BASE CATALYZED REACTIONS OF 2,6-DICHLORO-4-NITRO- AND 2,4-DINITROBENZENEDIAZONIUM IONS WITH WATER

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The substitution of 2-nitro group by OH group in 2,4-dinitrobenzenediazonium ion is base catalyzed. In the first (rate-determining) step the base reacts as a nucleophilic reagent and displaces the nitro group. In the second step the intermediate formed reacts with water to give 5-nitro-2-diazophenol. In the case of 2,6-dichloro-4-nitrobenzenediazonium ion both the nitro group and chlorine are substituted at comparable rates. The reaction proceeds by the same mechanism as the previous one. In acetate buffer of pH about 4 a formation of an intermediate could be observed spectrophotometrically; its reaction with water is only 2·5 times faster than its formation. Besides the nucleophile catalyzed hydrolysis the reversible formation of diazotate proceeds at pH $\geqq$ 5 with the both benzenediazonium ions.

In our previous work[1] we studied the base catalyzed substitution of halogen in 3-nitro-4-halogenobenzenediazonium ions by OH group. It was found that the so called nucleophilic catalysis[2] operated, so that the mechanism of this reaction could be represented by the scheme (A). If the rate is controlled by the first reaction step of the substitution, the nitro group is far more reactive than halogens except for fluorine.

$$+ \; RCO_2^{(-)} \xrightarrow{k_1} \qquad + \; X^{(-)} \xrightarrow[k_2]{H_2O} \qquad \qquad (A)$$

$$+ \; RCO_2H + H^+$$
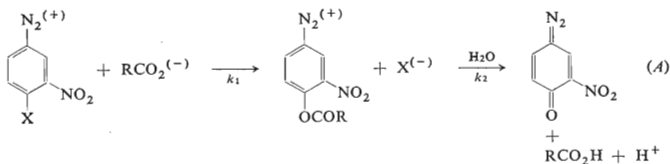
Although the substitution of 2-nitro group by OH group in 2,4-dinitrobenzenediazonium ion is used in technology for preparation of metal complexes of azo dyestuffs[3], no kinetic study of the substitution of nitro group by OH group in this or some other nitro derivative of benzenediazonium ion has been published so far. The only published paper deals with nucleophilic substitution of nitro group of 2,6-dichloro-4-nitrobenzenediazonium ion by chloride ion[4].

For these reasons we decided to study the kinetics of the base catalyzed substitution of nitro group by OH group (or, eventually, the simultaneous substitutions

of nitro group and chlorine by OH group) in these benzenediazonium ions. The study has been complicated by that the both ions are very reactive and change into diazotates even in slightly acid medium.

EXPERIMENTAL

Reagents. 2,6-*Dichloro-4-nitroaniline* (m.p. 193—194°C; ref.[5]. 195°C) was prepared by chlorination of *p*-nitroaniline[6] and purified by recrystallization from ethanol. 2,4-*Dinitroaniline* (m.p. 180·5°C; ref.[7] 182°C) was obtained by recrystallization of a raw product (VCHZ Synthesia) from ethanol. 2,6-*Dichloro-4-nitrobenzenediazonium fluoroborate.* The solution of the respective diazonium bisulphate in concentrated sulphuric acid prepared by diazotization of 2,6-dichloro-4-nitroaniline by nitrosylsulphuric acid[8] was diluted with water and ice and filtered into a saturated aqueous solution of sodium fluoroborate. The precipitated diazonium fluoroborate was collected by suction, washed with ethanol and ether and dried in a vacuum dissicator (decomposition point 178°C; ref.[9] 181°C). 2,4-*Dinitrobenzenediazonium fluoroborate* (decomposition point 193°C) was prepared in an analogous way. 2,6-*Dichloro-4-nitrophenol* (m.p. 124—125°C; ref.[10] 125°C) was prepared by chlorination of *p*-nitrophenol with potassium perchlorate in hydrochloric acid.

Kinetic Measurements

All the kinetic measurements were carried out at 20°C, and the ionic strength 0·5 was adjusted by addition of potassium chloride solution.

$5 . 10^{-3}$M Solutions of 2,6-dichloro-4-nitrobenzenediazonium fluoroborate and 2,4-dinitrobenzenediazonium fluoroborate were prepared by dissolving the respective amounts of solid fluoroborates in 0·01M-HCl. Because of their low stability, it was necessary to prepare fresh solutions every day and keep them in dark at 0°C. $1 . 10^{-4}$M Solutions of 2,6-dichloro-4-nitrobenzenediazotate and 2,4-dinitrobenzenediazotate were prepared by injecting 2 ml of the respective $5 . 10^{-3}$M diazonium fluoroborate solution into 98 ml 0·01M borax.

For kinetic measurements analogous methods were used to those of the previous work[1]: *1.* At regular time intervals, spectra were recorded in the region of 450—250 nm by means of a Unicam SP 800 spectrophotometer. *2.* The time change of the extinction of 2,6-dichloro-4-nitrobenzenediazonium ion (at 275 and 350 nm) and 2,4-dinitrobenzenediazonium ion (at 420 nm) was measured by means of a VSU-2P apparatus (Zeiss, Jena). *3.* The decrease of the diazonium ions was also followed by coupling with an excess of 1,8-dihydroxynaphthalene-3,6-disulfonic acid or 2-hydroxynaphthalene-3,6-disulfonic acid and measuring the extinction of the dyestuffs formed at 505 and 490 nm respectively. Experimental rate constants were obtained graphically according to Eqs (*1*) and (*2*) depending on whether the decrease of starting substances or the

$$kt = -2·303 \log (E_t - E_\infty) + \text{const. ,} \tag{1}$$

$$kt = -2·303 \log (E_\infty - E_t) + \text{const.} \tag{2}$$

increase of products was followed. E_t and E_∞ are the extinctions of the samples measured at a time t and $t = \infty$ respectively. The time change of the concentration of the intermediate formed by reaction of 2,6-dichloro-4-nitrobenzenediazonium ion with acetate ion was followed by extinction measurement of the reaction solution at 296 nm using the VSU-2P spectrophotometer. The time concentration change of 2,4-dinitrobenzenediazonium ion and the respective diazotate anion during the substitution reaction in acetate buffers was measured as follows: 5 ml $5 . 10^{-3}$M 2,4-dinitrobenzenediazonium fluoroborate was added into 245 ml acetate buffer

(pH 4·8—5·6) at the time $t = 0$. Then two 5 ml samples were withdrawn simultaneously at definite time intervals. The first of the samples was injected into a flask containing 10 ml $1 . 10^{-3}$M 2-hydroxynaphthalene-3,6-disulfonic acid, and 2 ml 0·1M borax was added immediately. The second sample was added into a flask containing 10 ml $1 . 10^{-3}$M 2-hydroxynaphthalene-3,6-disulfonic acid, and 2 ml 0·1M borax was added after about 1·5 hours. Extinction of the both series of samples were measured at 490 nm. The extinctions of the first series of samples correspond to the concentrations of the diazonium ion, those of the second series correspond to the sums of concentrations of the diazonium ion and the respective diazotate. In the same way the time concentration change of 2,6-dichloro-4-nitrobenzenediazonium ion and its diazotate was determined in acetate buffers at pH 4·8. In several cases the time concentration change of 2,4-dinitrobenzenediazotate was determined directly by measuring the extinction of the reaction solution at 300 nm by means of the VSU-2P spectrophotometer (Zeiss, Jena).

The rate of the conversion of 2,4-dinitrobenzenediazotate to the respective diazonium ion in acetate buffer (pH 5·6) was measured as follows: The same solution was prepared as in the procedure of simultaneous determination of the concentrations of diazonium ion and diazotate. At the moment when the diazotate concentration reached its maximum value, 5 ml $1 . 10^{-2}$M 2-hydroxynaphthalene-3,6-disulfonic acid was injected into 50 ml of the reaction solution, and the time dependence of the extinction increase was measured at 490 nm immediately.

Determination of Nitrous Acid

0·5 ml $5 . 10^{-3}$M benzenediazonium fluoroborate was added to 25 ml chloroacetate resp. citrate buffer (pH 1·7—2·8). After about six half-lives of the substitution reaction, 1 ml m-nitroaniline hydrochloride was added. The solution was acidified with 5 ml 2·5M-HCl, and after 5 min, 5 ml $1 . 10^{-2}$M 1,8-dihydroxynaphthalene-3,6-disulfonic acid solution and 5 ml 5M sodium acetate were added and the volume adjusted to 50 ml. A similar solution, to which 0·5 ml $5 . 10^{-3}$M-NaNO$_2$ was added instead of benzenediazonium fluoroborate, was worked up in an analogous way. The extinctions of the both solutions were then measured at 505 nm, and from their ratio the amount of the nitrous acid evolved during the substitution reaction of diazonium ion was calculated.

Gravimetric Analysis of Diazophenols as Iodophenols

Preparation of iodophenols from 2,6-dichloro-4-nitrobenzenediazonium fluoroborate. 200 ml buffer containing 9·5 g chloroacetic acid and 2·6 g sodium hydroxide was added to 300 ml water containing 2·0 g (6·5 . 10^{-3} mol) 2,6-dichloro-4-nitrobenzenediazonium fluoroborate with stirring. After 3 hours, 30 ml 50% H$_2$SO$_4$ and 30 g potassium iodide were added to the reaction mixture. The temperature of the solution was raised to about 60°C during 2 hours with stirring and maintained for another 1 hour. Then the solution was refluxed 30 minutes, cooled at 80°C, and some resinous substances (about 0·1 g) were removed by filtration. On the day after, the crystals precipitated were collected by suction and washed with water. The mother liquors were extracted with 2 × 100 ml ether. Ether was evaporated, the residue was dissolved in 20 ml 10% NaOH and filtered with charcoal. The second portion of iodophenols precipitated on acidification of the filtrate. The overall yield of iodophenols was 1·8 g. The ratio of the both iodophenols was determined from the NMR spectrum of the mixture.

A) *Isolation of 2-iodo-3-chloro-5-nitrophenol.* 1 g of the iodophenol mixture was dissolved in 3 ml warm 4M-NaOH. The sodium 2-iodo-3-chloro-5-nitrophenolate precipitated on cooling was collected by suction and washed with a small amount of ice water. The phenolate was dissolved

in 5 ml water, the phenol was precipitated by addition of 2 ml concentrated hydrochloric acid and recrystallized from aqueous methanol. Yield 0·15 g, m.p. 136°C. For $C_6H_3ClINO_3$ (299·5) calculated: 24·06% C, 1·01% H, 4·67% N; found: 24·08% C, 1·24% H, 4·68% N.

B) *Isolation of 3,5-dichloro-4-iodophenol.* 1 g of the iodophenol mixture was dissolved in a warm mixture of 2·5 g $SnCl_2.2 H_2O$, 10 ml conc. hydrochloric acid and 10 ml water. The crystals precipitated on cooling were collected by suction, washed with water and recrystallized from aqueous methanol. Yield 0·1 g, m.p. 146°C. For $C_6H_3OCl_2I$ (288·9) calculated: 24·94% C, 1·05% H; found: 24·90% C, 1·21% H. The diazophenols formed in other buffers were determined in the same way.

Determination of Concentrations of 5-Nitro-2-diazophenol and 2,4-Dinitrophenol in Reaction Products of 2,4-Dinitrobenzenediazonium Ion with Acetate and Phosphate Buffers

4-ml Portions of $4 . 10^{-3}$ M 2,4-dinitrobenzenediazonium fluoroborate were added to each 36 ml citrate buffer, two acetate and two phosphate buffers. After 3 hours standing in dark, each reaction mixture was divided into 4 parts. Three parts were used for determination of 5-nitro-2-diazophenol by various methods (*a*, *b*, *c*) and the fourth part was used for determination of 2,4-dinitrophenol *d*). *a*) The first part was acidified with 3 ml 2M-HCl and its extinction measured at 420 nm. *b*) 5 ml 0·2M borax, enough tert-phosphate to bring pH at about 10, and 15 ml $1 . 10^{-1}$ M 2-hydroxynaphthalene-3,6-disulfonic acid were added to the second part. After 3 hours, the solution was acidified with 2M-HCl at pH about 1, its volume was adjusted at 50 ml, and the extinction was measured at 505 nm. *c*) The third part was alkalized in the same way as *b*), and 5 ml $1 . 10^{-3}$ M 1-naphthol was added thereto. After 30 minutes, the solution was acidified with 5 ml 2M-HCl and the dyestuff formed was extracted in 25 ml chloroform. The extinction of the extract was measured at 485 nm. *d*) The fourth part was acidified with 5 ml 2M-HCl and extracted with 10 ml ether. The ether extract was extracted with 10 ml 0·1M-NaOH and the solution of phenolate was adjusted at a volume of 25 ml. The same procedure was also used for the buffer solution consisting of 10 ml buffer and 2 ml $2 . 10^{-4}$ M 2,4-dinitrophenol. By comparing the extinctions at 395 nm, the amount of 2,4-dinitrophenol formed in reaction of 2,4-dinitrobenzenediazonium ion in buffers was determined.

pH *of reaction solutions* was measured at 20°C with the use of a PHM 4c Radiometer apparatus (Copenhagen) and a glass and a saturated calomel electrodes. NMR spectra were measured with the use of a Tesla BS 487 A apparatus at 80 MHz. Saturated solutions of the substances in $CDCl_3$ with tetramethylsilane as an internal standard were used for the measurements.

RESULTS AND DISCUSSION

Both the nitro group or chlorine of 2,6-dichloro-4-nitrobenzenediazonium ion can be substituted by OH group in aqueous buffers (*B*). When attempting to prepare diazophenols under the conditions similar to those of successful preparation of 2-nitro-4-diazophenol in a high yield[1], we obtained a considerable amount of resinous substances. The reaction led predominantly to diazophenols only under the conditions when the reaction products remained in solution. Our attempts to isolate the diazophenols from the solutions after finishing the reaction were not successful, and, therefore, we isolated the iodophenols prepared therefrom. The 3,5-dichloro-4-iodophenol and 2-iodo-3-chloro-5-nitrophenol formed are stable and can be well isolated and relatively easily separated from each other. On the basis of integrated NMR spectrum (2 doublets 2·12τ and 2·33τ, $J = 3·0$ Hz, and one singlet 3·13τ in the case of nitro and chloro derivatives respectively) it was found that the iodophenols were formed at a ratio about 1 : 1. The same ratio was found by determination of the nitrous acid evolved in the reactions carried out under the same condi-

tions ($44 \pm 6\%$). Therefrom it follows that the nitro group is about twice as much reactive as chlorine during the substitution reaction.
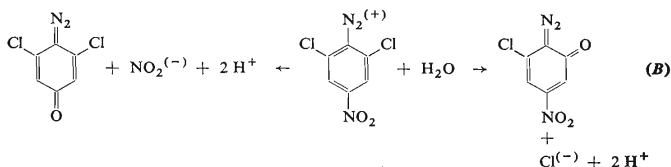
5-Nitro-2-diazophenol is formed on addition of solution of 2,4-dinitrobenzenediazonium ion into sodium carbonate solution[3]. Morgan and Porter[11] prepared 5-nitro-2-diazophenol by diazotization of 2-amino-5-nitrophenol and submitted it to coupling with alkaline 2-naphthol solution whereupon a dark blue dyestuff was formed which turned red on acidification. The authors failed to obtain the dyestuff in crystalline form. We have used the same coupling reaction conditions for alkaline 2-naphthol solution and the 5-nitro-2-diazophenol prepared, on the one hand, according to the abovementioned patent[3] and, on the other hand, by the reaction of 2,4-dinitrobenzenediazonium fluoroborate in citrate buffer under the conditions similar to those of kinetic experiments. It was found by chromatographic comparison that the both dyestuffs are identical. The dyestuff prepared from 2,4-dinitrobenzenediazonium fluoroborate was purer. Therefrom it can be presumed that, also under the conditions of kinetic experiments, the substitution of o-nitro group is the main reaction, the side reaction being not significant. The amount of nitrous acid formed during the reactions was determined by parallel experiments ($86 \pm 6\%$).

The first kinetic experiments were carried out in 0·1M and 0·01 M-HCl and in chloroacetate and citrate buffers. Isosbestic points were found in the spectra of 2,6-dichloro-4-nitro- and 2,4-dinitrobenzenediazonium ions in the region of $450 - 250$ nm. Spectral records of the reaction of 2,6-dichloro-4-nitrobenzenediazonium ion were very similar to those of nucleophilic substitution of 3-nitro-4-halogenobenzenediazonium ions[1]. A marked decrease and increase of extinction at 275 nm and 350 nm respectively correspond to the decrease of the diazonium ion and increase of the diazophenols respectively (Fig. 1a). On the contrary, the character of spectra of 2,4-dinitrobenzenediazonium ion was quite different, and the difference between the starting substances and products was less distinct (Fig. 1b). All the reactions were 1. order in diazonium ion and independent of pH. Experimental rate constants k were directly proportional to the concentration of basic buffer component (Table I). The increasing of chloroacetic acid concentration at a constant chloroacetate concentration resulted in a progressive increase of decomposition rate of diazonium ions. The increasing of citric acid concentration in citrate buffers did not bring about such an acceleration. We suppose that the increase of the rate constant k_B is caused by the change of medium (the lowering of dielectric constant) which results in acceleration of a reaction between two ions carrying opposite charges. This opinion is supported by that a similar acceleration of the reaction was brought about by addition of tert-butanol (instead of chloroacetic acid) to the chloroacetate buffer (Fig. 2).

Reactions of 2,4-Dinitrobenzenediazonium Ion

The course of substitution of *o*-nitro group of 2,4-dinitrobenzenediazonium ion in acetate buffers of pH < 4·7 was similar to the cases discussed so far. The reaction proceeded more rapidly in accord with the acetate ion being stronger nucleophilic reagent. The dependence of experimental rate constants on acetate concentration was measured at pH 4·1 (Table II). This dependence is linear, giving an intercept of 0·028 min^{-1} at *y* axis. Supposing that this value corresponds to the reaction with OH$^-$ ion, we get $k_{OH^-} = (2·2 \pm 0·5) . 10^8$ l mol^{-1} min^{-1} and $k_B = (5·47 \pm \pm 0·74)$ l mol^{-1} min^{-1}. In more alkaline acetate buffers the character of the spectra measured in the region of 450—250 nm changed, and the change was increasingly distinct with increasing pH. Spectral records of the reaction courses showed no isosbestic points. In the initial interval of the reaction, some further substance was formed very rapidly, and its concentration, after reaching maximum, slowly decreased. As it was found by measuring the absorption at 300 nm, the increasing of pH resulted
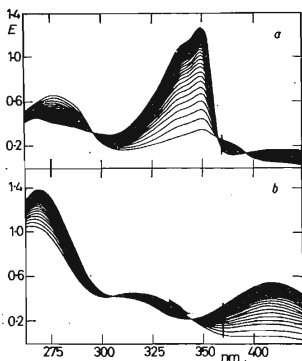

Fig. 1

Spectral Record of Reaction *a* 2,6-Dichloro-4-nitrobenzenediazonium ion in chloroacetate buffer at 20°C and ionic strength 0·5; pH 2·72, [ClCH$_2$CO$_2^{(-)}$] = 0·1M, [ArN$_2^{(+)}$] = 5 . . 10^{-5} M. *b* 2,4-Dinitrobenzenediazonium ion in chloroacetate buffer at 20°C and ionic strength 0·5; pH 3·81, [ClCH$_2$CO$_2^{(-)}$] = = 0·1M, [ArN$_2^{(+)}$] = 5 . 10^{-5}M.

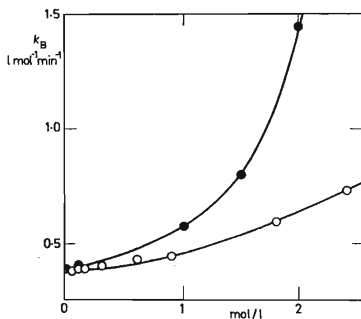

Fig. 2

Dependence of Rate Constant k_B on Concentrations of Chloroacetic Acid ○ and Butanol ● during the Reaction of 2,6-Dichloro-4-nitrobenzenediazonium Ion in Chloroacetate Buffer at 20°C and Ionic Strength 0·5

Table I

Rate Constants of Reactions of 2,6-Dichloro-4-nitrobenzenediazonium Ion and 2,4-Dinitro-benzenediazonium Ion with Water, Citrate and Chloroacetate at 20°C and Ionic Strength 0·5 k_B, l mol^{-1} min^{-1}.

| pH	[B], mol l^{-1}	k, min^{-1}	pH	[B], mol l^{-1}	k, min^{-1}
		2,6-Dichloro-4-nitrobenzenediazonium ion			
		Water[a] $k_B = (1·61 \pm 0·15) . 10^{-5}$			
0·29	55·5	$1·01 . 10^{-3}$	1·21	—	$8·25 . 10^{-4}$
1·05	—	$9·03 . 10^{-4}$	1·99	—	$8·35 . 10^{-4}$
		Citrate $k_B = (2·06 \pm 0·17)$			
1·37	0·05	$1·06 . 10^{-1}$	2·57	0·05	$1·08 . 10^{-1}$
1·48	0·05	$9·76 . 10^{-2}$	2·22	0·04	$9·43 . 10^{-2}$
1·68	0·05	$1·13 . 10^{-1}$	2·17	0·06	$1·13 . 10^{-1}$
1·79	0·05	$1·03 . 10^{-1}$	2·15	0·07	$1·44 . 10^{-1}$
2·36	0·05	$9·36 . 10^{-2}$	2·10	0·10	$1·82 . 10^{-1}$
		Chloroacetate $k_B = (3·75 \pm 0·13) . 10^{-1}$			
2·54	0·4	$1·54 . 10^{-1}$	4·19	0·4	$1·47 . 10^{-1}$
2·76	0·4	$1·52 . 10^{-1}$	2·71	0·1	$3·76 . 10^{-2}$
2·91	0·4	$1·56 . 10^{-1}$	2·72	0·15	$5·87 . 10^{-2}$
3·26	0·4	$1·47 . 10^{-1}$	2·73	0·2	$7·37 . 10^{-2}$
3·53	0·4	$1·52 . 10^{-1}$	2·72	0·3	$1·12 . 10^{-1}$
3·65	0·4	$1·41 . 10^{-1}$			
		2,4-Dinitrobenzenediazonium ion			
		Water[a] $k_B = (2·45 \pm 0·15) . 10^{-5}$			
1·05	55·5	$1·28 . 10^{-3}$	2·05	—	$1·44 . 10^{-3}$
		Citrate $k_B = (5·29 \pm 0·25)$			
1·85	0·025	$1·46 . 10^{-1}$	2·89	0·05	$2·52 . 10^{-1}$
2·89	0·025	$1·38 . 10^{-1}$			
		Chloroacetate $k_B = (7·80 \pm 0·31) . 10^{-1}$			
1·82	0·1	$8·24 . 10^{-2}$	2·86	0·2	$1·54 . 10^{-1}$
2·73	0·1	$7·62 . 10^{-2}$	2·75	0·3	$2·24 . 10^{-1}$
3·82	0·1	$7·97 . 10^{-2}$			

[a] pH was adjusted by addition of 2M-HCl.

TABLE II

Experimental Rate Constants of Reactions of 2,4-Dinitrobenzenediazonium Ion with Acetate and Phosphate Buffers at 20°C and Ionic Strength 0·5

pH	[B], mol l^{-1}	k, min^{-1}	pH	[B], mol l^{-1}	k, min^{-1}
	Acetate			sec-Phosphate	
4·08	0·01	$6·41 . 10^{-2}$	6·03	0·01	$1·48 . 10^{-2}$
4·12	0·02	$1·12 . 10^{-1}$	6·02	0·05	$2·96 . 10^{-2}$
4·11	0·03	$1·58 . 10^{-1}$	6·55	0·01	$3·08 . 10^{-3}$
4·07	0·05	$2·31 . 10^{-1}$	6·58	0·05	$5·33 . 10^{-3}$

in an increase of this maximum concentration, and, at the same time, the interval necessary for reaching the maximum concentration diminished. A further study of the reaction proceeding under these conditions showed that the compound is the diazotate formed reversibly according to:

$$(C)$$
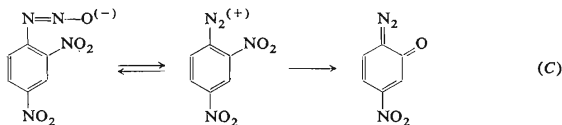
The following facts support the ascription of the structure of diazotate to the compound absorbing at 300 nm: *1*. A solution of 2-hydroxynaphthalene-3,6-disulfonic acid was added to the reaction solution at the moment when the extinction of the compound mentioned reached its maximum value. The extinction at λ 485 nm increased almost immediately due to azo dyestuff formation from 2,4-dinitrobenzenediazonium ion. This rapid extinction change was then followed by a further slow increase of extinction which obeyed the 1. order kinetics, the half-life being several minutes. This second phase corresponded to the formation of diazonium ion from diazotate and its subsequent rapid coupling with 2-hydroxynaphthalene-3,6-disulfonic acid[12]. *2*. The time dependence of both the diazonium ion concentration and the sum of diazonium ion and diazotate was followed simultaneously in one kinetic experiment (Experimental) (Fig. 3a). The time dependence of diazotate concentration has the same character as that found by measuring the extinction at 300 nm. The time change of the sum of concentrations of diazonium ion and diazotate corresponds to the conversion of the diazonium ion into 5-nitro-2-diazophenol. In Fig. 3 it can be seen that this change is large at the beginning and gradually diminishes. The rate of formation of diazophenol is proportional to the diazonium ion concentration at any moment, and it is given by Eq. (*3*).

$$k_{exp} = - (d([ArN_2^{(+)}] + [ArN_2O^{(-)}])/dt) (1/[ArN_2^{(+)}]) . \qquad (3)$$

3. A solution of the respective diazotate was used instead of 2,4-dinitrobenzenediazonium fluoro-

borate. Fig. 3b presents the time dependence of concentrations of diazonium ion, diazotate, and their sum. In this case, too, the dependences found agree with the mechanism suggested.

The rate of establishing of equilibrium between 2,4-dinitrobenzenediazonium ion and the respective diazotate is greater than that of the conversion of the diazonium ion into 5-nitro-2-diazophenol, so that, soon after the beginning of the reaction, the equilibrium or, more precisely, the steady state is established (in 4 minutes at pH about 5). This is obvious, on the one hand, from the ratio $[ArN_2^{(+)}]/[ArN_2O^{(-)}]$ remaining constant at this reaction phase (Table III) and, on the other hand, from that the dependence of logarithm of extinction (corresponding to the sum of concentrations of diazonium ion and diazotate) on time is linear. The ratio $[ArN_2^{(+)}]/[ArN_2O^{(-)}]$ equals 0·30 and 1·2 at pH 5·14 and 4·80, respectively. This means that pH_m of 2,4-dinitrobenzenediazonium ion is about 4·85 (pH_m is the pH value corresponding to the ratio[13] $[ArN_2^{(+)}] : [ArN_2O^{(-)}] = 1$). The rate constant of the conversion of diazonium ion into diazophenol (or, more correctly, of the diazonium ion decrease, because further reaction products are formed in more alkaline buffers, too) in acetate buffers, calculated according to Eq. (3), increases linearly with increasing OH^- concentration. This is caused by nucleophilic substitution with OH^- ions taking place besides the reaction with acetate ion under these conditions. The rate constant k_{OH^-} calculated from the dependence of k_{exp} on $[OH^-]$ at a constant

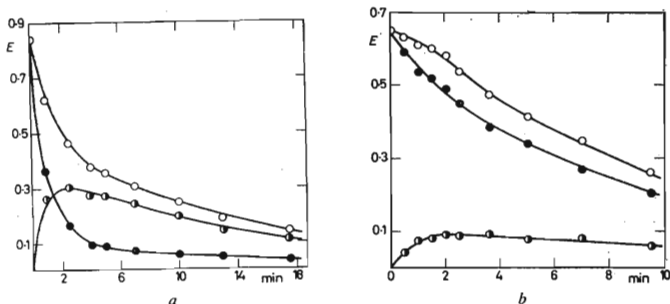**FIG. 3**

Time Dependence of Concentrations

a 2,4-Dinitrobenzenediazonium ion (●), its diazotate (◐) and their sum (○) during the reaction of 2,4-dinitrobenzenediazonium ion in acetate buffer; pH 5·14, $[CH_3CO_2^{(-)}] = 0·01M$, $[ArN_2^{(+)}] = 1 \cdot 10^{-4}M$. *b* 2,4-Dinitrobenzenediazonium ion (◐), its diazotate (●) and their sum (○) during the reaction of 2,4-dinitrobenzenediazotate in acetate buffer; pH 5·18, $[CH_3CO_2^{(-)}] = 0·01M$, $[ArN_2O^{(-)}] = 1 . 10^{-4}M$.

The Time Dependence of the Ratio of 2,4-Dinitrobenzenediazonium Ion to its Diazotate in Acetate Buffer at 20°C and Ionic Strength 0·5

$[CH_3CO_2^{(-)}] = 0.01 \text{ mol l}^{-1}$.

t, min	Extinctions of dyestuffs corresponding to			$[ArN_2^{(+)}]$: $: [ArN_2O^{(-)}]$
	$[ArN_2^{(+)}]$	$([ArN_2^{(+)}] + [ArN_2O^{(-)}])$	$[ArN_2O^{(-)}]$	
pH 4·81, $[ArN_2^{(+)}]_0 = 1 . 10^{-4} \text{ mol l}^{-1}$				
0·0	0·725	0·725	—	—
0·5	0·515	0·580	0·065	7·92
1·0	0·456	0·568	0·112	4·07
2·0	0·337	0·490	0·153	2·20
3·0	0·260	0·425	0·165	1·58
4·5	0·195	0·354	0·159	1·23
7·0	0·135	0·253	0·118	1·14
9·2	0·111	0·205	0·095	1·18
11·0	0·092	0·171	0·079	1·16
13·0	0·077	0·136	0·059	1·30
pH 5·14, $[ArN_2^{(+)}]_0 = 1 . 10^{-4} \text{ mol l}^{-1}$				
0·0	0·837	0·837	—	—
1·0	0·360	0·620	0·260	1·38
2·5	0·160	0·460	0·300	0·53
4·0	0·091	0·373	0·272	0·33
5·0	0·084	0·350	0·266	0·32
7·0	0·064	0·300	0·236	0·27
10·0	0·052	0·244	0·192	0·27
13·0	0·043	0·182	0·139	0·31
17·5	0·032	0·138	0·106	0·30
pH 5·18, $[ArN_2O^{(-)}]_0 = 1 . 10^{-4} \text{ mol l}^{-1}$				
0·0	—	0·652	0·652	—
0·5	0·042	0·635	0·593	0·07
1·0	0·075	0·612	0·537	0·14
1·5	0·082	0·602	0·520	0·16
2·0	0·090	0·582	0·492	0·18
2·5	0·087	0·539	0·452	0·19
3·6	0·090	0·475	0·385	0·23
5·0	0·076	0·415	0·339	0·22
7·0	0·079	0·348	0·269	0·29
9·5	0·058	0·272	0·204	0·28

acetate concentration has a value of $2 \cdot 6 \cdot 10^8 \, l \, mol^{-1} \, min^{-1}$ which is practically the same value as that calculated from the dependence of k_{exp} on acetate concentration at pH $4 \cdot 1$.

The reactions of 2,4-dinitrobenzenediazonium ion were studied in phosphate buffers at pH $6 \cdot 0$ and $6 \cdot 6$ at two different buffer concentrations, too. Under these conditions, the equilibrium diazonium ion–diazotate was established even sooner than the first sample could be withdrawn (i.e. in a time shorter than $0 \cdot 4$ min). The linear dependence between the logarithm of extinction (corresponding to the sum of diazonium ion and diazotate concentrations) and time was fulfilled far worse in these cases due obviously to side reactions. The experimental rate constants k were computed according to Eq. (3) again. The concentration of diazonium ion was calculated on the basis of the value $pH_m \approx 4 \cdot 85$ and an assumption that it is indirectly proportional to $[OH^-]^2$. From the values given in Table II it is obvious that the k_{exp} value found is a sum of $k_B[HPO_4^{2-}]$ and $k_{OH}[OH^-]$ again. With respect to the bad linear dependence of $\log E$ on t, it was not possible to obtain any significant k_B values for HPO_4^{2-}. According to a very rough estimate this constant k_B equals $50 \, l mol^{-1} \, min^{-1}$.

In order to ascertain the way in which 2,4-dinitrobenzenediazonium ion reacts with OH^- ion, we determined the amount of 5-nitro-2-diazophenol and 2,4-dinitrophenol formed in two phosphate buffers. For comparison, the same reaction was carried out in citrate buffer where practically only 5-nitro-2-diazophenol was formed. The results are presented in Table IV. The relative accuracy of determination of 2,4-dinitrophenol in reaction products was about $\pm 30\%$. From the Table it follows that the reaction with OH^- ion gives 5-nitro-2-diazophenol only partially (maximum 50%), and 2,4-dinitrophenol forms only a part of the other products. We did not determine these products.

Reaction of 2,6-Dichloro-4-nitrobenzenediazonium Ion

When studying the acetate catalyzed conversion of 2,6-dichloro-4-nitrobenzene-diazonium ion into diazophenols by spectral measurements in the range of 450 to 250 nm, we failed to find any isosbestic points even in the most acidic acetate buffers (pH $3 \cdot 9$). The character of spectra was independent of pH up to pH about 5. At pH > 5 an increasingly more distinct decrease of extinction in the region of 275 nm (corresponding to the absorption of the original diazonium ion) was encountered. The spectral records of the kinetic experiments carried out at pH < 5 suggest that some further compound is temporarily formed besides the diazonium ion decrease and diazophenol increase. By measuring the dependence of extinction at λ 296 nm (corresponding to the isosbestic point of the original diazonium ion and diazophenols) on time, the time concentration dependence of the transient compound was determined. For the same experiment, the time dependence of extinctions of diazonium ion (λ 275 nm) and diazophenols (λ 350 nm) were determined, too. The dependences found are given in Fig. 4 (the concentrations were calculated from the extinc-

tions). The course of diazonium ion concentration has an exponential character, and the concentration increase of diazophenols has a shape typical for compound C in a reaction sequence A → B → C. From the linear time dependence of log E_{275} the experimental rate constant of formation of the intermediate was computed. This constant is directly proportional to acetate ion concentration (Table V). From the found experimental rate constants k_1 of formation of the intermediate and t_{max} (the time when the concentration of the intermediate reaches maximum) the pseudomono-molecular rate constants k_2 of the decomposition of intermediate in reaction (A) were computed according to Eq. $(4)^{14}$.

$$t_{max} = (\ln (k_2/k_1))/(k_2 - k_1). \tag{4}$$

These constants are proportional to acetate ion concentration, too (Table V). The maximum concentration (%) of the intermediate was calculated from the rate constants of its formation and decomposition according to Eq. $(5)^{14}$ where $[I]$ is the concentration of the intermediate at t_{max}. The average value of this concentration*

$$\frac{[I] \cdot 100}{[ArN_2^{(+)}]_0} = \frac{k_1}{k_2 - k_1} ((\exp. -k_1 t_{max}) - (\exp. -k_2 t_{max})) \tag{5}$$

was $(22 \cdot 3 \pm 3 \cdot 0)$ % of the diazonium ion concentration present at the time $t = 0$, and it was independent of buffer concentration. Thus the first reaction phase consists
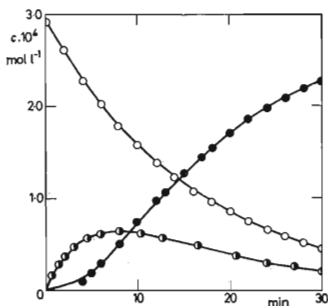

FIG. 4

Time Dependence of Concentrations of 2,6-Dichloro-4-nitrobenzenediazonium Ion (○), Diazophenol Mixture Formed in the Reaction (●) and Intermediate (◑) during the Reaction of 2,6-Dichloro-4-nitrobenzenediazonium Ion in Acetate Buffer

pH 3·92, $[CH_3CO^{(+)}] = 0.025$M, $[ArN_2^{(-)}] = 2·9 . 10^{-4}$ mol l^{-1}.

*   The values given hold under the condition that only one intermediate (and, hence, only one product) is formed in the reaction. When the both products are formed at a ratio 1 : 1 in acetate buffer, too, the value k_1 and the maximum concentration of the intermediate determined spectrophotometrically are half; the k_2 value remains the same.

in the substitution reaction of 2,6-dichloro-4-nitrobenzenediazonium ion with acetate ion giving the substituted diazophenyl acetate (= the intermediate). The second phase consists in the base catalyzed hydrolysis of the intermediate giving diazophenols and regenerating acetate ion. In contrast to the other conversions of diazonium ions into diazophenols (with nucleophilic catalysis by acetate or other ions) studied by us so far, the hydrolysis of the ester is not far faster than its formation in this case. Therefore, it is possible to follow spectrophotometrically the time course of concentration of the intermediate and thus to confirm the mechanism suggested.

TABLE IV

Amounts of 2,4-Dinitrophenol and 5-Nitro-2-diazophenol in Reaction Products of 2,4-Dinitrobenzenediazonium Ion with Acetate and Phosphate Buffers at 20°C and Ionic Strength 0·5

Base	pH	$\dfrac{[B]}{\text{mol l}^{-1}}$	5-Nitro-2-diazophenol, %			2,4-Dinitrophenol %
			a	*b*	*c*	
Citrate	2·84	0·05	100	100	100	—
Acetate	4·05	0·05	88	94	95	5
	5·27	0·05	69	71	77	10
sec-Phosphate	6·04	0·0125	36	40	35	35
	6·02	0·05	63	65	60	20

a Determined by coupling with 1-naphthol, *b* determined by coupling with 2-hydroxynaphthalene-3,6-disulfonic acid, *c* 5-nitro-2-diazophenol measured directly after acidification.

TABLE V

Rate Constants of Formation (k_1) and Decomposition (k_2) of Intermediate during Reaction of 2,6-Dichloro-4-nitrobenzenediazonium Ion in Acetate Buffers at 20°C, Ionic Strength 0·5 and pH 3·93

$\dfrac{[\text{CH}_3\text{CO}_2^{(-)}]}{\text{mol l}^{-1}}$	$\dfrac{t_{max}}{\text{min}}$	$\dfrac{k_1{}^a}{\text{min}^{-1}}$	$\dfrac{k_2{}^b}{\text{min}^{-1}}$
0·025	8·2	0·0653	0·205
0·05	5·0	0·125	0·300
0·05	5·2	0·117	0·295
0·10	2·35	0·243	0·672
0·10	2·45	0·235	0·650

a $k_B = 2·45 \pm 0·11$ l mol^{-1} min^{-1}, *b* $k_B = 6·67 \pm 0·92$ l mol^{-1} min^{-1}.

Although we failed to ascertain whether the formation of the intermediate observed was due to the substitution of nitro group or chlorine, we consider the first alternative to be more probable. Nitro group is much more reactive in nucleophilic substitutions[15] so that the difference in velocities of the first and second steps is less in the case of substitution of nitro group than that of chlorine.

TABLE VI

The Time Dependence of the Ratio of 2,6-Dichloro-4-nitrobenzenediazonium Ion to its Diazotate in Acetate Buffers at 20°C and Ionic Strength 0·5

pH 5·28, $[CH_3CO_2^{(-)}] = 0.005$ mol/l, $[ArN_2^{(+)}]_0 = 1 . 10^{-4}$ mol/l.

t, min	Extinctions of dyestuffs corresponding to			$[ArN_2^{(+)}]$: $: [ArN_2O^{(-)}]$
	$[ArN_2^{(+)}]$	$([ArN_2^{(+)}] + + [ArN_2O^{(-)}])$	$[ArN_2O^{(-)}]$	
0·0	0·595	0·595	—	—
1·0	0·505	0·535	0·030	16·83
3·0	0·380	0·460	0·080	4·75
5·0	0·298	0·387	0·089	3·35
8·0	0·215	0·299	0·084	2·56
12·0	0·135	0·222	0·087	1·55
16·0	0·092	0·176	0·084	1·09
20·0	0·067	0·146	0·077	0·87
25·0	0·052	0·117	0·065	0·80

A rapid decrease of diazonium ion concentration (measured at 275 nm) was observed at the initial reaction phase in acetate buffers of pH > 5. On the basis of analogy with 2,4-dinitrobenzenediazonium ion, we ascribe this decrease to a reversible formation of diazotate. In accord to this, the extinction increase at 350 nm (increase of diazophenols) did not agree with the simple kinetic equation A → B → C. The concentration change of diazonium ion and diazotate, in this pH range, was followed by coupling with 2-hydroxynaphthalene-3,6-disulfonic acid as in the case of 2,4-dinitrobenzenediazonium ion. Table VI presents the extinctions corresponding to the concentrations of diazonium ion, diazotate, and their sum. From the Table it is obvious that the equilibrium between diazonium ion and diazotate is established in the case of 2,6-dichloro-4-nitrobenzenediazonium ion far more slowly than in the case of 2,4-dinitrobenzenediazonium ion, so that the system does not attain the steady state until the end of measurement. Although it is not possible to obtain the accurate value of pH_m from experimental data, it is obvious that 2,6-dichloro-4-nitrobenzene-

diazonium ion is a weaker "acid" than 2,4-dinitrobenzenediazonium ion, because the ratio $[ArN_2^{(+)}]/[ArN_2O^{(-)}]$ is smaller with 2,4-dinitrobenzenediazonium ion at the same pH.

Similarly to the 2,4-dinitrobenzenediazonium ion, in the case of 2,6-dichloro-4-nitrobenzenediazonium ion, too, the rate of decrease of the sum of concentrations of diazonium ion and diazotate is proportional to diazonium ion concentration at any moment. Therefore, it was possible to calculate (on the basis of Eq. (3)) the experimental rate constants (Table VII), which are again linearly dependent on $[OH^-]$; it means that the overall reaction rate is equal to the sum of reactions with acetate ion and OH^- ion. The calculated rate constant $k_{OH^-} = (5 \cdot 2 \pm 1 \cdot 5) \cdot 10^7 \, l \, mol^{-1} \, min^{-1}$ is about four times smaller than the rate constant of the analogous reaction of 2,4-dinitrobenzenediazonium ion. From the spectral records of the course of kinetic experiments it can be seen that diazophenols are predominantly formed by the reaction with OH^- ion. We did not ascertain their accurate amount.

TABLE VII

Experimental Rate Constants of Reaction of 2,6-Dichloro-4-nitrobenzenediazonium Ion with Acetate Buffer at 20°C and Ionic Strength 0·5

pH	$[CH_3COO^{(-)}]$ mol l^{-1}	k, min^{-1}	pH	$[CH_3COO^{(-)}]$ mol l^{-1}	k, min^{-1}
4·93	0·005	$6 \cdot 03 \cdot 10^{-2}$	5·37	0·005	$1 \cdot 38 \cdot 10^{-1}$
5·17	0·005	$9 \cdot 80 \cdot 10^{-2}$	5·45	0·005	$2 \cdot 04 \cdot 10^{-1}$
5·22	0·010	$1 \cdot 07 \cdot 10^{-1}$	5·67	0·0156	$2 \cdot 62 \cdot 10^{-1}$
5·28	0·005	$1 \cdot 06 \cdot 10^{-1}$			

The equilibrium diazonium ion–diazotate was established within less than 0·5 min in phosphate buffers (pH ~6). During this time, about $15-20\%$ of the original diazonium ion changed into a mixture of diazophenols and other reaction products. Further reaction proceeded very slowly and was 1. order in overall diazonium ion concentration. The half-life of this reaction was about 1 hour at pH 6·0. The half-life doubled on increasing the OH^- concentration to the double which can be explained by that the velocity is 1. order in OH^- ion, whereas the diazonium ion concentration is inversely proportional to $[OH^-]^2$. In borax buffers (pH 9·2) the conversion of 2,6-dichloro-4-nitrobenzenediazonium ion into the respective diazotate proceeds almost instantaneously. The diazotate solution formed is very stable; its concentration decrease is slower under these reaction conditions than in mineral acid solutions by several orders of magnitude.

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