

The NO_x System in Homogeneous and Heterogeneous Nuclear Waste

Research Objective — This project focuses on the development of reliable theoretical and efficient computational descriptions of the chemistry of high-level waste simulants in highly concentrated solution and the experimental validation of this approach. It is an extension of previous work which:

- a) Determined the mechanism of H₂ formation in waste simulants allowing quantitative prediction of H₂ generation in nuclear waste storage tanks;
- b) Predicted and confirmed NO₂ as a key oxidant in the tanks
- c) Determined relative rates of reaction of NO₂ with chelators thus helping to resolve the "Organic Tanks" safety issue;
- d) Measured rates of NO₂ and NO₂⁻ with some model organic radicals;
- e) Quantified the redox potentials of two major reductants, NO₂⁻ and NO₃⁻;
- f) Discovered a new radiolytic route to the reductant NO₃²⁻ and demonstrated its potential persistence in irradiated alkaline aqueous media;
- g) Demonstrated that while radiolytic electrons escape from solid suspended silica particles to disrupt the surroundings, holes remain trapped thus storing oxidative equivalents.

To further advance our knowledge of the basic principles underlying tank chemistry, theoretical models are being developed to account for the effect of high salt concentrations on the reactivity of radicals and radical ions generated radiolytically in the nuclear waste and the corresponding computer codes are presently being implemented. The electronic structure of key NO_x species is being determined including the specific influence of first-shell solvent molecules as well as bulk dielectric, and ionic strength effects on their reactivity with model complexants and radicals derived therefrom. The theoretical predictions will be validated by experimentally measuring the absolute rate constants of key reactions between NO_x radicals and the complexants and NO_x⁻ ions and the organic radicals. Product distributions, yields, and relative rates will be quantified by contact experiments with dilute NO₂ gas. The resulting validated theoretical models will allow unambiguous determination of pathways for oxidation of organic reductants, accurate quantification of rate constants for degradation under various conditions, and reliable prediction of the radiolysis products. Combined with our earlier studies and ongoing related projects at PNNL, we will provide a comprehensive, quantitative description of useful predictive capability

for chemistry in nuclear waste storage and treatment streams. Reduced funding levels have forced us to reluctantly remove the heterogeneous component of our initial proposal.

Research Progress and Implications — We are now six months into the first year of the Renewal period. Initial steps have been taken to lay the groundwork for derivation of appropriate boundary element equations to describe the influence of solvent ionic strength on solute properties. These first steps provide for the use of general cavity surface dipole distributions to describe the relevant solvent reaction field. Computer code to determine and utilize such dipole distributions has now been implemented. The electronic structure and spectroscopic signatures have been computed for radicals derived from a number of model complexants using the density functional theory (DFT) method. We predicted that radiolytic oxidation of substituted glycines in basic aqueous solution should yield reducing carbon-centered radicals from both H-abstraction and decarboxylation in addition to previously unobserved aminyl radicals. The production of these oxidizing species was subsequently confirmed by time-resolved electron spin resonance (TRESR) spectroscopy directly in systems specifically chosen to amplify their yield, and indirectly by selective spin-trapping in other cases. We have configured hardware and developed software for digital acquisition of TRESR spectra, an essential component for reliable radical fingerprinting with both this technique and steady-state methods. We expect the reconfigured system to allow us an order of magnitude increase in the speed of data acquisition, particularly of ESR spectra of short-lived radicals. Calculations have been initiated to determine the mechanism of attack on formate, for which we have previously measured the rate of oxidation to carbonate. Transition states have been located using DFT methods for pathways that involve attack at the carboxylate group (electron transfer) and abstraction of H from carbon.

NO_2 gas-contact experiments with tank waste simulants, using ion chromatography and nuclear magnetic resonance spectroscopy for product analysis (often with C-13 labeled substrates), have identified reaction products and measured rates for glycolate and glycinate ions. Glycolate is oxidized to formate, carbonate and oxalate; with formate favored over oxalate by a factor of 3. The reaction competes with hydrolysis of NO_2 . While reaction of glycolate ions with NO_2 produces nitrite ions, NO_2 hydrolysis produces equal amounts of nitrate and nitrite ions. Using the known rate of NO_2 hydrolysis, we determined the rate constant for NO_2 attack on glycolate ($18 \text{ M}^{-1} \text{ s}^{-1}$). Glycinate is even more reactive than glycolate. We determine a rate constant of

$\sim 75 \text{ M}^{-1} \text{ s}^{-1}$ for glycinate by letting it compete with glycolate for NO_2 . Reaction of glycinate with NO_2 is more complex. Adducts of glycinate, as well as, formate, carbonate, and oxalate are produced. One major adduct is hydroxyaspartate. The adducts are suppressed by high concentrations of nitrite by a still unclear mechanism. We have seen by pulse-radiolysis techniques that nitrite oxidizes organic radicals that would otherwise couple or added to substrates. These observations suggest that nitrite concentrations in tank wastes strongly influence the products of waste aging. In the absence of sufficiently high nitrite concentrations aging may not much reduce the complexing ability and energy content of the aminocarboxylate chelators.

Planned Activities —In the next year the theoretical building blocks already developed will be utilized to produce a computer program module capable of solving the general Poisson-Boltzmann equation that describes ionic strength effects, and this module will be interfaced to a standard electronic structure program package. A visit of an NDRL PI to PNNL will be made in late July 2001, to construct a parallel version of the electronic structure program that includes the solvation codes.

The validity of preliminary DFT determination of structure and properties of one-electron oxidized radicals from models of common complexant will be carefully assessed against results of high-level molecular-orbital based treatments. This will ensure that the predicted chemistry is not influenced by deficiencies in present-day functionals specific to the treatment of these unusual odd-electron species. Calculations on the rate and mechanism of formate oxidation to carbonate will be completed. The relevance of channels uncovered in the hydroxyl radical induced oxidation of the glycinate to NO_x attack will be explored by theoretically characterizing the reactants, intermediates, products, and transition states connecting them. We will determine mechanism and product selectivity of reactions of nitrate and nitrite ions with organic radicals formed in the oxidative degradation. We will evaluate the structure and magnetic hyperfine coupling constants for the resultant radicals from spin-trapping by the *aci*-anion of nitromethane to facilitate the interpretation of the ESR subtask of the project. We will extend the NO_2 contact experiments to address larger aminocarboxylate substrates, e.g., iminodiacetate and nitrilotriacetate. We will also identify the adducts formed in the oxidations and elucidate their formation mechanisms.

Publications

REDUCING RADICALS IN NITRATE SOLUTIONS. THE NO_3^{2-} SYSTEM REVISITED

A.R. Cook, N. Dimitrijevic, B.W. Dreyfus, D. Meisel, L.A. Curtiss and D.M. Camaioni, *J. Phys. Chem. B*, **105**, 3658-66 (2001).

RADIATION-INDUCED PROCESSES IN AQUEOUS SUSPENSIONS OF NANOPARTICLES AND NANOSCALE WATER FILMS.

Thom Orlando and Dan Meisel, *ACS Symposium Series 778*, "Nuclear Site Remediation," Ed. G. Eller and W. R. Heineman, pp. 284-296, 2001.

RADIATION AND CHEMISTRY IN NUCLEAR WASTE: THE NO_x SYSTEM AND ORGANIC AGING

Dan Meisel, Donald Camaioni, and Thom Orlando, *ACS Symposium Series 778*, "Nuclear Site Remediation," Ed. G. Eller and W.R. Heineman, pp. 342-361, 2001.

Interactions

Kick-off coordination meeting of project renewal at PNNL, Feb. 12, 2001. Present Dan Meisel, Ian Carmichael and Gordon Hug from Notre Dame and Don Camaioni from PNNL, and representatives from TFA, CH2M Group, DOE-RL and others.

Coordination of computer code development, July, 2001. Two-week planned visit of Dan Chipman from Notre Dame with Don Camaioni and computational components from PNNL.

Coordination meeting of the PNNL and NDRL components at the ACS National meeting in Chicago planned for end of August 2001

Presentations

EARLY EVENTS IN THE RADIOLYSIS OF AQUEOUS AMINO ACID COMPLEXANTS: INSIGHTS FROM THEORY

Ian Carmichael, Invited Talk, PNNL, Feb 12, 2001.

THE NO_x SYSTEM IN NUCLEAR WASTE: IMPACT AND PERSPECTIVES

Dan Meisel, Don Camaioni, Ian Carmichael, Invited Talk, DOE's Tank Focus Area Mid-Year Review, March 12-14, 2001, Salt Lake City, UT.

THE NO_x SYSTEM IN HOMOGENEOUS AND HETEROGENEOUS NUCLEAR WASTE

Ian Carmichael, Gordon Hug, Dan Meisel, and Don Camaioni, Invited Talk, EMSP Symposium, Annual Meeting, Am. Chem. Soc., Chicago, IL, Aug 26-31, 2001.

THE RADIATION CHEMISTRY OF DEFENSE NUCLEAR WASTE

Don Camaioni and Dan Meisel, Invited talk, EMSP Symposium, Annual Meeting, Am. Chem. Soc., Chicago, IL, Aug 26-31, 2001.