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

Dr. Donald G Truhlar (University of Minnesota), Bruce C. Garrett (PNNL), Keiji Morokuma (Emory University)

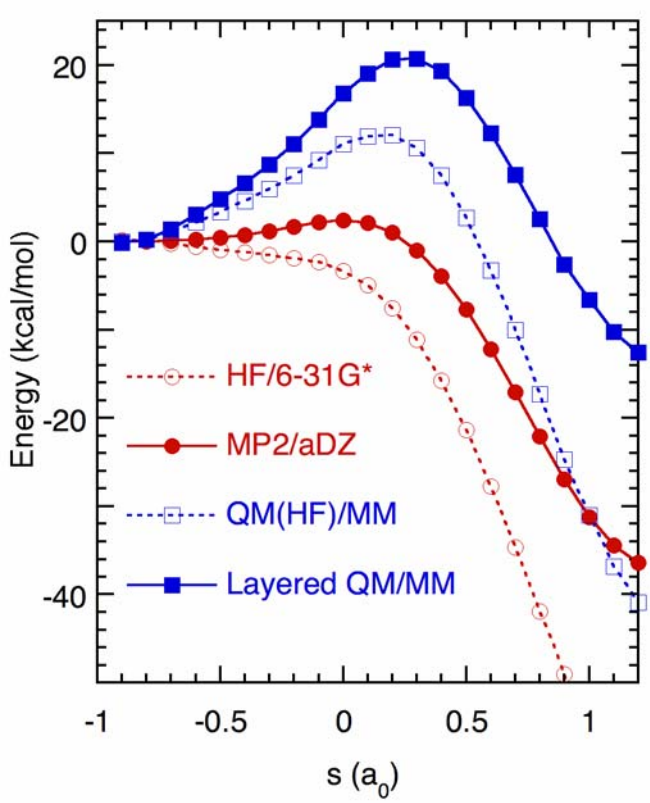
Chlorinated hydrocarbons (CHCs), which can be carcinogens, are the most common contaminant found at hazardous waste sites and are the most prevalent contaminants on Department of Energy (DOE) weapons production sites. Chlorinated hydrocarbons are resistant to biodegradation, but can degrade by abiotic processes such as hydrolysis, nucleophilic substitution, and dehydrochlorination. Unfortunately, disagreement still exists about the mechanisms and rates of many of the key reactions. Our work is focused on modeling the reactions involved in the degradation of chlorinated hydrocarbons in the groundwater. The goals of the research proposed here are fourfold: 1) development of a computational approach that will allow reaction pathways and rate constants to be accurately calculated, 2) development of more approximate approaches, evaluated against the more accurate approach, which will lay the groundwork for exploratory studies of more complex CHCs, and 3) application of these approaches to study the degradation pathways of CHCs in aqueous liquids. A major focus of this work is on the development of continuum solvation models, which are based upon the solvation models of Truhlar and Cramer, and which are appropriate for calculations using density functional theory (DFT). Applications are focused on the initial elementary steps in reactions of OH^- with chlorinated methane molecules, $CH_nCl_{(4-n)}$, and studies of reactions of OH - with chlorinate ethylene molecules, $C_2H_nCl_{(4-n}$

Significant progress has been made on development of continuum solvation methodology needed to simulate the reactions of hydroxide with chlorinated hydrocarbons. In our initial work on this, the need for diffuse functions to get the thermochemistry right became clear. However, our solvation models and charge models were not stable when diffuse functions are used. The progress we made to solve this is:

- First we derived a new type of population analysis that is stable to diffuse functions: "More Reliable Partial Atomic Charges When Using Diffuse Basis Functions," J. D. Thompson, J. D. Xidos, T. M. Sonbuchner, C. J. Cramer, and D. G. Truhlar, PhysChemComm 5, 117-134 (2002).
- Then we used this new type of population analysis to develop charge models that give stable charges with diffuse basis sets: "Charge Model 3: A Class IV Charge Model Based on Hybrid Density Functional Theory with Variable Exchange," P. Winget, J. D. Thompson, J. D. Xidos, C. J. Cramer, and D. G. Truhlar, Journal of Physical Chemistry A106, 10707-10717 (2002); "Parameterization of Charge Model 3 for AM1, PM3, BLYP, and B3LYP," J. D. Thompson, C. J. Cramer, and D. G. Truhlar, Journal of Computational Chemistry 24, 1291-1304 (2003).
- Finally, we are making excellent progress in using the new charge models to create new solvation models, and we almost have a publication ready on that. The originally planned large computations will use this methodological development on this aspect of the project. Although it was more efficient to do the preliminary work on desktop workstations and compute servers, the grand challenge work on this part of the project using this methodology requires the supercomputers in the MSCF.

The use of the computers in the MSCF have been essential for the applications to the reactions of OH^- with chlorinated methane molecules, $CH_nCl_{(4-n)}$ with n=1-4. In previous work we completed a hierarchy of calculations for the gas phase reactions for all n and for microsolvated reactions (with up to two water molecules) for n=1-3. Recent work on this project has focused primarily on the high-level electronic structure calculations (e.g., methods that include electron correlation such as Møller-Plesset perturbation theory, e.g., second-order is denoted MP2, and couple cluster methods) for the microsolvated reactions of carbontetrachloride (n=4), which are a significant computational challenge and require the use of advanced software such as NWChem on the massively parallel computers in the MSCF. These calculations show a significant increase in the reaction barrier for the nucleophilic substitution (S_N2) reaction as the number of water molecules is increased.

To account for the effects of bulk solvation (i.e.., increase of the amount of water molecules to a macroscopic number), we use a computationally tractable and efficient procedure for the calculation of potentials of mean force using mixed Hamiltonian models of electronic structure where quantum subsystems are described with computationally intensive ab initio wavefunctions. The mixed Hamiltonian is mapped into an all-classical Hamiltonian that is amenable to a thermodynamic perturbation treatment for the calculation of free energies. A small number of statistically uncorrelated (solute-solvent) configurations are selected from the Monte Carlo random walk generated with the all-classical Hamiltonian approximation. Those are used in the averaging of the free energy using the mixed quantum/classical Hamiltonian. Application of this methodology is illustrated for the S_N2 substitution reaction of methyl chloride by hydroxide in the figure. In this figure the dashed and solid lines with circles and are calculations of the energies for the gas-phase reaction using Hartree-Fock theory with a 6-31G* basis set (dashed curve with open circles) and MP2 with an aug-cc-pVDZ basis set (solid curve with filled circles). The energies are computed at geometries along a minimum energy path for the gas-phase reaction that is calculated using MP2/aDZ theory. The



dashed line with open squares show the results of bulk solvation on the HF/6-31G* results using the QM/MM approach described above. The most accurate values of the solvated potential energy curve is given by combining the MP2 results with those of the QM(HF)/MM and HF.6-31G* results, using a layered electronic structure approach, to give the solid curve with filled squares.

Another aspect of this work is the development of efficient DFT methods to study chemical reactivity. In another research effort at the University of Minnesota, which is not directly mentioned in the original proposal but is a complement to that work, we are developing new force fields for aluminum nanoparticles that are important to energy research because of their potential as high-energy materials. The computer hardware and software at PNNL has been essential to the latest stage of this work. In particular, we have been studying the transition from small-molecule properties to their bulk limit in Al molecules, clusters, and nanoparticles, specifically the evolution of the binding energy per particle as the cluster gets bigger. We have also studied the multiplicities of the clusters. We have recently developed a new effective core potential (ECP) method for use with hybrid density functional theory (HDFT) that provides accurate energies and geometries. This development was done on local computers at Minnesota, but we have been able to use the resulting technology to run large production runs on Al19, Al43, Al55, Al79, and Al87 on the PNNL computer system with NWChem. For nanoparticle sized Al (more than 50 atoms), the capabilities of the PNNL software and hardware for this work are impressive. We have therefore been taking advantage of the parallel capabilities of NWChem and anticipate running even larger systems that will take full advantage of the computing power of the EMSL for this kind of research.