52. Dediazoniation of Arenediazonium Ions in Homogeneous Solutions. Part XVII. Kinetics and Mechanisms of Dediazoniation of *p*-Chlorobenzenediazonium Tetrafluoroborate in Weakly Alkaline Aqueous Solutions in the Presence of Oxygen[1]

by **Jacques Besse** and **Heinrich Zollinger**

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

(5.XII.80)

Summary

The kinetics of dediazoniation of *p*-chlorobenzenediazonium tetrafluoroborate have been studied in buffer solutions in the pH-range 9.0-10.0, ionic strength $I = 0.10$, at 20.0° in glass and polytetrafluoroethylene vessels. The presence of oxygen (<5 ppb of O_2, 60 to 100 ppb of O_2, air, $>99\%$ of O_2) has a decisive influence on the rate and kinetic order of the dediazoniation. Iodoacetic acid inhibits the reaction, whereas *p*-chlorophenol has a catalytic effect, and in air and $>99\%$ of O_2 it acts as an autocatalyst. The reaction is subject to general-base catalysis by water, hydroxyl ions, hydrogen carbonate and carbonate ions. The kinetic results are interpreted in conjunction with data concerning the reaction products [2] and a ^{15}N-CIDNP. investigation of a related system [3]. Specific radical chain mechanisms are consistent with the results.

1. Introduction. - In previous papers we have described investigations of the structure and distribution of products formed in dediazoniations of *p*-chlorobenzenediazonium ions in weakly alkaline aqueous solutions in the presence and absence of O_2 [2] and also the kinetics and mechanisms of these systems under N_2 (<5 ppb of O_2) [1] [3]. The analyses of the decomposition products [2] indicate that the mechanism of dediazoniations under these conditions is influenced by O_2 present in the solution and in the supernatant atmosphere. In the present paper we report the kinetics of dediazoniations under N_2 containing traces of O_2 (60 to 100 ppb of O_2) as well as in air, and under $>99\%$ of O_2.

2. Results. - 2.1. *Basic parameters which influence the kinetics.* Dediazoniations of *p*-chlorobenzenediazonium tetrafluoroborate in aqueous hydrogen carbonate/carbonate buffers (pH 9 to 10) in glass vessels show clean first-order kinetics with respect to diazonium ions and are subject to general-base catalysis [1]. At 20° half-life times are in the range of 30 min to 4 hours.

Figures 1 and *2* demonstrate that considerable changes occur if only traces of O_2 (60 to 100 ppb) are present. Further, the kinetics are strongly influenced by the

---

[1] For part XVI, s. [1].

0018-019X/81/2/0529-18$01.00/0

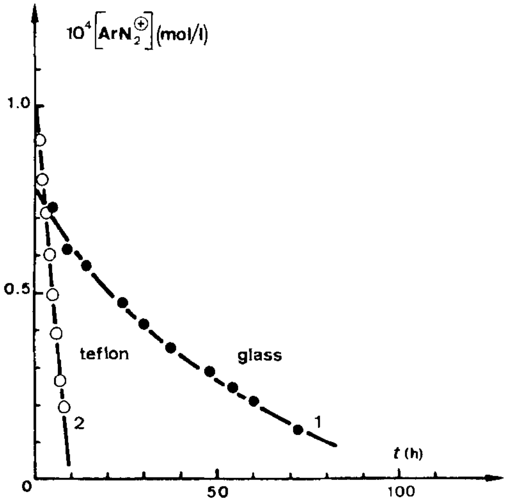


Fig. 1. *Kinetics of the decrease in concentration of* p-*chlorobenzenediazonium tetrafluoroborate under* N_2 *containing 60 to 100 ppb of* O_2 (pH = 9.00 ± 0.02 ($Na_2B_4O_7 + HCl$), $I = 0.0296$, $T = 20.0 \pm 0.1°$). Curve 1: glass vessel; curve 2: *Teflon* vessel.

nature of the reaction vessel. Curves 1 and 2 *(Fig. 1)* represent two experiments carried out in a glass vessel and in a polytetrafluoroethylene *(Teflon)* vessel under N_2 in the presence of 60 to 100 of ppb O_2. In *Teflon* (curve 2) the dediazoniation is about four times faster and, except for a short initiation phase (not seen in *Fig. 1*), strictly order zero; in glass (curve 1) the kinetic order lies between 0 and 1[2]).

Figure 2 shows two experiments in air. The dediazoniations are much faster (note the time scale of the abscissa!), the half-lives are about two hours, and the nature of the vessel has no influence on the rate. The Z-shaped curves of the

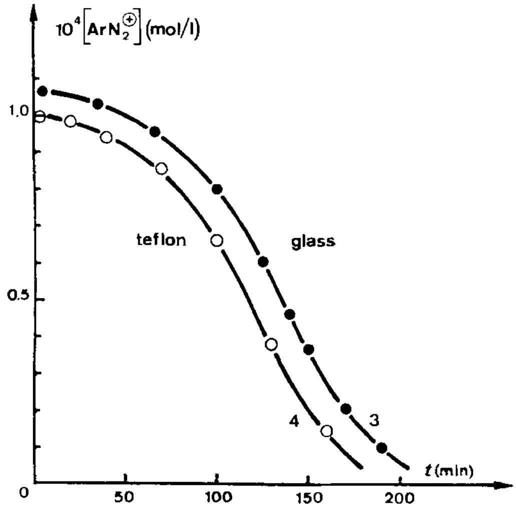


Fig. 2. *Kinetics of the decrease in concentration of* p-*chlorobenzenediazonium tetrafluoroborate under air* (same conditions as given in *Fig. 1*). Curve 3: glass vessel; curve 4: *Teflon* vessel.

---

[2]) The experiments described in *Figures 1* and *2* were run in borate buffers, whereas all the other experiments in this and the preceeding [1] kinetic investigation were carried out in hydrogen carbonate/carbonate buffers. Apart from the general-base effect there is no influence of the chemical nature of the buffers.

decrease in diazonium ion concentration are not compatible with simple kinetics, but suggest an autocatalyzed reaction.

Based on these preliminary results we decided to carry out a systematic investigation of the dediazoniation in *Teflon* vessels (because of the apparent simpler kinetics) using hydrogen carbonate/carbonate buffers (in which interpretations of general-base effects are less complex than in borate buffers) under two extreme conditions with respect to O_2, namely under N_2 containing 60 to 100 ppb of O_2 and pure O_2 ($>99\%$ of O_2).

2.2. *Kinetics under N_2 containing 60 to 100 ppb of O_2.* These particular conditions are obtained when N_2 is deoxygenated by washing three times with a 20% (*w/v*) solution of the trisodium salt of 1,2,3-benzenetriol - a method used often for 'deoxygenation' of gases. However, the gas still contains 60-100 ppb of O_2[3]. To obtain gas with lower O_2-content the method described by *Schwarz* [4a] must be used.

Figure 3 demonstrates that, apart from the initial period, plots of the diazonium ion concentration as a function of time are linear; the straight lines are almost parallel. The reaction is therefore of order zero with respect to time ($n_t = 0$) and to concentration ($n_c = 0$). The equality $n_c = n_t$ indicates in *Letort*'s analysis [5] [7c] that under these conditions the reaction is neither autocatalyzed, nor inhibited. Kinetic curves under argon are identical to those under N_2.

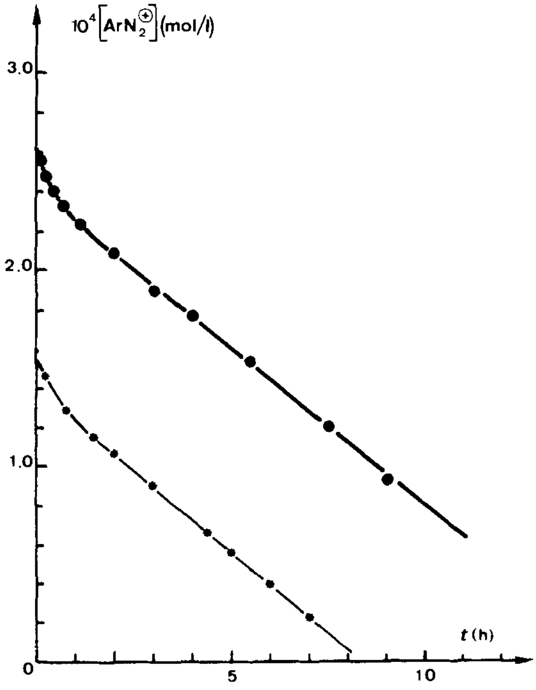


Fig. 3. *Two kinetic runs of the dediazoniation of p-chlorobenzenediazonium tetrafluoroborate in aqueous hydrogen carbonate buffer* (pH 9.00 ± 0.02; $I = 0.10$, $T = 20.0 \pm 0.1$°; under N_2 (60 to 100 ppb of O_2) in a *Teflon* vessel)

---

[3] We thank Dr. *W. Schwarz* for these O_2-determinations; see also [1].

Table 1. *Constants of order zero for the dediazoniation of* p-*chlorobenzenediazonium tetrafluoroborate in aqueous buffers under* N_2 (60 to 100 ppb of O_2; at 20.0±0.1°; I = 0.10)

B	k_B [s^{-1}]	$-\log k_B$	$-\log K_b$ [6]
HO^-	4.87×10^{-6}	5.31	− 1.60
CO_3^{2-}	1.26×10^{-8}	7.90	3.69
HCO_3^-	5.67×10^{-10}	9.25	7.82
H_2O	1.58×10^{-11}	10.80	15.60

The rate constants calculated for the straight parts of the two curves in *Figure 3* are $k_{obs} = (4.55\pm0.08)\times10^{-9}$ mol · l^{-1} · s^{-1} and $(4.70\pm0.08)\times10^{-9}$ mol · l^{-1} · s^{-1}.

Sodium tetrafluoroborate has no influence on the rate constants if the ionic strength is kept constant. However, the rates are influenced by buffer concentrations, buffer ratios and also, therefore, by pH. By varying buffer concentrations with constant buffer base/buffer acid ratios and varying buffer acid (or base) keeping buffer base (or acid, respectively) constant, we could demonstrate that the rates increase linearly with the concentrations of all bases present, *i.e.* $[HO^-]$, $[HCO_3^-]$, $[CO_3^{2-}]$, and that part of the reaction proceeds by a pathway which is independent of these bases. It is likely that this pathway involves catalysis by water molecules.

The measured rate constant k_{obs} of order zero is given by equ. 1 as a sum of first-order constants multiplied by the respective base concentrations.

$$k_{obs} = k_{H_2O}[H_2O] + k_{HO}[HO^-] + k_{HCO_3}[HCO_3^-] + k_{CO_3}[CO_3^{2-}] \quad (1a)$$

$$k_{obs} = \sum_B k_B[B] \quad (1b)$$

The evaluation is described in the experimental part; it yields the values given in *Table 1*. They give a reasonably good *Brönsted* plot *(Fig. 4)*; $G_B = 4.76\times10^{-7}\,s^{-1}$ and $\beta = 0.31$ ($r = 0.9740$).

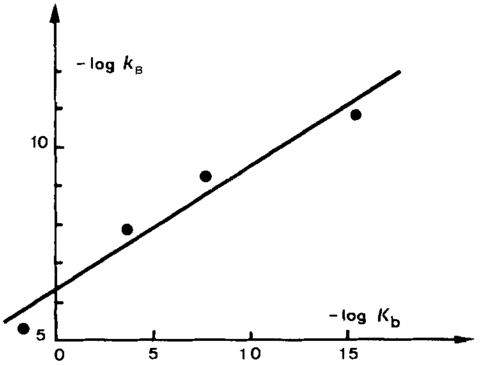


Fig. 4. Brönsted *relationship for base-catalyzed dediazoniations under* N_2 (data of *Table 1*)

The results of the preliminary experiments (chap. 2.1) indicate clearly a complex mechanism, probably homolytic and perhaps even a chain reaction. It was logical therefore to check the influence of radical trapping reagents. Iodoacetic acid was chosen because of its solubility in water. Additions of 5.0×10^{-4} mol/l of

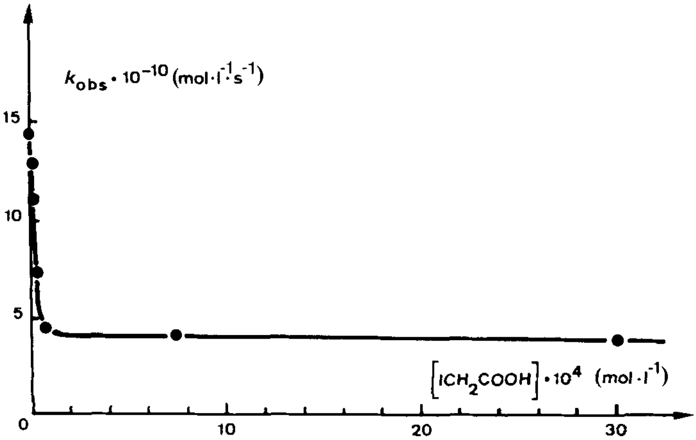


Fig. 5. *Influence of iodoacetic acid on the rate of dediazoniation* (at pH 10.00±0.05, T=20.0±0.1°, I=0.1)

ICH_2COOH to a buffered solution of 1.5×10^{-4} mol/l of diazonium salt at pH 9.00±0.05 decreased rate constant of order zero from 4.73×10^{-9} to 4.21×10^{-10} mol $\cdot l^{-1} \cdot s^{-1}$, *i.e.* by a factor of 11.

In *Figure 5* the rate constants of a series of experiments at pH 10.00±0.02 are plotted as a function of the initial concentration of iodoacetic acid.

As *Figure 3* shows, there is an initiation period accounting for approximately one tenth of the total reaction. The order during this period is higher than zero; this is easily recognized from the nonlinear relationship between diazonium ion concentration and time. It was, however, not possible to determine the order and rate constant accurately.

The initiation period disappears in the presence of *p*-chlorophenol. In *Figure 6* four kinetic runs are shown with increasing initial concentrations of *p*-chlorophenol.

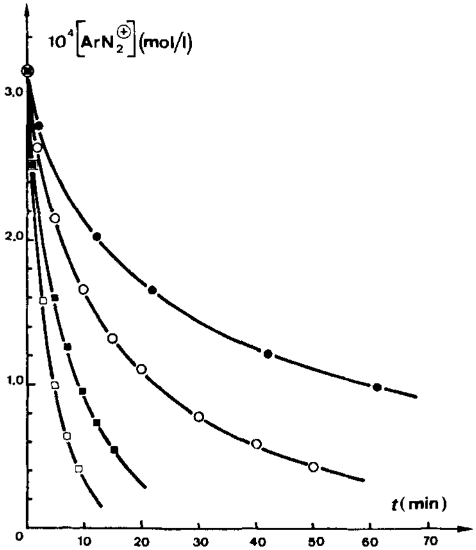


Fig. 6. *Effect of initial concentration of* p-*chlorophenol on the rate of decrease of diazonium ion concentration* (pH 10.00±0.02, T=20.0±0.1°, I=0.1). ● 0.33×10^{-4} mol/l of *p*-chlorophenolate; ○ 0.65×10^{-4} mol/l of *p*-chlorophenolate; ■ 1.30×10^{-4} mol/l of *p*-chlorophenolate; □ 2.61×10^{-4} mol/l of *p*-chlorophenolate.

Table 2. *Initial rates* (v_0) *and kinetic constants for dediazoniations of* p-*chlorobenzenediazonium ions in the presence of* p-*chlorophenol and* N_2 *containing 60–100 ppb of* O_2

Run no.	pH ($\pm$0.02)	$\log v_0$	$\log c_0$ $[ArN_2^+]_0$	$[Cl\text{-}C_6H_4\text{-}O^-]_0$	n_c $[ArN_2^+]$	$[Cl\text{-}C_6H_4\text{-}O^-]$	k_{obs} $(l\cdot mol^{-1})^{0.4}\cdot s^{-1}$
30	10.00	−4.18	−3.52	−3.58			
31	10.00	−4.28	−3.52	−3.89		0.63	6.65
32	10.00	−4.58	−3.52	−4.18			
33	10.00	−4.72	−3.52	−4.49			
34	9.00	−4.45	−3.40	−3.86			
35	9.00	−4.71	−3.70	−3.86	0.77		3.00
36	9.00	−4.91	−4.00	−3.86			

There is an increase in rate, and in addition, the order with respect to diazonium salt is greater than zero.

For the experiments in *Figure 6* as well as additional experiments with different initial concentrations of diazonium ions (1.0 to 4.0×10^{-4} mol/l) but constant concentrations of *p*-chlorophenol, initial rates were determined using *van't Hoff's* method [7b]. Results are given in *Table 2.* When the equilibrium *p*-chlorophenol ⇄ *p*-chlorophenolate ion ($pK_a = 9.18$ [8]) are taken into account, the reaction orders n_c for the decomposition of the diazonium salt are n_c $(ArN_2^+) = 0.77$ and n_c (*p*-chlorophenolate ion) = 0.63. The increase in the rate constant between pH 9.0 and pH 10.0 is due to a (weak) base catalysis which was not investigated further.

2.3. *Kinetics under* >*99% of* O_2. The time dependence of the decrease in the diazonium ion concentration under O_2 is a Z-shaped curve indicative of an autocatalyzed reaction. This was confirmed by the study of a reaction that was run in the solution of a previous dediazoniation. As shown in *Figure 7,* the second reaction has a significantly higher rate, the half-life time decreased from 51 min to 9 min. In addition the reaction profile is no longer Z-shaped.

Experiments under O_2 with increasing concentrations of *p*-chlorophenol *(Fig. 8)* demonstrate that *p*-chlorophenol is responsible for a major part of the auto-

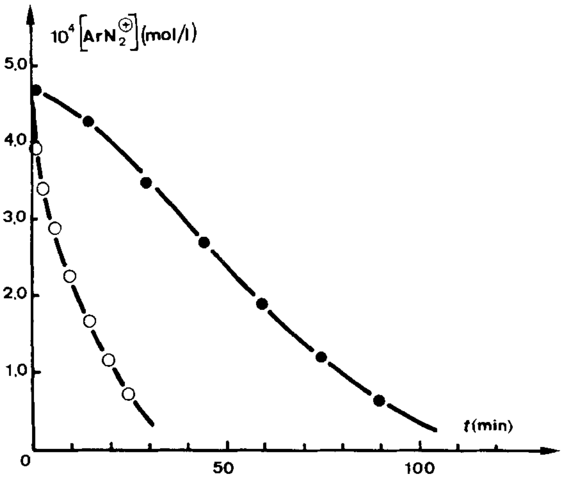


Fig. 7. *Evidence for catalysis by products of dediazoniations under* O_2. pH 9.00 ± 0.02, $T = 20.0 \pm 0.1°$, $I = 0.0296$). Upper curve (●): first run; lower curve (○): second run in solution of first run.

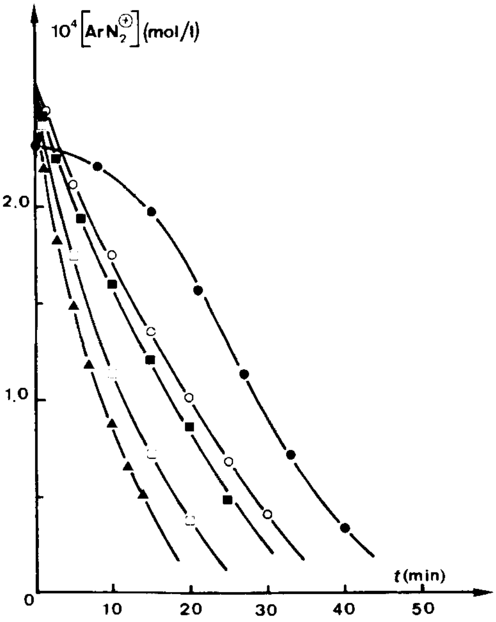


Fig. 8. *Influence of added* p-*chlorophenol on the rate of dediazoniation of* p-*chlorobenzenediazonium ions* (pH 9.00 ± 0.02, $T = 20.0 \pm 0.1°$, $I = 0.10$).
● 0.0 mol/l of *p*-chlorophenolate ion;
○ 1.99×10^{-5} mol/l of *p*-chlorophenolate ion;
■ 3.98×10^{-5} mol/l of *p*-chlorophenolate ion;
□ 10.0×10^{-5} mol/l of *p*-chlorophenolate ion;
▲ 19.9×10^{-5} mol/l of *p*-chlorophenolate ion.

catalysis[4]). Clearly the autocatalytic character of the reaction disappears with increasing concentration of *p*-chlorophenol.

Kinetic runs with *p*-chlorophenol added at the outset were evaluated in the same manner as those under N_2 (60–100 ppb of O_2) described in chap. 2.2. Results are given in *Table 3*. Under O_2, the reaction catalyzed by *p*-chlorophenol has the order

Table 3. *Initial rates* (v_0) *and kinetic constants for dediazoniations of* p-*chlorobenzenediazonium ions in the presence of* p-*chlorophenol*[5]) *under* > *99%* O_2 (pH = 9.00 ± 0.05, 20°)

Run no.	$\log v_0$	$\log c_0$		n_c		k_{obs}
		$[ArN_2^+]_0$	$(Cl\text{-}C_6H_4OH)_0$	$[ArN_2^+]$	$(Cl\text{-}C_6H_4OH)_0$	$(l \cdot mol^{-1})^{0.42} \cdot s^{-1}$
58	−5.01	−3.60	−4.70			
59	−4.93	−3.60	−4.40			
60	−4.74	−3.60	−4.00		0.35	3.05
61	−4.68	−3.60	−3.70			
62	−5.04	−4.00	−3.70			
63	−4.72	−3.70	−3.70	1.06		3.21
64	−4.53	−3.52	−3.70			
65	−4.91	−4.00	−3.40			
66	−4.55	−3.70	−3.40	1.08		5.02
67	−4.40	−3.52	−3.40			

---

[4]) Possibly the other reaction products found by us [2] also catalyze the dediazoniation. It is, however, unlikely that they are as important as *p*-chlorophenolate ions.

[5]) Concentrations of *p*-chlorophenol in *Table 3* and in equ. 1 are given in parentheses ( ), not in brackets [ ]. With parentheses we designate the total concentration of the sum of all equilibrium forms, *i.e.* undissociated *p*-chlorophenol *and p*-chlorophenolate ion.

$n_c = 1.07$ with respect to the diazonium ion and $n_c = 0.35$ with respect to *p*-chlorophenolate.

Table 3 contains rate constants k_{obs} for the decomposition; k'_{obs} is a second-order constant, first-order with respect to the diazonium ion and to *p*-chlorophenolate as autocatalyst, corresponding to the rate equation 2.

$$\frac{1}{[ArN_2^+]_0 + (PCP)_0} \ln \frac{[ArN_2^+]_0((PCP)_0 + (PCP)_t)}{(PCP)_0([ArN_2^+]_0 - (PCP)_t)} = k'_{obs} \cdot t \qquad (2)^{5)}$$

PCP = *p*-chlorophenol

Equ. 2 is applicable only if the concentration of *p*-chlorophenolate at time $t = 0$ is *not* zero, as it should be for a reaction which proceeds exclusively by autocatalysis. For the application of eq. 2 in this paper we assume a) that *p*-chlorophenol is the only catalyst formed during the decomposition and that it is formed quantitatively, *i.e.* $(PCP)_t = [ArN_2^+]_0 - [ArN_2^+]_t$, and b) that in runs without addition of *p*-chlorophenol the ratio of the initial concentrations $[ArN_2^+]_0/(PCP)_0$ is 100:1.

An example of the application of equ. 2 is given in *Figure 9* which shows the dependence of the rate on buffer concentration at pH = 9.00. The evaluation of these and additional rate data with respect to base catalysis will be given in chap. 3.

Finally our results are summarized in *Table 4* which shows the influence of the atmosphere and the material of the vessel on the approximate half-life times and the kinetics of the dediazoniations studied in this work and in previous work [1] at extremely low O_2-concentrations (< 5 ppb of O_2).

Table 4 provides the basis for the mechanistic discussion in the following section:

3. Discussion. - 3.1. *Semiquantitative interpretation.* The data in *Table 4* demonstrate that, if half-life times are taken as a measure of the rates of dediazoniations6), a change with reaction conditions, *e.g.* the nature of the vessel and the

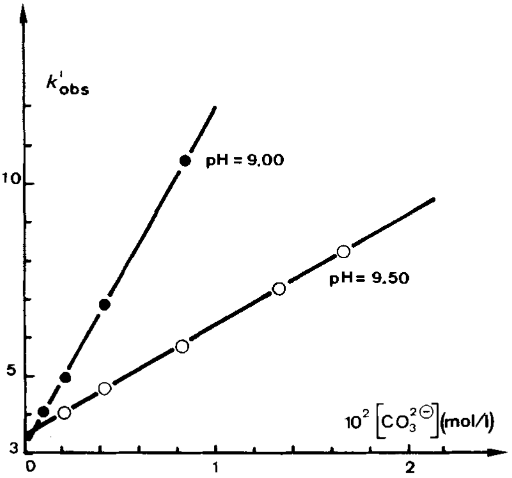


Fig. 9. *Rates of dediazoniations of* p-*chlorobenzenediazonium ions in solutions of hydrogen carbonate/carbonate ions of increasing concentration at pH = 9.00 ± 0.02 and 9.50 ± 0.02* ($I = 0.10$, $T = 20.0 \pm 0.1$°, under O_2)

---

6) We are, of course, aware of the fact that the half-life times are different functions of initial concentrations $[ArN_2^+]$ if reactions of different kinetic orders are compared.

Table 4. *Summary of the experimental results* (20.0°; pH 9.0-10.0; various buffers, $I = 0.10$)

Group of exper.	Atmosphere	Vessel	Additive	Half-life time $T_{1/2}$ (hours)	Kinetic order (n) n_{ArN_2}	$n_{additive}$
I	N_2(< 5 ppb of O_2)	glass	-	> 80[a]	1[c]	-
II	N_2(60-100 ppb of O_2)	glass	-	30	~0.5-1[b]	-
III	N_2(60-100 ppb of O_2)	*Teflon*	-	5	0	-
IV	N_2(60-100 ppb of O_2)	*Teflon*	ICH_2COOH	50	0	- 1[c]
V	N_2(60-100 ppb of O_2)	*Teflon*	PCP[d]	0.1-0.6	0.77	0.63
VI	air	glass	-	2.2	n.d.; autocat.[e]	-
VII	air	*Teflon*	-	1.8	n.d.; autocat.[e]	-
VIII	O_2 (> 99%)	*Teflon*	-	0.5-1.3	1	1[f]
IX	O_2(> 99%)	*Teflon*	PCP	0.1-0.3	1	1

[a]) Data from [1]. [b]) Data in part from [4b]. [c]) See text. [d]) PCP = *p*-chlorophenol. [e]) n.d. = not determined; autocat. = autocatalysis. [f]) With respect to autocatalyst *p*-chlorophenol.

atmosphere and addition of product can cause a change in rate of at least three powers of ten.

It is appropriate to choose as a reference point the reactions carried out under N_2 (< 5 ppb of O_2) (*Table 4*, group I). Traces of O_2 (60-100 ppb of O_2) and high O_2-concentrations in the atmosphere (18 to 99% of O_2) influence rate and kinetic characteristics dramatically. This observation together with the influence of iodoacetic acid (group IV) and the polymeric nature of the products (see [2] and [9]) is a strong indication of *radical chain mechanisms.*

As the experiments in group I have the slowest rates this suggests that under the other conditions species are present which either catalyze the initial reaction (formation of one or several chain carriers) or the chain propagation[7]).

The data for group II (60-100 ppb of O_2, glass vessel) can not be discussed in detail as a complete investigation of the dediazoniation was not carried out. A comparison of II with the well documented group III demonstrates, however, that *Teflon* catalyzes the reaction strongly. The rate is increased further by addition of *p*-chlorophenol (group V), but is decreased by iodoacetic acid (group IV). As iodoacetic acid does not change the kinetic order with respect to diazonium ion (n_{ArN_2}), it is probable that the acid is a scavenger in the initial or chain propagating reaction, but does not change the chain mechanism itself.

p-Chlorophenol, however, does change the order; this suggests the incursion of an additional mechanism, a conclusion which is supported by a partial change in products [2] for experiments in group V.

In the presence of a large excess of O_2 (groups VI-IX) autocatalysis is clearly indicated by the shape of plots of the concentration [ArN_2^+] as a function of time *(Fig. 2)* and by the increase in rate when the product solution of a previous experiment is used as solvent in a kinetic run *(Fig. 7)*.

Figure 8 demonstrates that *p*-chlorophenol acts as a catalyst. Our work on the products of these dediazoniations [2] has shown that *p*-chlorophenol (and its

---

[7]) There is also the possibility of a particularly effective chain termination reaction in group I. This is, however, unlikely as group I conditions are the 'cleanest' with respect to species which might be potential radical scavengers.

subsequent decomposition products) are formed in much higher concentrations in the presence of O_2 (*cf.* conditions of groups I–III). The evaluation of the experimental data with eq. 2 for second-order autocatalysis (first-order in reagent and autocatalyst) given in *Figure 9* suggests that this is the only reaction occurring under these conditions. This is, however, a simplification. Applications of *Letort's* method [5] [7b] to our data in the presence of relatively high concentrations of *p*-chlorophenol shows that the reaction order with respect to concentration is still higher than that with respect to time ($n_t < n_c = 1.07$). Furthermore, the straight lines in *Figure 9* do not pass through the origin as equ. 2 would predict. If these two observations are not due to experimental artefacts, the possibility that the second-order autocatalytic reaction is not the only reaction occurring under conditions of large excess of oxygen cannot be excluded.

3.2. *Application of steady-state chain kinetics.* Here we apply the principles of steady-state chain kinetics (see *e.g.* [10]) to the data for groups III–V and VIII–IX, *i.e.* those groups which have been investigated intensively.

It is, however, necessary to qualify what follows with a word of warning. A chain reaction consists of an initiation, a propagation and a termination reaction. Usually several chemically feasible reactions can be written for each stage. For example, if 5 reactions are possible for each of the three stages, there are 5^3 combinations, *i.e.* 125 potential mechanisms! It is highly probable that *more* than one mechanism will show kinetic orders with respect to reagents, catalysts *etc.* which fit the experimental kinetic data, and these mechanisms cannot be differentiated without additional data. We emphasize that this should be borne in mind in the following discussion. Our experimental results only *corroborate* the mechanisms discussed here; we hesitate even to say that there is strong or convincing evidence for these mechanisms. Nevertheless, it is instructive to evaluate the mechanistic possibilities particularly since the reactivity of these compounds which have been of huge preparative and technical importance for many decades, has not been investigated in the most widely used solvent for diazonium salts[8]), *i.e.* water, with modern methods.

The results of groups III–V and XIII–IX have at least one common feature. They show base catalysis by hydroxyl ions, carbonate and hydrogen carbonate ions, and a pathway independent of these bases which, in all probability, represents base catalysis by water molecules. Results of group III but not of group VIII correlate fairly well with *Brönsted's* law for general-base catalysis.

In a previous paper [1] an evaluation of kinetic results in the (practically) complete absence of O_2 (<5 ppb of O_2) showed that the formation of *trans*-diazotate is general-base catalyzed. This result together with clear evidence from ^{15}N-CIDNP. data [3] for the formation of diazoanhydrides ($Ar\text{-}N_2\text{-}O\text{-}N_2\text{-}Ar$) led us to propose that diazoanhydrides are key intermediates in homolytic dediazoniation in weakly alkaline aqueous solution. As in the case of the *Gomberg-Bachmann* arylation [12] diazoanhydrides are the most likely precursors of the radicals formed under our conditions in the initial reaction of the chain process, *provided* no additives are present which form radicals with diazonium ions, diazohydroxides or diazotate ions easier than direct ('spontaneous') homolytic dissociation of diazoanhydrides.

---

[8]) Mechanisms of dediazoniations of arenediazonium salts are much better known in other solvents, particularly in methanol thanks to the work of *Bunnett et al.* (s. [11] and earlier papers of *Bunnett et al.*). Mechanisms in methanol are, however, not as complex as in water with respect to kinetics and products.

This conclusion allows a simple explanation of the observation[8]) that dediazoniations in methanol and other alcohols [11] probably follow a homolytic pathway, but show less complex kinetics and simpler products than in water: *In the absence of water the formation of diazoanhydrides is scarcely possible.*

Concerning our kinetic data, dediazoniations in group III, *i.e.* *Teflon* vessels under N_2 containing 60 to 100 ppb of O_2 show general-base catalysis with HO^-, CO_3^{2-}, HCO_3^- and H_2O. They are of order zero with respect to $[ArN_2^+]$ except for an initial period of 2-5% of reaction which has an order higher than zero. If *Teflon* is replaced by glass, the rate is slower (group IV), and the order is between 0.5-1.0 [4b] [7b]. Intermediate values of rate and order are obtained if the reaction is carried out in glass in the presence of a *Teflon*-coated magnetic stirrer [4b]. This suggests that *Teflon* very probably catalyzes the formation of the chain carrier and that its surface area enters the kinetic equation (*Teflon* is known to absorb O_2 on its surface).

We were not able to find *reasonable* combinations of mechanisms for the initiation, propagation and termination which fit our kinetic data and, at the same time involve diazoanhydrides as precursors. Diazoanhydride formation is likely to be second-order with respect to $[ArN_2^+]$; we found $n_{ArN_2} = 0$ which could be explained by a termination mechanism second-order with respect to $[ArN_2^+]$ coupled with a propagation process kinetically independent of the concentration of diazonium ion. Such processes are completely unrealistic. An additional argument against the formation and 'spontaneous' homolytic dissociation of diazoanhydrides as key intermediates for group III dediazoniations is the fact that comparable runs of group I are much slower. Here, the involvement of diazoanhydrides is highly probable as our kinetic and CIDNP. work shows [1] [3].

The observed general-base catalysis, however, indicates that formation of *trans*-diazotate (equ. 3) [1] followed by an involvement of *Teflon* (equ. 4) is a reasonable supposition for the initiation, *i.e.* the formation of the arenediazenyl radical chain carrier (equ. 5):

$$\text{Ar-N}_2^{\oplus} + \text{B} \longrightarrow \text{Ar-N=N-O}^{\ominus} \qquad (3)^{9)}$$

$$\text{Ar-N=N-O}^{\ominus} + \text{PTFE} \longrightarrow (\text{Ar-N=N-O-PTFE})^{\ominus} \qquad (4)$$

$$(\text{Ar-N=N-O-PTFE})^{\ominus} \longrightarrow \text{Ar-N}_2\cdot + (\dot{\text{O}}\text{-PTFE})^{\ominus} \qquad (5)$$

PTFE = *Teflon*

As a large number of products are formed in the decomposition of aqueous diazonium salt solutions under our conditions [2], it is intrinsically impossible to postulate *one* propagation process. The major product by weight is the polymeric diazo tar. It is reasonable to assume that, in principle, its formation is analogous to that of radical polymerisation products in general, namely by repetitive steps, each involving a molecule and a radical.

How can such a process take place in the formation of diazo tar, a polymer which, in contrast to polyvinyl derivatives *(etc.)*, does not have the structure of a

---

[9]) For a detailed discussion of these steps s. [1].

chain molecule of repeating monomeric units? A possible answer to this question lies in the initial reaction (first 2-5%) of the dediazoniation where the kinetic order is >0. In our opinion, in this initial reaction oligomeric diazo tar is formed which afterwards acts as a substrate with a *multiplicity* of reaction sites which have, at a first approximation, the same (high) reactivity with radicals. After the initial period of 2-5% the 'concentration' of the reactive sites is therefore *constant*, or more exactly, in large excess relative to the amount of radicals formed.

This leads to the following proposal for the subsequent chain propagation:

$$\text{Ar-N}_2 \longrightarrow \text{Ar}\cdot + \text{N}_2 \tag{6}$$

$$\text{Ar}\cdot + \text{Polymer-H} \longrightarrow (\text{Ar-Polymer-H})^{\cdot} \tag{7}$$

$$(\text{Ar-Polymer-H})^{\cdot} + \text{Ar-N}_2^+ \longrightarrow \text{Ar-Polymer} + \text{Ar-N}_2 + \text{H}^+ \tag{8}$$

Step 8 is corroborated by the observation that in unbuffered diazonium salt solutions the pH value decreases during diazo tar formation. In chain cycles subsequent to steps 6-8, the compound Ar-Polymer will again add aryl radicals (and probably diazenyl radicals as the final polymer contains azo groups) and this will be followed by electron transfer to a diazonium ion and release of a proton, *i.e.* analogous to equ. 6-8.

Many potential termination processes have been discussed in the literature (see *e.g.* [13]). A reasonable reaction involves the combination of an aryl radical with a diazonium ion (equ. 9), forming an azoarene radical cation and finally an azoarene, as *Opgenorth & Rüchardt* [13], *Clusius et al.* [14] and others have discussed.

$$\text{Ar}\cdot + \text{Ar-N}_2^+ \longrightarrow (\text{Ar-}\dot{\text{N}}_2\text{-Ar})^+ \twoheadrightarrow \text{Ar-N}_2\text{-Ar} \tag{9}$$

Application of steady-state chain kinetics to the sequence (3)-(9) gives equ. 10. It is consistent with our experimental results.

$$v = \frac{k_{\text{in}} k_{\text{pr}}}{k_{\text{ter}}} [\text{B}][\text{PTFE}][\text{Po}] \tag{10}$$

$k_{\text{in}}, k_{\text{pr}}, k_{\text{ter}}$	Overall rate constants for the initiation (equ. 3-5), propagation (equ. 6-9) and termination (equ. 10), respectively
[B]	Base concentration[10])
[PTFE], [Po]	'Concentration' of *Teflon* and polymeric diazo tar, respectively

Iodoacetic acid (group IV experiments) decreases the rate, but does not change the kinetic order n_{ArN_2} or the base catalysis. The rate decreases linearly with increasing concentration of iodoacetic acid as long as its concentration does not exceed that of the diazonium salt: higher concentrations of iodoacetic acid influence the rate only to a small extent *(Fig. 5)*. The kinetic order with respect to iodoacetic acid is therefore $n_{\text{add}} = -1$, if $[\text{ICH}_2\text{COOH}]_0 < [\text{ArN}_2^+]_0$. Iodoacetic acid forms *p*-chloroiodobenzene with chlorobenzene radicals (Ar·) and 7-9% of *p*-chloroiodo-

---

[10]) For simplicity, we write eq. 10 with one base only. More correctly, the rate is equal to the *sum* of respective terms with $\Sigma_{\text{B}_i} k_{\text{in}}$ and $[\text{B}]_i$.

benzene can indeed be found in the products [2]. *Bunnett et al.* and *Cadogan et al.* [15] have demonstrated that iodobenzene is a scavenger for aryl radicals. It is therefore probable that in our system *p*-chloroiodobenzene, the primary product of the trapping of chlorobenzene radicals, is also a potential scavenger of aryl radicals as is the other fragment of iodoacetic acid, namely the radical $\cdot CH_2COOH$. Iodoacetic acid is therefore an effective scavenger even if it is present in initial concentrations smaller than that of the diazonium ion ($[ICH_2COOH]_0 < [ArN_2^+]_0$).

In the *presence of* p-*chlorophenol* (group V) the kinetic evaluation is based on *initial* rates. The dediazoniation is significantly faster; the kinetic order n_{ArN_2} increases from 0 to 0.73; the order with respect to *p*-chlorophenol is 0.63; and the order with respect to bases is less than 1[11]. In chain reactions fractional kinetic orders such as 0.5 and 1.5 are consistent with one (or more) specific mechanism. Orders such as $n_{ArN_2} = 0.73$ indicate that at least two mechanisms operate simultaneously, one with $n_{ArN_2} = 1.0$, 1.5 or 2.0, the other with $n_{ArN_2} = 0.5$ or 0. In the present case it is likely that the mechanism given by equ. 3–10 discussed above ($n_{ArN_2} = 0$) occurs in parallel with a mechanism with $n_{ArN_2} \geq 1.0$. This second mechanism has a faster rate than the first and is subject to catalysis by *p*-chlorophenol and/or *p*-chlorophenolate ion. Therefore, the catalyst is involved in the initiation and/or the propagation process. The following mechanism (equ. 11–16) is consistent with all our experimental results:

Initiation:

$$\text{Ar-N}_2^+ + {}^-\text{O-Ar}'\text{-H} \longrightarrow \text{Ar-N}_2\text{-O-Ar}'\text{-H} \qquad (11)^{12)}$$

$$\text{Ar-N}_2\text{-Ar}'\text{-H} \longrightarrow \text{Ar-N}_2\cdot + \cdot\text{O-Ar}'\text{-H} \qquad (12)$$

Propagation:

$$\text{Ar-N}_2^{\cdot} \longrightarrow \text{Ar}\cdot + \text{N}_2 \qquad (13)$$

$$\text{Ar}\cdot + {}^-\text{O-Ar}'\text{-H} \longrightarrow \text{Ar-}\dot{\text{A}}\text{r}'\text{(H)-O}^- \qquad (14)$$

$$\text{Ar-}\dot{\text{A}}\text{r(H)-O}^- + \text{Ar-N}_2^+ \longrightarrow \text{Ar-Ar}'\text{-O}^- + \text{Ar-N}_2^{\cdot} + \text{H}^+ \qquad (15)$$

Termination:

$$\text{Ar}\cdot + \cdot\text{O-Ar}'\text{-H} \longrightarrow \text{Ar-O-Ar}'\text{-H} \qquad (16)$$

The kinetic equ. 17 corresponds to the mechanism given by equ. 11–16.

$$v = \frac{k_{in} k_{prop}}{k_{ter}} [\text{ArN}_2^+][{}^-\text{O-Ar}'\text{-H}] \qquad (17)$$

According to equ. 17 there is no general base-catalysis in this mechanism, but a specific influence of hydroxyl ion concentration on the prior acid-base equilibria

---

[11]) We did not carry out a detailed analysis of base catalysis; the data in *Table 2* (increase in rate by a factor of 2.2 for an increase in pH from 9.0 to 10.0) indicate, however, kinetic order $0 < n_{OH} < 1$.

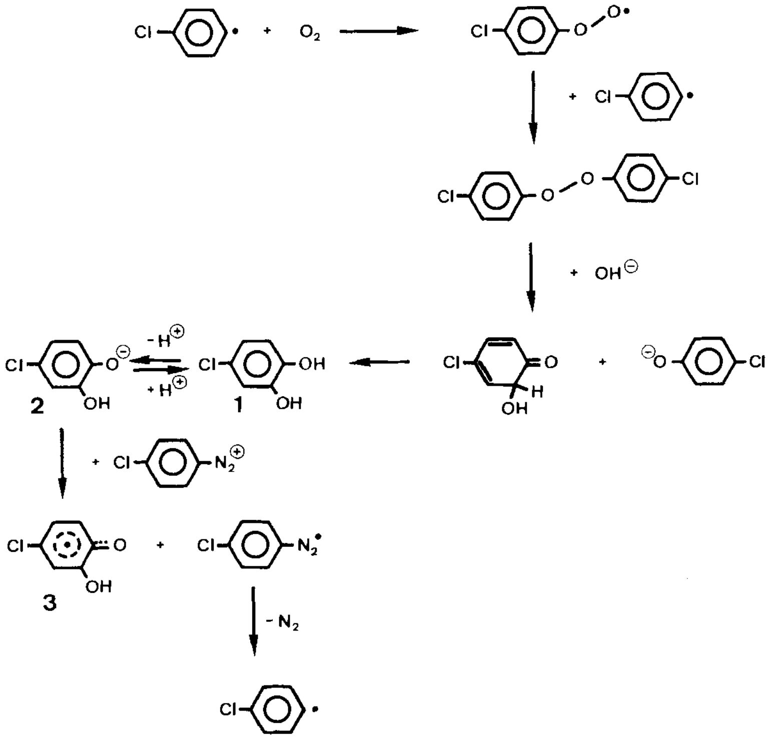
[12]) There are various electron donors (ArO^-) and various bases B which are effective in this system; equ. 18 is therefore only a summarized form of the complete equation which should allow for all cross-combinations of reagents.

of the diazonium$\rightleftarrows$*cis*-diazotate and the *p*-chlorophenol$\rightleftarrows$*p*-chlorophenolate systems. As the reactions 11-16 are competitive with the reactions 3-9, it is impossible for reasons of experimental accuracy to evaluate reliably base-catalytic effects in group V.

Further conclusions concerning the effects of bases are possible for the reactions under >99% of O_2 (groups VIII and IX). Experiments of group IX (>99% of O_2, *p*-chlorophenol added at $t = 0$)are the fastest of allruns investigated. The observation that the kinetic order with respect to diazonium ion *and* to *p*-chlorophenol is 1, corroborates our above claim that in the presence of *p*-chlorophenol and traces of O_2 (group V) the mechanism given by equ. 3-9 is still partly effective occurring together with the mechanism catalyzed by added *p*-chlorophenol equ. 11-16. The latter is dominant under >99% of O_2 (group VIII) where the autocatalyst *p*-chlorophenol is formed rapidly.

Under these conditions *p*-chlorophenol is the major autocatalyst. As we have argued previously [2], it can scarcely originate from a heterolytic hydroxy-dediazoniation as this reaction is, at 20°, about 500 times slower [16] than the reactions which we describe in this paper. In addition the product analyses [2] demonstrate that in the absence of O_2 (< 5 ppb of O_2) only traces of *p*-chlorophenol and its subsequent product of diazo coupling are found (<0.2%), whereas in the presence of 60 ppb or more O_2 significant amounts of *p*-chlorophenol and its azo

Scheme 1



derivative are formed (> 3%). As *Russel et al.* [17] have shown, aryl radicals react with O_2 to form finally phenols and dihydroxybenzenes. The sequence of reactions shown in *Scheme 1* corresponds to literature data (see *e.g.* [18]) applied to the system of group VIII. 4-Chlorobenzene-1,2-diol (**1**), its conjugate base **2** and/or the corresponding semiquinone **3** were not detected; they are probably part of the polymeric products.

It is therefore reasonable to postulate that in a *primary* initiation process aryl radicals are formed in the same manner as in the absence of high concentrations of O_2, *i.e.* following equ. 3–6. These aryl radicals, however, react with O_2 faster than with oligomeric tars (equ. 7). The products are mono- and dihydroxybenzenes of the type described in *Scheme 1.* These products are good electron donors and can form diazenyl radicals from diazonium ions, *e.g.* by the mechanism given in equ. 11–12, followed by the propagation and termination processes discussed for the reaction in the presence of *p*-chlorophenol without O_2 (group V) *i.e.* equ. 13–16.

The kinetic equation 18 for this process corresponds to our experimental results. The constant k_{in} includes in this case the primary initiation 3–6 and the reactions with O_2 (s. *Scheme 1*); the origin of the term $[HO^-]$ is shown in *Scheme 1,* whereas [B] originates from equ. 3.

$$v = \frac{k_{in}k_{pr}}{k_{ter}}[ArN_2^+][ArO^-][B]^{1/2}[O_2]^{1/2}[HO^-]^{1/2} \qquad (18)^{12)}$$

With equ. 18 we have reached the limit of a reasonable analysis of our kinetic results. Equ. 18 cannot be evaluated rigorously in a quantitative way as ArO^- refers

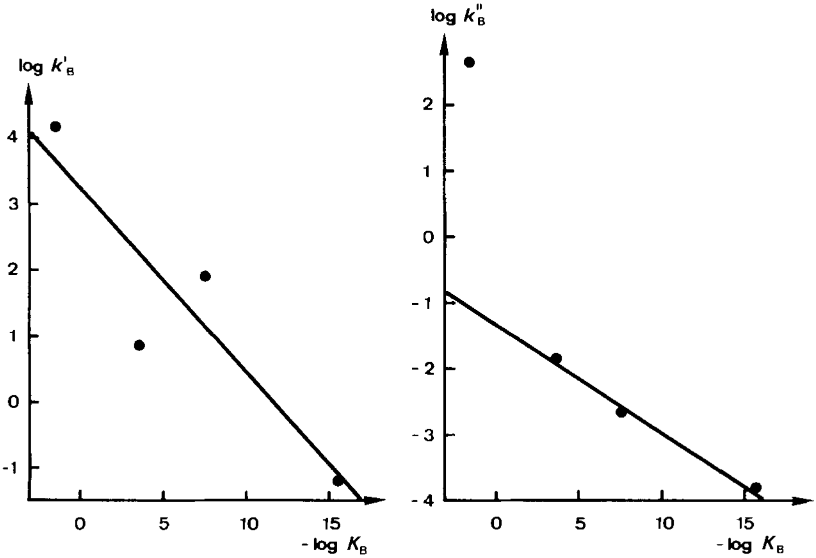


Fig. 10. *Calculated rate constants of dediazoniations of* p-*chlorobenzenediazonium ions under* > *99% of* O_2, *autocatalyzed by* p-*chlorophenol* (pH 9.00 and 9.50 (HCO_3^-/CO_3^{2-} buffers), 20.0°, $I = 0.10$) *as a function of the basicity of the bases.* a) Calculated on the basis of the total concentration of *p*-chlorophenol; b) Calculated on the basis of the equilibrium concentration of *p*-chlorophenolate ions; straight line does not include k''_{OH} (see text).

to more than one potential electron donor and the rate constants are different for each of these donors.

Semiquantitatively, however, one can demonstrate that equ. 18 is not mere speculation. We evaluated the observed rate constants of the runs of group VIII for general-base catalysis by HO^-, CO_3^{2-}, HCO_3^- and H_2O on the basis of the kinetic equ. 2. A *Brönsted* plot *(Fig. 10a)* gives a very poor result. Hydrogen carbonate appears to be a better catalyst than carbonate!

As these experiments were carried out at pH 9.00 and 9.50, *i.e.* near the pH value where [p-chlorophenol] = [p-chlorophenolate] ($pK_a = 9.18$), we recalculated the rate constants on the assumption that the reactivity of the phenolate ions is more than 100 times higher than that of the phenol. The results is given in *Figure 10b*. There is a *Brönsted* relationship for $B = H_2O$, HCO_3^- and CO_3^{2-}, but for HO^- the rate is much faster than predicted. However, equ. 18 contains the general base term [B] which includes, of course, $B = HO^-$ and also as additional term specifically for $[HO^-]$. It is therefore understandable that the hydroxyl ion is a 'better' base than one expects on the basis of a simple *Brönsted* plot.

3.3. *Final remarks.* These considerations lead us to conclude for the investigations described in parts XIV-XVII of this series that it is possible to elucidate *some* mechanistic phenomena of the decomposition of arenediazonium ions in weakly alkaline aqueous systems. But we wish to emphasize that the mechanisms are extremely complex. It is therefore understandable that little work has been carried out in this field in spite of the great technical and synthetic importance of reactions of diazonium ions in such systems.

This work was supported by the *Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung* (projects 2.406-0.75 and 2.120-0.78).

Experimental Part

1. *General.* Unless otherwise specified, all reagents were obtained commercially and used without further purification. p-Chlorobenzenediazonium tetrafluoroborate was prepared using established procedures [3] and kept at 0° in the dark. Deionized water was purified by distillation from $KMnO_4$/$Ba(OH)_2$ using a 1.5-m-*Vigreux* column (average carbon content: 0.06 ppm), and deoxygenated or oxygenated water by boiling for 1 h under continuous bubbling of purified N_2 or O_2 through the solution just prior to a kinetic run. Nitrogen (> 99%) was purified by washing with a 20% 1,2,3-benzenetriol-solution [2]. All kinetic experiments were conducted in a 100-ml-*Teflon* apparatus described elsewhere [2] [7d]. Optical densities of azo solutions were obtained on a *Beckman*-ACTA-III-UV./VIS. spectrometer at 494 nm. Rate constants were calculated with a least squares program. The reproducibility of the observed rate constants determined at least twice with different stock solutions was good (± 10%).

2. *Kinetic methods.* Decomposition reactions were studied in buffered aqueous solutions (pH 9.0 to 10.0) at $20 \pm 0.1°$ and constant ionic strength ($I = 0.1$), in the dark and under continuous magnetic stirring. The vessel was flushed with the purified gas (O_2 or N_2) for 2 h prior to each kinetic run and kept under a light flow of the gas during the whole experiment. In a typical kinetic experiment 50 ml of a freshly prepared buffer solution (deoxygenated or saturated with O_2) was introduced *via* a syringe (*Hamilton*-type, 1050 LL) into the reaction vessel and allowed to equilibrate for 30 min. Then 1 ml of a solution of 2.5×10^{-2} mmol of p-chlorobenzenediazonium tetrafluoroborate in 100 ml of (oxygenated or desoxygenated) water was added to the solution ($t = 0$) and the decomposition monitored by withdrawing 1 ml samples at appropriate time intervals. The aliquots were immediately quenched with solutions of 2-hydroxynaphthalene-3,6-disulfonic acid (2 ml, 10^{-2}M, pH 10), and the optical densities of the resulting azo solutions were measured at 494 nm. Computation of the concentrations of the diazonium salt was made with a calibration curve.

3. *Kinetic parameters.* Rate constants k_{obs} for reactions of order zero were obtained from the least-squares slopes of $[\mathrm{ArN}_2^+]_t$ *vs.* time.

For the general-base catalysis the individual rate constants, k_{B}, were determined from equ. 1a of chap. 2.2. Rearrangement of equ. 18 affords:

$$k_{\mathrm{obs}} = (k_{\mathrm{HCO_3}} \cdot z + k_{\mathrm{CO_3}})[\mathrm{CO_3^{2-}}] + k_{\mathrm{HO}}[\mathrm{HO^-}] + k_{\mathrm{H_2O}}[\mathrm{H_2O}],$$

where z is the ratio of concentrations of the buffer species, *i.e.* $z = [\mathrm{HCO_3^-}]/[\mathrm{CO_3^{2-}}]$.

To determine the four individual rate constants we carried out two sets of experiments, each at a different pH-value, and analyzed the results graphically (plots of k_{obs} *vs.* $[\mathrm{CO_3^{2-}}]$). From the slopes we obtained values for $k_{\mathrm{HCO_3}} \cdot z + k_{\mathrm{CO_3}}$ and from the intercepts values for $k_{\mathrm{HO}}[\mathrm{HO^-}] + k_{\mathrm{H_2O}}[\mathrm{H_2O}]$.

The data which yielded the values shown in *Table 1* of chap. 2.1 (decomposition under N_2) are listed in *Table 5.*

Table 5. *Influence of the buffer concentration and buffer ratio on the rate of dediazoniation under N_2* (60–100 ppb of O_2, $T = 20.0 \pm 0.1°$, $[\mathrm{ArN}_2^+] = 1.5 \times 10^{-4}$ mol/l)

Run no.	Buffer conc. in mol/l $[\mathrm{HCO_3^-}]$ $\times 10^2$	 $[\mathrm{CO_3^{2-}}]$ $\times 10^2$	z[a])	I[b])	k_{obs}	pH
11	9.80	3.40	2.884	0.2	$8.99 \cdot 10^{-9}$	9.50 ± 0.03
8	5.02	1.66	3.020	0.1	$7.97 \cdot 10^{-9}$	9.50 ± 0.03
12	2.51	0.83	3.020	0.1	$6.67 \cdot 10^{-9}$	9.50 ± 0.03
13	5.86	14.70	0.398	0.5	$2.15 \cdot 10^{-8}$	10.25 ± 0.02
14	3.73	8.76	0.427	0.3	$1.71 \cdot 10^{-8}$	10.25 ± 0.02
15	2.70	5.77	0.468	0.2	$1.54 \cdot 10^{-8}$	10.25 ± 0.02
16	1.58	2.81	0.562	0.1	$1.24 \cdot 10^{-8}$	10.25 ± 0.02
17	0.90	1.37	0.661	0.05	$1.13 \cdot 10^{-8}$	10.25 ± 0.02

[a]) $z = [\mathrm{HCO_3^-}]/[\mathrm{CO_3^{2-}}]$. [b]) Ionic strength.

For the decomposition under O_2, the values of the second-order autocatalytic rate constants k'_{obs} were determined from the least-squares slopes of the left side of equ. 2 of chap. 2.3 *vs.* time with correlation coefficients ≥ 0.99. k''_{obs} values were obtained by multiplying k'_{obs} by the fraction of *p*-chlorophenol present as *p*-chlorophenolate ions at the respective pH, assuming that only the latter species was catalytically active in the decomposition. These values of k'_{obs} and k''_{obs} can be evaluated in terms of a general-base catalysis by hydrogen carbonate ions, carbonate ions, hydroxyl ions and water molecules with an equation analogous to equ. 1a and 1b of chap. 2.2. Values are listed in *Tables 6* and *7. Brönsted* plots of these data are given in *Figure 10a* and *10b*, respectively.

Table 6. *Kinetic runs of dediazoniations in aqueous buffer under O_2* ($T = 20.0 \pm 0.1°$, $I = 0.10$, $[\mathrm{ArN}_2^+]_0 = 2.5 \times 10^{-4}$ mol/l)

Run no.	Buffer conc. in mol/l $[\mathrm{NaHCO_3}]$ $\times 10^2$	 $[\mathrm{Na_2CO_3}]$ $\times 10^2$	$[\mathrm{NaCl}] \cdot 10^2$ in mol/l	pH	$\tau_{1/2}$ min	k'_{obs} $\mathrm{l \cdot mol^{-1} s^{-1}}$	k''_{obs} $\mathrm{l \cdot mol^{-1} s^{-1}}$
49	8.11	0.84	0.00	9.00 ± 0.05	27	10.58	4.20
50	4.06	0.42	5.00	9.00 ± 0.05	39	6.86	2.72
51	2.03	0.21	7.50	9.00 ± 0.05	51	4.96	1.97
52	1.01	0.10	8.75	9.00 ± 0.05	67	4.07	1.62
53	5.02	1.66	0.00	9.50 ± 0.03	24	8.25	5.58
54	3.67	1.23	2.50	9.50 ± 0.03	29	7.29	4.93
55	2.51	0.83	5.00	9.50 ± 0.03	37	5.78	3.91
56	1.25	0.42	7.50	9.50 ± 0.03	49	4.69	3.17
57	0.63	0.21	8.75	9.50 ± 0.03	65	4.04	2.73

Table 7. *Catalytic constants for the second-order dediazoniation of* p-*chlorobenzenediazonium tetrafluoroborate in aqueous buffers under* O_2 (20.0 ± 0.1°, $I = 0.10$; k'_B and k''_B: s. text)

B	k'_B ($l^2 \cdot mol^{-2}s^{-1}$)	k''_B ($l^2 \cdot mol^{-2}s^{-1}$)	$\log k'_B$	$\log k''_B$	$-\log K_b$ [6]
HO^-	1.59×10^4	4.89×10^2	4.20	2.69	− 1.60
CO_3^{2-}	7.75	1.29×10^{-2}	0.89	− 1.89	3.69
HCO_3^-	91.9	2.14×10^{-3}	1.96	− 2.67	7.82
H_2O	5.33×10^{-2}	1.70×10^{-4}	− 1.27	− 3.83	15.60

REFERENCES

[1] *W. Schwarz & H. Zollinger,* Helv. Chim. Acta *64,* 513 (1981).

[2] *J. Besse, W. Schwarz & H. Zollinger,* Helv. Chim. Acta *64,* 504 (1981).

[3] *E.-L. Dreher, P. Niederer, A. Rieker, W. Schwarz & H. Zollinger,* Helv. Chim. Acta *64,* 488 (1981).

[4] *W. Schwarz,* Ph.D. thesis ETH Zürich 1979; a) p. 168; b) p. 62.

[5] *M. Letort,* J. Chim. Phys. *34,* 206 (1937); *idem,* Bull. Soc. Chim. Fr. *9,* 1 (1942); *K.J. Laidler,* 'Chemical Kinetics', McGraw-Hill, New York, 2nd edition 1965, p. 15.

[6] *B. Glutz,* Ph.D. thesis ETH Zürich 1966, p. 86.

[7] *J. Besse,* Ph.D. thesis ETH Zürich 1976; a) p. 25; b) p. 104; c) p. 110; d) p. 95.

[8] 'Handbook of Chemistry and Physics', 56th ed. Rubber Comp. Cleveland, Ohio, p. D-150.

[9] *H. Gies & E. Pfeil,* Liebigs Ann. Chem. *578,* 11 (1952).

[10] *A.A. Frost & R.G. Pearson,* 'Kinetics and Mechanism', John Wiley, New York, 2nd edition 1965, p. 241.

[11] *J.F. Bunnett & Ch. Yijima,* J. Org. Chem. *42,* 639 (1977); *T.J. Broxton, J.F. Bunnett & C.H. Paik,* J. Org. Chem. *42,* 643 (1977); *T.J. Broxton & J.F. Bunnett,* Nouv. J. Chimie *3,* 133 (1979).

[12] *C. Rüchardt & E. Merz,* Tetrahedron Lett. *1964,* 2431; *C. Rüchardt, E. Merz, B. Freudenberg, H.J. Opgenorth, C.C. Tan & R. Werner,* J. Chem. Soc. Spec. Publ. *24,* 51 (1970).

[13] *H.J. Opgenorth,* Ph.D. thesis University of Münster 1972, p. 28; *H.J. Opgenorth & Ch. Rüchardt,* Liebigs Ann. Chem. *1974,* 1333.

[14] *K. Clusius & F. Endtinger,* Helv. Chim. Acta *43,* 566 (1959).

[15] *J.F. Bunnett & C.C. Wasmer,* J. Am. Chem. Soc. *88,* 5534 (1966); *D.L. Brydon & J.I.G. Cadogan,* Chem. Commun. *1966,* 744.

[16] *D. Schulte-Frohlinde & H. Blume,* Z. Phys. Chem. *59,* 299 (1968).

[17] *G.A. Russel & R.F. Bridger,* J. Am. Chem. Soc. *85,* 3765 (1963).

[18] *Th. König,* in 'Free Radicals', ed. J.K. Kochi, John Wiley, New York 1973, vol. I, p. 121, 157; *K.U. Ingold,* ibid., vol. I, p. 57.