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Mechanisms and Kinetics of Organic Aging in High-Level Wastes

Summary/Progress Report

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Research Objective

The goal of this project is to develop a fundamental understanding of organic aging and to assemble a model that describes and predicts the thermal and radiolytic aging of organic compounds in high-level wastes (HLW). To reach this goal, we will measure kinetics and elucidate products and mechanisms of organic reactions occurring under conditions of waste storage, retrieval, and processing. Initial emphasis will be placed on studying thermal effects, because organic reaction mechanisms and effects of varying conditions are uncertain, and because we benefit from collaborations with earlier Environmental Management Science Program (EMSP) projects that have worked on radiation effects. Organic complexants are of greatest concern regarding both safety and pretreatment because they have been found to degrade to gases, combust in dry wastes, and interfere with radionuclide separations. Therefore, efforts will focus on studying the reactions of these organic chemicals and associated degradation products.

In preliminary work, the authors have used mechanistic kinetic modeling techniques to successfully model the radiolytic degradation of formate to carbonate in HLW simulants. The research will continue development of the model using an iterative process that measures degradation products and kinetics of increasingly complex molecules while adapting the model to reproduce the results each step of the way. Several mechanistic probe experiments have been designed to learn the fundamental mechanisms that operate during thermal degradations so that thermal and radiolytic processes may be integrated within the model. Key kinetic data and thermodynamic properties relating to thermal reactivity will also be acquired so that rate-controlling and product-forming reactions can be predicted. Thermochemical properties of key intermediates will be experimentally and/or theoretically determined to facilitate mechanism verification, structure/reactivity correlation, and prediction of reaction rates.

We expect a comprehensive understanding of organic reactivity in HLW will accrue from the work. This understanding will be embodied in organic reaction models capable of predicting distributions of species, including gases, with respect to time, temperature, and radiation history. These models will assist waste management decisions by predicting impacts of organic chemicals on safe storage, waste retrieval, and pretreatment of HLW.

Problem Statement

Uranium and plutonium production at the Hanford and Savannah River Sites produced large quantities of radioactive byproducts and contaminated process chemicals that are stored in underground tanks awaiting treatment and disposal. Scientific information is needed to support decisions and issue resolutions for safe, effective, and efficient waste storage and processing activities, including development of the Hanford Phase II privatization request for proposals (Foreman 1998a, b). Tanks that contain organic process chemicals have many issues, including the following:

- If allowed to dry out, wastes can be at risk for fuel-nitrate deflagration accidents (Meacham et al. 1998).
- The generation of flammable gases by organic-containing wastes is a major safety concern. Radiolytic and thermochemical processes degrade (“age”) organic solutes into smaller fragments of lower energy content, thereby reducing the hazard, while contributing to the generation of toxic, flammable and potentially explosive gases (i.e., volatile organic chemicals, NH_3 , H_2 , and N_2O) (Meisel et al. 1993; Ashby et al. 1994; Camaioni et al. 1998).

- Aging of organic chemicals also produces toxic volatile organic vapors. Release of these vapors by the wastes causes concern for the health and safety of personnel working about the waste tanks.
- Changing waste storage conditions may alter organic aging to increase gas and organic vapor production. However, changes that accelerate aging of organic complexants also decrease the potential for combustion reactions and facilitate separation of radionuclides.
- Organic complexants in wastes interfere with radionuclide separation and affect the subsurface transport characteristics of metal ions. Partitioning of radionuclides between the liquid and solid phases in the waste is hindered by organic complexants present in the wastes. The complexation of radionuclides must be controlled to separate the waste into high- and low-level fractions effectively. This may entail destroying the complexants or removing the dissolved radionuclides using advanced separation processes.

Organic reactions induced by heat and radiation need to be studied to assess hazards, better understand methods for organic destruction, and be able to predict rates of production of gases in the wastes. The studies should include organic chemicals that were added to tank wastes and their aging products as well as organic chemicals and materials that may be used in processing the wastes.

Research Progress

In this first year of the project, we have developed a broadly applicable approach to obtaining kinetic and thermochemical measurements of nitrite ester reactions, especially those derived from organic complexants (e.g., glycolic acid, hydroxyethylethylenediaminetriacetic acid [HETDA], citric acid). The approach takes advantage of the facile exchange reactions that occur between nitrite esters and alcohols. By measuring the effects of added substrate on reaction rates, we extract absolute rate constants for generation and reaction of nitrite esters derived from complexants and their thermodynamic stabilities. In the sections that follow, we provide background to specific problems on which we are working and report progress to date.

Background

The major complexants used in Hanford nuclear materials processing were the sodium salts of N-(2-hydroxyethyl) ethylenediaminetetraacetic acid (HEDTA), glycolic acid, ethylenediaminetetraacetic acid (EDTA), and citric acid (Meacham et al. 1998). Of these, only HEDTA and glycolate ion are readily oxidized by thermally activated reactions to give flammable gases (Ashby et al. 1994). EDTA, which is structurally quite similar to HEDTA, is relatively unreactive (Delegard 1987; Ashby et al. 1994; Camaioni et al. 1998). Nitrite ion appears to supply the oxidizing equivalents for thermal oxidation. Aluminate ions, or other aluminum species, are catalysts, and hydroxide ion promotes the oxidation (Delagard 1980, 1987; Ashby et al. 1994).

Products from HEDTA include oxalate, formate, carbonate, ethylenediaminetriacetate, nitrogenous gases (N_2 and N_2O), and H_2 (Ashby et al. 1994; Barefield et al. 1996; Camaioni et al. 1998). Glycolate ion gives formate, oxalate, carbonate, and the gases as well (Ashby et al. 1994; Barefield et al. 1995). Mechanisms and rate controlling steps are poorly understood. Barefield et al. (1995, 1996) and Ashby et al. (1994) hypothesize that the reactions occur as depicted in Equations 1 and 2, where $R = (^-O_2CCH_2)_2NCH_2CH_2N(CO_2^-)CH_2$ and CO_2^- .

Reaction 1 is endothermic, and activation barriers for the reverse, Reaction -1 (alkaline hydrolysis), are relatively large (Oae et al. 1978). Even in molar hydroxide solutions, hydrolyses of alkyl nitrites occur slowly. Thus Reaction 1 is very unfavorable in alkaline conditions such as those encountered in Hanford tank wastes. Accordingly, it has been suggested that $\text{Al}(\text{OH})_4^-$ serves to catalyze Reaction 1 (see Figure 1) (Ashby et al. 1994; Barefield et al. 1996).

Alkyl nitrite esters may undergo internal redox reactions (Equation 3) to give NO^- and ketone/aldehyde products competitively with hydrolysis:

Reaction 3 was shown to occur quantitatively in basic anhydrous media by Friedman and Bayless (1969). They observed that 2-methylpentyl nitrite yielded N_2O and 2-methylpentanal when reacted with sodium *t*-amyloxide in *t*-amyl alcohol. This type of reaction has been proposed by Ashby et al. (1994) to explain the formation of oxalate during thermal decomposition of methyl nitrosyloxyacetate in aqueous hydroxide solutions. However, product studies by Oae et al. (1978) of reactions of benzyl nitrite and phenylethyl nitrite in 0.1 M HO^- showed quantitative conversion to hydrolysis products, benzyl alcohol, and phenylethyl alcohol (no benzaldehyde or phenethylaldehyde were observed). Thus, Reactions 1-3 are not understood well enough to predict the outcome for simple alkyl nitrites, let alone for more functionalized structures involving glycolate and HEDTA.

To test the hypothesis expressed in Figure 1 and obtain predictive reaction parameters, we are measuring the rates of alkaline hydrolysis of nitrosyloxyacetate ion (nitrite ester of glycolate ion) in the presence and absence of $\text{NaAl}(\text{OH})_4$. In the sections that follow, we report on 1) the reactions of ethyl nitrite in alkaline solutions, 2) nitrosyl exchange reactions between simple alkyl nitrite esters and glycolate ion, and 3) kinetic measurements of the effect of glycolate ion on the hydrolysis of ethyl nitrite.

Hydrolysis and Internal Redox Reactions of Ethyl Nitrite

We opened our investigations by revisiting the reactions of alkyl nitrites in sodium hydroxide solution as a preliminary step toward studying nitrite esters of complexants. Figure 1 shows absorbance spectra recorded during and after decomposition of EtONO in sodium hydroxide solution and the expected products for Reactions 1 and 3.

Figure 1. Potential Energy Diagram Showing How $\text{Al}(\text{OH})_4^-$ May Catalyze Oxidation of Glycolate and HEDTA (Ashby et al. 1994)

At the end of the reaction, the nitrite ester absorbance bands have disappeared to be replaced by nitrite ion (355 nm) and aldehyde (275 nm) bands. Neither sodium nitrite (see Figure 2) nor ethanol exhibits a maximum at 275 nm. However, acetaldehyde (Figure 2) does absorb at this wavelength and, as discussed above, could be produced as shown in Reaction 3 ($\text{R} = \text{H}$). The spectra taken after alkaline hydrolysis provide evidence for a competition between Reactions -1 and 3 for EtONO at ambient temperatures.

This is an important finding; the observation of products from competing reactions justifies further work into acquiring rate constants for reactions such as Equation 3. These results will provide the necessary thermochemical kinetic data to develop a model for thermal degradation of organic complexants in HLW.

Nitrosyl Exchange Reactions

Doyle et al. (1983) measured the rates of hydrolysis of a series of alkyl nitrites and examined the nitrosyl exchange reactions with *t*-BuONO with a series of aliphatic alcohols, as in Equation 4.

They found that equilibrium constants for reactions of primary alkanols with *t*-BuONO are uniformly near 10. The rate of exchange occurred within 1 minute at room temperature. For primary alcohols containing β electron withdrawing groups, e.g., 2-ethoxyethyl nitrite, *K* decreased to 5.8. Given these favorable equilibria, *t*-BuONO has been used to synthesize a variety of nitrite esters.

Figure 2. Absorbance Spectra of Ethyl Nitrite at Start (—) and Completion (— · —) of Alkaline Hydrolysis Reaction Compared with Spectra for NaNO₂ (- - -) and for Acetaldehyde (.....)

Exchange equilibrium constants (K_4) for glycolate ion, methyl glycolate, and ethanol reacting with *t*-BuONO were determined by ^1H -NMR spectroscopy. Measurements for EtOH and methyl glycolate were obtained in CDCl_3 solvent. The measurement for glycolate ion was made in DMSO-d_6 solvent. The protons attached to the carbon adjacent to the nitrosyl group are slightly broadened and shifted downfield from the protons attached to the carbon adjacent to the hydroxyl group by approximately δ 1 – 1.1 ppm. The fractions, $[\text{RONO}]/[\text{ROH}]$ and $[\text{t-BuOH}]/[\text{t-BuONO}]$, were determined from the normalized integrated areas of the ^1H -NMR resonances. The product of these equate to the equilibrium constant for exchange values, and K_5 for any alcohol with *t*-BuONO can be determined according to Equation 5:

$$K_4 = \frac{[\text{t-BuOH}][\text{RONO}]}{[\text{t-BuONO}][\text{ROH}]} \quad (5)$$

Using this method, we obtain $K_4 = 9.8$ for *t*-BuONO reacting with EtOH. The literature value is 10.6 (Doyle et al. 1983). For *t*-BuONO reacting with methyl glycolate in CDCl_3 and with sodium glycolate in DMSO-d_6 , we obtain $K_4 = 0.15$. The equilibrium constant for exchange between EtONO and sodium glycolate is about 0.015. The observation that the equilibrium constant is much less than unity shows that nitrosyloxyacetate ion is much less stable than simple alkyl nitrite esters. Using Equation 6, we calculate that nitrosyloxyacetate is 2.5 kcal/mol less stable than ethyl nitrite:

$$\Delta G = -RT\ln(K_4) \quad (6)$$

The exchange equilibrium constant provides a direct measure of the relative stability of nitrite esters. In addition to the thermodynamic data obtainable by nuclear magnetic resonance (NMR) spectroscopy, kinetic analysis of the equilibrium mixtures will provide rate constants for base-induced decomposition of unstable, difficult-to-prepare nitrite esters.

Effect of Glycolate Ion on the Alkaline Hydrolysis of Ethyl Nitrite

There is no report in the literature for the synthesis and isolation of the nitrosyloxyacetate ion. Kornblum (1956) prepared ethyl nitrosyloxyacetate and found that hydrolysis to ethyl glycolate occurred within a few seconds at room temperature. We prepared nitrosyloxyacetate ion and nitrosyloxyacetic acid in situ by reacting sodium nitrite with glycolic acid in the presence of a drying agent in dimethyl sulfoxide (DMSO) and by reacting glycolic acid with *t*-BuONO in DMSO. Identifications were made by proton NMR, which showed the appearance of a new methylene resonance ($\delta \sim 5.1$ ppm) downfield from the methylene resonance ($\delta \sim 4$ ppm) of glycolate ion/glycolic acid. Nitrosyloxyacetate ion hydrolyzed within seconds on mixing with water, aqueous sodium carbonate, or 0.1 M NaOH. The absorbance spectra recorded after mixing showed only the characteristic nitrite ion band at 355 nm. Clearly, the nitrosyloxyacetate ion is less stable than alkyl nitrite esters and more reactive toward hydrolysis. Because the equilibrium constants for nitrosyl exchange and rate constants for hydrolysis of ethyl nitrite are readily measured, we take the approach of measuring the effect of glycolate ion on the hydrolysis kinetics of ethyl nitrite. Preliminary results already provide new thermochemical kinetic data and insight to the potential energy surface for formation and reaction of the nitrosyloxyacetate ion.

Figure 3 shows absorbance at 355 nm of aqueous alkaline EtONO solutions (2 M HO^- , room temperature, 33% DMSO) as a function of time in the presence and absence of glycolate. The absorbance decays by a first-order kinetic process giving satisfactory fits to Equation 7:

$$A_t = (A_o - A_\infty)e^{-k_{\text{OH}}[\text{HO}^-]t} + A_\infty \quad (7)$$

where A_{∞} is the absorbance due to sodium nitrite at completion of hydrolysis.

Figure 3. Lifetime of Ethyl Nitrite in 2 M NaOH is *Shorter* When Glycolate Ion is Present than When it is Absent: $\tau = 2170$ s, 0.01 M EtONO; $\tau = 366$ s with 0.009 M EtONO and 0.65 M Glycolate Ion. Solutions are 33 vol% DMSO/water with ~ 0.09 M EtOH at start. Absorbance measured at 355 nm.

When glycolate ion is present at 0.65 M, the lifetime of EtONO is much shorter, suggesting that a reaction system such as Scheme 1 is operating.

Scheme 1. Mechanism for Promotion Alkaline Hydrolysis of Ethyl Nitrite by Glycolate Ion: Steps *b* and *c* are Faster than Step *a*

Given that the reaction in the presence of glycolate follows first-order kinetics, nitrosyl transfer (step *b* in Scheme 1) must be rate-limiting under the reaction conditions. If step *c* were rate-limiting, then a more complex time-dependence would be observed. Analysis of the experimental data leads to rate constants, as shown in Table 1.

Table 1. Rate Constants and Estimated Free Energies for Reactions in Scheme 1

Rxn Step	k $M^{-1} s^{-1}$	$\bullet G^\ddagger$ kcal/mol	$\bullet G^\circ$ kcal/mol
<i>a</i>	2.3×10^{-4}	23.9 ^(a)	-17.4 ^(b)
<i>b</i> ^(c)	3.49×10^{-3}	22.2	2.8
<i>c</i> ^(c)	$\bullet 0.2$	$\bullet 19.8$	-20.2

(a) Oae et al. 1978.

(b) Alred et al. 1982.

The rate constant for nitrosyl transfer step *b* is more than 10 times larger than EtONO alkaline hydrolysis step *a*. The rate constant for alkaline hydrolysis of nitrosyloxyacetate ion is more than 1000 times larger than the rate constant for EtONO hydrolysis. These rate data have been converted to free energies of activation and are included in Table 1 with corresponding reaction free energies. Figure 4 depicts the potential energy diagram based on data given in Table 1. Consistent with the observed kinetic behavior, the transition state for nitrosyl transfer and nitrosyloxyacetate hydrolysis are lower in energy than the transition state for EtONO hydrolysis. Therefore, addition of glycolate ion accelerates hydrolysis of EtONO even though formation of nitrosyloxyacetate ion is endergonic by ca. 2.5 kcal/mol.

Figure 4. Free-Energy Diagram for Alkaline Hydrolysis of Ethyl Nitrite Promoted by Glycolate Ion. Barriers for reaction of EtONO going to the right are lower than the barrier for reaction with hydroxide ion such that glycolate ion promotes EtONO hydrolysis.

The rate constant we obtained for alkaline hydrolysis of EtONO at 25°C is ca. 2.5 times faster than that observed by Oae et al. (1978) for n-butyl nitrite at 35°C in 60% dioxane/water. The faster reaction may be due to the use of a different solvent system or possibly the participation of Reaction 3 at the higher hydroxide concentrations we used. The short lifetime ($\bullet$ 5 seconds) for nitrosyloxyacetate ion in alkaline solution is an interesting observation to consider. The result requires decomposition Reactions 8 and 9 to be comparably rapid if they are to compete according to the mechanism originally envisioned (Figure 1), in which nitrosation of glycolate ion is catalyzed by aluminate ion.

The energy of the transition state leading to the formation of nitrosyloxyacetate from glycolate ion and sodium nitrite is an upper limit (see Figure 4). If the energy is much lower, then it may be feasible to generate the nitrosyloxyacetate without having to invoke aluminate catalysis, as proposed in Figure 1. Therefore, we must consider the possibility that aluminate ion catalyzes Reactions 8 and 9 instead of Reaction 1. We are in the process of determining whether aluminate may accelerate alkaline hydrolysis of EtONO and nitrosyloxyacetate ion.

Planned Activities

The research planned for the coming year will continue the current investigations into thermal oxidation mechanisms of glycolate ion. We will alter conditions in subsequent experiments to make step *c* in Scheme 1 rate-limiting so that accurate rate data for this reaction may be obtained. For example, lowering the hydroxide ion concentration, increasing the glycolate ion concentration, and/or lowering the ethanol concentration may cause step *c* to be rate-limiting. Kinetic measurements will be made at different temperatures to determine thermochemical kinetic parameters for nitrosyl transfer, nitrite ester hydrolysis, and elimination of NO^- . Also, we will perform measurements in the presence and absence of aluminate to determine catalytic effects. Investigation of the analogous system based on HEDTA will also begin. Preliminary results suggest aluminate has little effect on hydrolysis of EtONO. If this is true and subsequent experiments do not show aluminate to catalyze Reactions 8 and 9, then we will abandon the hypothesis that nitrite esters are intermediates and alternative mechanisms and intermediates will be examined.

This project builds on two earlier collaborative EMSP projects that focused primarily on radiolytic processes in tank wastes.^(a) Because these projects will conclude in FY 1999, we will continue with those aspects of the projects that concern mechanisms and kinetics of organic aging by radiolytic processes. Specifically, we will continue experiments that measure the rates of NO_2 reacting with complexants in alkaline solutions. Prior work has examined the reactions of formate ion and glycine, and performed preliminary studies of iminodiacetate (IDA) and nitrilotriacetate (NTA) ions. We will carry the IDA and NTA work to completion and extend the NO_2 oxidation studies to HEDTA-related systems and to glycolate, acetate, and citrate ions. Concurrent with these activities, we will incorporate rate and mechanistic data into a predictive kinetic model.

Finally, a collaborative effort will theoretically characterize organic intermediates generated in HLW. This work will involve the Principal Investigators of this project and theorist colleagues at PNNL and Notre Dame Radiation Laboratory. The effort will foster understanding of organic aging and the development of mechanistic kinetic models by calculating thermochemical properties that are difficult to measure by experiment.

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