

# KINETICS AND MECHANISM OF FORMATION OF SUBSTITUTED BENZENEDIAZONIUM IONS FROM BENZENEDIAZOHYDROXIDES

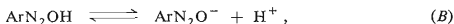
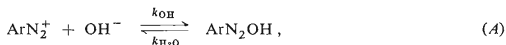
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The rate constants of N—O bond splitting and the dissociation constants have been determined for six *m*- and *p*-substituted benzenediazohydroxides and the respective Hammett  $\rho$  constants of the both reactions have been calculated. The N—O bond splitting of benzenediazohydroxides is subject to general acid catalysis, the value of the Brønsted coefficient  $\alpha$  being 0.19.

The substituted benzenediazonium ions react reversibly with  $\text{OH}^-$  ions in aqueous buffer solutions<sup>1,2</sup> to give benzenediazotate ions<sup>1</sup>. The equilibrium is established practically within a fraction of a second; in the equilibrium there is only a slight concentration of the diazohydroxide<sup>1</sup>, so that only the ratio of diazotate ion to diazonium ion can be determined experimentally.



$$K = K_1 K_2 = \frac{[\text{ArN}_2\text{O}^-][\text{H}^+]}{[\text{ArN}_2^+][\text{OH}^-]} = \frac{[\text{ArN}_2\text{O}^-][\text{H}^+]^2}{[\text{ArN}_2^+]K_w}. \quad (I)$$

The rate constants of the reaction (A) cannot be determined by usual methods, because the half-lives of this reaction are substantially smaller than 1 s. Only recently the rate constants  $k_{\text{OH}}$  of the reaction (A) were determined for *m*- and *p*-substituted benzenediazonium ions by means of the spectral stopped-flow method<sup>2,3</sup>.

The kinetics and mechanism of the reverse step of the reaction (A) could be studied by usual spectral methods with 2,6-dichloro-4-nitro derivative, because in this case the substituents present decreased the reaction velocity considerably. It was found that, besides the non-catalyzed N—O bond splitting (Eq. (A)), a generally acid-catalyzed splitting occurs, the value of the Brønsted coefficient<sup>4</sup>  $\alpha$  being 0.34. The general acid catalysis was proved in the case of 2,4-dinitrobenzenediazohydroxide, too<sup>5</sup>. However, it was not certain, whether the results obtained could be generalized, because in both the cases the very reactive diazonium ions had substituents in *o*-positions.

In this work we have studied the splitting of diazohydroxides into diazonium ions in aqueous buffer solutions and dilute HCl with six *m*- and *p*-substituted ions using

the spectral stopped-flow method. None of these diazonium ions had a *p*-substituent of -M type, so that the formation of *anti*-diazotate might be excluded. The main goal of this work was the verification of the reaction mechanism, determination of the rate constant  $k_{H_2O}$  and of the partial equilibrium constants  $K_1$  and  $K_2$  for the reactions (A) and (B) respectively, and their quantitative dependence on substituents in the form of the Hammett equation.

## EXPERIMENTAL

*m*- and *p*-Substituted benzenediazonium fluoroborates were prepared for kinetic measurements<sup>3</sup>. Spectra of their solutions in 0.1M-HCl and 0.1M-NaOH were measured with a Unicam SP 800 apparatus. From the spectral data the respective  $\lambda_{max}$  were read and the concentrations suitable for kinetic measurements were determined. These measurements were carried out in borax, phosphate, acetate and chloroacetate buffers and in dilute HCl in the pH range 9.5–1.0 using a Durrum-Gibson stopped-flow spectrophotometer at 20°C. Equal volumes of a freshly prepared syndiazotate solution (the diazonium salt solution in  $10^{-3}M$ -HCl was injected into 0.1M-NaOH) and of the buffer solution adjusted at the ionic strength 0.5 with KCl were injected into the mixing chamber of the apparatus. The resulting ionic strength had thus the value 0.25. The experiments with phosphate buffers were carried out at a wavelength corresponding to the maximum difference of the extinctions of the both forms. As the increasing diazohydroxide concentration resulted in a change of this difference, it was necessary to find experimentally new wavelengths with sufficiently large difference of extinctions between the equilibrium mixture diazohydroxide-diazotate ion and diazonium ion.

The experimental rate constants were calculated from the reaction half-life (read from the screen of the apparatus) according to the relation  $k_{exp} = 0.694/t_{1/2}$ . Each kinetic experiment was repeated at least three times at one pH value. The half-lives were within 10–0.4 ms. The experimental error was  $\pm 5$ –10% up to the half-life of 1 ms., whereas it steeply increased with decreasing half-life, being as much as  $\pm 50\%$  in the case of the most rapid reactions. The pH of the separately prepared solutions was measured by means of a Radiometer apparatus (Copenhagen).

## RESULTS AND DISCUSSION

The equilibrium between diazohydroxide and benzenediazotate is established practically immediately on mixing benzenediazotate solution and buffer solution. The relation between the value of the experimentally determined rate constant and the extent of dissociation of diazohydroxide is expressed by Eq. (2).

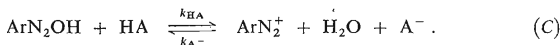
$$k' = k_{H_2O}[\text{ArN}_2\text{OH}]/([\text{ArN}_2\text{OH}] + [\text{ArN}_2\text{O}^-]) = k_{H_2O} ([\text{H}^+]/[\text{H}^+] + K_2). \quad (2)$$

In acetate buffers almost all benzenediazotate is transformed into benzenediazohydroxide. The rate constant  $k'$  does not depend on pH and (within experimental error) buffer concentration (maximum acetic acid concentration 0.05M), and hence it corresponds to  $k_{H_2O}$  of the reverse step of Eq. (A), i.e. non-catalyzed resp. water-catalyzed N—O bond splitting of diazohydroxide.

In dilute hydrochloric acid, the experimental constant  $k'$  increases linearly with proton concentration:

$$k' = k_{\text{H}_2\text{O}} + k_{\text{H}^+}[\text{H}^+]. \quad (3)$$

The rate constant  $k_{\text{H}^+}$  of the proton-catalyzed bond splitting was determined graphically from the dependence on the hydrochloric acid concentration. The experiments carried out in chloroacetate buffers at constant pH gave a linear dependence on concentration of undissociated chloroacetic acid, too. The rate constant  $k_{\text{HA}}$  was determined analogously as  $k_{\text{H}^+}$ . The determination of the catalytic influence of chloroacetic acid confirms the validity of general acid catalysis of the N—O bond splitting and, hence, of the reaction mechanism Eq. (C).



From the rate constants  $k_{\text{H}_2\text{O}}$ ,  $k_{\text{H}^+}$  and  $k_{\text{HA}}$ , the value of the Brönsted coefficient  $\alpha$  was calculated to be  $0.19 \pm 0.02$ . This value is smaller than that of 2,4-dinitro- and 2,6-dichloro-4-nitro derivatives<sup>4</sup> by 0.15. This can be caused by larger reactivity and hence lower selectivity of *m*- and *p*-substituted benzenediazohydroxides or by some specific influence of substituents in *o*-position on the structure of the activated complex. The low value of the coefficient  $\alpha$  indicates that the bond between the proton of catalyst acid and the OH<sup>-</sup> group being split off is formed only to a small extent in the activated complex.

In borax and phosphate buffers (3,4-dichloro derivative)  $k'$  decreases with increasing pH, because the ratio benzenediazohydroxide: benzenediazotate decreases. From the dependence of  $\log k'$  on pH the values  $\text{p}K_2$  were determined (Table I).

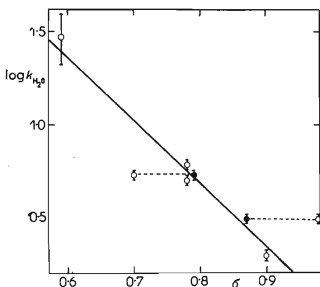


FIG. 1  
Dependence of  $\log k_{\text{H}_2\text{O}}$  on  $\sigma$  Constants  
○ The values of  $\sigma$  constants from ref.<sup>7</sup>,  
● the  $\sigma$  values calculated.

In the case of 3,4-dichloro derivative this dependence was used also for determination of the approximative value of  $k_{\text{H}_2\text{O}}$ , because the rate was so large in acetate buffers that the reaction half-life could not be determined from the oscilloscopic record.

3,4,5-Trichloro derivative (strongly) and 3-nitro derivative (to a considerable extent) deviate from the correlation of  $\log k_{\text{H}_2\text{O}}$  with the Hammett  $\sigma$  constants (Fig. 1). The both derivatives deviated considerably also in correlation of  $\log k_{\text{OH}}$  and  $\text{pH}_m$  (ref.<sup>3</sup>) with  $\sigma$  constants ( $\text{pH}_m = \text{pH}$  of the solution containing equal concentrations of diazonium and diazotate ions<sup>6</sup>), whereas for the remaining substituents the linear dependence was very good. At the same time the correlation of  $\log k_{\text{OH}}$  vs  $\text{pH}_m$  gave a very good linear dependence even when 3,4,5-trichloro- and 3-nitro derivatives were included ( $r$  0.988) which indicates that the effects which cause the deviations of the two derivatives in correlations with  $\sigma$  constants are the same in the both reaction series, so that they cancel each other in mutual correlation. A very good linear dependence with a slope  $-1.6 \pm 0.13$  is obtained for correlation of  $\log k_{\text{H}_2\text{O}}$  with  $\log k_{\text{OH}}$  including all substances (3,4,5-trichloro- and 3-nitro derivatives, too). If for these two derivatives the constants are calculated from the Hammett equations<sup>3</sup> for  $\log k_{\text{OH}}$  and  $\text{pH}_m$  and then used, practically all values of  $\log k_{\text{H}_2\text{O}}$  (Fig. 1) lie, within experimental error, on the line defined by Eq. (4).

$$\log k_{\text{H}_2\text{O}} = -3.4 \sum \sigma + 5.4. \quad (4)$$

A similar linear dependence (5) holds also for dissociation constants of the substituted benzenediazohydroxides.

$$\text{p}K_2 = -1.3 \sum \sigma + 8.1. \quad (5)$$

TABLE I

Dissociation Constants of Substituted Benzenediazohydroxides and Rate Constants of their N—O Bond Splitting at 20°C and Ionic Strength 0.25

Substituted benzenediazonium ion	$10^{-2}k_{\text{H}_2\text{O}},^a$ $\text{s}^{-1}$	$10^{-3}k_{\text{H}^+},$ $1 \text{ mol}^{-1} \text{ s}^{-1}$	$10^{-2}k_{\text{HA}},$ $1 \text{ mol}^{-1} \text{ s}^{-1}$	$\text{p}K_2^b$	Diazohydroxide %
3-NO <sub>2</sub> -4-Cl	1.95	8 ± 2	6.5 ± 2	6.90	2.05
3,4,5-Cl <sub>3</sub>	3.05	13 ± 3	10 ± 3	6.90	1.39
3,5-Br <sub>2</sub>	4.96	—	—	7.00	0.79
3,5-Cl <sub>2</sub>	6.03	20 ± 10	30 ± 15	7.05	0.90
3-NO <sub>2</sub>	5.34	20 ± 10	30 ± 15	7.15	1.11
3,4-Cl <sub>2</sub>	30.0	—	—	7.30	0.28

<sup>a</sup>Mean error ±5%; in the case of 3,4-dichloro derivative ±30%. <sup>b</sup>Mean deviation ±0.05; in the case of 3,4-dichloro derivative ±0.10.

The error in determination of  $\rho$  for  $pK_2$  is not greater than 0.15. Although the differences in reactivities of the substituted benzenediazohydroxides are considerable and it was possible to obtain the rate constants  $k_{H_2O}$  only for the five least reactive derivatives, we suppose that the  $\rho$  value lies within the limits  $-3.1$  to  $-3.6$ , the reasons being as follows: a similar value  $-3.3$  was obtained *a*) from the slope  $-1.6$  of the dependence of  $\log k_{H_2O}$  on  $\log k_{OH}$  and the  $\rho$  constant 2.06 (Eq. (6)) of the reaction of benzenediazonium ion with  $OH^-$  ion<sup>3</sup>, *b*) from the same value  $\rho$ , *i.e.* 2.06 and the  $\rho$  constants 6.66 (ref.<sup>3</sup>) and 1.3 for  $\log K$  (defined by Eq. (1)) and  $pK_2$ , respectively.

$$\log k_{OH} = (2.06 \pm 0.05) \sigma + (3.97 \pm 0.03) \quad (6)$$

Eqs (4)–(6) determine quantitatively the both reactions (A) and (B) and the dependence of their constants on substituents. From the values of equilibrium constants the maximum concentrations of substituted benzenediazohydroxides were calculated and are also given in Table I. The highest concentration is in the case of 3-nitro-4-chloro derivative; the concentration of diazohydroxide decreases with decreasing value of  $\sigma$  constants.

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