Bull. Environ. Contam. Toxicol. (1990) 45:149–156

Bulletin of Environmental Contamination and Toxicology

Reduction of Halogenated Hydrocarbons with Magnesium Hydrolysis Process

Tsen C. Wang and Chee K. Tan

Department of Chemical and Environmental Engineering, Harbor Branch Oceanographic Institution, Ft. Pierce, Florida 34946, USA

Magnesium reacted with water at room temperature and platinum colloid catalyst produces hydrogen. In the presence of the platinum catalyst, metal bonded hydrogen radicals generated in situ can be used to reduce halogenated hydrocarbons to hydrocarbons. Trichloroethylene, bromoform and carbon tetrachloride in the contaminated water were reduced to ethane and methane in this study. A material balance for each experiment was established to verify the reactions. The process can be used to degrade halogenated compounds from the contaminated water.

Halogenated hydrocarbons such as halomethanes, halogenated ethanes and ethenes, etc. are introduced into the environment by man (Burmaster, 1982). They have been found to be ubiquitous contaminants in air, water, and food (Parson, et al., 1984; Wang, et al., 1985; Marx, 1974). The use of chlorine in conventional drinking water disinfection contributes to the formation of chlorinated organic compounds (Arguellow, 1979; Rook, 1976; Stevens, et al., 1980). Halogenated hydrocarbons have been shown to be toxic and possibly carcinogenic and pose a serious threat to public health (Dowty, et al., 1975; Simon and Tardiff, 1978). A novel water photolysis system, with catalysts for oxidation or reduction of organics in situ, has recently drawn attention for detoxifying these compounds in the water. Photooxidation of organic compounds to CO_2 and HCl in aqueous suspension of titanium dioxide (Carey, 1976; Matthews, 1986; Ollis, et al., 1983, 1984) and photoreduction of CO_2 and halogenated hydrocarbons to hydrocarbons were recently published (Maiden and Wilner, 1986; Wang and Tan, 1987).

Hydrogen has been used to reduce trihalomethanes to hydrocarbons catalytically (Hoke, et al., 1984) and thermally (Chung and Bozzelli, 1986). Hydrogen can be produced by the addition of an active metal such as magnesium to steam. However, the reaction of magnesium with water to form hydrogen is negligible at room temperature. The reduction of water by magnesium is a thermally

---

Send reprint requests to T. Wang at the above address.

favorable process: $Mg + 2H_2O \rightleftharpoons Mg^{2+} + 2OH^- + H_2$ $\Delta G^0 = -369$ KJoule/mole.

Unfortunately, the formation of metal hydroxide shielded the metal surface from the further spontaneous reaction (Hohne and Jager, 1981). The addition of nobel catalyst such as platinum will generally enhance the reaction process (Rylander, 1968; Jolly, 1971; Archer and Spiro, 1970). In the aqueous system, platinum catalyzes the reaction between magnesium and water at ambient temperature and generate hydrogen gas. This process is a spontaneous electron transfer reaction which does not require an energy supply. With the aid of superfine colloidal platinum, the generated hydrogen radical in situ can be used as a reducing agent in the aqueous system (Tan, et al., 1987). This study is intended to degrade halogenated contaminated water such as trichloroethylene (C_2HCl_3), bromoform ($CHBr_3$), and carbon tetrachloride (CCl_4) in situ with hydrogen generated from magnesium hydrolysis process. These compounds can be reduced to low molecular weight hydrocarbons such as methane and ethane.

MATERIALS AND METHODS

Three liters of colloidal platinum catalyst were prepared by reducing hexachloroplatinic acid (1.5×10^{-3} mole) with excess of potassium citrate (6.7×10^{-3} mole) and 1% polyvinyl alcohol. This suspension was then centrifuged at 1.2×10^3 rpm for 1.5 hours (Brugger, et al., 1981). The pH of the colloid was adjusted to 7.0 with 3N NaOH. Twenty milliliters of this platinum colloid was placed into a 28 mL glass vial equipped with a screw cap and teflon faced septum. One gram of magnesium (325 mesh) was added to the reaction vial and evacuated immediately. The vial was then stirred vigorously at room temperature. Hydrogen produced was collected using an inverted graduated cylinder filled with water. Hydrogen generated from the reaction gradually replaced the water and collected in the cylinder.

The substrates tested were 2.1 μℓ of bromoform ($CHBr_3$), 1.3 μℓ of carbon tetrachloride (CCl_4), 4.1 and 13.7 μℓ of trichloroethylene (C_2HCl_3), respectively. For each test, a fresh solution was prepared. During the degradation process, samples were taken from both gas and liquid phases of the system at different time intervals for analysis. A Perkin Elmer 900 gas chromatograph equipped with a 1.5 m x 0.32 cm stainless steel column packed with Carbosive-G 60/80 mesh (Supelco) together with a Flame Ionization Detector was used to analyze the hydrocarbon gas samples in the headspace. The liquid samples were analyzed for halogenated compounds by a 5700A Hewlett Packard gas chromatograph in series with a Tekmar Liquid Sample Concentrator (LSC-2). The chromatograph was equipped with a 1.5 m x 0.32 cm glass column packed with Carbopack-B and an Electrolytic Conductivity Detector. A 5730A Hewlett Packard gas chromatograph using a glass column (1.8 m x 0.64 cm) packed with Carbopack-B and an Electron Capture Detector was used to analyze the halogenated compounds by direct injection of the headspace samples. The final solution was analyzed by an ion chromatograph (Dionex QIC model) for the resulted anions. The chromatograph was equipped with a HPLC AS4A column (Dionex). The efluent was 0.75M $NaHCO_3$/ 2.0M Na_2CO_3 at 2 mℓ/min. The regenerant was 0.025M H_2SO_4 at 4 mℓ/min.

RESULTS AND DISCUSSION

Figure 1 demonstrates the H_2 evolution with various amounts of magnesium added. One gram of magnesium reacted with 20 mℓ of water for seven hours at room temperature (23°C) produced 48 mℓ of H_2. When platinum (5×10^{-4} M) was present in the mixture of same water and 1.5 g of magnesium, H_2 generation was increased to 380 mℓ.

Figure 2 indicates the initial concentration of 45.6 µmol of trichloroethylene was reduced in a 20 mℓ of Pt-colloid mixed with 1 g of Mg. After twenty minutes of reaction, there was no trichloroethylene detected in the liquid phase and approximately 3 µmol of trichloroethylene, 39.1 µmol of ethane and 1.70 µmol of methane were detected in the gas sample. At the end of 30 minutes, only a trace amount of trichloroethylene (0.02 µmol) was detected in the headspace sample and the amount of methane and ethane in the gas phase were 2.92 and 47.5 µmol, respectively. The amount of ethane formed was dependent on the amount of trichloroethylene present in the system initially. Table 1 and Figure 2 show that 145 µmol of ethane was formed in 30 minutes with a 152 µmol trichloroethylene initially present in the reaction vial. The end products formed vary with the initial substrates in the system. Figure 3 shows that 23.7 µmol of bromoform after twenty minutes of degradation was reduced to 1.01 µmol of dibromomethane 17.3 µmol of methane and 4.92 µmol of ethane. Ethane and dibromomethane were possible intermediate compounds during the degradation process and they were not detected at the end of the experiment.

The reduction of CCl_4 at 38.9 µmol to 30.5 µmol of CH_4 is shown in Table 1 and Figure 4. After 140 minutes of reaction, chloroform and dichloromethane detected in the sample were possible intermediate compounds. The probable transformation of CCl_4 or $CHCl_3$ to CH_4 could be: CCl_4 ---> $CHCl_3$ ---> CH_2Cl_2 ---> CH_3Cl --> CH_4. This proposed transformation pathway is not proven in this paper. Without pt-colloid present in the system, the reduction process could not be effectively carried out. A blank test with 45.6 µmol of trichloroethylene added to the system was performed. After a period of 2 hours, 37.5 µmol of trichloroethylene still remained and only trace amounts of methane (3.45 µmol) and ethane (3.14 µmol) were detected. Another blank test was conducted with an excess amount of pure H_2 added to a reactor containing 9.08 µmol of $CHBr_3$ in 20 mℓ of H_2O. Magnesium and platinum colloid

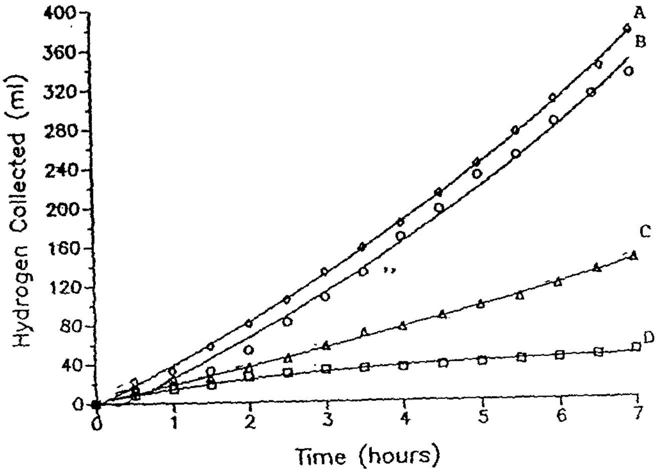

Figure 1. Generation of hydrogen from Mg/Pt-colloid (20ml, 0.0005M), except for D: (A) 1.5g Mg; (B) 1.0g Mg, (C) 0.5g Mg, (D) 1.0g Mg in Blank H_2O.

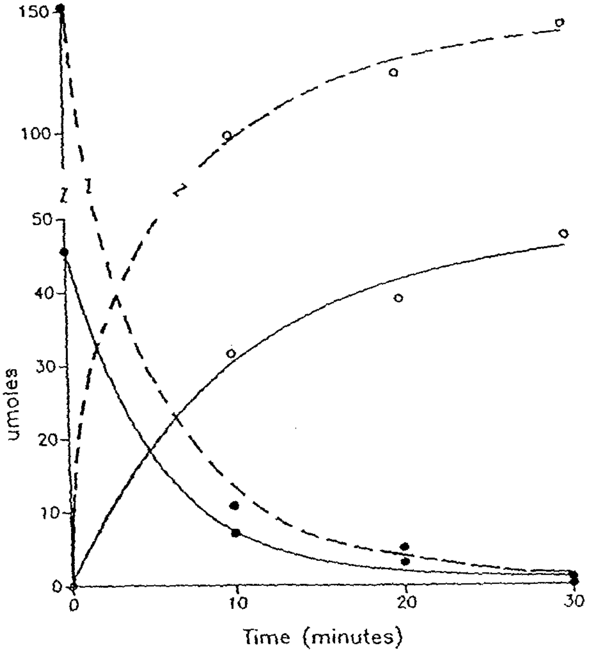

Figure 2. Reduction of trichloroethylene (——45.6 µmol, --- 152 µmol) to ethane in Mg (1g, 0.04mol)/Pt-colloid (20ml, 0.0005M): (•) trichloroethylene, (o) ethane.

Table 1. Mass Balance of the Degradation Process in the Mg-Hydrolysis Process with Pt-Colloid as the Catalyst.

Substrate (μmol)		Reaction Time, min.	Detected (μmol)		Ratio=Detected Prod.* / Substrate (C	Cl	Br)
TCE	45.6	30	CH_4 C_2H_6 Cl^-	2.91 47.5 133	1.05	0.97	----
TCE	152.0	30	CH_4 C_2H_6	2.50 145	0.97	NA	----
$CHBr_3$	23.74	40	CH_4 Br^-	21.5 68.4	0.91	----	0.96
CCl_4	38.96	140	$CHCl_3$ CH_2Cl_2 CH_4 C_2H_6 Cl^-	1.21 6.10 30.5 1.50 131	1.05	0.95	----

* Detected Prod.: Detected Products, NA: not analyzed

were not added to this system. Samples analyzed at 24 hours contained 6.99 μmol of $CHBr_3$, 2.18 μmol of CH_2Br_2 and 0.46 μmol of CH_4. The results of these blank tests are shown in Table 2. These tests indicate that without a Pt catalyst, Mg cannot effectively reduce halogenated hydrocarbons to low molecular weight hydrocarbons. However, with the presence of a platinum catalyst in the system, H_2 molecules would be able to transform to active hydrogen atoms or the metal-bonded hydride form. The hydrogen atoms could then reduce halogenated hydrocarbons to low molecular weight hydrocarbons and halogen ions.

Table 2. Stability tests of TCE and $CHBr_3$ (no catalyst added to the system, 20 mℓ H_2O)

Substrate (μmol)		System used for the study	Reaction Time hours	Detected Compound (μmol)		Ratio= C-Detected / C-Substrate
TCE	45.6	Mg (1g)/ H_2O (20 mℓ)	2	TCE CH_4 C_2H_4 C_2H_6	37.5 3.45 2.94 3.14	0.99
$CHBr_3$	4.53	H_2 (1 atm)/ H_2O (20 mℓ)	24	CH_2Br_2 CH_4	2.85 2.09	1.09
$CHBr_3$	9.08	H_2 (1 atm)/ H_2O (20 mℓ)	24	$CHBr_3$ CH_2Br_2 CH_4	6.99 2.18 0.46	1.06

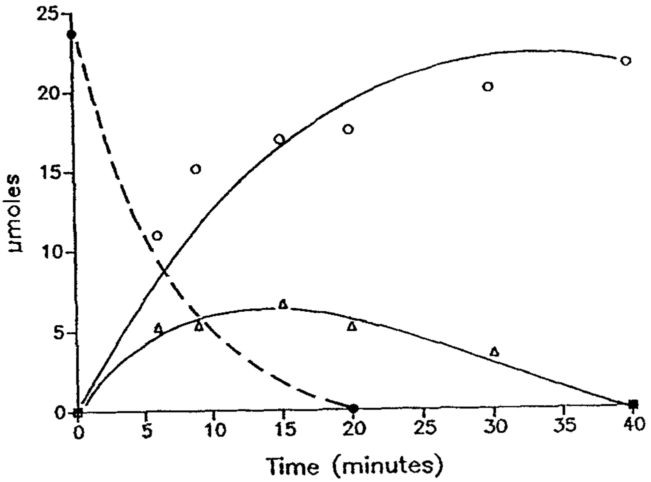

Figure 3. Reduction of bromoform (300ppm, 23.7µmol) to methane in Mg (1g, 0.04mol)/Pt-colloid (20ml, 0.0005M): (●) bromoform, (○) methane, (△) ethane.

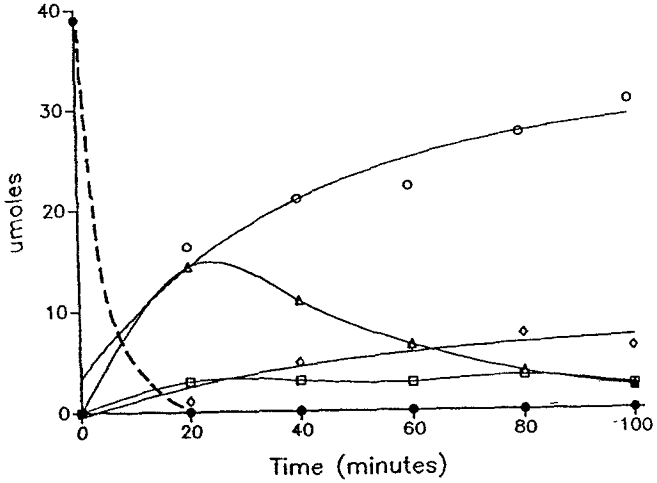

Figure 4. Reduction of corbon tetrachloride (300ppm, 39.0µmol) in Mg (1g, 0.04mol)/Pt-colloid (20ml, 0.0005M): (●) carbon tetrachloride, (○) methane, (◇) ethane, (△) chloroform, (□)dichloromethane.

At the end of each experiment, the resulting solution was analyzed for any anion concentration. The concentrations of Br^- or Cl^- detected for each test is shown in Table 1. A mass balance based on the detected compounds for C, Br, and Cl atoms was established and included in Table 1. The ratios of detected products to initial substrates for each experiment ranged between 0.91-1.05 for C, 0.95-0.97 for Cl, and 0.96 for Br.

This study shows that the reduction of trichloroethylene, bromoform, and carbon tetrachloride can be carried out at room temperature with a platinum catalyst present in the Mg-hydrolysis process. These halogenated compounds can be reduced to low molecular weight hydrocarbons such as CH_4 or C_2H_6, etc. The process can be effective to degrade trichloroethylene or other halogenated organic chemicals in the contaminated water.

Acknowledgments. We thank Ms. D. Farb for typing the manuscript and Mr. T.E. Kadlac for analyzing the anion concentrations. This manuscript is Harbor Branch Contribution No. 754.

REFERENCES

Archer MD, Spiro M (1970) Heterogeneous catalysis in solution. VIII. Catalysis of the aquation of the bromopentamine cobolt (III) ion by Metallic Platinum. J Chem Soc 1:78-81

Arguello MD (1979) THM in water. J Am Water Work Assoc 71:504

Burmaster DE (1982) Groundwater Contamination. Environment 24(2):6-13

Brugger PA, Cuendet P, Gratzel M (1981) Ultrafine and specific catalysts affording efficient hydrogen evolution from water under visible light illuminator. J Am Chem Soc 103:2923-2927

Carey JH, Lawrence J, Tosine HM (1976) Photodechlorination of PCBs in the presence of titanium dioxide in aqueous suspensions. Bull Environ Contam Toxic 16:697-701

Chuang SC, Bozzelli JW (1986) Conversion of chloroform to HCl by reaction with hydrogenated water vapor. Environ Sci Technol 20:568-574

Dowty BJ, Carlisle D, Laseter JL, Stern J (1975) Halogenated hydrocarbons in New Orleans drinking water and blood plasma. Science 187:75-77

Hohne K, Jager P (1981) Hydrogen generation of means of catalyzed Mg-Al hydrolysis. Siemens Forsch.-u. Entwickl.-Ber. Bd. 10(5):323-326.

Hoke SH, Baxter LJ Burns M (1984) Catalytic degradation of trihalomethanes. U.S. Army Medical Research and Development Command, Fort Detrick: Frederick, MD, AD-A151516

Jolly WL (1971) Preparative inorganic reactions, Interscience-Wiley, New York

Maiden R, Wilner I (1986) Photoreduction of CO_2 to CH_4 in aqueous solutions using visible light. J Am Chem Soc 108:8100-8101

Matthews RW (1986) Photo-oxidation of organic material in aqueous suspensions of titanium dioxide. Wat Res 20:569-578.

Marx JL (1974) "Drinking Water: Another source of carcinogens?". Science 186:809-811.

Ollis DF, Hsio CY, Budiman L, Lee CL (1984) Heterogeneous photo-assisted catalysis: Conversion of perchloroethylene, dichloroethane, chloromatic acids & chlorobenzenes. J Catal 88:89-96

Parsons F, Wood PR, DeMarco J (1984) Transformation of tetrachloroethylene in micro-organisms and groundwater. J Am Water Work Assoc 76:56-50

Pruden AL, Ollis DF (1983) Degradation of chloroform by photo-assisted heterogeneous catalysis in dilute aqueous suspensions of titanium dioxide. Environ Sci Tech 17:628-631

Rook JJ (1976) Haloforms in drinking water. J Am Water Work Assoc 615:68-168

Rylander PN (1968) Catalytic Hydrogenation Over Platinum Metals, Academic Press, New York

Simmon VF, Tardiff RG (1978) Water Chlorination. Ann Arbor Sci Pub, Ann Arbor, Michigan

Stevens AA, Slocum CJ, Robock GG (1976) Chlorination of organics in drinking water. J Am Water Work Assoc 615:68-71

Tan CK, Wang TC (1987) Reduction of trihalomethanes in a water photolysis system. Environ Sci Technol 21:508-511

Tan CK, Newberry V, Webb TR, McAuliffe CA (1987) Water photolysis, Part 2. J Chem Soc Dalton Trans:1299-1303

Wang TC, Tan CK (1987) Photodegradation of trichloroethylene in microheterogeneous aqueous systems. Environ Int 13:359-362

Wang TC, Lenahan R, Kanik M (1985) Impact of trichloroethylene contaminated groundwater discharged to the Main Canal and Indian River Lagoon. Bull Environ Contam Toxicol 34:578-586

Wang TC, Tan CK (1988) Reduction of chlorinated hydrocarbons with natural sunlight in a platinum-catalyzed water photolysis system. Environ Sci Technol 22:916-919

Received May 8, 1989; accepted January 10, 1990.