

# Studies on Bleaching Mechanism of Dyes. Part II: Identification of Decomposition Products of Hydroxyazobenzenes by Sodium Hypochlorite and Bleaching Mechanism

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Two isomeric azoic dyes, 2-hydroxy- and 4-hydroxyazobenzenes synthesized by diazotization of aniline and coupling with phenol, were bleached by sodium hypochlorite solutions at room temperature under acidic conditions by use of two-phase system of dichloromethane and water. The decomposition products extracted with the dichloromethane layer were analyzed by GC, and the structure was mainly determined by GC-MS. The results were as follows;

1. The bleaching agent caused the cleavage of the azo group of the dyes to afford many bleaching products: five compounds for 2-hydroxyazobenzene and six compounds for 4-hydroxyazobenzene were identified. In particular, chlorine-substituted phenols, ones of the decomposition products will cause dermatological problems, provided that these compounds accumulate in the fabrics.
2. Judging from the assigned bleaching products, it was estimated that under the acidic bleaching conditions occurred the electrophilic chlorination reaction toward the benzene ring on the side of phenol and then chloro-dediazotization at the primary step, and then further chlorination of the decomposition products at the secondary step.

## Introduction

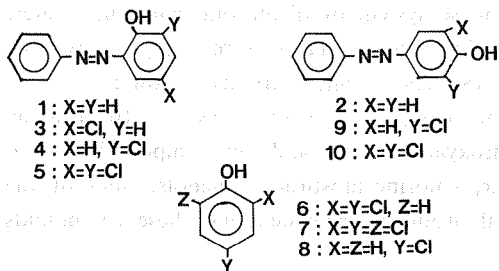
Many dermatological problems by dyes have been suspected since Wilson suggested in 1869 that a French soldier's foot lesions were due to his red aniline dyed socks.<sup>1)</sup> Recently, Hatch published the review about dermatological problems related to dyes, fiber content, and chemical finishes.<sup>2)</sup> In our country, the dermatological problem due to wearing brand-name yellow cotton-sweaters was of frequent occurrence particularly in Kansai-area in 1987.<sup>3)</sup> The cause was that excessive bleaching by hypochlorite in the after-treatment of yellow fabrics dyed with Naphthol Dye coupled with 2,5-dichloroaniline and naphthol AS-G induced decomposition of the dye to afford toxic compounds to human skin. The chemical structure of the compounds was suggested from two laborato-

ries.<sup>4,5)</sup> There is a possibility that such toxic compounds should be produced by bleaching not only in the yellow dye but also more conventional dyes. Therefore, dermatological safety in bleaching of colored fabrics by hypochlorite must be urgently established.

As reported previously,<sup>6)</sup> the bleaching of naphthol dyes with sodium hypochlorite solution using two-phase bleaching system containing water (bleaching agent) and dichloromethane, afforded many decomposition products such as chloro-naphthols and chlorophenols, which were irritant to the skin. Further we suggested the bleaching mechanism competitive with electrophilic chlorination and chloro-dediazotization reactions. In continuation of the previous report, we will describe here the bleaching of more simple dyes.

## Experimentals

**Materials.** As dyes were employed 2-hydroxy-(1) and 4-hydroxyazobenzenes(2), which were synthesized by the diazotization of aniline<sup>7)</sup> followed by the coupling reaction with phenol and were easily separated by silica-gel column chromatography (1 from first eluate and 2 from second eluate). Both compounds were purified by repeated recrystallization from a mixture of benzene-hexane. Sodium hypochlorite was purchased and titrated by iodometry before use (available chlorine 7.52%).



Structure

**Bleaching and Analysis.** According to the previous report,<sup>6)</sup> two-phase bleaching system of dichloromethane-water was adopted at pH4.1. Quantitative analyses were performed on a Shimadzu GC-7A gas chromatograph, using 1-m column containing 5% SE-30 on Diasolid L(60-80 mesh) equipped with a flame-ionization detector. The initial column oven temperature was 120°C, and after 4 min the temperature was programmed at a rate of 1°C/min to 180°C, and the final temperature held constant for 60 min. Quantitative analyses were performed by the method of internal standard. Benzophenone was chosen as an internal standard. GC-MS was recorded on a Shimadzu QP-2000A, using a capillary column (CBP1-M25-025, 25m×φ0.2mm). The initial column oven temperature was 70°C and after 5 min of isothermal operation, the temperature was programmed at a rate of 10°C/min to a maximum 250°C, and the final temperature held constant for

30 min.

## Results and Discussion

**Analyses of Bleaching Products.** During bleaching of 2-hydroxyazobenzene 1 in two-phase bleaching system, GC-MS analyses in the organic phase were performed at appropriate intervals. Fig.1 expresses the total ion chromatogram after disappearance of 1. Five peaks were observed on the chromatogram. Taking into account that the molecular ion peak (m/e 232) on the mass spectrum of peak-3 was larger by 34 than that(m/e 198) of 1 and appeared with the characteristic isotope peak(m/e 234) on the approximate ratio of 3:1, the structure was assigned as 3 in which chlorine atom bounded to 2-hydroxyazobenzene at the para position of the hydroxyl group. The mass spectrum and the retention time of 3 were in a good agreement with those of the authentic sample prepared by diazotization and coupling reactions of aniline and 4-chlorophenol. Similarly the peak-4 and the peak-5 were assigned on basis of the mass spectra as the isomer of the peak-3 4- (m/e 232) and dichlorinated compound 5 (m/e 266). The peak-1 and the peak-2 on the region of short retention time were due to decomposition products assigned as 2,4-dichlorophenol 6 and 2, 4, 6-trichlorophenol 7 on the basis of the mass spectra.

Concerning 4-hydroxyazobenzene, similar experiments were carried out. As the results of total ion chromatography were shown in Fig.3, the reaction was rather complex in comparison with 1. The peak-4 and the peak-5 were due to monochlorinated 9 and dichlorinated compounds 10 of 2, 2, 4-dichlorophenol and 2,4,6-trichlorophenol were also identified as the corresponding peak-1 and peak-3.

**Bleaching Mechanism.** Bleaching includes two types of reactions; the electrophilic chlorination of benzene ring on the side of phenol part and the cleavage reaction of the azo linkage. In order to elucidate the bleaching mechanism, it is necessary to obtain information on which reaction is faster, otherwise competitive. Using 2-hydroxyazobenzene, diluted sodium hypochlorite solution adjusted at

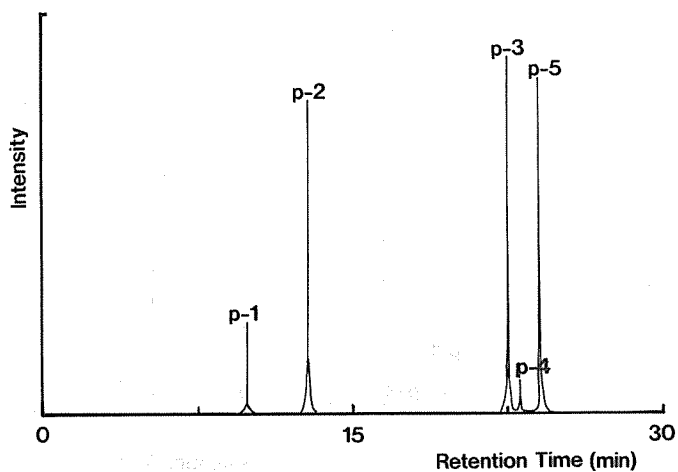


Fig. 1. Total ion chromatogram of bleaching of 2-hydroxyazobenzene

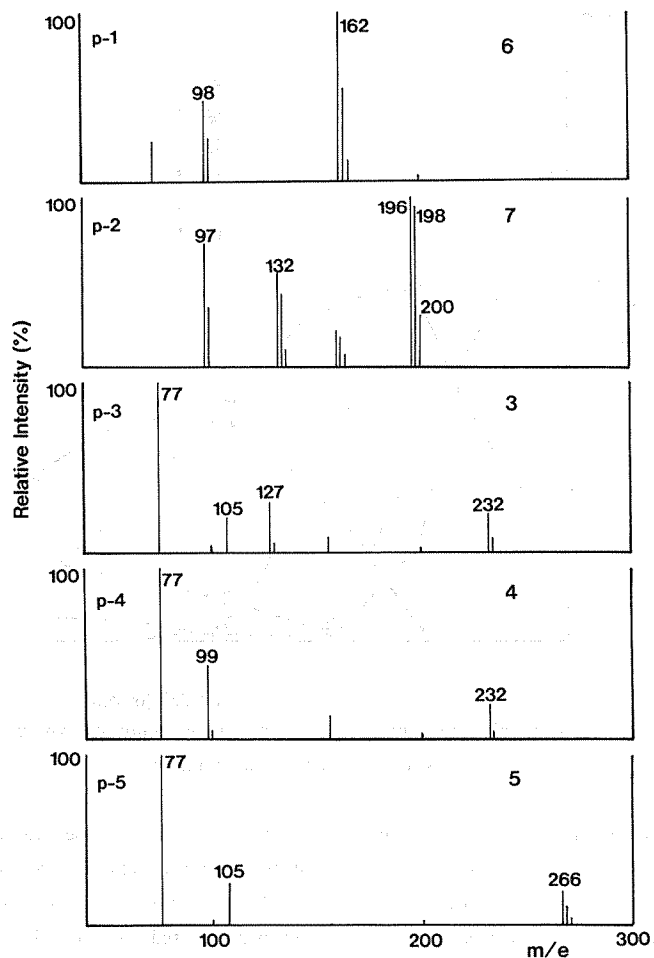


Fig. 2. Mass spectra of peak-1 ~ peak-5  
Numerals denote compound number.

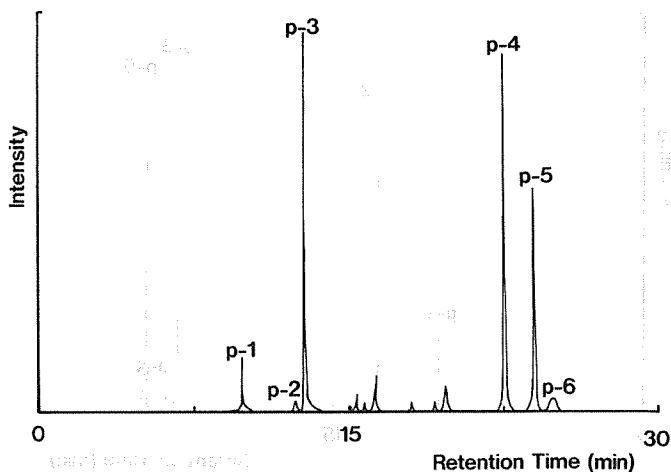


Fig. 3. Total ion chromatogram of bleaching of 4-hydroxyazobenzene

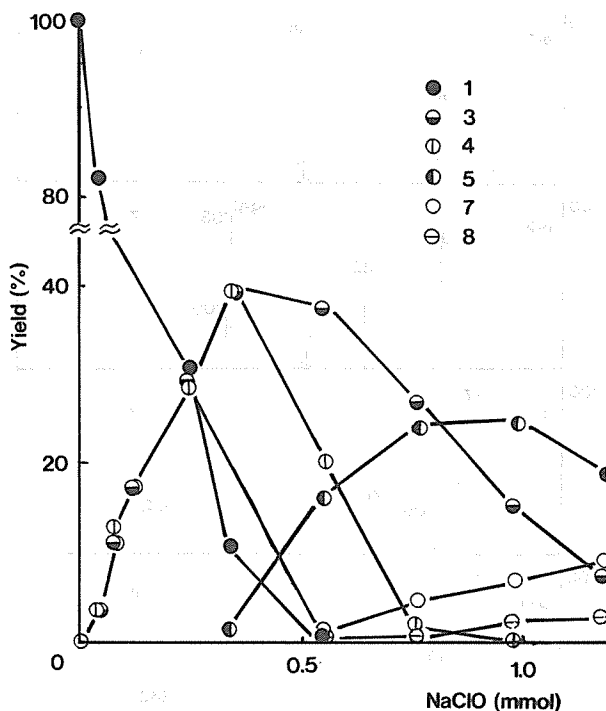
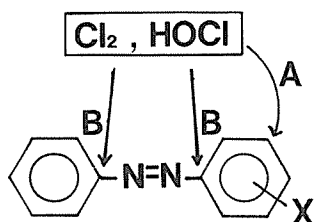


Fig. 4. Yields of bleaching products dependent on amount hypochlorite  
Numerals denote compound number

pH4.1 was added slowly from below equivalent amount to over equivalent amount of 1 (0.13 mmol) in the two-phase system and the organic layer was analyzed quantitatively by means of GC. The results were presented in Fig.4. As increase in added amount of hypochlorite the remaining

starting material decreased rapidly and the addition of 0.5 mmol of chlorine resulted in disappearance of 1, and on the contrary both isomers of monochlorinated compounds, 3 and 4 increased with the increasing addition of hypochlorite at first and then decreased with further increasing addition

of hypochlorite. At the same time as decrease in the amount of monochlorinated compounds, the dichlorinated compound 5 began to produce. On the other hand, decomposition products dichlorophenol and trichlorophenol yielded rather slowly in the excess of hypochlorite. These facts indicate that the consecutive chlorination of 1 is much faster than the cleavage of the azo linkage.



Taking into account that 1 and 2 were extremely stable to basic hypochlorite solution, hypochloric acid and/or molecular chlorine not hypochlorite ion,<sup>8)</sup> should play important roles in the bleaching. Since both bleaching species were strong electrophile,<sup>9)</sup> the electrophilic chlorination occurs predominantly at the electron-rich parts. These are cases for 3, 4, 5, 9, and 10. On the other hand, attack of the electrophiles to the carbon bound at the azo group (chloro-dediazoti-

zation) results in the formation of chlorophenols from chlorohydroxyazobenzenes. Finally, attention must be paid to the formation of chlorophenols, irritant to the skin from hypochlorite-bleaching of hydroxyazobenzenes. We feel that repeated washing is necessary after bleaching of colored-fabrics.

### References

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