

Transformation of Halogenated Aliphatic Compounds by the Reductive Dehalogenation Process

Dong-Suk Han^{*}, Seh-Hwan Park, Sung-Kuk Kim^{*}, Dae-il Hong^{**},
and Sang-Won Park

Faculty of Environmental Science and Engineering,
Keimyung University

^{**} Department of Chemistry, Keimyung University

1. Introduction

Halogenated aliphatic compounds (HACs) are used in a broad range of industrial, agriculture, and domestic applications. They are found in groundwaters, as a result of past practices in landfilling and in toxic chemical disposal. They are also major compounds of landfill leachates and hazardous disposal. The production and use of HACs and their potential hazard to human health have prompted investigations concerning their fate in the aquatic environments, and in the treatment facilities. Air-stripping and sorption onto activated carbon have been used for above groundwater treatment of contaminated water. These methods merely transfer the contaminants from one environmental compartment to another, without destroying them. Studies of carbon tetrachloride reduction by iron sulfides and other reducing agents suggest possible reaction pathways for the reduction of halogenated aliphatic compounds (HACs). It has been hypothesized that iron sulfide and other reducing agents are electron transfer mediators which form highly reactive and reduced intermediates, being able to reduce the oxidized contaminant (1,2). Once the electron transfer mediator is oxidized by the contaminant, it can be assumed to be reduced back to the initial state by a "bulk" electron donor, which may be present in excess of the mediator. For example, some hydroquinones have been found to be efficient electron transfer mediators with either Fe^{2+} or HS^- as the bulk

electron donor(3). NOM(Natural Organic Matter) has recently been shown to increase the rate of reduction of HACs in the presence of HS , and it was proposed that the hydroquinone/quinone type couple was the electron transfer mediator(4). This is consistent with the known properties of model hydroquinones and the redox properties of NOM.

This hydroquinone/quinone-type couple is believed to dominate the redox properties of humic acid(5). The objectives of this work are to test the hypothesis that carbon tetrachloride could be reduced by reducing agents and to determine the reduction of CCl₄ with HS as the bulk electron donor if iron sulfide and pyrite can mediate.

2. Methodology

Experimental Approach. The experiments described here evaluate the influence of environmental variables such as pH, ionic composition, and the presence of organic molecules similar to these found in natural waters on the rates and products of reductive dehalogenation of CCl₄ by iron sulfide and pyrite. Carbon tetrachloride was chosen for study since it represents a major class of drinking water pollutant, and because it was expected to undergo rapid dechlorination due to its high standard reduction potential.

Equipment. The atmosphere in the glove box was 90%N₂/10%H₂. The gas chromatographic used was a Younglin, Model M600D, equipped with PDD detector. The column was type DB-1, 50m×0.2mm with a 0.11 μm film thickness from Hewlett Packard. The column, injector, and detector temperature were 50°C, 150°C, and 200°C, respectively. The make-gas was 95%He/5%CH₄ and a pressure of approximately 2.5kg/cm². The flow rate of the carrier gas, He, was 8ml/min

3. Results and Discussion

Effect of Solids Concentration. Figure 1.2 illustrate the relationship in terms of two parameters : g of FeS/L (or g of FeS₂/L) of reaction volume, which is operationally the most convenient, and m² of surface area/L, which should incorporate most of the effects of grain size and shape.

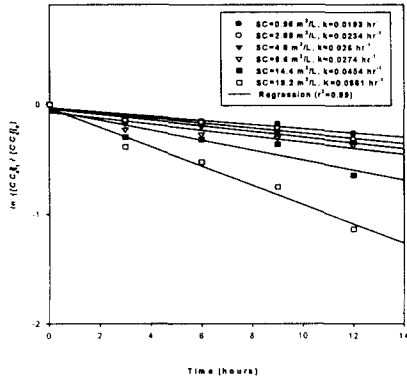


Figure 1. Effect of FeS, surface concentration(SC) on pseudo-first-order rate constants for carbon tetrachloride dehalogenation. The experimental conditions were as follows: Tris buffer 0.1M, Fe²⁺ 1M, pH 7.8

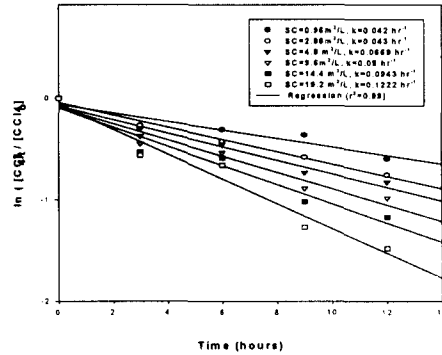


Figure 2. Effect of FeS surface concentration on pseudo-first-order rate constants for carbon tetrachloride dehalogenation. The experimental conditions were as follows: Tris buffer 0.1M, ionic strength 0.1M, pH 7.8

A relationship of k vs SC (Surface Concentration) shows an increasing rate constant with increasing surface concentration

4. Conclusions

Carbon tetrachloride undergoes rapid reductive dehalogenation in the presence of iron sulfide and pyrite. In our closed system, the overall chemistry of the system is dominated by anaerobic corrosion; i.e., oxidative dissolution of Fe^{2+} to Fe^{3+} . The chloromethanes apparently substitute for water in this reaction, providing an alternative oxidant for iron sulfide and pyrite, and a mechanism has been proposed involving direct electron transfer to the adsorbed halocarbon. Dehalogenation of carbon tetrachloride was faster at more acidic pH, but this effect was modest. The most important predictor of dechlorination rate was found to be FeS (or FeS_2) surface area concentration.

5. References

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