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[Lab. of Pharm. Analytical Chemistry]

Electrocatalytic Oxidation of Carbohydrates at Copper(II)-Modified Electrodes and its Application to Flow-Through Detection.

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Electrochemical oxidation of carbohydrates at several copper-oxide-modified electrodes in alkaline solution has been studied using cyclic voltammetry and rotating-disk voltammetry. It has been found Cu(II) oxide on the electrode surface is essential for the electrode process, in which some electrogenerated higher Cu(III) oxide seems to serve substantially as a catalyst. Each mole of xylose, glucose and sorbitol was found to be oxidized to 5 mol, 6 mol and 6 mol of formic acid respectively with the transfer of 10, 12 and 14 electrons. The electrodes allowed the highly sensitive amperometric detection of carbohydrates down to picomole level in flow-through systems.

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Novel Redox Behavior of [5]Radialenes with 1,3-Dithiol Groups.

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Only one pair of reversible waves involving a net four-electron transfer has been observed in the redox process of pentakis(1,3-benzodithiol-2-ylidene)cyclopentane (1). This is the first case of a single-wave four-electron transfer with only one macroscopic redox site in organic redox systems. Digital simulation have shown that 1 mainly follows a two-step two-electron transfer and is converted to the tetracation via the dication. The estimated redox potentials indicates that three electrons are transferred at no cost in energy after the first electron is transferred.

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Spectroscopic Study of the Conformational Dependence on Acid Dissociation of Phenoxy pyridinium Cations.

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Thermodynamic constants for acid dissociation of the 2-, 3- and 4-phenoxy pyridinium, and 2-(2,6-xyllyloxy)pyridinium cations were estimated by the spectroscopic method, and are extensively discussed in relation to the conformations around the bridging oxygen atom and the electronic states. The protonation to the nitrogen atom of 2-phenoxy pyridine (2PP) causes a conformational alteration from the stable skew form to the twist. Further evidence for twisting around the C-O bonds of 2PP with protonation has been given by the small ΔH° value concerning the protonation to 2PP.