

Environmental Management Science Program

Project ID Number 55103

Utilization of Kinetic Isotope Effects for the Concentration of Tritium

Dr. Gilbert M. Brown
Oak Ridge National Laboratory
Bldg. 4500S
MS 6119
P.O. Box 2008
Oak Ridge, Tennessee 37831-6119
Phone: 423-576-2756
E-mail: gbn@ornl.gov

Thomas J. Meyer
University of North Carolina at Chapel Hill
Chapel Hill, North Carolina 27599-3290
Phone: 919-962-6319
E-mail: TJMSEC@net.unc.edu

June 1, 1998

Utilization of Kinetic Isotope Effects for the Concentration of Tritium

Dr. Gilbert M. Brown, Oak Ridge National Laboratory

Thomas J. Meyer, University of North Carolina at Chapel Hill

Research Objective

The objective of this research program is 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. Because tritium (generally present as HTO) is in a rapidly established equilibrium with protio-water, it moves with groundwater and separation from water cannot be achieved by the usual pump-and-treat methods using sorbants. The general methodology developed in this work will be applicable to a number of DOE waste streams, and as a consequence of the process tritium will be incorporated into an organic compound that will not readily exchange the tritium with groundwater. We intend to develop a process to 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 and T₂O 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 along several fronts in the first 21 months of this project with much of the work directed toward demonstrating the individual steps required for the concentration of tritium in water. An early research objective is to carry out a proof-of-principle "cold" experiment in which the electrochemical reduction of carbon dioxide in an aqueous solution containing deuterium shows the incorporation of deuterium in the product substrate. This will be coupled to the catalytic oxidation of the formate anion demonstrating the fractionation of the deuterated component in a mixture of proteo- vs. deuterio-organic compounds. The ruthenium(IV) oxo species chosen for this early work was the complex [Ru(IV)(terpy)(bpy)O]²⁺ where terpy is 2,2',2''-terpyridine. In terms of more long range goals, additional themes have been explored. One is a continuing investigation of the magnitude of kinetic isotope effects to identify the most promising metal catalytic system. The second is to develop the catalytic chemistry in redox active films and membranes appropriate for device applications. The third general theme is to evaluate C-H/C-T kinetic isotope effects in the oxidation of several functionally different organic substrates by various Ru(IV) oxo complexes.

Tritium kinetic isotope effects are unknown, but they are expected to be as high or higher than the deuterium effect. Work is in progress to measure the tritium isotope effect for the oxidation of formate anion to carbon dioxide with [Ru(IV)(terpy)(bpy)O]²⁺. The deuterium kinetic isotope effect ($k(\text{C-H})/k(\text{C-D})$) for oxidation of formate by [Ru(IV)(terpy)(bpy)O]²⁺ was observed to be 25 which is comparable to but larger than the ratio measured by Roecker and Meyer ($k\text{H}/k\text{D} = 19$) while the value of the rate constant for oxidation of protio-formate was 3.85 M⁻¹s⁻¹ also in good agreement with the value reported by Roecker and Meyer for oxidation of formate by [Ru(IV)(bpy)₂(py)O]²⁺ (4.2 M⁻¹s⁻¹). Measurement of the kinetic isotope effect for oxidation of tritiated formate anion is in progress with measurements being made at the tracer level by measuring the rate of transfer of tritium from the formate anion to HTO. The concentration of tritium in water is being determined by

scintillation counting. Preliminary results indicate the tritium isotope effect is larger than the deuterium effect as expected. The formate anion is an attractive substrate for a "cold" demonstration involving the removal of deuterium from water because the tritiated formate anion can be separated by ion exchange from the reaction mixture. We have been able to confirm reports in the literature that CO_2 is reduced to formate at an indium electrode. We anticipate that large levels of formate can be generated by electrolysis, and this will be important for reducing the number of stages needed to effect a separation. Work is in progress to demonstrate the fractionation of deuterium by observing the build up of deuterated formate in the catalyzed oxidation of a mixture of deuterio and proteo-formate. We have investigated the electrochemical kinetics of the Ru(III)/Ru(IV) redox reaction using cyclic voltammetry and utilizing a chemically modified electrode. Previous results have shown that it is very difficult to observe the III/IV redox couple on a glassy carbon electrode because of kinetic sluggishness. However, we observed that an ITO electrode coated with $\text{Ru}(\text{terpy})((4,4' -(\text{PO}_3\text{H}_2)\text{-bpy})(\text{H}_2\text{O})^{2+}$ enhanced the response of the III/IV redox wave during a cyclic voltammetric experiment in which $\text{Ru}(\text{terpy})(\text{bpy})(\text{H}_2\text{O})^{2+}$ dissolved in solution was undergoing oxidation. ITO electrodes coated with TiO_2 and $[\text{Ru}(\text{IV})(\text{terpy})((4,4' -\text{PO}_3\text{H}_2)\text{bpy})\text{O}]^{2+}$ have also been used to study the catalyzed oxidation of benzyl alcohol and these electrodes with a surface immobilized catalyst were found to be active. Finally, a deuterium kinetic isotope effect of 61 has been observed for the second stage in the oxidation of benzyl alcohol by the Ru(VI) oxidant, $\text{trans-}[\text{Ru}(\text{VI})(\text{tpy})(\text{O})_2(\text{S})]^{2+}$ ($\text{S} = \text{CH}_3\text{CN}$). This is part of a systematic effort to identify catalyst-substrate combinations that maximize the isotope effect.

Planned Activities

By the end of FY 1998, we plan to complete a preliminary determination of the kinetic isotope effect for oxidation of formate by the complex $[\text{Ru}(\text{IV})(\text{terpy})(\text{bpy})\text{O}]^{2+}$, and these results will be reported at the American Chemical Society Meeting in Boston. Following our report on the formate based fractionation experiments in the literature, we hope to be able to report the experimental realization of a complete cyclic system for deuterium separation from water. Other suitable substrate/electrode combinations for cyclic reduction /oxidation will be investigated. Use of electrodes with the Ru catalyst bound to the surface are highly desirable, and they will be further investigated.

Other Access To Information

Lebeau, E.L. and Meyer, T.J., "Oxidation of Benzyl Alcohol by a Dioxo Complex of Ru(VI)," submitted for publication.
Trammel, S.; Meyer, T.J., "Mechanisms of Surface Electron Transfer. Proton Coupled Transfer," submitted for publication.
Narula, P.; Brown, G.M., Sloop, F.V., Meyer, T.J., "H-D Isotopic Separation by Exploiting Kinetic Isotope Effects," manuscript in preparation.