

ELECTROCHEMICAL REDUCTIONS OF ALKYL (HET)ARYL KETOXIMES AND THEIR Ni²⁺, Cu²⁺ AND Zn²⁺ COMPLEXES ON MERCURY

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This contribution is dedicated to
Professor Jean-Michel Savéant.

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Ketoximes and their metal chelate complexes are both active as catalysts in hydrolysis of esters. Since the oximate anion is the nucleophile attacking the ester function of the substrate, the different activity of oximes and their complexes is caused by

- a) different acidity of the oxime group;
- b) different nucleophilicity of the oximate anion.

However, these effects are contradictory: the higher is the acidity (and thus the concentration of oximate anions), the lower is their nucleophilicity. Coordination causes higher acidity of the oxime grouping. Similarly, the acidity of the oxime grouping (and hence the nucleophilicity of the oximate anion) are influenced by neighbor substituents and/or presence of heteroatoms.

Electroreductions of hydroxyimino group of four series of substituted ketoximes on mercury electrodes were studied using dc polarography, coulometry and preparative electrolysis. Depending on pH, double-protonated, single-protonated and neutral forms of the ketoximes are transformed in a four-electron reduction to the corresponding amine. Reducibility of the oximes correlates with the enhancement of their hydrolytic activity towards 4-nitrophenyl acetate. The influence of the structure and substitution on the reduction potential and reduction pathway of various oximes are discussed.

Electroreductions of Ni²⁺, Cu²⁺ and Zn²⁺ complexes of methyl azinyl (azinyl = pyridin-2-

yl, pyridazin-3-yl, pyrimidin-2-yl, pyrimidin-4-yl, pyrazinyl) ketoximes on mercury electrode were studied using dc polarography. Three different types of complex behaviour on the mercury electrode were observed: whereas Ni²⁺ complexes are reduced on the hydroxyimino group of the ligand, reduction of Cu²⁺ complexes proceeds on the metal ion. In the case of Zn²⁺ complex of methyl pyridin-2-yl ketoxime, only reduction waves of uncoordinated ligand and metal were observed due to rapid decomplexation pre-equilibrium.

The structure of the complex with the formula [Zn(methyl pyridin-2-yl ketoxime)₂(NO₃)₂] isolated from water-ethanolic solution, was determined from X-ray diffraction data.

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