

BEHAVIOR OF THE PORPHYRIN CATION RADICAL.

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Decay rates of hematoporphyrin-Mn(IV) (II) to the Mn(III) complex (I) had been shown to increase with decrease of pH of the solution. In acidic media at $\text{pH} < \sim 6$, the reaction did not follow simple pseudo-first order kinetics. At pH 1.1, change of the absorption at $\lambda_{\text{max}} 440\text{m}\mu$ was detected by a rapid-scan spectrophotometer. The nature of the intermediate was discussed on the basis of the results of chemical oxidation of (I) with Ce^{4+} at pH 0.8 and the oxidation-reduction potential of (II). The cation radical of (I) was most probable candidate for the short lived intermediate.

Hydrogen peroxide was detected in 7% yield as a product of the reaction of (II) to (I) at pH 7.4 by the potentiometric titration with Ce^{4+} . Further, 30% of water soluble peroxide was detected by iodometry as a product of the reaction at pH 2.0.

REACTIONS OF 7- ~~α~~ -D-ARABINOFURANOSYLHYPOXANTHINE

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A new type of ketosugar nucleoside, 7-(5-trityl-2,3-dideoxy-2-oxo- ~~α~~ -D-pentofuranosyl)hypoxanthine (1) and a new type of purinecyclo nucleoside, 5'-0-trityl-3',6-anhydro-7- ~~α~~ -D-arabinofuranosylhypoxanthine (2) were synthesized from 5'-0-trityl-2',3'-di-0-mesy- ~~α~~ -D-arabinofuranosylhypoxanthine. Mass fragmentation pattern and mode of formation of 1 and 2 have been also discussed