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Degradation of Bromoform and Chlorodibromomethane in a Catalyzed H_2-Water System

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Oxidation of halogenated organic compounds to CO_2 and HCl in aqueous suspension of a photocatalyst, TiO_2, was reported by Carey et al. (1976), Matthews (1986), Ollis et al. (1984, 1985). Photoreduction of CO_2 and trihalomethane compounds to CH_4 was also reported by Maiden and Willner (1986), Wang and Tan (1987), respectively. Recently, catalytic and thermal reductions of trihalomethanes by hydrogen was conducted by Hoke et al. (1984) and Chuang et al. (1986). This study is to obtain the quantitative information of CH_4 generated from trihalomethanes in a hydrogen enriched enclosure. Langmuir adsorption model was applied to describe the reaction mechanism.

MATERIALS AND METHODS

The system examined was composed of 20 ml of colloidal platinum ($\approx 5\times10^{-4}$M) which was prepared by the citrate reduction method (Tan et al. 1987). The reactor was a 60 ml Savillex teflon bottle which included an on-off valve and a teflon-faced septum. Hydrogen was bubbled through the colloid at the rate of 3.5 ml/minute for an hour. A required amount (0.4, 0.8, 1.2, or 1.6 µl) of the substrate ($CHBr_3$ or $CHBr_2Cl$) was then spiked into the colloid. The aqueous mixture was then stirred vigorously at room temperature. Gas chromatographic analyses were conducted on samples taken from both headspace and liquid phases of the system at different time intervals (Wang and Tan 1988). The final solution was analyzed by a Dionex QIC ion chromatograph for the resulted anions. All of the reactions were repeated twice for consistency and reproducibility of the reduction process. The precision of these experiments were within 5%.

RESULTS AND DISCUSSIONS

Blank tests with $CHBr_3$ (9.08 µmol) and $CHClBr_2$ (18.8 µmol) in the H_2-water system without catalysts were performed. The samples analyzed after 24 hours of agitation showed that most of the starting substrates were not completely reduced to CH_4.

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Approximately 5% and 18% of both substrates were reduced to CH_4, respectively. The results indicate that hydrogen alone is not an effective reducing reagent. However, with colloidal platinum catalyst added into the reactor, $CHBr_3$ and $CHBr_2Cl$ were completely reduced to CH_4. Table 1 summarizes the amount of CH_4 obtained with various amounts of initial substrates. The initial concentrations of the reactant in this study ranged between 0.23-0.91 µmol/ml (4.53-18.1 µmol) for $CHBr_3$ and 0.24-0.94 µmol/ml (4.71-18.8 µmol) for $CHBr_2Cl$. The results of CH_4 formation at different time intervals were presented in Figures 1 and 2 for $CHBr_3$ and $CHBr_2Cl$, respectively. Both figures show that the initial CH_4 production rates depended on the type of reactants and their initial concentrations. A relationship between initial CH_4 production rates and reactant's concentrations is shown in Figure 3.

Table 1. Mass balance of the substrates during degradation in the system of H_2 (1 atm.)/Pt-colloid (20ml.).

Substrate (µmol)		Detected Prod. (µmol)		Ratio= Detected Prod.* / Substrate (C	Cl	Br)
$CHBr_3$	4.53	CH_4	4.62	1.02	----	0.96
		C_2H_6	0.01			
		Br^-	13.1			
$CHBr_3$	9.08	CH_4	9.16	1.01	----	0.92
		C_2H_6	0.02			
		Br^-	25.1			
$CHBr_3$	13.6	CH_4	12.8	1.02	----	0.98
		C_2H_6	0.51			
		Br^-	39.8			
$CHBr_3$	18.1	CH_4	17.5	1.04	----	0.97
		C_2H_6	0.68			
		Br^-	53.8			
$CHClBr_2$	4.71	CH_4	4.83	1.05	0.92	0.93
		C_2H_6	0.06			
		Br^-	8.71			
		Cl^-	4.37			
$CHClBr_2$	9.41	CH_4	7.06	0.95	0.96	1.00
		C_2H_6	0.92			
		Br^-	18.8			
		Cl^-	9.06			
$CHClBr_2$	14.1	CH_4	11.2	0.91	0.89	0.85
		C_2H_6	0.82			
		Br^-	24.0			
		Cl^-	12.6			
$CHClBr_2$	18.8	CH_4	14.9	0.91	0.85	0.94
		C_2H_6	1.12			
		Br^-	35.5			
		Cl^-	16.0			

* Detected Prod.: Detected Products.

In this reduction study, H_2 molecules introduced into the catalyst particle could be dissociated into metal bonded hydrogen atoms (H) (Bau 1978). These active species, surface-bound atoms, could then reduce the halogenated methanes to CH_4 (Wang and Tan 1887, 1988). The reduction of CHX_3 (X:halides) to CH_4 can be described as the formation of the adsorbed CHX_3 on the catalyst sites and follows a simple Langmuir isotherm behavior (Ollis et al. 1984):

$$CHX_3 + \theta_V \text{ (catalyst site)} \xrightleftharpoons{K_e} CHX_3 \text{ (ads., } \theta_{CHX_3}) \quad (1)$$

Thus, the coverage θ_{CHX_3} and the rate equation can be obtained by an adsorbed intermediate:

$$\theta_{CHX_3} = \frac{K_e C}{1 + K_e C}, \quad \text{C: initial } CHX_3 \text{ concentration} \quad (2)$$

$$R(\text{rate}) = k_r \bullet \theta_{CHX_3}, \quad k_r\text{: reaction constant} \quad (3)$$

$$R(\text{rate}) = k \bullet \left(\frac{K_e C}{1 + K_e C} \right) \quad (4)$$

or

$$\frac{1}{R} = \frac{1}{k_r} + \left(\frac{1}{k_r \bullet K_e} \right) \bullet \frac{1}{C} \quad (5)$$

Equation (5) indicates a linear relationship between 1/R vs. 1/C for a Langmuir adsorption model. Figure 4 shows the plots of the experimental results for $CHBr_3$ and $CHBr_2Cl$ conducted in this study. A linear characteristic was established for both molecules. The values of k_r and K_e for $CHBr_3$ and $CHBr_2Cl$ were obtained from this figure. These parameters are summarized in Table 2. The ratios of k_r between $CHBr_3$ and $CHBr_2Cl$ was approximately 2:1. This indicates that $CHBr_3$ is more reactive than $CHBr_2Cl$. This reactivity could be due to the relative stronger C-Cl bond than a C-Br bond. The bond energy and bond length for C-Cl and C-Br bonds are 327 kj/mol, 1.76Å; 285 kj/mol, 1.91Å, respectively. Similarly, K_e value of $CHBr_2Cl$ was found to be 1.6 times more than that of $CHBr_3$. This indicates a relative stronger surface binding characteristic of $CHBr_2Cl$ than $CHBr_3$.

At the end of the experiment, mass balance for each reaction was calculated and shown in Table 1. CH_4 was a major product and ethane was a minor product. The yield of ethane was probably due to the dimerization of methyl radicals. During the course of reaction, ethylene was detected as an intermediate species. It was not detected at the end of experiment. The ratios of C-atom base on the detected products and reactants were 0.91-1.05, while the ratios of Br and Cl atoms were 0.92-1.0 and 0.85-0.96, respectively.

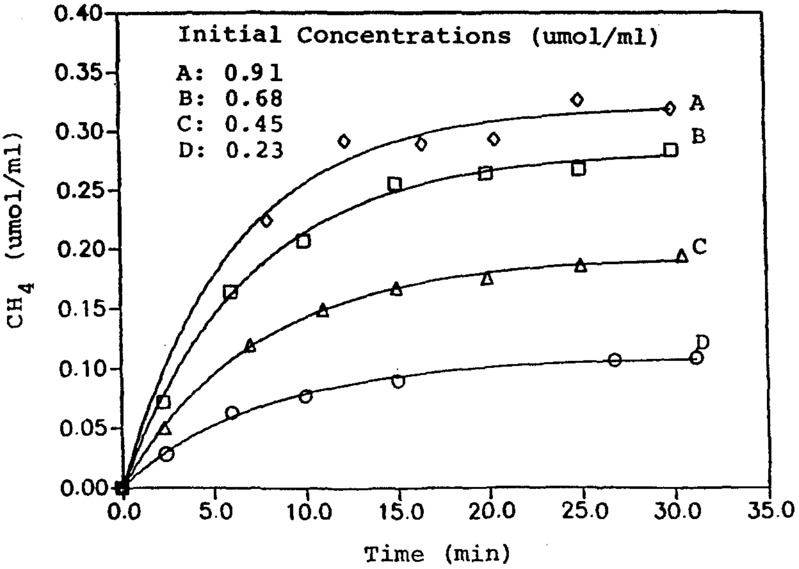

Figure 1. Reduction of bromoform to methane.

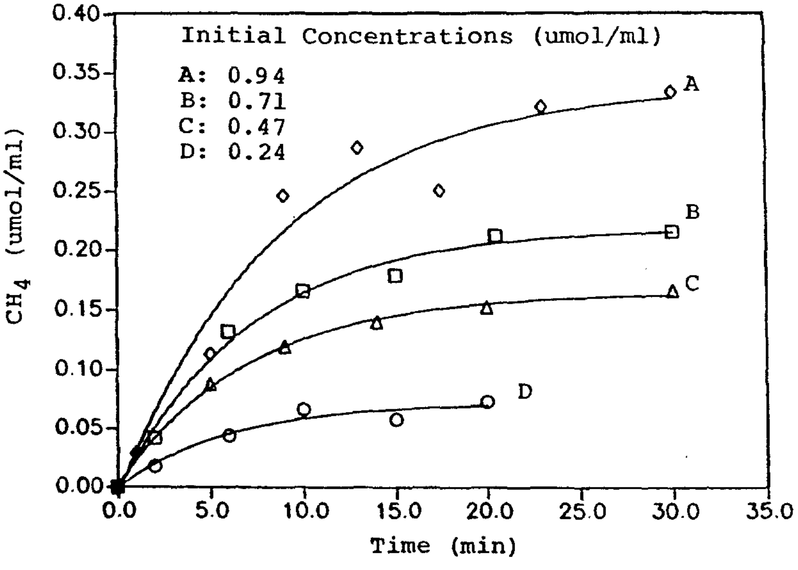

Figure 2. Reduction of chlorodibromomethane to methane.

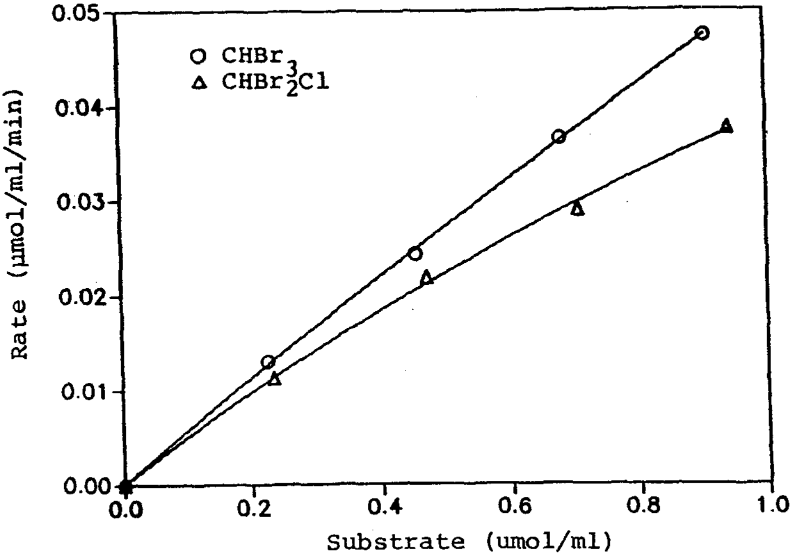

Figure 3. Initial reaction rate vs. substrate concentration.

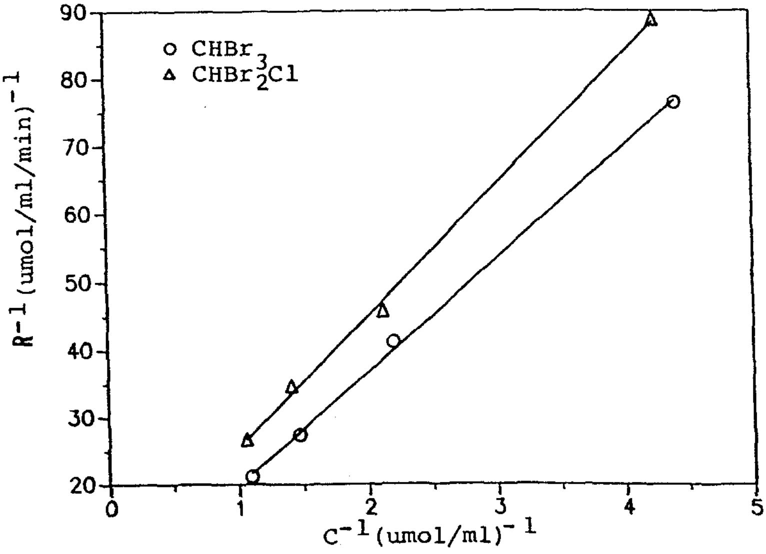

Figure 4. Reciprocal initial rates vs. reciprocal initial concentrations of bromoform and chlorodibromomethane.

Table 2. Parameter values for trihalogenated methane conversions.

Substrate	k_r $\frac{\mu mol}{ml\ min}$	K_e $\frac{ml}{\mu mol}$	$k_r K_e$ $\frac{1}{min}$
$CHBr_3$	0.31	0.19	0.059
$CHBr_2Cl$	0.17	0.31	0.053

This study shows that colloidal platinum is an effective catalyst in reducing CHX_3 to CH_4 in a H_2 enriched enclosure at room temperature. The Langmuir adsorption model can be applied in this reduction process.

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