

THE ELECTROCHEMISTRY OF FLUORINATED β -KETOAMINES, THEIR SULFUR ANALOGUES AND METAL CHELATES IN NONAQUEOUS MEDIA

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ABSTRACT

The electrochemistry of eighty fluorinated β -ketoamines, β -thioketoamines, monothio- β -diketones and their complexes of Cu(II) and Ni(II) in dimethylformamide has been investigated. The reduction products of the ligands (LH_2) are found to be unstable anion-radicals; the chemical and electrochemical transformations of the latter result in the elimination of the F^- ion. Metal complexes are characterized by reversible electron transfer. According to ESR data either Ni(I)(LH)_2 or Ni(II)(LH)_2^- are formed as the one-electron reduction products. The dependence of the electrochemical and ESR parameters of complexes on the ligand structure is discussed.

INTRODUCTION

β -Diketones, monothio- β -diketones, dithio- β -diketones, β -ketoamines and β -thioketoamines represent structurally related ligands with oxygen, sulfur and nitrogen as the donor atoms. Acetylacetonates were the first of the series to be studied electrochemically [1–4]. This group of complexes was shown to undergo multi-electron irreversible reduction, usually accompanied by chemical reactions. Substitution of oxygen by sulfur as a donor atom has been found to affect the redox processes both thermodynamically and kinetically [5,6]. Thus, sulfur-based compounds are reduced at more positive potentials and with higher rates of heterogeneous transfer than their oxygen analogues. Among the sulfur analogues of β -diketones only dithioacetylacetonates were extensively investigated by Bond et al. [7,8]. This group of chelates was found to undergo stepwise one-electron reversible reduction either with a central atom [7,8] or a ligand [9] being reduced. In our opinion, additional study is necessary to draw certain conclusions on the nature of the boundary orbitals. There are only a few papers dealing with the nonaqueous electrochemistry of β -ketoamines, β -thioketoamines and monothio- β -diketones [1]. Nevertheless the ligands and chelates are of great practical importance due to their volatility, and their catalytic and biological activity. Fluorinated derivatives are the most volatile but their electrochemical characteristics have not been described earlier. Besides the electrochemical characteristics, the sulfur and nitrogen derivatives provide informa-