166. Nucleophilic Aromatic Substitutions. Part XIV[1]). Investigation of the Mechanism of Hydroxy-denitration of 4,2- and 2,4-Chloronitrobenzenediazonium Ions as a Function of pH

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(16. VI. 81)

Summary

4,2-Chloronitrobenzenediazonium ions in aqueous buffer solutions between pH 2.9 and 7.9 do not hydrolyze by dediazoniation as previous authors have assumed, but by denitration. The isomeric 2,4-compound reacts by denitration (*ca.* 70%) and dechlorination (*ca.* 30%). The reactions are general base catalyzed. The products and kinetics are consistent with an S_NAr-mechanism in which the general base-catalyzed addition of a hydroxyl group at the reacting C-atom is rate-limiting. The rate maxima at or near the pH-values corresponding to $(\mathrm{p}K_1+\mathrm{p}K_2)/2$ of the diazonium $\rightleftarrows$ *cis*-diazotate equilibria can be rationalized on the assumption that the diazonium ion is the only equilibrium form of the diazo compound which enters the substitution proper, and the superposition of rate term $\sum_\mathrm{B} k_\mathrm{B}[\mathrm{B}]$ of all nucleophiles involved (H_2O, OH^- and buffer bases).

1. Introduction. – In nucleophilic aromatic substitution the diazonio group is an interesting substituent for two reasons: *a*) It is one of the best (if not the best) nucleofugial leaving group in substitution by nucleophiles in an S_N1-like[2]) substitution; *b*) It is by far the most activating substituent for nucleophilic aromatic substitutions (S_NAr-type) in the *o*- or *p*-position. This property is due to the strong –*M* and –*I* effect of the diazonio group as exemplified by the *Hammett* substituent constants of $-N_2^+$: $\sigma_m=1.7$; $\sigma_p=2.0$; $\sigma_p^-=3.0$ [3].

Depending on the type and number of substituents in the 2-, 4- and 6-position of benzenediazonium ions and the nature and concentration of a nucleophilic reagent, either dediazoniation (reaction A), or nucleophilic substitution of one of the groups in the 2-, 4- or 6-position (reaction B) will dominate. It is difficult to predict the ratio of the two reactions in a specific case. This is exemplified by two investigations of *Štěrba et al.*: Depending on pH and added buffers, 3-nitro-4-chlorobenzenediazo-

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[1]) Part XIII, see [1].

[2]) It has been shown recently [2] that heterolytic dediazoniations of arenediazonium ions are not classical S_N1-reactions as the formation of the aryl cation is preceeded by a molecule-ion pair.

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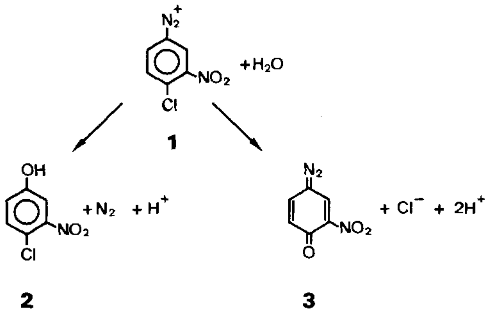
nium ions (**1**) in aqueous solution yields predominantly 3-nitro-4-chlorophenol (**2**) (reaction A) or 4-diazo-2-nitro-2,5-cyclohexadien-1-one (**3**) (reaction B) [4]; under similar conditions with 2,4-dinitrobenzenediazonium ions the nitro group in the 2-position is substituted at pH 2.84 whereas at pH values between 4.05 and 6.02 dediazoniation takes place in addition to denitration [5].



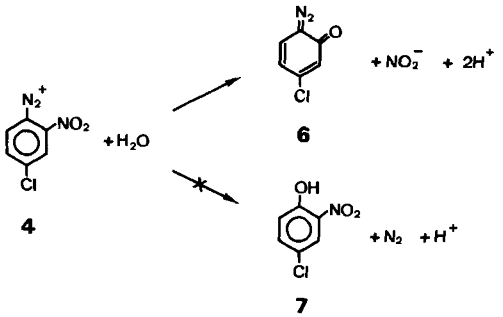
We are interested in reactions of such systems primarily from the point of view of the mechanism of dediazoniations of aromatic diazonium ions under weakly acidic to slightly alkaline conditions. It is known that below *ca.* pH = 2, dediazoniations follow the heterolytic S_N1-like mechanism and that, with increasing pH, the rate increases to a maximum at medium to slightly alkaline pH-values. Under such conditions product ratios and kinetics are very sensitive to various additives and oxygen [6] [7]. CIDNP.-measurements [8] and kinetics indicate strongly that dediazoniation follows a homolytic pathway.

In the elucidation of these mechanisms the search for rate maxima as a function of the hydroxyl-ion concentration would appear to be a potentially fruitful approach. A particularly clear case of such a maximum was reported by *Štěrba et al.* [9] for the reaction of 4-chloro-2-nitrobenzenediazonium ions (**4**) measured in aqueous buffer solutions between pH 2.0 and 8.0 (rate maximum at *ca.* pH 6.5). Without giving details of product analyses the authors mention that 4-chloro-2-nitrophenol is formed.

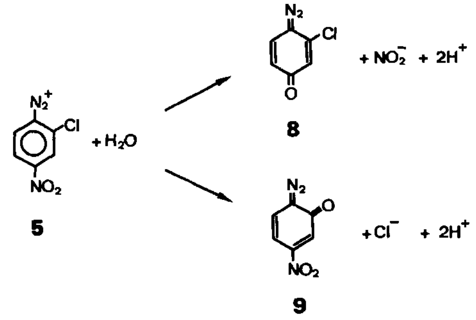
We decided therefore to investigate this reaction in more detail as well as that of the isomeric 2-chloro-4-nitro-benzenediazonium salt (**5**).

2. Results. – 2.1. *Reaction products.* In the hydrolysis of the tetrafluoroborate of 4-chloro-2-nitrobenzenediazonium ions (**4**) in concentrations $[ArN_2^+ \ BF_4^-] \leqslant 5 \times 10^{-4}$ M in various buffer systems (pH 4 to 8, I=0.5, 30°, λ_{max}=305 nm) always the same product with λ_{max}=390 nm is formed in practically constant yield. Above pH 6.5 the formation of *cis*-4-chloro-2-nitrobenzenediazotate in a rapid side equilibrium can be observed (λ_{max}=276 nm) [10a]. The occurrence of the *cis*-diazotate is expected on the basis of the acid-base equilibrium constant $(pK_1 + pK_2)/2 = 7.21 \pm 0.01$ (see exper. part). The product was identified by MS. and by comparison with the product of an independent synthesis as 5-chloro-2-diazo-3,5-cyclohexadien-1-one (**6**). The yield at pH 6.6 is practically quantitative, but is lower at higher pH-values owing to base catalyzed decompositions of **6** and **4**. We were not able to detect the main product 4-chloro-2-nitrophenol (**7**) mentioned by *Štěrba et al.* [9]. In the hydrolysis of **4**

therefore, reaction B (denitration) and not reaction A (dediazoniation) takes place. The diazonium ion **4** is therefore not a suitable candidate for the investigation of the pH-dependence of hydroxy-dediazoniations[3], as we had originally hoped; it is, however, suitable for a study of the mechanism of hydroxy-denitrations[3], a reaction, for which only few comprehensive and unambiguous mechanistic data are available [12]. We decided therefor to elucidate the *mechanism of hydroxy-denitrations of nitrobenzenediazonium ion derivatives* in detail.



Besides the hydrolysis of **4**, we also investigated the isomeric compound 2-chloro-4-nitrobenzenediazonium ion (**5**) under the same conditions. The main product in the hydrolysis of **5** also results from a nucleophilic substitution of the nitro group. The yield of 3-chloro-4-diazo-2,5-cyclohexadien-1-one (**8**) is, however, only *ca.* 70%; 30% 2-diazo-5-nitro-3,5-cyclohexadien-1-one (**9**), *i. e.* the product of a hydroxy-dechlorination is also formed.



2.2. *Kinetics. Štěrba et al.* [9] report a plot of their rate constants for the hydrolysis of **4** as a function of pH at 30°, but give no numerical figures for these constants nor any information on the buffers used. We measured therefore these rates, first in citric acid/phosphate buffers between pH 2.90 and 7.90, then in $H_2PO_4^-/HPO_4^{2-}$, acetate and propionate buffers, always at ionic strength I=0.5. In the first-mentioned buffer we determined also the kinetic orders for the diazonium ion with respect to

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[3] We use in this paper the systematic nomenclature for reactions in organic chemistry, proposed recently by the IUPAC Commission for Physical Organic Chemistry [11].

concentration (n_c) and time (n_t). Under all conditions, the rate constants were determined from the decrease in the concentration of the diazonium ion which was measured spectroscopically at 495 nm by coupling unreacted diazonium ion with 2-hydroxynaphthalene-3,6-disulfonic acid. Some measurements were checked by also measuring the increase in the concentration of the product **6** (λ_{max}=390 nm).

In *Figure 1* the logarithms of the observed first-order rate constants (k_{obs}) are plotted against pH. Full circles (●) correspond to the runs carried out in citric acid/phosphate buffers; the straight lines are based only on these measurements. The other symbols refer to rate constants determined in solutions of the other buffers mentioned and in an pH-stat (see below). With two exceptions all points are mean values of 2 to 4 kinetics runs.

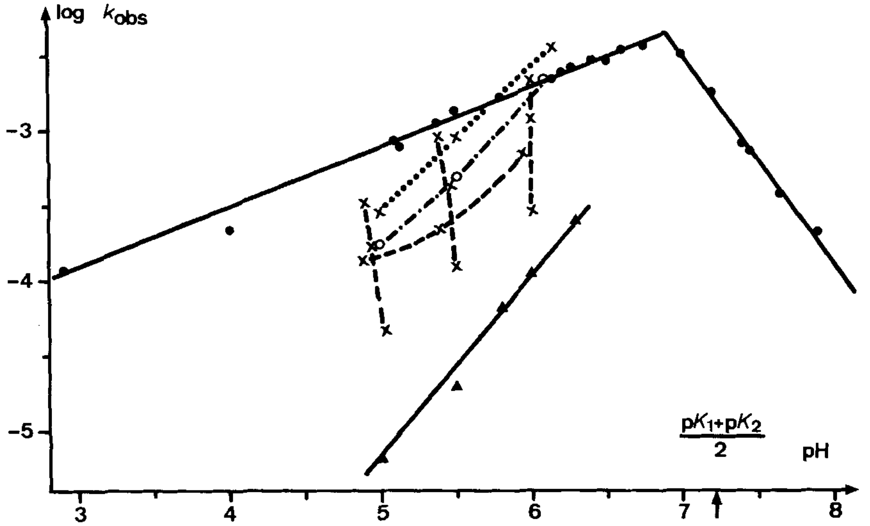


Fig. 1. *Relationship between the logarithms of observed rated constants* (k_{obs}) *of the hydrolysis of 4-chloro-2-nitrobenzenediazonium tetrafluoroborate* (**4**) *and pH of buffer solutions* (I=0.50) *at 30°.*
● Citric acid/phosphate buffer (——); * $H_2PO_4^-/HPO_4^{2-}$ buffer (– – –); ○ AcOH/AcO$^-$ buffer (–·–·); × $CH_3CH_2COOH/CH_3CH_2COO^-$ buffer (.....); ▲ Unbuffered solutions in pH-stat (——). The curves with the designations in parentheses above connect runs of the same buffer series (numerical figures for buffers see exper. part).

These measurements indicate a rate maximum at pH=6.90 ± 0.05. It corresponds roughly to the acid-base equilibrium constant of the diazonium/*cis*-diazotate system, $(pK_1 + pK_2)/2 = 7.21 \pm 0.01$. The difference is outside experimental error. The slopes of the straight lines are 0.41 ± 0.01 (pH 2.90–6.75) and –1.32 ± 0.04 (pH 7.00–7.90).

The rate constants obtained with the other buffers indicate strongly a general base catalysis. We will return to this question in section 3.

The slowest rates were those found in an unbuffered solution in a pH-stat and were determined by measuring the amount of NaOH as a function of time (△ *in Fig. 1*). Such plots correspond to a first-order reaction at pH $\geqslant$ 5.8; those at pH 5.0 and 5.5 are, however, sigmoidal indicating an autocatalytic reaction. For the interpretation of these plots and the calculation of the corresponding k_{obs} values in *Figure 1,* see experimental part.

In the calculation of the kinetic orders n_t and n_c with respect to diazonium ions the methods of *van't Hoff* and *Letort* respectively [13] were used. Below pH 6.5 n_t and n_c are 1 within the experimental limits; they are, however, greater than above pH 6.5. The following values are characteristic:

pH	n_t	n_c
6.0	1.09	1.02
7.0	1.71	1.37
7.9	1.20	1.67

Their interpretation is difficult. A reaction with orders higher than 1 should give $n_t = n_c > 1$; as relatively small concentrations of (unidentified) products besides **6** are formed at pH ≥ 6.5 they might be the cause of autocatalysis ($n_c > n_t$) and/or autoinhibition ($n_t > n_c$). We did not investigate this problem further.

The hydrolysis of 2-chloro-4-nitrobenzenediazonium tetrafluoroborate (**5**), the isomer of **4**, shows very similar kinetics; the rate is three to five times slower than that of **4**. In *Figure 2* the logarithms of the observed rate constants are plotted against the pH-value of citric acid/phosphate buffers.

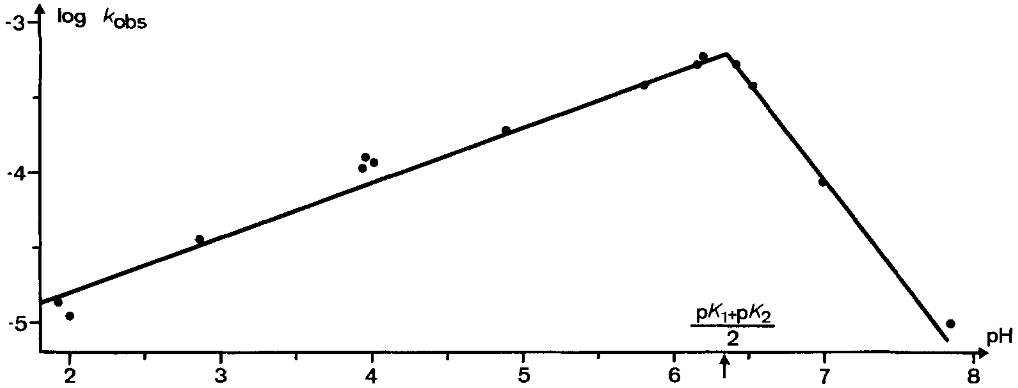


Fig. 2. *Relationship between the logarithms of observed rate constants* (k_{obs}) *of the hydrolysis of 2-chloro-4-nitrobenzenediazonium tetrafluoroborate* (**5**) *and pH of citric acid/phosphate buffers* (I=0.50) *at 30°*

There is a rate maximum at pH = 6.30 ± 0.05. It corresponds within experimental error to the equilibrium constant $(pK_1 + pK_2)/2 = 6.32 \pm 0.05$. The slopes of the straight lines in this *Figure* have the values 0.38 ± 0.02 and –1.19 ± 0.20.

The influence of buffer concentration was determined only in one experiment at pH=6.20. A fivefold increase in buffer concentration gave a 12% increase in rate. The effect of other buffers was not examined.

On the other hand, the influence of a radical scavenger, iodoacetic acid, was tested at pH 6.20 and 7.00. At the lower pH-value, 0.0002 to 0.010 M ICH_2COOH had no influence, but at pH 7.00, 0.0010 M ICH_2COOH decreased the rate constant by 30%.

The hydrolysis of 2-chloro-4-nitrobenzenediazonium ions was not further investigated as the measured rate constants are the sums of the constants of two competitive reactions, namely hydroxy-denitration and hydroxy-dechlorination, forming compounds **8** and **9** respectively.

3. Discussion. – The most important result of hydroxy-denitrations of the two isomeric chloro-nitrobenzenediazonium ions **4** and **5** is the catalysis by various bases. By varying the concentrations of buffer bases and buffer acids in the usual way [10b], one can demonstrate that the rates are first-order with respect to the concentration of the bases OH^-, HPO_4^{2-}, $CH_3CH_2COO^-$ and AcO^- and the catalytic rate constants k_B in the general rate equation 1 can be determined. The logarithms of the constants k_B show a good linear relation with the pK_a-values of the conjugate acids of the bases mentioned above *(Fig. 3);* they obey therefore the *Brönsted* relationship for *general* base catalysis. The slope in *Figure 3* corresponds to $\beta = 0.61 \pm 0.05$ in the *Brönsted* equation.

$$-\frac{d[ArN_2^+]}{dt} = k_{obs}[ArN_2^+] = \sum_B k_B[B][ArN_2^+] \qquad (1)$$

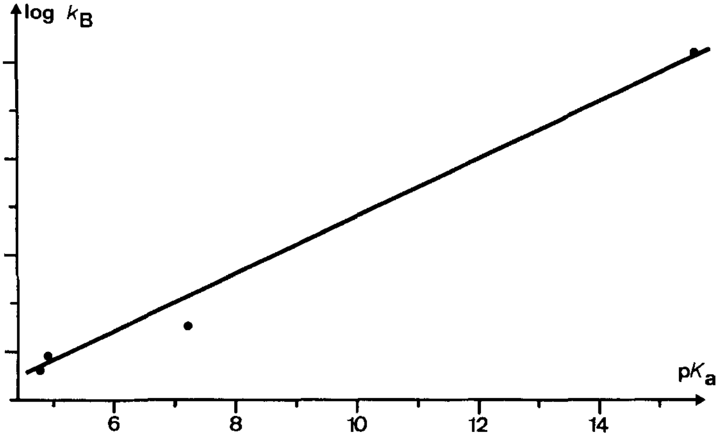
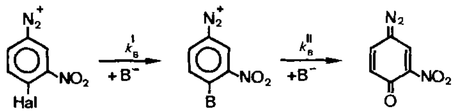


Fig. 3. Brönsted *relationship for the general base catalysis of the hydrolysis of 4-chloro-2-nitrobenzenediazonium ions* (**4**) *by* OH^-, HPO_4^{2-}, $CH_3CH_2COO^-$ *and* AcO^-.

The general base catalysis is compatible with either a rate-limiting proton transfer or with a nucleophilic catalysis, but hardly with the specific catalysis proposed by *Izzo* [14] for the methoxy-denitration of 1,3,5-trinitrobenzene in methanol/water mixtures in the presence of hydrogen carbonate. With *Izzo*'s mechanism one would expect an increased effect for hydrogen phosphate, as HPO_4^{2-} is the only one of our four catalysts which is, like HCO_3^-, bifunctional.

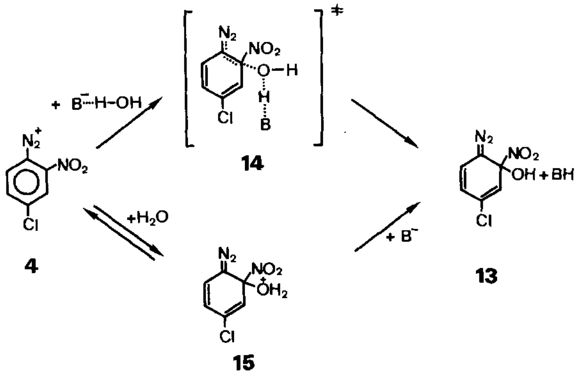
In the nucleophilic substitution of halogen atoms in 4-halogeno-3-nitrobenzene- and 2,6-dichloro-4-nitrobenzenediazonium ions *Štěrba et al.* [4] [5] proposed a nucleophilic catalysis by hydrogen phosphate, acetate, propionate, citrate *etc.* forming first the phenyl esters **11** which are hydrolyzed in a second, base-catalyzed step to 4-diazo-2-nitro-2,5-cyclohexadien-1-one (**12**). It is, however, unlikely that the hydroxy-denitration of **4** in this work follows a two step mechanism analoguous to **10**→ **11**→ **12**: *Gold et al.* [15] determined hydrolysis rates of substituted phenol acetates under similar conditions to ours. Extrapolating his results to 5-chloro-2-diazophenol acetate – the intermediate which would be formed in our case if a mechanism analoguous to **10**→ **11**→ **12** is followed – one can calculate a rate constant for the second step which is about the same as our observed rate constant k_{obs} [10c]. As acetate is, however, also involved in the first step, such a mechanism should give overall second-order kinetics with respect to acetate. This was not found. Furthermore, the isosbestic point in the UV.-spectra observed during the reaction demonstrate that a potential intermediate can be present only in steady-state (*i. e.* very low) concentrations. These experimental results bring us to the conclusion that a nucleophilic catalysis of the type **10**→ **11**→ **12** can be excluded for our reactions.



10 **11** **12**

B = HPO_4^{2-}, $CH_3CH_2COO^-$, AcO^-, citrate *etc.*

General base catalysis, *i. e.* a rate-limiting proton transfer, is, however, consistent with all our results as well as with literature data for related reactions. We propose that **4** forms the steady-state intermediate 5-chloro-2-diazo-1-nitro-3,5-cyclohexadien-1-ol (**13**) either *via* the transition state **14** or by water addition to **4** forming **15** followed by rate-limiting proton transfer as suggested for similar reactions by *Bernasconi et al.* [16]. In consecutive steps the intermediate **13** loses a proton and a nitrite ion in that order or the reverse; a third possibility could involve concerted loss of HNO_2. As these steps are fast, we can not differentiate between these possibilities.



The phenomenon of general base catalysis might also be due to specific base catalysis (by OH^-) followed by general acid catalysis. In the second step the release of nitrite ion must be induced by a proton donor. As nitrite is a good nucleofugal leaving group [12] [17] and as, to our knowledge, no cases of a catalyzed dissociation of a $C(sp^3),NO_2$-bond are known, we do not consider such a mechanism very likely.

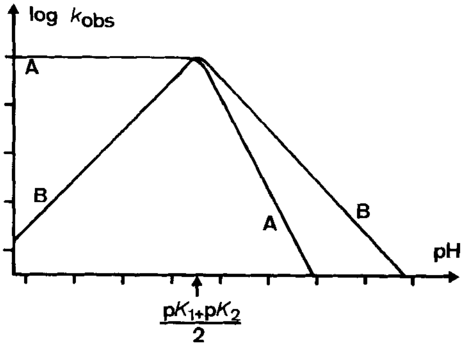
In the results section we mentioned that at pH $\leqslant$ 5.5 in unbuffered solution the hydroxy-de-nitration appears to be autocatalyzed. This observation is explainable by the nitro-dediazoniation of diazonium ions by nitrite ions: *Opgenorth & Rüchardt* [18] showed that this is a relatively fast radical chain reaction. In all our hydroxy-denitrations, nitrite ions are formed. The two experiments in unbuffered solutions at pH 5.0 and 5.5 had by far the slowest initial rate; only in these cases is nitro-dediazoniation an effective competitive reaction. It is autocatalyzed by the nitrite ion formed in the main reaction **4** → **6** (for details see exper. part).

Finally, the pH-dependence of the hydroxy-denitrations of compounds **4** and **5** (*Fig. 1* and *2*) will be considered. As the diazonio group (but not the *cis-* or *trans*-diazotate groups) is a powerful activating substituent for nucleophilic aromatic substitution of the S_nAr-type, we assume that the reactivity of the diazotates can be neglected. The observed rates as a function of pH should therefore be proportional to the *equilibrium* concentration of the diazonium ion. On the acidic side of the pH-value which corresponds to $(\mathrm{p}K_1 + \mathrm{p}K_2)/2$, this concentration approaches 100% of the total (= sum of diazonium ion + *cis*- + *trans*-diazotate ion) concentration. On the alkaline side the equilibrium concentration of the diazonium ion decreases by a factor of a hundred per pH-unit [19].

For an S_NAr-substitution of an arenediazonium salt with a nucleophilic reagent the reactive form of which is present in a constant, *i. e.* pH-independent concentration, one expects the rate profile A in the following *Scheme*[4]. The slopes on both sides of $\mathrm{pH} = (\mathrm{p}K_1 + \mathrm{p}K_2)/2$ are 0.0 and –2.0 respectively. The other extreme case is a hydrolysis in which only hydroxyl ions are the reactive species. It is described by the rate equation 2 and therefore by the rate profile B with a rate maximum at $\mathrm{pH} = (\mathrm{p}K_1 + \mathrm{p}K_2)/2$ and slopes of 1.0 and –1.0 respectively. This has been observed for the hydrolysis of 4-halogeno-3-nitrobenzenediazonium ions by OH^- ions [4]. Our results indeed show a slope of *ca.* 1.0 between pH 5.0 and 6.3 for the unbuffered solutions of the hydrolysis of **4** (*Fig. 1*)! These are, however, the *only* experiments which correspond to the *Scheme*. This is understandable as we demonstrated that our reactions are *general* base catalyzed. We can increase or decrease the rates at a *constant* pH-value by changing buffer concentrations.

$$\text{rate} = k[\mathrm{ArN_2^+}][\mathrm{OH^-}] \qquad (2)$$

Scheme



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[4] This would be the case for a hydrolysis if only water molecules were reactive.

What is the reason for the linear, but numerically fractional slopes with citrate/phosphate buffers over ranges of up to 4 pH-units? These buffers are prepared by a "continuous" change in concentrations of citric acid, phosphate, mono- and dihydrogen phosphate ions [20]. This results in apparent fractional orders with respect to hydroxyl ions. In reality it is, however, the sum of first-order terms in the *Brönsted* equation 1. The slopes on both sides of the maxima in *Figures 1* and *2* are therefore more negative than those expected for a reaction with the hydroxyl ion as sole nucleophile.

Our final point in discussion of the pH-dependences relates to the observation that the rate maximum for the hydrolysis of **5** *(Fig. 2)* occurs at $pH = pK_1 + pK_2)/2$, but that the maximum for the rates of **4** is at a slightly lower pH-value than expected *(Fig. 1)*.

In our opinion this discrepancy is due to the fact that $(pK_1 + pK_2)/2$ relates only to the equilibrium 3 and that this equilibrium constant neglects the relatively slow *cis-trans* equilibrium K_3 (4). In all known cases *trans*-diazotates are thermodynamically more stable than the respective *cis*-diazotates. The numerical value $(pK_1 + pK_2 + pK_3)/3$ for the overall equilibrium 4 is therefore *lower* than $(pK_1 + pK_2)/2$. Examples can be found in a review by *Štěrba* [21] and in a paper we published recently [7] on the equilibria of the *p*-chlorobenzenediazonium ion: $(pK_1 + pK_2)/2 = 10.84$ (25°, $I = 0{,}1$); $(pK_1 + pK_2 + pK_3)/3 = 9.75$ (20°, $I = 0{,}1$);

$$ArN_2^+ + 2\,OH^- \overset{K_1K_2}{\rightleftharpoons} cis\text{-}ArN_2O^- + H_2O \qquad (3)$$

$$ArN_2^+ + 2\,OH^- \overset{K_1K_2K_3}{\rightleftharpoons} trans\text{-}ArN_2O^- + H_2O \qquad (4)$$

We conclude therefore that in the hydrolysis of **4** the *cis/trans* equilibrium influences the overall kinetics whereas in the case of **5** the *cis/trans* transformation appears to be so slow that there is little or no influence on the rate of hydrolysis.

Experimental Part

1. *General.* – Melting points (m.p.) are uncorrected. IR. spectra (*Beckman* Acculab-4): Wave-numbers are given in cm^{-1}. UV/VIS.-spectra (*Beckman* Acculab II and III): λ_{max} are given in nm, molecular extinction coefficients ε (in brackets) in $l\ mol^{-1}\ cm^{-1}$. ^1H-NMR.-spectra (*Bruker* HX-90E and *Bruker* WH-90): Internal standard tetramethylsilane ($\delta = 0$ ppm); d = doublet, $d \times d$ = doublet of doublets. MS.-sprectra (*Hitachi-Perkin Elmer* RMV-6M): Signals are given in *m/z*. pH-values were measured with a *Metrohm* digital pH-meter E512 using *Metrohm* standard buffers for calibration. The pH-stat used was a *Metrohm* Kombi-Titrator 6B4-3D; a solution of 0.004 M NaOH in 0.5 M KCl was added.

2. *Syntheses.* – 2.1. *4,2-Chloronitrobenzenediazonium tetrafluoroborate* (**4**). The corresponding aniline derivative (8.6 g, 0.05 mol) was suspended in 50% aqueous HBF_4-solution (70 ml) and diazotized at 0° to 5° with sodium nitrite (3.4 g, 0.05 mol). After 15 min the precipitate was separated and washed with ethanol and ether. After reprecipitation from acetonitrile with ether a white salt was obtained which was stored over P_2O_5 in a refrigerator, m.p. 130° (dec.).

2.2. *2,4-Chloronitrobenezenediazonium tetrafluoroborate* (**5**). This was obtained in the same manner as a light yellow salt, m.p. 156° (dec.).

2.3. *5-Chloro-2-diazo-3,5-cyclohexadien-1-one* (**6**). 4-Chloro-2-hydroxyaniline (350 mg, 2.4 mmol) was diazotized in 2.7 ml 3 M HCl with sodium nitrite and carefully neutralized at 0° with K_2CO_3. The yellow precipitate was separated and purified by column chromatography (aluminium oxide/$CHCl_3$). All work-up operations had to be carried out in the dark [22]. – UV/VIS. (H_2O): 390 (5500). – IR. (KBr):

2120, 1620, 1560, 1500, 1300, 1170, 1100, 1045, 920, 855. – ^{1}H-NMR. ($CDCl_3$): 7.14 (*d*, 1H); 6.75 (*d*, 1H); 6.25 (*d*× *d*, 1H). – MS. (direct injection, temp. < 100° C): 156/154, 128/126, 100/98, 63.

2.4. *3-Chloro-4-diazo-2,5-cyclohexadien-1-one* (**8**). This was obtained using similar procedure from 2-chloro-4-hydroxyaniline [23]. – UV/VIS. (H_2O): 348 (34700). – IR. (KBr): 2120, 1600, 1450, 1380, 1270, 1235, 1120, 1020, 870, 855. – ^{1}H-NMR. ($CDCl_3$): 7.39 (*d*, 1H); 6.55 (*d*, 1H); 6.36 (*d*× *d*, 1H).

2.5. *2-Diazo-5-nitro-3,5-cyclohexadien-1-one* (**9**). This was prepared from 2-hydroxy-4-nitroaniline [24]. – UV/VIS. (H_2O): 432 (4340). – IR. (KBr): 3100, 2180, 1630, 1570, 1515, 1440, 1355, 1320, 1230, 1160, 1090, 1040, 950, 890, 820, 740. – ^{1}H-NMR. ($CDCl_3$): 7.57 (*d*× *d*, 1H); 7.45 (*d*× *d*, 1H); 7.03 (*d*× *d*, 1H).

2.6. *Hydrolysis of* **4**. After leaving for several hours in the dark 250 ml of a 0.001 M solution of the diazonium salt **4** in a pH 6.6 buffer the products were extracted with ether or $CHCl_3$. The solvent was evaporated and the residue investigated spectroscopically. – UV/VIS. (H_2O): 390. – IR. ($CHCl_3$): 2120, 1620, 1560, 1500, 1300, 1170, 1100, 1045, 920, 855. – ^{1}H-NMR. ($CDCl_3$): 7.14 (*d*, 1H); 6.75 (*d*, 1H); 6.25 (*d*× *d*, 1H). – MS. (direct injection, temp. < 100°C): 156/154, 128/126, 100/98, 63.

2.7. *Hydrolysis of* **5**. This was carried out in the same manner using a 0.0004 M solution in a pH 5.6 buffer and $CHCl_3$ as solvent for the extraction. – UV/VIS. (H_2O): 347, shoulder at 425. – IR. (KBr): 2120, 1580, 1520, 1450, 1380, 1360, 1310, 1270, 1235, 1120, 1080, 1020, 870, 855, 820, 800, 730. – ^{1}H-NMR. ($CDCl_3$): two arom. 3-proton-systems, rel. intensities A : B = *ca.* 2.5 : 1. A: 7.44 *(d)*; 6.59 *(d)*; 6.41 *(d*× *d)*; B: 7.57 *(d)*; 7.44 *(d)*; 7.03 *(d*× *d)*.

3. *Kinetics.* All experiments were carried out at 30° at 0.5 ionic strength established with KCl.

A solution of 27.1 mg (0.0001 mol) of the diazonium salt in 5 ml water at 0° was prepared and 1 ml of this solution was added to 49 ml of a thermostated buffer solution in a glass reactor with a teflon stirrer in air with exclusion of light. Aliquots (1 ml) were coupled with a solution of 2-hydroxy-naphthalene-3,6-disulfonic acid (0.01 M in 0.1 M $Na_2B_4O_7$). After dilution to 10 ml the absorption at 495 nm was determined and used to calculate k_{obs}.

At pH-values above 6.75 first 2.5 ml of 0.1 N HCl were added to the aliquot samples; coupling was carried out after 10 min as above.

3.1. *Hydrolysis of* **4**. In citric acid/phosphate-buffers [20] (each constant calculated from one kinetic run):

pH	k_{obs} $[10^{-4}s^{-1}]$	n_t	pH	k_{obs} $[10^{-4}s^{-1}]$	n_t
2.90	1.17		6.40	29.34	1.22
	1.17			29.29	1.14
4.00	2.26		6.50	27.58	1.22
	2.22			26.35	1.25
5.10	8.88	0.89	6.60	34.85	1.29
	8.67	1.06		32.41	1.24
	8.91	1.29	6.75	39.01	1.36
	9.03	0.97		35.87	1.58
5.12	8.18	1.38		36.04	1.33
	8.29	1.03		39.43	0.98
5.40	11.08	1.09		33.97	0.96
	11.68	0.92	7.00	32.73	1.20
5.50	13.14	1.13		36.06	1.34
	14.14	1.21		26.63	1.64
5.80	16.20	1.02	7.20	15.55	
	16.39	1.09		18.37	
6.00	19.49	1.03	7.40	8.05	
	19.13	1.09	7.45	7.62	
6.14	23.05	1.05	7.65	4.07	
	21.02	1.09		3.84	
6.20	24.83	1.10	7.90	2.07	
6.25	25.72	1.38		2.13	

Experiments at pH 2.9 were monitored up to 50% reaction from pH 4.0 to 5.8 up to at least 74%, from pH 6.0 to 7.0 with two exceptions up to at least 80%, at pH 7.2 and higher between 47–68%. Values for n_t were only calculated for over 75% reaction. The regression coefficients r^2 were usually better than 0.99. All rate constants k_{obs} in the following tables are average values of two independent runs.

In phosphate buffer:

pH	$[NaH_2PO_4]$ [mol/l]	$[Na_2HPO_4]$ [mol/l]	k_{obs} $[10^{-4}s^{-1}]$	pH	$[NaH_2PO_4]$ [mol/l]	$[Na_2HPO_4]$ [mol/l]	k_{obs} $[10^{-}s^{-1}]$
4.90	0.468	0.013	3.27	5.99	0.299	0.080	22.13
4.94	0.234	0.006	1.70	6.00	0.149	0.040	11.63
5.04	0.047	0.001	0.45	6.01	0.030	0.008	2.80
5.40	0.412	0.035	8.96	4.90	0.211	0.005	1.35
5.47	0.206	0.018	4.40	5.40	0.211	0.016	2.17
5.52	0.041	0.004	1.17	5.95	0.211	0.053	7.42

In acetate buffer:

pH	$[CH_3COOH]$ [mol/l]	$[CH_3COONa]$ [mol/l]	k_{obs} $[10^{-4}s^{-1}]$
5.01	0.020	0.05	1.68
5.50	0.020	0.15	4.88
6.08	0.020	0.50	18.92

In propionate buffer:

pH	$[C_2H_5COOH]$ [mol/l]	$[C_2H_5COONa]$ [mol/l]	k_{obs} $[10^{-4}s^{-1}]$
5.02	0.025	0.05	2.77
5.53	0.025	0.15	8.93
6.13	0.025	0.50	33.55

In the pH-stat (*i. e.* unbuffered solutions) applying first-order kinetics to the experimental data:

pH	5.0	5.5	5.8	6.0	6.3
k_{obs} $[10^{-4}s^{-1}]$	0.065	0.18	0.73	1.13	2.50

The experimental data at pH ≥ 5.8 gave good first-order kinetics, in contrast to those at pH = 5.0 and 5.5. Plots of concentrations of the reagent **4** as a function of time are slightly sigmoidal, indicating an autocatalyzed reaction. We evaluated these runs on the basis of the following two competitive reactions:

$$\mathbf{4} + OH^- \xrightarrow{k_1} \mathbf{6} + NO_2^- + 2H^+ \qquad (5)$$

$$\mathbf{4} + NO_2^- \xrightarrow{k_2} \text{4-chloro-1.2-dinitrobenzene} + N_2 \qquad (6)$$

As $[OH^-]$ = constant, the reaction system (5)+(6) corresponds to the kinetic model (7)+(8) which we evaluated following *Cappelos & Bielski* [25].

$$A \xrightarrow{k_1} B + \ldots \qquad (7)$$

$$A + B \xrightarrow{k_2} C + \ldots \qquad (8)$$

The following rate constants were obtained:

pH	k_1 (= k_{obs})	k_2
5.0	$6.54 \times 10^{-6} s^{-1}$	2.29×10^{-5} l $mol^{-1}s^{-1}$
5.5	$1.85 \times 10^{-5} s^{-1}$	3.91×10^{-5} l $mol^{-1}s^{-1}$

For the determination of n_c-values and the rate constants of product formation, see *Weber* [10d].

3.2. *Hydrolysis of* **5**. Rate constant calculations are based on the measurement of the concentration of the diazonium salt.

In citric acid/phosphate buffers [20] *of varying pH-values:*

pH	k_{obs} $[10^{-4}s^{-1}]$	pH	k_{obs} $[10^{-4}s^{-1}]$
1.94	0.14	5.80	3.87
2.00	0.11	6.20	6.03
2.85	0.36	6.17	5.40
3.95	1.04	6.42	5.08
3.96	1.24	6.54	3.86
3.99	1.18	7.00	0.86
4.92	1.85	7.85	0.10

In citric acid/phosphate buffers of varying buffer concentration (constant pH and constant ionic strength):

pH	$[Na_2HPO_4]$ [mol/l]	[Citric acid] [mol/l]	k_{obs} $[10^{-4}s^{-1}]$
6.20	0.133	0.029	5.53
	0.066	0.014	5.33
	0.027	0.006	4.95

Effect of the radical scavenger on the rate of decomposition:

pH	$[CH_2ICOOH]$ [mol/l]	k_{obs} $[10^{-4}s^{-1}]$	pH	$[CH_2ICOOH]$ [mol/l]	k_{obs} $[10^{-4}s^{-1}]$
6.20	—	5.82	7.00	—	1.66
6.20	0.0002	6.08	7.00	0.0010	1.09
6.20	0.0010	5.91	7.00	0.0010	1.00
6.20	0.0100	5.59			

4. *Determination of* $(pK_1 + pK_2)/2$. To 50 ml of a diazonium salt solution (0.0004 M in 0.5 M KCl) thermostated at 30° 1.5 equivalents of sodium hydroxide (3 × 1 ml of 0.01 M NaOH) were added. After each addition the pH-value of the solution was recorded and the values for $(pK_1 + pK_2)/2$ were calculated to be 7.21 (±0.02) for **4** and 6.32 (±0.03) for **5** using equation 9:

$$\frac{pK_1 + pK_2}{2} = pH + ½\log\frac{[ArN_2^+]}{[ArN_2]} \tag{9}$$

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