51. Dediazoniation of Arenediazonium Ions in Homogeneous Solutions. Part XVI. Kinetics and Mechanisms of Dediazoniation of *p*-Chlorobenzenediazonium Tetrafluoroborate in Weakly Alkaline Aqueous Solutions under Nitrogen Gas[1])

by **Wolfgang Schwarz** and **Heinrich Zollinger**

Technisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule (ETH), CH-8092 Zürich

(5.XII.80)

Summary

The kinetics of reactions of *p*-chlorobenzenediazonium ions in aqueous buffer solutions (pH 9.0-10.6) under N_2 (< 5 ppb of O_2) have been measured between 20 and 50 °C. The formation of *trans*-diazotate is first-order with respect to the concentration of hydroxyl ions and to the equilibrium concentration of diazonium ions, if the diazonium ion $\rightleftarrows$ *cis*-diazotate equilibrium is considered as a fast prior equilibrium. This indicates that the *p*-chlorobenzenediazonium ion, in contrast to all previous investigations with the *p*-nitrobenzenediazonium ion and benzenediazonium ions carrying similar substituents with a $-M$ effect, rearranges from the *cis*- to the *trans*-configuration as diazohydroxide and not as diazotate. The formation of *trans*-diazotate is catalyzed by carbonate and inhibited by hydrogen carbonate ions; mechanisms of these catalyses are discussed, and the solvent isotope effect K_{H_2O}/K_{D_2O} measured by an ^{1}H-NMR. technique reported. The kinetics of the dediazoniations can be analyzed as a mixture of two reactions, a relatively fast first reaction, reaction A, which is responsible for about 5% of the total reaction, and a second reaction F. Both are first-order with respect to diazonium ion; reaction A is also first-order in hydroxyl ions. There are some indications that reaction A corresponds to the hydrolysis of the diazonium ion to give eventually amine and nitrite ions. Reaction F shows a complex dependence on hydroxyl ions; it is related to the homolytic dediazoniation.

1. Introduction. - Weakly alkaline aqueous solutions of arenediazonium salts are important in the synthesis of azo compounds, including the majority of technical azo dyes. On the other hand, it has been known qualitatively for many years [2] that their stability is lowest under these conditions. It is therefore surprising that the mechanisms of such decompositions have not been investigated in detail; however, the reactions which occur in such systems are very complex.

In the present paper we report on the equilibria and kinetics of the reactions of *p*-chlorobenzenediazonium ions in aqueous buffer solutions between pH 9.0 and 10.6 under strict exclusion of oxygen (< 5 ppb of O_2). In the presence of even

---

[1]) Part XV: s. [1].

0018-019X/81/2/0513-16$01.00/0

small concentrations of O_2 (60 to 100 ppb) the kinetics are significantly different as we shall show in a subsequent paper [3].

The kinetic results in the absence of O_2 will be discussed mechanistically in this communication in conjunction with investigations of the structure of the products formed in the reaction [1] and CIDNP. data of such systems [4]. The complex problem of the reaction mechanism is therefore approached from three sides, namely by measurement of the kinetics of the decrease in the diazonium ion concentration, analysis of steady-state intermediates with the help of CIDNP., and product analysis.

In several investigations [5-7] (s. summary by *Štěrba* [8]) the kinetics of formation of *cis*-diazohydroxides and *cis*-diazotates (*syn*-diazotates) by reaction of diazonium ions with hydroxyl ions have been investigated. The experiments were, however, designed in such a way that dediazoniations and other reactions leading to products which can not regenerate diazonium ions are avoided as much as possible.

However, the influence of pH on decompositions of diazonium ions has been studied by *Ishino et al.* [9] in the range of pH 1 to 7. In the more acidic region they found for eleven monosubstituted benzenediazonium ions a reaction which is kinetically independent of pH; it corresponds therefore to heterolytic dediazoniation by the S_N1 mechanism involving rate-limiting formation of aryl cations [10]. At higher pH values ($pH \geqslant 4$), the measured rate increased with pH, but in most cases the order with respect to the concentration of hydroxyl ions was less than unity, *e.g.* for *p*-chlorobenzenediazonium ions $d(\log k)/d(pH) = 0.38$ between pH 4.0 and 6.2 (50.4°) [9]. This indicates a complex mechanism.

2. Results. - 2.1. *Kinetics of the formation of* trans-*diazotate.* In buffered solutions the absorption maximum of the diazonium ion ($\lambda = 282$ nm) decreases and is replaced by a maximum at 276 nm. The latter can be identified as arising from *trans*-diazotate by comparison with the spectrum of an authentic sample. The sum of the concentrations of diazonium and *trans*-diazotate ion can be determined by diazo coupling of the solution with 2-hydroxynaphthalene-3,6-disulfonic acid. Typical half-life times of the reaction are 300 min at pH 10.08 and 20° and 12 min at pH 10.06 and 50°.

An example of a kinetic run is given in *Figure 1*. The sum of the two concentrations $[ArN_2^+] + [trans\text{-}ArN_2O^-] = [diazo]_{tot}$ decreases slowly due to subsequent decomposition reactions. These will be discussed in the next section.

An equilibrium between diazonium ion and *trans*-diazotate is established which is not completely on the side of the diazotate. The pH-dependence of the equilibrium follows equations 1, 2 and 3.

$$ArN_2^+ + 2\,HO^- \rightleftarrows trans\text{-}ArN_2O^- + H_2O \tag{1}$$

$$\frac{[trans\text{-}ArN_2O^-]_{eq}}{[ArN_2^+]_{eq}} = K'_{trans}[HO^-]^2 \tag{2}$$

or

$$\frac{[trans\text{-}ArN_2O^-]_{eq}[H^+]^2}{[ArN_2^+]_{eq}} = K_{trans} = K'_{trans} \cdot K_w^2 \qquad (3)[2]$$

---

[2] The water concentration is included in K_{trans}. Our constants K_{trans} and K_{cis} are the reciprocal of those of *Štěrba* [8].

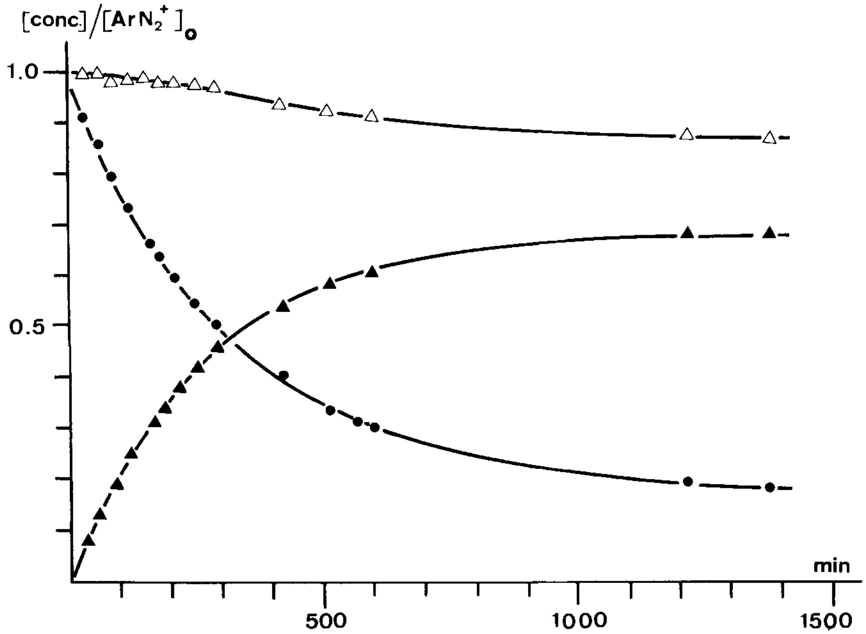


Fig. 1. *Kinetics of the* trans-*diazotate formation of* p-*chlorobenzenediazonium ion.* pH = 10.08, T = 20.0°, $[ArN_2^+]_0 = 4 \times 10^{-4}$ mol/l. ● [conc.] = $[ArN_2^+]$, ▲ [conc.] = [*trans*-ArN_2O^-], △ [conc.] = $[diazo]_{tot}$ = $[ArN_2^+]$ + [*trans*-ArN_2O^-].

Equations 2 and 3 can be verified (s. *Fig. 2*). The values for the equilibrium constant K_{trans} are:

$$K_{trans} = 10^{-18.62(\pm 0.02)}\ \mathrm{mol^2/l^2}\ (50.0°;\ I = 0.1)$$

$$K_{trans} = 10^{-19.5(\pm 0.1)}\ \mathrm{mol^2/l^2}\ (20.0°;\ I = 0.1)$$

This equilibrium can be compared with the equilibrium 4 between diazonium ion and *cis*-diazotate which we determined in the usual way by potentiometric titration [11].

$$ArN_2^+ + 2\,HO^- \overset{K_{cis}}{\rightleftarrows} cis\text{-}ArN_2O^- + H_2O \qquad (4)$$

$$K_{cis} = 10^{-21.68}\ \mathrm{mol^2/l^2}\ (25°;\ I = 0.1)\ \text{or (see [11])}\ \sqrt{K_1 K_2} = \sqrt{K_{cis}} = 10^{-10.84}\ \mathrm{mol/l}$$

This value is consistent with earlier measurements ([11]: $10^{-11.21}$, 20°, $I = 1.0$; [12]: $10^{-10.97}$, 20°, $I = 0.25$).

The rate of decrease in the concentration $[ArN_2^+]$ is first-order if the concentrations are plotted logarithmically against time. The measured rate constant k is independent of the initial concentration between $[ArN_2^+]_0 = 2 \times 10^{-4}$ to 2×10^{-3} mol/l. An evaluation using *Letort*'s method [13] demonstrated that the *orders* with respect to concentration (n_c) and time (n_t) are 1 within experimental error. A plot of log k against $1/T$ is a straight line in the temperature range 293-333 K indicating no change in mechanism with temperature. The *Arrhenius* parameters are: $E_a = 104 \pm 4$ kJ/mol (25.2 ± 1.0 kcal/mol), $\log A = 13.5 \pm 0.7$.

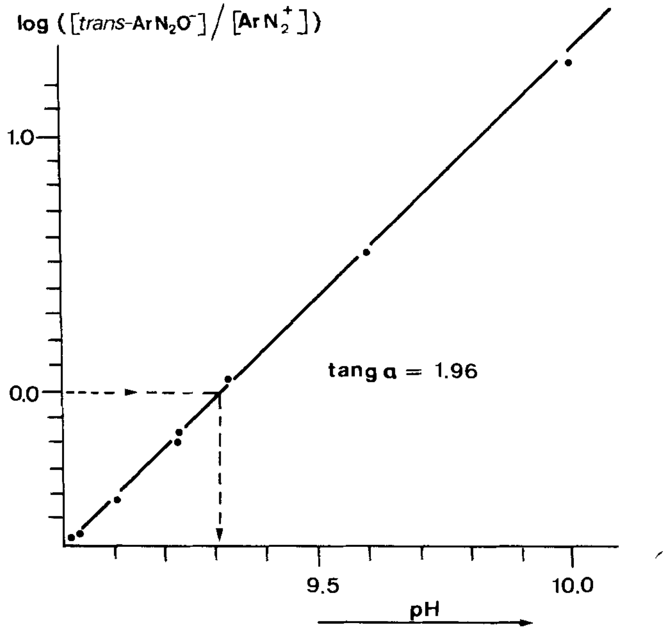


Fig. 2. *Relationship between equilibrium ratio* $[\text{trans-}ArN_2O^-]/[ArN_2^+]$ *and pH* (50.0°)

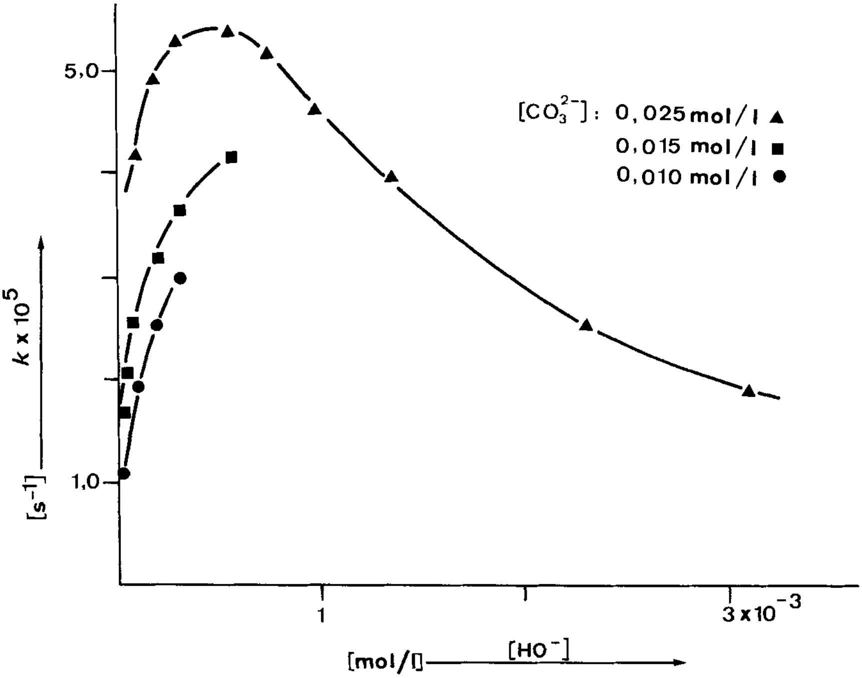


Fig. 3. *Rate constants* k *as a function of hydroxyl ion and carbonate concentrations* (T = 20.0°; I = 0.10)

The rate is a complex function of the hydroxyl ion concentration *(Fig. 3)*. At a given pH-value, *i.e.* at a constant ratio of hydrogen carbonate/carbonate buffer concentrations it increases linearly with buffer concentration at constant ionic strength *(Fig. 4)*.

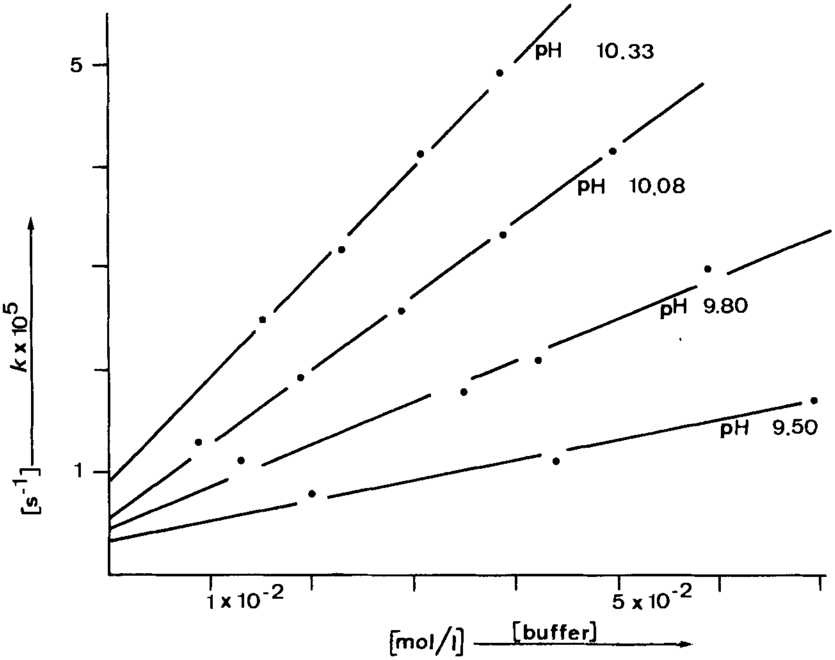


Fig. 4. *Rate constants as a function of* $[HCO_3^-]/[CO_3^{2-}]$ *concentrations* ($T = 20.0°$; $I = 0.10$)

Obviously this reaction is subject to general base catalysis and equation 5 should be applicable.

$$\frac{d[\textit{trans}\text{-}ArN_2O^-]}{dt} = [ArN_2^+]\sum_i k_iB_i = [ArN_2^+](k_{H_2O}[H_2O] + k_{OH}[HO^-] + k_{HCO_3}[HCO_3^-] + k_{CO_3}[CO_3^{2-}]) \quad (5)$$

Above pH 10.1 the equilibrium 4 of *cis*-diazotate formation can not be neglected[3]. The equilibrium concentration of diazonium ions is then given by equation 6 where (ArN_2^+) is the sum of the concentrations of diazonium ions and *cis*-diazotate in the equilibrated system. Equation 6 has to be introduced in 5. *Figure 5* demonstrates the linear relationship of the measured rate constants with the hydroxyl ion concentration if the equilibrium concentration of diazonium ion is calculated using equation 6. From the slope of the straight lines k_{OH} can be calculated. The intercepts correspond to the sum of the three other terms in equation 6.

$$[ArN_2^+] = (ArN_2^+)\Big/\left(1 + \frac{K_1K_2}{[H^+]^2}\right) \quad (6)$$

---

[3] This equilibrium is established very rapidly as *Ritchie et al.* [6] have shown. They determined the rate constant for the hydroxyl ion addition to *p*-chlorobenzenediazonium ion to give *cis*-diazohydroxide and finally *cis*-diazotate at 23°: $k_1 = 1.6 \times 10^4$ l/mol s^{-1}.

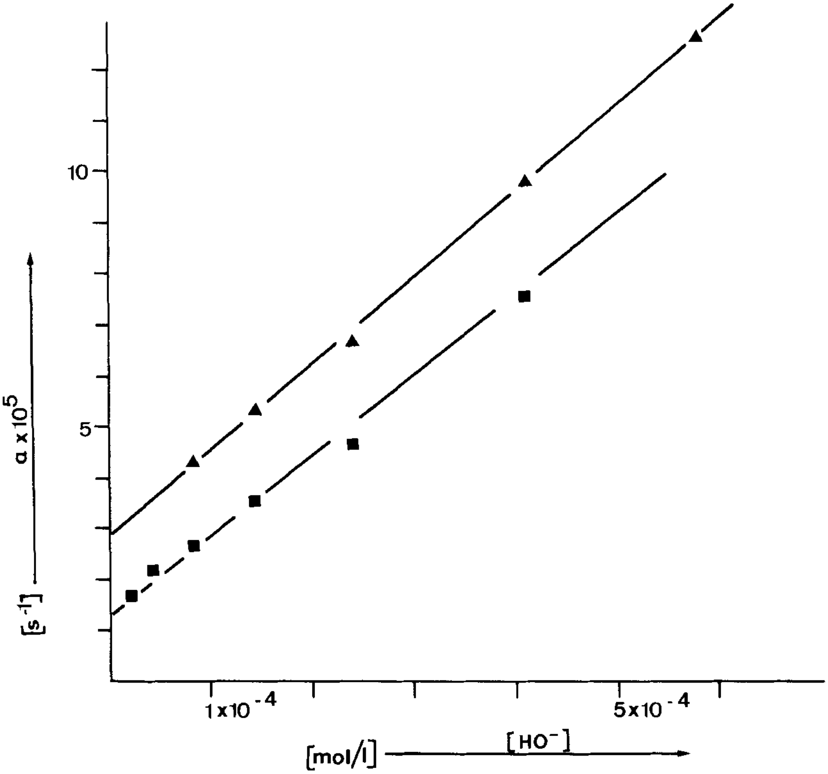


Fig. 5. *Rate constants as a function of the hydroxyl ion concentration, calculated on the basis of the equilibrium concentration of diazonium ions.* ▲ $[CO_3^{2-}] = 0.025$ mol/l, ■ $[CO_3^{2-}] = 0.015$ mol/l

For the determination of the four rate constants in equation 5, three series of kinetic runs were performed with constant $[HO^-]$, $[HCO_3^-]$ or $[CO_3^{2-}]$. Some of these data are shown in *Figures 3-5*. We obtained the following constants:

$$k_{OH} = (3.4 \pm 0.4) \times 10^{-2}\ mol^{-1}\ s$$
$$k_{CO_3} = (1.74 \pm 0.17) \times 10^{-3}\ mol^{-1}\ s$$
$$k_{HCO_3} = -(3.4 \pm 1.5) \times 10^{-4}\ mol^{-1}\ s$$
$$k_{H_2O} = (2.1 \pm 0.4) \times 10^{-6}\ mol^{-1}\ s$$

We shall interpret these constants in chap. 3 (below); in particular we shall discuss the negative value for k_{HCO_3} which implies that the hydrogen carbonate ion has not a catalyzing but an inhibiting effect on the formation of *trans*-diazotate.

In order to examine whether this remarkable effect of hydrogen carbonate ion is specific, the influence of species similar to HCO_3^-, *i.e.* both *Brönsted* acid and base, was investigated: Monohydrogen phosphate has a p*K*-value (6.50) comparable to that of hydrogen carbonate (6.35). A kinetic run at pH 10.32 containing phosphates in addition to the carbonate buffer system (s. exper. part) at the same ionic strength ($I = 0.10$) gave a rate constant $k = (2.50 \pm 0.07) \times 10^{-5}\ s^{-1}$ which, within experimental error, is the same as that for the phosphate-free run: $k = (2.55 \pm 0.20) \times 10^{-5}\ s^{-1}$.

2.2. *Kinetics of the back reaction.* The rate of formation of the diazonium ion was measured in a buffer solution (pH = 9.70) at 50° to which pure sodium *trans*-

diazotate was added. Samples taken at various times were added to an excess of a solution of 2-hydroxynaphthalene-3,6-disulfonic acid which reacts rapidly with the diazonium ion (but not with *trans*-diazotate) to form an azo compound. The

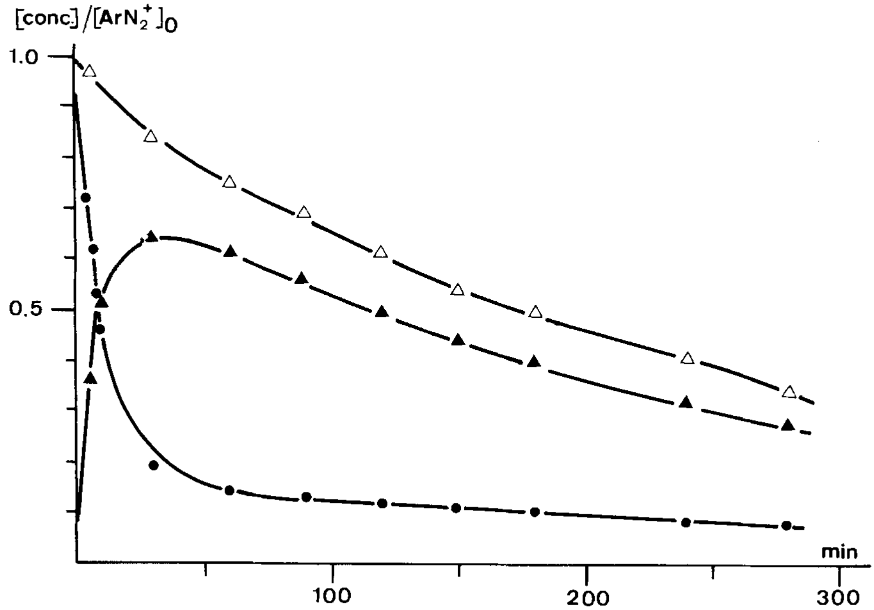


Fig. 6. *Kinetics of decomposition at pH 9.70, 50.0°*, $[CO_3^{2-}] = 0.01$ mol/l. ● $[conc.] = [ArN_2^+]$, ▲ $[conc.] = [trans\text{-}ArN_2O^-]$, △ $[conc.] = [diazo]_{tot} = [ArN_2^+] + [trans\text{-}ArN_2O^-]$

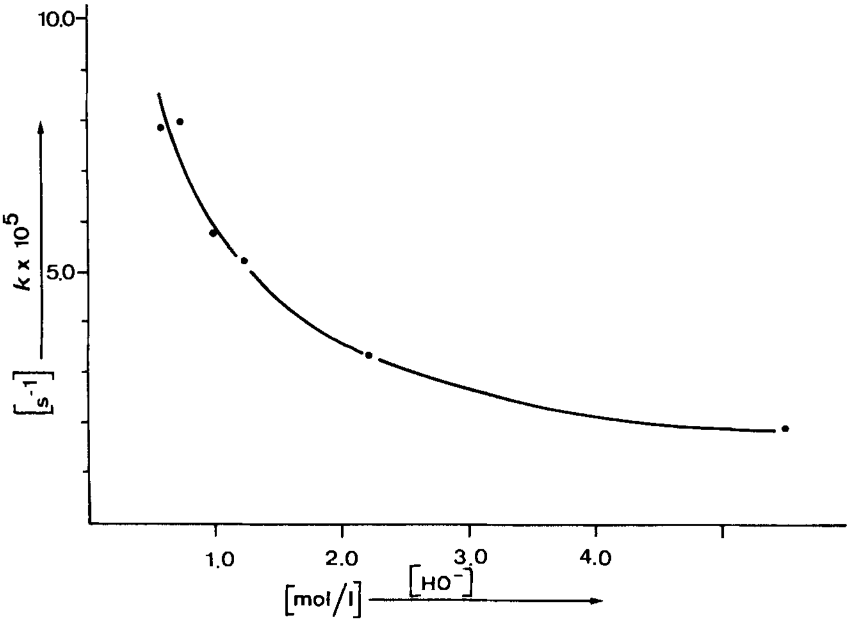


Fig. 7. *Rate constant* k_F *of the decomposition reaction at 50.0° as a function of* $[HO^-]$

concentration of the azo compound was determined spectrophotometrically. The rate was first-order in *trans*-diazotate with a rate constant $k_{-trans} = (2.07 \pm 0.01) \times 10^{-4} s^{-1}$.

The rate of formation of *trans*-diazotate and the equilibrium $[trans\text{-}ArN_2O^-]/[ArN_2^+]$ were determined under the same conditions, which gave $k = (8.70 \pm 0.05) \times 10^{-4} s^{-1}$ and $[trans\text{-}ArN_2O^-]/[ArN_2^+] = 4.8 \pm 0.2$. The latter value corresponds reasonably well to the ratio of concentrations calculated from the equilibrium constant K_{trans} for pH = 9.70 in equ. 3: $[trans\text{-}ArN_2O^-]/[ArN_2^+] = 5.8$.

The measured rate constants k and k_{-trans} are *initial* rate constants; we also applied the data to equations for simultaneous forward and back reactions (s. *e.g.* [14]). The results [15a] are consistent with the rate constants reported above.

2.3. *Kinetics of the decomposition reactions. Chemical method.* In *Figure 1* it can be seen that the total concentration of diazo compounds, $[diazo]_{tot}$, decreases slowly at 20°. For the determination of the rate constants for the formation of *trans*-diazotate, this decrease can be neglected. The rate of decomposition increases at higher temperatures as shown in *Figure 6* (50°). The total concentration of diazo

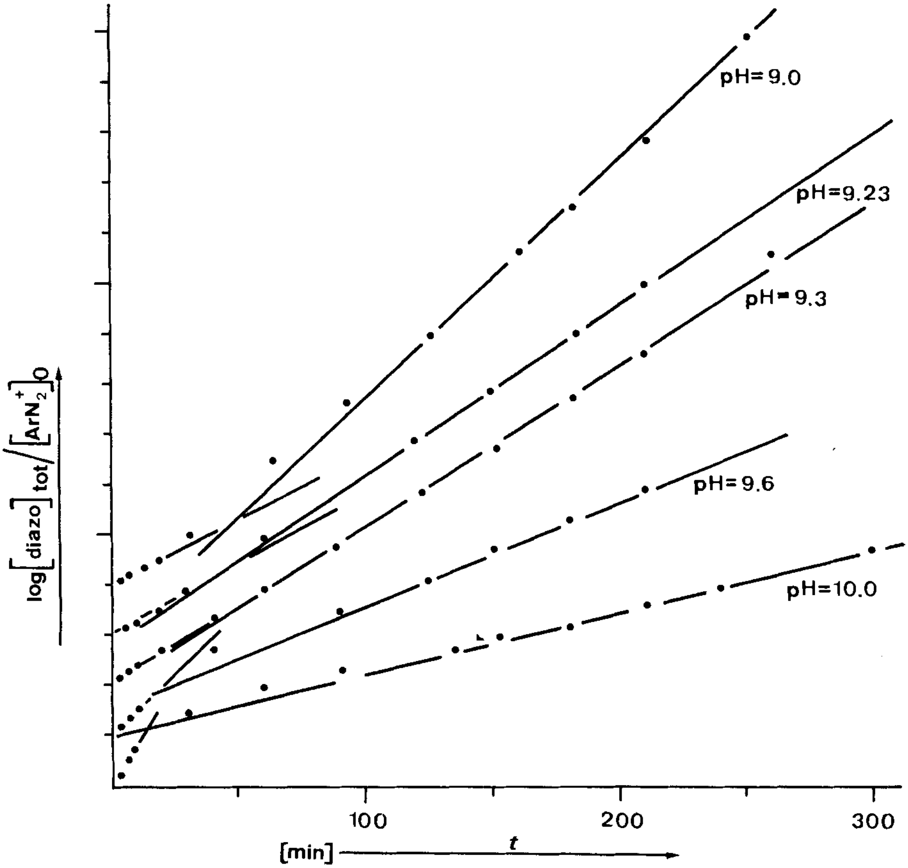


Fig. 8. *Evaluation of the kinetics of decomposition at 20.0° as a function of the pH-value*

compounds decreases with a half-life time of *ca.* 200 minutes, the concentration of *trans*-diazotate reaches a maximum of about 63% after 40 minutes, whereas at 20° *(Fig. 1)* a maximum is not attained after 1500 minutes.

In the measured range of initial concentrations of diazonium salt (2.0 to 20.0×10^{-4} mol/l) the rate is first-order. It is a complex function of the hydroxyl ion concentration as shown in *Figure 7.*

The rates of decomposition have also been evaluated at 20°. Plots of $\log([\text{diazo}]_{tot}/[ArN_2^+]_o)$ against time demonstrate that there is an initial reaction A (rate constant k_A) and a subsequent reaction F (k_F) which have a different dependence on the pH-value of the solutions *(Fig. 8).*

An *Arrhenius* treatment [15b] shows that the reaction measured at 50° is reaction F which dominates at the higher temperature. Reaction F has the following *Arrhenius* parameters: $E_a = 77.6 \pm 2.9$ kJ/mol (18.8 ± 0.7 kcal/mol), $\log A = 9.4 \pm 0.5$. The induction phase is too short at 50° to detect reaction A, but at 20° the kinetic order with respect to $[HO^-]$ is $n_c = 0.9 \pm 0.2$.

The above data for reaction F are supplemented by the kinetic ^{1}H-NMR. data in the following section.

2.4. *Kinetics of the decomposition reactions. ^{1}H-NMR. method.* In order to obtain sufficiently strong signals, the concentrations of all species had to be increased significantly. We measured the decrease of the ^{1}H-NMR. signals of the diazonium ion in D_2O solutions containing 0.04 to 0.06 mol/l of diazonium salt at pD = 9.3 and 9.7, $I = 1.0$. An example of a kinetic run measured by the ^{1}H-NMR. method is given in the exper. part.

The diazonium ion $\rightleftarrows$ *trans*-diazotate equilibrium 1 shows a solvent isotope effect *(Table 1)*, neglecting the change in ionic strength from H_2O ($I = 0.1$) to D_2O ($I = 1.0$). If the influence of ionic strength on the *trans*-diazotate equilibrium 1 is similar to that of the *cis*-diazotate equilibrium 4, the solvent isotope effect of 1 would be even greater than the values given in *Table 1.*

Table 1. *Solvent isotope effect of the diazonium ion* $\rightleftarrows$ trans-*diazotate equilibrium 1 at 50.0°*

pH (pD)	K_{H_2O}[a])	K_{D_2O}[a])	K_{H_2O}/K_{D_2O}
9.3	1.0	0.07	14.3
9.7	4.2	0.28	15.0

[a]) $K = [trans\text{-}ArN_2O^-]_{eq}/[ArN_2^+]_{eq}$.

As the rate of formation of *trans*-diazotate in D_2O is relatively fast due to the high concentration of CO_3^{2-} ($\tau_{1/2}$ *ca.* 5 min), accurate rate constants could not be determined. At pD 9.7 and 50.0° we obtained the value $k_F^{NMR.} = (1.6 \pm 0.2) \times 10^{-4}\ s^{-1}$. This value is about two times greater than that in H_2O, determined chemically. Considering the change in solvent, the solvent isotope effect on the equilibrium 4, which is probably similar to that of 1, and the different carbonate concentration and ionic strength employed, the agreement is satisfactory and verifies that the same reaction is measured by the ^{1}H-NMR. method.

3. Discussion. - 3.1. *Mechanism of the* trans-*diazotate formation.*

As found by *Lewis, Littler, Ritchie, Štěrba, Virtanen, Yoshito et al.* [5-7] *p*-nitrobenzene-*trans*-diazotate and other *trans*-diazotates carrying substituents with $-M$ effect (NO_2, CN, $COCH_3$) in the *o*-, *m*- or *p*-positions are formed in alkaline aqueous solution from diazonium ions by rearrangement of the *cis*-diazotate *via* the *cis*-diazohydroxide (equ. 7–9).

$$\mathrm{ArN_2^+} + \mathrm{HO^-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} cis\text{-}\mathrm{ArN_2OH} \tag{7}$$

$$cis\text{-}\mathrm{ArN_2OH} + \mathrm{HO^-} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} cis\text{-}\mathrm{ArN_2O^-} + \mathrm{H_2O} \tag{8}$$

$$cis\text{-}\mathrm{ArN_2O^-} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} trans\text{-}\mathrm{ArN_2O^-}. \tag{9}$$

If equations 7 and 8 are fast prior equilibria and the concentration of *cis*-diazohydroxide is negligible, the measured rate corresponds to the fraction of the diazo compound present as *cis*-diazotate multiplied by the rate constant k_3 (equ. 10). With the equilibrium constant K_{cis} (s. above) equ. 11 is obtained for the reciprocal of the observed rate constant k.

$$-\frac{\mathrm{d(ArN_2^+)}}{\mathrm{dt}} = \frac{\mathrm{d}(trans\text{-}\mathrm{ArN_2O^-})}{\mathrm{dt}} = k_3[cis\text{-}\mathrm{ArN_2O^-}] = k_3\frac{[cis\text{-}\mathrm{ArN_2O^-}]}{[\mathrm{ArN_2^+}]+[cis\text{-}\mathrm{ArN_2O^-}]}[\mathrm{ArN_2^+} + cis\text{-}\mathrm{ArN_2O^-}] \tag{10}$$

$$\frac{1}{k} = \frac{1}{K_1K_2k_3} \cdot \frac{1}{[\mathrm{HO^-}]^2} + \frac{1}{k_3} \tag{11}$$

A linear relation between $1/k$ and $1/[\mathrm{HO^-}]^2$ was indeed found for the benzenediazonium ions carrying substituents with $-M$ effect mentioned above [7].

If we apply the same considerations to our data for *p*-chlorobenzenediazonium ions, we find *no linear relationship (Fig. 9).*

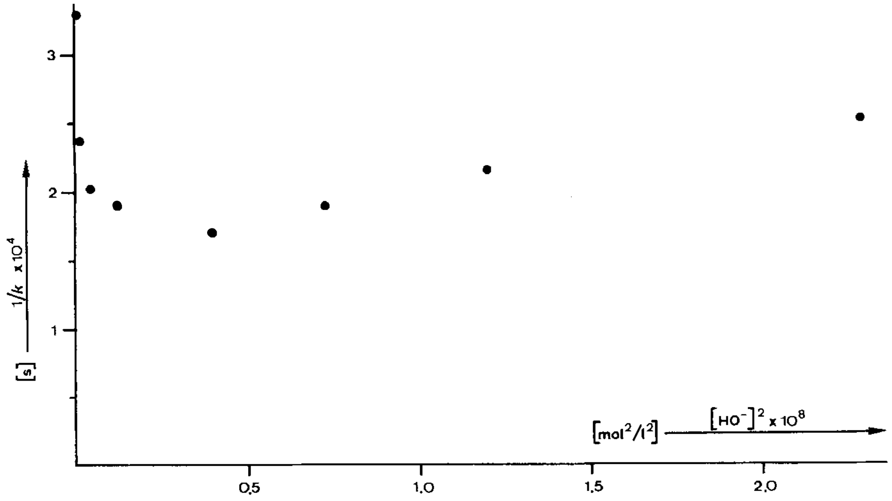
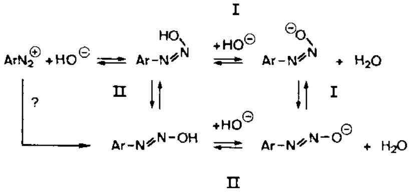


Fig. 9. *Plot of reciprocals of measured rate constants* k *for the decrease in concentration of diazonium salt against* $[HO^-]^2$

As shown in chap. 2 the dependence of the rate of *trans*-diazotate formation on pH becomes clear, however, if the rapid diazonium ion/*cis*-diazotate equilibrium 4 is taken into account and only the effective diazonium ion concentration $[\mathrm{ArN_2^+}]$ is used in the rate equation. The result is a linear relation between rate and the *first* power of hydroxyl ion concentration *(Fig. 5).*

Mechanistically this leads to the conclusion that the *cis/trans* rearrangement in the *p*-chloro substituted diazo compound does not take place *via* diazotate as with the *p*-nitro and other compounds carrying *o*-, *m*- and *p*-substituents with $-M$ effect, but *via* the diazohydroxide. The situation is summarized in the general *Scheme 1* where the two pathways between the diazonium ion and the *trans*-diazotate are shown, namely I for *p*-nitrobenzene- and related diazonium ions, and II for the *p*-chloro derivative.

Scheme 1



Scheme 1 also includes the possibility that the *trans*-diazohydroxide may be formed by direct combination of a hydroxyl ion with the N(β)-atom of the diazonium ion. Such a mechanism is consistent with our kinetic results. This mechanism will be discussed below in the context of the carbonate catalysis.

The remarkable change in mechanism of the *cis/trans*-rearrangement on going from diazonium ions carrying substituents with $-M$ effect to the *p*-chlorobenzenediazonium ion can be rationalized on the basis of the investigations of *Haberfield et al.* [16] on the *cis/trans*-isomerization of azobenzene derivatives. They found that azobenzene itself and monosubstituted derivatives rearrange by inversion at one of the N-atoms, whereas azobenzene derivatives with an electron donor in one benzene ring and an acceptor in the other rearrange by rotation of the N,N double bond as this bond now has less double bond character.

p-Nitrobenzenediazotate can be considered as an azo compound comparable to an azobenzene having one electron acceptor and donor on the two sides of the azo group; the acceptor-donor relationship is more dominant in the *cis/trans*-diazotate pair than in the diazohydroxide pair. The N=N rotation mechanism of the diazotate pair is therefore the favoured process ($E_a = 84$ kJ/mol [17]). On the other hand, *p*-Cl is not a substituent with $-M$ effect; therefore it does not decrease the double bond character of the N=N bond and the inversion mechanism at the N(β)-atom becomes dominant. Its activation energy ($E_a = 104$ kJ/mol, s. chap. 2.1) is higher than that of the N=N rotation mechanism of the *p*-nitro derivative, but it is reasonable to assume that it is lower than the N=N rotation in the *p*-chloro derivative. Furthermore, one can conclude that N-inversion is more favourable in the diazohydroxide than in the diazotate[4]).

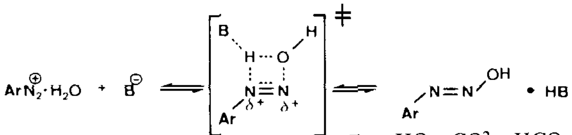
The formation of *trans*-diazotate differs for the *p*-nitro- and *p*-chlorobenzenediazonium ion also in another respect. In the present work we have found catalysis by carbonate ions, and catalysis of the back reaction by hydrogen carbonate ions.

The catalysis by carbonate ions is either a general-base catalysis or a specific nucleophilic catalysis. The *general-base catalysis* can be formulated as shown in

---

[4]) A mechanism which can not be excluded with our data involves the isomerization of the diazohydroxide into *N*-nitroso-*p*-chloroaniline, rotation of the N–N bond and deprotonation.

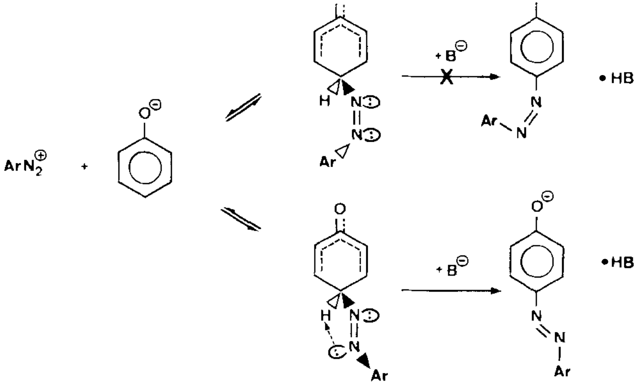
Scheme 2



$B^- = HO^-, CO_3^{2-}, HCO_3^-, H_2O$ etc.

Scheme 2. The mechanism of *Scheme 2* is rather unconventional as it leads 'directly' from the diazonium ion to the *trans*-diazotate[5]. There is, however, indirect support for the structure of the proposed transition state from the fact that in diazo coupling reactions always the *trans*-azo compound is formed. This observation is understandable from a consideration of the deprotonation of the σ-complex of a diazo coupling reaction, assuming either a *cis*- or a *trans*-configuration in the σ-complex (s. *Scheme 3*). Proton release from the *trans*-isomer is facilitated either by hydrogen bonding with the lone electron pair of the N(α)-atom of the diazo group or by the easier approach of an external proton acceptor to the proton (or by both these effects).

Scheme 3



It is impossible to decide from kinetic experiments whether *trans*-diazotate formation with $B^- = HO^-$ follows the mechanism of *Scheme 2* or *1* or both. The former with $B^- = HO^-$ has been discussed briefly by *Štěrba* [8b]. With carbonate ions, however, the mechanism of *Scheme 1* is very improbable. With *Scheme 2* the catalysis of the back reaction by hydrogen carbonate can be explained. The calculated 'negative' rate constant is the sum of the rate constants for the forward reaction with $B^- = HCO_3^-$ and the acid catalyzed back reaction with $HB = HCO_3^-$. In the same way we may explain the non-effect of monohydrogen phosphate as a cancellation of the catalytic effects on the forward and the back reaction[6].

---

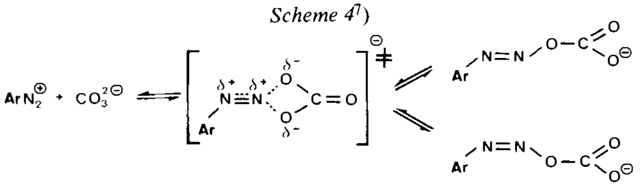
[5] In the mechanism of *Scheme 2* the diazonium ion is written as an ion solvated with *one* water molecule. This is of course a simplification as diazonium ions have more than a water molecule in the first solvation shell. S. *e.g.* CNDO/2 calculations by *Simonetta et al.* [18].

[6] Catalysis of the back reaction by hydrogen carbonate could be eliminated if the rate constants of the forward dediazoniation reaction could be determined very accurately from initial rates. This is unfortunately not possible as the decrease in $[\text{diazo}]_{\text{tot}}$ is determined by the (relatively small) difference between the initial concentration $[ArN_2^+]_0 - ([ArN_2^+]_t + [\textit{trans}\text{-}ArN_2O^-]_t)$.

In this context it is interesting to recall that *Štěrba et al.* [19] found general-acid catalysis for the formation of diazonium ions from *cis*-diazohydroxides. The reverse reaction is therefore general-base catalyzed. It is an open question whether there is a mechanistic analogy between *Štěrba*'s and our results.

A mechanism with *specific nucleophilic catalysis* by carbonate ions is shown in *Scheme 4*. The isomeric diazocarbonic acid esters hydrolyze in consecutive steps into *cis*- and *trans*-diazotates. As the *cis*-diazotate is in a relatively rapid equilibrium with the diazonium ion, the net reaction will give *trans*-diazotate.

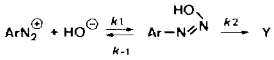
Scheme 4[7]



We consider this mechanism to be less probable, as the back reaction of *trans*-diazotate with hydrogen carbonate is unlikely.

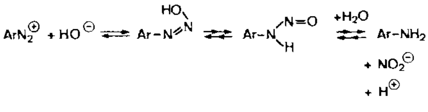
3.2. *Mechanism of the decomposition reactions.* Little can be said about the mechanism of the reaction which is only kinetically detectable at 20° within the first few minutes of a run. This process (*reaction A*, s. chap. 2.3) is first-order with respect to diazonium ion and hydroxyl ion; it is therefore probable that the formation of the *cis*-diazohydroxide is at least partially rate determining. The addition of hydroxyl ion to the diazonium ion cannot be exclusively rate-limiting as *Ritchie et al.* [6] and others have shown that this reaction is much faster than our observed rates. Our data are, however, consistent with a mechanism in which the *cis*-diazohydroxide is a steady-state intermediate. A mechanism as shown in *Scheme 5* fits our results if $k_{-1} \gg k_2$.

Scheme 5



As about 2-5% of the diazonium ions undergo reaction A, it is possible that the steps subsequent to the formation of *cis*-diazohydroxide involve rearrangement to *N*-nitrosamine (*i.e.* Y=Ar-NH–NO) and denitrosation to give *p*-chloroaniline and nitrite ion (s. *Scheme 6*). This pathway is supported by our observation [1] of 2.3% of *p*-chloraniline and 0.2% of *p*-nitrochlorobenzene among the products and the detection by *Matrka et al.* [20] of 5.4% of nitrite in the hydrolysis of *p*-chlorobenzenediazonium ions.

Scheme 6



Reaction F (s. chap. 2) is kinetically the main decomposition process. The dependence of its rate on the hydroxyl ion concentration is very complex (s. *Fig. 7*).

---

[7] We write for simplicity *one* transition state and leave open the question whether two different transition states are involved.

We applied the data to several hypothetical mechanisms [15c], but none of them was completely satisfactory. From our CIDNP. results [1] it is probable that one or several of the isomeric diazoanhydrides are key intermediates. Diazoanhydrides are probably formed by reaction of a diazonium ion with a *cis*- or *trans*-diazotate. If this is indeed the case, diazoanhydride formation can not be rate-limiting for simple kinetic reasons. Such a reaction (with fast consecutive steps to products and neglect of the back reaction to diazonium ion and diazotate ion) would be second order in diazo compound and its rate would be independent of pH. This is not the case.

There are several indications that the homolytic part of the decomposition is a chain reaction. It is well known that kinetic orders of chain reactions can differ completely from expectations based on the stoichiometry of the overall reaction. In the field of dediazoniations we refer *e.g.* to the extensive discussion of potential mechanisms of the reaction of diazonium ions with nitrite ion given by *Opgenorth* [21] or to our following paper on the decomposition of *p*-chlorobenzenediazonium ion solutions in glass and in polytetrafluoroethylene vessels [3].

It is possible to accomodate our kinetic data - first order in diazo compound, complex order in hydroxyl ions - with the diazoanhydride mechanism postulated in our previous paper [1], *if* one assumes 'suitable' initiation and termination steps. At present, such an exercise is, of necessity, speculative, and we shall not describe it here. For the same reason we will not discuss if our CIDNP. results [4] are compatible in principle with a chain mechanism. This problem was discussed briefly by *Gragerov et al.* [22].

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* (Project 2.120-0.78).

Experimental Part

1. Syntheses. - p-*Chlorobenzenediazonium tetrafluoroborate* was synthesized according to *Starkey* [23]: m.p. 134,4° ([24]: 135°).

Sodium p-*chlorobenzene*-trans-*diazotate* was obtained in 58% yield by nitrosation of *p*-chlorophenylhydrazine with isopentyl nitrite in anhydrous diethyl ether in the presence of sodium methoxide according to *Lewis & Hanson* [17]. - UV.: 276 (11700), 215 (11100) ([17]: 276 (12000)). - ^{1}H-NMR. (0.1N NaOD, reference: sodium 3-(trimethylsilyl)tetradeuteriopropionate): *AA'BB'*-system at 7.500, 7.495, 7.470, 7.430, 7.400, 7.348, 7.318, 7.278, 7.249.

The purity was determined by UV./VIS. absorption of 1) the product at 276 nm, giving 97.7%, 2) the diazonium ion at 282 nm after addition of 0.1N HCl, giving 94.6%, and 3) the azo dye formed with 2-hydroxynaphthalene-3,6-disulfonic acid [15] at 494 nm ($\varepsilon = 24700$) giving 99.6%.

p-*Chlorophenylhydrazine* was synthesized from *p*-chlorobenzenediazonium chloride with sodium metabisulfite by the method of *Bullock* [25]. Yield 50%, m.p. 88°.

Purification of N_2 with BET-catalyst and *deoxygenation of water* have been described previously [1].

2. Kinetic experiments. - *General remarks.* The kinetic experiments were run in an all-glass reactor vessel as described in [1]. For details see [15]. All experiments were run in aqueous buffered solutions in the pH range 9.0-11.7 with exclusion of oxygen (< 5 ppb) and under a N_2-atmosphere ($p = 150$ Torr). In the pH range 9.0-11.0 sodium carbonate *(Merck, ultrapur.)* and sodium hydrogen carbonate *(Merck, puriss. p.a.)* were used as buffer salts whereas sodium carbonate and sodium hydroxide *(Merck, puriss. p.a.)* were used at pH > 11.0. The ionic strength $I = 0.1$ was maintained by addition of sodium chloride *(Merck, puriss. p.a.)*. pH values were measured with a *Metrohm* Digital-pH-meter E 512. The oxygen content of the reaction solution was measured with a *Beckman* Oxygen Monitor 7001.

Procedure. The calculated amount of buffer salt and sodium chloride were weighed into the reactor vessel. O_2 was removed by flushing the apparatus with purified N_2, and 100 ml of deoxygenated water from a storage flask were then added. The solution was allowed to reach the required temp. and the reaction started by injection of 1-2 ml of a deoxygenated solution of the diazonium salt in purified water.

The concentration of $[ArN_2^+]$ was determined by measuring the absorption of the azo dye, formed by diazo coupling with 2-hydroxynaphthalene-3,6-disulfonic acid (R-salt), at 494 nm. The concentration of $[\text{diazo}]_{\text{tot}}$ was determined as follows: 1.5 ml of the reaction solution were mixed with 2 ml of 0.1N HCl. After 30 s, 1.5 ml of 0.01M R-salt solution (pH = 10.5) were added and the solution was neutralized by addition of 2 ml of 0.1N NaOH and sodium hydrogen carbonate. For details see [15].

Influence of phosphates on the kinetics of trans-*diazotate formation.* Two kinetic runs A and B were performed in a HCO_3^-/CO_3^{2-} buffer; in one run NaCl was used to adjust the ionic strength to $I = 0.10$, in the other phosphates were used:

	run A	run B
$[NaHCO_3]$	0.0052 mol/l	0.0052 mol/l
$[Na_2CO_3]$	0.010 mol/l	0.010 mol/l
[NaCl]	-	0.0475 mol/l
$[NaH_2PO_4]$	4.6×10^{-6} mol/l	-
$[Na_2HPO_4]$	0.0213 mol/l	-
$[Na_3PO_4]$	2.2×10^{-4} mol/l	-
pH	10.32	10.32
k (s^{-1})	$(2.50 \pm 0.07) 10^{-5}$	$(2.55 \pm 0.20) 10^{-5}$

The difference between the two rate constants (1.5%) is within the standard deviation of these measurements (± 5%).

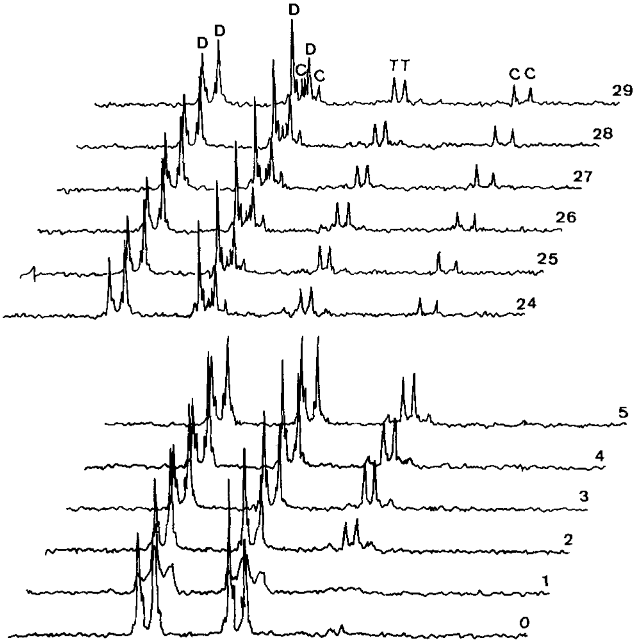


Fig. 10. *Part of a series of ^1H-NMR. spectra used for kinetic measurements in D_2O* (pD = 9.7, 50°, $[ArN_2^+]_0 = 0.06$ mol/l). D = diazonium ion, T = *trans*-diazotate, C = 4-diazo-2,5-cyclohexadien-1-one. *Spectra 0-5 and 18-23* are the first six and last six spectra, respectively, of a series of 30 taken at 90 s intervals.

Kinetic ^{1}H-NMR. measurements. The ^{1}H-NMR. spectra were measured on a *Bruker* WH 90 (90 MHz) instrument. A T_1-programme (T I/II) from *J. W. Cooper* (B 14-60421) was used to obtain spectra at constant time intervals. Pulse angle: 24.5°, acquisition time: 1.7 s, pulse/spectrum: 20-60, Hertz/point: 0.439. In *Figure 10*, the first six and the last six spectra out of 30 spectra of a typical kinetic ^{1}H-NMR. run are shown (time interval between the spectra: 90 s).

Chemical shifts. p-Chlorobenzenediazonium tetrafluoroborate: ^{1}H-NMR. (reference sodium 2-(trimethylsilyl)-tetradeuterioproprionate): *AA'BB'*-system at 8.65, 8.62, 8.60. 8.54, 8.52, 8.49, 8.08, 8.05, 8.03, 7.97, 7.94, 7.92.

p-Chlorobenzene-*trans*-diazotate: ^{1}H-NMR. (reference tetramethylsilane): *AA'BB'*-system at 7.23, 7.13, 6.79, 6.69, 5.01, 3.60.

p-4-Diazo-2,5-cyclohexadien-1-one: ^{1}H-NMR. (D_2O/NaOD, reference tetramethylsilane): *AA'BB'*-system at 7.98, 7.88, 6.64, 6.53. - ^{1}H-NMR. (D_2O/DCl): 8.49, 8.38, 7.32, 7.21.

REFERENCES

[1] *J. Besse, W. Schwarz & H. Zollinger,* Helv. Chim. Acta *64,* 504 (1981).
[2] *K. H. Saunders,* 'The Aromatic Diazo Compounds and their Technical Application', E. Arnold, London, 2nd ed. 1949, p. 99.
[3] *J. Besse & H. Zollinger,* Helv. Chim. Acta *64,* 529 (1981).
[4] *E.-L. Dreher, P. Niederer, A. Rieker, W. Schwarz & H. Zollinger,* Helv. Chim. Acta *64,* 488 (1981).
[5] *E. S. Lewis & H. Suhr,* J. Am. Chem. Soc. *80,* 1367 (1958); *M. Yoshito, K. Hamamoto & T. Kubota,* Bull. Chem. Soc. Jpn *35,* 1723 (1962); *J. S. Littler,* Trans. Faraday Soc. *59,* 2296 (1963); *J. Jabelka, O. Macháčková, V. Štěrba & K. Valter,* Collect. Czech. Chem. Commun. *38,* 3290 (1973).
[6] *C. D. Ritchie & D. J. Wright,* J. Am. Chem. Soc. *93,* 2425, 6574 (1971).
[7] *P. O. I. Virtanen & T. Kuokannen,* Acta Univ. Ouluensis A *53,* Chem. 4, 3 (1977).
[8] *V. Štěrba,* in 'The Chemistry of Diazonium and Diazo Groups' (ed. S. Patai), Interscience, New York 1978, Part I, a) p. 71, b) p. 83.
[9] *Y. Ishino, T. Hirashima & O. Manabe,* Nippon Kagaku Kaishi *76,* 968 (1976).
[10] *H. Zollinger,* Angew. Chem. *90,* 151 (1978), Angew. Chem. Int. Ed. *17,* 141 (1978).
[11] *C. Wittwer & H. Zollinger,* Helv. Chim. Acta *37,* 1954 (1954).
[12] *M. Beranek, V. Štěrba & K. Valter,* Collect. Czech. Chem. Commun. *37,* 3313 (1972).
[13] *M. Letort,* J. Chim. Phys. *34,* 206 (1937); Bull. Soc. Chim. Fr. *9,* 1 (1942); *K. J. Laidler,* Chem. Kin., McGraw-Hill, New York, 2nd ed., 1965, p. 15-17.
[14] *Ch. Capellos & B. H. J. Bielski,* 'Kinetic Systems, Mathematical Description of Chemical Kinetics in Solution', Wiley, New York 1972, p. 34.
[15] *W. Schwarz,* Ph. D. thesis ETH Zürich 1979; a) p. 84, b) p. 110, c) p. 117-134.
[16] *P. Haberfield, P. M. Block & M. S. Lux,* J. Am. Chem. Soc. *97,* 5804 (1975).
[17] *E. S. Lewis & M. P. Hanson,* J. Am. Chem. Soc. *89,* 6268 (1967).
[18] *A. Gamba, M. Simonetta, G. Suffritti, I. Szele & H. Zollinger,* J. Chem. Soc. Perkin II *1980,* 493.
[19] *O. Macháčková & V. Štěrba,* Collect. Czech. Chem. Commun. *37,* 3313 (1972); *J. Jahelka, O. Macháčková & V. Štěrba,* Collect. Czech. Chem. Commun. *38,* 706 (1973).
[20] *M. Matrka, Z. Sagner, V. Chmetal & V. Štěrba,* Collect. Czech. Chem. Commun. *32,* 2697 (1967).
[21] *H. J. Opgenorth,* Ph. D. thesis Universität Münster 1972, p. 27-29.
[22] *T. G. Sterleva, L. A. Kiprianova, A. F. Levit & I. P. Gragerov,* Dokl. Akad. Nauk SSSR *219,* 1140 (1974).
[23] *E. B. Starkey,* 'Organic Synthesis', Vol. II, 225 (1966).
[24] *D. Schulte-Frohlinde & H. Blume,* Z. Phys. Chem. *59,* 299 (1968).
[25] *M. W. Billock,* in «Houben-Weyl, Methoden der organischen Chemie», Vol. 8, 575, E. Thieme, Stuttgart 1952.