

## KINETICS AND MECHANISM OF THE AZO COUPLING REACTION OF 1-AMINONAPHTHALENE-4-SULFONIC ACID

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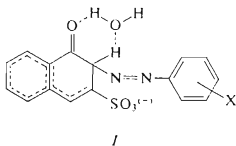
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Kinetics of the azo coupling reaction of 1-aminonaphthalene-4-sulfonic acid with nine substituted benzenediazonium chlorides was investigated at four temperatures. The results were processed in terms of the isokinetic relationship and of an isoparametric relationship with temperature and  $\sigma$  constant as independent variables. There is a great similarity to the coupling reaction of 1-hydroxynaphthalene-4-sulfonic acid; all the results are consistent with a cyclic transition state implying variable association of a water molecule.

The general features of the azo coupling reaction have been clarified in the 1950's by Zollinger<sup>1,2</sup>. Certain coupling reactions, for example those taking place in the *ortho* position to a hydroxy or amino group, reveal characteristic features as compared with the general pattern. According to a kinetic study of the azo coupling with 1-hydroxynaphthalene-3-sulfonic acid a structure near to *I* was suggested<sup>3</sup> for the transition state. The main argument originated in the large difference of activation entropies for *para* and *ortho* coupling. On the basis of the azo coupling with 1-hydroxynaphthalene-4-sulfonic acid, Demian<sup>4</sup> formulated a reaction mechanism implying variable association of a water molecule in the transition state.

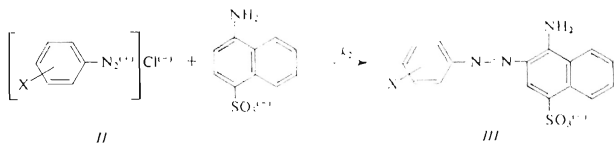


Seeking for further support of the above mechanism, we have extended the investigations to 1-aminonaphthalene-4-sulfonic acid, and report in this paper the kinetic data of its coupling reaction with substituted benzenediazonium chlorides *II*. This

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reaction takes place exclusively in *ortho* position to the amino group, yielding the azo dye III. The kinetic data obtained have been correlated using extrathermodynamic relationships<sup>5</sup>, in particular the Hammett equation<sup>5</sup> at different temperatures<sup>6</sup> and the isokinetic relationship<sup>7</sup>. All the results have been compared to the previously investigated reactions of the same type<sup>4</sup>.

The reaction under investigation



X = *m,p*-NO<sub>2</sub>, *m,p*-Cl, *m,p*-CH<sub>3</sub>, H, and *m,p*-OCH<sub>3</sub>

follows the kinetic equation:

$$\frac{d[Az]}{dt} = k_2 [D] \cdot [C], \quad (1)$$

where [Az] is the concentration of the formed azo dye, [D] the concentration of benzenediazonium cation (equal to the concentration of benzenediazonium tetrafluoroborate) and [C] concentration of the acid anion. The latter is conditioned by the equilibrium with the free acid:

$$[C] = \frac{K_a \cdot c_i}{K_a + [H^+]}, \quad (2)$$

where  $K_a$  is the acidity constant ( $pK_a = 2.81$ , ref.<sup>8</sup>) of the amino group,  $c_i$  the initial concentration of 1-aminonaphthalene-4-sulfonic acid. Using the coupling component C in large excess, the pseudomonomolecular conditions were provided and the pseudo-first-order rate constants  $k_\psi$  obtained from the equation:

$$\frac{d[Az]}{dt} = k_\psi [D], \quad (3)$$

By combining relations (1)–(3) the second-order rate constants  $k_2$  were calculated:

$$k_2 = \frac{k_\psi (K_a + [H^+])}{K_a \cdot c_i}. \quad (4)$$

The values of  $k_2$  at four temperatures are listed in Table I, the activation parameters<sup>o</sup> in Table II.

When processing our kinetic data (reaction series A) within the framework of correlation analysis, reference will be made to the mentioned azo coupling reactions with 1-hydroxynaphthalene-4-sulfonic acid<sup>4</sup> as the passive component (reaction series B).

TABLE I

Rate constants  $k_2$  for the azo coupling reaction of 1-aminonaphthalene-4-sulfonic acid<sup>a</sup>

Substituent in the diazonium cation	log $k_2$ at $T$			
	283.2 K	288.2 K	293.2 K	298.2 K
4-NO <sub>2</sub>	5.060	5.170	5.255	5.350
3-NO <sub>2</sub>	4.730	4.845	4.940	5.025
4-Cl	2.870	3.005	3.135	3.250
3-Cl	3.615	3.745	3.825	3.950
4-CH <sub>3</sub>	1.815	1.970	2.105	2.280
3-CH <sub>3</sub>	1.930	2.070	2.210	2.350
H	2.240	2.370	2.505	2.620
4-OCH <sub>3</sub>	1.210	1.365	1.515	1.670
3-OCH <sub>3</sub>	2.595	2.730	2.860	2.985

<sup>a</sup>  $k_2$  in  $l \text{ mol}^{-1} \text{ s}^{-1}$ .

TABLE II

Activation parameters  $\Delta H^\ddagger$  ( $\text{kJ mol}^{-1}$ ) and  $\Delta S^\ddagger$  ( $\text{J mol}^{-1} \text{ K}^{-1}$ )

Substituent	Free fitting		Isoentropic constraint <sup>a</sup>
	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$
4-NO <sub>2</sub>	28.5	-47	27.3
3-NO <sub>2</sub>	29.3	-50	28.9
4-Cl	38.6	-53	38.4
3-Cl	32.6	-60	34.7
4-CH <sub>3</sub>	47.0	-44	43.6
3-CH <sub>3</sub>	42.8	-56	43.2
H	38.8	-64	41.6
4-OCH <sub>3</sub>	47.0	-55	46.8
3-OCH <sub>3</sub>	39.6	-55	39.8

<sup>a</sup>  $\Delta S^\ddagger = -54 \text{ J mol}^{-1} \text{ K}^{-1}$  for all the reactions.

The kinetic data were processed in terms of the isokinetic relationship<sup>7</sup> (IKR) on the one hand, and in terms of the Hammett equation<sup>5</sup> and its extensions<sup>6,10</sup> on the other. A preliminary test of the IKR was accomplished by plotting  $\Delta H^\ddagger$  vs  $\Delta G^\ddagger$  according to Krug and coworkers<sup>11</sup>. In the reaction series A the substituent 4-OCH<sub>3</sub> deviated significantly from the linear dependence, in the series B the same was observed with 4-NO<sub>2</sub> and 4-OCH<sub>3</sub>. The anomalous behaviour of these substituents was confirmed by a plot of  $\log k$  vs substituents constants<sup>12</sup>  $\sigma^0$ : within the series B the substituents 4-NO<sub>2</sub> and 4-OCH<sub>3</sub> were off the line and in A only 4-OCH<sub>3</sub>. The behaviour of the 4-methoxy group can be either accounted for by variable direct conjugation or by specific solvation in water solution. On the contrary, we have no straightforward explanation for the deviations of the 4-nitro group which belongs usually to well-behaved substituents.

The statistical treatment of the IKR was carried out by a method<sup>13</sup> based on the least squares condition in the coordinates  $\log k$  vs  $T^{-1}$ . In this concept, the existence of IKR is equivalent to the condition that the Arrhenius lines intersect in one point with the coordinates  $(\beta^{-1}, y_0)$ :

$$\log k_{ij} = y_0 + b_i(T_j^{-1} - \beta^{-1}). \quad (5)$$

For the reasons discussed in some detail elsewhere<sup>7,13</sup> we preferred to take all the rate constants with the same weight, irrespective of their experimental error estimated from individual kinetic runs. The most important statistics are listed in Table III. The

TABLE III  
Statistics of the isokinetic relationship

Parameter	Series A	Series B <sup>a</sup>
Standard deviations $\cdot 10^4$ (degrees of freedom)		
$s_{00}$	82 (18)	139 (8)
$s_0$	98 (25)	137 (14)
$s_\infty$	275 (26)	220 (15)
$s_s$	98 (26)	133 (15)
$s_R$	12 959 (8)	10 712 (7)
Isokinetic temperature $\beta$ , K	-3 860	5 188
Validity of IKR: $\psi$	0.008	0.013
$\alpha$	0.25	>0.25

<sup>a</sup> Without 4-NO<sub>2</sub> and 4-CH<sub>3</sub>O.

precision of IKR is given by the standard deviation  $s_0$ , or by the standard deviations  $s_{\infty}$  or  $s_S$  which would be operative if the reactions series were isoenthalpic or isoentropic, respectively. The standard deviation  $s_{00}$  refers to freely fitted Arrhenius lines (*i.e.* without the constraint of a common point of intersection) and serves as an estimate of the overall experimental error.

The salient feature of the data is that IKR is accepted as a useful empirical relationship for series A since the statistic  $\psi$  (relating  $s_0$  to the variance between individual reactions as expressed by  $s_R$ ) is significantly lower than 0.1. The IKR is also valid within the limits of experimental error according to the confidence level  $\alpha$  (relating  $s_0$  to  $s_{00}$ ). According to the value of  $s_{\alpha}$ , the reaction series cannot be isoenthalpic but according to  $s_S$  it may be well isoentropic. This is in accord with the high negative value of the isokinetic temperature  $\beta$  which could be actually infinite. In such cases we accept the isoentropic hypothesis as the simpler one<sup>13</sup>. The values of  $\Delta S^\ddagger$  in Table II are by far not constant and reveal how little dependable is the determination from a single reaction. More dependable are  $\Delta H^\ddagger$  values: when we calculated  $\Delta H^\ddagger$  with the isoentropic constraint ("isokinetic"  $\Delta H^\ddagger$ , ref.<sup>13</sup>), they differ but little from the unconstrained ones (Table II). All the conclusions apply for series B, too. The pertinent statistics are very similar in the two series, the only difference is the higher experimental accuracy now attained for series A.

The treatment in terms of the Hammett type equations was carried out for all temperatures together. If both substituent and temperature are varied, the general form of the correlation equation is the isoparametric relationship<sup>6,14</sup> with  $\sigma$  and  $T^{-1}$  as independent variables:

$$\log k_{ij} = -\beta \rho_0 (\sigma_i - \vartheta) (T_j^{-1} - \beta^{-1}) . \quad (6)$$

The isokinetic temperature  $\beta$  has the same meaning as above and  $\vartheta$  represents the extrapolated value of  $\sigma$  constant which should make the reactivity independent of temperature.

The relationship (6) differs from (5) only by an additional requirement that the slopes  $b_i$  are proportional to the substituent constants  $\sigma$ . Of various sets of constants<sup>12</sup> the best results were obtained with standard constants  $\sigma^\circ$  for all substituents except 4-OCH<sub>3</sub>, for which the value 0.28 was used (derived from dissociation constants in water<sup>12</sup>). In this way the importance of hydration processes is expressed. The 4-nitro substituent was omitted in both series, although this was necessary in the series B only. The statistics listed in Table IV reveal again great similarity of the series A and B; (see particularly the values of  $\vartheta$  and  $\beta$ , the latter being virtually infinite in the two series). In all cases the isoparametric relationship is adequate and its standard deviation  $s_{\text{ISOP}}$  is lower than for independent correlations at each separate temperature ( $s_{\text{LIFER}}$ ). The similarity of both reaction series is revealed most distinctly

in the reaction constant  $\rho_{25}$  valid for 25 °C, whereas the values of  $\rho_0$  are immaterial as products of a far reaching extrapolation. Similarly, the values of  $\vartheta$  represent an extrapolation which cannot be reached experimentally.

An alternative set of constants can be obtained from the Yukawa-Tsuno treatment<sup>10</sup> as:

$$\sigma = \sigma^0 + r(\sigma^+ - \sigma^0), \quad (7)$$

where the adjustable parameter  $r$  expresses the variable conjugation of substituent with the reaction centre. Our data do not allow a precise treatment since  $r$  is determined mainly by the substituent 4-OCH<sub>3</sub> and hence estimated very roughly. The direct conjugation seems not to be of much importance if present at all. The precision of Yukawa-Tsuno treatment is slightly lower in the series A than in B.

In conclusion, the results of correlation analysis are compatible with an essentially common mechanism of the two series and with a sigma-complex transition state. The association of a water molecule in a cyclic structure may assist in proton transfer, this effect being probably responsible for characteristic deviations observed with the most powerful electron acceptors as well as donors.

TABLE IV  
Statistics of the isoparametric relationships with  $\sigma$ , T<sup>-1</sup>

Parameter	Series A <sup>a</sup>	Series B <sup>a</sup>
$\sigma^{\circ}$ Constants and $-0.28$ for 4-OCH <sub>3</sub>		
$\rho_{25}$	3.35	3.96
$\vartheta$	2.32	3.26
$\beta$ , K	-40 260	-4 071
$-\beta\rho_0$ , K	994	1 103
Standard deviations: $s_{\text{ISOP}}$	0.092	0.151
$s_{\text{L呢ER}}$	0.094	0.158
$\sigma$ Constants from the Yukawa-Tsuno equation		
$\rho_{25}$	3.29	3.63
$r$	0.26	0.43
$\vartheta$	2.32	4.01
Standard deviations: $s_{\text{ISOP}}$	0.100	0.065
$s_{\text{L呢ER}}$	0.108	0.067

<sup>a</sup> Without 4-NO<sub>2</sub>.

## EXPERIMENTAL

1-Aminonaphthalene-4-sulfonic acid has been purified by repeated precipitation with HCl from alkaline solution<sup>15</sup>. The aromatic amines were purified by crystallization and vacuum distillation. The diazotization of the amines was performed according to ref.<sup>15</sup>.

The concentration of 1-aminonaphthalene-4-sulfonic acid was  $3 \cdot 10^{-3} \text{ mol l}^{-1}$ , while the concentration of benzenediazonium chlorides was about  $5 \cdot 10^{-5} \text{ mol l}^{-1}$ . The coupling component was dissolved in aqueous buffer solutions (sodium citrate-HCl, pH 1.10–4.96,  $I = 0.2$ ). The pH range was selected in such a way that the rate constant  $k_{\psi}$  (equation (3)) should be at least two orders of magnitude greater than the rate constant of the parallel thermal decomposition reaction of the diazonium salt<sup>16</sup>.

The pH measurements were performed with a precision pH-meter MV85 Präcitronic, DDR). The kinetics of the azo coupling reactions was followed spectrophotometrically at  $\lambda = \lambda_{\text{max}}$  of the formed azo dye. The kinetic runs were accomplished in the thermostated cell of a UNICAM SP-800 spectrophotometer equipped with SP-820 and SP-870 accessories, the exit signal being recorded with a Philips PM 8100 recorder. The temperature in the cell was measured by a mercury thermometer of  $\pm 0.1^{\circ}\text{C}$  precision. The pseudo-first-order rate constant  $k_{\psi}$  was determined by linearization (the method of least squares) of  $\log(E - E_{\infty})$  vs  $t$ ,  $k_{\psi}$  being the slope of regression line. Four to six runs were performed at each temperature.

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