

GENERAL ACID CATALYSIS DURING TRANSFORMATION OF 2,4-DINITROBENZENEDIAZOTATE ION INTO DIAZONIUM ION

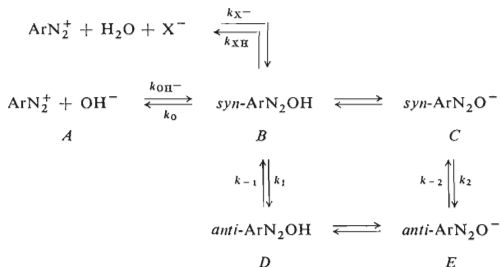
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The rate-determining step of the transformation of *anti*-2,4-dinitrobenzenediazotate ion into the respective diazonium ion consists in splitting of the *syn*-diazohydroxide at $\text{pH} > 4.5$ and in isomerization of the *anti*-diazohydroxide into the *syn*-diazohydroxide at $\text{pH} < 1$. The splitting of *syn*-diazohydroxide is subject to general acid catalysis, the value of the Brönsted coefficient α being 0.31. The rate constant of the reaction $\text{ArN}_2^+ + \text{OH}^- \rightarrow \text{syn-ArN}_2\text{OH}$ has been found, and therefrom and from the rate constant of the transformation of the *anti*-diazotate into the diazonium ion the value of the equilibrium constant was also calculated for the reaction $\text{ArN}_2^+ + \text{H}_2\text{O} \rightleftharpoons \text{anti-ArN}_2\text{O}^- + 2\text{H}^+$.

In a previous paper¹ we studied the kinetics of acid-catalyzed transformation of a mixture of *syn*- and *anti*-2,6-dichloro-4-nitrobenzenediazotate ions into the corresponding diazonium ion (Scheme 1).



SCHEME 1

In contrast to monosubstituted benzenediazonium ions, where the rate-determining step is the transformation of *anti*- into *syn*-diazohydroxide or direct splitting of *anti*-diazohydroxide², in the case of 2,6-dichloro-4-nitrobenzenediazotate ion at higher pH values the rate-determining step consists in a non-catalyzed (resp. water-catalyzed) splitting of *syn*-2,6-dichloro-4-nitrobenzenediazohydroxide. At lower pH values an acid-catalyzed splitting of *syn*-diazohydroxide becomes more and more significant kinetically, and the rate of this reaction begins to be compar-

able with the reverse rate of *syn-anti* isomerization of the diazohydroxide. At $\text{pH} < 1$ the rearrangement of *anti-* to *syn-*diazohydroxide becomes rate-determining as it is the case with the monosubstituted benzenediazonium ions. In contrast to the monosubstituted benzenediazohydroxides and their diazotates, very small values of isomerization equilibrium constants were found for this compound.

With the aim of ascertaining to what extent the different behaviour of the 2,6-dichloro-4-nitro derivative is caused by polar effects and to what extent by the steric ones, we studied an analogous reaction system of 2,4-dinitrobenzenediazonium ion in this work. The polar effects towards usual nucleophilic reagents are comparable for the both ions studied which is in accord with that the sum of the respective substituent σ constants has roughly the same value for both the cases. It must be remarked that, as far as mesomeric effects are concerned, the value of $\sum\sigma^-$ is much greater with 2,4-dinitro- than 2,6-dichloro-4-nitro derivative. In the case of 2,4-dinitro benzenediazonium ion, however, there is only one *ortho* position occupied, which results in a great decrease of steric effects. The rate of formation of 2,4-dinitrobenzenediazonium ion from the mixture of *syn-* and *anti-*2,4-dinitrobenzenediazotates in solutions of buffers or dilute hydrochloric acid depends on both pH and acid buffer component concentration. The dependence of $\log k'$ on pH (k' are the experimental rate constants k measured in dilute HCl or in buffers and extrapolated to zero buffer concentration) (Fig. 1) as well as that of the experimental rate constants k on the acid buffer component concentration at a constant pH (Fig. 2) are similar to those in the case of 2,6-dichloro-4-nitrobenzenediazonium ion¹. Therefrom it can be concluded that in the case of 2,4-dinitrobenzenediazonium ion the reaction mechanism is similar.

For $\text{pH} > 4.5$ (and low acid buffer component concentrations) we can define the reaction as rapid antecedent equilibrium between *syn-* and *anti-*diazohydroxides and their anions and a subsequent rate-determining splitting of the *syn-*diazohydro-

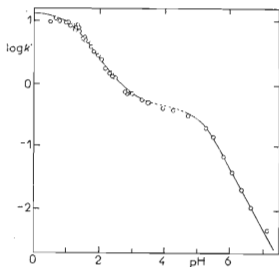


FIG. 1

Dependence of Logarithm of Rate Constants k' (extrapolated to zero buffer concentration) on pH

The full line was calculated for $\text{pH} < 3.4$ from Eq. (2) and for $\text{pH} > 4.5$ from Eq. (1) where $[\text{HX}] = 0$.

xide into the diazonium ion. Hence, for the kinetics Eq. (I) can be written, where $[M] = [B] + [C] + [D] + [E]$ (Scheme 1), k_0 , k_{H^+} and k_{HX} are the rate constants

$$v = k[M] = (k_0 + k_{H^+}[H^+] + k_{HX}[HX])[B] = (k_0 + k_{H^+}[H^+] + k_{HX}[HX]) \frac{1}{(1 + K_1^{iso})} \left(\frac{[H^+]}{[H^+] + K'_A} \right) [M]. \quad (I)$$

of the non-catalyzed, proton-catalyzed and acid-catalyzed (the acid buffer component HX) splitting of *syn*-diazohydroxide into diazonium ion respectively, K_1^{iso} is the isomerization equilibrium constant of the transformation *syn*- to *anti*-diazohydroxide, K'_A is the apparent dissociation equilibrium constant of the mixture of *syn*- and *anti*-diazohydroxides.

The value $K'_A = (1.0 \pm 0.2) \cdot 10^{-5}$ was determined from the dependence $\log K'$ on pH for pH > 4.5 using Eq. (I) where $[HX] = 0$. For obtaining the other constants it would be necessary to measure directly the rate of the acid-catalyzed splitting of *syn*-diazohydroxide for at least one acid. In the previous paper¹ the rate constant

TABLE I

Products of Rate Constants k_{HX} of Acid-Catalyzed Splitting of *syn*-2,4-Dinitrobenzenediazohydroxide into the resp. Diazonium Ion

HX	pH	φ^a $l \text{ mol}^{-1} \text{ min}^{-1}$	$(K'_A + [H^+])/[H^+]$	$k_{HX}/(1 + K_1^{iso})$, $l \text{ mol}^{-1} \text{ min}^{-1}$
H ₃ O		$2.8 \cdot 10^2$	1	$2.8 \cdot 10^2$
ClCH ₂ COOH	2.32	$1.35 \cdot 10^1$	1	$(1.26 \pm 0.08) \cdot 10^1$
	2.80	$1.25 \cdot 10^1$	—	
	3.27	$1.19 \cdot 10^1$	—	
CH ₃ COOH	3.95	2.15	1.09	(2.35 ± 0.20)
	4.25	1.85	1.18	
	4.66	1.80	1.45	
	5.25	0.85	2.78	
	5.47	0.57	3.95	
H ₂ PO ₄ ⁻	5.79	$2.15 \cdot 10^{-1}$	7.17	(1.52 ± 0.15)
	6.11	$1.13 \cdot 10^{-1}$	13.86	
	6.36	$5.50 \cdot 10^{-2}$	23.9	
	6.66	$3.50 \cdot 10^{-2}$	46.7	
	7.14	$1.13 \cdot 10^{-2}$	139.0	
H ₂ O ^b	—	—	—	$9 \cdot 10^{-4}$

^a φ Are the slopes of the tangent to the dependence $k' = f([HX])$ at a point $[HX] = 0$, ^b It corresponds to $k_0/(1 + K_1^{iso}) \cdot 55.5$ which was calculated from Eq. (I); see the text.

k_{H^+} was determined directly. We tried to obtain k_{H^+} for 2,4-dinitrobenzenediazohydroxide in the same way. Even though the time between the preparation of the diazotate and the injection of acid was shortened to 1 s., the rate constant obtained had the same value as in the case using a mixture of diazotates prepared several hours before. The dependence $\log(E_\infty - E_t)$ on time was linear in the whole range and its extrapolation to $t = 0$ gave practically the same value as that obtained for logarithm of the extinction of the solution after finishing the reaction. Therefrom it follows that a) the half-life of the isomerization reaction is far shorter than 1 s. (the same values of experimental rate constants obtained with the solutions of diazotates prepared immediately and after a longer period) and b) the equilibrium mixture contains practically only *anti*-2,4-dinitrobenzenediazotate ion: if it contained more than 5% *syn*-2,4-dinitrobenzenediazotate, the dependence $\log(E_\infty - E_t)$ on time would have a steeper course at the beginning¹ and, hence, also the value $\log(E_\infty - E_t)$ extrapolated from the linear part to zero time would be smaller than the value of the extinction logarithm after finishing the reaction.

The much smaller content of *syn*-diazotate with 2,4-dinitro derivative as compared to that of 2,6-dichloro-4-nitro derivative stands in accord with the statement¹ that the steric hindrance of *anti*-isomer formation due to occupation of the both *ortho* positions is the decisive reason for the low isomerization equilibrium constant of 2,6-dichloro-4-nitrobenzenediazotate. From the results obtained it can be estimated that the isomerization rate constant of *syn*-2,4-dinitrobenzenediazotate to the *anti*-isomer is greater than that of the 2,6-dichloro-4-nitro derivative by at least 3 orders of magnitude,* even though the sum of σ constants has a slightly smaller value.** This difference is caused first by the steric hindrance of the *anti*-isomer formation in the case of 2,6-dichloro-4-nitrobenzenediazotate (estimated retardation about 2 orders of magnitude)¹ and second by that a mesomeric effect causing acceleration of the isomerization reaction² makes itself felt in the case of the *o*-nitro derivative.

As the rate constants k_0 , k_{H^+} and k_{HX} could not be determined for the very rapid isomerization *syn*- to *anti*-2,4-dinitrobenzenediazotate, we have determined only their products with the expression $1/(K_1^{iso} + 1)$. In the case of k_0 Eq. (1) and the rate constants k' experimentally determined for $pH > 4.5$ were used for the calculation. The products of the rate constants k_{HX} and k_{H^+} were determined as the slopes (φ) of the tangent to the dependence $k = f([HX]$ resp. $[H^+])$ at a point ($[HX]$ resp. $[H^+] = 0$); in the case of acetic and phosphoric acids these products had to be multiplied by the expression $(K'_A + [H^+])/[H^+]$ (Table I).

* Note added in proof: In addition we have measured the isomerization rate with the use of the Durrum stopped-flow spectrometer; the half-life of the reaction was 34 ms., i.e. the isomerization rate constant is $3000\times$ greater in the case of 2,4-dinitrobenzenediazotate than that of 2,6-dichloro-4-nitrobenzenediazotate.

** The necessary *o*-substituent σ constants 0.71 and 0.45 for nitro³ and chloro⁴ groups respectively were obtained from coupling kinetics measurements.

Assuming that the concentration of *syn*-2,4-dinitrobenzenediazohydroxide in dilute HCl is far smaller than that of *anti*-diazohydroxide, we can use the steady-state treatment and express the dependence of k' on $[H^+]$ by Eq. (2), where

$$\frac{1}{k'} = \frac{k_1}{k_{-1}k_{H^+}([H^+] + k_0/k_{H^+})} + \frac{1}{k_{-1}}, \quad (2)$$

k_1 resp. k_{-1} are the isomerization rate constants (Scheme 1). The dependence of $1/k'$ on $1/([H^+] + k_0/k_{H^+})$ is linear in the whole pH range studied (0.5–3.4), the slope being $k_1/k_{-1}k_{H^+} = 3.7 \cdot 10^{-3} \text{ l mol}^{-1} \text{ min}^{-1}$, correlation coefficient 0.995, and standard deviation 0.03. The reciprocal of the slope is $270 \text{ l mol}^{-1} \text{ min}^{-1}$, and it is the same as the value for $k_{H^+}/(K_1^{150} + 1)$ (Table I) in accord with the both expressions being practically identical for $K_1^{150} \gg 1$. The reciprocal of the intercept of y axis corresponds to the isomerization rate constant $k_{-1} = 14.5 \text{ min}^{-1}$. This constant is only $4 \times$ greater than that of the rearrangement of *syn*-2,6-dichloro-4-nitrobenzenediazohydroxide, which agrees with the statement¹ that the polar effect of the substituents is far less significant for the rate of rearrangement of diazohydroxides than for that of their diazotates.

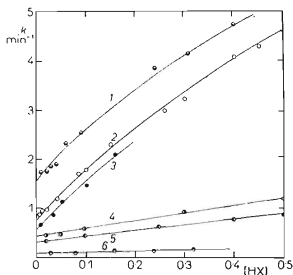


FIG. 2

The Dependences of Experimental Rate Constants on Acid Buffer Component Concentration Obtained for Acid-Catalyzed Splitting of *syn*-2,4-Dinitrobenzenediazohydroxide

Buffers: $\text{CH}_2\text{ClCO}_2\text{H}$ – pH 2.32 (1), pH 2.80 (2), pH 3.27 (3); $\text{CH}_3\text{CO}_2\text{H}$ – pH 3.95 (4), pH 4.66 (5); H_2PO_4^- – pH 5.80 (6).

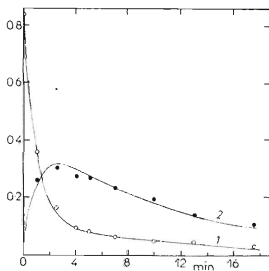


FIG. 3

Time Dependence of Concentration Change of 2,4-Dinitrobenzenediazotates (1) and the respective Diazotates (2) in Acetate Buffer pH 5.14 at 20°C and Ionic Strength 0.5

The full lines correspond to the theoretical concentrations calculated according to ref.¹ For the values of rate constants see the text.

The splitting of *syn*-2,4-dinitrobenzenediazohydroxide into the corresponding diazonium ion is subject to general acid catalysis, the value of the Brønsted α coefficient (calculated from the equation $k_A/p = G_A(qK/p)_\infty$)⁵ being 0.31, correlation coefficient 0.995, standard deviation 0.23. The value of α is, within the experimental error, the same as that of the acid-catalyzed splitting of *syn*-2,6-dichloro-4-nitrobenzenediazohydroxide¹, wherefrom it can be judged that the configuration of the activated complex is similar for the both cases.

The ratio of the rate constants k_{H^+}/k_1 is 350 and 18.6 in the cases of *syn*-2,6-dichloro-4-nitrobenzenediazohydroxide and 2,4-dinitrobenzenediazohydroxide respectively. We suppose that this large difference is due to the rate constant k_1 being far greater for 2,4-dinitro- than for 2,6-dichloro-4-nitrobenzenediazohydroxides, because the isomerization rate is not so lowered by steric effects. A rough estimate of the proper constants k_{H^+} , k_1 and the equilibrium constant K_1^{iso} can be obtained by the following reasoning: The difference between the rate constants of non-catalyzed splitting of *syn*-diazohydroxide into diazonium ion for 4-nitro-² and 2,6-dichloro-4-nitrobenzenediazohydroxides is about 4 orders of magnitude, the difference in σ constants being 0.9. This corresponds to a reaction constant ρ about 4 for this splitting. The value of σ constants of 2,4-dinitrobenzenediazohydroxide is smaller than that of 2,6-dichloro-4-nitrobenzenediazohydroxide by 0.2, so that the splitting rate of *syn*-2,4-dinitrobenzenediazohydroxide should be about 5–10 \times greater than that of 2,6-dichloro-4-nitro derivative. For the latter the value $k_{H^+} = 1350 \text{ l mol}^{-1} \text{ min}^{-1}$ was measured, so that for 2,4-dinitrobenzenediazohydroxide the value k_{H^+} should be about $1 \cdot 10^4 \text{ l mol}^{-1} \text{ min}^{-1}$. The values of 500 min^{-1} and $3.5 \cdot 10^1$ should then follow for the rate constant k_1 and the isomerization equilibrium constant K_1^{iso} respectively.

The rate constant of the reaction of 2,4-dinitrobenzenediazonium ion with OH^- ion was measured directly in the pH range 6.0–7.4, where the reverse reaction is already slower by several orders of magnitude. As 5-nitro-2-diazophenol, eventually further reaction products⁶, are formed during this reaction, the rate constant k_{OH^-} was calculated from the experimentally obtained rate constant k'_{OH^-} after subtraction of the proportion due to formation of the by-products¹ (Table II). The rate constant k_{OH^-} is independent of pH in the pH range studied.

The equilibrium constant K of the reaction $\text{ArN}_2^+ + \text{H}_2\text{O} \rightleftharpoons \sum \text{ArN}_2\text{O}^- + 2\text{H}^+$ was obtained from the experimental rate constants k'_{OH^-} and experimental rate constants k' of the reverse reaction of the diazotate giving the respective diazonium ion. This constant was calculated in quite the same way as that of 2,6-dichloro-4-nitrobenzenediazonium ion¹. The rate constants k'_{OH^-} and k' for calculation of K were also obtained by measuring the concentration change of 2,4-dinitrobenzenediazonium ion and its diazotate in acetate buffer pH 5.14 and comparing these measured concentrations with the calculated ones in the same way as in the previous paper¹. In the calculation of the theoretical concentrations the value of $k_r = 0.41$

TABLE II

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

pH	$(k_r + k'_{\text{OH}^-})$ min^{-1}	5-Nitro-2-diazo- phenol, %	k'_{OH^-} , min^{-1}	$k_{\text{OH}^-} \cdot 10^{-8}$, ^a $\text{l mol}^{-1} \text{min}^{-1}$
6.11	12.0	47.5 ± 10	6.30	4.88
6.45	19.3	37.0 ± 10	12.15	4.31
6.78	34.7	24.5 ± 5	26.20	4.35
7.07	59.7	12.5 ± 5	52.30	4.44
7.33	112.2	12.5 ± 5	98.10	4.58

^a $k_{\text{OH}^-} = (4.51 \pm 0.20) \cdot 10^8 \text{ l mol}^{-1} \text{ min}^{-1}$.

min⁻¹ was used, which was ascertained by following the substitution of the nitro group in acetate buffer⁶ at pH 5.14. For the rate constant k' the value 0.22 min⁻¹ was used, which was obtained by direct measurement of the reverse reaction. For the rate constant k'_{OH^-} was obtained 0.49 min⁻¹ as the optimum value determined by this comparison; this corresponds to $k_{\text{OH}^-} = 3.55 \cdot 10^8 \text{ l mol}^{-1} \text{ min}^{-1}$ which is lower than the values obtained in direct measurements in phosphate buffers by about 20% (Table II). The value $-1/2 \log K = 5.08$ calculated from the constants thus obtained is by about 0.07 higher than the values obtained by direct measurement of rate constants at pH > 6 (5.01). The values given correspond practically to the equilibrium between the diazonium ion and the *anti*-diazotate. The respective equilibrium constant for 2,4-dinitrobenzenediazotate ion cannot be obtained by direct measurement, because the isomerization reactions proceed far more rapidly than the reaction between 2,4-dinitrobenzenediazonium ion and its *syn*-diazohydroxide. This value can only be calculated from the Hammett equation⁷ (4), where K^{syn} and

$$\log (K^{\text{syn}}/K_0^{\text{syn}}) = 6.3\sigma \quad (4)$$

K_0^{syn} are the equilibrium constants of the reaction $\text{ArN}_2^+ + \text{H}_2\text{O} \rightleftharpoons \text{syn-ArN}_2\text{O}^- + 2 \text{H}^+$. In the case of 2,4-dinitrobenzenediazonium ion the calculation gave $-1/2 \log K^{\text{syn}} \approx 7$. Ref.² gives the value 5.58 obtained by direct potentiometric measurement at pH 5.5. From our results it follows that at this pH the rate of the isomerization reactions is greater than the rate of establishing of the equilibrium diazonium ion \rightleftharpoons diazotate, so that no correct value of the equilibrium constant K^{syn} can be obtained in this way.

EXPERIMENTAL

All the kinetic measurements were carried out at 20°C in aqueous buffer or HCl solutions of the ionic strength 0.5 adjusted by addition of KCl. $5 \cdot 10^{-3} \text{M}$ 2,4-dinitrobenzenediazonium fluoroborate solution in 0.01M-HCl and $1 \cdot 10^{-4} \text{M}$ 2,4-dinitrobenzenediazotate solution in 0.01M- $\text{Na}_2\text{B}_4\text{O}_7$ were prepared as in ref.⁶ The same procedures were used for kinetic experiments and their evaluation as those described in ref.¹ for 2,6-dichloro-4-nitrobenzenediazonium ion.

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