

8976 C

The Two-Step Oxidation-Reduction of Phthiocol.

EDGAR S. HILL. (Introduced by P. A. Shaffer.)

*From the Department of Biochemistry, Washington University School of
Medicine, St. Louis.*

Having found that semiquinones can be formed from the anthraquinone sulfonates¹ in alkaline solution, it was suspected that phthiocol, a pigment contained in the human tubercle bacillus, isolated by Anderson and Newman² and proved by them to be 2-methyl-3-hydroxy-1, 4 naphthoquinone,^{3, 4} might behave similarly. Ball⁵ studied the electrochemical behavior of phthiocol at pH's ranging from 1.12 to 12.56 and reported no indication of a 2-step oxidation.

Our suspicions were partially confirmed colorimetrically when solutions of phthiocol at pH > 10 were reduced slowly and an intermediate violet color was observed. Solutions of phthiocol were titrated reductively over a pH range from 7.53 to 14.3 (3M-NaOH), and it was found from an analysis of the titration curves that the separation of the 2 steps begins at about pH 9.0 and is more distinct at greater pH's. The separation never becomes so great as to produce a jump of the potential at 50% of the whole titration. The maximum amount of the ratio semiquinone: total dye is about 50% at pH 13.4-14.3. The E'_o curve (midpoint potentials of the system: fully oxidized-fully reduced dye) changes from a slope of .06 to .03 at pH 11.5 (pK_{r_2}) and from .03 to 0.0 in the neighborhood of pH 14.3 (pK_{r_3}). The curves of the midpoint potentials of the systems: semiquinone form-fully reduced form, and totally oxidized form-semiquinone form (E_1 and E_2 , respectively as per Elema⁶) cross the E'_o curve at pH 12.9, at a potential of -0.540 volt.

¹ Hill, Edgar S., and Shaffer, Philip A., *Proc. Am. Soc. Biol. Chem.*, 1936, p. li.

² Anderson, R. J., and Newman, M. S., *J. Biol. Chem.*, 1933, **101**, 773.

³ Anderson, R. J., and Newman, M. S., *J. Biol. Chem.*, 1933, **103**, 197.

⁴ Anderson, R. J., and Newman, M. S., *J. Biol. Chem.*, 1933, **103**, 405.

⁵ Ball, E. G., *J. Biol. Chem.*, 1934, **106**, 515.

⁶ Elema, B., *J. Biol. Chem.*, 1933, **100**, 149.