

Mechanisms and Kinetics of Organic Aging in High-Level Waste

(Project Number: 65408)

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Research Objective

The objective is to develop predictive models of organic degradation in high-level wastes (HLW). We make this information available to facility operators on the Hanford Site to support decision-making processes regarding safety, retrieval, and treatment issues. Emphasis is placed on the aging of organic complexants because they have direct impacts on safety issues such as the organic/nitrate salt and flammable gas problems. They also affect waste treatment efforts to separate radionuclides and reduce the volume of HLW.

Research Progress and Implications

This project, now in its third year, studies thermally- and radiolytically-induced reactions of organic compounds in waste simulants. The work on radiolytically induced reactions is coordinated closely with an EMSP project at the Notre Dame Radiation Laboratory. Together, we also explore the use of computational chemistry to characterize solution properties of intermediates in HLW.

Thermally Induced Organic Aging

At the start of the project, it was known that complexants with hydroxyl groups are thermally most reactive, nitrite ion is required, and aluminate is a catalyst. Other researchers have advanced a mechanism in which a nitritoaluminate species, e.g., $\text{ONOAl}(\text{HO})_3^-$, catalyzes nitrosation of hydroxyl groups [$\text{ROH} + \text{ONOAl}(\text{HO})_3^- \rightarrow \text{RONO} + \text{Al}(\text{OH}^-)_4$] and the resulting nitrite ester decomposes to precursors of H_2 and N_2O . We set out to measure the kinetics of aluminate catalysis of the reverse reaction, nitrosyl transfer from RONO to OH^- , but found none. Subsequent work investigated the extent to which nitritoacetate degrades to gas precursors and ultimately to formate and oxalate at 60° and 90°C . This is key test of the nitrite ester mechanism because the kinetic order of aluminate ion in the rate law requires decomposition to be approximately 5 times faster than hydrolysis.

The results show that decomposition of nitritoacetate to gas precursors cannot be faster than hydrolysis, even at elevated temperatures. Therefore, organic nitrite esters and nitritoaluminates seem unlikely intermediates in the thermal reactions of complexants in the tank wastes, and alternative mechanisms must be considered. We suggest that the role of $\text{Al}(\text{III})$ may be to bind the charged glycolate dianion and nitrite anion, thereby lowering the coulombic contribution to the reaction barrier (Figure 1). In this way, Al serves as a bridge for electron transfer. Alternatively, or in addition, Al binding of the organic complexant may activate adjacent C-H and C-C bonds (Figure 1).

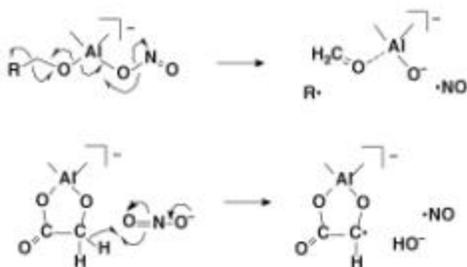


Figure 1. Role of Aluminate in Catalyzing Oxidations of Complexants by Nitrite: $R = \text{CO}_2^-$, or $\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2^-)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2^-)_2$

Kinetic Simulation of Radiolytically Induced Reactions

This work was performed in collaboration with the EMSP project at Notre Dame Radiation Laboratory and the Waste Tank Safety Program at Hanford. The underlying premise of the Notre Dame project is that the dominant radical in the irradiated HLW is the NO_2 radical. This premise was verified early, and work since has focused on measuring rate constants, elucidating mechanisms for formation of NO_2 and for its reactions with organic complexants, and modeling the overall kinetics. We contribute to the modeling effort under this project because our overall goal is to develop combined thermal and radiolytic predictive kinetics models.

Our collaboration led to a discovery that the strongly reducing radical, NO_3^{2-} , is produced by the strongly oxidizing O^- radical ($\text{NO}_2^- + \text{O}^- \rightarrow \text{NO}_3^{2-}$) that is a major water-fragmentation product at high pH typical for HLW. Prior to this discovery, O^- was believed to react only via electron transfer leading to NO_2 directly. This observation highlights the delicate balance between reducing and oxidizing reactions in HLW. The work involved fitting a complex multistep mechanism to the time-resolved electron spin resonance signal for NO_3^{2-} . Because most of the rate constants were known, it was possible to fit the kinetic behavior and derive a rate constant. We then extended the model to explain results for radiolysis of formate in HLW simulants. A useful feature of the model is that it allows extrapolation of results obtained from high-dose-rate laboratory studies to lower-dose-rate conditions typical of actual wastes.

Theoretical Characterization of Intermediates

A survey and benchmark calculations of methods for computing aqueous properties of molecules and ions were performed. Benchmark studies were deemed necessary because few radical and zwitterion radical species are usually included in the evaluation sets used in the development of these methods. We used solvation models based on a continuum dielectric representation of the solvent with the solute molecule inside a molecule-shaped cavity embedded in the continuum. In these models, the interaction of the solute with the solvent is modeled by means of effective charges induced by the solute electron density at the cavity boundary.

An important outcome of our benchmark comparisons of experiment and theory has been the development of a powerful *semi-empirical* protocol that allows computational results to be equated directly with experimental measurements. This protocol relies on accurate semi-empirical estimates of the free energy of a proton in water, of a hydroxide ion in water, and for

the standard hydrogen electrode. These two ions are known to be difficult to theoretically characterize because of their strong interaction with the solvent. Using *semi-empirical estimates* of their solvation free energies circumvents these difficulties. When combined with *calculated* solvation energies of a given species, these estimates lead to a direct correlation between the cavity radii and the experimental acidities or half-reaction potentials. This correlation puts us in a position to determine species-specific radii that reproduce experimental reaction energies for reactions involving these selected species. Although these species-specific radii may not be universally transferable, we believe that this protocol will provide a path to predicting accurately the chemistry of many species important to the redox chemistry in the HLW.

Planned Activities

In the remaining months of the current project, we will continue to investigate the role of Al in the thermally initiated organic aging and calibrate the computational solvation model to predict aqueous properties of oxoanions. A renewal proposal has been submitted. Under the renewal, we would extend the computational models to predict aqueous properties of organic complexes of technetium and its oxoanions in response to Hanford Site needs to understand the distribution of soluble technetium species in wastes.

Information Access

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