

[Colloid Polym. Sci., 266, 745 (1988)]

Reactivity of Singlet Oxygen Generated by the Photosensitization of Tetraphenylporphyrin in Liposomes.

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A hydrophobic porphyrin derivative, tetraphenylporphyrin (TPP), was used as a sensitizer, and an anionic dye, methyl orange (MO), was employed as a substrate of photooxidization. TPP was incorporated into the hydrophobic environment of phosphatidylcholine (PC) bilayer membranes, liposomes. When oxygen was purged out of the liposome suspension by nitrogen bubbling, the degradation of MO was completely inhibited. A specific superoxide scavenger, superoxide dismutase, had no effect on the MO degradation. The replacement of H₂O by D₂O resulted in a 10 times enhancement in the photodegradation of MO.

[Bull. Chem. Soc. Jpn., 61, 1431 (1988)]

New Description of the Substituent Effect on Electronic Spectra by Means of Substituent Constants. V. $n-\pi^*$ Transition of Aliphatic Carbonyl Groups.

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The substituent (X) effect on the carbonyl $n-\pi^*$ band of CH₃COX is discussed on the basis of a general equation, theoretically derived in order to express the substituent effect on electronic spectra using substituent constants. The results have been successful and are supported by molecular orbital calculations. Our present treatment made it possible to estimate the $n-\pi^*$ transition energy of CH₃CONH₂, the data estimated by many authors being contradictory to each other.

[J. Electroanal. Chem., 246, 385 (1988)]

Electrocatalytic Reduction of Oxygen at a Pyrolytic Graphite Electrode Modified by Adriamycin and its 7-Deoxyaglycone.

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Anthracycline antibiotics, adriamycin and 7-deoxyadriamycinone, adsorbed on a basal-plane pyrolytic graphite electrode catalyze the reduction of molecular oxygen in pH 7.0 phosphate buffer. Cyclic and rotating-disk voltammetric studies show that the semiquinone radical intermediate is an active species in the catalytic reduction. Theoretical treatment newly developed here gives support to this mechanism. The cyclic and rotating-disk voltammograms were then simulated by means of a non-linear least-squares curve-fitting technique. The results are quite good, and the kinetic parameter values thus evaluated by the curve-fitting method and also by the Koutecký-Levich-type equation are discussed.