FINAL REPORT

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

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Executive Summary

The premise of this project was that if we understood the fundamental chemistry that controls the branching among product formation pathways for the degradation of CCl_4 , we could design remediation strategies that minimize the formation of CHCl_3 and thereby provide badly needed alternatives for remediation of the large plumes of CCl_4 that contaminate several DOE sites. To this end, we performed a series of coordinated batch, spectroscopic, and modeling experiments, to study the effect of a variety of factors on the yield of CHCl_3 from CCl_4 during reduction with zero-valent iron (Fe^0). The factors studied include those with direct implications for field performance (e.g., the concentration of CCl_4 relative to the amount of iron surface area) and others chosen for diagnosis of the reaction mechanism (e.g., incorporation of deuterium into CCl_4 reduction products in the presence of D_2O). The key mechanistic findings of this study are (i) that $\text{CCl}_3^\bullet$ probably is not an intermediate in the formation of CF, but CCl_3^- probably is, (ii) the high reductive capacity of the Fe^0 core favors the concerted $2e^-$ reduction, and (iii) magnetite on Fe^0 favors the benign product formation pathway.

The latter conclusion is based on the observation that one type of nano-sized Fe^0 that is coated with magnetite shell produces low yields of chloroform (0-40%), whereas others produce the higher yields of chloroform (60-100%) that are typical of most methods for reducing CCl_4 (including biodegradation). Since nano- Fe^0 can, in principle, be introduced into the deep subsurface by injection, our results would suggest that the right type of nano- Fe^0 introduced in the right way might be highly effective at dechlorinating CCl_4 with minimal formation of CHCl_3 or other undesirable by-products. This conclusion may offer a breakthrough in the search for remediation technologies that are suitable for the deep CCl_4 -contamination at DOE sites such as the 200-W area of Hanford.

Project Results

Research Objectives

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 (Scheme 1). Both of these products are more persistent and problematic than the parent compound. Fortunately, competing reaction pathways produce the more desirable products carbon monoxide (CO) and/or formate (HCOO^-), albeit with lower yield. Results scattered throughout the chemical and environmental engineering literature show that the branching between these two reaction pathways is highly variable, and that the controlling factors had not been identified.

Scheme 1. General conceptual model for branching among the two major product formation pathways in the reduction of CT.

The premise of this project was that if we understood the fundamental chemistry that controls the branching among these 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 was designed to 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 (Table 1).

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 CCl₄ 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.

Details of the results of this project are summarized below in four sections:

- Tasks 1 and 4: Batch experiments with analysis mainly by gas chromatography: Led mainly by Tratnyek and coworkers at OHSU.
- Task 2: Batch experiments analyzed by microscopy and spectroscopy: Led mainly by Amonette at PNNL.
- Task 3 and 5: Modeling studies based on electronic structure theory: Led by Bylaska at PNNL.
- Tasks 6 and 7: Column experiments: descoped.

Results—Tasks 1 and 4

We developed and validated the necessary experimental protocols and analytical methods for determining all of the reaction products of CCl₄ reduction over an experimental time course. Then we applied these protocols on a number of batch experiments to test the effects of various experimental conditions (pH, buffer type, iron type, initial concentration of CCl₄, 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 CHCl₃ (Y_{CF}), as well as the disappearance of CCl₄ (k_{CT}).

Based on Scheme 1, we can write equations 1 and 2, with equation 3 to define the yield of chloroform (Y_{CF}). We fit this model in several ways: “globally” within an experiment, by fitting equations 1 and 2 together, globally between several experiments belonging to a subset, also by fitting equations 1 and 2 together, and “locally” by fitting equation 1, then equation 2, separately. In either case, we tried letting $[CT]_0$ float and fixing it at its nominal value. Most of the results shown in this report are obtained by globally fitting equations 1 and 2 within several experiments in a subgroup, and letting $[CT]_0$ float.

$$[CT]_t = [CT]_0 e^{-k_{CT}t} \quad [1]$$

$$[CF]_t = [CT]_0 Y_{CF} (1 - e^{-k_{CT}t}) \quad [2]$$

$$Y_{CF} = k_{CF} / k_{CF} + k_{unk} \quad [3]$$

From the above, it is apparent that k_{CT} and Y_{CF} are related and possibly covariant, but this does not appear to be a significant problem (Baer et al. 2007). Below, we summarize our key results with respect to both k_{CT} and Y_{CF} .

Types of Iron

Though most of our experiments were performed with Fe^{H2} , a type of nano-sized iron, a fairly wide range of types of iron and iron oxides was studied to analyze for effect of type of iron on Y_{CF} (Table 2). These iron types vary in size, shell composition, and surface structure, all of which may affect the rate and product branching. They were selected not only for their suitability in mechanistic studies, but also for their potential relevance to field-scale remediation applications. (Several materials used in this work are among the leading commercial products currently available.) We have studied Fe^{AR} , Fe^{OM} , Fe^{H2} , Fe^{BH1} , Fe^{BH2} , Fe^{EL} and Fe^{PL} (defined in Table 2) for reactivity with CT. The first five are nano-sized materials, Fe^{EL} consists of micron-sized particles, and Fe^{PL} has millimeter dimensions.

Table 2. Names, sizes, composition and sources of different irons used.

Name	Source	Particle Size	Surface Area	Major Phase	Minor Phase
Fe^{H2}	Toda Americas, Inc., IL	70 nm	29 m ² /g	$\alpha\text{-Fe}^0$	Magnetite
Fe^{BH1}	W.-X. Zhang, Lehigh U.	10-100 nm	33.5 m ² /g	Fe^0	Goethite, Wustite
Fe^{BH2}	J. Linehan, PNNL	10-100 nm	28.6 m ² /g	Fe^0	Goethite, Wustite
Fe^{AR}	Arcadis, CO	nm	2-3 m ² /g	Fe^0	-
Fe^{OM}	OnMaterials, CA	nm	15 m ² /g	Fe^0/Pt	-
Fe^{EL}	Fisher Scientific, PA	150 mm	0.1-1 m ² /g	99% Fe^0	-
Fe^{PL}	Peerless, MI	mm	<0.1 m ² /g	Fe^0	Iron Oxide

Among the different types of iron, Fe^{H2} consistently gave the lowest yield of CHCl_3 . This confirms the result we reported in our first publication from this study (Nurmi et al., 2005), and is the discovery from this study that has the greatest potential implications for remediation application. We speculate that the low Y_{CF} shown by Fe^{H2} may be due to its magnetite shell (magnetite is thought to promote the benign pathway producing little CF). This result is addressed further in detail in the subsection focused on aging.

Figure 1. Variation of Y_{CF} with iron type: the experiments are color-coded with respect to the sparging method used. The nomenclature used on the x-axis is defined in Table 2. Error bars indicate the goodness of fit of the data to equations 1-3.

Contrary to a common perception that nano-sized iron particles have higher reaction rates than larger bulk sized iron, a comparison of the rates of reaction of the nano irons (Fe^{BH} and Fe^{H2}) and the micron sized iron (Fe^{EL}) with CT shows that there is not a significant difference in surface area normalized rate constants, k_{SA} , between different types of nano- and micron-sized zero-valent irons, though both were faster on a surface area and mass basis, than impure iron types like Fe^{PL} . We published a preliminary version of this analysis in (Nurmi et al., 2005), a simplified illustration in Tratnyek and Johnson (2006), and a manuscript with a more thorough treatment is in preparation (Sarathy and Tratnyek, 2007). The key result is illustrated by Fig. 2.

Effect of mixing

We varied the mixing rate of the rotary shaker on which reaction vials were placed, in order to confirm that the reactions were not mass transport limited. Glass beads were added to replicates, in order to increase the efficiency of mixing of the system. Though there was no significant effect of increasing the mixing rate on k_{CT} , the addition of glass beads did increase k_{CT} (by 10-100%). We speculate that the addition of glass beads may have served to break up aggregates of nano particles, thus increasing the surface area. It may have also added an additional dimension of mixing, thus making mass transport more efficient. Our conclusion is that the rate of mixing (24 rpm) in our experiments keeps us in a regime where kinetics are not mass transport limited, though aggregation does affect the rate.

Effect of $[CT]_0$

We varied $[CT]_0$ from 4×10^{-7} M to 10^{-4} M for three types of iron— Fe^{H2} , Fe^{BH} , and Fe^{EL} . Sparging gas (N_2 vs. Ar) was a third variable. There is a small decrease in k_{SA} with increase in $[CT]_0$ observed in both nano irons— Fe^{BH} and Fe^{H2} —which can be rationalized by the fact that surface sites of iron may get increasingly saturated at higher $[CT]$. However, there is no evidence of complete saturation, since reactions do not digress into zero-order at high $[CT]_0$. The data (not shown) reveal no trend in Y_{CF} with change in $[CT]_0$.

Effect of aging

The oxide layer on iron mediates contaminant

reduction in solution, and therefore may be a factor in determining Y_{CF} (Johnson et al. 1996). Since we expect the oxide layer to change with exposure to water, aging of the iron could be a significant contributor to changes in surface chemistry of the oxide film, and hence changes in Y_{CF} . Here, we use the term aging only as a measure of time spent by iron in solution. We used fresh Fe^{H2} (which had never been exposed to water) to reflect short-term aging; and Fe^{H2} that had been in slurry for approximately a year (aged Fe^{H2}) to give us a model of long-term aged iron.

Assuming that trends in k_{CT} values reflect changes in oxide layer, the short term experiments show a rapid de-passivation of the existing oxide layer on the fresh Fe^{H2} , followed by a (re)growth of a fresh oxide film, known to be magnetite from XRD studies (Amonette et al. 2007). In the long-term experiments, the observation that k_{CT} decreased with increasing aging was interpreted to indicate that the existing oxide layer (magnetite) was gradually growing in thickness (Amonette et al. 2007). Since the core is Fe^0 , we expect the kinetics to be slower with increasing thickness of oxide layer.

In the short-term batch experiments, Y_{CF} was seen to follow a trend similar to k_{CT} , that is there was a rapid increase and gradual lowering of Y_{CF} with time (Fig. 3A), while in the long-term reactions Y_{CF} was stable at a low value of ~ 0.25 (Fig. 3B). This is consistent with the

Figure 2. Comparison of rate constants for reduction by nZVI and two types of micro-sized Fe^0 . Ovals are based on ~ 50 data for reduction of CCl_4 compiled from a variety of sources. C.f., Fig. 5 in Nurmi et al. (2005). This version, Fig. 3 from Tratnyek and Johnson (2006).

depassivation of oxide layer in the beginning, leading to exposure to Fe^0 , which may have caused the spike in Y_{CF} . As the oxide layer (magnetite) begins to build up, Y_{CF} decreases. This observation adds further support to our hypothesis that magnetite is responsible for favoring the carbene pathway. The explanation for this phenomenon may be found in the structure of magnetite.

Magnetite is known to have an “inverse spinel” lattice structure with both octahedral sites that contain equal amounts of Fe^{3+} and Fe^{2+} , and tetrahedral sites that contain only Fe^{3+} . In previous studies of CT dechlorination by magnetite, it has been suggested that the higher electron density and delocalization in octahedral sites may be effective at stabilizing carbenes which are highly electrophilic—and thus reducing CF yield—than iron oxides with no structural Fe^{2+} (Pecher et al. 2002; Danielsen and Hayes 2004).

Figure 3. Variation of Y_{CF} with pre-exposure time for (A) fresh $\text{Fe}^{\text{H}2}$, and (B) slurry aged $\text{Fe}^{\text{H}2}$. Error bars represent one standard deviation from fitting. $[\text{CT}]_0 = 4.01 \mu\text{M}$.

Variation of chloride concentrations

Previous studies have suggested that chloride could affect the rate of CT degradation by Fe^0 , possibly due to pitting on the iron-oxide surface (Johnson et al. 1996). However, evidence for this hypothesis is still weak. In this study, we varied chloride concentrations to test an alternate hypothesis—that it would influence Y_{CF} via one or more potentially reversible steps involving Cl^- shown in Fig. 4. Chloride concentrations were varied from 0 to 40 mM. In the same set of experiments, the age of the iron (in solution) was also simultaneously varied up to 20 days.

Figure 4. Detailed conceptual model showing feasible steps in the dechlorination of CT. In general horizontal, vertical, and diagonal arrows represent electron transfers, atom transfers, and concerted electron and atom transfers, respectively. Dashed arrows indicate multiple steps that are not listed here.

Neither k_{CT} nor Y_{CF} showed any trend with either increasing chloride concentration or with aging (data not shown). We hypothesize that this is because: (i) pitting and aging work against each other resulting in no net effect, (ii) chloride by itself does not cause sufficient change in oxide surface chemistry to affect either k_{CT} or Y_{CF} , and (iii) the reaction $CCl_3^- \rightarrow CCl_2 + Cl^-$ is not reversible in our system.

Effect of pH and H donor

Batch experiments performed on micron sized Fe^{EL} at two different pHs—7.3 and 8.4—confirmed that rate decreased with increasing pH as did earlier experiments (Pecher et al. 2002; Nurmi et al., 2005), but showed no significant difference in Y_{CF} . These experiments were done with a pre-exposure time of 24 hours, which we later concluded may not have been sufficient for complete equilibration of surface sites with the solution. However, the Y_{CF} data does suggest that if CCl_3^- is active, it is on the oxide surface, and not in solution, since pH does not have an effect on Y_{CF} .

Of course, changing pH can affect various reaction conditions, including oxide composition, pitting, rate, etc. Knowledge of the role of [H⁺] and [H[•]] can help elucidate pathways of dechlorination, by helping us understand the relative roles of $CCl_3^\bullet$ and CCl_3^- in the formation of CF (Fig. 4). For a more controlled way of investigating the role of [H⁺] and [H[•]] with respect to the anion intermediate, experiments were conducted in D₂O by adding D[•] and D⁺ donors that should give diagnostic products that we could analyze via GC/MS. We conducted

experiments in H₂O, D₂O, and H₂O with 3.9 uM d8-isopropanol, with Fe^{H2} as the reductant, and 0, 1, and 3-day pre-exposures in each set-up. The different pre-exposures were carried out to account for possible slow kinetics of H⁺/D⁺ exchange between surface hydroxyls and the solvent.

The products obtained under each experimental condition are summarized in Table 3. Had surface hydroxyls been donating protons to CCl₃⁻, we would expect to see an increase in CDCl₃ or CHCl₃ production in the 1- and 3-day pre-exposure systems relative to the 0-day pre-exposure system in the D₂O case (due to H⁺/D⁺ exchange), but there was no effect (Table 3), possibly in part due to the high pH (~10).

Table 3. Products formed under different H⁺/D⁺/D⁻ donor conditions.

Solvent system with Fe ^{H2}	Products observed: 0-day pre-exposure	Products observed: 1-, 3-day pre-exposure
H ₂ O	CHCl ₃	CHCl ₃
H ₂ O with d8-isopropanol	CHCl ₃	CHCl ₃
D ₂ O	CDCl ₃	CDCl ₃

Starting with the assumption that in the heavy water system D₂O only provides D⁺ and not D⁻, the fact that we saw only CDCl₃ produced in the reactions conducted in D₂O indicates that CCl₃⁻ + D⁺ → CDCl₃ is the pathway by which products are formed, and CCl₃[•] does not lead directly to products. In contrast, in Fe²⁺/goethite systems with CCl₂Br₂ and D₂O, CHCl₂Br rather than CDCl₂Br has been observed as the major product (Pecher et al. 2002).

The Y_{CF} values for both H₂O systems (with and without d8-isopropanol) showed similar values and trends. They were ~0.5 for the 0-day pre-exposure system, and ~0.3 for the 1-day pre-exposure system. This decrease in Y_{CF} may be related to the aging of the iron, and has been attributed to an increase in oxide (magnetite) upon increased pre-exposure, in the discussion about aging.

d8-isopropanol, was injected in roughly equimolar concentrations to CT and therefore should have been in excess of any CCl₃[•] produced in the system. It is a D[•] donor and was therefore expected to act as a trap for, and hence test for the presence of, CCl₃[•] radicals. However, since no CDCl₃ was produced, we must conclude that CCl₃[•] radicals are not active in producing CF either because: (i) they are not formed (the trichloromethyl anion being formed from CT in a concerted 2 e⁻ transfer with cleavage of one chloride), or (ii) they are very short lived and therefore do not react even with a radical-trap like D[•].

In contrast, in both Fe²⁺/goethite systems, and biogenic magnetite systems, the presence

of $\text{CCl}_3^\bullet$ was confirmed by d8-isopropanol experiments, and radical trapping experiments using dimethylbutene (DMB) respectively (Danielsen and Hayes 2004; Elsner et al. 2004). We hypothesize that these results contradict our results because of the higher reducing capacity of $\text{Fe}^{\text{H}2}$ nanoparticles, which have an Fe^0 core, and may therefore favor a concerted 2e^- reduction to CCl_3^- . In fact, a 2e^- transfer (with simultaneous cleavage of 2 C-Cl bonds) is thermodynamically favored over 1e^- reduction to form $\text{CCl}_3^\bullet$ (Balko and Tratnyek 1998). However studies on goethite/ Fe^{2+} systems have shown that this does not occur (Elsner et al. 2004), and we do not consider cleavage of 2 C-Cl bonds to be likely.

CCl_3^- , which maybe the Y_{CF} determining reactive intermediate in our system, can exist as a surface stabilized species though the pH that we studied (~ 10 , which is higher than the point of zero charge—pzc—of magnetite) would cause the magnetite surface to be negatively charged. Since we expect CCl_3^- to be formed on the surface, it can either dissociate to the more surface stable carbene, or abstract protons from surface hydroxyls (unlikely due to high pH) or solution.

Results—Task 2

In Task 2, we attempted to improve our fundamental understanding of the factors affecting the reaction branching ratio. For this work, we focused on the nano-sized Fe^0 that produced low yields of CHCl_3 from CCl_4 and used the age of particles in water as a variable since we knew that the yield of CHCl_3 varied somewhat with this factor. We measured changes in the nano-particle properties with length of exposure to water and correlated these changes with the reactivity and CHCl_3 yield. Changes in particle properties were followed by in-situ and ex-situ methods.

For in-situ measurements we used electron paramagnetic resonance (EPR)

Figure 5. EPR signals for DMPO reduced by direct electron transfer (top) and atomic hydrogen (middle) from RNIP-TODA Fe nanoparticles after 18 and 147 h in H_2O . Changes in the relative proportion of direct electron-transfer and hydrogen-transfer products with aging time in H_2O are shown in the bottom panel.

spectroscopy with a nitrogen-centered spin-trapping agent (DMPO, 5,5-dimethyl-1-pyrroline-N-oxide) to probe the surface. This agent yields no EPR signal until it is reduced and, if reduced by a radical species, forms an adduct having a distinctive EPR signal thus allowing identification of the reductant. The experimental set-up allowed us to record the EPR signal as a function of time. The data showed that nano-Fe⁰ reduces DMPO in two ways (electron transfer and hydrogen atom transfer) and that the relative significance of these two pathways changed with time. Initially, only electron transfer was observed (Fig. 5). After 24 hours, however, a signal for hydrogen-atom transfer appeared, and this signal grew over the next few days while the electron-transfer signal decreased. After a week, roughly 90% of the reduced DMPO was in the form of the hydrogen adduct. Mechanistically, these results suggested that the oxide shell initially present on the dry nano-particles shields the Fe⁰ core for about 24 hours. Thereafter, breaches in the oxide shell occur to allow direct reaction of solution with Fe⁰ and production of atomic H.

For ex-situ measurements, we used X-ray photoelectron spectroscopy (XPS) to follow the composition of the nano-particle surface. As one of our branching-ratio hypotheses involved the donation of hydrogen from surface hydroxyl species to form CHCl₃, we followed the changes in the O 1s spectrum, which allows quantification of the oxide, hydroxyl, and adsorbed H₂O concentrations at the surface of the nanoparticles (e.g., Grosvenor et al., 2004). We collected spectra for two sets of samples, one set that had been pre-exposed to H₂O for various periods, and a second set that had been reacted for a few hours with aqueous CCl₄ after pre-exposure to H₂O.

The results (Fig. 6) showed that when the nanoparticles were exposed to water (dashed lines) decreases in oxide O and adsorbed H₂O occur during the first 24 hours, and these are roughly compensated for by a substantial increase in OH (here OH refers to sum of lattice OH and surface OH using the terminology of Grosvenor et al. 2004). After about 100 hours, the OH starts to decrease and the oxide O to increase. If the samples are reacted with CCl₄ after H₂O exposure (solid lines), different results are obtained for

Figure 6. Changes in concentrations of O, OH, and H₂O at the surface of RNIP-TODA Fe after aging in water at room temperature for different periods (dashed lines) and the same aging treatment followed by reaction with CCl₄ (solid lines).

oxide O and OH. There is a slight increase in OH during the first six hours, but thereafter the OH decreases to less than the starting value for the next five days. During the same period, the oxide O remains the same or increases slightly relative to the starting value. After 20 days (data not shown) the oxide O falls to 33.1 atom % and the OH increase slightly to 16.1 atom %.

The lower values for OH concentration seen after reaction with CCl_4 are consistent with the donation of H from surface OH to form CHCl_3 . The timing coincides with maxima for both the rate of CCl_4 reaction and the yield of CHCl_3 shown in Fig. 3.

We interpreted the results of these studies largely along the lines presented in an extended abstract (Amonette, 2006) and to be formally documented in a forthcoming publication (Amonette et al., 2007). The evidence we have gathered, taken together with that in the literature, suggests that the nano-particles evolve from a zerovalent core with an oxide shell through an intermediate state consisting of a highly reactive green-rust-type compound (with very high hydroxyl content) eventually to form magnetite/maghemite. The green-rust compound does not persist and never occupies a major fraction of the surface, yet dominates the reductive chemistry of CCl_4 because of its high reactivity.

The key result of the work in this task, is the correlative evidence that surface hydroxyls associated with green rust, not atomic hydrogen generated by iron corrosion or adsorbed H_2O from the solvent, are the chief source of the hydrogen that ends up in CHCl_3 . The implication for remediation of CCl_4 is that the formation of green rust should be minimized during the time period that reaction with CCl_4 is expected. This can be accomplished either by starting with highly aged nanoparticles having magnetite/maghemite as the dominant phase, or through the use of bi-metallic nanoparticles (e.g., Cu-Fe) where the reaction site is presumed to be on the Cu surface and far enough removed from the sites where green rust occurs to prevent formation of CHCl_3 .

Results—Tasks 3 and 5

The results of Tasks 3 and 5 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 (Bylaska et al. 2002). We have extended this analysis to DDT, which (being an alkane that is per-chlorinated at one C) is a structural analog of CCl_4 (Bylaska et al. 2004). Electronic structure methods were also used to calculate the thermochemical properties of 37 different polychloroethylene-yl radicals, anions, and radical anions (Bylaska et al. 2005). 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. Most recently, electronic structure methods were used to calculate the aqueous reaction energies for hydrogenolysis, dehydrochlorination, and nucleophilic substitution by OH^- of 1,2,3-trichloropropane (Bylaska et al. 2007). These results demonstrate that ab initio electronic structure methods can be used to calculate the reduction potentials of solvated organic

compounds in order to help identify the potentially important environmental degradation reactions.

Equally important in understanding these reactions are the height and shape of activation barriers existing between the reactants and products. We have recently developed a strategy for estimating the activation barrier for the concerted electron transfer reaction (Bylaska 2005). In this strategy the activation energy is determined by finding the crossing point between the dissociation potential energy curves for the neutral $R-Cl$ and the radical anion $R-Cl^{\bullet-}$ as a function of the C-Cl bond length. Not surprisingly, the accuracy of the activation barrier was found to be highly sensitive to the level of ab initio theory. This is not that surprising since it is well known that many ab initio theories fail to correctly describe the interaction between a radical and a closed shell anion ($R-Cl^{\bullet-}$). However, we have found that the anion curve generated by lower-level (e.g., B3LYP) calculations parallels high-level CCSD(T) calculations, and that the accuracy of the lower level anion curves can be improved by correcting for the errors in the C-Cl bond dissociation energy and the electron affinity of chlorine.

We have recently used this strategy to estimate the activation barriers for the electron transfer reactions of polychloroethylenes. Both concerted and stepwise cleavages of R-Cl bonds were considered. It was found that stepwise cleavages yielded lower activation barriers than concerted cleavages for the reduction of C_2Cl_4 , $CHCl_3$, and trans-1,2- $C_2H_2Cl_2$ via strong reducing agents (Fig. 6). However, for typical ranges of reducing strength concerted cleavages were found to be favored (Bylaska, Dupuis, and Tratnyek, 2007). Most recently we have been directly estimating the effect of solvation on the activation barriers of chlorinated methanes by

Figure 6. Activation free energies of the stepwise π^* and concerted reactions for C_2Cl_4 , cis- C_2HCl_3 , and 1,2-trans- $C_2H_2Cl_2$ 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.

performing potential of mean force calculations using QM/MM simulations (QM/MM code developed by M. Valiev, available in NWChem). In the QM/MM approach the system is broken up into two parts: A localized quantum mechanical region surrounded by a molecular mechanical region (Fig. 7). This type of simulation allows for a water-pollutant complex to be modeled quantum mechanically, while at the same time the long-range effects of solvent are included with classical modeling.

Figure 7. Reaction barriers for concerted electron transfer reactions of chlorinated methanes were calculated using QM/MM methods (Valiev et al. 2007).

Results—Tasks 6 and 7

Mid-way through the project we decided to de-scope the testing of control strategies that formed tasks 6 and 7. This decision was made because we did not think we had made enough progress in the earlier tasks to adequately support any specific control strategies and that our best approach would be to continue to focus on developing a better understanding of the primary factors that control the reaction branching ratio.

Summary of Practical Implications and Future Needs

With respect to the ultimate, potential application of the results of this work to remediation of critical contaminations problems at DOE site, the key result is that some types of nano-sized zero-valent iron (nano-Fe⁰) produce low yields of chloroform (0-40%), whereas others produce the higher yields of chloroform (60-100%) that are typical of most methods for reducing CCl₄ (including biodegradation). Since nano-Fe⁰ can, in principle, be introduced into the deep subsurface by injection, our results would suggest that the right type of nano-Fe⁰ introduced in the right way might be highly effective at dechlorinating CCl₄ with minimal formation of CHCl₃ or other undesirable by-products. However, before field-scale applications can be pursued, a follow-up study to this one will be needed, in which the effects of scaling issues are addressed.

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Internet

Some results of this project are summarized—and products may eventually be disseminated—via the web at <http://cgr.ebs.ogi.edu/iron/>.