ASYMMETRIC DYES AND THE MECHANISM OF DYEING

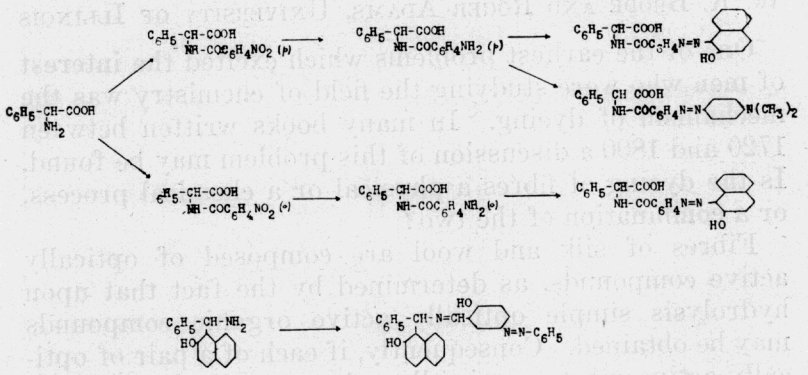
W. R. Brode and Roger Adams, University of Illinois

One of the earliest problems which excited the interest of men who were studying the field of chemistry was the mechanism of dyeing. In many books written between 1720 and 1800 a discussion of this problem may be found. Is the dyeing of fibres a physical or a chemical process, or a combination of the two?

Fibres of silk and wool are composed of optically active compounds, as determined by the fact that upon hydrolysis simple optically active organic compounds may be obtained. Consequently, if each of a pair of optically active substances is allowed to react with the fibres it may be expected that one would react more rapidly under similar conditions than the other. On the other hand, if the active substances were merely physically absorbed the rapidity of action should be the same for each of the pair. The problem, therefore, involved (1) the preparation of one or more pairs of optically active dyes, (2) the determination of the validity of the assumption that if the combination of such dyes with the fibre was purely physical in character the absorption would be the same for each of the pair, and (3) a determination of the speed with which the dyes react with the fibres under similar conditions. It was also necessary to be certain that the method for determining the amount of dye absorbed by the fibre was accurate.

The dyes which have been studied are of the azo type. One pair was made by the condensation of the active phenyl amino acetic acids with p-nitrobenzoyl chloride, reduction of the product to the corresponding amine, diazotiation of this latter substance and coupling with beta naphthol. A second pair of dyes was made by the same series of reactions except that the coupling was made with dimethyl aniline. A third pair was made by using o-nitrobenzoyl chloride in place of p-nitrobenzoyl chloride and the coupling with beta naphthol in the last step. A fourth pair was produced by taking the d and l forms of alpha beta-naphthol benzyl amine and condens-

ing with benzene azosalicyl aldehyde. The equations representing these syntheses are given below.



The degree of absorption of the optically active dyes by means of charcoal and kaolin was determined. With these absorbing agents there is no possibility of chemical reaction. All the experiments showed that a d dye was absorbed to the same extent as an l dye, and consequently the validity of the assumption that physical absorption of dyes by fibres would be the same for enantiomorphs was effected. The absorption of the racemic modification, however, was much greater than that of the active forms due to the fact that it was less soluble and more colloidal in character.

As the method for determining the amount of dye absorbed in a given time was by means of colorimeter readings before and after treatment of the standard dye solution with the fibres, the absorption spectra of the d and l forms of the dyes was determined. The bands were found to be of the same frequency both in the visible and ultra violet. A determination of the hydrogen ion concentration of a dye solution before and after treatment with the fibres indicated that there was a maximum change of 0.5 pH and that, therefore, the color change due to change in hydrogen ion concentration was negligible. A study of the effect of varying the hydrogen ion concentration showed that the absorption band does not change in wave length but merely in intensity, at least between 3 and 8.5 pH. Excess of acid or alkali causes sharp changes in the appearance of the band.

Repeated experiments under varying conditions with active dyes which had been very carefully purified showed that one form was absorbed to the same extent as its enantiomorph. The conclusion that can be drawn from these experiments is that the mechanism of dyeing is purely physical in character.