

## **Project 90107**

### **Hazardous and Corrosive Gas Production in the Radiolysis of Water/Organic Mixtures in Model TRU Waste**

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#### **RESULTS TO DATE: Scope.**

Experiments in combination with diffusion-kinetic modeling incorporating track structure simulations are used to examine the radiation chemistry of aqueous systems containing chlorinated hydrocarbons. Irradiations with both Co-60 gamma rays and alpha particles are employed in order to simulate typical mixed radiation environments encountered in waste management. The goal is to determine fundamental mechanisms, kinetics, and yields for the formation of potentially explosive gases and corrosive agents, such as H<sub>2</sub> and HCl, respectively, in the radiolysis of water-organic mixtures. The radiation chemical systems studied are found throughout the DOE portfolio and are important in radioactive waste remediation and management.

#### **Program Highlights.**

Products from the radiolysis of chlorinated hydrocarbons. The first studies explored the radiation-induced yield of molecular hydrogen and chloride anion from aqueous solutions of 1,2-dichloroethane (1,2-DCE) and 1,1-dichloroethane (1,1-DCE) over the concentration range 1-80 mM. Radiolysis experiments were performed with both Co-60 gamma rays and alpha particles, while the model studies incorporated stochastic Monte Carlo track chemistry calculations at short times (< microsecond) with a deterministic diffusion kinetic approach to the longer time kinetics. The agreement between experiment and model was excellent suggesting that proposed mechanisms are correct. The main conclusion reached in the radiolysis of the dichloroethanes was that both the hydrated electron and H atom react quantitatively to give chloride anion.



Similar results are observed for both 1,1-DCE and 1,2-DCE. The reaction with the hydrated electron was expected, but never proven to be quantitative. H atoms were expected to extract an H atom and not give the chloride anion. The observed result with H atoms was unexpected and leads to a higher chloride anion yield and lower molecular hydrogen yield than would normally be predicted. In conjunction with production of the chloride anion, the hydronium cation is observed. Production of the hydronium cation leads to a significant drop in pH and may prove to be a significant problem for maintenance of storage containers. Radiation chemistry studies of aqueous dichloromethane, chloroform, and carbon tetrachloride solutions are now in progress. These compounds are much more volatile than the dichloroethanes and required extensive modification of the experimental techniques. The preliminary results show that the chloride anion yield is greater than the sum of the hydrated electron and H atom yields suggesting a contribution due to hydrolysis of radicals. Aerated solutions show huge chloride anion yields, probably as a result of the chemistry of the peroxide intermediates. Model calculations to help explain these results are currently in progress.

#### **Rate coefficients for the reaction of the hydrated electron and OH radical with chlorinated hydrocarbons**

There was considerable discrepancy in the rate coefficients for the reaction of the primary radiation produced reducing and oxidizing radicals from water, hydrated electron and OH radical respectively, with the chloroethanes. These uncertainties made modeling the kinetics very difficult. Electron pulse-radiolysis

experiments were used to measure the rate coefficients while paying special attention to the volatility of the samples. The rate coefficients of the hydrated electron were obtained from its measured rate of decay with different solute concentrations. Competition studies with thiocyanate were used to measure OH radical rate coefficients. The mechanism for the radiation-induced formation of thiocyanate dimer radical anion from thiocyanate is complex and involves a number of equilibria. Careful electron pulse radiolysis experiments were performed and analyzed using the full reaction mechanism. The rate coefficient for the reaction of the OH radicals with a chloroethane was then obtained by examining the change in the radiation-induced yield of thiocyanate dimer radical anion from an aqueous thiocyanate solution. The results show an increase in the rate coefficient for hydrated electron reaction with increasing number of chlorine atoms on the chloroethane, except for hexachloroethane. Apparently the presence of H atoms on the carbon atom facilitates the reaction with hydrated electron. No particular trend is observed for the rate coefficients of the OH radical. A complete set of accurate rate coefficients will aid in understanding further radiolysis experiments measuring product yields

#### **DELIVERABLES: EMSP Sponsored Publications in 2005**

B. Milosavljevic and J. A. LaVerne, Pulse Radiolysis of Aqueous Thiocyanate, *J. Phys. Chem. A*, 2005, 109, 165.

B. Milosavljevic, J. A. LaVerne, and S. M. Pimblott Rate Coefficient Measurements of Hydrated Electrons and Hydroxyl Radicals with Chlorinated Ethanes in Aqueous Solutions, *J. Phys. Chem. A*, 2005, 109, 7751.

S. M. Pimblott, B. Milosavljevic, and J. A. LaVerne, Radiolysis of Aqueous Solutions of 1,1- and 1,2-Dichloroethane, *J. Phys. Chem. A*, in press.

#### **EMSP Sponsored Submissions in 2005**

P. Rajesh, J. A. LaVerne, and S. M. Pimblott, Radiolysis of Aqueous Solutions of Dichloromethane, Chloroform, and Carbon Tetrachloride, *J. Phys. Chem. A*, submitted.

#### **EMSP Sponsored Presentations in 2005**

J. A. LaVerne, Rate Coefficients of Chlorinated Ethanes in Aqueous Solutions, *PacificChem2005*, December 18, 2005.

S. M. Pimblott, Hazardous and Corrosive Gas Production in the Radiolysis of Water/Organic Mixtures, *PacificChem2005*, December 19, 2005.