

SUMMARY/PROGRESS REPORT

Mechanisms and Kinetics of Organic Aging and Characterization of Intermediates in High Level Waste

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Research Objective

The objective of this project is to characterize significant chemical degradation pathways of organic chemicals in stored high-level waste and waste treatment streams. The underlying chemistries of high-level waste are 1) the chemistry initiated by radioactive decay and the reactions initiated by heat from radioactive decay and 2) the chemistry resulting from waste management, and treatment activities (e.g., waste transfers, concentration through evaporators, caustic and other chemical additions, and separations operations). Recognizing that experiments cannot reproduce every conceivable scenario, the project works to develop predictive computational models of these chemistries. The effort is closely coordinated with a Notre Dame Radiation Laboratory project (EMSP No. 73832, "The NO_x System in Nuclear Waste," D. Meisel, Principal Investigator) that focuses on radiolytically-induced degradation of organic complexants in waste simulants. Investigators combine experimental observations, electronic structure computations, and theoretical methods development to achieve this goal. The resulting models will facilitate accurate evaluation of the hazardous material generated, including flammable gases, and will support decision-making processes regarding safety, retrieval, treatment, and tank closure issues.

Research Progress and Implication

This project, now in its 5th year after being renewed in 2001, is presently focused on obtaining thermochemical properties and chemical kinetics of reaction intermediates for mechanism verification, structure/reactivity correlation, and prediction of reaction rates. At the start of the project, the investigators set out to model the thermal degradation of complexants in Hanford wastes. It was known that complexants with hydroxyl groups are thermally most reactive, nitrite ion is the oxidant, and some form of aluminum ion is a catalyst. A mechanism had been advanced by Ashby et al. (*ACS Sym Ser*, **1994**, 554, 247), in which aluminate ions catalyze the nitrosation of complexants. The resulting nitrite esters subsequently decompose to aldehydes,

which degrade to H₂ and carboxylate ions in the strongly alkaline wastes. However, while attempting to further elucidate this mechanism, the investigators obtained contradictory results (Camaioni and Autrey, *ACS Sym Ser*, **2000**, 778, 299). In a study of the decomposition of nitritoacetate (ONOCH₂CO₂⁻) in waste simulants, they determined that it hydrolyzes much faster than it decomposes to either glyoxal or formaldehyde. Furthermore, they observed that aluminate ion did not accelerate hydrolysis of nitritoacetate or ethyl nitrite, a model for HEDTA. These results suggest that aluminate ion cannot be in the rate-determining step of the Ashby mechanism. An alternative mechanism would first have Al(III) bind with glycolate anion and then have the complex react with nitrite ion. In this way, Al(III) would serve to lower the repulsive forces between nitrite and glycolate ions, as well as be a bridge for electron transfer. In addition, binding Al(III) to glycolate ion may activate it to undergo H-atom transfer to nitrite ion (induced homolysis). Novel methods to assess and accurately model these mechanisms for organic aging, as well as others, are now being developed by this project. Specifically, the project is 1) developing and applying Photoacoustic Calorimetry (PAC) for measuring aqueous thermochemistry and reaction kinetics of transient intermediates and 2) improving solute cavity definition in a dielectric continuum solvation model for the purpose of computing thermochemical properties of radicals and ions in aqueous solutions.

In addition to these fundamental investigations, the PI has interacted with Savannah River and Hanford site operators on site-specific issues. In FY2002, the PI helped prepare a report (PNNL-13935) that assessed the chemical stability of the solvent components to be used in the Caustic Side Solvent Exchange process to be used at the Savannah River Site. Currently, the PI is assisting the Bechtel Hanford Waste Treatment Research and Technology Department in addressing issues concerning H₂ generation by waste streams in the Hanford Waste Treatment and Immobilization Plant.

Thermodynamics and Kinetics of Aqueous 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 related to the heats, reaction volumes and rates of the induced reactions. The investigators have developed methods for recording the signals and resolving their time-dependent components so that reaction energies and kinetics can be determined. As a first step toward obtaining aqueous thermochemistry of organic radicals in water, they adapted the technique to use hydrogen peroxide as the photo-precursor and performed benchmark experiments. For H₂O₂(aq) → 2OH(aq), they measured $\Delta H_r = 195 \pm 6$ kJ/mol and $\Delta V_r = 6.6 \pm 0.4$ mL/mol. Using a Maxwell relation, $\Delta S_r = 4$ J/mol•K in water is estimated from the volume change such that $\Delta G_r^\circ = 194 \pm 6$ kJ/mol. Since the aqueous thermochemistry of H₂O₂ is known, the aqueous thermochemistry of OH radical is determined. The measurements yield $\Delta H_f^\circ = -1 \pm 6$ and $\Delta G_f^\circ = 31 \pm 6$ kJ/mol that are in agreement with literature estimates (e.g., Poskrebyshv et al. *J Phys Chem A*, **2002**, 106, 11488). The results provide confidence in the pulsed 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 Aqueous Solution. The investigators developed a new cavity definition protocol that yields accurate solvation energies and electrode potentials for selected oxoanions, XO_mⁿ⁻, including some for which other cavity protocols do not perform well enough (Camaioni, Dupuis and Bentley, *J. Phys. Chem. A*, **2003**, 107, 0000). In this

new definition scheme with cavities made up of interlocked atomic spheres, the radii are given by simple empirically-based expressions involving effective atomic charges of the solute atoms that fit the solute molecular electrostatic potential and a bond length-dependent factor to account for atomic size and hybridization. The scheme shows substantial qualitative differences with other previously proposed schemes, for example by assigning a large radius to the central atom of the oxoanions. This difference is put on a firm theoretical basis in the case of NO_3^- through an analysis of the molecular electrostatic potential of the NO_3^- and an analysis of its interaction with a 'solvent' water molecule (see Figure 1). Despite a large positive partial charge assigned to nitrogen in NO_3^- , the water 'solvent' molecule continues to act as an H-bond donor in the region of the central N-atom as a result of the electrostatic potential of the anion, although the water-nitrate interaction in that region is weaker than near the terminal-O atoms. From these results the investigators surmise that the solvent molecules remain further away from the nitrogen atom, a finding consistent with the large radius assigned by the new scheme for nitrogen. The same qualitative feature holds true for the ten oxoanions and six neutral oxides they considered.

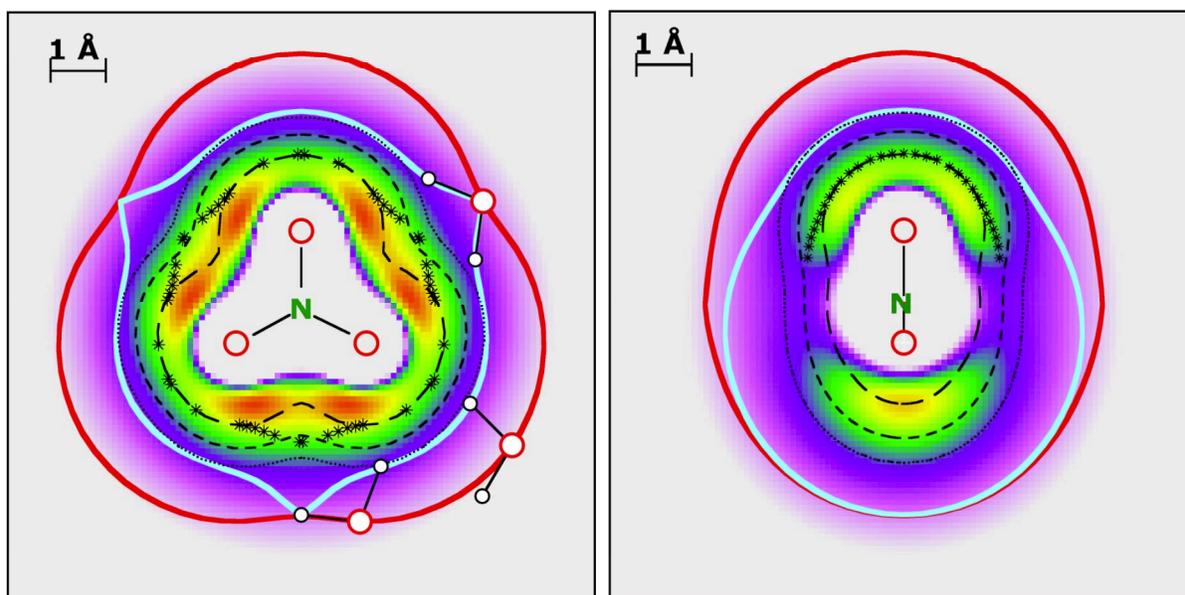


Figure 1: Colored-coded maps show electrostatic potential and electron density information for NO_3^- superimposed on $\text{H}_2\text{O}-\text{NO}_3^-$ minimum interaction energy contours. The analysis yields novel anion cavities for solvation models: (left) view of the molecular plane and (right) view of the plane perpendicular to the molecular plane along one N–O bond. Electron Isodensity contours values: $\cdots 5 \times 10^{-4}$, $--- 2 \times 10^{-3}$, $- - - 1 \times 10^{-2} e^-/\text{au}^3$; Electrostatic Isopotential contour values for unit positive test charge (kcal/mol): $\square \geq -75$, $\blacksquare -94$, $\blacksquare -113$, $\blacksquare -132$, $\blacksquare -151$, $\blacksquare -169$; * H-bond critical points; (red line) water-oxygen MIE surface; (blue line) water-hydrogen MIE surface. Reproduced from DM Camaioni, M Dupuis, and J Bentley, *J Phys Chem A*, **2003**, *107*, 0000. Copyright © 2003 American Chemical Society.

Planned Activities

Having established that the PAC technique measures the aqueous thermochemistry of hydroxyl radical, the investigators will apply the technique to obtain the thermochemistry for reactions of

OH radical with substrates. Preliminary work has been performed on the reactions with hydrogen peroxide and glycolate ion to give OOH and glycolate radicals, respectively. As this work concludes, work will start (in latter part of 2003) on obtaining results for radicals derived from Al(III) complexes of glycolate ion. The computational effort will expand the new protocol to include oxoanion systems with hydroxyl and alkyl groups and the applicability to multiply-charged anions will be investigated. The protocol will be used to compute properties of reaction intermediates.

Information Access

Publications:

“Theoretical characterization of oxoanion XO_m^{n-} solvation.” DM Camaioni, M Dupuis and J Bentley, *J. Phys. Chem.*, in press.

“Decomposition pathways for the Savannah River Site Caustic-Side Solvent Sxtraction System.” LM Stock, DM Camaioni, D Wester, and D Gutsche, 2002, PNNL-13935, Pacific Northwest National Laboratory, Richland, Washington.

Presentations:

“Radiolysis effects in high level waste; modeling the chemistry in waste tanks.” J Bentley, I Carmichael, DM Chipman, G Hug, D Meisel, DM Camaioni and M Dupuis, *Amer. Nuc. Soc. Spectrum Conference*, August 4-8, 2002, Reno, NV.

“Towards ab initio cavities for dielectric continuum solvation models.” M Dupuis, DM Camaioni, DM Chipman, and J Bentley, *224th American Chemical Society Meeting, Symposium on Classical and Quantum Statistical Mechanics Studies of Solvation*, August 18-24, 2002, Boston MA.

“The effects of organics and their aging products on gas generation.” DM Camaioni, *Meeting on Gas Generation Information Needs for the Waste Treatment Plant*, October 23, 2002, Richland, WA.

“Thermochemical property measurements of hydrogen peroxide and hydroxyl radical in aqueous solution.” T Autrey, D Camaioni, A Getty, A Brown, and N Foster, *15th Symposium on Thermophysical Properties*, June 23, 2003, Boulder, CO,

“Food for thought. Molecular volume changes in photoacoustic calorimetry, for the better not the worst.” T Autrey, *Gordon Research Conference on Photoacoustic and Photothermal Phenomena*, June 8, 2003, Colby-Sawyer College, New London, NH.

“Mechanisms and kinetics of organic aging and characterization of intermediates in high level waste.” DM Camaioni, T. Autrey, M. Dupuis, W. J. Shaw, *FY2003 EMSP Principal Investigator Workshop*, May 6-7, 2003, Richland, WA.

“Aqueous thermochemistry of radicals by pulsed photoacoustic calorimetry.” DM Camaioni, T Autrey, A Getty, A Brown, and N Foster, *39th IUPAC Congress and 86th Conference of the Canadian Society for Chemistry*, August 10-15, 2003, Ottawa, Canada.

“Modeling the chemistry in high-level waste tanks: Effects of radiation and heat on waste simulants,” DM Camaioni, M Dupuis, T Autrey, WJ Shaw, D Meisel, I. Carmichael, DM Chipman, GL Hug, and J Bentley, *226th American Chemical Society National Meeting*, September 7-11, 2003, New York, NY.