



Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Spectroelectrochemistry: ESR of Paramagnetic Intermediates in the Electron Transfer Series $[\text{Cr}(\text{bpy})_3]^n$ ($n = 3+, 2+, 1+, 0, 1-$)



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ARTICLE INFO

Article history:

Received 7 July 2015

Received in revised form 13 September 2015

Accepted 13 September 2015

Available online 15 September 2015

Keywords:

Transition metal complexes

pyridine ligands

radical anion

cyclic voltammetry

electron spin resonance

ABSTRACT

A new method of cyclic voltammetry with simultaneous ESR spectra multiple recording (CV-MRESR) has been proposed and implemented. Along with cyclic voltammetry (CV) and electron spin resonance (ESR), the combined method involving cyclic voltammetry and ESR (CV-ESR) has been used for the study of electron transfer in a series of complexes $[\text{Cr}(\text{bpy})_3]^n$ ($n = 3+, 2+, 1+, 0, 1-$).

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1. INTRODUCTION

Organometallic metal complexes with α -diimine ligands like 2,2'-bipyridine, terpyridine, 1,10-phenanthroline, have gained an enormous interest in the last decade. The interest in this 'non-innocent ligands' is strongly motivated by their versatility as catalysts for important organic transformations. The understanding of ways of electron transfer in the course of redox-reactions and the detection of intermediates are extremely important for managing the choice of the most effective catalyst. Electron transfer to complex changes electronic configuration of metal complex, thus considerably raising its reactivity. Determining the effects of these redox non-innocent ligands on the reactivities of first-row transition metals during electron transfer processes is very important and requires a new and improved approaches and research methods.

ESR is a spectroscopic technique that is sensitive to systems with unpaired electrons, such as organic free radicals, [1–3] radical anions [4–6] and radical cations, [7,8] or to complexes of transition

metal ions [9,10]. The combination of electrochemical methods and ESR creates new opportunities for deeper studies of heterogeneous electron transfer and subsequent chemical reactions [11–14].

Improved cell configurations for simultaneous electrochemical ESR have been described in various articles published in recent years. Coaxial, [15] tubular flow, [16] channel [17] and flat [18] EI-ESR cell constructions are characteristic of the constant search for a successful solution to the problems of simultaneous electrochemistry and ESR experimentation.

The concept of a coaxial cavity [19] was used to create a three-electrode electrochemical-ESR (EI-ESR) cell with a large surface comprised of a helical working electrode for the purpose of increasing sensitivity and ensuring the accuracy of the electrochemical experiments due to the relatively small voltage drop between the working and reference electrodes. Placing the cell in the cavity and recording the ESR spectrum or measuring its intensity simultaneously with electrochemical characterization has led to interesting results in the potentiostatic mode as well as in the modes of voltammetry, chronopotentiometry and chronoammetry [7,10,14].

Transition metal complexes with pyridine ligands are widely used as active components in the photo- and redox-active polynuclear and supramolecular structures, given the prospects

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