Annual Report II

Overcoming Barriers to the Remediation of Carbon Tetrachloride through Manipulation of Competing Reaction Mechanisms

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1. Research Objective

Most approaches that have been proposed for the remediation of groundwater contaminated with carbon tetrachloride (CCl_4) produce chloroform ($CHCl_3$) as the major product and methylene chloride (CH_2Cl_2) as a minor product. Both of these products are nearly as persistent and problematic as the parent compound, but competing reaction pathways produce the more desirable products carbon monoxide (CO) and/or formate ($HCOO^-$). Results scattered throughout the chemical and environmental engineering literature show that the branching between these reaction pathways is highly variable, but the controlling factors have not been identified. If we understood the fundamental chemistry that controls the branching among these, and related, product-formation pathways, we could improve the applicability of a host of remediation technologies (both chemical and biological) to the large plumes of CCl_4 that contaminate DOE sites across the country. This project will provide the first complete characterization of the mechanisms and kinetics of competing degradation reactions of CCl_4 through laboratory experiments in simple model systems closely coordinated with theoretical modeling studies. The results provide strategies for maximizing the yield of desirable products from CCl_4 degradation, and the most promising of these will be tested in column model systems using real site waters and matrix materials.

2. Research Progress and Implications

As of June 2004, we are working on Tasks 1-3, beginning to shift to Task 4, and preparing to start Tasks 5-6 (See Table of Tasks on next page.)

Work on Task 1 is occurring mainly at the Oregon Health & Science University (OSHU), by Dr. Paul Tratnyek and an OHSU Ph.D. student, Vaishnavi Sarathy. Work on Task 2 is underway mainly at PNNL by Dr. James Amonette and an EMSL laboratory technician. Work on Task 3 is underway at EMSL by Dr. Eric Bylaska.

Under Task 1, we have developed and validated the necessary experimental protocols and analytical methods for routinely determining all of the reaction products of CCl_4 reduction over an experimental time course. We have applied these protocols on a numerous batch experiments to test the effects of various experimental conditions (pH, buffer type, buffer composition, iron type, initial concentration of CCl_4, etc.) We fit these data with an improved kinetic model—which we developed for the current purpose—that allows us to rigorously quantify the yield of $CHCl_3$. The most notable result is that one particular form of nano-sized iron metal apparently produces much less $CHCl_3$ than other types of Fe^0. Currently, we are focusing on the fundamental (Task 2) and practical (Tasks 4) implications of this result.

Table 1. Summary of major objectives and tasks.

Objective I. Characterize mechanisms & kinetics.
Task 1. **Batch Experiments:** Quantify the kinetics of all competing product-formation pathways, over a range of conditions relevant to groundwater remediation, using well-mixed batch reactors and analysis primarily by chromatography.
Task 2. **Characterization of Reactive Surfaces and Intermediate Species:** Determine how the composition and structure of reactive surfaces, and the formation and fate of key reaction intermediates, control the distribution of reaction products formed, using model systems similar to Task 1 but analyzed with complementary spectroscopic and molecular-trapping methods.
Task 3. **Theoretical Modeling:** Calculate the electronic structure and properties of all relevant contaminant species and intermediates using ab initio quantum mechanical models, and use these results to characterize the controls on branching among reaction products.
Objective II. Derive control strategies.
Task 4. **Batch Experiments:** Test the experimental variables that offer the most control of product distributions (as determined from Tasks 1-3), using procedures similar to those in Task 1.
Task 5. **Mechanistic Modeling:** Develop a comprehensive mechanistic framework for explaining the results of Tasks 1-4 and predicting product distributions as a function of key reaction parameters.
Objective III. Test control strategies.
Task 6. **Column Experiments:** Test the most promising strategies for optimizing the distribution of products from CCl_4 remediation (as determined from Tasks 4-5) in columns that provide realistic physical models for the overall process of reactive-transport in homogeneous porous media.
Task 7. **Reactive-Transport Modeling:** Develop a reactive-transport model that explains the results of Task 6 given the mechanistic model developed in Task 5, and that can be used to predict the performance of product-distribution control strategies in the field.

Progress on Task 2 has been limited. We have obtained the spin-trapping agents and assembled the stop-flow apparatus for EPR experiments to identify reaction intermediates. Batch experiments with Fe(II)-bearing smectite, in the presence of other catalysts/reductants such as Cu(m), elemental S, and free dithionite have shown little differentiation among product streams, but significant differences in the extent of reaction. For, example, with free dithionite in both the presence and absence of Cu(m), complete dechlorination was observed, wherease little reaction was observed with the Fe(II)-bearing smectite alone. Experiments with smectite in the presence of elemental S showed no effect of the S, suggesting that the strong effect of dithionite we observed was either a result of direct reaction with the dithionite anion/sulfoxyl radical or with nanoparticulate sulfides precipitated during the dithionite treatment of the smectite.

Progress on Task 3 includes ab initio calculation of the energetic and activation barriers of some of the steps involved in the mechanisms of reduction of chlorinated methanes and ethenes. Most recently, ab initio electronic structure methods were used to calculate the thermochemical properties of 37 different polychloroethylene-yl radicals, anions, and radical anions. On the basis of these thermochemical estimates, the overall reaction energetics (in the gas phase and aqueous phase) for several mechanisms of the first electron reduction of the polychlorinated ethylenes were predicted. These results demonstrate that ab initio electronic structure methods can be used to calculate the reduction potentials of organic compounds in order to help identify the potentially important environmental degradation reactions.

3. Planned Activities

For the remainder of Project Year 2, work at OHSU will focus on completing Task 1 and transitioning to Task 4, with emphasis on the particular type of iron that we have found with the most favorable (smallest) yield of $CHCl_3$. We have also begun a dialog with the manufacturer of this material regarding its potential availability for a field/pilot scale demonstration.

The PNNL effort on Task 2 will continue to focus on 1) identifying and quantifying the key intermediate species in the CCl_4 degradation reaction by trapping them with agents that can be detected by either UV or EPR spectroscopy, and 2) identifying the key agent(s) responsible for the complete dechlorination observed with dithionite/smectite suspensions.

The PNNL work on Task 3, we will perform a theoretical investigation of the thermodynamic properties of all relevant species and intermediates for the reduction and hydrolysis of CCl_4 using ab initio models and energetic data available from experiments.

In Project Year 3, Tratnyek (OHSU) will focus on Task 4, while Amonette (PNNL) completes Task 2, Bylaska (PNNL) completes Task 5, and Szecsody (PNNL) implements Tasks 6-7.

4. Information Access (Publications and Presentations)

4.1. Journal Articles

Miehr, R., Tratnyek, P. G., Bandstra, J. Z., Scherer, M. M., Alowitz, M., and Bylaska, E. J. (2004) "The diversity of Contaminant Reduction Reactions by Zero-valent Iron: Role of the Reductate." *Environ. Sci. Technol.*, 38(1): 139-147.

Bylaska, E. J., Dixon, D. A., Apra, E., Felmy, A. R., and Tratnyek, P. G. (2004) "The Energetics of the Hydrolysis, Dehydrohalogenation, and Reductive Dehalogenation for 4,4'-DDT and 1,1,1-Trichloroethane." *J. Phys. Chem., A.* Online version released 10 June 2004. DOI: 10.1021/jp0312316.

Nurmi, J. T.; Tratnyek, P. G.; Sarathy, V.; Baer, D. R.; Amonette, J. E.; Pecher, K.; Wang, C.; Linehan, J. C.; Matson, D. W.; Penn, R. L.; Driessen, M. D. Characterization and properties of metallic iron and iron-oxide nanoparticles: spectroscopy, electrochemistry, and kinetics. *Environ. Sci. Technol.*, submitted.

Bylaska, Eric J. Michel Dupuis, and Paul G. Tratnyek One-electron reduction of polychlorinated ethylenes as determined: from ab initio electronic structure theory. J. Phys. Chem. in prep.

4.2. Abstracts and Presentations

Bylaska, E. J., Dixon, D. A., Felmy, A. R., and Tratnyek P. G. 2003. One-electron reduction of substituted chlorinated methanes: Application of ab initio electronic structure theory. 58th ACS Northwest Regional Meeting, June 12-14, 2003, Bozeman, Montana.

Tratnyek, P. G., Amonette, J. E., and Bylaska, E. J. 2004. Overcoming barriers to the remediation of carbon tetrachloride through manipulation of competing reaction mechanisms. EMSP Vadose Zone Principal Investigators Workshop, Pacific Northwest National Laboratory, Richland, WA, 6-8 May 2003.

Tratnyek, P. G.; Amonette, J. E.; Bylaska, E. J. 2004. Overcoming barriers to the remediation of carbon tetrachloride through manipulation of competing reaction mechanisms; *227th National*

Meeting, 28 March - 1 April 2004, Anaheim, CA, American Chemical Society, Vol. 44, No. 1, pp. 456-460.

Rosso, K. M. and Bylaska, E. J. 2004. Theoretical approaches to electron-transfer chemistry at mineral surfaces: Helping optimize and interpret experimental efforts, Bouyoucos Conference on Electron Transfer and Biogeochemistry at the Clay-Water Interface, San Antonio, January 14-17, 2004.

Bylaska, E. J., et al. 2004. The energetics of the hydrogenolysis, dehydrohalogenation, and hydrolysis of 4,4'-dichloro-diphenyl-trichloroethane from ab initio electronic structure theory, 228th ACS National Meeting, Philadelphia, PA, August 22-26, 2004.

Table 2. Updated time line for the major objectives and general tasks.

Objectives/Tasks	Year I				Year II				Year III			
	1/4	2/4	3/4	4/4	1/4	2/4	3/4	4/4	1/4	2/4	3/4	4/4
I. Characterize Mechanism & Kinetics												
1. Batch experiments	Student & Tratnyek				Student & Tratnyek							
2. Reactive Surfaces & Intermediates	Staff & Amonette											
3. Theoretical calculations	Bylaska				Bylaska & Others							
II. Derive Control Strategies												
4. Batch experiments					Student & Tratnyek				Student & Tratnyek			
5. Mechanistic modeling					Bylaska & Others							
III. Test Control Strategies												
6. Column experiments									Technician & Szecsody			
7. Reactive-transport modeling									Szecsody			

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