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Mechanism of Azo Coupling Reactions: Part XXXV.* pH-Dependence and *Ortho/Para* Ratio in Coupling Reactions of Aminohydroxynaphthalenesulfonic Acids

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SUMMARY

We have found that the conclusions made by Freeman et al. *[*Dyes and Pigments, *7, 215 (1986)] in a recent investigation on the products of diazo coupling reactions with aminohydroxynaphthalenesulfonic acids are not correct. It was previously known that, with these coupling components, in the pH range 5 to 7, substitution takes place in the ring bearing the OH group and a mechanistic explanation of this fact appeared in the literature in 1952. With derivatives of 1-naphthol-3-sulfonic acid, coupling under alkaline conditions takes place preferentially in the 2-position. Literature data demonstrate that the ^{1}H-NMR signals for the OH protons found by Freeman originate from* ortho-*hydroxyazo compounds and not from their* para-*isomers.*

INTRODUCTION

In a recent paper Freeman *et al.*[2] reported data on products of diazo coupling reactions of four aminohydroxynaphthalenesulfonic acids (J-, γ-, H- and S-acid). The authors interpreted their results as follows:

(1) 'Contrary to previous reports, selective diazo coupling *ortho* to an amino group of an aminohydroxynaphthalenesulfonic acid does not occur in weakly acidic (pH 5–6) media ... (but) required a pH of 3·0–3·5 ...'.

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* Part XXXIV: see Diener and Zollinger.[1]

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(2) 'The structures of the dyes obtained were unambiguously determined with the aid of ^{1}H-NMR spectroscopy ... (H-, S- and J-acid) underwent diazo coupling exclusively *para* to the hydroxyl group under alkaline conditions ...'.

However, we show in this paper (i) that the first-mentioned claim is *not* in contradiction to previous reports; (ii) that diazo coupling reactions of aminohydroxynaphthalenesulfonic acids are never strictly 'selective' and that they do not take place 'exclusively' in the *para-* (or *ortho-*) position to the hydroxyl group of 1-hydroxynaphthalene-3-sulfonic acid and its derivatives under alkaline conditions; and (iii) that the ^{1}H-NMR spectra published by Freeman are consistent with published and unpublished data which clearly show that the products are *ortho*-hydroxyazo compounds.† We also indicate briefly that only *ortho-*, but not *para*-hydroxyazo dyes, fulfill the requirement of fastness properties for textile dyes.

THE pH-DEPENDENCE OF DIAZO COUPLINGS OF AMINOHYDROXYNAPHTHALENESULFONIC ACIDS

At the end of the 19th century it was found[3] that aminohydroxynaphthalenesulfonic acids give two different azo dyes when coupled under acid and alkaline conditions respectively. It must be emphasized that, at that time, the determination of hydrogen ion concentrations in aqueous solutions was in its infancy and that the concept of pH was developed in 1912.

It is therefore not surprising that a mechanistic explanation of this selectivity was given only much later, namely by Zollinger and Wittwer in 1952.[4] The explanation is based on the fact that 1- and 2-hydroxynaphthalene and their derivatives react in the anionic form of the naphthol/naphtholate acid/base equilibrium, and naphthylamines in the amine form but not in the ammonium form. These equilibria are, of course, pH-dependent and rates of diazo coupling reactions were shown to be proportional to the equilibrium concentrations of the naphtholate/naphthylamine forms of the coupling components. In aminohydroxynaphthalene derivatives, these two reactions are superimposed.

Naphtholate ions are stronger nucleophiles than naphthylamines. Therefore, at higher pH values, where the naphthol/naphtholate equilibrium

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† When this communication was in press, A. Lyčka and J. Jirman published a paper on extensive two-dimensional NMR spectroscopy of the alkaline azo coupling products of J-, H- and Gamma acid (*Dyes and Pigments*, **8**, 315 (1987)). The authors came to the same conclusions.

is almost completely on the side of the naphtholate (i.e. at pH > pK_{OH}), the reaction will dominate at that ring of naphthalene which bears the O^- atom. At lower pH values, however, the protonation of the amino group is not yet dominant (as long as pH > $pK_{NH_3^+}$), but the equilibrium concentration of the naphtholate is up to 10^5 times lower than that of the non-protonated naphthylamine.

On these basic principles postulated in 1952, two additional effects are superimposed. Ikeda *et al.*[5] found, in 1967, that when the OH-group is dissociated, the rate of coupling at the other ring with the NH_2-group is five to six times larger. The increased electron donor effect of a naphtholate oxygen relative to the naphthol OH group therefore brings about a slightly increased nucleophilicity in the *other* ring.

Secondly, we found in 1983[6] that micromixing can influence the ratio of coupling on the amino and hydroxy ring of an aminohydroxynaphthalenesulfonic acid (γ-acid) if the reaction is run in relatively concentrated solutions (5×10^{-2}–5×10^{-1} M). Micromixing effects occur because in diazo coupling reactions a proton is liberated; therefore the local pH decreases. If mixing in this local area is slower than the consecutive coupling reactions in the immediate (i.e. molecular) neighbourhood, the local pH determines the product ratio.

The explanation given in 1952[4] was tested at that time only by measuring *separated* diazo coupling rates of naphtholsulfonic and naphthylaminesulfonic acids. Aminohydroxynaphthalenesulfonic acid rates *per se* were investigated in 1969 by Panchartek and Sterba[7] (J-acid and phenyl-J-acid). Their results as well as those of Langfeld and Ionita[8] verified the predictions.

Figure 1 is a reproduction of a figure given in our 1983 paper.[6] The broken curve shows the rate profile of diazo coupling at that ring of naphthalene which contains the amino group. The higher rate between pH *ca* 10–11 corresponds to the effect found by Ikeda *et al.*[5] The arrows refer to the possibility of general base catalysis, an effect which we will not discuss further. The full line refers to coupling at the ring containing the hydroxyl group which, as mentioned before, reacts essentially only if the OH group is dissociated. [The reaction rate of an undissociated phenol or naphthol is *ca* 10^8 times slower than that of the conjugate base, as found by the group of Allan and Sterba (for summary, see Ref. 9)]. The decrease of both curves at pH $\geq$ 11 is due to the diazonium ion/diazotate equilibrium, which is not relevant to this discussion.

The schematic Fig. 1 shows that the full and the dashed curve cross at pH *ca* 6·2. In a solution of pH 6·2 the rates of coupling at the two rings are therefore the same and the yields of the two azo compounds (not considering the further isomers due to *ortho*/*para* differentiation) are expected to be 50:50.

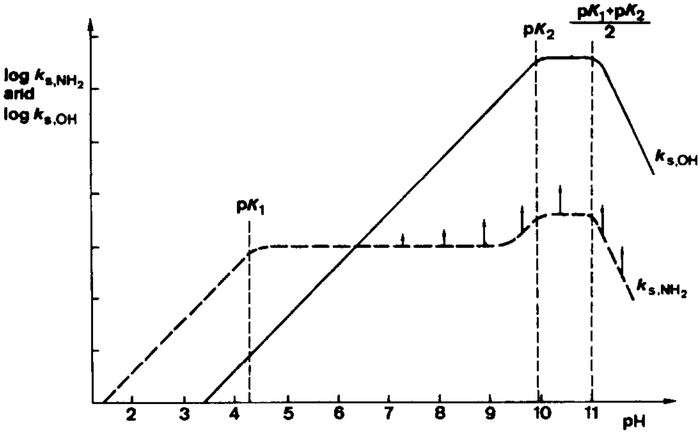


Fig. 1. Diazo coupling of aminohydroxynaphthalene derivatives as a function of pH (with permission from Kaminski *et al.*[6]): ---, reaction at the ring containing the amino group; ——, reaction at the ring containing the hydroxyl group; pK_1, pK_2 = pK_a values of the ammonium and the hydroxyl groups, respectively; (pK_1 + pK_2)/2 = acid-base equilibrium of diazo component.

The experimental data for diazo coupling of J-acid, as published by Panchartek and Sterba,[7] demonstrate that this crossing-point for their reaction is at pH 5·2. For a γ-acid coupling we[6] found pH 5·4. In buffer solution with *higher* pH values, the reaction at the ring bearing the OH group is dominant; Freeman *et al.*'s claim[2] that they found coupling at the OH-ring under acidic conditions for the first time is therefore not valid.

In a more generalized way, based on the rationale behind Fig. 1, one has to come to the conclusion that the location of the 50:50 'crossing point' will vary, depending, first of all on the aminohydroxynaphthalenesulfonic acid used, and second (as shown by Panchartek and Sterba[7]) on the electrophilicity of the diazonium ion. The location of the crossing point will be at higher pH values if the ratio of the intrinsic rate constants k_{OH}/k_{NH_2} is small, and will be at lower pH values if that ratio is large. (The ratio is given logarithmically by the difference of the levels of the flat portions of the full and dashed curves in Fig. 1. For the differentiation between intrinsic rate constants k and stoichiometric rate constants k_s see Ref. 6 and earlier papers, e.g. Ref. 4.) It is expected, for example, that the 50:50 point of couplings of H-acid (1-amino-8-hydroxynaphthalene-3,6-disulfonic acid) is at a lower pH value than that of the respective couplings with γ- or J-acid, because the intrinsic rate constant for coupling on the amino side is smaller because of steric hindrance by the sulfonic group in the 3-position, γ- and J-acid having coupling sites on the ring containing the amino group which are only slightly sterically hindered (however, see Ref. 10). In addition, Fig. 1 clearly shows that absolute selectivity is never obtained. Ratios of $\log(k_{S,OH}/k_{S,NH_2}) = 2·5$

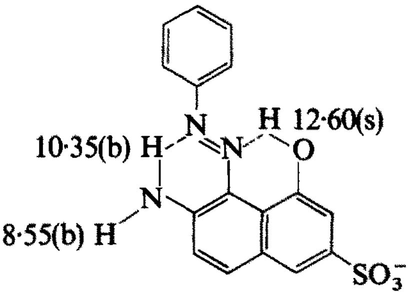
and 3·0, for example, found in that diagram at pH 9·0 and 10·5, respectively, mean that $10^{2\cdot5}$ and $10^{3\cdot0}$, i.e. *ca* 300 and 1000, times more product coupled at the OH-ring are found. This means that coupling at the amino-ring is not zero, but 0·3–0·1%, albeit these are small figures, they are, however, not zero!

DIAZO COUPLING IN THE *ORTHO*- OR *PARA*-POSITION?

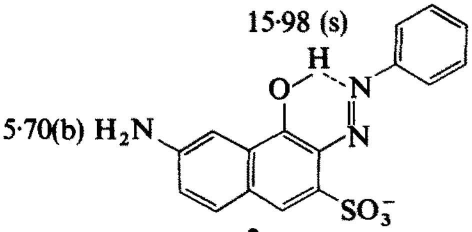
Based on ^{1}H-NMR spectra, Freeman *et al.*[2] concluded that, with the exception of γ-acid, J-, H- and S-acid react under alkaline conditions in the *para*-position to the hydroxyl group. This claim was based on an interpretation of the chemical shifts of the CH-protons of the benzene and naphthalene nuclei of the dyes. The very low-field OH proton signals at 15·5–16·1 ppm were explained by 'the increased acidity ... *ortho* or *para* to the strongly electron-withdrawing azo moiety'.

Whereas the assignment of CH- protons in multiple substituted aromatic rings on the basis of chemical shifts is often ambiguous, such low-field signals for OH protons are typical for protons involved in *intra*molecular hydrogen bonds. In phenols and naphthols this means that a proton-acceptor group has to be present in the *ortho*-position to the OH group. Isomeric compounds with the substituents in the *para*-positions have chemical shifts of the OH protons at much higher field. This has been known for some time, and is described in standard texts (e.g. Ref. 11). For hydroxyazo compounds it was established in 1968 by Mathias *et al.*,[12] who investigated the coupling of 2-naphthol with *para*-substituted benzene diazonium ions. They found, depending on the substituent, chemical shifts in the range of 15·61–16·06 ppm (in $CDCl_3$, 100 MHz). The presence of the hydrogen bond was shown by ^{14}N decoupling experiments. Saeva[13] compared the diazo coupling products of 4-methoxybenzenediazonium ions with 1- and 2-naphthol, resulting in (predominantly) *para*- and (exclusively) *ortho*-coupling, respectively. For the 1,4-hydroxyazo compound, chemical shifts of 10·19 and 3·59 ppm (the latter attributed to the ketohydrazone isomer) were obtained. For the 2,1-hydroxyazo isomer, the OH signal was found at much lower field (16·20 ppm in acetone-d_6, 60 MHz). For the γ-acid derivatives of our own investigation[6] we found the chemical shifts shown below in **1** and **2**[14] (DMSO-d_6, 300 MHz; b = broad singlet, s = sharp singlet).

As these aminohydroxynaphthalenesulfonic acids, with the exception of S-acid, are derivatives of 1-naphthol-3-sulfonic acid, the azo derivatives of 1-naphthol-3-sulfonic acid itself are also instructive: the coupling product with *o*-nitrobenzenediazonium ion in the 2-position shows an OH signal at 16·4 ppm (CD_2Cl_2), the 4-isomer at 11·75 ppm ($CDCl_3$, 300 MHz).[14]



1

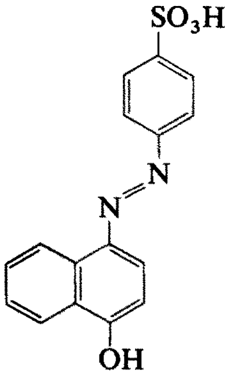


2

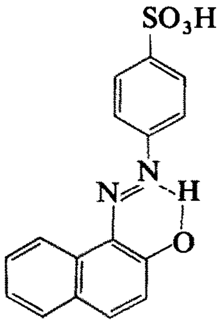
The dependence of azo coupling of 1-naphthol-3-sulfonic acid in the 2- and 4-position was studied in the 1950s by Stamm and Zollinger.[15] That work demonstrated that mixtures of the two isomers are always obtained, a result consistent with the earlier work of Gattermann *et al.*[16,17] The ratio of these isomers can be rationalized mechanistically.

The fact that both isomers are formed is important for the dyestuff industry, as we demonstrated some years ago[18] (and again more recently[19-21]) for the comparison of the isomeric dyes Naphthalene Orange I (C.I. Acid Orange 20; **3**) and Naphthalene Orange G (C.I. Acid Orange 7; **4**). In contrast with Orange G, Orange I is little used now because the tint changes in soda and washing tests. The pK_2 values show that Orange I is already present dominantly as a dibasic anion above pH 8·2, while Orange G splits off its phenolic proton in a pH range ($>$11·4) not attainable during washing. This is due to the intramolecular hydrogen bond. The effect of the hydroxyazo/ketohydrazone tautomerism is also significant, but we will not discuss it further here (see Ref. 22).

Dyes with the basic structure of those discussed by Freeman *et al.*[2] are, in fact, in commercial use (e.g. C.I. Acid Black 1). If those dyes had the *para*-hydroxyazo structure as suggested,[2] they would have unacceptably low



3
p$K_2 = 8{\cdot}2$



4
p$K_2 = 11{\cdot}4$

fastness properties under slightly alkaline conditions. There are some industrial dyes for which the diazo coupling reaction gives significant percentages of *para*-coupled products, so that, after diazo coupling, the *para*-isomer has to be destroyed, e.g. by degradation with hypochlorite, in order to obtain a final product which contains only traces of the *para*-dye.

The case of coupling of S-acid is an open question. Gattermann's work[16,17] demonstrates that 1,5-naphtholsulfonic acid is more prone to coupling in the 4-position than the 1,3-isomer. Freeman *et al.* suggest coupling in the *para*-position to the OH group at pH 8–10 and 5–6. Their published ^{1}H-NMR data do not however allow a decisive conclusion to be made.

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