BASE CATALYZED REACTIONS OF 3-NITRO-4-HALOGENOBENZENEDIAZONIUM IONS WITH WATER

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The reactions of 3-nitro-4-halogenobenzenediazonium ions with water in the presence of bases take a two step course. In the first step a base – nucleophilic reagent – displaces the halogen. In the second step the intermediate formed reacts with water to give 2-nitro-4-diazophenol. The formation of the intermediate could be proved spectroscopically using pyridine as the base. In the other cases the hydrolysis of the intermediate is much faster than its formation. The fluoro derivative reacts with water as well as with acetate ion faster than both the chloro and bromo derivatives by several orders of magnitude. The reaction of hydroxyl ion with 3-nitro-4-halogenobenzenediazonium ion gives 3-nitro-4-halogenophenol.

Aromatic nucleophilic substitution was observed to be catalyzed by bases in many instances. In such cases the experimental bimolecular rate constant k_2 can be expressed by Eq. (*1*) where k' and k'' are the rate constants of the non-catalyzed and catalyzed reactions respectively, and [B]

$$k_2 = k' + k''[\mathrm{B}]\,, \qquad (1)$$

stands for the base concentration. Bunnett[1] classified these base catalyzed nucleophilic aromatic substitutions into two groups according to the ratio k''/k'. The first category comprises those reactions where the displaced group splits off with a relative difficulty, and the decomposition of the intermediate formed into products is the rate-determining step. In these cases an addition of base accelerates the reaction considerably; the ratio k''/k' is often greater than $50\ \mathrm{l\ mol^{-1}}$. The value of k'' depends on the base stregth, and a good linear dependence between $\log k''$ and $\mathrm{p}K_\mathrm{a}$ of the conjugate acids of the catalysts is usually obtained. The second group comprises such reactions whose rate-determining step is the intermediate formation. The base addition accelerates the substitution reaction to a small extent, and the value of k'' does not usually depend on the $\mathrm{p}K_\mathrm{a}$ value of the corresponding conjugate acids. Nitro compounds and anions of carboxylic acids have usually comparative catalytic effects as amines or hydroxyl ion. The ability to bind the proton (by a hydrogen bond) and thus to stabilize the activated complex is decisive.

No cases of any strong facilitation of the intermediate formation by an addition of base during nucleophilic aromatic substitution have been reported in literature so far, although a number of such cases has been described concerning ester hydrolysis and further similar reactions[2] which also have an addition-elimination mechanism. Catalytic action of bases can take two courses in these cases (Scheme 1). The first case represents a so called nucleophilic catalysis where RCO_2^- reacts as a nucleophilic reagent. The second case represents a general base catalysis, where RCO_2^- behaves as a base and forms a bond to the proton of water in the moment of the attack of the aromatic nucleus by the water molecule. Nucleophilic catalysis makes itself felt in the case when the displaced group splits off of the intermediate formed more easily than the attacking nucleophilic reagent[2-4]. Base catalysis, as a rule, is significant in reactions with weak nucleophiles[5]. Aqueous buffer solutions are especially useful as a reaction medium for a study of such reactions.

Most aromatic nucleophilic substitution reactions were studied in non-aqueous media using relatively strong nucleophiles as amines and alkoxide ions because of the low reactivity of the substrates used. If a diazonium group is used as one of the activating groups of the substrate, the reactivity as well as the water solubility are increased so that the reaction can be studied under the conditions suitable for ascertaining base catalysis. Although the substitution of halogen, sulfonic acid group, nitro group or hydroxyl in aromatic diazonium ions belongs to important reactions of azo chemistry (*e.g.* the preparation of metal complexes of azo dyes[6]), these reactions have not yet been studied kinetically.

In the present paper we have focussed our attention on a study of base catalyzed substitutions of halogen by an OH group in aqueous solutions of 3-nitro-4-halogenobenzenediazonium ions.

EXPERIMENTAL

Reagents

3-*Nitro*-4-*fluoroaniline* (m.p. 96·5–97·5°C, ref.[7] 98°C), 3-*nitro*-4-*chloroaniline* (m.p. 101·5 to 103°C, ref.[8] 102·5–103°C), and 3-*nitro*-4-*bromoaniline* (m.p. 128·5–129·5°C, ref.[9] 131–132°C) were prepared by nitration of the respective 4-haloanilines with fuming nitric acid in concentrated sulphuric acid[10]; they were purified by crystallizations from aqueous ethanol.

2-*Nitro*-4-*diazophenol* was prepared by the decomposition of 3-nitro-4-chlorobenzenediazonium ion in acetate buffer[10]. The raw product was recrystallized from aqueous acetic acid and its identity was verified by the melting point of the corresponding azo dyestuff with 2-naphthol (m.p. 216–218°C; ref.[10] 216°C).

3-*Nitro*-4-*chlorophenol* was prepared by nitration of O,N-diacetyl-*p*-aminophenol, subsequent deacetylation, diazotization, and substitution of the diazo group by chlorine by the action of cuprous chloride. The use of copper powder as it is given in the original prescription[11] led to considerably lower yields. After a crystallization from diluted hydrochloric acid the product melted at 125·5–127°C (ref.[11] 127°C).

3-*Nitro*-4-*chloro*- and 3-*nitro*-4-*bromoanilines* were diazotized in a usual way[12].

3-*Nitro*-4-*fluorobenzenediazonium* ion changed quickly into 2-nitro-4-diazophenol in aqueous solutions. Therefore, the following procedure was used for diazotization of 3-amino-4-fluoroaniline: 0·0173 g ($2·5 . 10^{-4}$ mol) sodium nitrite was dissolved in 0·5 ml 65% H_2SO_4 and 2 ml 100% CH_3CO_2H. 0·039 g ($2·5 . 10^{-4}$ mol) 3-nitro-4-fluoroaniline was added to this cold mixture with stirring. The diazotization was finished after about 15 minutes and the solution of the diazonium salt was adjusted at 50 ml with 100% CH_3CO_2H. The solution of 5 . 10^{-3} mol/l diazonium salt prepared in this way contained about 20% 2-nitro-4-diazophenol after several days standing in a refrigerator.

Kinetic Measurements

All the kinetic measurements were carried out at 20°C and ionic strength 0·5. In the case of 3-nitro-4-chloro- and 3-nitro-4-bromobenzenediazonium ions, either their decrease was measured by a coupling with an excess of 1,8-dihydroxynaphthalene-3,6-disulfonic acid (Lachema), or the decrease of the diazonium ion and simultaneously the increase of 2-nitro-4-diazophenol by recording UV spectra at definite time intervals. In the case of ascertaining the decrease of diazonium ion by coupling with 1,8-dihydroxynaphthalene-3,6-disulfonic acid solution, 2·5 ml 5 . 10^{-3}M diazonium salt solution was added to 250 ml buffer solution having a certain concentration and the ionic strength adjusted at 0·5 by addition of 1M-KCl. 20 ml samples were withdrawn from the reaction mixture at definite time intervals and added into 50 ml calibrated flasks containing each 5 ml 5 . 10^{-3}M 1,8-dihydroxynaphthalene-3,6-disulfonic acid solution. After acidification with 5 ml 2·5M-HCl and adjusting at 50 ml volume the extinction of the dyestuff formed was measured at λ 505 nm using a spectrophotometer Zeiss VSU-2P (Zeiss, Jena). The rate constants were evaluated graphically according to Eq. (*2*) where E_t and E_∞ are the extinctions of the sample withdrawn at a time t and $t = \infty$ respectively.

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

The fast reaction of 3-nitro-4-chlorobenzenediazonium ion in borax buffers was followed by a method described below in connection with the fluoro derivative.

The diazonium ion decrease and the 2-nitro-4-diazophenol increase were followed simultaneously using a recording spectrophotometer Unicam SP-800 at 20°C. To 50 ml buffer solution having ionic strength 0·5 a sufficient amount of diazonium salt solution was added to make the final concentration 5 . 10^{-4} mol/l. After mixing, a part of the reaction solution was transferred into a 1 cm quartz sample cell located in a thermostated cell-holder of the spectrophotometer. The same solution without the diazonium salt was placed in the reference cell. At definite time intervals the spectra were recorded in the range of wavelengths 220—500 nm. The rate constants were calculated graphically from the extinctions read at the λ_{max} of the diazonium ion (278 and 289 nm for the chloro and bromo derivatives respectively) according to Eq. (*2*), as well as from those read at the λ_{max} of 2-nitro-4-diazophenol according to Eq. (*3*), where E_t and E_∞ are the extinctions of samples at a time t and $t = \infty$ respectively.

$$kt = -2{\cdot}303 \log (E_\infty - E_t) + \text{const.} \qquad (3)$$

A formation of an intermediate having λ_{max} 420 nm was observed spectroscopically when using the buffer pyridine–pyridinium chloride. The time dependence of the extinction at this wavelength was measured using the spectrophotometer Zeiss VSU-2P (Zeiss, Jena) at 20°C. The reaction solutions were prepared in the same way as those for the measurements with the use of the Unicam SP-800 apparatus.

The increase of 2-nitro-4-diazophenol during the decomposition of 3-nitro-4-fluorobenzenediazonium ion in diluted solutions of sulphuric acid was followed using the Unicam SP-800 apparatus by measuring the extinction in the range of λ_{max} of 2-nitro-4-diazophenol. The rate constant was calculated from Eq. (*3*). The determination of the decrease of 3-nitro-4-fluorobenzenediazonium ion in the buffer solutions of secondary and tertiary phosphates was carried out by coupling with 1,8-dihydroxynaphthalene-3,6-disulfonic acid as it is described in the case of 3-nitro-4-chloro- and 3-nitro-4-bromobenzenediazonium ions. For the buffer solutions in which the decrease was too fast (the half-life less than 1 minute) a different procedure was adopted: 0·5 ml 5 . 10^{-3}M diazonium salt solution was injected from a syringe into 50 ml thermostated buffer solution with stirring. The buffers used contained enough sodium hydroxide to neutralize the acetic acid used for the diazonium salt preparation. After a definite time interval the amount of the unreacted diazonium ion was determined by injecting 5 ml 5 . 10^{-3}M 1,8-dihydroxynaphthalene-3,6-disulfonic acid solution. After acidification with 5 ml 2·5M-HCl and adjusting at 100 ml the extinction was measured at λ 505 nm. About ten experiments with different time intervals were carried out to determine one rate constant. The Eq. (*2*) was used for calculation.

Two methods were used for decomposition rate determination of 2-nitro-4-diazophenol in phosphate and borax buffers. The slow reactions in borax (pH 9·1) were followed by direct measurement of the time dependence of the extinction decrease of 2-nitro-4-diazophenol using the VSU-2P apparatus (Zeiss, Jena) at 330 nm. For the fast reactions in phosphate buffer (pH 11·5) the abovementioned method using the syringe was modified: at definite time intervals the reaction was stopped by injecting 5 ml 4M-CH_3CO_2H, and the extinction of the samples was measured at λ 330 nm. An aqueous stock solution of 2 . 10^{-4} mol/l 2-nitro-4-diazophenol was prepared for these experiments.

For the pK_a determination the spectra of 5 . 10^{-4}M 2-nitro-4-diazophenol solution in 0·4 to 5·2M-H_2SO_4 were measured. As a shift of the spectra occured at higher sulphuric acid concentrations, the spectral lines were modified in such a way that they passed through the isosbestic point before the extinction reading. From the extinctions at λ 330 nm the pK_a was calculated according to Eq. (*4*) where E_A, E_{HA^+} and E are the extinction of 2-nitro-4-diazophenol in acetate buffer, that of the protonated 2-nitro-4-diazophenol in 5·2M-H_2SO_4, and that at the given H_0 respectively. The concentration of sulphuric acid in the samples was determined titrimetrically with 1M-NaOH using phenolphthalein as indicator, and the corresponding H_0 values were taken from the literature[13]. The pH values of the other reaction solutions were measured at 20°C after finishing each experiment, using a PHM 4c apparatus (Radiometer, Copenhagen) with a glass and a saturated calomel electrodes.

$$\mathrm{p}K_a = H_0 + \log\left((E_A - E)/(E - E_{HA^+})\right) . \qquad (4)$$

The amount of 2-nitro-4-diazophenol formed during the kinetic experiments was determined by measuring the samples extinctions at the respective λ_{max} 330 nm. The extinction coefficient of the aqueous 2-nitro-4-diazophenol solution at the abovementioned wavelength was calculated from the extinction of its solutions having precisely known concentrations.

The amount of 3-nitro-4-diazophenol formed in the reaction of 3-nitro-4-chlorobenzenediazonium ion with aqueous solution of phosphate buffer was determined as follows: 10 ml 5 . 10^{-3}M diazonium salt solution was added to 500 ml buffer solution containing the same amount of phosphates and potassium chloride as in the kinetic experiments. After the end of reaction the mixture was acidified at pH about 4 and extracted three times with 20 ml ether. Ether solutions were extracted with 0·1M-NaOH several times. The phosphate buffer containing a known amount of 3-nitro-4-chlorophenol was worked up in a quite analogous way. Spectra of the hydroxide extracts had the same character in the both cases. The amount of the phenol formed was calculated from the extinctions measured at λ 395 nm which is the λ_{max} of 3-nitro-4-chlorophenolate ion.

RESULTS

3-Nitro-4-chloro- and 3-nitro-4-bromobenzenediazonium ions are converted into 2-nitro-4-diazophenol slowly in diluted hydrochloric acid (pH 1). The reaction is of the first order with respect to the diazonium ion. All the spectral records of the kinetic experiments show clear isosbestic points. The reaction half-life of the chloroderivative is 96 hours in 0·1M-HCl at 20°C. As the diazonium salts (and especially 2-nitro-4-diazophenol) are sensitive towards light, the samples of kinetic experiments had to be kept in dark. Daylight caused a decomposition of 2-nitro-4-diazophenol giving the substances which were not identified. This decomposition is practically of the first order with respect to 2-nitro-4-diazophenol. The half-life of the reaction in an experiment where the decomposition was followed by means of coupling with resorcinol was about 1 hour.

The conversion of the diazonium ion into 2-nitro-4-diazophenol is accelerated by addition of bases, In the presence of monoacid anions of chloroacetic, acetic, trichloroacetic, citric, and phosphoric acids (pH $< 5·3$) the reaction proceeds as pseudo-

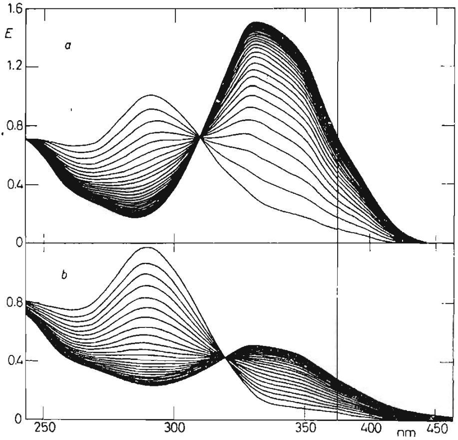

Fig. 1

Spectral Record of the Reaction of 3-Nitro-4-bromobenzenediazonium Ion at 20°C and Ionic Strength 0·5

a With acetate buffer (pH 5·3; [acetate] 0·5M; [diazonium ion] $8·5 . 10^{-5}$M; Δt 5 min); *b* with phosphate buffer (pH 6·29; [HPO_4^{2-}] 0·1M; [diazonium ion] $1 . 10^{-4}$M; Δt 2·5 min).

monomolecular. The spectral records show an isobestic point and 2-nitro-4-diazophenol is the only reaction product (Fig. 1*a*). The reaction rate is of the first order with respect to the anion of the acid, and it is independent of pH. At higher pH values hydroxyl ion began to make itself felt kinetically, too. The reaction was pseudomonomolecular again and the experimental rate constant k involved the rate constants of reactions with water, OH^-, and base (Eq. (5)).

$$k = k_{H_2O} + k_B[B] + k_{OH^-}[OH^-]\,. \tag{5}$$

The rate constants k_B were calculated from the angular coefficients of the straight lines obtained by plotting k against the base concentration at a constant pH. The intercept at the y-axis corresponded to $k_{OH^-}[OH^-]$. In this way the constants k_{OH^-} and k_B were determined at two different pH values in buffers of primary and secondary phosphates (Fig. 2). The rate constants calculated are summarized in Tables I and II. The proportion of 2-nitro-4-diazophenol among the reaction products decreased with increasing pH value (Fig. 1*b*). The amount of the 2-nitro-4-diazo-

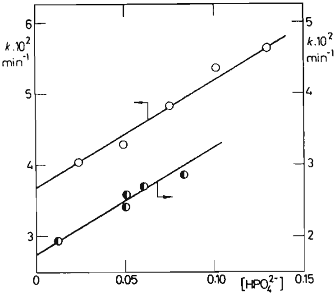

FIG. 2

Dependence of Experimental Rate Constant k on Concentration of HPO_4^{2-} at 20°C and Ionic Strength 0·5

pH 6·6 (○), 6·2 (◐).

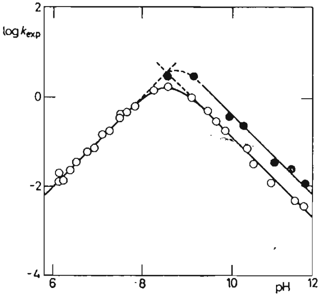

FIG. 3

pH Dependence of $\log k_{exp}$ for Reaction of 3-Nitro-4-chlorobenzenediazonium Ion with OH^- (○) and 3-Nitro-4-fluorobenzenediazonium Ion with OH^- (●) at 20°C and Ionic Strength 0·5

Full line was calculated from the equation $k_{exp} = k_{OH} - c[OH^-]/(1 + K[OH^-]^2)$, where c is the total diazonium ion concentration and $K = [ArN_2O^-]/([ArN_2^+][OH^-]^2 = 8 \,.\, 10^{10}$.

TABLE I

Rate Constants of Reactions of 3-Nitro-4-chlorobenzenediazonium Ion with Bases at 20°C and Ionic Strength 0·5

Base	pH	k, min^{-1}	[B], $\mathrm{mol\ l}^{-1}$	k_B, $\mathrm{l\ mol}^{-1}\ \mathrm{min}^{-1}$	K_a	2-Nitro-4-diazo-phenol, %	
						found	calculated
Water	1·075	1·20 . 10^{-4}	55·5	(2·28 ± 0·17) . 10^{-6}	55·5[a]	—	—
	1·254	1·33 . 10^{-4}	55·5				
Trichloroacetate	1·285	4·05 . 10^{-4}	0·5	(8·12 ± 0·82) . 10^{-4}	3·03 . 10^{-1}[b]	—	—
Chloroacetate	3·399	6·70 . 10^{-3}	0·5	(1·45 ± 0·14) . 10^{-2}	1·36 . 10^{-3}[a]	—	—
	3·942	7·70 . 10^{-3}	0·5				
Citrate	3·395	2·77 . 10^{-2}	0·5	(4·88 ± 0·78) . 10^{-2}	7·21 . 10^{-4}[c]	—	—
	3·413	1·27 . 10^{-2}	0·3				
o-Chlorobenzoate	4·315	3·33 . 10^{-2}	0·1	(6·66 ± 0·72) . 10^{-2}[d]	1·24 . 10^{-3}[c]	20·0	—
Acetate	4·605	3·82 . 10^{-2}	0·5	(7·71 ± 0·10) . 10^{-2}	1·75 . 10^{-5}[a]	—	—
	5·302	3·89 . 10^{-2}	0·5			—	—
Primary phosphate	2·890	4·97 . 10^{-4}	0·5	(9·94 ± 0·95) . 10^{-4}	7·46 . 10^{-3}[e]	—	—
Secondary phosphate	6·157	2·58 . 10^{-2}	0·05	(1·52 ± 0·15) . 10^{-1}	6·20 . 10^{-8}[a]	34·1	33·2
	6·188	1·93 . 10^{-2}	0·012			11·9	19·8
	6·190	2·31 . 10^{-2}	0·04	(9·97 ± 0·95) . 10^{5}[f]		26·4	29·3
	6·195	2·40 . 10^{-2}	0·05			29·1	30·6
	6·214	2·68 . 10^{-2}	0·06			36·5	35·5
	6·245	2·85 . 10^{-2}	0·083			40·3	42·8

TABLE I
(Continued)

Base	pH	k, min^{-1}	[B], mol l^{-1}	k_B, l mol^{-1} min^{-1}	K_a	2-Nitro-4-diazophenol, %	
						found	calculated
	6·392	3·11 . 10^{-2}	0·025			20·1	20·8
	6·585	4·20 . 10^{-2}	0·012			11·9	15·0
	6·589	4·38 . 10^{-2}	0·024			15·5	18·5
	6·600	5·09 . 10^{-2}	0·075			27·3	25·9
	6·613	5·33 . 10^{-2}	0·10			30·6	33·0
	6·615	5·73 . 10^{-2}	0·13			35·3	35·6
	6·775	6·83 . 10^{-2}	0·10			28·5	29·4
	7·210	2·07 . 10^{-1}	0·05			18·4	21·7
	7·524	4·01 . 10^{-1}	0·05			11·3	16·5
Borate	7·571	3·55 . 10^{-1}	—	(9·41 ± 1·00) . 10^{5}[f]	6·20 . 10^{-10}[a]	—	—
	7·675	5·23 . 10^{-1}	—			—	—
	7·829	6·32 . 10^{-1}	—			—	—
	8·165	1·249	—			—	—
	8·265	1·445	—			—	—
	8·571	1·690	—			—	—
	9·090	9·97 . 10^{-1}	—			—	—
	9·455	4·88 . 10^{-1}	—			—	—
	9·850	1·70 . 10^{-1}	—			—	—

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[a] Ref.[23]. [b] ref.[24]. [c] ref.[25]. [d] The rate constant k given was calculated from k_{exp} and the amount of 2-nitro-4-diazophenol formed (20%). [e] ref.[26] [f] k_{OH^-}.

phenol formed depends on the relative rates of the reactions of the diazonium ion with the base and OH^- according to Eq. (6). D_{max} is the maximum amount of 2-nitro-

$$D/D_{max} = k_B[B]/(k_B[B] + k_{OH^-}[OH^-])\,, \qquad (6)$$

4-diazophenol which could be formed if it were not for the reaction with OH^-, D is the 2-nitro-4-diazophenol amount formed during the given kinetic experiment. In the case of the 3-nitro-4-chlorobenzenediazonium ion the log k_{exp} value increased with increasing OH^- concentration till pH 8·5, and then decreased again (Fig. 3).

TABLE II

Rate Constants of Reactions of 3-Nitro-4-bromobenzenediazonium Ion with Bases at 20°C and Ionic Strength 0·5

Base	pH	k, min^{-1}	[B], mol/l	k_B, $l\ mol^{-1}\ min^{-1}$
Chloroacetate	3·683	$3·89 . 10^{-3}$	0·4	$(1·04 \pm 0·09) . 10^{-2}$
	3·699	$2·28 . 10^{-3}$	0·2	
	3·732	$4·98 . 10^{-3}$	0·5	
Citrate	3·300	$5·59 . 10^{-3}$	0·2	$(2·62 \pm 0·27) . 10^{-2}$
	3·342	$7·92 . 10^{-3}$	0·3	
	3·350	$1·02 . 10^{-2}$	0·4	
	3·362	$1·50 . 10^{-2}$	0·5	
	3·382	$1·13 . 10^{-2}$	0·5	
o-Chlorobenzoate[a]	4·275	$1·54 . 10^{-3}$	0·2	$(7·61 \pm 0·13) . 10^{-4}$
	4·755	$7·51 . 10^{-4}$	0·1	
Acetate	4·302	$2·61 . 10^{-2}$	0·5	$(5·53 \pm 0·39) . 10^{-2}$
	4·590	$5·87 . 10^{-3}$	0·1	
	4·600	$1·09 . 10^{-2}$	0·2	
	4·610	$2·08 . 10^{-2}$	0·4	
	4·625	$2·72 . 10^{-2}$	0·5	
	5·295	$3·12 . 10^{-2}$	0·5	
	5·312	$2·64 . 10^{-2}$	0·5	
Primary phthalate[b]	3·650	$4·51 . 10^{-3}$	0·3	$(1·20 \pm 0·25) . 10^{-2}$
	3·612	$3·90 . 10^{-3}$	0·3	
	3·700	$3·72 . 10^{-3}$	0·3	
	4·005	$8·03 . 10^{-4}$	0·1	
	4·075	$2·30 . 10^{-3}$	0·2	
Secondary phosphate	6·202	$2·77 . 10^{-2}$	0·05	
	6·270	$4·62 . 10^{-2}$	0·1	
	6·343	$5·25 . 10^{-2}$	0·1	

[a] k was calculated from k_{exp} and the amount of 2-nitro-4-diazophenol formed (20%). [b] k was calculated from k_{exp} and the amount of 2-nitro-4-diazophenol formed (17%).

In the ranges pH < 7·8 and pH > 9·2 the dependence is linear with angular coefficients +1 and −1 respectively. In the case of the reaction of 3-nitro-4-chlorobenzenediazonium ion in phosphate buffer (pH 6·9; HPO_4^{2-} concentration = 0·08 mol/l.) the amount of the products formed was determined: 65% 3-nitro-4-chlorophenol and 11% 2-nitro-4-diazophenol were found. Besides that an azo dyestuff was found chromatographically, but its amount and structure were not determined. The presence of the supposed reduction product of the reaction (*o*-nitrochlorobenzene) could not be proved reliably among the reaction products.

A very small amount of 2-nitro-4-diazophenol was formed in the buffers *o*-chlorobenzoic acid–sodium *o*-chlorobenzoate and phthalic acid–primary sodium phthalate. The experiments were less reproducible especially with phthalic acid. In the both cases the rate constant k_B was calculated from the experimental pseudomonomolecular rate constant k and the amount of the 2-nitro-4-diazophenol formed. The calculation was carried out under an assumption that k is composed of the rate constant k_B of the reaction producing 2-nitro-4-diazophenol and of the rate constant of reaction leading to formation of other products.

A fast formation of the intermediate was observed in the buffer pyridine–pyridinium chloride. The concentration of this intermediate reached its maximum value at a time t = 3·4 minutes (Fig. 4) when using the concentrations of pyridine and its hydro-

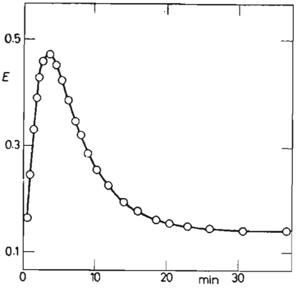


FIG. 4

Time Dependence of Extinction of Reaction Solution at λ_{max} of the Intermediate (420nm) during the Reaction of 3-Nitro-4-chlorobenzenediazonium Ion with Buffer Pyridine (0·025M)–Pyridinium Chloride (0·050M) at 20°C and Ionic Strength 0·5

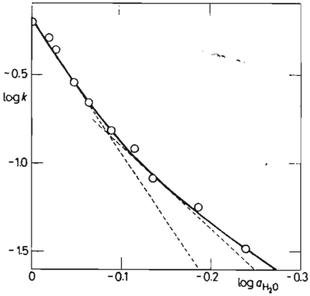


FIG. 5

Dependence of log k *vs* log a_{H_2O} during the Reaction of 3-Nitro-4-fluorobenzenediazonium Ion with Water in Diluted H_2SO_4 Solutions (0·4—5·2M) at 20°C chloride 0·025 and 0·050 mol/l respectively. The pseudomonomolecular rate constant $k = 0{\cdot}46\ \text{min}^{-1}$ of the intermediate formation was obtained from the time dependence of the extinction of 3-nitro-4-chlorobenzenediazonium ion (at λ 278 nm) and the pseudomonomolecular rate constant $k_2 = 0{\cdot}17\ \text{min}^{-1}$ of the intermediate decomposition was calculated from Eq. (7) [14].

$$t_{\max} = (1/(k_2 - k_1)) \ln (k_2/k_1) \,. \tag{7}$$

TABLE III

Rate Constants of Reactions of 3-Nitro-4-fluorobenzenediazonium Ion with Bases at 20°C and Ionic Strength 0·5

Base	pH	k, min^{-1}	k_{corr},[a] min^{-1}	[B] mol/l	k_B $\text{l mol}^{-1}\,\text{min}^{-1}$
Water	1·375	6·93 . 10^{-1}	—	55·5	(1·24 ± 0·18) . 10^{-2}
	2·178	6·66 . 10^{-1}	—	55·5	
	2·575	6·30 . 10^{-1}	—	55·5	
	2·575	7·70 . 10^{-1}	—	55·5	
Acetate	4·557	9·30 . 10^{-1}	2·41 . 10^{-1}	8·2 . 10^{-2}	(3·27 ± 0·61) .
	4·645	1·331	6·42 . 10^{-1}	2·47 . 10^{-1}	
	4·678	1·385	6·96 . 10^{-1}	1·77 . 10^{-1}	
	4·607	2·303	1·614	4·86 . 10^{-1}	
	5·312	2·008	1·32	5·01 . 10^{-1}	
	5·054	1·304	3·45 . 10^{-1}	1·20 . 10^{-1}	
	5·520	1·307	6·18 . 10^{-1}	1·46 . 10^{-1}	
	5·324	1·523	8·34 . 10^{-1}	2·92 . 10^{-1}	
Secondary phosphate[b]	6·231	1·100	—	2·70 . 10^{-2}	—
	6·255	1·320	—	6·50 . 10^{-2}	
	6·265	1·283	—	4·75 . 10^{-2}	
	6·304	1·170	—	7·05 . 10^{-2}	
Borate	7·005	1·165	(2·28±2·5) . 10^{-1}	—	—
	8·535	3·150	2·875	—	
	9·146	3·225	3·010	—	
	10·271	2·22 . 10^{-1}	2·21 . 10^{-1}	—	
Tertiary phosphate	9·921	3·96 . 10^{-1}	3·91 . 10^{-1}	—	—
	10·965	3·26 . 10^{-2}	3·26 . 10^{-2}	—	
	11·334	2·35 . 10^{-2}	2·35 . 10^{-2}	—	
	11·646	1·10 . 10^{-2}	1·10 . 10^{-2}	—	

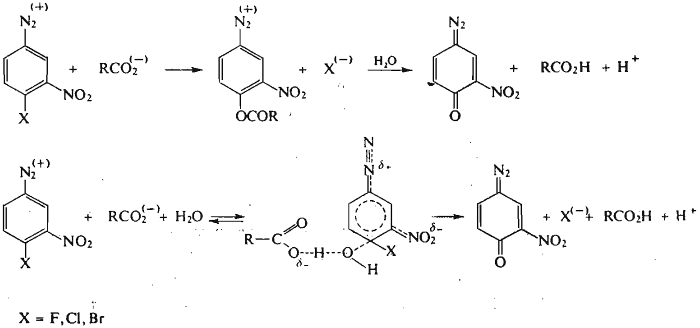
[a] k_{corr} is the rate constant k obtained from k_{exp} by subtracting k_{H_2O} eventually k_{AcO}-[AcO$^-$] (in phosphate and borax buffers). [b] k was calculated from the linear section of the dependence log E *vs* t (see the text).

The calculated concentration of the intermediate at the time t_{max} represents about 55% of the initial diazonium ion concentration. When using a half concentration of the buffer pyridine–pyridinium chloride (ionic strength 0·5) the time t_{max} necessary for reaching the maximum intermediate concentration was approximately twofold. This points to a fact that the intermediate decomposition is catalyzed by pyridine in such a way that the intermediate formation as well as its decomposition are reactions of the first order with respect to pyridine concentration.

The conversion of 3-nitro-4-fluorobenzenediazonium ion into 2-nitro-4-diazophenol was practically quantitative in acetate buffer, in water (pH 2), as well as in diluted sulphuric acid medium (0·4 – 5·2M-H_2SO_4), and the respective reactions were of the first order in the whole range studied. In the solutions of diluted sulphuric acid the reaction rate constant decreased with decreasing water activity (Fig. 5). In acetate buffers the reaction rate increased with increasing base concentration. The dependence of k on the base concentration was linear and the rate constant k_B was calculated from the angular coefficient. The yield of 2-nitro-4-diazophenol was practically quantitative in buffers primary – secondary phosphates, too. At the beginning the dependence of log E *vs* t was, however, much steeper than it would correspond to the rate constant of a reaction catalyzed by phosphate ion, and it became linear only after more than 50% conversion of the diazonium ion (Fig. 6). A similar anomaly was observed in some experiments in buffers secondary – tertiary phosphate (but to a substantially smaller extent only). In borax buffers the dependence log E *vs* t was linear again, and the influence of pH on the reaction rate began to make itself felt (Table III). The maximum velocity was reached in the range of pH 8·5 – 9. Above pH ~9·2 the dependence log k_{exp} *vs* pH is linear, the slope being −1, similarly as with 3-nitro-4-chlorobenzenediazonium ion (Fig. 3). The amount of the 2-nitro-4-diazophenol formed was determined in the borax buffers, too, and it was within 25 – 60%. The accurate amount of 2-nitro-4-diazophenol can be determined only with difficulty in this medium, because of its subsequent decomposition reactions taking place at higher pH values, and from Fig. 7 it can be seen that the time dependence of 2-nitro-4-diazophenol extinction has a shape characteristic for autocatalyzed reactions.

DISCUSSION

The rate of conversion of 3-nitro-4-halogenobenzenediazonium ion into 2-nitro-4-diazophenol is independent of pH and it is of the first order with respect to the base concentration. The value of the rate constant k_B depends on the base strength. Two reaction mechanisms can be considered for the catalytic action of bases in these cases (Scheme 1). When the intermediate decomposition into products is much faster than its formation, the both mechanisms are indistinguishable kinetically. In all the cases studied by us the reaction took a pseudomonomolecular course execept for the raction in the presence of pyridine and phosphate buffer (in the case of the fluoro derivative). An isosbestic point was observed in the spectral records which points to a fast decomposition of the intermediate eventually formed into the product (it is thus present at a concentration not perceptible spectrophotometrically).



SCHEME 1

In the case of acetate ion it is possible to calculate, from the available data, the decomposition velocity of the intermediate formed. Gold[4] measured the hydrolysis velocity of substituted phenylacetates in the presence of acetate ions. He ascertained that a nucleophilic catalysis by acetate ion operated in the hydrolysis of nitroderivatives, and that a roughly linear relation held between pK_a of the phenol formed and $\log k$ of the hydrolysis. On the basis of this relation and the pK_a value determined for 2-nitro-4-diazophenol (pK_a −0·273) we have calculated that the rate constant of the intermediate decomposition is about 50 l mol^{-1} min^{-1}. This value is greater than the calculated bimolecular rate constant k_B of the acetate catalyzed formation of 2-nitro-4-diazophenol in the case of the chloro resp. bromo derivatives by roughly 3 orders of magnitute, and about 20 times in the case of the fluoro derivative. This means that, in the case of the catalysis by acetate ion, the intermediate would be decomposed far more quickly than it would be formed. In the case of the reaction catalyzed by HPO_4^{2-} there was no sufficient basis available for calculation of the rate of the intermediate formation, but from the literature data[15] it can be supposed that the intermediate decomposition would be substantially faster than its formation at least in the case of chloro and bromo derivatives. If we use the relative tendencies of the halogen and base catalyst to split off from the intermediate formed as one of the criteria for the proposition of reaction mechanism, then nucleophilic catalysis would be preferred in the case of the bromo and chloro derivatives, whereas a borderline case[16] could operate in the case of the fluoro derivative. The intermediate formation observed spectroscopically in the reaction with pyridine is a further confirmation of the nucleophilic catalysis in the case of chloro resp. bromo derivatives. A far slower intermediate decomposition than in the previous cases is caused probably by the fact that the intermediate formed in the reaction with pyridine is attacked by the nucleophilic reagent at an aromatic carbon atom whereas the intermediate formed in the reaction with carboxylate ion is attacked at carbonyl carbon atom. In the case of generally base catalyzed reactions the Brönstedt relation is fulfilled relatively well even when the bases of different types are compared. On the other hand, in the case of nucleophilic catalysis differences of as much as several orders of magnitude often appear[2] between the rate constants of bases of comparable strength. *E.g.* pyridine is a 4× more effective catalyst than acetate ion during generally base catalyzed hydrolysis of ethyl dichloroacetate[17], but it is more effective at nucleophilic catalysis of acetanhydride hydrolysis[18] by more than 4 orders of magnitude. Fig. 8 represents the Brönstedt relation between log k_B and pK_a of the respective conjugate acids. The rate constant k_B of pyridine was calculated from the experimental rate constant of the intermediate formation and the pyridine concentration, considering the reaction to be of the first order with respect to pyridine ($k_B = 18{\cdot}4 \text{ l mol}^{-1} \text{ min}^{-1}$).

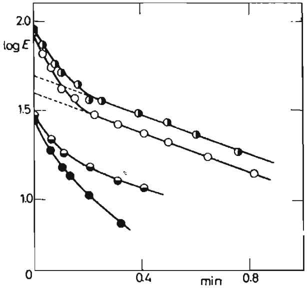


FIG. 6

Time Dependence of log E during the Reaction of 3-Nitro-4-fluorobenzenediazonium Ion with Phosphate Buffers at 20°C and Ionic Strength 0·5

pH 6·55: ⊖ [HPO_4^{2-}] = 0·03M; ● [HPO_4^{2-}] = 0·07M; pH 6·25: ◑ [HPO_4^{2-}] = = 0·05M, ○ [HPO_4^{2-}] = 0·07M.

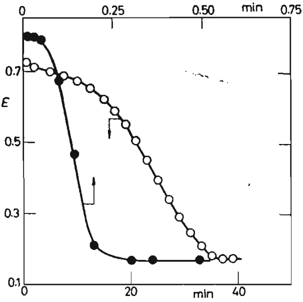


FIG. 7

Time Change of Extinction of 2-Nitro-4-diazophenol (4 . 10^{-5}M) in Phosphate Buffer pH 11·5 (●), Borax Buffer pH 9·1 (○) at λ 330 nm, 20°C and Ionic Strength 0·5

From Fig. 8 it can be seen that the anions of carboxylic acids, being bases of the same type, fulfil the Brönstedt relation relatively well, the slope being $\beta = 0{\cdot}47$. The both phosphates lie on a practically parallel line shifted downwards by a unit. Pyridine on the contrary, reacts more quickly than it should react according to its basicity by 2 orders of magnitude when compared with carboxylic acids. Also the anomalous behaviour of the anion of *o*-chlorobenzoic acid and expecially that of monoanion of phthalic acid rather point to a nucleophilic catalysis.

The reaction rate of the fluoro derivative with water is greater than that of the chloro resp. bromo derivatives by almost 4 orders of magnitude, the corresponding difference of the reactions with acetate ion being less than 2 orders of magnitude. The acceleration reaching several orders of magnitude in the case of the fluoro derivative points to the fact that, also here, the formation of the Meisenheimer complex and not the splitting off of fluoride ion is the rate-determining step. From the data obtained it cannot, however, be decided unambiguously whether the acetate ion acts in this case as a nucleophil or as a base.

The dependence of log k *vs* log a_{H_2O} is not linear (Fig. 5). The decrease becomes less steep with decreasing water activity. The value of $\Delta \log k / \Delta \log a_{H_2O}$ is about 7·5 and 5 in the concentration ranges of $0-2{\cdot}5\text{M-}H_2SO_4$ and $2{\cdot}5-5{\cdot}2\text{M-}H_2SO_4$ respectively. According to Bunnett[19] this can be interpreted in such a way that the formation of the activated complex necessitates, in average, 7 and 5 water molecules in the abovementioned concentration ranges of sulphuric acid respectively; one water molecule only acts as proper nucleophilic agent, the rest being involved in solvate sphere of the proton formed. The number of the water molecules solvating the proton decreases with increasing concentration of sulphuric acid. According to Robertson[20], the average number of water molecules is 10 in $2\text{M-}H_2SO_4$, whereas

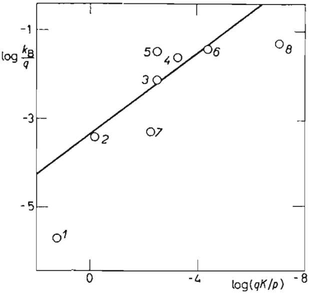


FIG. 8

Dependence of log k of the Conversion of 3-Nitro-4-chlorobenzenediazonium Ion into 2-Nitro-4-diazophenol on the pK_a Values of Catalysts[23] at 20°C and Ionic Strength 0·5

1 Water, *2* trichloroacetate, *3* chloroacetate, *4* citrate, *5* *o*-chlorobenzoate, *6* acetate, *7* primary phosphate, *8* secondary phosphate.

it is only about 7 in 4M-H_2SO_4. In our case the calculated number of water molecules in the conversion of 3-nitro-4-fluorobenzenediazonium ion into 2-nitro-4-diazophenol is lower by about one third in the abovementioned medium. This decrease can be caused by the fact that only 2 protons, which can bind further water molecules, are bound to the positively charged oxygen atom in the activated complex, in contrast to the hydroxonium ion H_3O^+.

In the phosphate buffer the initial decrease of the diazonium ion was many times faster than it would correspond to the catalytic activity of the phosphate anion HPO_4^{2-} (Fig. 6). The dependence obtained could be explained *e.g.* by a fast formation of a complex of the diazonium ion with HPO_4^{2-}, which might either decompose into the original substances or react further to give 2-nitro-4-diazophenol at last. The k values given in Table I for HPO_4^{2-} (calculated from the linear part of the dependence of $\log E$ *vs* t) cannot be compared with those of acetate ion in this case, because the kinetic course of the reaction is different. The value $3 \,.\, 10^3$ l mol^{-1} min^{-1} was estimated for the bimolecular rate constant of the complex formation from the angular coefficient of a tangent constructed to the experimental line at the point $t = 0$. Zollinger[21] described recently a formation of π complexes between *o*- resp. *p*-nitrobenzenediazonium fluoroborates and some naphthalene derivatives. It does not, however, seem very probable that a similar type of π complex was involved in that case, because no marked colour change of the reaction solution could be observed.

In the buffers of primary – secondary phosphates, 3-nitro-4-chloro- and 3-nitro-4-bromobenzenediazonium ions react either with the HPO_4^{2-} catalysis giving 2-nitro-4-diazophenol or with OH^- giving 3-nitro-4-chloro- and 3-nitro-4-bromophenols respectively. The reaction rate with OH^- is directly proportional to the concentrations of the diazonium ion and OH^-. The maximum velocity was attained at pH 8·56 in the case of 3-nitro-4-chlorobenzenediazonium ion. This pH value had to correspond to pH_m (ref.[22]) which means a pH value for which $[ArN_2^+]/[ArN_2O^-] = 1$. Two kinetically indistinguishable mechanisms can be considered for the phenol formation:

$$ArN_2^+ + OH^- \rightleftarrows \text{Meisenheimer complex} \rightarrow ArOH + N_2$$

and

$$ArN_2^+ + OH^- \rightleftarrows ArN_2OH \rightarrow ArOH + N_2 \,.$$

In the first case the reaction would proceed as a nucleophilic aromatic substitution with an intermediate formation of the Meisenheimer complex. In the second case the diazo hydroxide (which would be in equilibrium with the original benzenediazonium ion) would be formed first and then decomposed to give phenol and nitrogen. In our case the second mechanisms seems to be more probable, as we do not see any reason why OH^- should attack preferentially the carbon atom carrying the diazonium group whereas the other nucleophilic reagents attack preferentially the carbon atom bound to the halogen atom. In the case of the fluoro derivative, the competition reaction with OH^- ions leading to the phenol formation makes itself felt at higher pH values only (borax buffers), because fluorine (in contrast to chlorine and bromine) activates the carbon atom to which it is bound, whereas the influence on the reactivity of the diazonium group is similar with all the three substituents. The value pH_m 8·8 estimated for the fluoroderivative is higher than that for the chloro derivative by 0·3 (Fig. 3). This difference is the same as that between *p*-fluoro- and *p*-chlorobenzenediazonium ions[22].

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