

Chemical Fate of Contaminants in the Environment: Chlorinated Hydrocarbons in the Groundwater

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May 2006



**Molecular Science
Computing Facility**



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Abstract

Chlorinated hydrocarbons (CHCs) are the most common contaminant found at hazardous waste sites and are the most prevalent contaminants on U.S. Department of Energy (DOE) weapons production sites. Many of the CHCs are either known or suspected carcinogens and thus pose health risks to the public and/or site workers. Unlike simple hydrocarbons, CHCs are resistant to biodegradation, but can degrade by abiotic processes such as hydrolysis, nucleophilic substitution, and dehydrochlorination. Unfortunately, few studies of the reactions of chlorinated hydrocarbons have been reported in literature, and disagreement still exists about the mechanisms and rates of many of the key reactions.

In this work, we modeled the reactions involved in the degradation of CHCs in the groundwater. The goals of the research proposed are:

- development of a computational approach that will allow reaction pathways and rate constants to be accurately calculated
- development of more approximate approaches, evaluated against the more accurate approach, which will lay the groundwork for exploratory studies of more complex CHCs
- application of these approaches to study the degradation pathways of CHCs in aqueous liquids
- application of the more approximate approaches to study the mechanism of forming complex CHC polychlorinated benzene compounds and dioxins.

We examined elementary reactions involved in the aqueous-phase chemistry of chlorinated methanes and ethylenes in an attempt to obtain a detailed understanding of the abiotic processes involved in the degradation of this important class of contaminants. We began by studying the reactions of $\text{CH}_n\text{Cl}_{(4-n)}$ and $\text{C}_2\text{H}_n\text{Cl}_{(4-n)}$ with OH^- , as these are thought to be the dominant processes involved in the degradation of these chlorinated species. We used state-of-the-art theoretical techniques to model the elementary reactions of CHCs important in the groundwater. We employed high-accuracy electronic structure methods (*e.g.*, perturbation theory and coupled cluster methods with correlation-consistent basis sets) to determine the energies of the various stable species, intermediates, and transition states involved in the elementary reactions of CHCs. Effects of solvation on the reaction energetics were studied by including small numbers of solvent molecules (microsolvation). Our own N-layered molecular orbital + molecular mechanics (ONIOM) method was used because it allows the number of solvent molecules to be increased, and hybrid quantum mechanical/molecular mechanics (QM/MM) methods and continuum solvation models were used to estimate the effects of bulk solvation. Rate constants for the gas-phase, microsolvated, and bulk-phase reactions were computed using variational transition state theory (VTST).

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Number of hours allocated for the past three years

FY 2002: 150,000 node hours

FY 2003: 950,000 node hours

FY 2004: 1,282,884 node hours

Number of hours actually used

FY 2002: 137,208 node hours

FY 2003: 1,977 node hours

FY 2004: 382,774 node hours

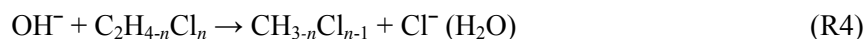
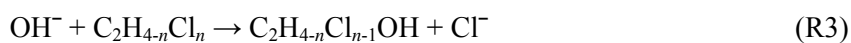
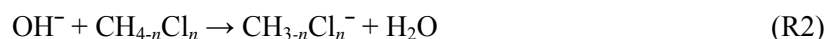
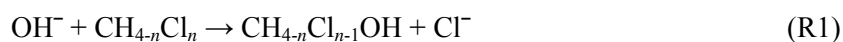
Overview of past three year’s accomplishments and activities [4-6 pages]

The major objective of this research project was to obtain *accurate* estimates of the lifetimes of chlorinated hydrocarbons (CHCs) in an aqueous environment determined from abiotic reactions and to identify any long-lived, potentially hazardous intermediates formed from the original CHCs. The challenges of accurately treating condensed-phase reactions are twofold. First, the molecular interactions or potential energy surface (PES) for the reaction must be accurately calculated. Electronic structure methods sufficient to predict accurate interaction energies for gas-phase reactions typically are not affordable for extended systems such as reaction in liquids. Application of electronic structure to condensed-phase reactions requires approximation to the reaction system or to the level of the electronic structure methods. A variety of approximate approaches have been taken, but few benchmarks are available to test these approximate approaches. Second, the reaction dynamics must be treated accurately. The most common approach to treating dynamics in condensed-phase systems is molecular dynamics (MD) approaches, which assume that classical mechanics is valid. Experience with gas-phase reaction dynamics indicates that classical mechanics is rarely sufficient to describe reaction rate constants accurately, particularly if hydrogen atoms are involved in the reaction. Quantum dynamical methods for

extended systems are necessarily approximate, and a variety of approximations have been proposed with few benchmark studies performed. Treating quantum mechanical effects for chemical reactions (both electronic structure and nuclear dynamics) in condensed-phase remains a significant (“grand”) challenge for theoretical and computational methods.

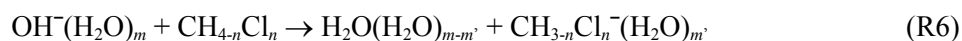
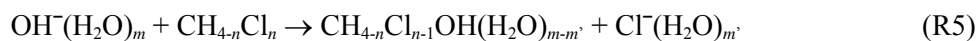
In this research project, *ab initio* electronic structure theory was the basis for the calculation of the reaction energetics. Aqueous solvation can have profound effects on the reaction energetics and we explored the effects of solvation using a number of different techniques. First, the effects of microsolvation on the electronic structure of the reacting species were studied using accurate *ab initio* calculations for the reactions with small numbers of solvent molecules added. The approach to bulk solvation was examined by extending the microsolvation studies using the Integrated Molecular Orbital Molecular Orbital (IMOMO) method or the more general ONIOM method. Finally, continuum solvation models and hybrid QM/MM methods were used to estimate the effects of bulk solvation on the reaction energetics. Rate constants for the reaction were computed using variational transition-state theory (VTST).

Work on this project focused on benchmark calculations of the gas-phase reactions, microsolvation studies, ONIOM calculations, and QM/MM studies for the reactions:



where $n = 1-4$. In previous years, reactants, reactant complexes, transition states, product complexes, and products were characterized for the nucleophilic substitution ($\text{S}_{\text{N}}2$) reaction (R1) and for the proton transfer (PT) reaction (R2). Critical geometries were optimized at the MP2/aug-cc-pVDZ level of theory. For reactions (R1) and (R2), single-point calculations were performed at these geometries using MP2, MP3, CCSD, and CCSD(T) with complete-basis-set (CBS) estimates obtained using the aug-cc-pVxZ basis sets with $x = 2,3,4$. For reactions (R3) and (R4), reaction OH^- abstracts a proton from the carbon atom with no chlorine atoms and with no barrier to the reaction. These systems have small barriers to the elimination of Cl^- to form acetylene and a hydrated chloride ion.

Work in the first year of the current project focused on the effects of solvation on reactions (R1) and (R2). Significant progress was made in completing the benchmark calculations for microsolvated versions of $\text{S}_{\text{N}}2$ and proton transfer reactions of OH^- with $\text{CH}_{4-n}\text{Cl}_n$:



Calculations for the reactions with $n = 1-4$ and $m = 0-2$ have been completed. Using the same protocol established for the reaction with no solvation by water molecules, critical geometries were optimized at

the MP2/aug-cc-pVDZ level of theory and single-point calculations were performed at these geometries using MP2, MP3, CCSD, and CCSD(T) with CBS estimates obtained using the aug-cc-pVxZ basis sets with $x = 2,3,4$. In addition, we used a two-point extrapolation formula to estimate the CBS limit. Geometries for the microsolvated S_N2 and PT reactions are depicted in Figure 1.

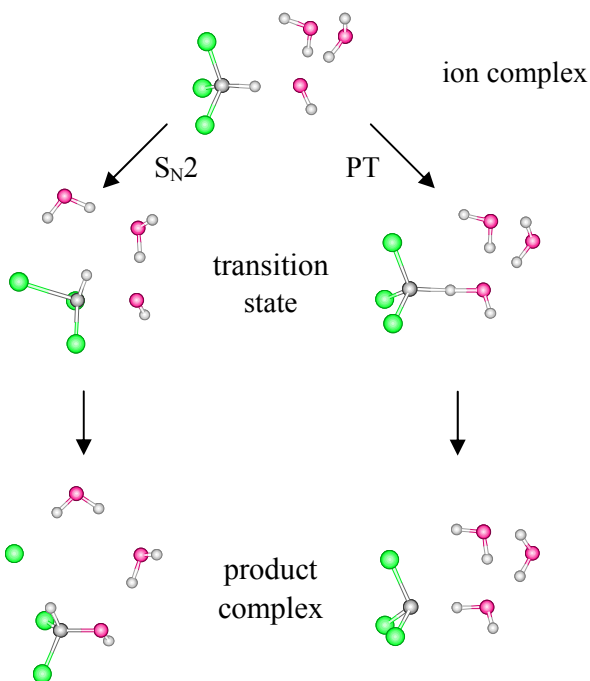


Figure 1. Geometries for the reactant complex, transition state, and product complex of the nucleophilic substitution (S_N2) and proton transfer (PT) reactions of OH^- with $CHCl_3$ solvated by two water molecules.

The energies for bound reaction complex transition states, product complexes, and products of the reactions $OH^-(H_2O)_m + CH_{(4-n)}Cl_n$ with $m = 0, 1, \text{ and } 2$ and $n = 1-4$ are shown in Figure 2. The results show that both the degree of chlorination and level of solvation on the reaction energetics have a profound effect on the reaction energetics.

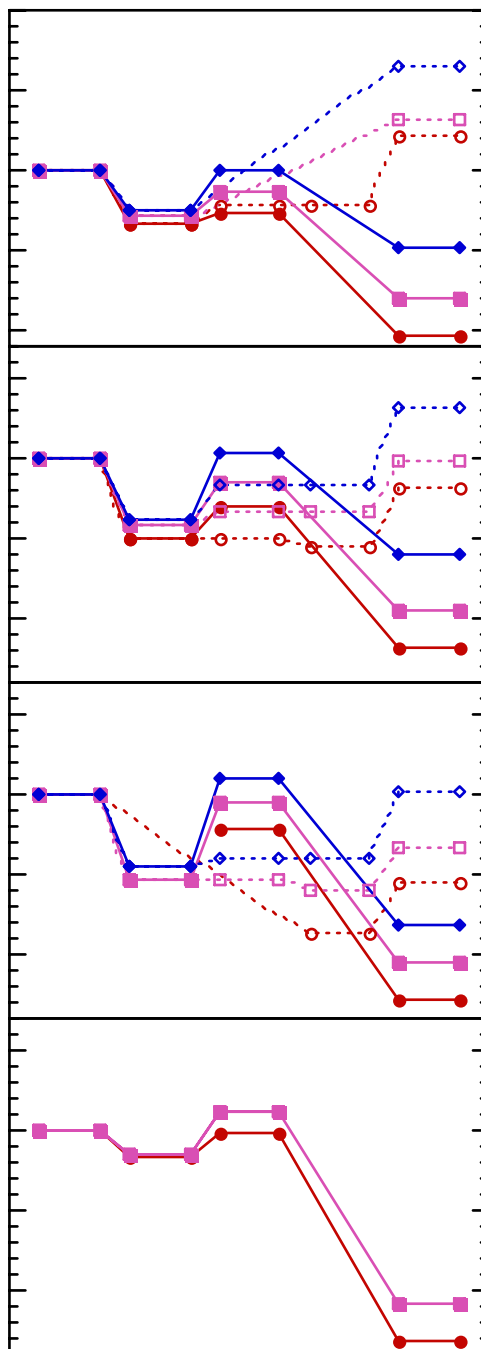


Figure 1. Energies (at the MP2/aug-cc-pVDZ level of theory) for bound reaction complexes, transition states, product complexes, and products of the reactions $\text{OH}^-(\text{H}_2\text{O})_m + \text{CH}_{(4-n)}\text{Cl}_n$ with $m = 0, 1,$ and 2 and $n = 1-4$. Solid lines represent the $\text{S}_{\text{N}}2$ reaction and the dashed lines represent the PT reaction.

Minimum energy paths (MEPs) have been computed at the MP2/aug-cc-pVDZ level of theory for both reactions (R5) and (R6) with $n = 1$ and 2. Information along the MEPs was used in VTST calculations of rate constants for these microsolvated gas-phase reactions. The MEPs were computed for the entrance channels as well as near the saddle points to compare the locations of the dynamical bottlenecks with those for the gas-phase reactions. For reactions (R1) and (R2), the saddle-point energy is below the reactant asymptote for the reaction, and we calculated the MEP in the entrance channel for the reaction to allow VTST calculations of the bimolecular rate constants. These calculations indicate that gas-phase rate constants for reaction (R1) with $n = 1-3$ are controlled by dynamical bottlenecks in the entrance channel, while reaction (R1) with $n = 4$ has the dynamical bottleneck near the saddle point. The computed rate constants are in good agreement with experimental values. For reaction (R5), the energy of the saddle point (relative to the asymptotic reactant energy) increases upon microsolvation and the dynamical bottleneck switches from the entrance channel to the saddle point. The calculated rate constants for the microsolvated reactions therefore are a better benchmark (than the gas-phase reaction rates) of the region of the potential that controls the rate of the bulk-phase reaction.

We are developing continuum solvation methods in order to model reactions between simple CHCs and the hydroxide ion. In particular, we are using hybrid density functional theory (DFT) and a continuum solvation model based on the generalized Born (GB) approximation. It has been shown that hybrid DFT calculations of barrier heights, energies of reactions, and conformational energies are more accurate when diffuse basis functions are included. However, partial atomic charges, which are key components of the GB method, can become unphysical when diffuse functions are used. We have therefore developed a method that alleviates some of the sensitivity to the inclusion of diffuse functions when calculating partial atomic charges from a Löwdin population analysis (see Figure 3). We have further improved these charges by mapping them to new charges so that they reproduce experimentally well-defined quantities, like the dipole moment.

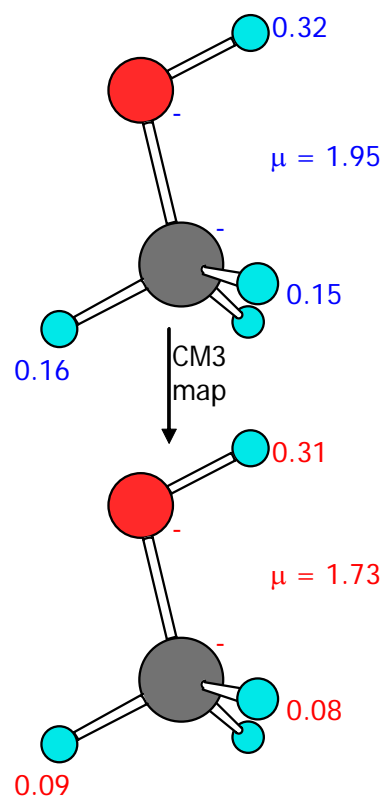


Figure 2. Redistributed Löwdin population analysis charges and dipole moment (blue) and CM3 charges and dipole moment (red) of methanol. The experimental dipole moment is 1.7 D.

List of publications resulting from this work

Borisov, YA, EE Arcia, SL Mielke, BC Garrett, and TH Dunning, Jr. 2001. “A Systematic Study of the Reactions of OH⁻ with Chlorinated Methanes: 1. Benchmark Studies of the Gas-Phase Reactions” *Journal of Physical Chemistry A* 105(32): 7724-7736, DOI: 10.1021/jp011447c.

Jasper AW, NE Schultz, and DG Truhlar. 2005. “Analytic Potential Energy Functions for Simulating Aluminum Nanoparticles.” *Journal of Physical Chemistry B* 109(9):3915-3920, DOI: 10.1021/jp044805v.

Schultz NE and DG Truhlar. 2005. “New Effective Core Method (Effective Core Potential and Valence Basis Set) for Al Clusters and Nanoparticles and Heteronuclear Al-Containing Molecules.” *Journal of Chemical Theory and Computation* 1(1):41-53, DOI: 10.1021/ct0400018.

List of presentations resulting from this work

Garrett, BC, GK Schenter, EA Arcia, YA Borisov, RP McRae, and DG Truhlar. 2002. “Environmental Effects on Chemical Reaction Rates.” In *Abstracts 223rd American Chemical Society National Meeting*, Phys 0269, April 2002, Orlando, Florida. [Invited speaker]

List of significant methods/routines or codes developed

Application of VTST with the PES information obtained using a QM/MM approach requires obtaining the potential of mean force (PMF), which is obtained by averaging solvent configurations for fixed geometries of the cluster model. Converged ensemble averages can require averaging over millions of solvent configurations and this approach can be computationally intensive, particularly if an electronic structure calculation is performed for each solvent configuration. These calculations will benefit greatly from the availability of a parallel implementation of the method.

The PMF is defined by

$$\frac{\partial U}{\partial \mathbf{x}} = \left\langle \frac{\partial V}{\partial \mathbf{x}} \right\rangle \quad (\text{Eq. 1})$$

where U is the PMF, which is a function of the solute coordinate \mathbf{x} only, V is the total potential, which is a function of solute coordinate and solvent coordinates \mathbf{r} , and the ensemble average is over solvent coordinates \mathbf{r} only for fixed values of the solute coordinate \mathbf{x} . The PMF along a reaction coordinate can be obtained by integrating Eq. 1 along the reaction coordinate, which is an example of thermodynamic integration. Alternatively, the PMF along a reaction path can be obtained in the following manner. The free-energy difference between two solute configurations i and j is given by

$$\Delta A_{ij} = -k_B T \ln \left\{ \left\langle \exp \left[-\frac{(V_i - V_j)}{k_B T} \right] \right\rangle_j \right\} \quad (\text{Eq. 2})$$

where k_B is Boltzmann's constant, T is temperature, V_j is the total interaction potential for the system with the solute in configuration j , and ensemble averages are defined by

$$\langle \dots \rangle_j = \frac{\int d\mathbf{r} \dots \exp[-V_j(\mathbf{r})/k_B T]}{\int d\mathbf{r} \exp[-V_j(\mathbf{r})/k_B T]} . \quad (\text{Eq. 3})$$

The PMF is obtained by summing the free-energy differences for points along the reaction path. We used the Metropolis Monte Carlo (MC) method to evaluate the averages in Eq. 3. In the QM/MM method, the electronic structure of the QM region includes the influence of electrostatic interactions (*e.g.*, charges, dipoles, etc.) with the solvent, and the potential in Eq. 3 requires that an electronic structure calculation be performed for every new solvent configuration, even though the solute coordinates do not change.

The Metropolis MC algorithm was implemented in HONDO to perform equilibrium ensemble averages for constrained geometries of the reactants. The code was adapted to run on any number of nodes on the MPP. The implementation generates independent initial random configurations of the solvent water molecules on each node. Independent calculations and MC simulations are performed on each node, with the resulting data sets being combined and averaged at the end of the job.