

[Spectrochim. Acta, 43A, 955 (1987)]

New Description of the Substituent Effect on Electronic Spectra by Means of Substituent Constants. IV. Charge Transfer Spectra of EDA Complexes of Tetracyanoethylen with *meta*-Disubstituted Benzenes.

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Charge transfer spectra of EDA complexes composed of TCNE and various kinds of *meta* disubstituted benzenes were discussed on the basis of a general equation, theoretically derived to express the substituent effect on electronic spectra. Molecular orbital calculation showed that the substituent effect on the CT spectra has been classified into two groups according to the HOMO character of *meta*-disubstituted benzenes (donors). This viewpoint was quite well supported by the application of the general equation to the CT spectra.

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Voltammetric and Spectroscopic Studies on the Carcinogen 4-(Hydroxyamino)quinoline *N*-Oxide (4HAQO) and its Analogues.

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Voltammetric studies of the oxidation processes of 4HAQO and related substances were carried out in aqueous solutions. 4HAQO forms a reversible redox couple with 4-nitrosoquinoline *N*-oxide through an intermediate free radical. The pH dependence of the redox potential gave the pK_a values, which agreed well with the data measured by UV spectral methods. The molecular structures of species formed by proton addition or dissociation were investigated by analyses of the pK_a and the electronic spectra, and also by their molecular orbital calculations. The *N*-oxide type structure was considered to be a main species in aqueous solutions of 4HAQO and its analogues.

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Electrochemical Study of the Mechanism and Kinetics of Reductive Glycoside Elimination of Adriamycin (ADM) Adsorbed on a Mercury Electrode Surface.

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Mechanism of the reductive glycoside elimination of an adsorbed ADM was studied by means of cyclic voltammetry (CV) and potential step chronoamperometry (PSC) at pH 7.6. The detailed analyses indicate that the hydroquinone species of ADM eliminates a C₇-glycoside to form a quinone methide intermediate, which brings about irreversible reactions in two pathways: the protonation-deprotonation process to the quinone species of 7-deoxyadriamycinone (7DADMN) and the one-electron reduction to the semiquinone species of 7DADMN. The theoretical equations of the reductive deglycosidation for PSC and CV were derived and the apparent rate constants were estimated.