Project ID: **55103**

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

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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. The process to be developed 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 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 toward demonstrating the individual steps required for the concentration of tritium in water in the first two years and 8 months of this project. An early research objective was 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 formate anion product. This was 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 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_D) for oxidation of formate by the complex [Ru(IV)(terpy)(bpy)O]²⁺. 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.

The tritium kinetic isotope effect for the oxidation of formate anion to carbon dioxide with [Ru(IV)(terpy)(bpy)O]²⁺ was measured. The deuterium kinetic isotope effect ($k(C-H)/k(C-D)$) for oxidation of formate by [Ru(IV)(terpy)(bpy)O]²⁺ was observed to be 25 which is comparable to but slightly larger than the expected value based on previous work by Roecker and Meyer. 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 HTO. The tritium isotope effect (k_H/k_T) was observed to be 125, one of the largest kinetic isotope effects ever measured at room temperature. The large isotope effect is attributed to nuclear tunneling. The

formate anion is an attractive substrate for a "cold" demonstration involving the removal of deuterium from water because the formate anion can be separated by ion exchange from the reaction mixture. We have been able to confirm reports in the literature that CO₂ is reduced to formate at an indium electrode. A demonstration of the fractionation of deuterium by observing the build up of deuterated formate in the catalyzed oxidation of a mixture of deuterio and proteo-formate was completed. We have investigated the electrochemical kinetics of the Ru(III)/Ru(IV) redox reaction using cyclic voltammetry and utilizing an 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 Ru(terpy)((4,4'-(PO₃H₂)-bpy)(H₂O)²⁺ enhanced the response of the III/IV redox wave during a cyclic voltammetric experiment in which Ru(terpy)(bpy)(H₂O)₂²⁺ dissolved in solution was undergoing oxidation. ITO electrodes coated with TiO₂ and [Ru(IV)(terpy)((4,4'-PO₃H₂)bpy)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

PLANNED ACTIVITIES

We will determine the tritium kinetic isotope effect for oxidation of a derivative of benzyl alcohol by the complex [Ru(IV)(terpy)(bpy)O]²⁺. Work will continue to demonstrate significant KIEs in oxidation reactions with modified electrode surfaces.

INFORMATION ACCESS

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