

KINETIC ISOTOPE EFFECTS IN OXYGEN ELECTRODE REACTIONS
 I. General Theory of Primary and Solvent H/D Isotope
 Effects in the Electrochemical Reduction of Oxygen

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INTRODUCTION

The effects of isotopic substitution on chemical reaction rates have been employed extensively to elucidate reaction mechanisms and to provide criteria for the identification of rate-determining steps.^{1,2} Although isotopic effects in chemical kinetics were first demonstrated experimentally³ by the electrolysis of water in 1932, it is only recently that this method has been applied successfully to detailed kinetic studies of electrochemical reactions.⁴ In the present communication, we discuss the kinetic theory of the effects of H/D isotopic substitution on the electrochemical reduction of oxygen in aqueous electrolytes. As a result of the calculations presented below, various mechanisms proposed for the reduction process can be distinguished on the basis of the magnitude of the H/D isotope effect. It is interesting to note that the ratio of standard rate constants for the electrolysis reaction may be very large, near unity, or inverse, depending upon the mechanism operative.

It has been well established⁵ that hydrogen peroxide may be formed as a stable intermediate species during the electrochemical reduction of oxygen to water. On electrode materials of high catalytic activity, however, hydrogen peroxide decomposes rapidly via a surface-catalyzed chemical reaction to regenerate oxygen. The effects of this coupled heterogeneous catalytic reaction on the kinetics of oxygen reduction have been discussed previously.^{6,7} To provide further criteria for establishment of the decomposition reaction mechanism, we have calculated the magnitude of H/D effects for several proposed schemes.

In the treatment which follows, we consider only the effects of complex isotopic substitution of the electrolyte. Species of mixed isotopic composition need not be considered therefore. The ratio of exchange current densities for an electrochemical reaction in light and heavy water electrolytes is given by

$$R_1 = \frac{i_o(H)}{i_o(D)}$$

where the subscript 1 denotes the step in the reaction sequence which is rate-controlling. In calculating this ratio from absolute rate theory we make the following simplifying assumptions:

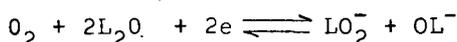
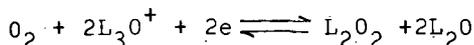
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- i) All pre-rate-determining steps are in quasi-equilibrium.
- ii) Ψ_1 -effects (Ψ_1 is the potential at the outer Helmholtz plane) can be neglected since they are small and we are only interested in their ratios (cf. reference (8)).
- iii) Limiting Langmuir adsorption conditions are applicable.
- iv) Secondary isotope effects are negligible.

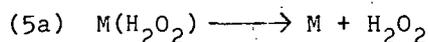
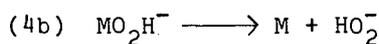
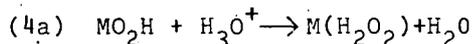
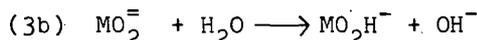
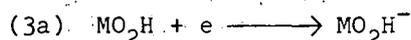
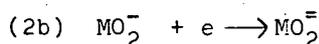
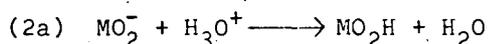
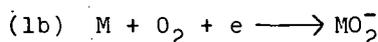
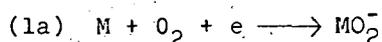
THEORY

I. Oxygen-Peroxide Electrode

This couple may be represented in acid and alkaline solutions, respectively, as



where L is either H or D. In light water electrolytes, the electrochemical production of H_2O_2 is believed to occur via the following schemes:⁵

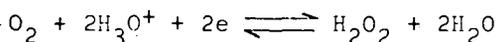
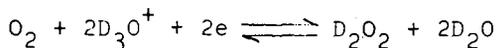


Other schemes are of course conceivable and will be considered in the full paper.¹⁰

If, in acid solutions, reaction step (1a) is rate-controlling, the ratio of exchange current densities is given by

$$R_{1a} = \frac{[O_2]_{H_2O}}{[O_2]_{D_2O}} \cdot \frac{q_{O_2(D_2O)}}{q_{O_2(H_2O)}} \cdot \frac{q_{O_2^{\ddagger}(H_2O)}}{q_{O_2^{\ddagger}(D_2O)}} \cdot \exp(\beta \Delta \phi F/RT)$$

where the bracketed terms denote the concentrations of molecular oxygen in H_2O and D_2O solutions, q is the molecular partition function of the species indicated (superscript \ddagger refers to the activated complex) and $\Delta \phi$ is the potential difference ($\phi_{D_2O_2} - \phi_{H_2O_2}$) for the two overall half-cell reactions



The contribution of the zero-point energy to the vibrational partition function is included in each q . It will be recalled that this term is principally responsible for the primary kinetic isotope effect of H/D substitution.^{1,2} The expression for the exchange current ratio with step (1a) rate-controlling reduces to

$$R_{1a} = \exp(\beta\Delta\phi F/RT)$$

By an analogous method we obtain the following expressions

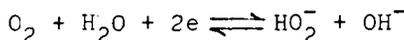
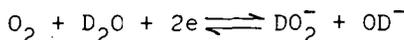
$$R_{2a} = \frac{q_{\text{D}_3\text{O}^+}}{q_{\text{H}_3\text{O}^+}} \cdot \frac{q_{\text{O}_2^{\ddagger}}(\text{H}_2\text{O})}{q_{\text{O}_2^{\ddagger}}(\text{D}_2\text{O})} \exp(\Delta\phi F/RT)$$

$$R_{3a} = \frac{q_{\text{D}_3\text{O}^+}}{q_{\text{H}_3\text{O}^+}} \cdot \frac{q_{\text{H}_2\text{O}}}{q_{\text{D}_2\text{O}}} \cdot \frac{q_{\text{O}_2^{\ddagger}}(\text{H}_2\text{O})}{q_{\text{O}_2^{\ddagger}}(\text{D}_2\text{O})} \exp[(1 + \beta)\Delta\phi F/RT]$$

$$R_{4a} = \left(\frac{q_{\text{D}_3\text{O}^+}}{q_{\text{H}_3\text{O}^+}} \right)^2 \cdot \frac{q_{\text{H}_2\text{O}}}{q_{\text{D}_2\text{O}}} \cdot \frac{q_{\text{O}_2^{\ddagger}}(\text{H}_2\text{O})}{q_{\text{O}_2^{\ddagger}}(\text{D}_2\text{O})} \exp(2\Delta\phi F/RT)$$

$$R_{5a} = \left(\frac{q_{\text{D}_3\text{O}^+}}{q_{\text{H}_3\text{O}^+}} \cdot \frac{q_{\text{D}_2\text{O}}}{q_{\text{H}_2\text{O}}} \right)^2 \cdot \frac{q_{\text{O}_2^{\ddagger}}(\text{H}_2\text{O})}{q_{\text{O}_2^{\ddagger}}(\text{D}_2\text{O})} \exp(2\Delta\phi F/RT)$$

Similarly, in alkaline solutions, we obtain for the reactions



where $\Delta\phi = \phi_{\text{DO}_2^-} - \phi_{\text{HO}_2^-}$, the following exchange current ratios.

$$R_{1b} = \exp(\beta\Delta\phi F/RT)$$

$$R_{2b} = \exp[(1 + \beta)\Delta\phi F/RT]$$

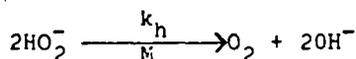
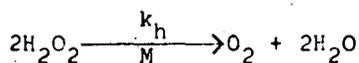
$$R_{3b} = \frac{q_{\text{D}_2\text{O}}}{q_{\text{H}_2\text{O}}} \cdot \frac{q_{\text{O}_2^{\ddagger}}(\text{OH}^-)}{q_{\text{O}_2^{\ddagger}}(\text{OD}^-)} \exp(2\Delta\phi F/RT)$$

$$R_{4b} = \frac{q_{D_2O}}{q_{H_2O}} \cdot \frac{q_{OH^-}}{q_{OD^-}} \cdot \frac{q_{O_2(OH^-)}}{q_{O_2(OD^-)}} \exp(2\Delta F/RT)$$

The evaluation of partition function ratios for the isotopic species L_2O , L_3O^+ and OL^- were carried out as before^{8,9} (cf. Appendix); those for the species L_2O_2 , LO_2 and LO_2^- were evaluated from spectroscopic and acid-base equilibrium data. The partition function ratios for the activated complexes were evaluated by assuming that the vibrational frequencies of the O-H and O-D bonds not directly participating in the reaction remain unchanged during the transition from the initial to the final state (cf. references 8, 9 where similar treatments have been employed). The results of these calculations show that a wide range of isotope effects can arise and that these effects are strongly dependent upon the nature of the solution employed (ie, acid or alkaline). An inversion of the exchange current ratio is predicted in some instances for the oxygen-peroxide electrode on changing from standard acid to standard alkaline conditions, owing to a solvent isotope effect.

II. Hydrogen Peroxide Decomposition

The overall decomposition reactions of hydrogen peroxide in acid and alkaline solution are

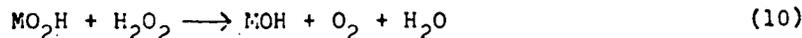


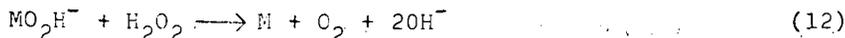
where k_h represents the heterogeneous chemical rate constant for the surface-catalyzed reaction. As examples of possible reaction mechanisms we consider the following schemes.

1) Oxygen Radical Mechanism



11) Modified Haber-Willstatter Mechanism



iii) Bimolecular Complex Mechanism

Other possible reaction mechanisms are considered in the final paper.¹⁰

For a given electrode material, the ratio of rate constants for the heterogeneous decomposition of peroxide in light and heavy water electrolytes is

$$R_{\pm} = \frac{k_h (H_2O_2)}{k_h (D_2O_2)}$$

This quantity may be evaluated from steady state polarization curves for oxygen reduction on a rotating-disk electrode.⁶ For the limiting current regions of the current-voltage scans we can make the simplifying assumption that the surface concentration ratios, $[H_2O_2]/[D_2O_2]$ and $[HO_2^-]/[DO_2^-]$, are unity.

Partition function ratios were evaluated as in the preceding section. We shall not present here the total list of expressions for calculation of the isotope effects involving reactions (6)-(12). Two representative calculations are shown below for reactions (6) and (10).

$$R_7 = \frac{q_{DO_2^-}}{q_{HO_2^-}} \cdot \frac{q_H^\ddagger}{q_D^\ddagger}$$

$$R_{12} = \frac{q_{D_2O_2}}{q_{H_2O_2}} \cdot \frac{q_{DO_2^-}}{q_{HO_2^-}} \cdot \frac{q_H^\ddagger}{q_D^\ddagger}$$

Representative rate constant ratios for these and other rate-controlling steps are summarized in Table I.

DISCUSSION

The predicted kinetic isotope effects vary over a wide range, depending upon the mechanism and rate-controlling step involved. Of particular interest is the prediction of an inverse isotope effect for the oxygen-peroxide electrode. Such an inverse isotope effect has also been found for the oxygen evolution reaction.^{4,9}

We have measured the exchange current ratios for the electrochemical reduction of oxygen on gold in acid and alkaline solutions in light and heavy water. In alkaline solutions the kinetic isotope effect is small and normal, but in acid solutions the effect is large and inverse. Small, normal kinetic isotope effects were also observed for the base-catalyzed decomposition of hydrogen peroxide

on gold electrodes and tend to confirm a mechanism involving an ion-molecule complex deduced from studies of pH effects on the kinetics of peroxide decomposition.¹² Details of these experiments will be reported elsewhere.¹³

The fact that predicted isotope effects for several reaction mechanisms are similar may make the assignment of one unique scheme difficult. A similar problem arises in classical electrode kinetic studies when the theoretical Tafel slopes are identical for differing mechanisms. Such results only serve to emphasize the fact that only one type of study is not sufficient to investigate the kinetics and mechanism of complex electrode processes. As with the oxygen and hydrogen evolution reactions, the strength of any conclusion concerning mechanisms lies in consistency of results from all types of studies. The kinetic isotope effect is a powerful tool when used in this sense.

APPENDIX

For initial state reactants, we have calculated or obtained from the literature, the partition function ratios shown below. All ratios include zero-point energy differences.

$$\frac{q_{D_2O}}{q_{H_2O}} = 1434 ; \quad \frac{q_{D_3O^+}}{q_{H_3O^+}} = 19,023 ; \quad \frac{q_{OD^-}}{q_{OH^-}} = 2615$$

$$\frac{q_{D_2O_2}}{q_{H_2O_2}} = 850 ; \quad \frac{q_{DO_2}}{q_{HO_2}} = 18.9 ; \quad \frac{q_{DO_2^-}}{q_{HO_2^-}} = 14.6$$

The standard potential difference (25°C) of the oxygen-peroxide couple in acidic light and heavy water electrolytes is:

$$\begin{aligned} \Delta\phi^{\circ} &= \phi_{D_2O_2}^{\circ} - \phi_{H_2O_2}^{\circ} \\ &= \frac{RT}{2F} \ln \left[\left(\frac{q_{H_3O^+}}{q_{D_3O^+}} \right)^2 \left(\frac{q_{D_2O}}{q_{H_2O}} \right)^2 \frac{q_{D_2O_2}}{q_{H_2O_2}} \right] \\ &= + 0.0202 \text{ volt} \end{aligned}$$

Similarly in alkaline solutions:

$$\begin{aligned} \Delta\phi^{\circ} &= \phi_{DO_2^-}^{\circ} - \phi_{HO_2^-}^{\circ} \\ &= \frac{RT}{2F} \ln \left(\frac{q_{H_2O}}{q_{D_2O}} \cdot \frac{q_{OD^-}}{q_{OH^-}} \cdot \frac{q_{DO_2^-}}{q_{HO_2^-}} \right) \\ &= - 0.0198 \text{ volt} \end{aligned}$$

TABLE I

H/D Isotope Effects in the Surface-Catalyzed
Decomposition of Hydrogen Peroxide

<u>Rate-Determining Step</u>	<u>Rate Constant Ratio, $k_h(\text{H}_2\text{O}_2)/k_h(\text{D}_2\text{O}_2)$</u>
6	1.67
7	1.0
8	1.8
9	5.2
10	1.5
11	1.67
12	2.61

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