

ABSTRACT

This study examines the oxygen reduction reaction (ORR) in a homogeneous catalyst system, comparing between the outer-sphere and inner-sphere electron-transfer mechanisms. The rate constants are measured using aqueous trifluoromethane sulfonic acid (TFMSA) and water-soluble M^* -meso-tetra(pyridyl)porphine chloride complexes [M^* TMPyP, $M^* = \text{Fe(III)}, \text{Co(III)}, \text{Mn(III)}$ and Cu(II)] at given pH and molar ratio of metal complexes to oxygen. An outer-sphere model consistent with Marcus theory explains that an outer-sphere electron transfer mechanism occurs in the activation-control region. However, higher rate constants than predicted suggests that a possible reaction pathway is a quasi-redox mechanism associated with the formation of an intermediate bond between M^* TMPyP [$M^* = \text{Fe(II)}, \text{Co(II)}, \text{Mn(II)}$ and Cu(I)] with O_2 followed by proton-activated decomposition. An increase in the catalyst turnover frequency was also observed upon addition of imidazole base, indicating the role of protonation is crucial to the ORR mechanism. The results are encouraging for replacement of platinum with non-noble metal-polymer complex systems for oxygen reduction in that the reorganization barrier for reaction pathway significantly decreases. The positive effect of proton activation on the catalytic activity of the homogeneous redox catalysts is of considerable interest for future studies. In a three-dimensional, molecular catalysis model, the predicted results using the measured reaction rate suggest that the non-noble metal catalysts can be used for practical electrochemical cell designs.