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Oxidation Electron Stoichiometry, Diffusion Coefficients and Formal Potentials of Two Di-nickel-bis(salen) Complexes ☆,☆☆

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Abstract

Two di-nickel complexes based on bis(salen) ligands are investigated by electrochemical and NMR techniques with respect to determination of their diffusion coefficients D and the number n of electrons involved in oxidation in organic electrolytes and at a Pt electrode. It is shown that in both cases the oxidation involves two electrons despite the appearance of the cyclic voltammograms which can not easily be distinguished from those of a one-electron process. The difference of the formal potentials of the two electron transfer processes is determined by simulation of the experimental cyclic voltammograms, and found to be below 60 mV.

Keywords: Nickel salen complexes, electron stoichiometry, diffusion coefficients, cyclic voltammetry, chronoamperometry, PGSE-NMR spectroscopy

1. Introduction

There are many examples of redox-active transition metal complexes with organic ligands which are stable in several successive oxidation states [3–5]. It is not uncommon that such complexes are catalysts for chemical or electrochemical transformations. Then, redox transitions are often involved [6] and effectively control their activity, for example in the form of redox-switchable catalysis [7, 8]. A particularly versatile ligand is the tetradentate bis(salicylidene)-ethylendiaminato or "salen" unit. For example, salen complexes with cobalt act as biomimetics of mono-oxygenases, dioxygenases, or peroxidases to catalyze oxygen transfer reactions [9, 10], and recently they have also been applied as water oxidation electrocatalysts [11]; Mn(salen) and derivatives are models for superoxide dismutase/catalase [12, 13], and successfully catalyze the asymmetric Jacobsen-Katsuki epoxidation [14]; salen complexes with nickel as the central atom act as electron transfer mediators in a large number of catalytic reductions [15].

Redox-active catalysts are characterized by electrochemical means with respect to their electron transfer properties. Generally, formal potentials E^0, electron transfer rate constants k_s, diffusion coefficients D, and the number n of electrons transferred between the redox states involved (electron stoichiometry) are accessible from cyclic voltammetry (CV) experiments [16, 17] under transient conditions.

The analysis of CV data typically uses peak currents i_p and peak potentials E_p. It relies on measurements of diffusion controlled i_p at an electrode with an electroactive surface A to determine in particular n and D. These parameters are related to i_p through the Randles-Ševčik equation (1) [18, 19], given as

$$i_p = 0.4463 \times n^{3/2} \times FAc^0\sqrt{FvD/RT} \quad (1)$$

(in a slightly modified form as derived from Nicholson and Shain's work [20]), where F is the Faraday constant, c^0 is the bulk concentration of the electroactive species, v is the potential scan rate, R is the gas constant, and T is the temperature. Thus, one of the quantities n or D can be calculated from

☆Electrochemistry of Transition Metal Complex Catalysts, Part 14 — Part 13, see ref. [1]; also: Two-Electron-Transfer Redox Systems, Part10 — Part 9, see ref. [2]

☆☆Dedicated to Professor K. Aoki on the occassion of his retirement.

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