198. Mechanism of Azo Coupling Reactions XXXIII[1])

pH-Dependence and Micromixing Effects on the Product Distribution of Couplings with 6-Amino-4-hydroxy-2-naphthalenesulfonic Acid. Evidence for *N*-Coupling of a Naphthylamine Derivative

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Summary

Azo coupling of 6-amino-4-hydroxy-2-naphthalenesulfonic acid (**1**) with 3-trifluoromethyl- and 4-nitrobenzenediazonium ion in relative highly concentrated aqueous alkaline solutions gave ratios of aminoazo to hydroxyazo compounds which are much higher than expected on the basis of the acid-base pre-equilibria of **1**. These product ratios are disguised by effects of micromixing. In dilute solution ($\leq 10^{-2}$ mol/l) product ratios and kinetics both correspond to the theory of acid-base pre-equilibria. A bisazo dye **10** was formed as a by-product in couplings with 3-trifluoromethylbenzenediazonium ion, as expected for reactions with micromixing effects. In the reaction with benzenediazonium ions, the products of azo coupling of diazotized **1** with **1** (compound **8**) and of the monoazo compound **8** with benzenediazonium ion (compound **9**) were found. It is likely that diazotized **1** is formed by *N*-coupling of **1** with benzenediazonium ion, tautomeric rearrangement and protonation of the triazene to diazotized **1** and aniline. This seems to be the first case of *N*-coupling of a naphthylamine which was assumed to be capable of *C*-coupling only.

1. Introduction. – Since 1891 it has been known that azo coupling reactions with aminonaphthol derivatives such as 6-amino-4-hydroxy-2-naphthalenesulfonic acid (**1**, γ-acid) [2a], 7-amino-4-hydroxy-2-naphthalenesulfonic acid (J-acid) and 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid (H-acid) [2b] give two types of isomeric azo compounds depending on the pH-value of the reaction medium. In alkaline solution it is the ring bearing the OH-group and in acidic solution it is the ring bearing the NH_2-group which is substituted (at positions *ortho* or *para* to the electron-releasing group). On the basis of this observation, many industrially important azo dyes belonging to one of these two types have been developed.

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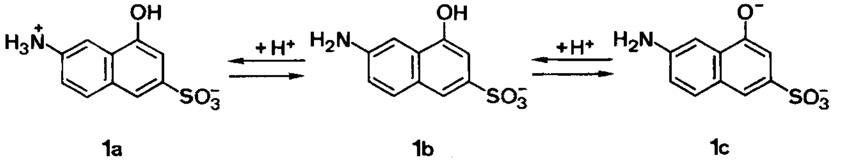
A mechanistic explanation of this selectivity was, however, only given in 1952 [3]. An aminonaphthol-coupling component can be considered as a superposition of a naphthol and a naphthylamine. The rates of azo couplings of both these components show characteristic pH-dependences. For a naphthylamine a tenfold increase in the rate of coupling is observed when the pH-value is increased by one unit to *ca.* pH = 4. Above pH = 5 the rate is independent of the pH-value. For naphthols an analogous dependence is observed. However, the change of the ratio log rate to pH from 1:1 to 0:1 occurs only at *ca.* pH = 10. The pH-values of both changes correspond to the pK_a-values of the naphthylammonium ion and naphthol, respectively. The rates are therefore proportional to the equilibrium concentrations of free (unprotonated) naphthylamine and of naphtholate anion. The decrease in rate at higher pH-values is caused by the diazonium ion ⇄ diazotate ion equilibrium [4].

Although naphtholate ions are stronger nucleophiles than naphthylamines, the rate of azo coupling of an aminonaphthol derivative will dominate at low pH-values (< 5) in that molecular segment containing the NH_2-group because the aminonaphthol equilibrium form (*e.g.* **1b** for γ-acid, *Scheme 1*) is present in $> 10^5$ times higher a concentration than the aminonaphtholate form (*e.g.* **1c**). At pH > 8, however, the ratio is reversed ([**1c**] ≫ [**1b**]) and substitution occurs predominantly at the molecular ring containing the O^--group.

Scheme 1



The rates of these reactions can be described in two ways. *Eqn. 1* gives the so-called stoichiometric rate constants (subscript s) and the overall (*i.e.* stoichiometric or analytical) concentrations of the diazo component (Dz) and the coupling component (in this case: **1a** + **1b** + **1c**). The k_s-values are second-order rate constants directly obtained from rate measurements, or, if **1** is used in large excess, in the usual way from the pseudo-first-order constant k_s', *i.e.* $k_s = k_s'/\mathbf{1}$. Stoichiometric concentrations are given in parentheses in *Eqn. 1*.

Eqn. 2 contains the second-order rate constants k for the substitution proper. They are independent of pH, as not stoichiometric concentrations of the reaction partners, but concentrations of those acid-base equilibrium forms are used which enter the substitution proper, *i.e.* the diazonium ion, the amine and the naphtholate ion. Such concentrations are given in square brackets.

$$v = (k_{s,NH_2} + k_{s,OH})(Dz)(\mathbf{1}) \tag{1}$$

$$v = k_{NH_2}[ArN_2^+][\mathbf{1b}] + k_{O^-}[ArN_2^+][\mathbf{1c}] \tag{2}$$

This explanation was corroborated later by *Štěrba et al.* [5]. They determined the pH-dependence of the kinetics of azo-coupling reactions of 7-amino-4-hydroxy-2-naphthalenesulfonic acid and related compounds.

An additional effect was found by *Ikeda et al.* [6] who measured the relative rates of azo-coupling reactions with the three sulfonated aminonaphthols mentioned above (γ-, J- and H-acid) in competitive experiments to the azo coupling reaction of 4-hydroxy-1-naphthalenesulfonic acid at pH = 5.5 to 9.1. They made the interesting observation that the rate at the position *ortho* to the NH_2-group is five to six times larger when the OH-group is dissociated. To our knowledge, this is the only clear case of an electrophilic substitution on naphthalene where an influence of the acid-base equilibrium of a substituent in one of the six-membered rings on the rate of substitution in the other ring has been measured quantitatively.

Figure 1 shows schematically the pH-dependence of azo-coupling reactions of aminonaphthols as a function of the pH-value as developed by *Zollinger et al.* [3] and including the observations of *Ikeda et al.* [6]. The latter are reflected in the increased level of curve k_{s,NH_2} at pH > 10. The curves refer to the rate-dependence on the pre-equilibria *(Scheme 1)*. They do not include the potential influence of general base catalysis. This additional effect will be discussed at the end of this paper for the case of the reaction of 3-trifluoromethylbenzenediazonium ion with **1** at C(5). The observed effect of general base catalysis for that reaction is symbolized in *Figure 1* by the arrows which indicate that k_{s,NH_2} can be higher than the value expected without general base catalysis, *i.e.* the corresponding curve.

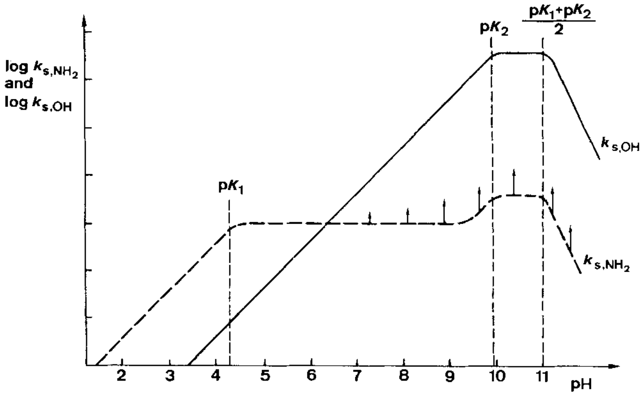
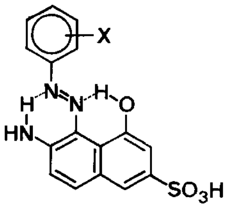


Fig. 1. *Azo coupling of aminonaphthol derivatives as a function of pH* (for meaning of arrows see text)

In the dyestuff industry [7] the observation was made that 3-trifluoromethylbenzenediazonium ion also couples in alkaline solution with γ-acid **1** at C(5). This result apparently violates the mechanism discussed above and prompted us to investigate this reaction in detail with respect to products and kinetics. Our work also includes the reactions with benzene- and 4-nitrobenzenediazonium ions.

2. Results. – 2.1. *Product Syntheses.* Dyes **2** to **9** (except **4** and **7**) were synthesized by azo couplings and purified. Dye **10** was obtained as a by-product in azo couplings of 3-trifluoromethylbenzenediazonium ions with **1** (see below) and purified by chromatography. The two arylazo residues are probably at C(1) and C(3). Dyes **4** and **7** have not been isolated, but their structure followed from a comparison of the products obtained at pH = *ca.* 2 and 11 (see *Exper. Part*).



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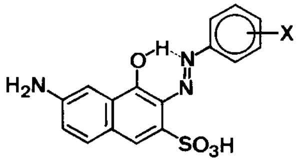
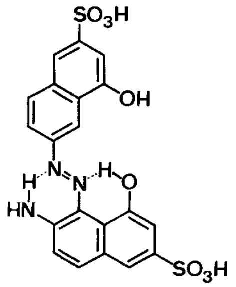


5-7

	2	**3**	**4**	**5**	**6**	**7**
X=	H	3-CF_3	4-NO_2	H	3-CF_3	4-NO_2



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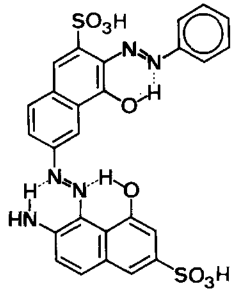

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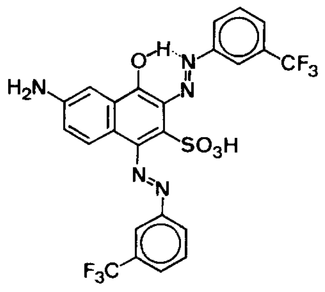

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2.2. *Product Analyses. Reactions in Relatively Concentrated Solutions* (5×10^{-1} *to* 5×10^{-2} M) (*cf. Table 1*). For solubility reasons only couplings with benzenediazonium ion could be carried out in buffered solutions. Products were analyzed by thick layer chromatographic separation and/or isolation, except for the products of azo coupling with 4-nitrobenzenediazonium ion which were estimated from thin layer chromatograms.

Benzenediazonium ion couples with **1** at pH = 3.6 to give dye **2**, together with 3% **8** and 0.2% **9**, and at pH = 9.6 to give only dye **5**. 3-Trifluoromethylbenzenediazonium ion gives exclusively dye **3** at pH *ca.* 3, but in alkaline solution (pH *ca.* 10) only 24% of the *o*-hydroxyazo compound **6** is obtained in addition to 31% of dye **3** and 16% of the bisazo compound **10**. Similarly 4-nitrobenzenediazonium ion in acidic solution gives dye **4**, whereas in alkaline solution only *ca.* 20% of the *o*-hydroxyazo compound **7**, but *ca.* 40% of **4** are obtained. The by-products were not analyzed in this case; they probably contain also bisazo compounds similar to **10**.

The classical rule that in alkaline systems aminonaphthol derivatives yield only the monoazo dye coupled at the molecular segment which contains the OH-group is therefore not correct for strongly electrophilic diazo compounds such as 3-trifluoromethyl- and 4-nitrobenzenediazonium ions.

2.3. *Product Analyses. Reactions in More Dilute Solutions (10^{-2} to 2.5×10^{-5}*M*) (cf. Table 1).* Coupling reactions were carried out in buffer solutions. Formation of by-products was negligible; therefore products were analyzed spectrophotometrically. The mol fractions X_5 and X_6 *(Eqn. 3)*[3]) for couplings at C(3) of γ-acid **1** with benzenediazonium ion (azo product **5**) and with 3-trifluoromethylbenzenediazonium ion (azo product **6**) were calculated by linear regression analysis of *Lambert-Beer*'s law at various wavelengths for 7 to 16 extinction measurements of each reaction solution. The mol fractions are shown in *Figure 2*.

$$X_5=\frac{(\mathbf{5})}{(\mathbf{2})+(\mathbf{5})}\qquad X_6=\frac{(\mathbf{6})}{(\mathbf{3})+(\mathbf{6})}\tag{3}$$

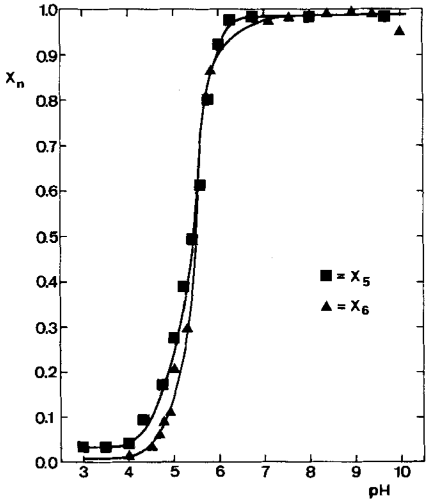

Fig. 2. *Mol fractions X_5 and X_6 of azo couplings at the 3-position of γ-acid* **1** *with benzene- and 3-trifluoromethylbenzenediazonium ion* (azo product **5** and **6**, respectively). Data from *Tables 3* and *4*.

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3) Mol fractions for other compounds and those including bisazo compounds are defined analogously. Yields of **9** and **10** have to be multiplied by 2, as they contain two arylazo groups.

4-Nitrobenzenediazonium ion was coupled at pH = 9.80 in buffered dilute (2.5×10^{-3} M) solution. As with the above diazonium ions only the *o*-hydroxy compound **7** was obtained.

2.4. *Kinetic Results.* Stoichiometric rate constants k_s corresponding to the sum of both reactions, *i.e.* $k_{s,NH_2} + k_{s,OH}$ in *Eqn. 1*, were obtained spectrophotometrically for the reaction of benzenediazonium ion with **1**. Measurements were made at 20.0 ± 0.1° in buffer solutions of ionic strength $I = 0.20$. In the pH-range from 3.00 to 6.25 the coupling component was used in 100-fold excess and the pseudo-first-order kinetics were evaluated as usual for second-order rate constants k_s. From pH = 7.00 to 10.00 no excess of **1** was used. The logarithms of the rate constants k_s are shown graphically in *Figure 3*. The logarithms of the constants k_{s,NH_2} and $k_{s,OH}$ are given by the solid lines. The experimental points are values for $\log k_s = \log(k_{s,NH_2} + k_{s,OH})$, *i.e.* for the *sum* of the two azo coupling reactions. The experimental points are therefore slightly *above* the two curves in the pH-range *ca.* 4.5 to 6.0, as the curves refer to $\log k_{s,NH_2}$ and $\log k_{s,OH}$ separately[4]).

The kinetics of the reaction of 3-trifluoromethylbenzenediazonium ion with **1** were also measured optically *(Fig. 4)*. The spectrophotometer was, however, operated with a computer programme which allowed the calculation not only of the *sum* of both stoichiometric rate constants, but also k_{s,NH_2} and $k_{s,OH}$ as well as the constants k_{NH_2} and k_{O^-} for the substitution proper (see *Exper. Part*). As this reaction

Table 1. *Products of Azo Couplings of γ-Acid* **1** *as a Function of pH and of Concentration*

Diazo component $X\text{-}C_6H_4\text{-}N_2^+$	pH	Azo products	Mol fractions X_n of azo products		
			Concentration range (M)		
			2.5×10^{-5} to 10^{-2}	5×10^{-2} to 5×10^{-1}	
				a)	b)
X = H	3.6	**5**	0.035	< 0.01	< 0.01
		2	0.965	> 0.99	> 0.96
		8 + **9**	0.00	–	0.03
	9.6	**5**	0.988	> 0.99	> 0.97
		2	0.002	< 0.01	< 0.01
		8 + **9**	0.00	< 0.01	< 0.01
X = 3-CF_3	4.0	**6**	0.010	< 0.01	< 0.01
		3	0.990	> 0.99	> 0.97
		10	0.00	–	< 0.01
	10.0	**6**	0.973	0.44	0.28
		3	0.027	0.56	0.36
		10	0.00	–	0.36
X = 4-NO_2	9.8	**7**	> 0.98	*ca.* 0.33	c)
		4	< 0.02	*ca.* 0.67	c)

a) Calculated on monoazo compounds only *(Eqn. 3)*. b) Calculated under inclusion of bisazo compounds. c) Yield of bisazo compounds not determined.

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[4]) Other deviations of the experimental values from the curves, *e.g.* those at pH 3.5, 7.0 and 8.0, are, however, due to experimental inaccuracies.

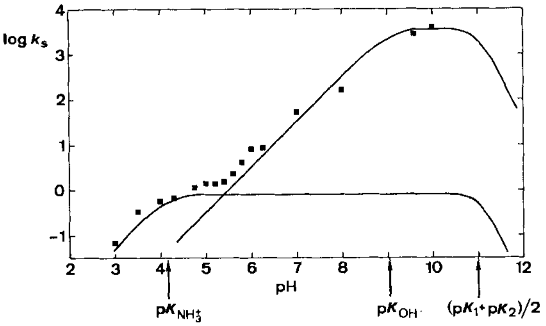

Fig. 3. *Logarithms of rate constants* k_s *of azo coupling reactions of benzenediazonium ion with γ-acid* **1** *as a function of the pH-value of the reaction solutions.* The curves correspond to calculated values (see Discussion); p$K_{NH_3^+}$ of **1** = 4.17 ± 0.03 [8], pK_{OH} of **1** = 9.03 ± 0.03 [8], (pK_1 + pK_2)/2 = 10.99 ± 0.12 (this work).

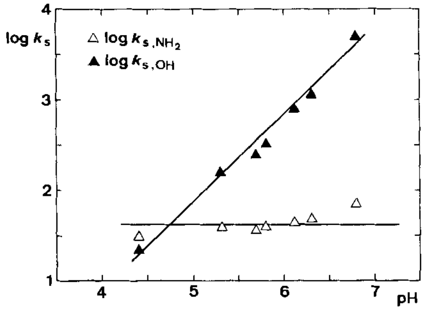

Fig. 4. *Logarithms of rate constants* k_{s,NH_2} *and* $k_{s,OH}$ *of azo coupling reactions of 3-trifluoromethylbenzenediazonium ion with γ-acid* **1** *as a function of the pH-value of the reaction solutions*

is relatively fast, accurate measurements were possible only for the pH-range 4.40 to 6.80 (T = 25.0 ± 0.2°, I = 0.10). The rate constants k_{s,NH_2} show an increasing trend above pH 6 relative to the expected independence on pH (horizontal line).

3. Discussion. – Product analyses demonstrate that the product ratios in azo coupling with γ-acid **1** are only independent of the concentrations of the reagents in a particular batch if a diazo component with a relatively low reactivity is used, in our case benzenediazonium ion. With this reagent the main products and kinetic results correspond to the scheme based on pre-equilibria *(Scheme 1)* of the coupling component as described in *Figure 1* and discussed in the *Introduction*. In acidic solution only that azo compound is formed which is based on electrophilic substitution of the segment of the naphthalene system which contains the NH_2-group; under alkaline conditions reaction occurs at that six-membered ring which contains the OH-group (we discuss the formation of compounds **8** and **9** below).

For azo couplings with more strongly electrophilic diazo components such as 3-trifluoromethylbenzenediazonium ion similar results were obtained in relatively dilute solutions ($\leq 10^{-2}$ M). Under 'preparative' conditions, however, *i.e.* concentrations in the range 0.05 to 0.5 M, this is only the case at pH = 4.0. Large changes were found at pH = 10.0 for couplings with 3-trifluoromethyl- and 4-nitrobenzenediazonium ions. The ratio of monoazo products **6**:**3** and **7**:**4** changed in favour of the substitution at the *o*-position to the NH_2-group (**3** and **4** respectively); in addition, very substantial amounts of the coupling product **10** containing two arylazo groups were found with 3-trifluoromethylbenzenediazonium ion.

We interpret these results as follows: 4-nitro- and 3-trifluoromethylbenzenediazonium ions are significantly more electrophilic than benzenediazonium ions. Therefore in the alkaline range the azo coupling of γ-acid with the two substituted diazo components reaches rates which can give rise to micromixing effects. This was shown by *Rys et al.* [9] even for the reaction of benzenediazonium ion with 5-hydroxy-2-naphthalenesulfonic acid dianion[5]). These authors found considerable amounts of 5-hydroxy-6,8-bisphenylazo-2-naphthalenesulfonic acid even when the ratio of reagents was 1:1. Their result corresponds to our observation that, with 3-trifluoromethylbenzenediazonium ion, γ-acid yields in a relatively concentrated system 16% bisazo product **10**. This is therefore a clear indication for a micromixing effect as described by *Rys et al.* [10] and by us [11] for nitrations.

In addition, we believe that the relative increase of the aminoazo dyes **3** and **4** in alkaline systems is also due to a micromixing effect. Compounds **3** and **4** are formed normally as the main products only under acidic conditions. At pH = 9 to 10 reaction takes place initially at the *o*-position to the O^--group. The proton released by this substitution is, however, not neutralized fast enough by mixing with the bulk of the solvent. As a result, the local pH-value becomes lower than the 'macroscopic' pH-value. In the mixing zones the acid-base equilibrium corresponds to the 'microscopic', lower pH-values and thus **3** and **4** are formed. The existence of local pH-gradients in the reaction zone and its influence on the product distribution of mixing-disguised reactions has been predicted theoretically as well as verified experimentally by *Rys et al.* [12]. We have also corroborated this interpretation experimentally: rapid combination of a relatively concentrated acidic solution of 3-trifluoromethylbenzenediazonium ion and an alkaline solution of γ-acid at pH = 10 from two syringes gives more efficient mixing, so practically only the *o*-hydroxyazo compound **6** was obtained, as expected for a solution of pH = 10. Another experiment demonstrated that the yield of the *o*-hydroxyazo compound can be increased: if the solution of γ-acid, at pH = 10, is mixed with a solution of 4-nitrobenzenediazonium ion which was neutralized immediately before adding it to the solution of γ-acid[6]), only *ca.* 10% aminoazo compound **4** was obtained, instead of 40%.

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[5]) 5-Hydroxy-2-naphthalenesulfonic acid is a stronger nucleophile than γ-acid; therefore micromixing effects were found with benzenediazonium ion.

[6]) Usually in azo couplings the solutions of the diazo component are kept acidic after diazotization and added as such to the coupling component. If they are neutralized the probability of homolytic decomposition is increased.

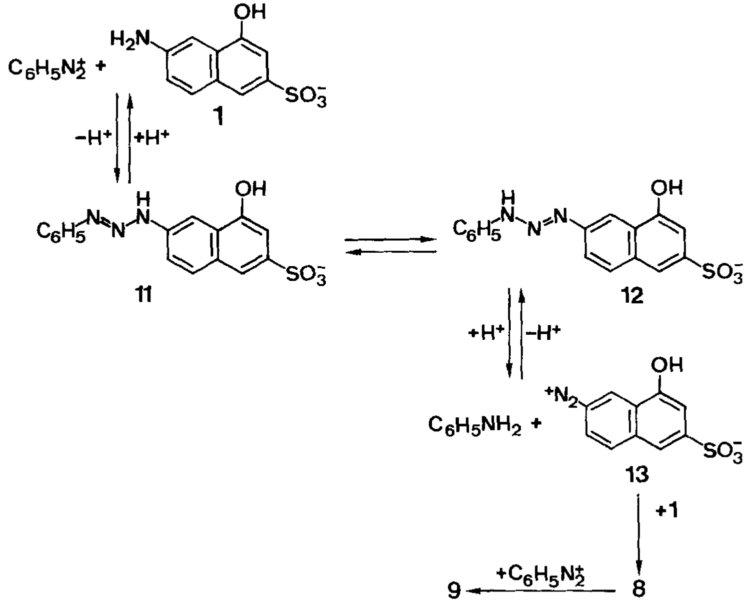
The present case of micromixing is slightly different from that of azo coupling of 5-hydroxy-2-naphthalenesulfonic acid mentioned above. In that reaction azo coupling occurs at the *para*-position to the O^--group. In the formation of compounds **5**–**7**, however, substitution occurs at the *ortho*-position and one might argue that in the σ-complex formed the proton to be substituted may not be released to the solvent, but intramolecularly to the O^--group. Such an apparently simple rearrangement was shown not to occur owing to the general base catalysis observed many years ago [13] and to stereochemical evidence [14]. It was recently discussed also from the point of view of the *Woodward-Hoffmann* rules [15].

The by-products **8** and **9** in the coupling of benzenediazonium ion with γ-acid at pH = 3.60 are obtained in yields of 3% and 0.2%, respectively. Bisazo compound **9** is obviously formed by consecutive azo coupling of benzenediazonium ion with **8**. The monoazo compound **8** is interesting, as it is the reaction product of diazotized γ-acid with γ-acid. The formation of diazotized γ-acid can be rationalized by the reaction sequence in *Scheme 2*, in which the benzenediazonium ion adds first to the NH_2-group of γ-acid (*N*-coupling) to give the diazoamino (or triazene) compound **11**, which subsequently gives, *via* the tautomeric equilibrium, the triazene **12**. Protonation of **12** yields aniline and diazotized γ-acid **13**.

Formation of **8** and **9** therefore contradicts all experience, namely that only *C*-, but no *N*-coupling of naphthylamines occurs except in cases in which the *o*- or *p*-position of the NH_2-group is substituted or where there is steric hindrance of the reaction site for *C*-coupling by *peri*-substituents.

Compound **8** and the coupling product corresponding to **9** were not found in couplings with 3-trifluoromethylbenzenediazonium ion. This is probably due to

Scheme 2



the fact that, as shown by *Lüttke et al.* and others [16], electron-withdrawing substituents in the *m*-position of the 1-phenyl ring in 1,3-diphenyltriazenes shift the equilibrium of the two tautomeric triazenes to that tautomeric form in which the proton is bonded to the N-atom in the 3-position. The equilibrium **11** $\leftrightarrows$ **12** in *Scheme 2* is therefore more on the side of **12** than the corresponding equilibrium in the coupling with 3-trifluoromethylbenzenediazonium ion. In the latter system the equilibrium **11** $\rightleftarrows$ **12** is predominantly on the side of the analogue of **11**; therefore no significant amount of diazotized γ-acid **13** is formed and no dye **8** is detectable.

The kinetic results (*Fig. 3* and *4*) correspond to expectation from the theory based on acid-base pre-equilibria *(Fig. 1)* for couplings with benzenediazonium ions and with 3-trifluoromethylbenzenediazonium ions as kinetics of *both* reactions were performed in highly dilute solution (2.5×10^{-5} M). The solid curves in *Figure 3* correspond to the rates of reaction at C(3) and C(5). They cross at pH 5.4, the value at which the mol fractions $X_5 = X_2 = 0.5$, as found experimentally.

The experimental values for the rate constant k_{s,NH_2} in *Figure 4* increase slightly above pH = 6. This effect is due to general base catalysis observed for all determinations of k_{s,NH_2} (but not for $k_{s,OH}$). The values for k_{s,NH_2} in *Figure 4* and in *Table 8 (Exper. Part)* are extrapolated to buffer base and γ-acid concentrations of zero in order to eliminate the catalytic effects of buffer and γ-acid. The fact that the extrapolated rate constants become still higher at increasing pH-values is obviously due to the higher concentration of hydroxyl ions which, of course, also act as general base catalysts. We did not investigate further the structural reasons for this general base catalysis. A similar effect was found also by *Štěrba et al.* [5].

The rate constants of the coupling of 3-trifluoromethylbenzenediazonium ion *(Fig. 4)* are larger than those for couplings of benzenediazonium ion *(Fig. 3)* by a factor of *ca.* 100 which is in part due to the difference in reaction temperature (25.0° and 20.0°, respectively). It is, however, also in good agreement with rate constants calculated with the help of a *Hammett* $\rho\sigma$ relationship with $\sigma_m = 0.43$ for the 3-trifluoromethyl group [17] and $\rho_{NH_2} = 4.26$ and $\rho_{OH} = 3.85$ for azo coupling reactions with 6-amino-2-naphthalenesulfonic acid and 6-hydroxy-2-naphthalenesulfonic acid [18].

Experimental Part

1. General. – *Chemicals.* Aniline was distilled under vacuum and stored as the hydrochloride in the refrigerator. 3-Trifluoromethylaniline for kinetic measurements was recrystallized as the hydrochloride once from H_2O and once from $MeOH/CHCl_3$ (1:2). 4-Nitroaniline (*puriss.* p.a., *Fluka AG*) was used as received. 6-Amino-4-hydroxy-2-naphthalenesulfonic acid (**1**, γ-acid; techn., *Fluka AG*) was purified twice by decoloration of a hot solution in aq. NaOH (60 g **1**, 140 ml H_2O, 10 g NaOH) with 10 g of charcoal and filtration into hot dil. H_2SO_4 [19] and was obtained as the monohydrate. In addition, **1** was recrystallized from H_2O for kinetic measurements.

Analytical Techniques. Pre-coated plastic sheets of silica gel *60* F_{254} and glass plates of silica gel *PSC 60* F_{254} (*Merck AG*, Darmstadt) were used for thin- and thick-layer chromatography, respectively. IR spectra (KBr) were run on a *Beckman IR-4250*, UV/VIS spectra and kinetics on a *Beckman Acta III*, ^1H- and ^{19}F-NMR spectra on a *Bruker WH-90*. The pH-values were measured using digital pH-meters *Metrohm E 604* and *E 532*, which were calibrated with standard buffer solutions (pH = 4.00, 7.00, 9.00).

2. Syntheses of Dyes 2–10. – *6-Amino-4-hydroxy-5-phenylazo-2-naphthalenesulfonic acid* (**2**) [19] [20]. Aniline hydrochloride (1.295 g, 10 mmol) in 7.5 ml 2M HCl and 40 ml H_2O was diazotized with 704 mg (10.2 mmol) $NaNO_2$ in 10 ml H_2O and poured into 50 ml of a cold buffer solution (7.40 g HCOONa, 3.63 g 100% HCOOH). The buffered diazonium salt solution was poured into an ice-cold suspension of **1**, obtained from a concentrated solution of 2.70 g (10.5 mmol) **1** in aq. Na_2CO_3 and

50 ml buffer solution (7.06 g HCOONa, 3.98 g 100% HCOOH). After 15 h the solution was diluted with H_2O to 200 ml, heated to 95° and neutralized with conc. NaOH. Dye **2** was precipitated by addition of 11 g NaCl. The crude product was dissolved in 150 ml boiling EtOH and the hot solution filtered. After cooling 1.53 g (42%) of **2** were obtained. UV/VIS (H_2O, pH = 7.00): 482 (17300). ^{1}H-NMR ((D_6)DMSO): 7.13–7.92 (*m*, 9 H, arom. H); ≈ 8.6 (br. *s*, 1 H, NH); ≈ 10.3 (br. *s*, 1 H, NH); 12.62 (*s*, 1 H, OH).

6-Amino-4-hydroxy-5-(3-trifluoromethylphenylazo)-2-naphthalenesulfonic acid (**3**), *6-amino-4-hydroxy-3-(3-trifluoromethylphenylazo)-2-naphthalenesulfonic acid* (**6**) *and bisazo dye* **10**. 3-Trifluoromethylaniline (1.66 g, 0.01 mol) was added to 12.5 ml 2 M HCl (25 mmol). The resulting suspension of the hydrochloride was diazotized in an ice bath with 10 ml 1 M $NaNO_2$ over a period of 15 min. The solution was filtered and during 10 min added to an ice-cold solution of 2.57 g (0.01 mol) of **1**, 0.40 g NaOH (0.01 mol) and 1.59 g Na_2CO_3 (15 mmol) in 40 ml H_2O. After additional stirring for 30 min in the ice bath the precipitated dyes were centrifuged, washed with H_2O and dried (P_4O_{10}) *in vacuo* to give 3.30 g of a mixture of dyes **3**, **6** and **10**. Chromatography of 50 mg of the mixture (7 plates *PSC 60* F_{254}, acetone/CH_2Cl_2/2-propanol 12:4:1) yielded 20 mg **3**, 16 mg **6** and 8 mg **10** (31, 24 and 16%, respectively). The pK_{OH}-value for **6** of 11.3 ± 0.1 was determined spectrophotometrically with buffer solutions [21] between pH = 9.5 and 12.5. UV/VIS (H_2O, pH = 7.00): **3**: 490 (13990); **6**: 508 (11650). ^{1}H-NMR (CD_3OD): **3**: 7.10 (*d*, *J* = 9.2, 1 H, H–C(7)); 7.38–7.96 (*m*, 7 H, arom. H). – **6**: 7.04 (*dd*, *J* = 2.4 and 8.3, 1 H, H–C(7)); 7.38–8.11 (*m*, 7 H, arom. H). – **10**: ≈ 7.3–8.2 (*m*, 10 H, arom. H); ≈ 8.3–8.4 (*m*, 1 H, arom. H). ^{19}F-NMR (CD_3OD, internal reference C_6F_6): **3**: 101.11. **6**: 101.17. **10**: 101.06, 101.17.

6-Amino-4-hydroxy-5-(4-nitrophenylazo)-2-naphthalenesulfonic acid (**4**) [20] *and 6-amino-4-hydroxy-3-(4-nitrophenylazo)-2-naphthalenesulfonic acid* (**7**) [20] [22]. Dyes **4** and **7** were not isolated. They were identified by TLC comparison of azo coupling products at pH = *ca.* 2 and 11 from concentrated (*ca.* 10^{-1}M) and diluted (*ca.* 10^{-3}M) solutions (see *Product Analyses*).

6-Amino-4-hydroxy-3-phenylazo-2-naphthalenesulfonic acid (**5**) [19] [20] [22]. Aniline hydrochloride (1.295 g, 10 mmol) was diazotized as described for dye **2**; under vigorous stirring the diazonium salt solution was poured into a cold solution of 1.84 g (17 mmol) Na_2CO_3 in 50 ml H_2O and immediately mixed with an ice-cold solution of 2.70 g (10.5 mmol) **1**, 9.01 g (85 mmol) Na_2CO_3 and 5.96 g (71 mmol) $NaHCO_3$ in 150 ml H_2O. After stirring for 15 h the solution was diluted with 200 ml H_2O, heated to 90° and then cooled to r.t. to give 3.01 g (88%) crude **5**, which was recrystallized from H_2O. UV/VIS (H_2O, pH = 7.00): 513 (15870). ^{1}H-NMR ((D_6)DMSO): 5.70 (*s*, 2 H, NH_2); 6.97 (*dd*, *J* = 2.4 and 8.6, 1 H, H–C(7)); 7.12–7.83 (*m*, 8 H, arom. H); 10.68 (*s*, 1 H, OH).

Dye **8**. A solution of 257 mg (1 mmol) **1** in 1 ml 1 M NaOH was diluted with H_2O to 18 ml. After addition of 70 mg (1.01 mmol) $NaNO_2$ in 2 ml H_2O the solution was poured onto a mixture of 1.5 ml (9 mmol) 2 M HCl and 10 g ice. The resulting suspension of diazotized **1** was mixed with a suspension of 257 mg (1 mmol) **1**, prepared by dissolving **1** in 1 ml 1 M NaOH, dilution with H_2O to 10 ml and addition to 750 mg (11 mmol) HCOONa and 370 mg (8 mmol) HCOOH in 5 ml H_2O. The mixture was stirred for 36 h with cooling in the dark, then **8** was precipitated by addition of NaCl and purified by reprecipitation from an aq. solution with acetone (170 mg, 35%). UV/VIS (H_2O, pH = 7.00): 500 (21910). ^{1}H-NMR ((D_6)DMSO): 4.47 (br. *s*, 2 H, NH, OH); 7.14–8.47 (*m*, 9 H, arom. H); ≈ 10.5 (br. *s*, 1 H, NH); 12.76 (*s*, 1 H, OH).

Dye **9**. A mixture of 2 ml (0.2 mmol) 0.1 M aniline hydrochloride in H_2O and 0.15 ml (0.3 mmol) 2 M HCl was diluted with H_2O to 8 ml and diazotized with 2 ml (0.2 mmol) 0.1 M $NaNO_2$. The diazonium salt solution was poured with stirring into a solution of 107 mg (0.22 mmol) **8** and 53 mg (0.5 mmol) Na_2CO_3 in 30 ml H_2O. Dye **9** was precipitated and purified as described for **8** (30 mg, 25%). UV/VIS (H_2O, pH = 7.00): 549 (22670). ^{1}H-NMR ((D_6)DMSO): 7.15–8.18 (*m*, 10 H, arom. H); 8.58 (*m*, 3 H, arom. H); 8.60 (*s*, 1 H, OH); ≈ 8.6 (br. *s*, 1 H, NH); ≈ 10.6 (br. *s*, 1 H, NH); 12.70 (*s*, 1 H, OH).

3. Product Analyses. – *Reactions in Relatively Concentrated Solutions* (5×10^{-1} *to* 5×10^{-2}M). For the product analysis of coupling of *benzenediazonium ion* at pH = 3.6, 94 mg of the crude product of dye **2** were chromatographed (1 plate *PSC 60* F_{254}, PrOH/25% NH_4OH 2:1). Precipitation of separated dyes from MeOH-solutions with acetone yielded 78 mg **2**, 2.2 mg **8** and 4.4 mg **9**, corresponding to *ca.* 75, 3 and 0.2%, respectively. At pH = 9.6 only dye **5** was obtained (see *Syntheses of Dyes*).

Azo coupling of *3-trifluoromethylbenzenediazonium ion* in acidic solution (pH *ca.* 3) according to [23] gave only dye **3**. For product analysis of coupling at pH *ca.* 10, see synthesis of dyes **3**, **6** and **10**. Rapid mixing experiment: **1** (129 mg, 0.5 mmol) and 200 mg Na_2CO_3 were dissolved in 50 ml H_2O (10^{-2}M solution of **1**, pH *ca.* 10). 3-Trifluoromethylaniline (800 mg, 5 mmol) was dissolved in 6.3 ml 2M HCl and the necessary amount of H_2O to give a volume of 50 ml. From 5 ml of this solution, 0.5 ml 1M $NaNO_2$ and H_2O, a 10^{-2}M solution of diazonium salt was obtained. Both solutions were cooled in an ice bath and 10 ml of each were expelled from two syringes into a beaker. After 1 h at r.t. the product was precipitated with NaCl, centrifuged and analyzed by TLC (SiO_2, acetone/CH_2Cl_2/2-propanol 3:1:1). Only dye **6** was detectable.

The product analyses of coupling reactions of *4-nitrobenzenediazonium ion* is based on qualitative estimates of the respective spots on TLC (*DC 60 F_{254}*, BuOH/EtOH/H_2O 6:1:2). 4-Nitroaniline (276 mg, 2 mmol) was dissolved by warming in 0.6 ml H_2O and 0.6 ml conc. HCl. After addition of 1.6 g ice a suspension of the hydrochloride was obtained which was diazotized with 138 mg (2 mmol) $NaNO_2$. After filtration the solution of the diazonium salt was divided into two halves. One was added with cooling to a solution of 257 mg (1 mmol) **1** and 200 mg (5 mmol) NaOH in 2 ml H_2O (pH *ca.* 11). The second was added with cooling to a suspension of 257 mg (1 mmol) **1** in 0.1 ml conc. HCl and 2 ml H_2O (pH *ca.* 2). After additional stirring of both mixtures for 2 h at 0° the products were analyzed by neutralizing samples of the mixtures and adding the minimum amount of acetone to obtain homogeneous solutions for TLC. In acidic solution **4** (*ca.* 80%) and some by-products were obtained; at pH *ca.* 11, *ca.* 20% of **7** and *ca.* 40% of **4** and by-products were obtained. In a coupling reaction in alkaline solution as above but with a neutralized diazonium salt solution the amount of **4** was reduced to *ca.* 10%, but the by-products increased.

Reactions in More Dilute Solutions (10^{-2} to 2.5×10^{-5}M). For coupling reactions of *benzenediazonium ion* the following stock solutions were prepared: 77.2 mg (0.3 mmol) **1** and 0.31 ml

Table 2. *Composition of Buffer Solutions* (100 ml, I = 0.2) *for Product Analyses and Kinetics of Azo Coupling of Benzenediazonium Ion with* **1**

pH			ml of 1M KCl
3.0	50 ml 0.1M Sodium hydrogen phthalate	+ 22.3 ml 0.1M HCl	15.00
3.5	50 ml 0.1M Sodium hydrogen phthalate	+ 8.2 ml 0.1M HCl	15.00
4.0	50 ml 0.1M Sodium hydrogen phthalate	+ 0.1 ml 0.1M HCl	15.00
4.3	50 ml 0.1M Sodium hydrogen phthalate	+ 4.7 ml 0.1M NaOH	14.06
4.5	50 ml 0.1M Sodium hydrogen phthalate	+ 8.7 ml 0.1M NaOH	13.26
4.75	50 ml 0.1M Sodium hydrogen phthalate	+ 13.6 ml 0.1M NaOH	12.28
5.0	50 ml 0.1M Sodium hydrogen phthalate	+ 22.6 ml 0.1M NaOH	10.48
5.2	50 ml 0.1M Sodium hydrogen phthalate	+ 28.8 ml 0.1M NaOH	9.24
5.4	50 ml 0.1M Sodium hydrogen phthalate	+ 34.1 ml 0.1M NaOH	8.18
5.6	50 ml 0.1M Sodium hydrogen phthalate	+ 38.8 ml 0.1M NaOH	7.16
5.8	50 ml 0.1M KH_2PO_4	+ 3.6 ml 0.1M NaOH	14.28
6.0	50 ml 0.1M KH_2PO_4	+ 5.6 ml 0.1M NaOH	13.88
6.25	50 ml 0.1M KH_2PO_4	+ 8.9 ml 0.1M NaOH	13.22
6.5	50 ml 0.1M KH_2PO_4	+ 13.9 ml 0.1M NaOH	12.21
6.75	50 ml 0.1M KH_2PO_4	+ 20.9 ml 0.1M NaOH	10.82
7.0	50 ml 0.1M KH_2PO_4	+ 29.1 ml 0.1M NaOH	9.18
8.0	50 ml 0.1M KH_2PO_4	+ 46.7 ml 0.1M NaOH	5.66
9.6	50 ml 0.05M $NaHCO_3$	+ 5.0 ml 0.1M NaOH	17.00
10.0	50 ml 0.05M $NaHCO_3$	+ 10.7 ml 0.1M NaOH	16.43
10.9	50 ml 0.05M $NaHCO_3$	+ 22.0 ml 0.1M NaOH	15.30
12.0		6.0 ml 0.1M NaOH	20.65
12.9		66.0 ml 0.1M NaOH	14.65

(0.31 mmol) 1M NaOH, diluted with H_2O to 10 ml; 3 ml (0.3 mmol) 0.1M aniline hydrochloride, 3 ml (0.3 mmol) 0.1M $NaNO_2$ and 0.23 ml (0.46 mmol) 2M HCl, diluted with H_2O to 10 ml. The compositions of buffer solutions are given in *Table 2*. Coupling reactions: to 5 ml of the respective ice-cold stirred buffer solution 0.5 ml of each stock solution were added from syringes to give a final concentration of *ca.* 3×10^{-3}M of diazonium salt and **1**, respectively. The solution was kept for 4 h in an ice bath in the dark. Then 0.07 ml were diluted with 3 ml of buffer solution of pH = 7.00 to give a maximum dye concentration of *ca.* 5.8×10^{-5}M with a maximum absorbance of *ca.* 0.9. The experimental mol fractions X_5 *(Table 3)* were calculated by linear regression analysis of the *Lambert-Beer*'s law for 7 to 16 absorbance measurements between 380 and 530 nm per pH-value of reaction solutions (standard deviations for $0.15 \leq X_5 \leq 0.85$ less than 1%). The calculated mol fractions X_5 in *Table 3* have been obtained from *Eqn. 4*, where $k_{s,NH_2,max}$ is the maximum second-order rate constant for the 5-position in **1**, directly obtained from rate measurements, and pH* is that pH at which $X_5 = X_2 = 0.5$. *Eqn. 4* is obtained from *Eqn. 3* for X_5, assuming that the product ratio $\mathbf{5/2} = k_{s,OH}/k_{s,NH_2}$ and that $\log k_{s,OH} = pH - pH^* + \log k_{s,NH_2,max}$ (solid curve in *Fig. 3*), at $pK_{NH_3^+} \leq pH \leq pK_{OH}$. At pH-values $pH < pK_{NH_3^+}$ with $pH = pK_{NH_3^+}$ constant mol fractions X_5 are obtained.

$$X_5 = \frac{10^{(pH - pH^* + \log k_{s,NH_2,max})}}{k_{s,NH_2,max} + 10^{(pH - pH^* + \log k_{s,NH_2,max})}} \tag{4}$$

Table 3. *Mol Fractions X_5 of Azo Coupling of Benzenediazonium Ion with* **1** (final concentration of **1** and diazonium ion *ca.* 3×10^{-3}M, 0°, I = 0.2)

pH	Mol fractions X_5		pH	Mol fractions X_5	
	Exp.[a])	Calc.[b])		Exp.[a])	Calc.[b])
3.0	0.034	0.054	5.8	0.800 ± 0.009	0.711
3.5	0.034	0.054	6.0	0.918	0.795
4.0	0.036	0.054	6.25	0.980	0.873
4.3	0.095 ± 0.046	0.072	6.5	0.987	0.925
4.75•	0.170 ± 0.007	0.179	6.75	0.988	0.956
5.0	0.278 ± 0.003	0.280	7.0	0.988	0.975
5.2	0.390 ± 0.003	0.381	8.0	0.988	0.997
5.4	0.495 ± 0.004	0.494	9.6	0.988	–
5.6	0.610 ± 0.001	0.608			

[a]) From absorbance measurements and *Lambert-Beer*'s law. [b]) From *Eqn. 4*.

Table 4. *Mol Fractions X_6 of Azo Coupling of 3-Trifluoromethylbenzenediazonium Ion with* **1** (final concentration of **1** and diazonium ion *ca.* 10^{-3}M, 0°, I = 0.1)

pH	Mol fractions X_6	pH	Mol fractions X_6
4.0	0.010 ± 0.002	7.36	0.973 ± 0.003
4.5	0.034 ± 0.002	7.56	0.993 ± 0.003
4.7	0.063 ± 0.002	8.0	0.990 ± 0.004
4.8	0.088 ± 0.002	8.39	0.992 ± 0.003
4.9	0.106 ± 0.002	8.59	0.994 ± 0.003
5.0	0.205 ± 0.002	8.94	0.996 ± 0.004
5.3	0.294 ± 0.003	9.0	1
5.8	0.865 ± 0.003	9.17	0.994 ± 0.003
6.0	0.909 ± 0.002	9.44	0.994 ± 0.004
6.87	0.975 ± 0.003	9.46	0.995 ± 0.004
7.0	0.982 ± 0.004	10.0	0.973 ± 0.004
7.11	0.972 ± 0.009	11.0	1

The mol fractions X_6 *(Table 4)* of the coupling reactions of *3-trifluoromethylbenzenediazonium ion* were obtained as described above. The buffer solutions were prepared according to [21]. The buffers used were: for pH-values <5.8 potassium hydrogen phthalate, pH = 5.8 to 7.5 sodium phosphate, pH = 7.6 to 9.5 borax and pH = 9.5 to 11.0 sodium bicarbonate.

Coupling reactions of *4-nitrobenzenediazonium ion* in a buffered solution at pH = 9.8: 41.5 mg (0.3 mmol) 4-nitroaniline were diazotized at 0° in 3 ml 0.1 M HCl and 0.46 ml 1 M HCl with 20.7 mg (0.3 mmol) $NaNO_2$ in 5 ml H_2O, diluted with H_2O to 10 ml and filtered. A solution of **1** (77.2 mg, 0.3 mmol) in 3.1 ml 0.1 M NaOH was diluted with H_2O to 10 ml. The buffer solution was obtained from 210 mg $NaHCO_3$, 10.7 ml 0.1 M NaOH and 16.5 ml 1 M KCl, which were diluted to 100 ml. Solutions of **1** and 4-nitrobenzenediazonium ion (0.5 ml) were added dropwise to 5 ml of buffer solution at 0°. After additional stirring for 15 min the reaction product was analyzed by TLC as described above. Only dye **7** could be detected.

4. Kinetics. – *Azo Couplings of Benzenediazonium Ion with* **1**. The $pK_{NH_3^+}$ and pK_{OH} values of **1** (4.17 ± 0.03 and 9.03 ± 0.03, respectively) were taken from [8]. The $(pK_1 + pK_2)/2$ of benzenediazonium ion was calculated from *Eqn. 5*, where p is the degree of neutralization, and was 10.99 ± 0.12. To aliquots of a benzenediazonium ion solution, obtained from a stock solution (40 ml 0.1 M aniline hydrochloride, 3 ml 2 M HCl, 40 ml 0.1 M $NaNO_2$, diluted with H_2O to 100 ml) and an equal volume of 2 M KCl (for an ionic strength I = 0.2) were added increasing amounts of 0.1 M NaOH and after 1 min of stirring the pH of the solution was measured *(Table 5)*.

$$\frac{pK_1+pK_2}{2} = pH + \frac{1}{2}\log\frac{[ArN_2^+]}{[ArN_2O^-]} = pH + \frac{1}{2}\log\frac{1-p}{p} \qquad (5)$$

For kinetic measurements a 1-cm cell, thermostatted at 20.0 ± 0.1°, was filled with 3.00 ml buffer *(Table 2)* and the appropriate amount of the stock solution of **1** (20–100 µl of 3×10^{-1} M **1**). The

Table 5. *Determination of* $(pK_1 + pK_2)/2$ *of Benzenediazonium Ion* (I = 0.2, 20°)

p	pH	$(pK_1 + pK_2)/2$
0.125	10.53	10.95
0.250	10.79	11.00
0.375	10.98	11.09
0.500	11.10	11.10
0.625	11.19	10.79
0.750	11.26	11.00
		10.99 ± 0.12

Table 6. *Rate Constants* k_s *of Azo Coupling of Benzenediazonium Ion with* **1** (T = 20.0 ± 0.1°, I = 0.2)

pH	k_s[a]) ($l \cdot mol^{-1} \cdot s^{-1}$)	pH	k_s[a]) ($l \cdot mol^{-1} \cdot s^{-1}$)
3.00	0.067[b])	5.80	4.30
3.50	0.336[b])	6.00	7.98
4.00	0.577	6.25	8.36
4.30	0.676	7.00	51.2[b])
4.75	1.13	8.00	160
5.00	1.41	9.60	2660
5.20	1.40	10.00	3720
5.40	1.52	12.00	1570
5.60	2.33		

[a]) $k_s = k_{s,NH_2} + k_{s,OH}$ in *Eqn. 1*. [b]) Corrected values, see text.

diazonium salt solution (1.5×10^{-2}M) was added as one drop from a 10-µl syringe onto the stopper of the cell and the reaction started by closing and turning the cell. Absorbances were measured from pH = 3.00 to 5.60 and pH = 5.60 to 12.00 at 490 and 510 nm, respectively. The stoichiometric second-order rate constants were calculated from 10 absorbance measurements per pH-value. Where indicated in *Table 6* they have been corrected for the decomposition of the diazonium ion according to [18].

Azo Couplings of 3-Trifluoromethylbenzenediazonium Ion with **1**. The reactions were run in a thermostatted cell in a *Beckman Acta III* spectrophotometer which was connected on line with a teletype for computer evaluation. The 1-cm cell was filled with 3.00 ml buffer *(Table 7)*. The appropriate amount of the stock solution of **1** was added through a 10-µl syringe. The solution of the diazonium salt was added as one drop from a 100-µl syringe on the stopper of the cell. The reaction was started by closing and turning the cell. Absorbance was measured 10 times at such intervals that the last measurement was not taken earlier than after 20 half-lives. After that time the whole visible spectrum was measured. The computer programme which we applied to the measurements was based on the visible spectra of dyes **3** and **6**, pH, initial concentrations of diazonium ion and **1**, and $pK_{NH_3^+}$ and pK_{OH} of **1** in order to calculate k_s as well as k for both competitive reactions, *i.e.* coupling at the *o*-positions to the NH_2-group and the OH-group. We varied the concentration of both reagents (**1** always in 1.3 to 3 times excess), the concentrations of buffer base and buffer acid, and the pH-value. Ionic strength was always I = 0.10. A total of 223 kinetic runs was evaluated by the computer.

The results showed that the reaction at the *o*-position to the amino group (formation of dye **3**) was slightly catalyzed by buffer base (HPO_4^{2-}) and by excess **1** (which is also a base). To eliminate this effect, all data were extrapolated to zero buffer concentration. They are given in *Table 8*.

Table 7. *Composition of Buffer Solutions* ($mol \cdot l^{-1}$) *for Kinetics of Azo Coupling of 3-Trifluoromethylbenzenediazonium Ion with* **1**. The ionic strength was corrected to I = 0.1 with 0.1M KCl

pH	NaH_2PO_4	Na_2HPO_4
4.40	0.0989	0.0004
5.32	0.0880	0.0048
5.69	0.0822	0.0071
5.80	0.0786	0.0086
6.12	0.0698	0.0121
6.30	0.0537	0.0186
6.80	0.0225	0.0310

Table 8. *Results of Kinetic Measurements of the Reaction of 3-Trifluoromethylbenzenediazonium Ion with* **1** *at 25.0 ± 0.2° and I = 0.10* ($l \cdot mol^{-1} \cdot s^{-1}$)

pH	k_{s,NH_2}	$k_{s,OH}$
4.40	31.0	21.2
5.32	38.7	147.0
5.69	37.4	237.5
5.80	39.1	312.7
6.12	44.1	791.3
6.30	47.6	1065
6.80	71.0	4917

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