

RATE AND EQUILIBRIUM CONSTANTS OF THE SYSTEM
 DIAZONIUM ION, *syn*-, *anti*-DIAZOHYDROXIDE, *syn*-, *anti*-DIAZOTATE

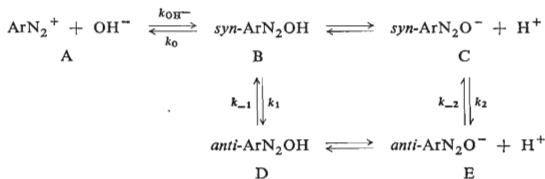
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Splitting of N—O bond of *syn*-diazohydroxide and rearrangement of *anti*-diazohydroxide into *syn*-diazohydroxide are the rate-determining steps of conversion of 2,6-dichloro-4-nitrobenzenediazotate into diazonium ion at $\text{pH} > 4.5$ and $\text{pH} < 1.5$ respectively. The splitting of *syn*-2,6-dichloro-4-nitrobenzenediazohydroxide is subject to general acid catalysis. The rate and equilibrium constants of the isomerization reactions have been found. The rate constants found for the reaction of 2,6-dichloro-4-nitrobenzenediazonium ion with OH^- ion enabled the calculation of equilibrium constants of the system 2,6-dichloro-4-nitrobenzenediazonium ion, *syn*-, *anti*-diazohydroxide, *syn*-, *anti*-diazotate.

Hantzsch¹ found the formation of two isomeric diazotates on alkalization of solutions of arenediazonium salts. Recently this reaction was studied by a number of authors in more detail²⁻⁸. There arose doubt as to the existence of both the *anti*-³ and *syn*-diazotates⁴, and the reaction was considered as rapid and reversible^{2,5,7} or slow⁴. The existence of *syn*- and *anti*-diazotates was, however, proved experimentally^{7,8}, and the reversibility and rapidity of the reaction of benzenediazonium ion with OH^- ion was confirmed by potentiometric studies of equilibria in the system diazonium ion, diazotate⁷. On the basis of those studies, Scheme 1 can be given which can be characterized by a series of equilibria expressed (except for the isomerization equilibrium constants K^{iso}) as acid-base equilibrium constants irrespective of the proper mechanism of the reactions considered.



SCHEME 1

The equilibria described by the constants K_2 , K_4 , K_6 (Table I) are established instantaneously, because the only reaction in this case is a proton transfer between a water and a *syn*- resp. *anti*-diazotate molecules. In the case of the other reactions the equilibrium can be established either within a fraction of a second or after several hours or even days according to the reaction type, structure

of the benzenediazonium ion and reaction conditions. In the case of all the benzenediazonium ions studied up to now^{7,9} except for 4-diazobenzenediazonium ion was $K_2 \gg K_1$, so that only their product, *i.e.* K_3 could be measured experimentally. From the rate constants referring to these equilibrium constants, the rate constants of reactions of 4-nitro- and 4-diazobenzenediazonium ions with OH^- ion were established on the basis of experiment⁷. The rate of rearrangement of *syn*-diazotate into *anti*-diazotate was measured for several substituted benzenediazonium ions, and it was found that the rearrangement is accelerated first of all by *p*-substituents having $-M$ effect^{6,7}. Both the *anti*-diazotate and *anti*-diazohydroxide are much more stable than the corresponding *syn*-isomers, which enabled the measurement of both the acid-base equilibrium constants K_4 ^{7,8} and the rate of their conversion into diazonium ion⁸. In the case of the substituted benzenediazotates having the substituent σ constant lower than 0.4 a direct conversion of *anti*-diazohydroxide into diazonium ion probably occurs⁸. In the case of 4-nitro- and 4-diazobenzenediazotates and 2-pyridinediazotate this reaction proceeds through *syn*-diazohydroxide and the isomerization reaction is rate-limiting⁸.

When studying the nucleophilic substitution of chlorine and nitro group by OH^- group in 2,6-dichloro-4-nitrobenzenediazonium ion, we found that in this case (obviously due to polar and steric effect of chlorine atoms) it is possible to measure under normal kinetic conditions also the further rate and equilibrium constants referring to the reaction of 2,6-dichloro-4-nitrobenzenediazonium ion with water. Therefore we have submitted the Scheme 1 to a detailed study the result of which was the finding of rate and equilibrium constants and elucidation of the whole mechanism.

EXPERIMENTAL

All the kinetic experiments were carried out at 20°C in aqueous buffer or hydrochloric acid solutions having the ionic strength 0.5 adjusted by additions of KCl . $5 \cdot 10^{-3} \text{M}$ 2,6-dichloro-4-nitrobenzenediazonium fluoroborate solution in 0.01M HCl and $1 \cdot 10^{-4} \text{M}$ 2,6-dichloro-4-nitrobenzenediazotate solution in 0.1M $\text{Na}_2\text{B}_4\text{O}_7$ were prepared according to ref.¹⁰. pH of solutions was measured by means of a PHM 4c apparatus (Radiometer, Copenhagen) after finishing each experiment. The course of the kinetic experiments was followed by means of a VSU-2P spectrophotometer (Zeiss, Jena).

Two methods were used for determination of rate constants of conversion of 2,6-dichloro-4-nitrobenzenediazotate into the diazonium ion depending on whether the reaction half life was shorter or longer than 5 s. In the case of slower experiments, 1 ml $1 \cdot 10^{-4} \text{M}$ 2,6-dichloro-4-nitrobenzenediazotate was injected into a 3 cm cell containing 4 ml buffer with $1 \cdot 10^{-5} \text{mol}$ 2-hydroxynaphthalene-3,6-disulfonic acid. The reaction was followed by measuring the extinction change at 485 nm. In the experiments in which pH of reaction solutions was lower than 2.5, 1,8-dihydroxynaphthalene-3,6-disulfonic acid was used instead of 2-hydroxynaphthalene-3,6-disulfonic acid and the reaction course was followed by extinction measurements at 505 nm. The rate constants were obtained graphically by plotting $\log(E_\infty - E_t)$ against time. In experiments having the half-life shorter than 5 s the following procedure was adopted: 0.5 ml $5 \cdot 10^{-4} \text{M}$ 2,6-dichloro-4-nitrobenzenediazonium fluoroborate was injected into 7.5 ml 0.06M $\text{Na}_2\text{B}_4\text{O}_7$ containing the necessary amount of KCl . After a definite time (2–3 s in the case of measuring the rate of conversion of *syn*-diazotate into the diazonium ion or 10 min in that of conversion of equilibrium mixture of *anti*- and *syn*-diazotates into the diazonium ion) 2 ml of a mixture containing 2-hydroxynaphthalene-3,6-disulfonic acid and such an amount of 2M HCl to attain the requested pH value (pH 1–2) was injected into the reaction mixture. At various time intervals the reaction was stopped by injecting 5 ml 0.1M $\text{Na}_2\text{B}_4\text{O}_7$ and the extinction of the dyestuff formed was measured immediately at 485 nm. pH of these solutions were within 7–8. The rate

constants were evaluated in the same way as in the previous case, the time interval between the injections of acid and borax being plotted in x -axis.

In the case of measurements of the reaction rate of 2,6-dichloro-4-nitrobenzenediazonium ion with OH^- ion in phosphate buffers having pH 6.5–7.5, 1 ml $1 \cdot 10^{-3}\text{M}$ 2,6-dichloro-4-nitrobenzenediazonium fluoroborate was injected into 20 ml buffer containing KCl. At various time intervals 2 ml $1 \cdot 10^{-2}\text{M}$ 2-hydroxynaphthalene-3,6-disulfonic acid was injected into these reaction mixtures, and the extinction of the dyestuffs formed was measured immediately at 485 nm. Under the same reaction conditions a further series of kinetic experiments were carried out, in which a mixture of 2 ml 2-hydroxynaphthalene-3,6-disulfonic acid and 3 ml $4\text{M-CH}_3\text{CO}_2\text{H}$ was added instead of mere 2 ml 2-hydroxynaphthalene-3,6-disulfonic acid, and the extinction was measured after 30 min of reaction.

The reaction rate of 2,6-dichloro-4-nitrobenzenediazonium ion with OH^- ion and that of the reverse reaction, *i.e.* diazotate \rightarrow diazonium ion, were measured at pH 5.2–5.6. The same method was adopted as that in ref.¹⁰ for determination of the time concentration change of 2,4-dinitrobenzenediazonium ion and the respective diazotate in acetate buffers at pH 4.8–5.6.

The rate of the isomerization *syn*-diazotate \rightarrow *anti*-diazotate was being measured in phosphate and borax buffers in the pH range 6.6–9.2. 0.5 ml $1 \cdot 10^{-4}\text{M}$ 2,6-dichloro-4-nitrobenzenediazonium fluoroborate was injected into 5 ml buffer solutions and the extinction measured immediately at 310 resp. 340 nm.

RESULTS AND DISCUSSION

Kinetics and Mechanism of Formation of 2,6-Dichloro-4-nitrobenzenediazonium Ion from syn- and anti-2,6-Dichloro-4-nitrobenzenediazotates

When 2,6-dichloro-4-nitrobenzenediazonium fluoroborate solution is injected into a borax buffer of pH about 9, the diazonium ion is transformed into the respective diazotate immediately (the estimated reaction half-life is about 0.01 s). A slower subsequent step produces an equilibrium mixture of *syn*- and *anti*-isomers, the half-life being about 1.4 min and independent of pH in the range of pH 7.2–9.2. On injecting this equilibrium mixture into buffer solutions containing 2-hydroxynaphthalene-3,6-disulfonic acid or into dilute hydrochloric acid solutions containing 1,8-dihydroxynaphthalene-3,6-disulfonic acid, the mixture of the diazotates is converted into the diazonium ion (Scheme 1) which reacts with the coupling component present giving the azo dyestuff. The rate of formation of the dyestuff is first order in total diazotate and diazohydroxide concentration and independent of concentration of the other coupling component. This means that one of the steps leading to diazonium ion formation (or several of these steps) and not the reaction of the diazonium ion with the coupling component must be rate-determining. The pseudomonomolecular experimental rate constant depends both on the proton and acid buffer component concentrations. In order to enable the determination of the dependence of the rate constant of diazonium ion formation on the proton concentrations, the rate constants measured in buffer solutions were extrapolated to zero buffer concentration. Logarithms of the rate constants determined in this way and those determined in dilute HCl are plotted in Fig. 1.

This dependence is more complicated than that given by Lewis⁸ for the formation of mono-substituted benzenediazonium ions from the respective diazotates. Besides that Lewis did not find the dependence of reaction rate on acid buffer component concentration in a single case. This means that in our case some further steps, too, are significant as rate-limiting besides the mere rearrangement of *anti*-diazohydroxide into *syn*-diazohydroxide proposed by Lewis. We made sure about it in the following way: 2,6-dichloro-4-nitrobenzenediazotate solution was injected several seconds after its preparation into acetate and phosphate buffers (pH 4.6 and 6.0 respectively). The both buffers gave the same rate constant as that obtained with the equilibrium mixture of diazotates containing predominantly the *anti*-isomer. It means that the rate of the rearrangement from *anti* to *syn* is not rate-limiting at least in this pH range.

The dependence given in Fig. 1 for pH > 4 can be explained as follows: the *syn*-diazohydroxide, which is in a rapid mobile equilibrium with *anti*-diazohydroxide and both diazotates, is split into diazonium and OH⁻ ions in a rate-determining step. For the velocity of the reaction in this pH range it can be written:

$$v = -d(M)/dt = k'(M) = (k_0 + k_{H^+}[H^+]) [B] = \\ = (k_0 + k_{H^+}[H^+]) [M] [H^+] / ((K_1^{iso} + 1) ([H^+] + K_6)), \quad (I)$$

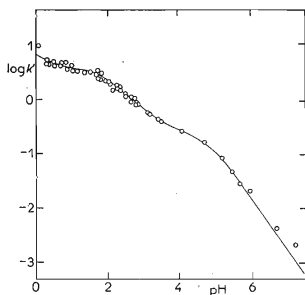


FIG. 1

Dependence of Experimental Rate Constants (extrapolated to zero buffer concentration) on pH

The full line was calculated from Eqs (I) and (6).

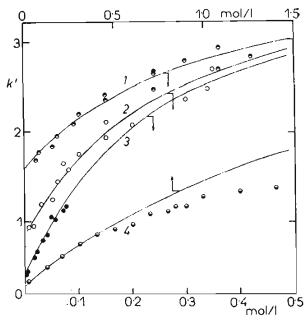


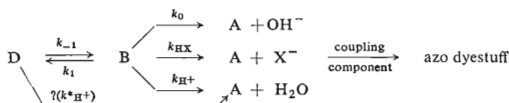
FIG. 2

Dependence of Experimental Rate Constants on Acid Buffer Component Concentration obtained from Acid-Catalyzed Splitting of *syn*-2,6-Dichloro-4-nitrobenzenediazohydroxide

Buffer: CH₂ClCO₂H—pH 2.33 (1), pH 2.80 (2), pH 3.50 (3); CH₃CO₂H—pH 4.06 (4). The full lines were calculated from Eq. (7) in which the term λ₂ was supplemented by the expression k_{HX}[HX].

where $[M] = [B] + [C] + [D] + [E]$ (Scheme 1), and k' is the experimental rate constant of the conversion of the mixture of diazohydroxides and diazotates into diazonium ion. On the basis of experimental dependence $\log k'$ vs pH and Eq. (1) the value of the equilibrium constant $K_6 = (2.0 \pm 0.2) \cdot 10^{-5}$ was found.

At pH < 4.5 the acid-catalyzed splitting of *syn*-2,6-dichloro-4-nitrobenzene diazohydroxide into the diazonium ion begins to make itself felt kinetically. Besides the proton, the acid buffer components are effective, too, which indicates general acid catalysis. However, the experimental rate constant k' is not linearly dependent either on the proton concentration or on the concentration of the acid used (acetic, chloroacetic) (Fig. 2). Therefrom it follows that, at increasing velocity of the acid-catalyzed splitting of *syn*-diazohydroxide, the reaction cannot be defined as a mere rapid equilibrium with a subsequent rate-determining splitting of *syn*-diazohydroxide, but that the overall mechanism is kinetically more complicated. Of several mechanisms considered only that given in Scheme 2 turned out to be consistent with all the experimental data. Here k_0 stands for the rate constant of non-catalyzed event. water-



SCHEME 2

catalyzed splitting of *syn*-diazohydroxide into diazonium ion, k_{H^+} and k_{HX} are the rate constants of the proton- and acid(HX)-catalyzed splitting respectively, and $k_{\text{H}^+}^*$ is the rate constant of direct (?) conversion of *anti*-diazohydroxide into diazonium ion. At low concentration of acids, the reaction rate depends predominantly on the rate of acid-catalyzed splitting of *syn*-diazohydroxide, and the reaction rate is roughly proportional to concentrations of the acids. With increasing concentration of the acids, the rate of isomerization of *syn*-diazohydroxide into *anti*-diazohydroxide becomes comparable to that of its splitting and the overall reaction rate becomes a complex function of individual rate constants and acid concentrations. At high proton concentrations the rate of splitting of *syn*-diazohydroxide is far greater than the rate of reverse isomerization, and the formation of *syn*-diazohydroxide becomes the rate-determining step. The reaction rate becomes independent of the proton concentration. This mechanism was confirmed as follows: a mixture of hydrochloric acid and 2-hydroxynaphthalene-3,6-disulfonic acid was injected into a freshly prepared solution of 2,6-dichloro-4-nitrobenzenediazotate containing practically only the *syn*-isomer, pH of the resulting mixture being within the limits 1.10–1.39 (see Experimental, the experiments with half-lives shorter than 5 s), and the formation of azo-dyestuff was then measured. The rate of formation of 2,6-dichloro-4-nitro-

benzenediazonium ion was far higher under these conditions than with the use of the equilibrium mixture of the diazotates, and it was directly proportional to the proton concentration. The rate constant found was $k_{H^+} = (1.35 \pm 0.10) \cdot 10^3 \text{ l. mol}^{-1} \text{ min}^{-1}$. On the basis of the mechanism suggested it is, at the same time, possible to explain a repeated acceleration of the reaction at $\text{pH} < 1$ as a consequence of acid-catalyzed conversion of *anti*-diazohydroxide into diazonium ion. In this case it can no longer be ascertained from kinetic experiments whether this conversion proceeds directly or *via syn*-diazohydroxide.

The approximative value of isomerization constant K_1^{iso} , which makes it possible to determine the *syn*-diazohydroxide concentration, was obtained in the following way: the slope of the tangent (ψ) to the curve $k' = f([\text{H}^+])$ at the point $[\text{H}^+] = 0$ was determined. This value was introduced into Eq. (2) wherefrom the approximate* value $K_1^{\text{iso}} 2.4$ was obtained.

$$\psi([\text{B}] + [\text{D}]) = k_{-1}k_{H^+}[\text{B}]/k_1 = k_{H^+}([\text{B}] + [\text{D}])/(1 + K_1^{\text{iso}}). \quad (2)$$

The small value of the isomerization equilibrium constant found is rather surprising, because according to present data^{6,9} the concentrations of *syn*-diazohydroxide and *syn*-diazotate are lower than those of the respective *anti*-isomers by at least 2–3 orders of magnitude. At the same time the high concentration of the *syn*-diazohydroxide made it impossible to calculate the rate constants by the steady state treatment. It was, therefore, necessary to use the non-simplified kinetic equations^{11,12} holding for the Scheme 2 and to determine the rate constants given in the Scheme by comparison with experimental rate constants k' .

For the solution of kinetic equations of the reactions taking place according to Scheme 2, the original rate constants were replaced by their combinations λ_1 and λ_2 (ref.¹¹).

$$\lambda_{1,2} = \frac{1}{2}(k_{-1} + k_1 + k_0 + k_{H^+}[\text{H}^+]) \pm \sqrt{((k_{-1} + k_1 + k_0 + k_{H^+}[\text{H}^+])^2 - 4k_{-1}k_0 + k_{H^+}[\text{H}^+])}. \quad (3)$$

If $\lambda_1 \gg \lambda_2$ (which holds for our case of transformation of diazohydroxide into diazonium ion, too), then, at the time $t > 1/\lambda_1$, the reaction course is described by Eq. (4)¹².

$$-2.303 \log ([\text{D}]_0 + [\text{B}]_0 - [\text{A}]_t) = \lambda_2 t + \text{const.} \quad (4)$$

This equation is analogous to that used for calculation of k' with the only difference that concentrations are given instead of extinctions in this case. Therefrom it follows that $\lambda_2 = k'$. The rate constants k_{-1} and k_1 , found by comparison of the experimental rate constants k' with the theoretical ones (λ_2), are given in Table I. From the rate constants thus obtained and from the experi-

* This value is approximate due to the dependence of k' vs $[\text{H}^+]$ being not quite linear even for the lowest proton concentrations attainable experimentally and, hence, the presumption of preliminary equilibrium being not wholly fulfilled.

TABLE I
Survey of Rate and Equilibrium Constants

Reaction	Constants
$\text{ArN}_2^+ + \text{OH}^- \xrightleftharpoons[k_0]{k_{\text{OH}^{(-)}}} \text{syn-ArN}_2\text{OH}$	$k_0 = (0.95 \pm 0.10) \text{ min}^{-1}$ $k_{\text{OH}} = 3.3 \cdot 10^7 \text{ l mol}^{-1} \text{ min}^{-1} \text{ }^a$ $K_1 = (k_{\text{OH}^{(-)}} \cdot K_{\text{W}})/k_0 = 3.33 \cdot 10^{-7}$
$\text{syn-ArN}_2\text{OH} + \text{HX} \xrightleftharpoons[k_{\text{X}^{(-)}}]{k_{\text{HX}}}$ $\rightleftharpoons \text{ArN}_2^+ + \text{H}_2\text{O} + \text{X}^-$	$k_{\text{HX}_1} = (48 \pm 4) \text{ l mol}^{-1} \text{ min}^{-1}$ $k_{\text{HX}_2} = (7.5 \pm 0.5) \text{ l mol}^{-1} \text{ min}^{-1}$ $k_{\text{HX}_3} = (1.4 \pm 0.2) \text{ l mol}^{-1} \text{ min}^{-1}$ HX_1 chloroacetic acid HX_2 acetic acid HX_3 primary phosphate
$\text{syn-ArN}_2\text{OH} + \text{H}^+ \xrightleftharpoons[k_{\text{H}_2\text{O}}]{k_{\text{H}^{(+)}}}$ $\rightarrow \text{ArN}_2^+ + \text{H}_2\text{O}$	$k_{\text{H}^{(+)}} = (1.35 \pm 0.10) \cdot 10^3 \text{ l mol}^{-1} \text{ min}^{-1}$ $k_{\text{H}_2\text{O}} = (4.55 \pm 0.25) \cdot 10^{-4} \text{ min}^{-1}$
$\text{anti-ArN}_2\text{OH} + \text{H}^+ \xrightleftharpoons{k_{\text{H}^{(+)}}} \rightarrow \text{ArN}_2^+ + \text{H}_2\text{O}$	$k_{\text{H}^{(+)}}^* = (3.0 \pm 0.5) \text{ l mol}^{-1} \text{ min}^{-1}$
$\text{syn-ArN}_2\text{OH} \xrightleftharpoons[k_{-1}]{k_1} \text{anti-ArN}_2\text{OH}$	$k_1 = (8.0 \pm 0.5) \text{ min}^{-1}$ $k_{-1} = (3.85 \pm 0.25) \text{ min}^{-1}$ $K_1^{\text{iso}} = k_1/k_{-1} = (2.1 \pm 0.3)$
$\text{syn-ArN}_2\text{O}^- \xrightleftharpoons[k_{-2}]{k_2} \text{anti-ArN}_2\text{O}^-$	$k_2 = (0.33 \pm 0.05) \text{ min}^{-1}$ $k_{-2} = (0.11 \pm 0.02) \text{ min}^{-1}$ $K_2^{\text{iso}} = k_2/k_{-2} = (3.0 \pm 0.5)$
$\text{syn-ArN}_2\text{OH} \rightleftharpoons \text{syn-ArN}_2\text{O}^- + \text{H}^+$	$K_2 = 1.55 \cdot 10^{-5}$
$\text{anti-ArN}_2\text{OH} \rightleftharpoons \text{anti-ArN}_2\text{O}^- + \text{H}^+$	$K_4 = 2.22 \cdot 10^{-5}$
$\sum \text{ArN}_2\text{OH} \rightleftharpoons \sum \text{ArN}_2\text{O}^- + \text{H}^+$	$K_6 \equiv K_A' = (2 \pm 0.2) \cdot 10^{-5}$
$\text{ArN}_2^+ + \text{OH}^- \rightleftharpoons \sum \text{ArN}_2\text{OH}$	$K_7 = [(k_{\text{OH}^{(-)}} \cdot K_{\text{W}})/k_0] (1 + K_1^{\text{iso}}) = 1.03 \cdot 10^{-6}$
$\text{ArN}_2^+ + \text{H}_2\text{O} \rightarrow \text{syn-ArN}_2\text{O}^- + 2\text{H}^+$	$K_8 = [k_{\text{OH}^{(-)}} \cdot [\text{H}^+]^2/k'] \cdot (K_6/K_6 + [\text{H}^+]) = 2.19 \cdot 10^{-11}$
$\text{ArN}_2^+ + \text{H}_2\text{O} \rightarrow \text{anti-ArN}_2\text{O}^- + 2\text{H}^+$	$K_3 = K_8 \cdot 1/(1 + K_2^{\text{iso}}) = 5.48 \cdot 10^{-12}$ $K_5 = K_8 \cdot K_2^{\text{iso}}/(K_2^{\text{iso}} + 1) = 1.64 \cdot 10^{-11}$

^a The value given for bimolecular rate constant $k_{\text{OH}^{(-)}}$ was obtained by comparison of the theoretically calculated concentrations of 2,6-dichloro-4-nitrobenzediazonium ion and its diazotate with those experimentally found in acetate buffer at pH 5.22.

mental ones found for the transformation of diazohydroxide into diazonium ion catalyzed by chloroacetic and acetic acids the rate constants k_{HX_1} and k_{HX_2} were calculated.* In these cases a good agreement between the theoretical (λ_2) and experimental (k') rate constants was reached only at lower acid concentrations (Fig. 2). At higher acid concentrations the experimental values are smaller than the theoretical ones, and these deviations gradually increase. This is obviously due to decreasing polarity of medium.

In the case of phosphate buffers the rate constant was calculated from the experimental data of buffers having pH 6. As the dependence of the experimental rate constant on the concentration of the acid HX_3 (i.e. H_2PO_4^-) is linear in this range, and as the presumption of a rapid antecedent equilibrium is already practically fulfilled at such a high pH, the rate constant k_{HX_3} has been calculated from Eq. (5), where φ is the slope of the dependence of the experimental rate constant

$$k_{\text{HX}_3} = \varphi(1 + K_1^{\text{iso}})(K_6 + [\text{H}^+])/[\text{H}^+] \quad (5)$$

on the concentration of the acid HX_3 . The rate constant $k_{\text{H}^+}^*$, which becomes significant kinetically at $\text{pH} < 1$, was calculated from Eq. (6).

$$k' = \lambda_2 + k_{\text{H}^+}^*[\text{H}^+]. \quad (6)$$

The overall dependence of $\log k'$ on pH can be expressed by Eq. (6); at $\text{pH} > 3.5$ the dissociation of diazohydroxides and the gradually more and more kinetically significant rearrangement of *syn*-diazotate into *anti*-diazotate must, of course, be taken into account in calculating λ_2 . This complicates the calculation of λ_2 considerably, on the other hand, however, the whole system approaches kinetically more and more to a state expressed by a rapid antecedent equilibrium and a subsequent rate-determining splitting of *syn*-diazohydroxide (Eq. (1)). In the range of pH 3.5 to 5.5 the values k' calculated according to Eq. (1) are higher than those calculated according to Eq. (6) by about 5%, at $\text{pH} > 6.5$ the both values are practically the same. Therefore, the theoretic curve in Fig. 1 was calculated from Eq. (6) for $\text{pH} < 3.5$, and for the rest from Eq. (1) with the corresponding correction for $\text{pH} < 6.5$.

Determination of Equilibrium Constants of Rearrangement *syn*-Diazotate \rightleftharpoons *anti*-Diazotate

At pH about 1 the acid catalyzed splitting of *syn*-2,6-dichloro-4-nitrobenzenediazohydroxide into 2,6-dichloro-4-nitrobenzenediazonium ion is many times more rapid than the reverse rearrangement into *anti*-diazohydroxide. The rearrangement of *anti*-diazohydroxide into *syn*-diazohydroxide is here practically the only rate-determining step. The dependence of $\log(E_\infty - E_t)$, which corresponds to the yet unreacted diazohydroxide, on time was linear in the whole range studied in these experiments, but the value $\log(E_\infty - E_t)$ extrapolated to zero time was in average by 25% smaller than it would correspond to the total concentration of the original diazotate. This

* In calculation of k_{HX_2} ($\text{HX}_2 = \text{CH}_3\text{CO}_2\text{H}$) it must be taken into account that the both diazohydroxides as well as the mixture of the respective diazotates are present side by side in the reaction mixture.

can be explained in such a way that about 25% of *syn*-diazohydroxide was present in the equilibrium mixture of the starting diazotates, and this diazohydroxide was transformed into diazonium ion sooner than the first record of extinction of the reaction mixture could be made, *i.e.* about 10 s. This was proved by an experiment in which the reaction course was followed discontinuously with the shortest time interval of 0.3 s. From Fig. 3 it can be seen that this overall reaction falls into two stages, from which the first, corresponding to a far quicker transformation of *syn*-diazohydroxide into diazonium ion, is finished practically within 2.5 s. From this first part the rate constant $k_{H^+} = (1.3 \pm 0.1) \cdot 10^3 \text{ l mol}^{-1} \text{ min}^{-1}$ was determined. From the second part of the dependence extrapolated to zero time the ratio $[\textit{anti}\text{-diazotate}]/[\textit{syn}\text{-diazotate}] = 2.6 \pm 0.3$ was determined in the starting equilibrium mixture. The average value of the equilibrium constant $K_1^{\text{iso}} = 3.0 \pm 0.5$ from all the experiments. The rate constant of formation of the equilibrium mixture *syn*-diazotate \rightleftharpoons *anti*-diazotate (measured spectrometrically) is $k_{\text{eq}} = k_2 + k_{-2} = 0.44 \text{ min}^{-1}$. From this constant and from the equilibrium constant $K_2^{\text{iso}} = k_2/k_{-2}$, the constants k_2 and k_{-2} were determined.

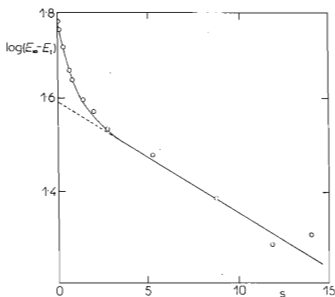


FIG. 3

Time Dependence of Extinction Logarithm (corresponding to concentration of mixture of diazohydroxides) during Proton-Catalyzed Splitting of Mixture of *syn*- and *anti*-2,6-Dichloro-4-nitrobenzenediazohydroxides in Dilute HCl (pH 1.24) at 20°C and Ionic Strength 0.5

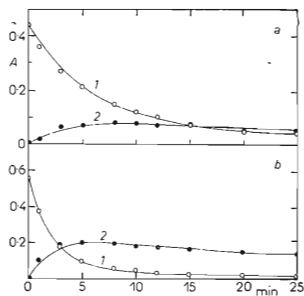


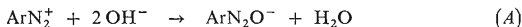
FIG. 4

Time Dependence of Change of Concentration of 2,6-Dichloro-4-nitrobenzenediazonium Ion (1) and its Diazotates (2) in Acetate Buffers at 20°C and Ionic Strength 0.5

The full lines were calculated according to Eqs (11) and (12). The rate constants obtained at the following conditions were used in the calculation: a) pH 5.22, k_r 0.105 min^{-1} , k'_{OH^-} 0.0525 min^{-1} , k' 0.075 min^{-1} ; b) pH 5.62, k_r 0.170 min^{-1} , k'_{OH^-} 0.138 min^{-1} , k' 0.038 min^{-1} .

Reaction of 2,6-Dichloro-4-nitrobenzenediazonium Ion with OH⁻ Ion and Determination of Equilibrium Constant K₈

The direct determination of the rate constant k_{OH^-} of the reaction $\text{ArN}_2^+ + \text{OH}^- \rightarrow \text{syn-ArN}_2\text{OH}$ was carried out in phosphate buffers at pH 6.5–7.5 when the reverse reaction was practically insignificant. As diazophenols, 2,6-dichloro-4-nitrophenol and other unidentified products¹⁰ are formed simultaneously along with diazotates during the reaction, we followed side by side both *a*) the overall decrease of the diazonium ion and *b*) the formation of the reaction products other than diazotates. From the first series of experiments *a*) the overall experimental rate constant ($k_r + k'_{\text{OH}^-}$) was determined (Scheme 3), from the second experimental series *b*) the proportion was determined corresponding to the proper reaction of diazonium ion with OH⁻ leading to formation of diazotates (Table II). As it can be seen from this Table, the rate constants k_{OH^-} increase with increasing pH value. At the same time the percentage of side products decreases. This decrease goes on with increasing pH, so that in borax buffers they are formed to an extent of maximum few per cent¹⁰. The increase of bimolecular rate constant k_{OH^-} with increasing pH value could be caused by an increased participation of the reaction (A). This would, of course, mean that the diazonium ion could be formed by the reaction of diazotate with water



besides the reactions given in Schemes 1 and 2. Such a mechanism stands in accord with the finding that at pH > 6 the log k' value decreases more slowly than it corresponds to the pH increase (Fig. 1). Hardly explainable, of course, is the great value

TABLE II

Rate Constants of Reaction of 2,6-Dichloro-4-nitrobenzenediazonium Ion with OH⁻ Ion in Phosphate Buffers at 20°C and Ionic Strength 0.5

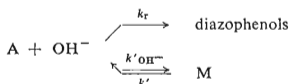
pH	$(k_r + k'_{\text{OH}^-})$ min ⁻¹	Diazophenols %	k' min ⁻¹	$k_{\text{OH}^-} \cdot 10^{-8}$ l mol ⁻¹ min ⁻¹
6.56	4.38	25 ± 5	3.29	0.90 ± 0.10
6.67	6.24	25 ± 5	4.68	1.00 ± 0.12
6.81	7.60	25 ± 5	5.70	0.88 ± 0.10
7.18	20.30	23 ± 5	15.63	1.03 ± 0.10
7.22	27.40	20 ± 5	21.90	1.32 ± 0.13
7.41	44.20	20 ± 5	35.40	1.37 ± 0.15

of the rate constant for reaction (A) viz. $5 \cdot 10^{14} \text{ l mol}^{-1} \text{ min}^{-1}$ which is practically the same as the rate constant of the reaction $\text{H}^+ + \text{OH}^-$ in ice crystals¹³.

One of the reasons for the determination of the rate constant k_{OH^-} was the determination of equilibrium constant K_8 on the basis of a condition that Eq. (7) holds for the equilibrium. It is not possible to determine this equilibrium constant

$$k'_{\text{OH}^-}[\text{A}] = k'([\text{C}] + [\text{E}]) \quad (7)$$

by direct measurement of concentration of the diazonium ion and the diazotate mixture, as the equilibrium is disturbed all the time due to simultaneous conversion of 2,6-dichloro-4-nitrobenzenediazonium ion into diazophenols¹⁰. From Eq. (7) and from the rate constants obtained at pH 7.18 the equilibrium constant K_8 $3 \cdot 16 \cdot 10^{-11}$ was calculated. This constant should be independent of pH which, however, could not be confirmed on the basis of the experimentally obtained rate constants k_{OH^-} , as it was not known how the value k_{OH^-} depended on pH lower than 6.5. Therefore, the rate of the reversible reaction $\text{ArN}_2^+ \rightleftharpoons \text{ArN}_2\text{O}^-$ taking place simultaneously with irreversible reaction $\text{ArN}_2^+ \rightarrow$ diazophenols (Scheme 3) was followed in acetate buffers at pH 5.22 and 5.62 (corresponding approximatively to $-1/2 \log K_8$), in order that the k_{OH^-} values might be calculated for these pH's.



SCHEME 3

k'_{OH^-} is the experimentally measured pseudomonomolecular rate constant (*i.e.* $k'_{\text{OH}^-} = k_{\text{OH}^-}[\text{OH}^-]$). The rate constant k_r was obtained from Eq. (8). The con-

$$k_r[\text{A}] = -d([\text{A}] + [\text{M}])/dt \quad (8)$$

centrations $[\text{A}]$ and $[\text{M}]$ were plotted against time and compared with the theoretical concentrations calculated according to Eqs (9) and (10)^{11,14}:

$$[\text{A}]_t = [\text{A}]_0 \left[\frac{(k_r + k'_{\text{OH}^-}) - \lambda_2}{\lambda_1 - \lambda_2} \cdot e^{-\lambda_1 t} + \frac{\lambda_1 - (k_r + k'_{\text{OH}^-})}{\lambda_1 - \lambda_2} \cdot e^{-\lambda_2 t} \right], \quad (9)$$

$$[\text{M}]_t = [\text{A}]_0 \frac{k'_{\text{OH}^-}}{\lambda_1 - \lambda_2} (-e^{-\lambda_1 t} + e^{-\lambda_2 t}), \quad (10)$$

where $\lambda_{1,2} = (k_r + k' + k'_{\text{OH}^-})/2 \pm \sqrt{((k_r + k' + k'_{\text{OH}^-})^2 - 4k'k_r)}$. Such rate constants k'_{OH^-} and k' were used for calculation of K_8 which gave the best agreement between the theoretically and experimentally determined concentrations (Fig. 4a,b). The equilibrium constant K_8 was calculated in this case from those constants according to Eq. (11), where the second fraction represents a correction for the pre-

$$K_8 = \frac{[\text{M}][\text{H}^+]^2}{[\text{A}]} \cdot \frac{K_6}{K_6 + [\text{H}^+]} = \frac{k'_{\text{OH}^-}[\text{H}^+]^2}{k'} \cdot \frac{K_6}{K_6 + [\text{H}^+]} \quad (11)$$

sence of *syn*- and *anti*-diazohydroxides in the reaction mixture. For the expression $-1/2 \log K_8$ (i.e. pH_m ; ref.⁶) there follows an almost the same value (5.37 ± 0.01) as if the experimental values obtained at $\text{pH } 7.18$ were used ($\text{pH}_m \ 5.25$).

Comparison of the Constants Obtained and the Mechanism Suggested with Literature Data

The value of the equilibrium constant K_2^{iso} is about $200 \times$ smaller than those⁷ calculated for 4-nitro- resp. 4-diazobenzene diazotates. This decrease is most probably due to steric effects of the both chlorine atoms in 2,6 positions on the stability of the *anti*-diazotate. This steric effect makes itself felt in the case of *anti*-isomer having the *cis* configuration which is quite contrary to what has been supposed so far⁷. The rate constant of the formation of *anti*-2,6-dichloro-4-nitrobenzene diazotate, $k_2 = 0.33 \text{ min}^{-1}$, is about $5 \times$ smaller than that of the rearrangement of 4-nitrobenzene diazotate², whereas that of the reverse reaction k_{-2} is about $50 \times$ higher as compared with 4-nitro derivative. The isomerization velocity increases in the both directions with increasing value of σ constants of substituents. From the rate constants of isomerization of benzenediazotate and 4-chlorobenzenediazotate⁶ the reaction constant ρ was estimated to be $1-1.5$ for this reaction, and therefrom the presumed acceleration by $1-1.5$ orders of magnitude as compared to the 4-nitro derivative. The rate of formation of the *syn*-isomer stands in overall agreement with the presumed effect of substituents, whereas that of *anti*-isomer is smaller by about 2 orders of magnitude.

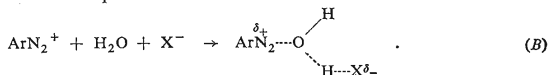
By the splitting of N—O bond in *syn*-diazohydroxide the diazonium ion is formed.* At $\text{pH} > 6.5$ the main reaction leading to formation of *syn*-diazohydroxide is the rearrangement of *anti*-diazotate, whereas at $\text{pH} < 6.0$ *syn*-diazohydroxide is formed mainly by the rearrangement of *anti*-diazohydroxide. If there is a small amount of acids present in the reaction medium, the splitting of N—O bond of *syn*-

* In the previous section two further possibilities of diazonium ion formation were considered, too, viz. the reaction of diazotate with a water molecule (Eq. (A)) for $\text{pH} > 6$ and the acid-catalyzed splitting of *anti*-diazohydroxide (Scheme 2) for $\text{pH} < 1$. There is little evidence for these mechanisms so far.

diazohydroxide is non-catalyzed (resp. water-catalyzed) and far slower than the reverse isomerization to *anti*-diazohydroxide and *anti*-diazotate. Under such conditions all the components M (Eq. (1)) are in equilibrium and the rate of the overall reaction depends on the concentration of *syn*-diazohydroxide and the rate of its splitting. In this respect it differs from monosubstituted derivatives e.g. 4-nitro- and 3-chlorobenzenediazotates and 2-pyridinediazotate⁸, with which the rearrangement of *anti*- into *syn*-isomer is rate-determining. This difference is caused by that the decrease of the overall inductive and mesomeric effects of substituents increases the rate of N—O bond splitting and, on the contrary, slows down the isomerization reactions, so that a change in rate-determining step occurs. In the case of the 4-nitro derivative this change is caused by an increase in the N—O bond splitting rate (the rate constant of this reaction is about $1.2 \cdot 10^4 \text{ min}^{-1}$ (ref.⁷) which is greater than that for 2,6-dichloro-4-nitrobenzenediazohydroxide by 4 orders of magnitude). In the case of 4-chloro-, 4-methyl- and unsubstituted benzenediazotates the *anti*-*syn* rearrangement rate is so small that this way ceases to be significant kinetically, and the direct splitting of N—O bond of the *anti*-diazohydroxide is the main reaction leading to diazonium ion formation⁸.

The acid-catalyzed splitting of *syn*-diazohydroxide into diazonium ion becomes more and more significant with increasing concentration of acids HX. The rearrangement of *anti*- into *syn*-diazohydroxide becomes rate-determining at sufficiently high concentration and strength of the acids. In our case the rate constant of the rearrangement $k_{-1} = 3.85 \text{ min}^{-1}$ is about $13 \times$ larger than that of 4-nitro derivative⁸. This difference is substantially smaller than that given for the rearrangement of the respective diazotates which is perhaps due to that diazohydroxides rearrange far more rapidly than diazotates and, therefore, the influence of substituents makes itself felt to a smaller extent.

N—O Bond splitting of a *syn*-diazohydroxide is subject to general acid catalysis. The dependence of $\log k_{\text{HX}}$ on $\text{p}K_{\text{a}}$ of the acids HX is practically linear with the slope $\alpha = 0.34 \pm 0.01$, correlation coefficient 0.998 and standard deviation 0.12. A relatively small value of the Brönsted coefficient α^{15} indicates that the bond between the proton of the acid catalyst and the leaving OH group is formed only to a small extent in the activated complex. In the reverse direction a base-catalyzed reaction (B) of the diazonium ion with water must be significant, the value of the coefficient β being correspondingly high (0.66). This means that the O—H bond is split to a greater extent in the activated complex.



The rates of the non-catalyzed and proton-catalyzed splittings of *syn*-diazohydroxide become equal at pH 3.15, i.e. at this pH diazonium ion reacts in the reverse

reaction equally rapidly with water as with OH^- . The rate constant k_{OH^-} ($3.3 \cdot 10^7 \text{ l. mol}^{-1} \text{ min}^{-1}$) is $2.5 \times$ greater than that obtained for the reaction of 4-nitrobenzenediazonium ion with OH^- ion⁷ and about $3 \times$ smaller than that roughly estimated for the reaction of 4-diazobenzenediazonium ion with OH^- ion⁷. The influence of a substituent on the reaction of diazonium ions with OH^- is very small in these cases in contrast to the reactions proceeding in opposite direction, *i.e.* the splitting of *syn*-diazohydroxide. Therefrom it can be concluded that the N—O bond is formed to a small extent in activated complex, resp. it is mainly split in the reaction proceeding in opposite direction. It is interesting that the rate constant of the reaction of 2,6-dichloro-4-nitrobenzenediazonium ion with 1-naphtholate ion¹⁶ is greater than that with OH^- ion by more than 3 orders of magnitude (the rate of the former reaction is limited by diffusion rate of the reactants), although 1-naphtholate ion is a weaker base than OH^- ion by 6 orders of magnitude. In spite of the reaction with 1-naphtholate ion being far quicker, the influence of substituents of the benzene nucleus of diazonium ions is far higher (the value of the reaction constant $\rho = 4.1$). The relatively low reactivity of OH^- ion is probably due to the necessity of partial desolvation of OH^- ion in the reaction with 2,6-dichloro-4-nitrobenzenediazonium ion which is little affected by a substituent in the nucleus.

From the equilibrium constant K_8 and from the isomerization equilibrium constants it is possible to calculate the equilibrium constants K_3 and K_5 . The

$$K_3 = K_8 / (1 + K_2^{\text{iso}}) \quad K_5 = K_8 K_2^{\text{iso}} / (1 + K_2^{\text{iso}}).$$

difference between the both constants is small (Table I), as the isomerization equilibrium constant K_2^{iso} has a small value, too. The equilibrium constant K_3 can be defined as a product $K_1 K_2$ of two subsequent equilibrium reactions ($K_2 \gg K_1$) (Table I) as in the case of all the benzenediazonium ions studied so far except for 4-diazo derivative⁷. That is also why in the reaction mixtures of these diazonium ions the concentration of the *syn*-diazohydroxide is so minute that it cannot be directly measured neither its reactions studied. In contrast to these benzenediazonium ions, in the case of 2,6-dichloro-4-nitrobenzenediazonium ion considerably high concentrations of the *syn*-diazohydroxide can be obtained (about 25% *syn*-diazohydroxide on acidifying the equilibrium mixture of diazotates and (transiently) a still far greater amount on acidifying immediately a freshly prepared mixture of diazotates). This is caused by a decreased rate of splitting of N—O bond of the *syn*-diazohydroxide and, further, by a small value of isomerization constants. These circumstances made it possible to determine all the rate and equilibrium constants given in the reaction Schemes 1–3.

Although high *syn*-diazohydroxide concentrations were reached in the reaction mixtures containing coupling component, the final extinction of the azo dyestuff formed was practically the same as in the case of direct coupling of the corresponding

amount of 2,6-dichloro-4-nitrobenzenediazonium ion with the same coupling component. This indicates that *syn*-2,6-dichloro-4-nitrobenzenediazohydroxide does not take part in formation of such by-products as *e.g.* diazophenols and 2,6-dichloro-4-nitrophenol.

REFERENCES

1. Hantzsch A.: Ber. 27, 1702 (1894).
2. Lewis E. S., Suhr H.: J. Am. Chem. Soc. 80, 1367 (1958).
3. Le Fevre R. J. W., Roper R., Reece I. H.: J. Chem. Soc. 1959, 4104.
4. Porai-Koshits B. A.: Tetrahedron 11, 30 (1960).
5. Wittwer C., Zollinger H.: Helv. Chim. Acta 37, 1954 (1954).
6. Lewis E. S., Suhr H.: Chem. Ber. 91, 2350 (1958).
7. Littler J. S.: Trans. Faraday Soc. 59, 2296 (1963).
8. Lewis E. S., Hanson M. P.: J. Am. Chem. Soc. 89, 6268 (1967).
9. Zollinger H.: *Azo and Diazo Chemistry*, p. 58. Interscience, New York 1961.
10. Macháčková O., Štěrba V., Valter K.: This Journal 37, 2197 (1972).
11. Frost A. A., Pearson R. G.: *Kinetics and Mechanism*, p. 195. Wiley, New York 1961.
12. Chong Wha Pyun: J. Chem. Soc. 48, 194 (1971).
13. Eigen M.: Angew. Chem. (internat. edit.) 3, 1 (1964).
14. Lewis E. S., Johnson M. D.: J. Am. Chem. Soc. 82, 5399 (1960).
15. Bell R. P., Ewans P. G.: Proc. Roy. Soc. (London) A 291, 297 (1966).
16. Kropáčová H., Panchartek J., Štěrba V., Valter K.: This Journal 35, 3287 (1970).

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