

Hair colorants

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INTRODUCTION

Modern hair dyeing methodology was established in the 1950's. Since that time the sales of hair colorants have shown continued growth, rising to an annual total of \$600 million in the United States during 1981. Thus, dyes are the third largest product type in the hair care category, following shampoos and conditioners. Accompanying this growth have been extensive research efforts into dye synthesis, the physical and organic chemistry of color producing processes, and the development of aesthetically acceptable formulations.

This area was last reviewed in 1973 (1). At that time the colorant market had segmented into three separate product types. The permanent, or oxidative, dyes use hydrogen peroxide to oxidize aromatics, such as *p*-diamines and *p*-aminophenols, to active intermediates which then react with a variety of color couplers to give the final, shampoo-fast dyes. Semi-permanent products incorporate amino- or hydroxy-nitrobenzenes which readily diffuse into hair, but also diffuse out again over the course of several shampoos. Temporary dye products generally consist of high molecular weight acid dyes which are deposited on the hair surface to give a coloring effect removable by a single shampoo. These categories have remained virtually unchanged.

Outstanding research tasks as seen at the previous review involved additional fundamental spectral studies more closely relating dye color to chemical structure, more extensive investigations of the color forming reactions of oxidative dyeing, and the development of data on diffusion rates of dyes into hair. While some of this work has been undertaken in the intervening ten years, the effort seems to have been unevenly applied since the major emphasis has been on color forming reactions.

Although unforeseen several years ago, major research attention has recently been given to in depth studies of the toxicological properties of the dyes. In particular, the mutagenic and carcinogenic potentials of many dyes have been evaluated. This topic has been reviewed (2) and will be discussed only briefly in this article. Its influence on the directions of hair dye research has, however, been significant, and it has markedly curtailed the introduction of novel ingredients.

SPECTRAL STUDIES

There have been several recent attempts to correlate the color of dyes to their chemical constitution. Most of these have been based on empirically determined rules whereby

the maximum absorption wavelength of a substituted compound is calculated on the basis of the number and nature of substituents, each of which has a characteristic hypso- or bathochromic effect on the spectrum of the parent compound. This process has worked well with nitroanilines and nitrophenylenediamines (3).

Molecular orbital calculations have been used to predict spectral maxima for a series of nitro- and dinitro-phenylenediamines (4) and several other classes of dyes (5). Generally good agreement is obtained for spectra measured in cyclohexane, except for compounds with severe steric crowding. Similar restrictions are found with the empirical rules, so the MO calculations, even though more soundly based, are of little better predictive value and neither method is useful in predicting absorption intensity. Presumably such studies will be extended and refined in the future.

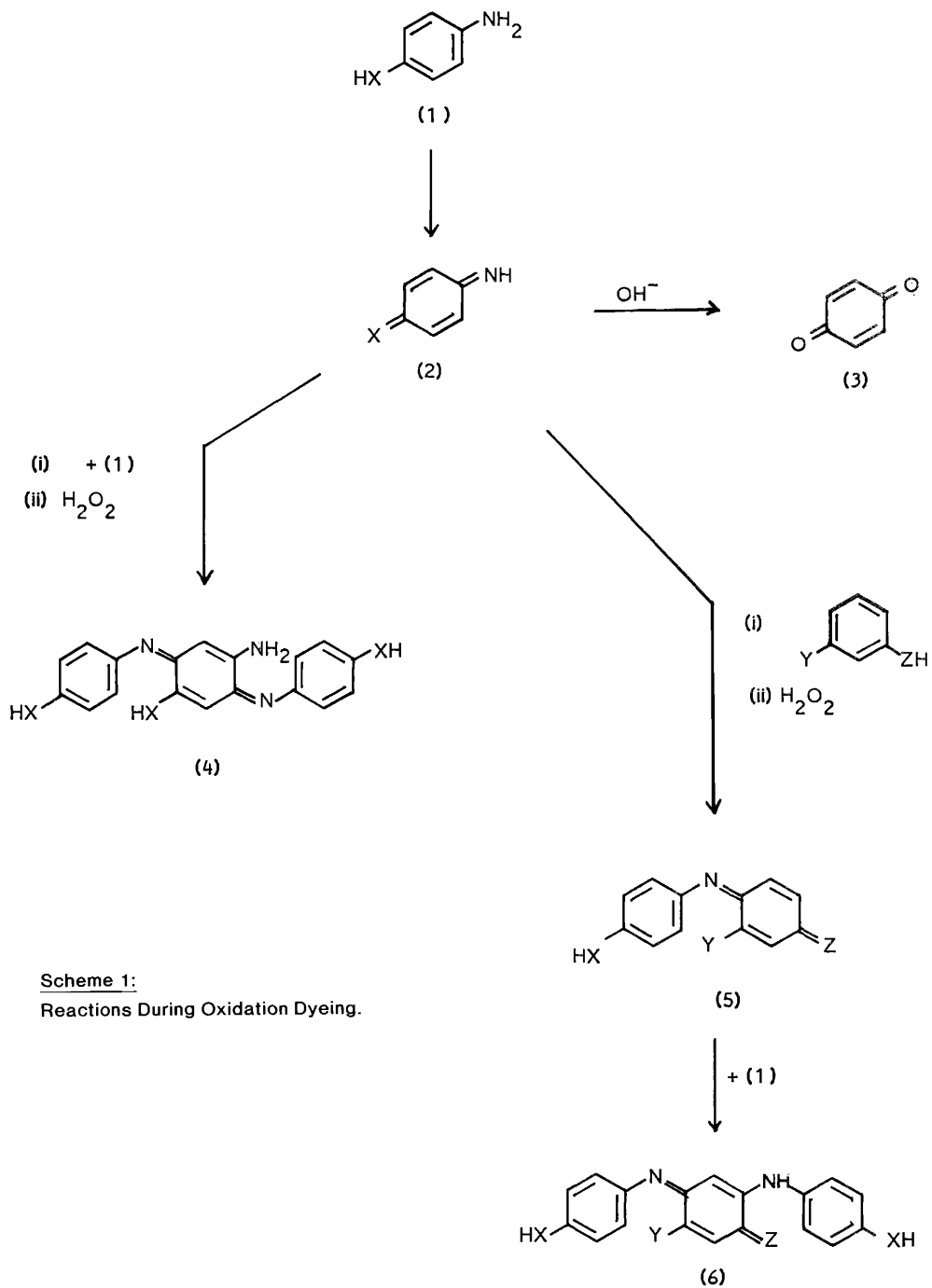
OXIDATION DYES

Oxidation dye compositions have remained relatively unchanged over the last few years. However, the color forming reactions from oxidation dye mixtures have been extensively studied, and a generalized scheme is represented in Scheme 1. The chemistry of reactions with *p*-phenylenediamine (1: X = NH), has been known for some time (6). Recent work (7) has now extended these investigations to *p*-aminophenol (1: X = O).

Kinetic studies have shown that *p*-aminophenol is oxidized to benzoquinone monoimine (2: X = O) which is slowly hydrolyzed to *p*-benzoquinone (3) in alkaline solution. However, in the presence of other reactants, dye formation occurs. Thus, monoimine reacts with excess *p*-aminophenol (8) to give the brown trinuclear dye (4: X = O) and with color couplers to give indo dyes, e.g., with phenols (9) to give blue indophenols (5: X = Z = O; Y = H). In many cases, excess *p*-aminophenol will add to the 5-position of the indo dye, if vacant, to give tri-nuclear dyes such as (6). In general, these trinuclear dyes have significantly less distinct spectra than the di-nuclear indo dyes (5), and this may be a cause of the browns and yellows frequently obtained from *p*-aminophenol-based dyes.

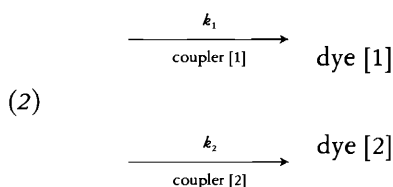
Bandrowski's base (4: X = NH) has been shown to have some mutagenic properties and its potential formation from dye solutions containing *p*-phenylenediamine had been considered a problem. However, kinetic studies show that the rate of self-coupling of *p*-phenylenediamine (and of *p*-aminophenol) is very much slower than their rate of coupling with typical color modifiers. Thus, in any commercial formulation, none of the self-coupled products can be formed.

Application of the results of these *in-vitro* experiments to hair dye practice has not yet been fully developed. It is clear that dyes formed from individual couples in solution and on hair are similar, even though different oxidants may have been used to form them. This has been confirmed chromatographically (10) using dye formulations as well as synthetic mixtures of components. Of course, as the concentration of reactants is increased, the opportunity for bimolecular reactions such as (5) to (6) increases, and the number of products increases. In addition, commercial compositions consist of mixtures of dye ingredients blended to give the required shade, and the final color results from a complex combination of competing reactions. The author has used the published rate constants to predict relative product yields from mixtures of compo-



nents and, where possible, to compare these predictions with experimentally determined yields.

So far results have been evaluated only for a single competition (i.e., one primary intermediate and two couplers, or two primary intermediates and one coupler). These results may not be directly translated into colors produced on hair from similar mixtures because factors such as diffusion rates of the various species also have to be considered. However, when dye yield in solution is compared with that predicted from the appropriate competing rate constants, generally good agreement is obtained. For example, when imine (2) was formed by ferricyanide [FC] oxidation in the presence of ten-fold molar excesses of two couplers, the ratio of the two indo dyes were, as predicted, for a first-order competition, in the ratio of the two coupling rate constants:



then: dye [1]/dye [2] = k_1/k_2

This is demonstrated in Table I for competition of either *p*-phenylenediamine [PPD] or *p*-aminophenol [PAP] with *m*-phenylenediamine [MPD] and *m*-aminophenol [MAP].

Table I
Competition for *meta* Couplers Under First-order Kinetic Conditions at pH 8.6 and 30°

Relative Concentrations ^a				% Para-MPD ^b	
PPD	PAP	MPD	MAP	Expt	Theory ^c
1	—	10	—	100	100
1	—	0	10	0	0
1	—	10	10	12	20
1	—	15	5	30	43
1	—	17.5	2.5	49	63
—	1	0	10	0	0
—	1	10	0	100	100
—	1	10	10	17	18
—	1	15	5	31	40
—	1	17.5	2.5	61	61

^aMultiples of 9.3×10^{-3} M.

^bDetermined spectrophotometrically.

^cRate constants: PPD-MPD, 298; PAP-MPD, 11; PPD-MAP, 1200; PAP-MAP, 49 l. mol⁻¹s⁻¹.

Significant error is involved in determining experimental product yields spectrophotometrically since the two products generally have similar spectra. Even so, the agreement between experiment and theory is good.

A second example is shown in Table II, for competition of *m*-phenylenediamine and *m*-aminophenol for *p*-aminophenol (molar ratio 10:10:1) at various pH values.

Table II
Competition for PAP by MAP and MPD at Various pH Values and 30°

pH	% PAP – MPD Product	
	Experimental	Calculated
6.5	80	68
7.1	65	62
7.8	34	30
7.9	34	27
8.7	18	17
9.4	4	8
10.1	0	0

The trends predicted from the effects of pH on the individual coupling rate constants are reflected closely in the product yields from the competition experiments.

Although these *meta* competition reactions are easy to evaluate, the corresponding *para* competitions are much more difficult because first-order kinetic conditions cannot be used. Thus a reaction stoichiometry such as a 10 PPD: 10 PAP: 1 coupler would show significant product formation from *para* self-coupling or cross-coupling or *para* addition to the coupled product. In addition, if a deficit of oxidant is used, some competition for oxidant will be evident and equilibria such as



will be established, resulting in consecutive rather than competitive product formation (6).

Product yields for the competitive system PPD - PAP - MAP are given in Table III.

Table III
Competition between PAP and PPD for MAP at pH 8.6 and 30°

Relative Concentrations ^a			% PPD Product in Mixture	% PAP Reacted		% PPD Reacted	
PPD	PAP	MAP		Found	Theory	Found	Theory
1	—	1	100	0	0	100	100
1	0.5	1.5	74	50	50	75	75
1	1	2	52	48	50	53	50
0.5	1	1.5	43	57	50	86	100
—	1	1	0	100	100	0	0

^aConcentrations are multiples of 9.87×10^{-3} M; 4 molar equivalents of FC added.

Kinetic equations for competing second-order reactions have not been derived, but they are not needed for a quantitative understanding of these data.

When a deficit of oxidant is used with a mixture of PPD and PAP, the PAP product is formed first even when the PAP coupling rate constant is very much less than the PPD rate constant. This is due to oxidation of PAP to monoimine by diimine by equilibrium (i), which effectively means that all the PAP is oxidized first. Any remaining ferricyanide is then used to oxidize PPD to diimine. Since diimine couples faster than monoimine under the experimental conditions, any remaining ferricyanide is used to

oxidize leucodiimine product to the final dye. Since there is no more ferricyanide, any further oxidations will use diimine initially (since it disappears the fastest) and then monoimine. Thus, in these experiments no more than 50% of the total PAP can be converted to monoimine dye. The theoretical yields of PAP and PPD dyes can therefore be calculated and are shown in Table III.

The agreement between theory and experiment is excellent, thus supporting this interpretation of the mechanism of oxidation of mixtures of PPD and PAP.

As a further extension of this theory, the product distribution should be independent of the coupler, since the product ratio depends only on the relative ratios of monoimine and diimine available for coupling and not on their coupling rates. This was confirmed experimentally with the couplers 1-naphthol, resorcinol, MPD and MAP where $53 \pm 8\%$ PPD product was formed from a 1:1 PPD/PAP mixture, $74 \pm 7\%$ from a 2:1 mixture, and $32 \pm 7\%$ from a 1:2 mixture (theory: 50, 75, 33%).

These results demonstrate the utility of the basic kinetic data in predicting results for more complex reactive mixtures.

This procedure may be extended further, but better techniques must be used to analyze the mixtures experimentally.

Polarography (11) has been used to investigate the oxidation-reduction properties of the primary intermediates used in oxidation dyeing; this leads to an alternate way of determining coupling rate constants for these reactions. The second-order rate constant evaluated in this study for coupling *p*-phenylenediamine with *m*-aminophenol agrees very well with the value determined spectrophotometrically (12).

During the review period there have been no significant introductions of novel primary intermediates although it has been suggested that a dyeing system can be based on tetra-aminopyrimidine (13) as well as several other N-heterocycles. In contrast, there has been intense activity in developing new couplers. Particular attention has been given to substitutes for 2,4-diaminoanisole, for which many analogues have been claimed. Probably the most useful of these is 2,4-diaminophenoxyethanol (14). Couplers that produce red shades have also been investigated and many *m*-aminophenols have been claimed in the patent literature.

It is interesting to note that there has been a marked increase in claims for less damage from oxidative products. This is usually achieved by the addition of cationics such as quaternary amines (15) or polymers (16) which mask the effects of damage rather than reduce it.

For many years, oxidative colors faded or changed shade under the influence of sunlight or perspiration. This problem is not as severe with current products. A recent survey (17) has compared the performance of most currently used dye components in relation to perspiration. It shows that coupled products from *p*-aminophenol had the least stability, while 4-aminodiphenylamine gave dyes with the greatest stability. Although most of the information was already available, the inclusion of several recently introduced components is useful.

Chemical processes occurring during these color fading reactions have been shown to involve hydrolytic fission of the dye molecule at low pH, and cyclization to azine dyes at higher pH. These reactions are particularly easy with *p*-aminophenol-derived dyes (18,19).

Despite the significance of these investigations, it has to be remembered that hair is not a passive substrate. While it allows the smaller dye precursors to diffuse in, it limits the diffusion of the larger dye molecules out. In addition, it provides a catalytic surface for peroxide decomposition, accelerating dye forming reactions but apparently protecting the dyes inside from the oxidative decolorization reactions they readily undergo in solution. Finally, hair can be dyed selectively in the presence of the scalp, although the larger pore sizes in the skin may allow for easier removal of dye during subsequent rinsing and shampooing. Thus, there are major areas of this dyeing process that are still incompletely understood.

DIRECT DYES

The chemistry of these dyeing systems is relatively simple since no chemical changes are involved during the dyeing process, and the dye color is transferred directly to the hair.

Typical shades contain 10-12 different dyes, of which the most common are 2-nitro-*p*-phenylenediamines. A variety of N¹ and N⁴ substituents has been added to the wide range of substituents already patented. Despite this, none seems to have a major advantage over the methyl or hydroxyethyl substituents previously claimed and widely used. Some substituted nitro-aminophenols have also been claimed (20).

Of particular interest with this class of dye is their resistance to shampoo and rinsing. This property is carefully balanced in commercial shades and appears to be related to the dyes' structure and molecular weight (21).

There has been a study of impurity content of these dyes in relation to product stability (22). Surprisingly, the nature of these impurities has not been determined, nor, in general, have purification techniques been widely applied in dye synthesis. It seems likely that purity of the dyes must affect many properties of the dyes, and more attention will be given to it in the near future.

OTHER HAIR COLORING SYSTEMS

Most hair coloring is performed with products of the previous two types. However, there is a significant market for products which perform more specialized functions and involve different chemistry.

Development of a permanent hair coloring system based on direct dyes has been the subject of many patent claims over the years. An obvious advantage to the consumer is the direct transfer of solution color to the hair (unlike conventional permanents where the solution is initially almost colorless). A common approach is to use the reactive dyes developed for other fibers, e.g., wool (23), with curing conditions moderated for use on live heads. Dye is thus bonded covalently to the hair and cannot be removed during subsequent shampooing. The practicality of such systems remains to be proven since except for the relevant patents there is a distinct lack of published scientific information.

Progressive dyeing systems are appropriate for the user who needs a gradual change in hair color. Most systems rely on aerial oxidation of the reactants. For example, a recent

patent covers the auto-oxidations of 1,2,4-benzotriol with *p*-diaminobenzenes added to modify the shades (24). However, the metal salt-based compositions (e.g., lead acetate) are apparently still the only product for this type of dyeing effect, since no organic dye-based system is on the market.

Patents have been issued at a steady rate for dyeing systems incorporating either colored resins (25) or natural melanin precursors (26). The lack of commercialization in these areas suggests major drawbacks both in performance and cost of such systems. In any case, the materials are not available in quantities where objective testing is possible. Significant advances in the technology are needed to overcome these problems.

HAIR DYE TOXICOLOGY

Over the last few years, this area has received substantial literature coverage which has recently been summarized by Corbett (2). During this time, most dye ingredients have been subjected to extensive toxicological evaluation including animal feeding studies. In general, adverse effects have not been observed and only three important dye ingredients were found to be carcinogenic in bioassay: 2,4-diaminoanisole, 2-nitro-*p*-phenylenediamine, and 2-nitro-4-aminophenol. Even if such studies are assumed to be valid, conservative risk assessment and human experience seem to support the position that there are no chronic untoward effects from the use of hair dyes. Thus, while such studies may reflect inherent properties of a dye ingredient, usage conditions must be considered. For example, the concentration of 2,4-diaminoanisole during the dyeing process has been monitored chromatographically (27). With a black shade, the concentration falls to around 10% of its original level within 15 minutes and to 5% within 30 minutes. This reflects rapid utilization of such intermediates and suggests that much less than the formulation amount is available during most of the dyeing step. In addition, dye must penetrate the scalp to cause many of the adverse effects. Skin penetration data on radiolabelled dyes after topical application show relatively low dye permeation rates which, however, depend on the area of application (28). Translating such results into actual dye usage is difficult.

More recent work (29) has attempted to quantitate dye penetration under actual usage conditions. In essence, the data shows that with *p*-phenylenediamine, 2,4-diaminoanisole, or HC Blue #1 less than 0.2% of the applied dye was absorbed by human subjects during the coloring process. The remainder was located in the hair (5–20%), or in the rinse water.

One hopes that this type of study is extended to other common dye ingredients, so that a realistic picture of the toxicological risks associated with hair dye usage can be determined.

CONCLUSIONS

A theoretical understanding of the properties of dyes and the dyeing process has continued to develop as investigations of more complex and more realistic systems are undertaken. However, the interactions of such systems with hair and skin are still incompletely understood.

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