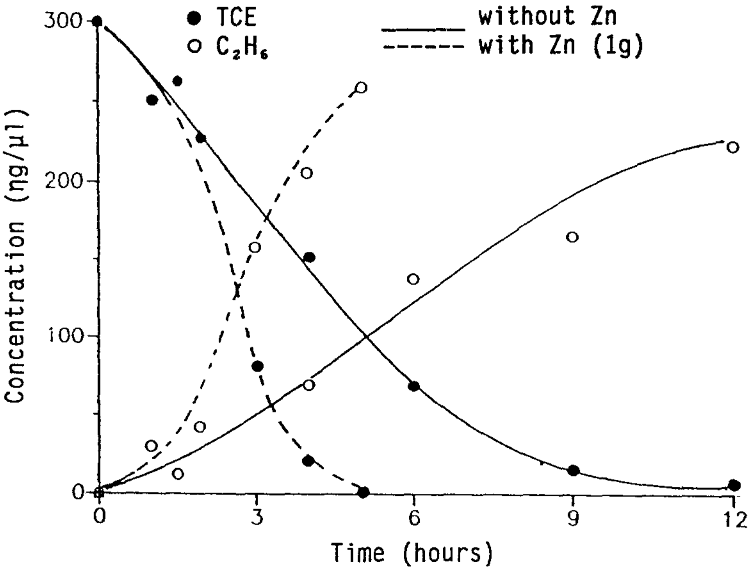


Figure 4. Photodegradation of trichloroethylene (TCE)-300 ηg/μl in the photolysis system.

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