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[Lab. of Pharm. Analytical Chemistry]

Characterization of Topa Quinone Cofactor

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Detailed theoretical analysis of the electrochemistry of topa quinone (TPQ), the organic cofactor of Cu-containing amine oxidase, has afforded the separated estimation of two overlapped one-electron redox potential and the acid-dissociation constants of the phenolic OH groups of TPQ, TPQ semiquinone and topa. The results were supported by electronic and ESR spectra. Redox catalytic activity of TPQ for the oxidation of amines and NADH was not observed. *Ab initio* energy minimization calculation of acid-dissociated TPQ anion indicates an intermediate electronic structure between the *p*- and *o*-quinone types. The lack of the redox catalytic activity of free TPQ is attributable to the partial contribution of the *p*-quinone-type structure.

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[Lab. of Pharm. Analytical Chemistry]

Surface-Redox Reaction Mechanism of Quinones Adsorbed on Basal-Plane Pyrolytic Graphite Electrodes.

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Reversible and quasi-reversible cyclic voltammograms of 9,10-phenanthrenequinone, 1,4-benzoquinone, chloranil, 1,4-naphthoquinone, 9,10-anthraquinone, and 5,12-naphthacenequinone adsorbed on basal-plane pyrolytic graphite electrodes have been theoretically analyzed in view of a one-step two-electron mechanism and a two-step one-electron mechanism. In each mechanism, the Frumkin-type interaction between the adsorbed molecules is taken into account and curve-fitting analysis of current-potential curves is presented. Detailed analysis has revealed that the electrochemistry of the adsorbed quinones can be well interpreted on the basis of the two-step mechanism rather than the one-step mechanism.

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Separation of Amino Acid-oxazole Derivatives of the Redox Coenzyme Pyrroloquinoline Quinone by Capillary Zone Electrophoresis

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Condensation products (oxazole derivatives) from the reaction of the coenzyme pyrroloquinoline quinone (PQQ) with several α -amino acids were successfully separated by capillary zone electrophoresis. Product analysis of the condensation reactions of PQQ with amino acids was performed by this method and the mechanism is discussed briefly. PQQ-spiked bovine serum was also analyzed. Unsubstituted type 1 oxazole derivative was predominantly detected. This result suggests that most of the PQQ in mammalian fluids, if any, exists as PQQ derivatives, probably as the type 1 oxazole derivative.