

**2006 ERSD Annual Report**  
*DOE-BER Environmental Remediation Sciences Project # 44076*

**The Reaction Specificity of Nanoparticles in Solution**

**PI: Donald R. Baer**

*Pacific Northwest National Laboratory, Richland, WA*

**Research Objective**

Iron-based metallic and oxide nanoparticles have been shown to have enhanced reactivity towards a variety of chemical species, including chlorinated hydrocarbons and reducible oxyanions, which frequently contaminate ground water at DOE and other government and industrial sites. Possibly of greater importance is the ability of these nanoparticles to select specific reaction pathways, potentially facilitating the formation of the most environmentally acceptable reaction products.

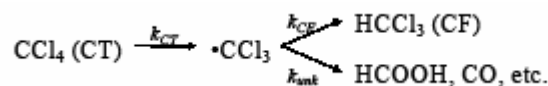
Since iron-based nanoparticles are oxidized by the surrounding water and the contaminant species, the ability of the particle surface and protective coatings to mediate or control the relative reaction rates has a major impact on the reactions that take place and the ultimate productive lifetime of the particles. Use of nanoparticles for environmental remediation requires understanding the impact of particle evolution or diagenesis on the reaction properties as a function of time.

The objective of this project is to develop a fundamental understanding of the mechanism(s) responsible for contaminant reduction and the overall reactivity, reaction selectivity and life cycle of iron-based metallic, bimetallic, and oxide nanoparticles with the intent of optimizing particle size, formulation and structure for reduction of environmental contaminants. Although the effects of coatings designed to enhance particle mobility on the overall particle reactivity (or non-reactivity) are not explicitly addressed by the tasks of this project, our work regarding the impact of particle coatings on reactivity is relevant to this important aspect of the technology.

**Research Progress and Implications**

This report summarizes results obtained during year one of a three year renewal of a multifaceted BER- and BES-funded research project that combines fundamental theoretical and experimental chemical studies with tasks that address issues important for scaling the laboratory results to field conditions. In this progress report we focus on two aspects of the work: 1) the aging (or diagenesis) of iron nanoparticles in a water solution and the impact of this aging on reduction of chlorinated hydrocarbons; and 2) theoretical determination of thermodynamic and kinetic properties of reactions of chlorinated hydrocarbons.

*Reaction Properties and Particle Aging.* We continue to focus on carbon tetrachloride (CT) as a probe contaminant because it is particularly relevant to DOE sites and is a good model for breakdown of chlorinated hydrocarbon contaminants in general. A significant issue in the breakdown of CT by zerovalent iron (ZVI) is controlling the branching ratio between the formation of toxic byproducts such as chloroform (CF) or the production of much more benign products such as formic acid (HCOOH) as shown in Scheme 1.



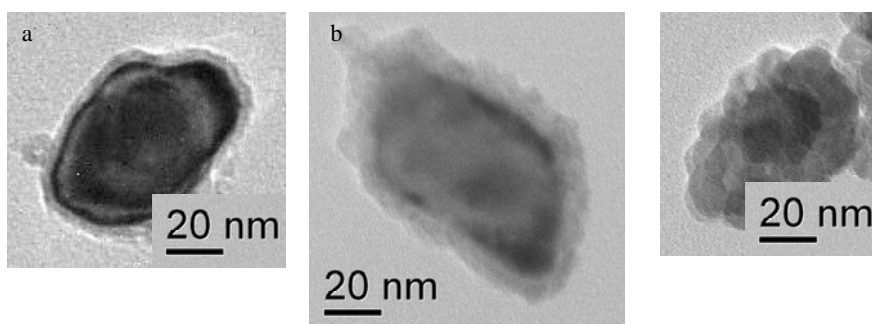
Scheme 1

One major result in earlier work was the demonstration that the nature of the nanoparticle coating can make more than a factor of four in the production of toxic versus non-toxic products during reduction of CT [Nurmi et. al. *Env. Sci & Tech.* 39 (2005) 1221-1230]. In particular, for one type of nanoparticle formed by hydrogen reduction of the iron oxide, the production of CF was 25% or less of that formed for micron-sized iron and many other types of nanoparticles.

One implication of this observation is that the chemical behavior of iron nanoparticles depend on the specific character of the particles. Consequently a significant portion of the research must be devoted to the synthesis and characterization of nanoparticles used in reaction studies. Because ZVI is oxidized during the reduction of contaminants, it is also important to understand how the properties of the nanoparticles may change as they age in solution. This has been the major focus of our most recent work.

Measurements of particles at different stages of reaction with pure or contaminant-bearing water show that the processes that control contaminant degradation evolve with time. Particle and surface characterization techniques include high-resolution transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), and x-ray diffraction (XRD). The chemical properties of the particles are measured by electrochemical, batch reactivity and electron paramagnetic resonance spin-trapping measurements.

Measurements by TEM, XPS, and XRD show that the ZVI nanoparticles with the low CF production are initially covered with an adherent iron oxide coating as shown in Fig 1a. As the

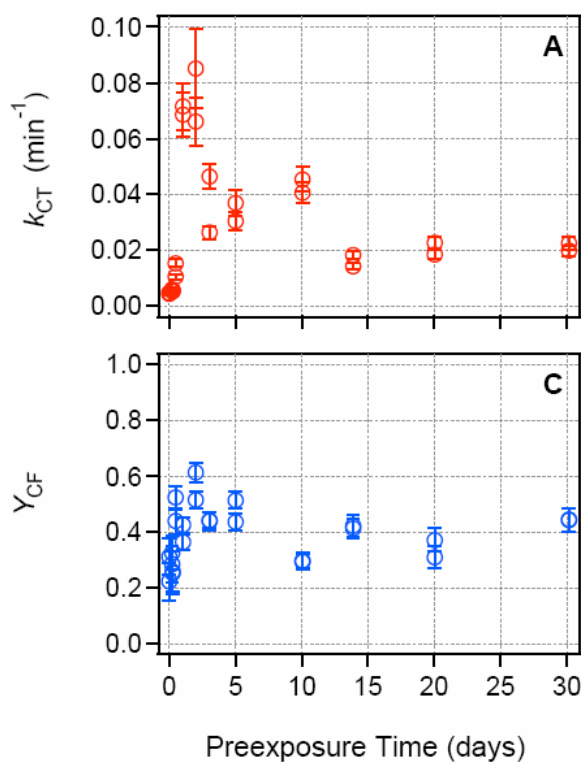


**Fig. 1.** TEM images of nanoparticles in as received condition (a) and after exposure to water for 1 day (b) and 5 days (c). The initial particles have an intact crystalline oxide shell that is broken down upon exposure to solution.

oxide is exposed to water solution for longer periods of time the oxide becomes less coherent and the metal content in the nanoparticles decreases as more material is oxidized (Figs. 1b and 1c).

Batch reaction studies were carried out on ZVI nanoparticles pre-exposed to water for

periods ranging up to 30 days. The data shown in Fig 2 indicate that the reaction rate was initially low and increased upon exposure to the water as the coating was damaged. With additional time the reaction rate decreased, but the rate remained significant for the duration of the experiments. The branching ratio showed a low yield of CF (relative to that observed for other types of iron) throughout the experiment, but there appeared to be an increase in CF yield during the time the initial surface scale was breaking down. These measurements show that the type of iron nanoparticles examined are highly reactive and produce relatively low amounts of



**Fig. 2.** Plots of reaction rate (A) and branching pathway (C) for iron nanoparticles pre-exposed to water. Although CF production ( $Y_{CF}$ ) increased slightly between 1 and 5 days, it remained significantly lower than values observed for micron sized iron particles and for several other types of nanoparticles.

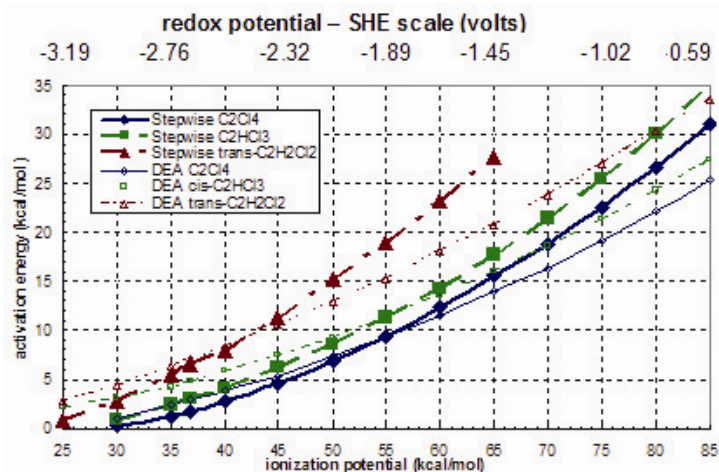
environment. We have developed strategies based on ab initio electronic structure methods for estimating thermochemical and kinetic properties of reactions with chlorinated hydrocarbons. Emphasis is placed on strategies that are computationally fast and can be used for large organochlorine compounds such as 4,4'-DDT.

As an example, we have applied this approach to the dechlorination of chlorinated ethylenes. Reaction barriers were calculated using ab initio electronic structure methods for the reductive dechlorination of the polychlorinated ethylenes:  $C_2Cl_4$ ,  $C_2HCl_3$ , trans-1,2- $C_2H_2Cl_2$ , cis-1,2- $C_2H_2Cl_2$ , 1,1- $C_2H_2Cl_2$  and  $C_2HCl_3$ .

Both concerted and stepwise cleavages of R-Cl bonds were considered. As shown in Fig. 3, stepwise cleavages yielded lower activation barriers than concerted cleavages for the reduction of  $C_2Cl_4$ ,  $C_2HCl_3$ , and trans-1,2- $C_2H_2Cl_2$  via strong reducing agents. However, for typical ranges of reducing strength, concerted cleavages were found to be favored. Both gas-phase and aqueous-phase calculations predicted  $C_2Cl_4$  to have the lowest reaction barrier. Additionally, the reduction of  $C_2HCl_3$  was predicted to have a significant amount of selectivity of cis-1,2- $C_2HCl_2^{\bullet}$  over the corresponding reactions leading to the, and 1,1- $C_2HCl_2^{\bullet}$  radicals. These results illustrate how ab initio electronic structure methods, by providing experimentally inaccessible thermodynamic properties and activation energies, are able to sort out possible reaction mechanisms for reactions that have broad relevance in environmental chemistry.

CF during a life cycle of up to one month. Although the reaction rate slows after the first five days, a reasonably high reaction rate and good branching ratio persists for at least thirty days.

*Theoretical determination of thermodynamic and kinetic parameters for dechlorination reactions.* As shown for CT (Scheme I), many different degradation reactions of chlorinated hydrocarbons are possible in natural groundwaters. In order to identify which degradation reactions are important, a large number of possible reaction pathways must be sorted out. Recent advances in ab initio electronic structure methods have the potential to help identify relevant environmental degradation reactions by characterizing the thermodynamic properties of all relevant contaminant species and intermediates for which experimental data are usually not available, and to provide activation energies for relevant pathways. Major challenges in these calculations include: determining the level of accuracy of calculation needed for reliable results, and developing approaches that accurately model the impacts of the solution



**Figure 3:** Activation free energies of the stepwise  $\pi^*$  reactions in the aqueous-phase versus the ionization potential reductant. The conversion of the ionization potential to standard hydrogen electrode redox potential is shown on the top x-axis. For comparisons, results are incorporated for the concerted dissociative electron attachment (DEA) reactions involving  $\text{C}_2\text{Cl}_4$ , cis  $-\text{C}_2\text{HCl}_3$ , and 1,2-trans  $-\text{C}_2\text{H}_2\text{Cl}_2$ .

### Planned Activities

This combined BER/BES program involves model-system experiments, theoretical calculations, nanoparticle synthesis and characterization, and nanoparticle reactivity studies involving PNNL, Oregon Health and Sciences University (Prof. Paul Tratnyek), the University of Minnesota (Prof. R. Lee Penn) and the University of Idaho (Prof. You Qiang). Current studies of the time dependence of the reaction properties of nanoparticles will be extended to longer times. We also plan to examine the impact of particle doping and surface contaminants and coatings on particle reactivity and time evolution. Theoretical efforts advance as both code developments and increased computational capability can be applied to the problem. The results described above focus on the dissociation of chlorinated hydrocarbons based on electron capture. Additional work is examining the localization and mobility of charge within the oxide shells as the source of that electron. As part of this effort a new approach to self-interaction correct density functional theory is being applied to iron oxides. The combination of fundamental chemical measurements and theoretical calculation are used to help validate and guide the approaches needed to fundamentally understand the reaction processes involved in the dechlorination process.

### Other Outreach

We have made a concerted effort to communicate the implications of our work to the practitioner community (consultants, engineers, regulators, etc.) because much of the information about this technology currently circulating is not well-founded on careful science. To this end, Paul Tratnyek has recently published a feature in *NanoToday*, a magazine that is widely distributed. The article can be obtained from <http://www.nanotoday.com> or <http://cgr.ebs.ogi.edu/iron/TratnyekJohnson06.pdf>. Baer and Tratnyek have also made numerous presentations on this work to diverse audiences (e.g., a workshop for regulators and consultants in Chicago sponsored by EPA Region 5 and a wide variety of scientific meetings). Results of this program are summarized at various places on the web, including <http://cgr.es.ogi.edu/iron/>, <http://www.ogi.edu/news/145>, <http://www.pnl.gov/cmsd/highlights/2006061306.stm>.

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