

KINETICS AND MECHANISM OF DIAZO COUPLING. XXI.*
KINETICS OF DIAZO COUPLING
WITH 1-NAPHTHOL AND 1-METHOXYNAPHTHALENE

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The ratio of the coupling rate constants of 2-chloro-4-nitrobenzenediazonium ion with 1-naphthol and 1-methoxynaphthalene decreases from 70 to 10 with increasing concentration of sulphuric acid in mixtures 32% by vol. acetic acid-sulphuric acid-water. In mixtures water-acetic acid, at first, this ratio increases with decreasing water concentration, and it reaches its maximum value 215 at a water concentration of 35% by weight. The dependences found have been explained by both the influence of medium on the activity coefficients of the starting species and activated complexes and the direct action of water in the splitting of the oxygen-hydrogen bond of 1-naphthol during the coupling reaction. The influence of water on the coupling kinetics of 1-naphthol has been studied in the mixture water-sulphuric acid, too. During the coupling with 1-methoxynaphthalene an acid catalyzed hydrolysis of the azo dyestuff formed takes place, the maximum rate of this reaction being at a concentration of about 45% by weight sulphuric acid. The ρ constants of coupling of undissociated 1-naphthol and 1-methoxynaphthalene with substituted benzenediazonium ions were ascertained, too.

Within our studies of coupling kinetics of 1-naphthol and its derivatives we determined the difference in the reactivities of 1-naphthol and its anion. This difference was somewhat greater than 8 orders of magnitude except for the most reactive diazonium ions¹ where the difference gradually diminished because the reaction rate was determined more and more by diffusion. We have now extended our studies by a comparison of reactivities of undissociated 1-naphthol and its O-methyl derivative.

The magnitude of the activating influence of methoxy group, eventually the difference in reactivities of methoxy and hydroxy derivatives, can be deduced only from the kinetic studies of phenol and anisol brominations in acetic acid^{2,3} and water⁴. In acetic acid, the bimolecular rate constant of phenol bromination is 92 times as large as that of anisol bromination². According to the authors, the higher reactivity of hydroxy derivatives is caused by the fact that O-H bond is partially split in the activated complex so that the mesomeric effect of the oxygen atom makes itself felt to a larger extent. The same opinion is expressed by Eaborn⁵ who presumes that this

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splitting is facilitated by a hydrogen bond to a solvent molecule. Also the decrease of the rate constant by a factor of 1.8–1.9 when carrying out the phenol bromination in deuterioacetic acid⁶ points to a considerable O—H bond splitting in the activated complex. The difference in the rate constants depends considerably on the reaction medium and substrate structure, resp. on the point of attack by electrophilic reagent. *E.g.* in water the bromination of phenol is only about four times as rapid as that of anisol⁴. This value is, of course, approximate only, because the reaction is very fast under these conditions. On the other hand, *p*-bromophenol reacts with bromine 600 times as rapidly as *p*-bromoanisol². There are only few data on diazo coupling with alkyl aryl ethers in literature. It is stated that they are considerably more reactive than alkylbenzenes but the diazo coupling, as a rule, takes place with strongly electrophilic diazonium ions only as *e.g.* 2,4-dinitrobenzenediazonium ion. Naphthyl alkyl ethers react more easily than the analogous phenyl ethers. A substitution of the alkyl group by hydroxyl group often takes place during coupling in mineral acid media. This substitution, which is acid catalyzed, follows the proper coupling reaction. Although the mechanism and kinetics of this hydrolysis were studied in detail^{7,8}, no data on kinetics of the proper diazo coupling reaction are given in literature up to now.

We have carried out the kinetic study of diazo coupling with 1-methoxynaphthalene in aqueous acetic acid. Both the influence of water or sulphuric acid concentration and the influence of substituents in benzenediazonium ion on the coupling rate were determined. The same conditions were adopted when following the diazo coupling kinetics with 1-naphthol. Besides that the influence of water activity on the velocity of coupling of 2,6-dichloro-4-nitrobenzenediazonium and 2-chloro-4-nitrobenzenediazonium ions with 1-naphthol were determined in diluted sulphuric acid.

EXPERIMENTAL

Reagents

A commercial sample of 1-naphthol was purified by crystallization from a benzene–cyclohexane mixture. The respective O-methyl derivative was prepared by usual methylation with dimethyl sulphate and distilled *in vacuo* (136°C/12 Torr; ref.¹⁰ 269°C/760 Torr). The substituted aromatic amines were either commercial products or prepared by known methods. Their purity was checked by melting point determination. The other chemicals were commercial products of p.a. purity grade.

Preparation of Stock Solutions

The solutions of diazonium salts (2,6-dichloro-4-nitro-, 2-chloro-4-nitro-, 2,4,6-trichloro-, and 3-nitro-4-chlorobenzenediazonium sulphates) were prepared by diazotization of the respective anilines in concentrated sulphuric acid with solid sodium nitrite⁹. Before each kinetic experiment a part of this solution was diluted with ice water at a concentration $5 \cdot 10^{-3}$ mol/l, and the excess nitrous acid was removed by a sulphamic acid addition. The solutions of the other diazonium salts were prepared in a usual way by diazotization in a small amount of 2.5M-HCl, removing the excess nitrous acid with sulphamic acid, and adjusting at a definite volume.

Kinetic Measurements

Various methods were used for the kinetic measurements according to the reaction rate and validity of the Lambert–Beer law for the respective dyestuff formed.

A) *Direct extinction measurement of the azo dyestuff formed.* This method was used for all the measurements in acetic acid medium. As a rule, 1 ml $5 \cdot 10^{-4}$ M diazonium salt solution was added to a thermostated solution, containing known amounts of sulphuric and acetic acids and substrate stock solution in acetic acid, located in a 50 ml calibrated flask. A part of the reaction solution was transferred to a 1 cm cell placed in the thermostated cell holder of a VSU-2P spectrophotometer (Zeiss, Jena), and the extinction was measured at definite time intervals. In the case of reactions of substituted benzenediazonium ions with 1-naphthol the extinction was measured at λ_{\max} of the azo dyestuff formed. In the case of reactions with 1-methoxynaphthalene the hydrolysis of methoxyl group took place in the azo dyestuff formed. The velocities of the both reactions were comparable in kinetic experiments with sulphuric acid concentrations up to 35% by weight, and, therefore, the extinction was measured at the isosbestic point of the hydroxy and methoxy derivatives. In the experiments with higher sulphuric acid concentrations the extinction was measured at λ_{\max} of the hydroxy derivative, because the subsequent reaction was faster by about 2 orders of magnitude. The reactions were followed up to 2–3 half-lives. After a time interval corresponding to about 7 half-lives the final extinction value was measured. The rate constant k' was obtained graphically according to Eq. (1) where E_t and E_∞ are the extinctions at a time t and $t = \infty$ (final solution) respectively.

$$k't = -2.303 \log (E_\infty - E_t) + \text{const.} \quad (1)$$

B) *Measurement of the diazo compound decrease.* This method was adopted for the measurements in aqueous mineral acid solutions. The diazonium salt solution was added to a reaction solution placed in the thermostat under stirring, and 5 ml samples were withdrawn with a pipette into 10 ml 10^{-2} M 1,8-dihydroxynaphthalene-3,6-disulphonic acid solution and 5 or 10 ml 2M- $\text{CH}_3\text{CO}_2\text{Na}$ depending on the amount of sulphuric acid in the reaction mixture. After finishing the experiment 5 ml ethanol was added to each sample and the volume was adjusted with distilled water. The dyestuffs formed by coupling with 1-naphthol are insoluble in 10% ethanol; the samples were filtered before the extinction measurements so that the extinction of the dyestuff from 1,8-dihydroxynaphthalene-3,6-disulphonic acid was measured only (λ_{\max} 510 nm). The rate constants were obtained graphically from Eq. (2).

$$k't = -2.303 \log (E_t - E_\infty) + \text{const.} \quad (2)$$

The measurements of the rate constants of hydrolysis of 4-(2-chloro-4-nitrophenylazo)-1-methoxynaphthalene in the mixtures water-sulphuric acid-acetic acid were carried out in two ways. In the case of reactions having half-lives higher than 10 min 5 ml $5 \cdot 10^{-4}$ M dyestuff solution in acetic acid was added into 45 ml of the mixture water-sulphuric acid-acetic acid and, after mixing, a part of the solution was transferred into a 1 cm cell located in the thermostated cell holder of a Unicam SP 800 B spectrophotometer. At definite time intervals spectra were recorded in the range 350–550 nm. The calculation was carried out according to Eq. (1), the extinction being used at a wavelength corresponding to the absorption maximum of the naphthol derivative formed. In the case of reactions with shorter half-lives, the following procedure was adopted: 5 ml $5 \cdot 10^{-4}$ M dyestuff solution in acetic acid was injected quickly from a syringe into 45 ml of the mixture water-sulphuric acid-acetic acid at 20°C, and then 1 ml samples were withdrawn from the solution by means of a special syringe and injected into 10 ml calibrated flasks containing each 5 ml 30% NaOH and 1 ml ethanol. After adjusting the volume with distilled water the extinctions were measured. The hydrolysis rate constant was computed graphically from Eq. (1).

Determination of Distribution Coefficients

The distribution coefficients of 1-naphthol and 1-methoxynaphthalene between cyclohexane and the reaction mixture were determined by the separation of the weighed substrate sample in both the media. 1-Naphthol concentration was determined by measuring the extinction of cyclohexane samples and that of the reaction mixture at 290 nm. As the 1-methoxynaphthalene concentrations in the reaction mixture were too low after the extraction with cyclohexane, the remaining 1-methoxynaphthalene was extracted into chloroform, and then the extinction of the chloroform solution was measured (Table I).

TABLE I

Distribution Coefficients of 1-Naphthol (X_{ArOH}) and 1-Methoxynaphthalene (X_{ArOCH_3}) between Cyclohexane and Mixture Sulphuric Acid-Water-32% by Vol. Acetic Acid

H_2SO_4 % by weight	CH_3CO_2H % by weight	H_2O % by weight	X_{ArOH}	X_{ArOCH_3}	$\gamma_{OH}/\gamma_{OCH_3}^a$
8.6	30.9	60.5	0.900	59	1.000
16.2	29.3	54.5	1.040	62	1.105
22.5	27.5	50.0	1.135	64	1.180
29.3	26.6	44.1	1.520	70	1.420
35.4	25.9	38.7	1.770	77	1.515
40.6	24.9	34.5	2.040	82	1.630
42.7	24.5	32.8	2.140	84	1.680
45.9	23.9	30.2	2.300	86	1.750
47.9	23.7	28.4	2.540	88	1.890

^a $\gamma_{OH}/\gamma_{OCH_3}$ is the ratio of the activity coefficients of the substrates. The mixture containing 8.6% H_2SO_4 was chosen as the standard mixture.

Preparation of Dyestuffs from 1-Methoxynaphthalene

The substituted 4-phenylazo-1-methoxynaphthalenes were prepared by diazo coupling of the respective benzenediazonium salts with 1-methoxynaphthalene in concentrated acetic acid⁷. The following azo dyestuffs were crystallized from aqueous acetone or a mixture acetone-methanol: 4-(3-Nitrophenylazo)-1-methoxynaphthalene, m.p. 141–142°C; for $C_{17}H_{13}N_3O_3$ (307.3) calculated: 66.50% C, 3.94% H, 13.66% N; found: 66.70% C, 4.24% H, 13.85% N. 4-(2-Chloro-4-nitrophenylazo)-1-methoxynaphthalene, m.p. 176–177°C; for $C_{17}H_{12}ClN_3O_3$ (341.7) calculated: 59.80% C, 3.54% H, 12.30% N; found: 60.07% C, 3.54% H, 12.44% N. 4-(3-Nitro-4-chlorophenylazo)-1-methoxynaphthalene, m.p. 215–216°C; for $C_{17}H_{12}ClN_3O_3$ (341.7) calculated: 59.80% C, 3.54% H, 12.30% N; found: 59.74% C, 3.50% H, 12.10% N.

RESULTS AND DISCUSSION

The first series of the kinetic measurements were carried out in media containing 32% by vol. acetic acid and various amounts of sulphuric acid and water. Lower concentrations appeared to be disadvantageous with respect to the rapidly decreasing 1-methoxynaphthalene solubility at lower acetic acid concentrations. 2-Chloro-4-nitrobenzenediazonium ion was used as the electrophilic reagent as it proved to be the most useful with respect to the coupling reaction rates with both the 1-hydroxy- and 1-methoxynaphthalenes. In all the cases a linear dependence of $\log E$ vs time t was obtained up to at least two half-lives. Results of the kinetic experiments are given in Table II.

The chromatography of the reaction products from kinetic experiments with 1-naphthol showed a presence of small amounts of 2-(2-chloro-4-nitrophenylazo) derivative besides the main 4-(2-chloro-4-nitrophenylazo)-1-naphthol as it was the case with coupling in aqueous medium⁶. The chromatography of the reaction products from the kinetic experiments with 1-methoxynaphthalene detected the formation of the respective hydroxy derivative besides the expected 4-(2-chloro-4-nitrophenyl-

TABLE II

Dependence of Coupling Rate Constant of 2-Chloro-4-nitrobenzenediazonium Ion with 1-Naphthol and 1-Methoxynaphthalene on Water Concentration

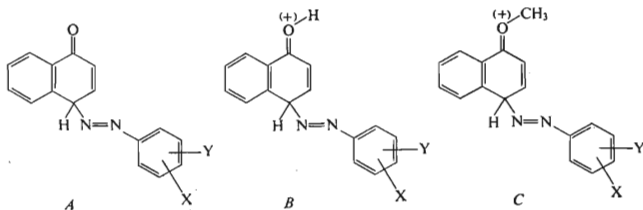
H ₂ SO ₄ % by weight	CH ₃ CO ₂ H % by weight	H ₂ O % by weight	1-Naphthol		1-Methoxynaphthalene	
			[S] · 10 ⁴ ^a mol l ⁻¹	k · 10 ⁻² l mol ⁻¹ min ⁻¹	[S] · 10 ⁴ ^a mol l ⁻¹	k · 10 ⁻¹ l mol ⁻¹ min ⁻¹
8.6	30.9	60.5	1	9.50	8	1.37
16.2	29.3	54.5	1	7.70	—	—
22.5	27.5	50.0	1	7.35	8	1.45
22.5	27.5	50.0	2	6.60	—	—
29.3	26.6	44.1	1	5.35	8	1.51
29.3	26.6	44.1	2	6.20	—	—
35.4	25.9	38.7	1	4.85	8	1.44
35.4	25.9	38.7	2	4.82	—	—
40.6	24.9	34.5	1	3.60	8	1.43
40.6	24.9	34.5	2	3.60	—	—
42.7	24.5	32.8	2	3.55	—	—
45.9	23.9	30.2	1	2.30	8	1.43
45.9	23.9	30.2	2	2.40	—	—
47.9	23.7	28.4	2	1.63	8	1.44
47.9	23.7	28.4	8	1.36	—	—

^a [S] is the concentration of 1-naphthol and 1-methoxynaphthalene respectively.

azo)-1-methoxynaphthalene, the ratio of hydroxy to methoxy derivatives being increased with increasing reaction time. This increasing hydroxy to methoxy derivative ratio stands in accord with the results of Bunnett⁷ showing that the formation of the hydroxy derivative is a consequence of hydrolysis of the methoxy compound originally formed.

In the case of the experiments using the maximum sulphuric acid concentration, the results obtained could be distorted by a simultaneous sulfonation of 1-naphthol resp. 1-methoxynaphthalene. We proved in two ways that this side reaction is not significant under the conditions given. 1. The coupling kinetics was measured either immediately after mixing the reagents or after six hours standing of the reaction mixture. In the both cases identical rate constants were obtained (within experimental error). 2. 1-Naphthol resp. 1-methoxynaphthalene was extracted from the reaction mixture into cyclohexane either immediately or after six hours. It was found that the amounts of the substances extracted were practically the same.

The rate constant of the coupling of substituted benzenediazonium ions with 1-naphtholate ion is greater than that of the undissociated naphthol by about 9 orders of magnitude. In the both cases the intermediate formation is the rate-determining step; the intermediate has the structure *A* in the case of coupling with 1-naphtholate ion, whereas in the case of coupling with undissociated 1-naphthol another possible structure *B* can be considered in addition to *A* (the structure *B* corresponds to the conjugate acid derived from the structure *A*). On the basis of analogy with conjugate acid of benzalacetophenone¹¹ we could consider a value in the range -5 to -6 for pK_a of this acid. Under the conditions usually adopted by us, only the intermediate *A* can be considered, so that a simultaneous splitting off of the proton takes place during the reaction with diazonium ion. In the undissociated molecule of 1-naphthol the hydrogen atom of the hydroxyl group is bound to a solvent molecule having an electron pair: $\text{—O—H}\cdots\text{X}$. In the activated complex the O—H bond is weakened, and, on the contrary, the H—X bond is strengthened. This proton-transfer is practically finished at the moment of the formation of the intermediate. The difference in the coupling rate constants between 1-naphtholate and 1-naphthol is caused by a different activation of the oxygen atom in the both activated complexes.



In the first case the oxygen atom is bonded by a hydrogen bond only to the molecule X, whereas in the second case the O—H bond is split partially only, so that the +M effect of the oxygen atom cannot make itself felt to such an extent. In coupling with 1-methoxynaphthalene the intermediate has the structure C. Therefrom it follows that, even in the activated complex, no significant O—CH₃ bond splitting took place. The lower reactivity of 1-methoxynaphthalene, as compared with the undissociated 1-naphthol, is caused, first of all, by the fact that +M effect of the oxygen atom bound to the methyl group is still smaller in the activated complex.

The influence of the molecules X on the coupling rate with the undissociated 1-naphthol will be the larger the higher is their basicity and concentration. Bunnett³ found that the reaction rate is, as a rule, dependent on the *n*-th power of water activity in the reactions where water acts as the proton-detaching reagent. The simplest interpretation of the *n* value is that it means the average number of water molecules binding the solvated proton.

In our case, according to Bunnett, the kinetic equation can be written in the form:

$$v_{\text{OH}} = k_0 [\text{D}] [\text{S}] a_{\text{H}_2\text{O}}^n (\gamma_{\text{S}} \gamma_{\text{D}} / \gamma^{\ddagger}) = k'_{\text{OH}} [\text{D}] [\text{S}],$$

where v_{OH} is the reaction rate, k_0 is the rate constant of the coupling in the standard state, $[\text{D}]$ stands for the concentration of the diazo compound, $[\text{S}]$ is the substrate concentration, $a_{\text{H}_2\text{O}}$ is the water activity, and γ_{S} , γ_{D} , and γ^{\ddagger} are activity coefficients of the substrate, the diazo compound, and the activated complex respectively.

The kinetic equation for 1-methoxynaphthalene would have an analogous form with the difference that it would not involve water activity. The ratio of the experimental rate constants k' is then expressed by:

$$k'_{\text{OH}} / k'_{\text{OCH}_3} = (k_0 \gamma_{\text{OH}} \gamma_{\text{OCH}_3}^{\ddagger} a_{\text{H}_2\text{O}}^n) / (k_0' \gamma_{\text{OCH}_3} \gamma_{\text{OH}}^{\ddagger}).$$

The symbols have the same meaning as above. The indices OH and OCH₃ denote the values of the respective substrates. The ratio of the activity coefficients of the substrates was determined experimentally, so that it can be transferred to the left side of the equation. If we assume that the ratio of the activity coefficients of the activated complexes does not differ substantially in different media (which, of course, cannot be proved experimentally, but which is generally accepted), we can rewrite the above equation in the form:

$$\log ((k'_{\text{OH}} \gamma_{\text{OH}}) / (k'_{\text{OCH}_3} \gamma_{\text{OCH}_3})) \approx \text{const.} + n \log a_{\text{H}_2\text{O}}.$$

As we do not know the real water activity in the media used, we have adopted the water activity for the case considering acetic acid to be inert. From Fig. 1 it can be seen that the product on the left side of the equation changes with the change of water

activity relatively slightly. The n value would be probably less than unity in this case. With respect to the assumption introduced about the constancy of the ratio of the activity coefficients of activated complexes, we can (from the values found) deduce only that the dependence on the water activity is substantially smaller in this case than in those given in literature³. In order to be able to use accurate values for the water activity, the coupling kinetics of 2-chloro-4-nitrobenzenediazonium ion with 1-naphthol was studied in aqueous sulphuric acid media (Table III). At the same time the dependence of the activity coefficient of 1-naphthol on the medium used was followed. The activity coefficient of 1-naphthol showed an upward trend with

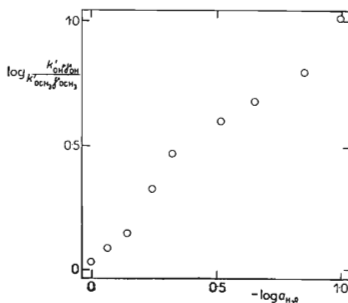


FIG. 1

Dependence of $\log ((k'_{OH}\gamma_{OH})/(k'_{OCH_3}\gamma_{OCH_3}))$
on Logarithm of Water Activity

Acetic acid is considered to be inert.

TABLE III

Dependence of Bimolecular Rate Constant of Coupling of Diazotized 2-Chloro-4-nitroaniline with 1-Naphthol on Water Activity in the Mixture Sulphuric Acid-Water

H_2SO_4 mol/l	a_{H_2O}	$[S] \cdot 10^4$ ^a mol/l	$k \cdot 10^{-2}$ $l \text{ mol}^{-1} \text{ min}^{-1}$	γ_{OH}
0.508	0.978	—	—	2.04
0.890	0.962	2	5.35	—
1.640	0.920	2	4.82	—
2.380	0.875	—	—	2.27
3.865	0.732	—	—	2.52
5.940	0.483	2	5.20	2.86
6.990	0.367	2	3.08	3.03

^a [S] means the 1-naphthol concentration.

increasing sulphuric acid concentration; similar trends were found with other hydroxy compounds, too^{12,13}. In the concentration range 0.4 to 7.7M- H_2SO_4 , the change of the rate constant was about 2 fold only, although the water activity dropped from 0.962 to 0.350. The results are presented in Table III. In this case the value n appears to be relatively small again (about unity). This value, however, can be taken as approximative and informative only, because during its determination the change of the ratio of the activity coefficient of the diazonium ion to that of the activated complex could not be taken into account. We ascribe the low effect of water activity on the coupling rate of the undissociated 1-naphthol to two factors: 1. The water molecule necessary for splitting off of the proton is present in the initial state already (bound by an hydrogen bond). 2. The extent of the O—H bond splitting is relatively small in the activated complex, so that the water molecule acquires a small positive charge only, and hence, the requirements for solvation with further water molecules are small, too. The small extent of the O—H bond splitting in the activated complex is also suggested by the fact that the difference between the coupling rate constant of the undissociated 1-naphthol (whose oxygen atom is bound, in the activated complex, to a water molecule by an hydrogen bond only) and that of 1-methoxynaphthalene is within 1–2 orders of magnitude, whereas the coupling rate constant of 1-naphtholate ion is larger than that of the undissociated 1-naphthol by about 9 orders of magnitude.

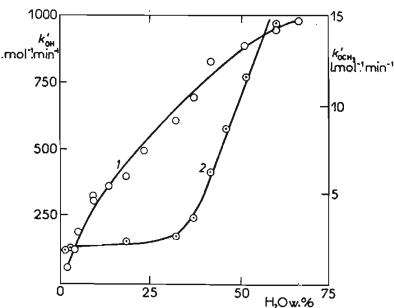


FIG. 2

Dependence of Coupling Rate Constants of 2-Chloro-4-nitrobenzenediazonium Ion with 1-Naphthol (1) and 1-Methoxynaphthalene (2) on Medium

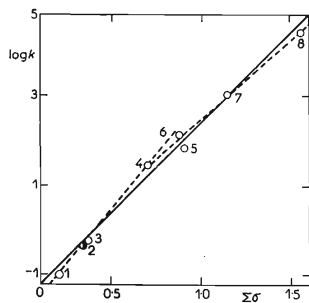


FIG. 3

Correlation of $\log k$ with the Hammett σ Constants for Coupling of Undissociated 1-Naphthol (in 2.5M-HCl)

ρ 3.96, r 0.993, $\log k_0$ - 1.60; for numbers see Table IV.

As we have already mentioned, the ratio of the rate constants of phenol and anisol brominations depends considerably on the reaction medium. *E.g.* its value is 92 in acetic acid² and about 4 in water⁴. We have, therefore, studied in detail the dependence of the coupling rate constants of 2-chloro-4-nitrobenzenediazonium ion with both 1-naphthol and 1-methoxynaphthalene on the water concentration in mixtures water-acetic acid where to a constant amount of sulphuric acid was added to suppress the dissociation of 1-naphthol. From Fig. 2 it can be seen that this dependence has entirely different courses for the two components, so that the rate constants ratio changes considerably with the water concentration change. Against the original expectations, this ratio increases steeply at first, and it decreases only below about 20% by weight water content. A rapid decrease of the activity coefficient of 1-methoxynaphthalene is probably the main reason for the initial increase of the ratio of the rate constants. That is to say, we have found that the addition of water causes an abrupt decrease of the solubility of 1-methoxynaphthalene in this range, whereas the corresponding change in 1-naphthol solubility is substantially smaller. The decrease of the ratio of the rate constants in the range of lower water concentrations, on the contrary, is caused by a rapid decrease of the coupling rate constant of 1-naphthol. The most probable explanation seems to be that the molecule of 1-naphthol including the hydroxyl group is solvated gradually more and more by acetic acid instead of water; acetic acid, being a far weaker base, cannot make itself felt to such an extent during the O—H bond splitting in the activated complex.

TABLE IV

Dependence of Logarithms of Coupling Rate Constants of Substituted Benzenediazonium Ion, with Undissociated 1-Naphthol ($\log k_a$) and 1-Methoxynaphthalene ($\log k_b$) in 60% by Vols Acetic Acid on the Hammett σ Constants

Compound	Substituent	$\Sigma\sigma$	$\log k_a$	$\log k_b$
1	4-Cl	0.20	-1.000	—
2	2-Cl	0.34 ^a	-0.325	—
3	3-Cl	0.37	-0.226	—
4	3-NO ₂	0.70	1.447	-1.509
5	3-NO ₂ -4-Cl	0.90	1.832	-0.717
6	2,4,6-tri-Cl	0.88	2.156	0.041
7	2-Cl-4-NO ₂	1.14	3.060	0.726
8	2,6-di-Cl-4-NO ₂	1.58	4.419	2.188

^a The value read.

The study of diazo coupling of substituted benzenediazonium ions with the undissociated 1-naphthol in 2.5M-HCl showed that the found dependence $\log k_a$ vs σ constants exhibits a trend to split into two independent relationships, the one having $\rho \approx 4.8$ for monosubstituted benzenediazonium ions, and the other having $\rho \approx 3.4$ for polysubstituted ones. (The σ constant used for *o*-chloro substituent was computed from the coupling rate constant of *o*-chlorobenzenediazonium ion with the use of the Hammett equation valid for the other monosubstituted benzenediazonium ions.) The results are given in Table IV and Fig. 3.

A similar tendency of the dependence $\log k$ vs σ to split into two independent relationships was observed formerly in the case of coupling of substituted benzenediazonium ions with acetoacetanilide¹⁴ and 2-hydroxynaphthalene-6-sulfonic acid¹⁵. It was shown that the break was situated in the range of $\sum \sigma \sim 1$.

The kinetic experiments designed for determination of the dependence between the rate and substituent constants in the coupling with 1-methoxynaphthalene were carried out in 60% by vol. acetic acid in order to be able to use high 1-methoxynaphthalene concentrations. Even under these conditions, *m*-nitrobenzenediazonium ion only could be used of all the monosubstituted diazo compounds, the respective reaction half-life being within 2–3 hours in this medium. The measurements were carried out in a similar way as in the preceding couplings with 1-methoxynaphthalene. The logarithms of the rate constants were correlated with σ constants too. The same σ constant was used for the *o*-chloro substituent as in the case of coupling with the undissociated 1-naphthol. The character of the dependence was analogous to that in the preceding case, the scattering of points being somewhat larger only. The value of the reaction constant was 4.03, that of the regression coefficient 0.968. The results are presented in Table IV.

TABLE V

Dependence of Hydrolysis Rate Constants of 4-(2-Chloro-4-nitrophenylazo)-1-methoxynaphthalene on Sulphuric Acid Content in 32% by Vol. Acetic Acid

H ₂ SO ₄ % by weight	CH ₃ CO ₂ H % by weight	H ₂ O % by weight	$k \cdot 10^2$ min ⁻¹	[S] · 10 ⁵ ^a mol/l
16.2	29.3	54.5	0.19	5
22.5	27.5	50.0	0.52	5
29.3	26.6	44.1	1.63	5
35.4	25.9	38.7	55.60	5
40.6	24.9	34.5	55.60	5
47.9	23.7	28.4	13.20	5

^a [S] is the dyestuff concentration.

The dependence of the hydrolysis reaction rate of 4-(2-chloro-4-nitrophenylazo)-1-methoxynaphthalene on the sulphuric acid concentration was followed in 32% by vol. acetic acid. The hydrolysis was of the first order with respect to the azo dye-stuff in all cases, and the overall reaction was pseudomonomolecular. When the reaction was followed by recording the spectra in the range 350–550 nm at definite time intervals, the spectral records showed good isobestic points; this suggests that no intermediates were formed in spectroscopically detectable concentrations, and that the hydrolysis was not complicated by any side or subsequent reactions. This was confirmed also by the chromatography of the reaction mixture: only one reaction product *viz.* the respective hydroxy derivative was found.

The rate constants reached their maximum values in the range of 40–50% by weight sulphuric acid, and then again they decreased slowly. This dependence of $\log k$ on sulphuric acid concentration has a similar character to that found by Bunnett⁸ in the study of hydrolysis kinetics of 4-(4-sulfophenylazo)-1-methoxynaphthalene in aqueous sulphuric acid. The results are presented in Table V. The velocity is maximum in the region of the greatest part of the azo dyestuff being in the respective protonated form; this form undergoes the hydrolytic reaction. The subsequent decrease is due to the decrease of water activity.

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