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Chemical Aspects of Bleaching Human Hair

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Synopsis—A review of HAIR BLEACHING, which describes reactions of bleaching agents with hair proteins and with hair pigments, is presented. The major emphasis is on the CHEMICAL ASPECTS of bleaching with special attention given to the oxidative degradation of the DISULFIDE BONDS in hair.

Introduction

During the past 20 years a great deal of progress has been made in determining the composition of amino acid residues (1–5) and hydrolyzates (6, 7) of oxidized keratin fibers, and in the isolation and analysis of fragments formed from the chemical degradation of natural pigments (8–12). Although many aspects are still controversial, general features of the structures of hair and of hair pigments, and of the reactions occurring during bleaching, may be described in terms of chemical structures and reaction mechanisms. The objective of this paper is to review and to describe some of this work in the language of physical-organic chemistry. Thus, the following discussion contains a brief description of current bleaching compositions followed by a review of the chemistry concerned with the oxidative degradation of hair proteins and hair pigments.

Reagents Used in Hair Bleaching

Modern bleaching preparations contain hydrogen peroxide as the primary oxidizing agent with salts of persulfate added as "accelerators" (13). The pH of these systems is generally in the range of 9.0 to 11.0, and stabilizers (e.g., sequestrants) are generally added to minimize decom-

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position of the peroxide. Additional details concerning bleaching formulae may be found in the book edited by Sagarin (14).

The Reaction of Bleaching Agents with the Proteins of Human Hair

The primary purpose in the bleaching of human hair is to lighten the hair; however, due to the severe reaction conditions required for destruction of the pigment chromophore, side reactions with the hair proteins occur simultaneously. Zahn (6) demonstrated that the reaction of oxidizing agents with the proteins of human hair occurs primarily at cystine. Robbins and Kelly (7) have shown that rather small amounts of degradation occur to the amino acid residues of tyrosine, threonine, and methionine during severe bleaching; however, in accord with Zahn, the main site of attack is at the disulfide bonds of the cystyl residues in the fibers. These authors have also shown that whereas 15 to 25% of the disulfide bonds in human hair are degraded during "normal" bleaching, as high as 45% of the cystine crosslinks may be broken during severe "in practice" bleaching.

Although a description of the kinetics of the reaction of human hair with bleaching agents could not be found, there is evidence to suggest that at least the oxidative cleavage of the disulfide bonds is diffusion controlled. Harris and Brown (15) have shown, by reduction and methylation of keratin fibers, that the wet tensile properties decrease almost linearly with the disulfide content. Alexander *et al.* (16) have arrived at this same conclusion after studying wool fiber oxidized with peracetic acid. A similar phenomenon has been observed, by this author, for hair that had been oxidized with alkaline hydrogen peroxide. These observations lead to the conclusion that the percentage loss of various parameters of the wet tensile properties of hair, that occur during bleaching, e.g., the 20% index (17), is a measure of the per cent cleavage of cystine crosslinks.

Edman and Marti (18) have described the change in the 20% index of hair fibers as a function of treatment time in 6% hydrogen peroxide, at 32°C, using a 25:1 solution:hair ratio at pH 9.52. Their data, plotted in Fig. 1, *versus* the square root of the time provides a straight line from which an approximate diffusion coefficient may be calculated. An equation developed by Crank (19) which describes diffusion from a stirred solution of limited volume into a cylinder of infinite length was used in this instance.

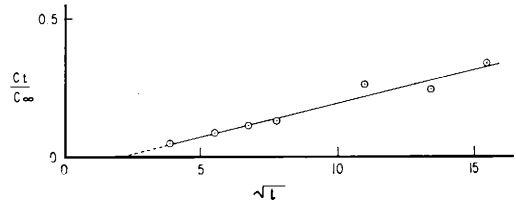

Figure 1. Rate of cleavage of cystine crosslinks estimated from tensile properties

$$C_T/C_\infty = 2\left[\frac{2}{\sqrt{\pi}}\,(Dt/a^2)^{1/2} + \ldots\right.$$

The term C_T is the 20% index at time (t), and represents the amount of cleaved disulfide at time (t); C, the 20% index at time zero represents the total amount of disulfide before oxidation, and a represents the fiber radius which is assumed to be 40 μ. Application of the Crank equation to the data in Fig. 1 provides an approximate diffusion coefficient of 1.8×10^{-9} cm^2/min, which is of the anticipated magnitude, suggesting that this reaction (the oxidative cleavage of the disulfide bond) is diffusion controlled.

Two types of mechanisms have been suggested for the oxidative degradation of disulfides (20), one involving S—S fission and the other C—S fission. The mechanistic schemes for S—S and C—S fission preferred by this author are summarized in Fig. 2, and the nomenclature used for several of the structures involved in these two schemes is described in Table I. A more comprehensive discussion of the oxidative degradation of cystine is given by Savige and Maclaren (20).

Two features that may be used to distinguish between these two reaction paths are the following: First of all, if the oxidation reaction proceeds totally *via* S—S fission, then two moles of sulfonic acid should be produced per mole of reacted disulfide. However, if the reaction goes totally

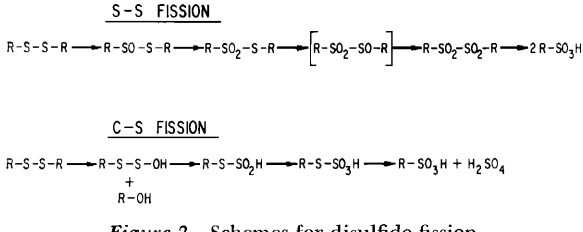

Figure 2. Schemes for disulfide fission

Table I
Cystine Oxides and Sulfur Acids

Cystine Oxides
R—SO—S—R Monoxide
$R—SO_2—S—R$ Dioxide
$R—SO_2—SO—R$ Trioxide
$R—SO_2—SO_2—R$ Tetroxide
$R = NH_2—\underset{\displaystyle |}{CH}—CH_2—CO_2H$
Sulfur Acids
R′—S—OH Sulfenic acid
$R'—SO_2H$ Sulfinic acid
$R'—SO_3H$ Sulfonic acid

through C—S fission, then only one mole of sulfonic acid can be produced from each mole of disulfide that reacts. Nachtigal and Robbins (5) have shown this ratio to be greater than 1.6:1 for one sample of severely bleached hair, suggesting that this reaction is occurring largely by S—S fission. Secondly, if this reaction occurs through the C—S fission route, the alcohol produced would be a seryl residue which, on hydrolysis, would provide significantly larger quantities of serine in bleached hair hydrolyzates than in hydrolyzates of unbleached hair. This is not the case (7). Therefore, the oxidative cleavage of the disulfide bond that occurs during the bleaching of human hair is predominantly an S—S fission process.

Since the bleaching of human hair is carried out in an aqueous alkaline oxidizing medium, hydrolysis of the cystine oxide intermediates (Fig. 3) should be competitive with oxidation. In fact, disproportionation of the cystine oxides (20) may also occur, adding to the complexity of the total reaction scheme.

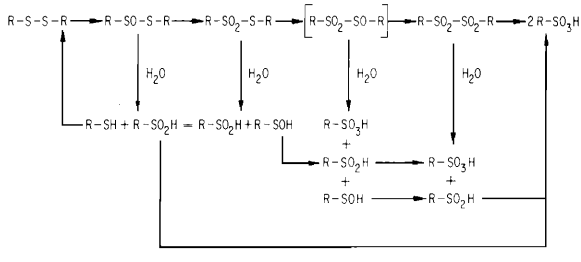

Figure 3. S—S fission of disulfides in aqueous alkaline oxidizing medium

Oxidation and hydrolysis reactions of the cystine oxides are summarized in Fig. 3. Disulfide trioxides have never been isolated, but may be inferred as possible intermediates in this scheme, since both disulfide dioxides (thiolsulfonates) and disulfide tetroxides (20) have been isolated. Cystine monoxide and dioxide are extremely sensitive to alkaline hydrolysis (21, 22) but have been isolated from aqueous acidic oxidations (22) and the tetroxide should be even more sensitive to alkali (20). Although the importance of hydrolysis relative to oxidation for each of the cystine oxides is not known, it is certain that hydrolysis should be increasingly important with increasing pH, and at the pH of current bleach products (pH 9 to 11) hydrolysis of these species should be highly competitive with oxidation.

In summary, sulfonic acid is the only established end product of the oxidative cleavage of the disulfide bond that occurs during the bleaching of human hair (3, 4). The mercaptan content of bleached hair, as one would predict, is lower than in unbleached hair (5), and neither the monoxide nor the dioxide occur as significant end products (5). Considering all the species from the oxidation of disulfides described in Fig. 3, the sulfinic acid is the only species of even moderate stability (23) remaining to be examined. Sulfenic acids are notoriously unstable (24) and trioxides and tetroxides are even more sensitive to alkali than dioxides and monoxides.

Oxidation of Hair Pigments

The principal pigments of human hair are the brown-black melanins and the less prevalent red pigments, the trichosiderins. Hair pigments reside within the cortex and medulla (25) in ovoid or spherical granules that generally range in size from 0.2 to 0.8 μ along their major axis (26). These particles generally comprise less than 3% of the total fiber mass as estimated by the residue weight after acid hydrolysis (27). Methods used for pigment granule isolation usually involve dissolving the hair from the granules (11, 26, 28–31). Funatsu (31) has found that the general composition of melanin granules consists of pigment, protein, and minerals. Flesch (11) reports a similar general composition for the trichosiderin-containing granules. Schmidli *et al.* (32, 33), after acid or alkaline hydrolysis of hair, were able to isolate melanin combined with protein, suggesting that melanin exists in combination with protein in the granules (melanoprotein).

Since the pigment granules are located in the cortical cells and in the medulla of human hair, it is reasonable to assume that pigment degrada-

tion is a diffusion-controlled process; however, the evidence supporting this contention is inconclusive at this time. In fact, determination of the rate-controlling step in this process is a large order task, since it is difficult to follow quantitatively the loss of pigment in hair, and since two important side reactions consume oxidizing agent—i.e., the previously described oxidation of amino acid residues (7), and dibasic amino acid residues associate strongly with many oxidizing agents including hydrogen peroxide and persulfate (34, 35).

The current knowledge of the structure of melanic pigments, the most preponderant pigments of human hair, has been described recently by Nicolaus (8) and Mason (9). Nicolaus has proposed that melanin is a complex random polymer formed from several species of the Raper scheme for the biological formation of 5,6-dihydroxyindole (36, 37) (Fig. 4), while Mason proposes that melanin is a homopolymer of 5,6-dihydroxyindole. Regardless of the differences, both theories suggest that the indole quinone grouping (or its reduced form) is a major repeating structural unit of melanins (Fig. 5).

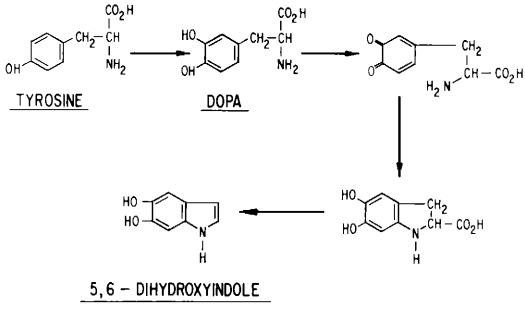

Figure 4. Raper's scheme for formation of 5,6-dihydroxyindole

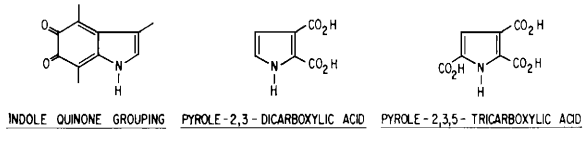

Figure 5. Repeating unit and fragments of melanins

Binns and Swan (38) oxidized synthetic melanins with alkaline hydrogen peroxide and identified only very small quantities of pyrole 2,3-dicarboxylic acid and pyrole 2,3,5-tricarboxylic acid as end products (Fig. 5). These same authors suggested that melanic acids are also products of this reaction; however, no evidence was provided to support this suggestion.

Small quantities of these same two pyrolic acids (and other pyrolic acids) have been isolated from the oxidation of sepiomelanin with permanganate or with hydrogen peroxide in acetic acid (39, 40). This latter reaction most likely involves attack by peracetic acid on melanin rather than attack by the hydroperoxide anion or the hydrogen peroxide molecule, as probably occurs in hair bleaching (41).

The isolation of pyrolic acids from the oxidation of melanin is consistent with the previous suggestion that the indole quinone grouping is a major repeating structural unit. The low yields of isolated pyrolic acids (generally less than 1%) may be explained on the basis that these fragments are themselves sensitive to oxidation; however, a second explanation suggests a multiplicity of sites in the pigment macromolecules that are susceptible to attack by oxidizing agents producing many unrecovered fragments. In more pertinent experiments, Wolfram *et al.* (10) have studied the reaction of alkaline hydrogen peroxide with melanin granules isolated from human hair. These authors suggest an initial solubilization followed by decolorization. Several products derived from melanoprotein were isolated from these reactions, including proteinaceous species rich in the dibasic amino acids, and several other products ranging up to 15,000 in molecular weight. Further identification of these fragments should provide interesting information concerning the structure of melanin and the mechanism of its oxidative degradation during bleaching.

The pigments in red hair are structurally different from the brown-black melanins (42). The chromophoric unit (Fig. 6) of the red pigments is of low molecular weight (560) as compared to the polymeric melanins. However, the aromatic rings of this structure are of high electron density and, as a consequence, should be sensitive to attack by oxidizing agents. One may conclude from the current knowledge of the structures of the melanins and the trichosiderins that they are similar enough to be sensitive to oxidation, yet dissimilar enough to react through different mechanistic schemes during oxidative degradation. A more complete understanding awaits further study.

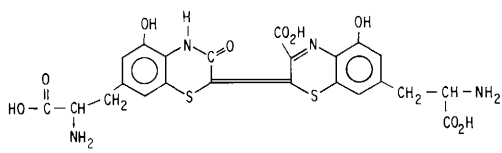

Figure 6. Structure of the pigment trichosiderin suggested by Prota

Summary

A review of hair bleaching describing reactions of bleach agents with the proteins of human hair and with hair pigments is presented. Support for diffusion-controlled oxidative cleavage of the disulfide bond during bleaching is described. Evidence for oxidation of cystyl residues in hair through S—S fission instead of C—S fission is presented and possible end products of the oxidation reaction are described. The low yields of products (pyrolic acids) isolated from the oxidation of melanins suggest that these species are themselves sensitive to oxidation, and/or that several different functional groups in the pigment macromolecule may be susceptible to attack by oxidizing agent.

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