

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

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## Principal Investigator

Donald M. Camaioni  
Pacific Northwest National Laboratory  
P.O. Box 999, MSIN K2-57  
Richland, WA 99352  
509-375-2739 (phone)  
509-375-6660 (fax)  
[donald.camaioni@pnl.gov](mailto:donald.camaioni@pnl.gov)

## Co-Investigators

S. Tom Autrey  
Pacific Northwest National Laboratory  
P.O. Box 999, MSIN K2-57  
Richland, WA 99352  
509-375-3792 (phone)  
509-375-6660 (fax)  
[tom.autrey@pnl.gov](mailto:tom.autrey@pnl.gov)

Michel Dupuis  
Pacific Northwest National Laboratory  
P.O. Box 999, MSIN K8-91  
Richland, WA 99352  
509-376-4921 (phone)  
509-376-0420 (fax)  
[michel.dupuis@pnl.gov](mailto:michel.dupuis@pnl.gov)

Wendy Shaw  
Pacific Northwest National Laboratory  
P.O. Box 999, MSIN K2-57  
Richland, WA 99352  
509-375-5922 (phone)  
509-375-6660 (fax)  
[wendy.shaw@pnl.gov](mailto:wendy.shaw@pnl.gov)

## Research Objective

The objective of this project is to characterize significant chemical degradation pathways of organic chemicals in nuclear waste storage and treatment streams. The effort at Pacific Northwest National Laboratory (PNNL) is closely coordinated with a Notre Dame Radiation Laboratory project (EMSP No. 73832, "The NO<sub>x</sub> System in Nuclear Waste," D. Meisel, Principal Investigator) that focuses on radiolytically induced degradation of organic complexants. An understanding of the chemistry of the organic chemicals present in tank wastes is needed to manage the wastes and related site cleanup activities. 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 activities (waste transfers between tanks, concentration through evaporators, caustic and other chemical additions). Recognizing that experiments cannot reproduce every conceivable scenario, the PNNL and Notre Dame projects work to develop predictive computational models of these chemistries. Participants in both projects combine experimental observations, electronic structure computations, and theoretical methods developed to achieve this goal. The resulting model will provide an accurate evaluation of the hazardous material generated, including flammable gases, and will support decision-making processes regarding safety, retrieval, and treatment issues. The utility of developing an understanding of tank chemistry has been demonstrated in earlier work. None of the Hanford tanks is currently on a watch list, partially due to predictive understanding of organic aging and flammable gas generation that resulted from previous research. Furthermore, concerns that arise from pretreatment and tank closure issues (e.g., Tc speciation) may be rationalized with the mechanistic knowledge provided by these projects.

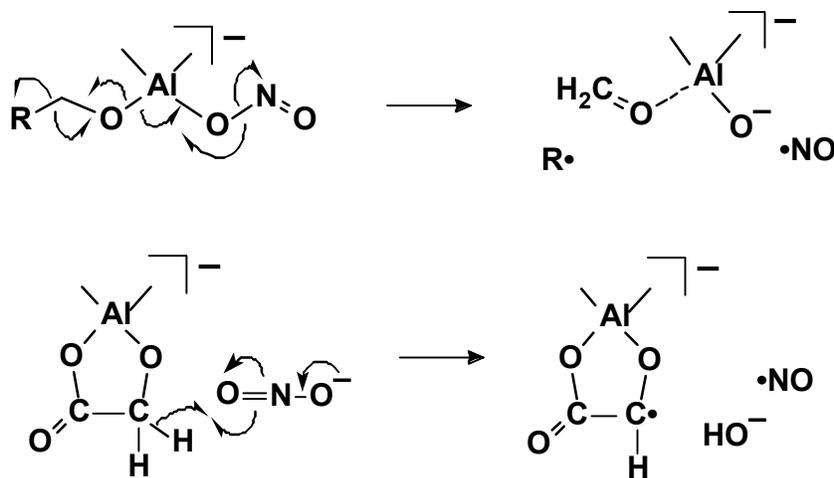
## Research Progress and Implications

At this stage of the project, which is in its fourth year after being renewed in 2001, we are obtaining data on the thermochemical properties and chemical kinetics of reaction intermediates for mechanism verification, structure/reactivity correlation, and reaction-rate prediction. Specifically, the project is 1) developing and applying photoacoustic calorimetry (PAC) for measuring aqueous thermochemistry and reaction kinetics of transient intermediates and 2) improving solvation models for use in computing the thermochemical properties of radicals and ions in aqueous solutions.

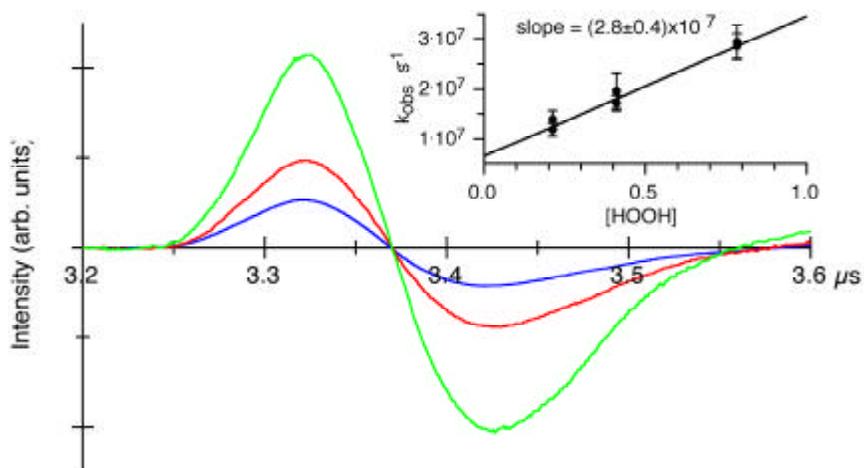
## Thermodynamics and Kinetics of Aqueous Intermediates

Complexants with hydroxyl groups are thermally the most reactive constituents in Hanford wastes. Nitrite ions also are required, and aluminate ions act as catalysts. The role of Al(III) may be to bind glycolate and nitrite anions, thereby lowering the coulombic contribution to the

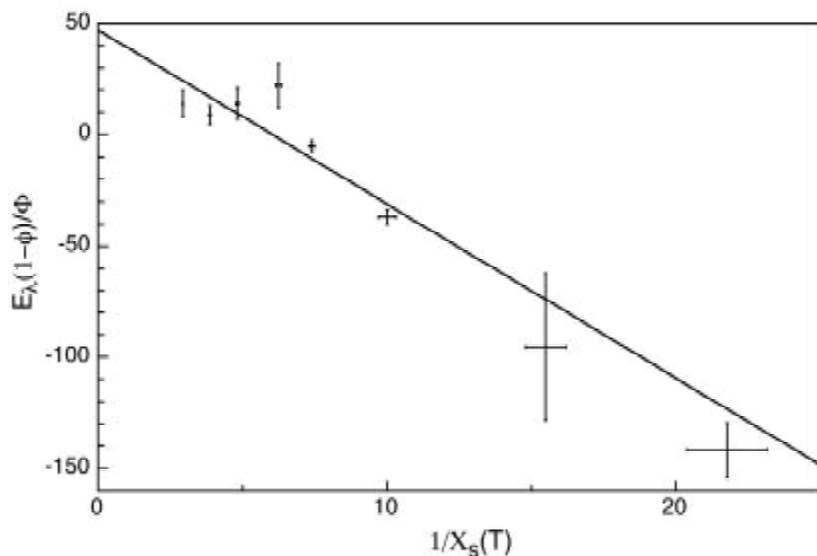
reaction barrier. In this way, Al serves as a bridge for electron transfer. Alternatively, or in addition, Al binding of the organic complexant may activate glycolate ions to undergo an H-atom transfer to nitrite. Suggested mechanisms for this reaction are shown in Figure 1. To assess these possibilities, the investigators are using PAC to measure the thermochemical and kinetic properties of the glycolate ion and its metal ion complexes in aqueous solutions. 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 relatable to the heats, reaction volumes, and rates of the induced reactions. The investigators have developed methods for recording the signals and for resolving their time-dependent components so that reaction kinetics, reaction heats, and reaction volumes can be obtained. We are adapting the technique to use hydrogen peroxide as the photo precursor, and some benchmark experiments have been performed. Example determinations of the O-O bond dissociation energy of  $\text{H}_2\text{O}_2$ , and the rate constants for reaction of OH with  $\text{H}_2\text{O}_2$  and with sodium glycolate are shown in Figures 2 through 4. The adapted technique provides an alternative to optical kinetic methods for measuring equilibrium constants and potentially could provide both enthalpy and free energies of proton transfer and electron transfer equilibria, and ultimately, solvation energies.



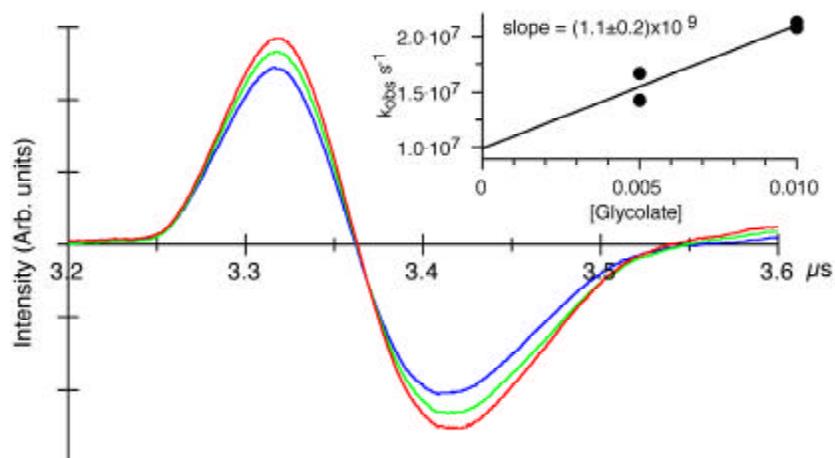
**Figure 1.** Suggested mechanism for Al(III)-catalyzed oxidation of glycolate ( $\text{R} = \text{CO}_2^-$ ), HEDTA ( $\text{R} = \text{CH}_2\text{N}(\text{CH}_2\text{CO}_2^-)\text{CH}_2\text{-CH}_2\text{N}(\text{CH}_2\text{CO}_2^-)_2$ ), and related structures by nitrite ion. The reactions are being studied to understand flammable gas generation and evolution of organic compounds over time. Aldehydes produced in these reactions degrade in caustic solutions to formate and oxalate ions and  $\text{H}_2$  gas and condense with enolizable compounds to make larger adducts. Nitroso compounds from combination of R and NO radicals decompose to ammonia and  $\text{N}_2\text{O}$  gases.



**Figure 2.** Acoustic signal from 308-nm pulsed laser light absorbed by aqueous  $\text{H}_2\text{O}_2$  (— 0.2 M, — 0.4 M, — 0.8 M). The signal increases with concentration of  $\text{H}_2\text{O}_2$  and shifts to longer time due to the exothermic reaction  $\text{HO} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{H}^+$ . The inset shows observed pseudo first-order rate constant extracted from the traces plotted against concentration of peroxide. The slope of the line yields the second-order reaction rate constant.



**Figure 3.** Photoacoustic signals, such as in Figure 2, are related to the changes in heat and volume associated with chemical reactions that occur within the time constant of the piezoelectric detector. The contributions add according to the equation,  $E_\lambda(1-\phi)/\Phi = DH^\circ(\text{aq}) - \Delta V_r/\chi_s(T)$ , where  $E_\lambda(1-\phi)/\Phi$  is the apparent heat released to the solution by photodissociation of  $\text{H}_2\text{O}_2$ ,  $DH^\circ$  is the bond dissociation energy of  $\text{H}_2\text{O}_2$ ,  $\Delta V_r$  is the solution volume change for  $\text{H}_2\text{O}_2$  dissociation, and  $\chi_s(T)$  is a function of the thermoelastic properties of water. The plot shows a least square fit to the  $E$  vs  $\chi_s(T)$  for data obtained over a temperature range of 8–35°C yielding  $DH^\circ(\text{aq}) = 47 \pm 5$  kcal/mol and  $\Delta V_r = 7.8 \pm 0.6$  ml/mol.

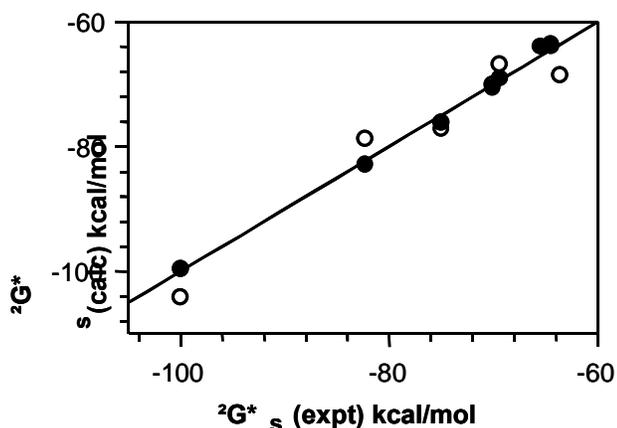


**Figure 4.** Photoacoustic signals from 0.2-M  $\text{H}_2\text{O}_2$  solutions containing 0 (—), 5 (—), and 10 (—) mM sodium glycolate. Deconvolution of the time dependence of the signal gives the pseudo-first order rate constant for reactions of HO radical. The inset shows a plot and least squares fit of the observed first-order rate constant vs. glycolate concentration. The slope equals the second-order rate constant for reaction with glycolate and the intercept equals the reaction with  $\text{H}_2\text{O}_2$  plus other background reactions. Rate constants agree with values found in the literature.

## Theoretical Characterization of Intermediates in Aqueous Solution

Mathematical models of solvation based on a dielectric continuum representation of the solvent combined with Molecular Orbital and Density Functional electronic structure theories are available. These models can be used to calculate free energies of solvation for solutes in various solvents so that thermochemical properties, such as acidity ( $K_a$ ), redox potentials ( $E^\circ$ ), and reaction energies ( $\Delta H$  and  $\Delta G$ ) can be determined. These methods are useful because they provide structural and energetics data that aid in verification of a reaction mechanism. Furthermore, the accuracy of computational methods is approaching that of experimental methods so a computational approach may be used when experimental data are either not available or are too difficult and expensive to obtain. A survey of various methods that can be used for computing aqueous solvation energies of molecules and ions and benchmark calculations using the methods were performed. These studies were necessary because few radical and zwitterion radical species usually are included in the evaluation sets used in the development of the methods. The work uses solvation models based on a continuum dielectric representation of the solvent with the solute molecule located within a molecule-shaped cavity embedded in the continuum. In these models, the interaction of the solute with the solvent is simulated by means of effective charges induced by the solute electron density at the cavity boundary. Thus, the shape and size of the cavity determines the strength of the interaction and, consequently, the magnitude of the solvation energy. The results of our benchmark comparisons of experimental and calculated data indicate that anions are not well represented by most

standard dielectric continuum models. Therefore, a powerful semi-empirical protocol that allows computational results to be directly equated with experimental measurements and a correlation of cavity shape with quantum mechanical descriptors was developed. The resulting methodology generates cavity shapes that capture the physics of anion-water interactions and reproduce anion hydration energies better than other methods [e.g., the United Atom Hartree Fock (UAHF) method (see Figure 5)]. Unlike the UAHF and other methods, our approach does not require knowledge of empirical parameters, such as the Van der Waals radii, or the hybridization of atoms.



**Figure 5.** Predicted Gibbs Hydration Free Energies for the Ions in Table 1 Plotted Against the Experimental Values: Open Circles - UAHF Radii Solid Circles - Radii Predicted by Quantum Descriptors, X-O Bond Distance and Potential-Derived Atomic (CHELPG) charges.

**Table 1.** Gibb's Free Energies of Hydration and Quantum Descriptors (Cavity Radii, Bond Distance, and Atomic Charges) That Reproduce the Energies Using the Gaussian 98 COSMO-Polarizable Continuum Model of Solvation

Species	$-\Delta G_s^*$ kcal/mol	$R_O$ Å	$D_{X-O}^{(a)}$ Å	$R_X$ Å	$Q_X^{(a)}$
$O^-$	100	1.46			
$O_2^-$	82	1.56			
$O_3^-$	70	1.59	1.352	2.12	0.076
$NO_2^-$	69	1.6	1.264	2.04	-0.087
$HCO_2^{-(b)}$	75	1.47	1.252	2.19	0.860
$NO_3^-$	65	1.53	1.260	2.42	1.180
$ClO_2^-$	64	1.53	1.634	2.71	0.432

(a) B3LYP/6-311+G\*\* CHELPG charges.  
(b) X = C-H group.

## Planned Activities

Our development and benchmarking of experimental and theoretical methods will continue. The experimental effort on applying the PAC technique in aqueous solution will focus on increasing the accuracy of heat measurements and on titrating the  $pK_a$  of OOH and glycolate radicals to determine the potential for measuring  $\Delta H$  and  $\Delta G$  for proton transfer. We then will initiate efforts to obtain results for Al complexes of glycolate. In our computational effort, we will develop quantum-descriptors for radii of hydroxyl and alkyl groups in oxoanions and for multiply charged oxyanions. Also, the solvation model will be used to characterize properties of species outside the training set as well as ones of interest to project objectives. Three manuscripts will be prepared and submitted.

## Information Access

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