KINETICS OF REACTION OF m- AND p-SUBSTITUTED BENZENEDIAZONIUM IONS WITH OH⁻ IONS

V.BERÁNEK, V.ŠTĚRBA and K.VALTER

Department of Organic Chemistry,
Institute of Chemical Technology, Pardubice

The rate constants of reactions of the substituted benzenediazonium ions with OH⁻ ions have been determined by spectral stopped-flow method and correlated with the Hammett σ constants. Lower values of the rate constants and ϱ constant, as compared to those of coupling reactions, have been explained by the desolvation of OH⁻ ion which precedes the proper very fast and slightly selective reaction.

At higher pH values the substituted benzenediazonium ions react with OH⁻ ions and give diazo hydroxides which split off the proton very quickly giving the respective diazotate[1]:

$$ArN_2^+ + OH^- \; \rightleftarrows \; ArN_2OH \tag{A}$$

$$ArN_2OH + OH^- \; \rightleftarrows \; ArN_2O^- + H_2O \tag{B}$$
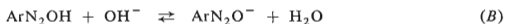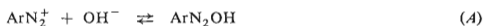
The reaction is reversible; in the resulting mixture there are diazonium ion, diazotate and a slight amount of diazohydroxide. The ratio of the both main components is given by Eq. (*I*).

$$K = [ArN_2O^-]/[ArN_2^+][OH^-]^2 \tag{I}$$

In order that the reaction course may be followed spectrophotometrically, it is necessary to work at such pH value that the overall extinction change due to the transformation of diazonium ion into diazotate may be sufficiently high. In the case of most diazonium ions the rate of establishing of the equilibrium under these conditions (pH > 9) is so large that it cannot be followed by usual methods. There have been only two data given in the literature so far, *viz.* the rate constant of reaction of 4-nitrobenzenediazonium ion with OH⁻ ion determined spectrophotometrically (stopped flow) and potentiometrically (continuous flow techniques)[2,3]. The rate constants of the same reaction of 2,4-dinitro- and 2,6-dichloro-4-nitrobenzenediazonium ions were determined recently[4,5]; these ions are more reactive than the 4-nitro derivative, but the reaction can be followed at considerably lower pH values (6·5 — 7·5). In all the cases the rate constants were lower than in the case of the reaction of these diazonium ions with anions of hydroxynaphthalenesulfonic acids and C-acids[6] which would indicate a relatively lower reactivity of OH⁻ ion. At the same time, however, the difference of the reactivity of OH⁻ ion towards different benzenediazonium ions was far smaller than in the case of coupling reactions which points to small selectivity of OH⁻ ion.

We measured the rates of the above reaction for nine *m*- and *p*-substituted benzene-diazonium ions to exclude the possibility of a lowering of the reactivity and selectivity by *ortho* substitution and to obtain more values of rate constants for correlation with the Hammett σ constants. The establishing of the equilibrium (B) is far faster than that of equilibrium (A). Hence, the reaction of benzenediazonium ion with OH^- ion and the N—O bond splitting of diazo hydroxide are the rate-determining steps in diazotate formation and in the reverse reaction respectively. The rate constant experimentally found is a sum of rate constants of diazo hydroxide formation and decomposition and can be expressed by Eq. (2) where K equals $[OH^-]^2$ at $pH = pH_M$ $([ArN_2^+] = [ArN_2O^-])$. The dependence of k_{exp} on $[OH^-]$ stands in accord

$$k_{exp} = k_2([OH^-] + 1/K[OH^-]) \qquad (2)$$

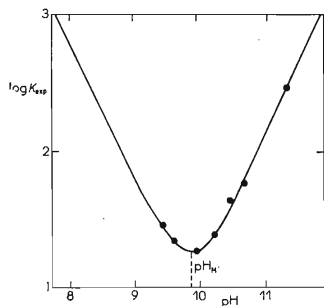with Eq. (2) as it can be seen in Fig. 1. The rate constants k_2 and pH_M values are

Fig. 1

Dependence of k_{exp} on pH for 3,4-Dichloro-benzenediazonium Ion

● The values found experimentally. Full line the dependence calculated according to Eq. (2).

TABLE I

Rate Constants and pH_M of Reactions of Substituted Benzenediazonium Ions with OH^- Ion Water, 20°C, ionic strength 0·25.

Substituent	pH_M	$(k_2 \pm 5\%).10^{-4}$ $1\,mol^{-1}\,s^{-1}$	Substituent	pH_M	$(k_2 \pm 5\%).10^{-4}$ $1\,mol^{-1}\,s^{-1}$
4-Cl	10·97 ± 0·04	2·60	3,5-di-Cl	9·09 ± 0·04	38·0
3-Br	10·37 ± 0·04	5·60	3,5-di-Br	9·10 ± 0·4	36·0
3-Cl	10·33 ± 0·04	6·00	3-NO₂-4-Cl	8·58 ± 0·04	74·0
3,4-di-Cl	9·83 ± 0·04	13·5	3,4,5-tri-Cl	8·75 ± 0·04	58·0
3-NO₂	9·10 ± 0·08	45·0			

given in Table I. Both the values log k_2 and pH$_M$ were correlated with the Hammett σ constants[8]. In the both cases the trichloro derivative deviated from the correlation considerably, the value $\sum\sigma$ read from the graph being always smaller than that obtained from the tabulated σ constants. Probably the additivity rule does not apply here, and, therefore, the trichloro derivative was not included in further calculations. The other derivatives correlated very well except for the 3-nitro derivative, as it can be seen from the equations calculated without and with 3-nitro derivative:

$$\text{pH}_M = (-3.33 \pm 0.12\ )\,\sigma + (11.67 \pm 0.07)\ ; \quad r = 0.9968\ , \tag{3}$$

$$\log k_2 = (\ 2.06 \pm 0.054)\,\sigma + (\ 3.97 \pm 0.03)\ ; \quad r = 0.9983\ , \tag{4}$$

$$\text{pH}_M = (-3.39 \pm 0.18\ )\,\sigma + (11.67 \pm 0.11)\ ; \quad r = 0.9920\ , \tag{5}$$

$$\log k_2 = (\ 2.13 \pm 0.15\ )\,\sigma + (\ 3.96 \pm 0.95)\ ; \quad r = 0.9854\ . \tag{6}$$

Lewis and Suhr[7] obtained ϱ 3.15 when correlating pH$_M$ for *m*- and *p*-substituted benzenediazonium ions. The correlation between pH$_M$ and log k_2 (Eq. (7)) is very good even if the both abovementioned derivatives, which fulfil the Hammett correlation badly, are included.

$$\text{pH}_M = (-1.59 \pm 0.04)\log k_2 + (17.32 \pm 0.23)\ ; \quad r = 0.9975\ . \tag{7}$$

In spite of OH$^-$ ion being a much stronger base than the anions of hydroxynaphthalenesulfonic acids and C-acids (acetoacetanilide, acetylacetone, nitroethane), the rate constants found are generally lower than those of the coupling reactions with the substrates mentioned by several orders of magnitude. At the same time the respective ϱ value (2.06 $\pm$ 0.054) is lower than that of the coupling reactions (3—4), too. This is inconsistent with the rule[9] (which often is not fulfilled) that a reagent is the more selective the more slowly it reacts. The reason is probably that OH$^-$ ion is strongly solvated in water, and partial desolvation must take place before the N—O bond can be formed. This process necessitates considerable energy and is obviously the main cause of the relatively lower reactivity of OH$^-$ ion. The proper N—O bond formation proceeds then very quickly and, therefore, this step is little selective. As the substituents in benzene nucleus of diazonium ion have practically no effect on the desolvation of OH$^-$ ion, the overall influence of substituents is relatively small which makes itself felt in a low value of ϱ constant. The overall reaction course can be represented as a formation of a so called solvent separated ion pair[10] which is transformed into an intimate ion pair, and only then the proper N—O bond formation takes place. On the contrary, the anions of the hydroxynaphthalenesulfonic acids and C-acids are far less solvated, and the carbon atoms which are involved in the

proper reaction do not form any hydrogen bonds, so that the predominant part of the activation energy is consumed in the proper coupling reaction (C—N bond formation).

EXPERIMENTAL

The substituted anilines were prepared by usual methods or were commercial samples of p.a. purity grade. For the proper measurements the diazonium tetrafluoroborates were prepared by diazotization of the substituted anilines in conc. HCl or nitrosylsulphuric acid and precipitation of the solution (eventually diluted) with $NaBF_4$ solution[11]. *Spectra* of solutions of the substituted benzenediazonium ions and diazotates were measured with the use of a Unicam SP 800 apparatus in $0.1M$-HCl or $0.1M$-NaOH solutions. From the spectral data λ_{max} and appropriate concentrations for kinetic measurements were determined. *Buffers used*: mixtures of solutions of prim-, sec- and tert-sodium phosphates, $NaHCO_3$—Na_2CO_3, borax–boric acid. *Kinetic measurements* were carried out with the use of a Durrum-Gibson Stopped flow spectrophotometer at 20°C. The same volumes of a substituted benzenediazonium fluoroborate solution adjusted at pH 3 with HCl and a buffer solution adjusted at ionic strength 0.5 with KCl were injected into the mixing chamber. Hence, the resulting ionic strength was 0.25. Experimental rate constants were calculated from the reaction half-life read from the screen of the apparatus according to the formula $k_{exp} = 0.694/t_{1/2}$. Each kinetic experiment was repeated at least three times at one pH. Most kinetic experiments were carried out in the range of pH $\geqq$ pH$_M$, in several cases at pH $<$ pH$_M$, too, to verify the validity of Eq. (4) for this region. The half-lives were within 3—100 ms. pH was measured in separately prepared mixtures with the use of a Radiometer apparatus (Copenhagen).

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