

Five digit Project ID number: 55103

Project Title: Utilization of Kinetic Isotope Effects for the Concentration of Tritium

Lead Principal Investigator: Gilbert M. Brown, Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS 6119, Oak Ridge, TN 37831-6119
Email: brownngm1@ornl.gov

Co-Principal Investigator(s): Thomas J. Meyer, Department of Chemistry, The University of North Carolina at Chapel Hill Chapel Hill, NC 27599-3290 (current address, Los Alamos National Laboratory, Los Alamos, NM) Email: tjmeyer@lanl.gov

Co-Investigator(s): C.-H. Ho, Leon Maya, Bruce A. Moyer, and Frederick V. Sloop, Jr, Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS 6119, Oak Ridge, TN 37831-6119

Post-Doctoral Fellows: Poonam M. Narula and My Hang V. Huynh, University of North Carolina

Specific DOE Problems. Tritium in groundwater is in the form of HTO which exchanges rapidly with normal isotopic composition water making it highly mobile. There is no currently identified, cost effective technology that is a solution to the problem of low level tritium contamination at a number of DOE sites. The most serious problems are at the Savannah River Site (SR00-3016 and SR004014) and the Hanford Site (RL-MW023) although a significant concern was identified at LLNL (OK99-13). The objective of our work is to develop an electrochemically based method to remove tritium from contaminated water, and as a consequence of the process tritium will be incorporated into an organic compound that will not readily exchange the tritium with groundwater.

Research Objective. Work is in progress to develop methods for concentrating tritium in water based on large primary isotope effects in catalytic redox processes. Basic research is being conducted to develop the chemistry of a complete cyclic process. The process will remove tritium from H₂O by concentrating it with respect to protio-water. This research involves developing chemical cycles that produce high concentration factors for HTO based on the discrimination of C-H and C-T bonds in oxidation reactions. Several steps are required in a cyclic process for the concentration of tritium in water. In the first step, the tritium is incorporated in an organic compound. H-T discrimination occurs as the tritium containing compound is oxidized in a step involving a Ru(IV) oxo complex. Strong primary kinetic isotope effects lead to the oxidation of C-H bonds in preference to C-T bonds, and this reaction leads to concentration of tritium in the organic compound. The reduced form of the ruthenium compound can be reoxidized so that the oxidation step can be made catalytic.

Research Progress and Implications. Progress has been made toward demonstrating the individual steps required for the concentration of tritium in water in the three years and 4 months of this project. An early research objective was achieved to demonstrate the individual steps for a proof-of-principle "cold" experiment to separate deuterium from water in a cyclic process. The electrochemical reduction of carbon dioxide in an aqueous solution containing deuterium shows the incorporation of deuterium in the formate anion product. In a cyclic process, reduction of CO₂ will be coupled to the Ru(IV) catalyzed oxidation of the formate anion. We demonstrated the fractionation of the deuterated component in a mixture of proteo- and deuterio-formate. The Ru(IV) oxo species chosen for this work was the complex [Ru(IV)(terpy)(bpy)O]²⁺ where terpy is 2,2',2''-terpyridine and bpy is 2,2'-bipyridine. We have determined the tritium kinetic isotope effect (k_H/k_T) for oxidation of formate by the complex [Ru(IV)(terpy)(bpy)O]²⁺. Measurement of the kinetic isotope effect for oxidation of tritiated formate anion was made at the tracer level by measuring the

rate of transfer of tritium from the formate anion to water. The tritium kinetic isotope effect, $k(H)/k(T)$, is dependent on ionic strength, and at μ 0.1 M it was observed to be in excess of 300. This result has both scientific and technological significance. It is the largest kinetic isotope effect observed at ambient temperatures, and it demonstrates the importance of nuclear tunneling in the hydride transfer mechanism. The technological significance is that tritium and protium can be separated in a single stage. In terms of more long-range goals, progress has been made in additional areas. We have begun to develop the catalytic chemistry in redox active films and membranes on the electrode surface, configurations that might be appropriate for device applications. The second general theme is to evaluate C-H/C-T kinetic isotope effects in the oxidation of several functionally different organic substrates by Ru(IV) oxo complexes. An investigation of the chemistry of related high oxidation osmium terpyridyl complexes has been rewarding. Oxo-like reactivity was observed for high oxidation state osmium hydrazido complexes. The proton-coupled electron transfer reaction of an osmium hydrazido complex was observed to have a N-H/N-D kinetic isotope effect of 41.4. These reactions may have significance for devising more effective catalyst-organic substrate combinations.

Planned Activities. As time and funding levels permit, the tritium isotope effect for oxidation of a derivative of benzyl alcohol by $[Ru(IV)(terpy)(bpy)O]^{2+}$ will be determined. Conditions will be investigated for reduction of the benzyl alcohol derivative by H_2 at low pressures.

Information Access.

Oxo-Like Reactivity of High Oxidation State Osmium Hydrazido Complexes. Huynh, M. H. V.; El-Samanody, E.; Demadis, K. D.; Meyer, T. J.; White, P. S. *J. Am. Chem. Soc.*, **1999**, *121*, 1403-1404.

Mechanisms of Surface Electron Transfer. Proton-Coupled Electron Transfer. Trammell, S. A.; Wimbish, J. C.; Odobel, F.; Gallagher, L. A.; Narula, P. M.; Meyer, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 13248-13249.

The Effect of Stepwise Oxidation on Molecular Structure in Osmium Hydrazido Complexes. Huynh, M. H. V.; El-Samonody, E.-S.; Meyer, T. J.; White, P. S., *Inorg Chem.*, **1999**, *38*, 3760.

Proton-Coupled Electron Transfer from Nitrogen. A N-H/N-D Kinetic Isotope Effect of 41.4". Huynh, M. H. V.; White, P. S.; Meyer, T. J. *J. Amer Chem Soc.*, **1999**, *121*, 4530-4531.

Intramolecular Oxidative Substitution on Coordinated Terpyridyl Ligand. Huynh, M. H. V.; Lee, D. G.; Meyer, T. J.; White, P. S., *J. Amer Chem Soc.*, **1999**, *121*, 10446-10447.

Surface Catalysis of Solution Electron Transfer. Narula;P. M.; Trammell, S. A.; Meyer, T. J., in preparation.

Reduction of Benzoquinone by trans-[OsIV(tpy)(Cl)₂(N(H)N(CH₂)₄O)](PF₆). Proton-Coupled Electron Transfer from Nitrogen. Huynh, M. H. V., Meyer, T. J., in preparation.

H/D Isotope Separation based on Kinetic Isotope Effects, P. M. Narula, F. V. Sloop, G. M. Brown, L. Maya, and T. J. Meyer, in preparation.

Deuterium and Tritium Kinetic Isotope Effects for the Oxidation of Formate by (Terpyridine)(bipyridine)-(oxo)ruthenium(IV), G. M. Brown, F. V. Sloop, Jr., B. A. Moyer, and T. J. Meyer, in preparation.