Chemical Fate of Contaminants in the Environment: Chlorinated Hydrocarbons (CHCs) in the Groundwater

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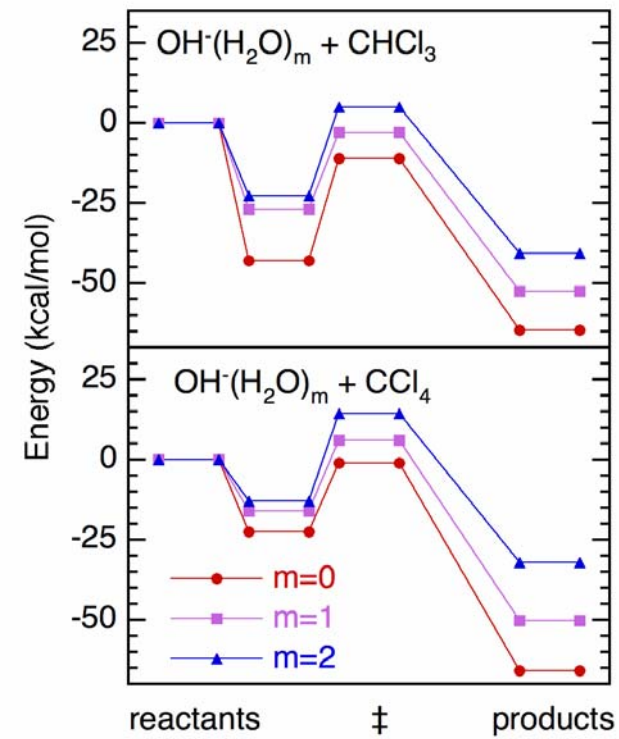
Energetics for the S_N2 Reactions
$OH^-(H_2O)_m$+$CHCl_3$ and $OH^-(H_2O)_m$+CCl_4



Microsolvation of the OH^- + $CHCl_3$ and CCl_4 Reactions

The reactions $OH^-(H_2O)_m$ + $CHCl_3$ and $OH^-(H_2O)_m$ + CCl_3 with m=0-2, present significant challenges for high level electronic structure theory because of the many electrons in the systems. We have used the high performance computers in the MSCF to perform calculations at the MP2, MP3 and CCSD(T) levels of theory with basis sets up to aug-cc-pVQZ basis sets. The results of these calculations are summarized in the figure, where we show the energetics (relative to the energy of the reactants with $OH^-(H_2O)_m$ infinitely separated from the chlorinated hydrocarbon) for reactant complexes, transition states, and products for the nucleophilic substitution (S_N2) reaction. The results clearly show that the effect of microsolvation is to decrease the energy for forming the reactant complex and increase the energy of the transition state.

E. E. Arcia, D. T. Chang, B. G. Garrett, and Y. A. Borisov, "A Systematic Study of the Reactions of OH^- with Chlorinated Methanes: 2. Effects of Microsolvation on Reaction Energetics and Rate Constants" (in prep.)

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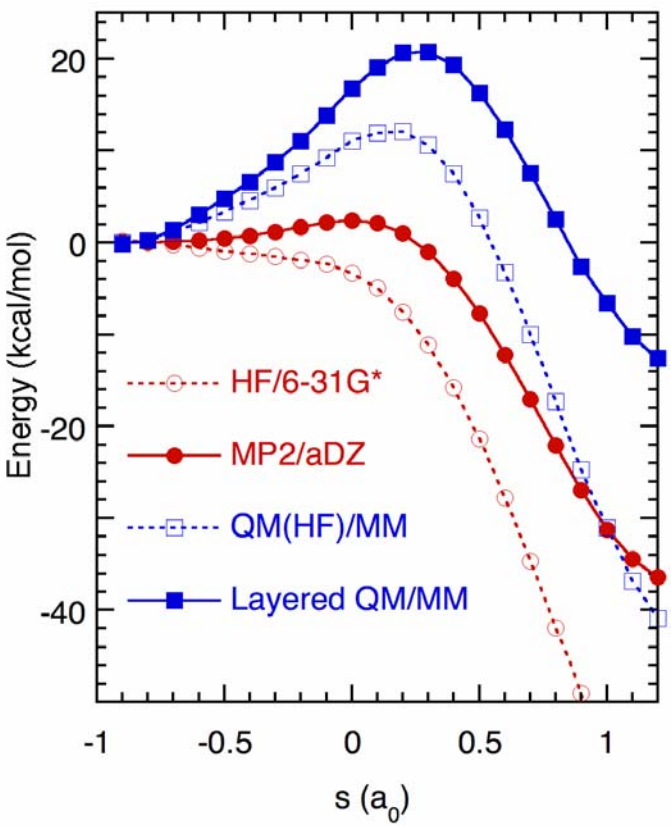
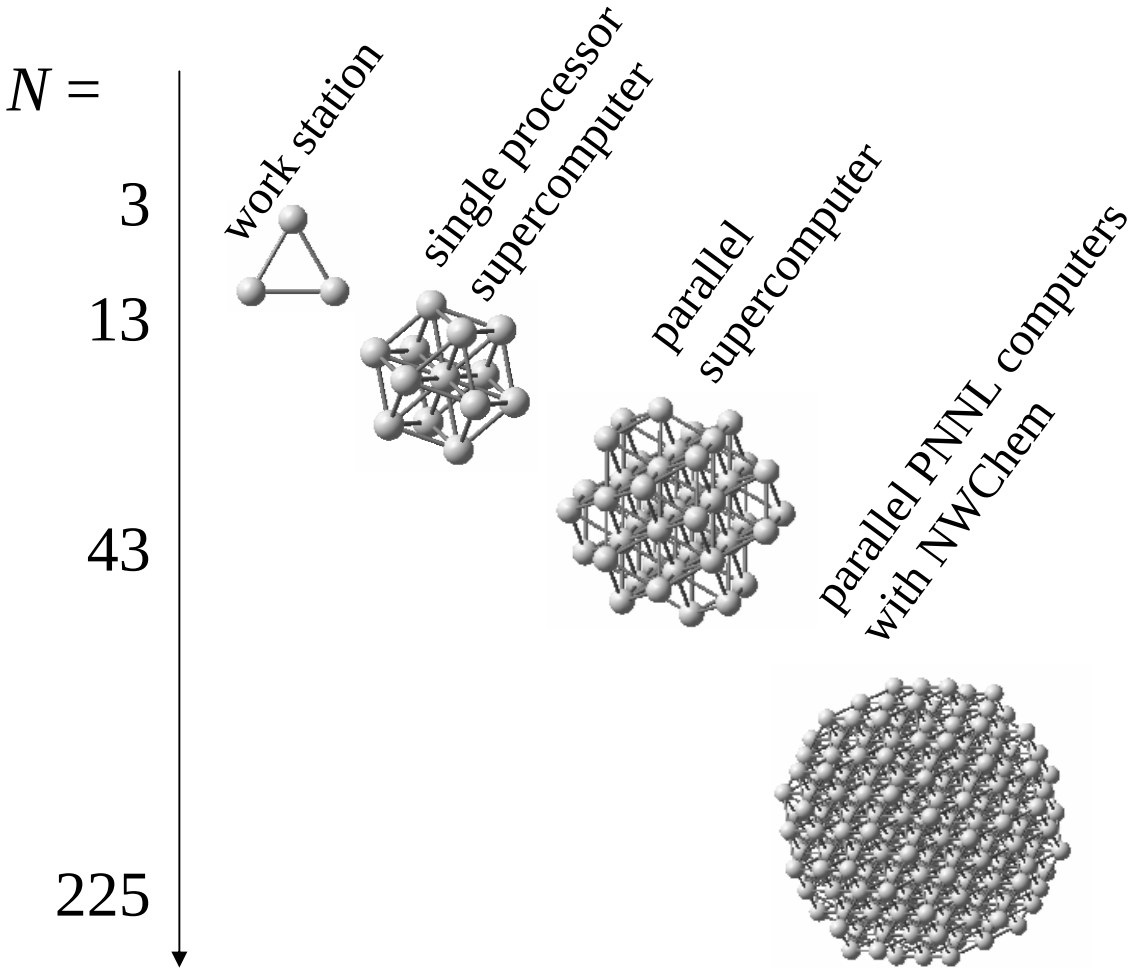


Solvation Effects on the OH^- + CH_3Cl Reaction

To account for the effects of bulk solvation, 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.

M. Dupuis, G. K. Schenter, B. G. Garrett, and E. E. Arcia, J. of Molec. Struct. (THEOCHEM), 173 (2003).



Properties of Al Nanoparticles

Hybrid density functional theory (DFT) calculations of the physical properties of Al_n nanoparticles (n = 19 - 225)

- binding energy / atom
- vacancy formation energy
- lattice constant