2005 SUMMARY/PROGRESS REPORT

Mechanisms and Kinetics of Organic Aging and Characterization of Intermediates in High Level Waste (Environmental Management Sciences Program project #95014)

Lead Principal Investigator:

Donald M. Camaioni, Pacific Northwest National Laboratory,[1] Chemical Sciences Divison, Richland, WA 99352, (509)375-2739, donald.camaioni@pnl.gov

Co-Investigators:

S. Tom Autrey, Pacific Northwest National Laboratory, Chemical Sciences Divison, Richland, WA 99352, (509)375-3792, tom.autrey@pnl.gov

Michel Dupuis, Pacific Northwest National Laboratory, Chemical Sciences Divison, Richland, WA 99352, (509)375-2617, michel.dupuis@pnl.gov

Research Objective

This project aims to develop quantitative understanding of the significant chemical changes that high-level waste (HLW) undergoes during storage, retrieval and treatment operations and computational capabilities to model that chemistry.

Research Progress and Implication

The project, which renewed in 2005, evolved from the PI's experience working with the Hanford Site and other Environmental Management Science Program projects to resolve issues concerning organic chemicals in HLW. The work combines theoretical, computational, and experimental efforts to achieve the project objective. In addition, the principal investigator maintains contact with DOE site operations staff and contributes to resolving issues within his expertise as they arise.

This report describes progress in developing and applying novel methods to assess and accurately model mechanisms of organic aging and related reactions occurring in HLW. The project is developing time-resolved photoacoustic calorimetry (PAC) to gain fundamental knowledge of the reactions of aqueous radicals in water. Specific information is being sought on the how Al(III) activates organic complexants to undergo redox reactions that lead to H_2 generation. Theoretical characterization is needed of organic radicals and radical ions in solution, including the calculation of reduction potentials, acidities, bond dissociation energies, and activation energies that are difficult to measure data but relevant to advancing chemical reaction models. A summary of information sharing activities is provided at the end of the report.

Thermochemistry and Kinetics of Radical Intermediates. The PAC technique is based on the phenomenon that chemical reactions induced by absorption of a light pulse produce a measurable sound pulse that is a function of the enthalpy changes, volume changes, and rates of the induced reactions. Of key importance, such information can be used to determine bond dissociation energies (BDEs) in solution. Thus, the investigators are interested in determining the bond energies of glycolate and its Al(III) complexes to determine if Al complexation activates glycolate ion to undergo homolytic hydrogen transfer reactions.

As a first step toward obtaining aqueous thermochemistry of organic radicals in water, the researchers worked to adapt the time-resolved PAC technique to use hydrogen peroxide as a photo-precursor. Initial

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[1]Operated by Battelle for the U.S. Department of Energy.

work surveyed the photodissociation reaction (1) of hydrogen peroxide and the follow up reaction (2) of hydroxyl radical with hydrogen peroxide.

$$HOOH(aq) \rightarrow 2OH(aq) \qquad (1)$$

$$OH(aq) + HOOH(aq) \rightarrow OOH(aq) + H_2O(l) \qquad (2)$$

Indeed, these preliminary experiments showed that the method provides valuable physical, thermochemical and kinetic data for radicals in water. The work then focused on measuring accurately the enthalpy and volume changes for reaction (1) from which the enthalpies of formation and hydration, and the partial molar volume of OH(aq) were determined.[2] In the past year, experimental conditions for study of reaction (2) were optimized to enable accurate measurements of Arrhenius rate parameters and reaction enthalpy and volume changes for (2). Recent work provides the first experimental measurements of the enthalpy of formation (-13 kcal/mol) and the partial molar volume (22 mL/mol) of HOO(aq). The partial molar volume of a solute is useful for predicting the pressure dependence of its reactions and provides insight to the interactions of the solute with water. As such it may also provide a useful benchnmark for solvation models.

Preliminary experiments to obtain the thermochemistry and rates of reaction (3) of OH with glycolate ion have been performed and described in the 2004 annual report. Work will continue on this system as studies of reaction (2) are completed.

$$OH(aq) + HOCH_2CO_2^-(aq) \rightarrow H_2O(l) + HOCHCO_2^-(aq) \qquad (3)$$

Overall, the results provide confidence in the time-resolved PAC technique for measuring aqueous thermochemistry and open the way to obtaining thermochemistry for radicals that can be formed by reaction of OH with aqueous substrates.

Theoretical Characterization of Intermediates in Solution. After extensive experimental characterization of tank wastes during the 1990s, theoretical input based on *ab initio* theories is needed to obtain improved understanding of chemical reactions in aqueous phase and to provide alternate routes to experiment for obtaining fundamental data (thermochemical, spectroscopic, and reactivity data of organic radical ions) that cannot be easily measured and yet are needed to develop of robust chemical kinetic models. For this purpose, the investigators use existing *continuum models* of solvation in the context of Density Functional Theory calculations. In these models, the solute resides in a molecular-shaped cavity embedded in a dielectric continuum representation of the solvent. Continuum solvation models provide a practical way to characterize solvation effects on the energetics of many chemical reactions; however, they are unable to yield **consistently** chemical accuracy for many systems outside the type of molecules used to calibrate the models. A systematic study by the project has found that current schemes for defining a solute's cavity do not reproduce well the detailed solute-solvent interactions. To address this limitation of the models, the project is developing more accurate and consistent chemical functionality-based schemes of defining cavities involving atomic radii dependent on atomic charges that capture specific solute-solvent interactions (see Figure 1). The protocol was initially defined for

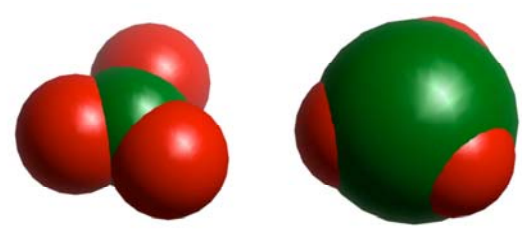

Figure 1. Shown are Cavity models based on Van der Waals radii (left) and atomic charges-dependent radii (right). The latter model captures well the specific interactions of the solute with the first solvation shell.

[2] Autrey, T.; Brown, A. K.; Camaioni, D. M.; Dupuis, M; Foster, N. S.; Getty, A. *J. Am. Chem. Soc.* **2004**, *126*, 3680-3681.

oxoanions[3] and is being extended to other organic functional groups.

Recent work has yielded cavity definitions for molecules and ions with O and OH functionalities. Theses definitions were used to calculate the activation barrier for hydrogen transfer reaction (2) in water (see Figure 2). The merit of relating cavity radii to atomic charges is underscored by this calculation because there is no ambiguity in defining the cavity radii for the transition state structure, or other structures along the reaction path. The cavity adjusts naturally to changes in the structural environment and partial atomic charges. The findings encourage extension of the protocol to include other functional groups to increase the applicability of the scheme and obtain greater accuracy in using continuum solvation models to predict properties of aqueous solutes.

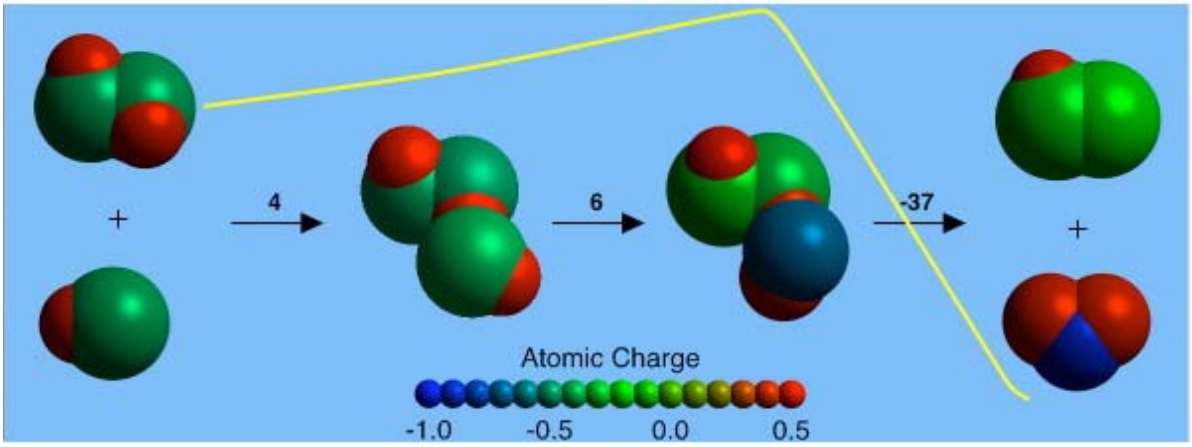

Figure 2. Simulation of reaction (2) in water using a continuum solvation model with cavities built up from interlocking spheres centered on the atoms with radii that are functions of the effective atomic charges and functional group type. Colors of spheres are coded to the atomic charge of the enclosed atom. The reaction proceeds from separated reactants, H_2O_2 and HO, to separated products, HO_2 and H_2O, via an hydrogen-bonded precursor complex (2nd from left) and the transition state complex (3rd from left). The "yellow" line traces the free energy of reaction. Changes for each step in kcal/mol are shown above connecting arrows. The reaction is accurately predicted to be slower in water compared to the gas phase reaction rate.

Modeling Radiolytic H_2 Generation Rates in the High Level Waste. The principal investigator collaborated with Hanford site contractors to develop models for predicting H_2 generation rates based on recent advances in fundamental understanding of the radiolytic process. Figure 3 shows the mechanism for H_2 formation from water radiolysis according to LaVerne and Pimblott.[4] The simplest second-order reaction that occurs on the fast time scales of H_2 formation in water radiolysis is dissociative recombination of a 'non-hydrated' electron (or 'precursor' to the hydrated electron) with the water cation. This process occurs in competition with hydration

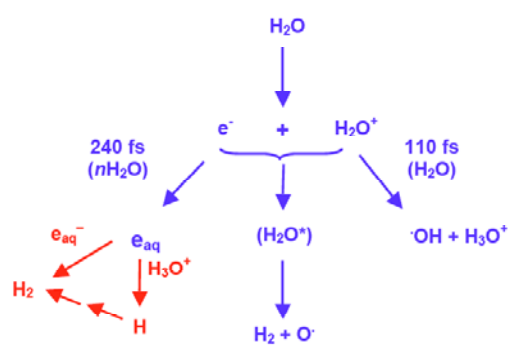

Figure 3. Mechanism for H_2 formation from water radiolysis.

[3] Camaioni, D. M.; Dupuis, M.; Bentley, J. *J. Phys. Chem. A*, **2003**, *107*, 5778.

[4] LaVerne, J. A.; Pimblott, S. A. *J. Phys. Chem. A*, **2000**, *104*, 9820.

of the electron and with proton transfer by the water parent cation and with scavenging of the unhydrated electron by solutes, *e.g.*, NO_3^- and NO_2^- which are among the dominant aqueous components of HLW. Some H_2 is generated by reactions of the hydrated electron and successor H atom ("red" portion of mechanism in Figure 3), which are also scavenged by NO_3^- and NO_2^-. LaVerne and Pimblott advanced the first term in equation (4) to describe the dependence on scavengers of the H_2 yield from dissociative recombination. To model the dependence of the total yield on scavengers, Camaioni added the second term.

$$G(\mathrm{H}_2) = G_0 \frac{\tau^{-1}}{\tau^{-1} + k[\mathrm{S}]} + \left(G_{[S]=0} - G_0\right) \frac{\tau_2^{-1}}{\tau_2^{-1} + k_2[\mathrm{S}]} \tag{4}$$

The Hanford River Protection Project is using equation (4) to evaluate design requirements for the Waste Treatment Plant.[5] Camaioni advised Albert Hu how to develop a variant of equation (4) that is being used in Hanford waste tank farm operations.[6,7] The Savannah River Site compared equation (4) for predicting H_2 yields in 4 tanks of their waste.[8] The predictions by equation (4) were in good agreement for 2 of the tanks but higher (more conservative) for the other 2.

Planned Activities

The investigators will work to continue experiments using PAC technique to measure thermochemistry and kinetics of aqueous reactions of OH radical with the goal of determining the effect that complexation with aluminum(III) has on the reactivity of complexants such as glycolate ion. The computational effort will work to extend the new cavity definition protocol to include solutes with nitrogen, oxygen and carbon containing functional groups. Extensions to metal complexes and multiply-charged ions will also be investigated. Computational efforts will determine reaction energies and activation barriers of key reactions.

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[5] Sherwood, D.J. and Stock, L. M., **2004**, *Modifying the Hu Correlation to Predict Hydrogen Formation in the Hanford Waste Treatment and Immobilization Plant*, 24590-WTP-RPT-RT-04-0002, Bechtel National, Inc., Richland, WA.

[6] Hu, T. A., **2004**, *Empirical Rate Equation Model & Rate Calculations of Hydrogen Generation for Hanford Tank Waste*, RPP-5926, Rev. 4, CH2M Hill, Hanford Group, Inc., Richland, Washington. http://198.232.211.23/pdwdocs/fsd0001/osti/2004/I0045564.pdf

[7] Hu, T. A., **2004**, S*teady State Flammable Gas Release Rate Calculation and Lower Flammability Level Evaluation For Hanford Tank Waste*, HNF-3851, Rev. 1, CH2M Hill, Hanford Group, Inc., Richland, Washington. http://198.232.211.23/pdwdocs/fsd0001/osti/2004/I0045881.pdf

[8] Crawford, C. L.; Bibler, N.E., **2005**, *Radiolytic Hydrogen Generation in Savannah River Site (SRS) High Level Waste Tanks – Comparison of SRS and Hanford Modeling Predictions*, American Institute of Chemical Engineers, Spring Conference. http://www.aiche.org/conferences/techprogram/paperdetail.asp?PaperID=773&DSN=spring05

Information Sharing (2004-5)

Publications:

1. "Comment on "Accurate Experimental Values for the Free Energies of Hydration of H^+, OH^-, and H_3O^+"," D. M. Camaioni and C. A. Schwerdtfeger, accepted for publication by *J. Phys. Chem. A.*
2. "EPR Detection of HNO_2^- in the Radiolysis of Aqueous Nitrite and Quantum Chemical Calculation of its Stability and Hyperfine Parameters," G. L. Hug, D. M. Camaioni, I. Carmichael, *J. Phys. Chem. A* **2004,** *108*, 6599-6604 (with EMSP project no. 73832).
3. "Thermochemistry of Aqueous Hydroxyl Radical from Advances in Photoacoustic Calorimetry and ab Initio Continuum Solvation Theory," T. Autrey, A. K. Brown, D. M. Camaioni, M. Dupuis, N. S. Foster, A. Getty, *J. Am. Chem. Soc.* **2004**, *126*, 3680-3681.

Presentations

1. "Mechanisms and Kinetics of Organic Aging and Characterization of Intermediates in High-Level Waste," D. Camaioni, EMSP High level Waste Principal Investigator Workshop, Savannah River, GA. http://srnl.doe.gov/emsp_news.htm
2. "Photoacoustic Calorimetry Studies of OH Radical in Aqueous Solution," (poster) Gordon Research Conference Photoacoustic & Photothermal Phenomena, T. Autrey, D. Camaioni, A. K. Brown, A. Getty, N. Foster, June 2005, Trieste, Italy.
3. "Experimental and Theoretical Investigation of Processes in the Radiolysis of Complex Aqueous Media," (poster) M. Dupuis, D. M. Camaioni, A. Furuhama, T. Autrey, A. K. Brown, and Q. Gilcrease, International Conference on Transient Chemical Structures in Dense Media. 14-16 march 2005, Paris, France
4. "Predicting Rates of Hydrogen Generation During Interim Storage and Treatment of Defense Nuclear Waste," (poster) D. M. Camaioni, D. J. Sherwood, and T. A. Hu, International Conference on Transient Chemical Structures in Dense Media. 14-16 March 2005, Paris, France.
5. "Using Variable Temperature Photoacoustic Calorimetry to Measure the H-OH Bond Dissociation Enthalpy of Water in Water," T. Autrey and D. Camaioni, 13th International Conference on Photoacoustic and Photothermal Phenomena, Rio de Janeiro, Brazil, July 5-8, 2004.

Reports in Collaboration with DOE Site Contractors:

1. *Gas Generation Testing and Support for the Hanford Waste Treatment and Immobilization Plant*, Bryan, S. A.; D. M. Camaioni, T. G. Levitskaia, B. K. McNamara, R. L. Sell, L. M. Stock. 2004. WTP-RPT-115 Rev. 0, Battelle, Pacific Northwest Laboratories, Richland, Washington.

Undergraduate Student Research Trainees

1. Aaron K. Brown, University of Washington, Seattle, Washington, Energy Research Undergraduate Fellow, summer 2004.
2. Quinn Gilcrease, Western Washington University, Bellingham, Washington, Science Undergraduate Laboratory Intern, summer 2004.
3. Christine Schwerdtfeger, University of Illinois at Urbana-Champaign, Science Undergraduate Laboratory Intern, summer 2005.