AZO COUPLING KINETICS OF BENZENEDIAZONIUM IONS WITH CITRAZINIC ACID

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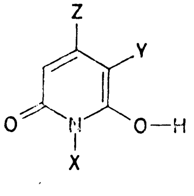
Azo coupling kinetics of 4-methoxybenzenediazonium ion with 1,2-dihydro-6-hydroxy-2-oxopyridine-4-carboxylic acid (citrazinic acid, *Ia*) have been measured in dilute solutions of hydrochloric acid and in chloroacetate, ethoxyacetate, acetate, and dihydrogenphosphate buffers. The reaction is subject to general base catalysis, i.e. splitting off of the proton from the tetrahedral intermediate is the rate-limiting step. The rate constants have been measured for the azo coupling reaction with monoanion *III* (splitting off of the proton from OH group) and dianion. The rate constant with the monoanion *III* is only 4× smaller than that with the dianion and practically the same as that with the anion of citrazinic acid ester *VIII*. The azo coupling rate constants of the monoanion *III* have been determined for various substituted benzenediazonium ions, the ϱ value found is 4·85.

Derivatives of 2-hydroxy-6-pyridone (general formula *I*) are important components of modern azo dyestuffs with brilliant greenish yellow hues.



I

The significance of this type of components for azo coupling reactions was recognized in the middle of the sixties, and the respective research activities in this field have led to more than 200 patents[1]. Recently increased attention has been paid to citrazinic acid *Ia* (X = Y = H, Z = COOH), 1,2-dihydro-6-hydroxy-2-oxopyridine-4-carboxylic acid [99-11-6], a quite new component from which e.g. the original reactive dyestuffs Ostazine Yellow H-7G and Ostazine Yellow S-7G were prepared[2].

Although there are a number of studies of kinetics and mechanism of azo coupling reactions with heterocyclic components described in literature[3], similar reactions with derivatives of 2-hydroxy-6-pyridone have not been studied yet. The aim of the present work is to study the coupling kinetics of citrazinic acid with selected monosubstituted benzenediazonium ions and to determine the pH profile of these reactions.

EXPERIMENTAL

Measurements

The melting points were measured on a Koffler apparatus. The electronic spectra were measured with a Zeiss Specord UV-VIS apparatus. The kinetic measurements were carried out spectrophotometrically with the same apparatus and the fast reactions ($\tau(1/2) < 5s$) were monitored by the stopped-flow technique using a Durrum D-150 apparatus. The ^1H and ^{13}C NMR spectra were measured at 99·602 and 25·046 MHz, respectively, in hexadeuteriodimethyl sulfoxide at 25°C with a JEOL JNM-FX 100 spectrometer. The chemical shifts are related to the solvent signal: $\delta(^1H)$ 2·55, $\delta(^{13}C)$ 39·6. The pH values of the buffer solutions were measured with an MV 870 apparatus (VEB Präcitronic, G.D.R.) using a combined glass and silver chloride electrode at 25°C.

Reagents

The substituted anilines, chloroacetic acid, ethoxyacetic acid, and acetic acid were commercial products of p.a. purity grade.

Citrazinic acid was supplied as a paste by the firm VCHZ Synthesia Semtín and was purified in the following way: 100 g of the acid was dissolved in a mixture of 130 ml 2·5 mol l^{-1} sodium hydroxide and water. The solution was hot filtered with charcoal and acidified with hydrochloric acid. The separated solid was collected by suction, washed with ethanol, and dried at 100°C. The citrazinic acid does not melt up to 300°C and decomposes above this temperature. Its purity was checked by both direct and indirect nitrosation titration[4] and was found to be above 99%. Solution of $4 . 10^{-3}$ mol l^{-1} monosodium salt of acid *Ia* was prepared in the following way: 62 mg ($4 . 10^{-4}$ mol) acid *Ia* was placed in a 100 ml calibrated flask, 40 ml 0·01M-NaOH was added along with 6·2 mg Chelaton III, and the volume was adjusted by addition of redistilled water. The fresh solution was prepared repeatedly every second day.

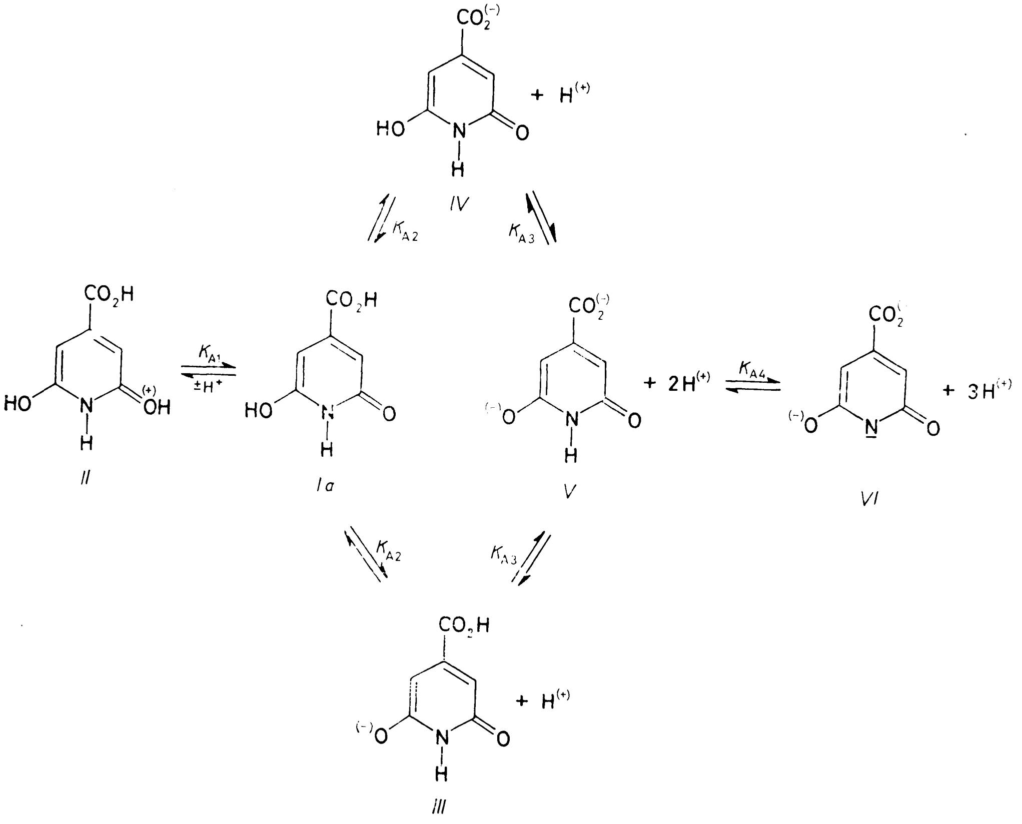
Methyl citrazinate (VII). Gaseous hydrogen chloride was introduced into a solution of 10 g citrazinic acid in 60 ml boiling methanol for 1·5 h. The hot reaction solution was decanted from an insoluble residue and cooled to 0°C. The separated crystals of hydrochloride of ester *VII* were washed with a small amount of ice-cold methanol (the hydrochloride is very soluble in methanol) which was removed by suction, and the solid was mixed with water. The liberated free base (6·5 g, 60%) was filtered off and recrystallized from methanol, m.p. 239—245°C (ref.[5] gives m.p. 232°C). The structure of the product was verified by NMR spectroscopy. ^1H NMR: 9·91 s, 2 H (NH + OH); 6·30 s, 2 H ($(CH_2)_2$); 3·85 s, 3 H (OCH_3). ^{13}C NMR: 165·44 (COO); 162·10 (C=O, C—OH); 143·04 (C-4); 98·16 (C-3, C-5); 52·76 (OCH_3).

Substituted benzenediazonium salts (IXa *unsubstituted compound*, IXb 4-*methyl*, IXc 4-*chloro*, IXd 4-*methoxy derivatives*). The respective substituted anilines were diazotized in 2·5 mol l^{-1} hydrochloric acid in the usual way. The solution of diazonium salt was filtered with charcoal and diluted to the required concentration. In the case of 4-chloroaniline the starting amine was —

at first — dissolved in hot 2·5 mol l^{-1} hydrochloric acid and then quickly cooled. The corresponding hydrochloride was precipitated in fine form; subsequent addition of sodium nitrite gave a clear solution of the diazonium salt. For the kinetic experiments fresh solutions of the salts *IXa—IXc* were prepared each day. The solution of 4-methoxy derivative *IXd*, which is very stable[6], was kept in a refrigerator and used for the whole set of experiments.

Measurements of Dissociation Constants (Scheme 1)

a) The equilibrium constant of the reaction $II \rightleftarrows Ia + H^+$: A 1 cm cell was charged with 0·2 ml 2 . 10^{-3} mol l^{-1} sodium citrazinate and 1·8 ml hydrochloric acid (0·01—5 mol l^{-1}), whereupon the spectrum was measured on the Specord UV VIS within the wavelength range of 250—350 nm at 25°C. The reference cell contained hydrochloric acid. The absorbance changes were read at 327 nm (the isosbestic point of the neutral species and monoanions). The dissociation constant was calculated from Eq. (*3*) (see Results and Discussion), where the quantity *R* is expressed by Eq. (*1*); here A, A_S, and A_{SH} stand for the absorbances in hydrochloric acid solutions, that of the neutral form in 2·5 . 10^{-3}M-HCl, and that of the protonated form of citrazinic acid



SCHEME 1

in 5M-HCl, respectively.

$$R = [II]/[Ia] = (A - A_S)/(A_{SH} - A) \qquad (1)$$

b) The equilibrium constant of the reaction $Ia \rightleftarrows III + IV + H^+$ was measured in similar way as that sub *a*) in chloroacetate and ethoxyacetate buffers at the ionic strength $I = 0{\cdot}5$ mol . l^{-1} which was adjusted by the addition of 2M-KCl. The absorbance changes were read at 312 nm (the isosbestic point of the mixture of the monoanions and dianion). The absorbance value of the neutral form was experimentally inaccessible and, therefore, was determined by the iterative method. The absorbance of the mixture of anions was measured in a 1 : 1 acetate buffer.

c) The equilibrium constant of the reaction $III + IV \rightleftarrows V + H^+$ was measured in acetate buffers again at $I = 0{\cdot}5$ mol l^{-1}. The absorbance changes were read at the wavelength of 327 nm (the isosbestic point of the neutral form and monoanion mixture). The absorbance of the dianion was determined by a measurement in a 1 : 1 phosphate buffer, and that of the mixture of monoanions in 5 . 10^{-3}M-HCl.

d) The equilibrium constant of the reaction $V \rightleftarrows VI + H^+$: A 1 cm was cell charged with 1·9 ml 1—5M-NaOH and 0·1 ml 4 . 10^{-3}M sodium citrazinate and the absorbance change was measured at 345 nm. The absorbance of the dianion was determined by the measurement in 1 . 10^{-3}M borax.

e) The dissociation constant of methyl citrazinate *VII* was measured in ethoxyacetate buffers at 384 nm: 25 μl 1 . 10^{-2} mol l^{-1} methyl ester *VII* was added into 2 ml ethoxyacetate buffer and potassium chloride. The absorbance of the neutral species *VII* was measured in 0·02 mol l^{-1} hydrochloric acid and that of the anion *VIII* in a 1 : 1 phosphate buffer.

Kinetic Measurements

The ester *VII* was dissolved in an equivalent amount of 0·1 mol l^{-1} sodium methoxide and methanol was added to adjust the concentration of 10^{-2} mol l^{-1}. For the kinetic measurements this methanolic solution was diluted with water to the concentration of 8 . 10^{-4} mol l^{-1}.

For the measurements on the Specord UV VIS apparatus (i.e. in chloroacetate, ethoxyacetate, and acetate buffers and hydrochloric acid) a 1 cm cell was charged with the required amount of 0·1M-HCl or buffer, citrazinic acid *Ia* or ester *VII*, and potassium chloride (to make the final ionic strength $I = 0{\cdot}5$ mol l^{-1}) and the volume was adjusted at 2 ml by addition of water. After attaining the temperature of 25°C, 10 μ 6 . 10^{-3} mol l^{-1} diazonium salt was injected and the absorbance increase was monitored at the λ_{max} of the azo dyestuff formed (4-methoxy 453 nm, 4-methyl 440 nm, 4-chloro 432 nm, H 440 nm). In all the cases the excess of citrazinic acid or ester *VII* was at least ten fold, so the reaction kinetics was of the pseudofirst order. The observed rate constants k_{obs} were evaluated by the Guggenheim method[7].

The kinetic experiments with citrazinic acid in acetate and phosphate buffers and in sodium hydroxide solutions were carried out by the stopped-flow technique (Durrum D-150 apparatus). One syringe contained the calculated amounts of buffer, citrazinic acid, and potassium chloride completed with water to the total volume of 20 ml; the other syringe contained the diazonium salt solution (3 . 10^{-5} mol l^{-1}) in redistilled water. The rate constants were calculated from the reaction half-lives read from the screen of oscilloscope or calculated graphically from Eq. (*2*).

$$k_{obs}t = -\log(A_\infty - A) + \text{const.} \qquad (2)$$

RESULTS AND DISCUSSION

Citrazinic acid *Ia* can exist in various forms in the media used: protonated *II*, neutral *Ia*, mixture of monoanions *III* + *IV*, dianion *V*, and – in strongly basic media – trianion *VI* (Scheme 1). The reactive forms which can be taken into account in the azo coupling reaction with diazonium salts include the monoanion *III*, dianion *V*, and possibly (at high pH values) trianion *VI*. The solution of monosodium salt turned dark rapidly, the citrazinic acid content (determined from the yield of the azo coupling reaction) decreased by ca 20% within two days. Therefore we added ethylenediaminetetraacetic acid (Chelaton III) to the solution (see Experimental): this addition in the amount of 10% with respect to citrazinic acid slowed down the undesirable reactions by 1 to 2 orders of magnitude. In order to find whether or not the presence of Chelaton III affects the reaction rate, we carried out – side by side – azo coupling experiments with as much as 10 fold concentration of Chelaton III. The reaction rate was the same in all the cases.

The protonation of neutral form *Ia* takes place at such high proton concentration that it is impossible to adopt pH, hence the dissociation constant $\mathrm{p}K_{a1}$ was calculated[8] from Eq. (*3*) where X is the so-called excess acidity function which reflects the difference between the acidity of medium related to a standard base and that corresponding to the proton concentration itself[8].

$$\log R - \log [\mathrm{H}^+] = \mathrm{p}K_a + mX \qquad (3)$$

The dissociation constants K_{a2} and K_{a3} and that of the ester (K_{a5}) were measured in buffer solutions and evaluated in usual way from Eq. (*4*). The values found are shown in Table I.

$$\mathrm{p}K_a = \log R + \mathrm{pH} \qquad (4)$$

TABLE I

The values of dissociation constant ($\mathrm{p}K_{a1-3}$) of dissociation of citrazinic acid *Ia* and ($\mathrm{p}K_{a5}$) of its ester *VII* in water at 25°C

$II \rightleftarrows Ia + \mathrm{H}^+$ ($\mathrm{p}K_{a1}$)	$Ia \rightleftarrows III + IV + \mathrm{H}^+$ ($\mathrm{p}K_{a2}$)	$III + IV \rightleftarrows V + \mathrm{H}^+$ ($\mathrm{p}K_{a3}$)	$VII \rightleftarrows VIII + \mathrm{H}^+$ ($\mathrm{p}K_{a5}$)
0·265 ± 0·015	2·78 ± 0·06	4·4 ± 0·03	3·52 ± 0·04

For determination of the equilibrium constant of reaction $V \rightleftarrows VI + H^+$ we plotted the log R values against the $H_=$ acidity function[9]. The dependence is linear with the slope of 1·35, and $\log R = 0$ for $H_= = 15{\cdot}45$ (2·2M-NaOH).

The greater part of the kinetic runs were carried out with 4-methoxy derivative *IXd*, since this ion is extraordinarily stable and shows the lowest reactivity allowing measurements within a wide pH range. The reaction course obeyed the pseudofirst-order kinetics in all the cases; k_{obs} was directly proportional to the concentration of citrazinic acid in the given medium. That means that the reaction is 1. order in each of the reacting components. The rate constants k_{obs} were transformed into the stoichiometric constants k_S by dividing them by the analytical concentration of citrazinic acid.

When measuring the azo coupling rates we found that the rate constants exhibited a linear increase with the buffer concentration. The dependence of k_S on concentration of some selected buffers is given in Fig. 1. For determination of the pH profile of the coupling reaction the k_S values were extrapolated to zero buffer concentration. The dependence of logarithms of the extrapolated values k_{ex} on pH is presented in Fig. 2. Table II presents the k_{ex} values and the buffers used.

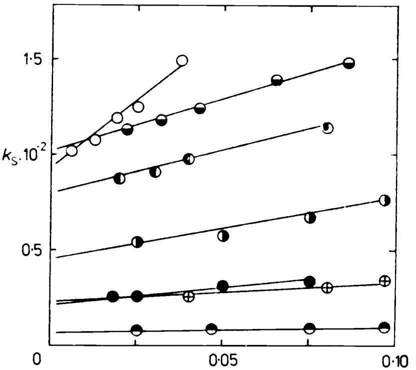


FIG. 1

The dependence of k_S (l mol^{-1} s^{-1}) on the molar concentration of basic component of buffer for the reaction of citrazinic acid (*Ia*) with 4-methoxybenzenediazonium ion (*IXd*) in 4 : 1 acetate buffer (○); 2 : 1 ethoxyacetate buffer (●); 1 : 1 (◑), 1 : 2 (◐), and 1 : 3 (◒) ethoxyacetate buffers; in 1 : 2 (⊕) and 2 : 1 (◓) chloroacetate buffer

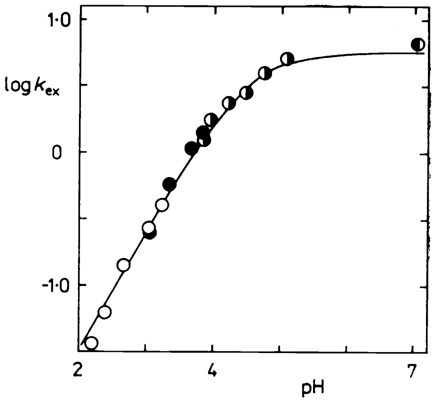


FIG. 2

The pH dependence of log k_{ex} (○ chloroacetate, ● ethoxyacetate, ◑ acetate, ◐ dihydrogenphosphate buffer)

The only forms practically existing in the buffer solutions used include the neutral form *Ia*, the mixture of monoanions *III* + *IV*, and the dianion *V*. The concentrations of the charged species are given by Eqs (*5*) and (*6*),

$$[III] + [IV] = K_{a2}a_{H}c_{I}/Z \tag{5}$$

$$[V] = K_{a2}K_{a3}c_{I}/Z\,, \tag{6}$$

where c_I is the analytical concentration of citrazinic acid, and $Z = (a_H)^2 + K_{a2}a_H + K_{a2}K_{a3}$.

The azo coupling rate extrapolated to zero buffer concentration is expressed in Eq. (*7*)

$$v = \frac{k_{34}a_{H}K_{a2} + k_{5}K_{a2}K_{a3}}{Z}\, c_{I}[ArN_2^+] = k_{ex}[ArN_2^+]\, c_I\,, \tag{7}$$

TABLE II

The rate constants k_{ex} (l mol^{-1} s^{-1}) of the reaction of *Ia* with *IXd* in chloroacetate (1), ethoxyacetate (2), acetate (3), and dihydrogenphosphate (4) buffers; the slope α from Fig. 1 and the values of r (αk_{ex}^{-1})

Buffer	[BH]/[B$^-$]	$k_{ex} . 10^{-1}$	$\alpha . 10^{-2}$	r
1	3 : 1	0·36	2·1	5·8
	2 : 1	0·60	3·3	5·5
	1 : 1	1·26	7·8	6·2
	1 : 2	2·28	12·0	5·3
	1 : 3	3·24	16·8	5·2
2	2 : 1	2·16	15·6	6·8
	1 : 1	4·50	30·0	6·7
	1 : 2	7·92	45·0	5·6
	1 : 3	10·20	55·2	5·4
3	4 : 1	9·36	138	147
	3 : 1	12·60	168	133
	2 : 1	16·20	222	138
	1 : 1	19·20	264	137
	1 : 2	26·40	324	123
	1 : 4	33·60	402	120
4[a]	1 : 2	42·00	7 200	1 700

[a] BH = $H_2PO_4^-$.

where a_H is the proton activity, k_5 is the rate constant of reaction of diazonium ion with dianion *V*, k_{34} is the overall rate constant of reaction of diazonium ion with the monoanions *III* and *IV* defined by Eq. (*8*).

$$k_{34}([III] + [IV]) = k_3[III] \qquad (8)$$

The relation (7) was transformed into Eq. (9), and the values of constants were calculated by linear regression: $k_{34} = (19 \pm 2)\,\mathrm{l\,mol^{-1}\,s^{-1}}$, $k_5 = (420 \pm 10)\,\mathrm{l\,mol^{-1}}\,.\,\mathrm{s^{-1}}$.

$$k_{ex}\left(\frac{(a_H)^2}{K_{a2}} + a_H + K_{a3}\right) = k_{34}a_H + k_5K_{a3} \qquad (9)$$

From Eq. (9) and from the found rate and equilibrium constants we calculated the curve of the dependence of log k_{ex} vs pH given in Fig. 2.

The rate constant k_5 is greater than k_{34} by the factor of 22, but the real rate constant k_3 of the reaction with anion *III* is much greater (see Eq. (*8*)). Its estimation necessitates the knowledge of K_{III} of the reaction $Ia \rightleftarrows III + H^+$. This constant K_{III} is experimentally inaccessible. As the constants σ have the same values for COOH and COOR (ref.[10]), we presumed the pK_{III} value to be the same as pK_a of ester *VII*, i.e. 3·52.

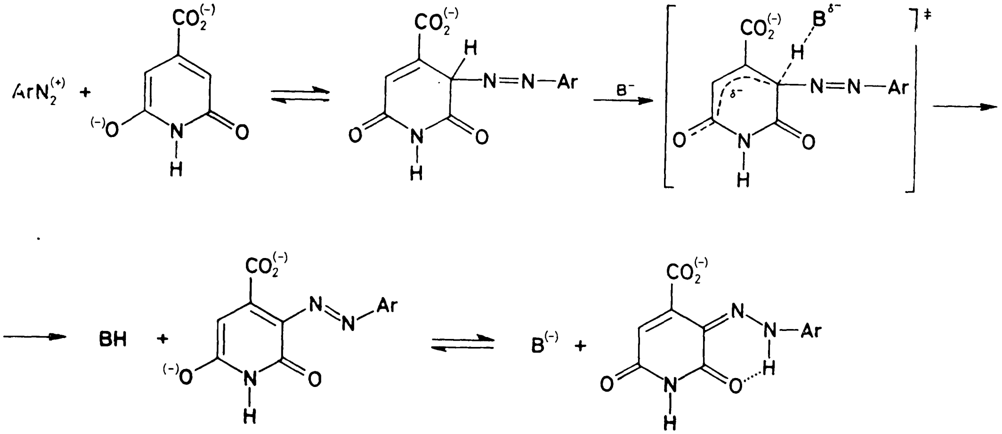
From the relation $K_{a2} = K_{IV} + K_{III}$ and from the values given for K_{a2} and K_{III} it was calculated that the fraction of anion *III* in the mixture of both anions is 0·18, wherefrom $k_3 = 19/0{\cdot}18 = 105{\cdot}6$, which means that the rate constant of the reaction with monoanion *III* is smaller than that with the dianion by the factor of only 4.

Under the fairly reasonable presumption that the sterical effect of *ortho*-methoxycarbonyl group is the same as that of *ortho*-carboxylic group the rate constant of azo coupling with ester *VII* should be comparable with the rate constant k_3. The dependence of the rate constant k_S of the azo coupling reaction of 4-methoxyderivative *IXd* with ester *VII* on the concentration of chloroacetate, ethoxyacetate, and acetate buffers is presented in Fig. 3. As there is only one reactive form (anion of ester *VIII*) present in the solution, the dependence of k_{ex} on the proton activity is much simpler (cf. Eq. (*10*)):

$$k_{ex} = k_8K_{a5}/(K_{a5} + a_H) = k_8f\,, \qquad (10)$$

where f is the fraction of the ester anion *VIII* in the equilibrium mixture of the ester and its anion, and k_8 is the rate constant of reaction of diazonium ion with anion *VIII*. The rate constant $k_8 = (85 \pm 3)\,\mathrm{l\,mol^{-1}\,s^{-1}}$ is comparable in value with the k_3 constant.

The dependence of k_{ex} on the concentration of the basic component of buffer (Figs 1 and 3) indicates that the rate-limiting step consists in the splitting off of the proton from the intermediate formed by addition of benzenediazonium ion to monoanion or dianion of citrazinic acid (or monoanion of ester *VIII*) and not in the formation of these intermediates as it is usual with azo coupling reactions[11] (Scheme 2).



SCHEME 2

This change in the rate-limiting step is caused by sterical effects in the intermediate (neighbouring groups), and similar situation was encountered with the azo coupling reactions of 1-hydroxynaphthalene-3-sulfonic acid and 7-hydroxynaphthalene-1-sulfonic acid[11]. In our case the steric hindrance is caused by the ester or carboxylic (or COO^-) group.

In the azo coupling reaction with anion of ester *VIII* the rate constant k_S in the given buffer is given by Eq. (*11*)

$$k_S = k_{ex} + \alpha[B] = f(k_8 + k_B[B])\,, \qquad (11)$$

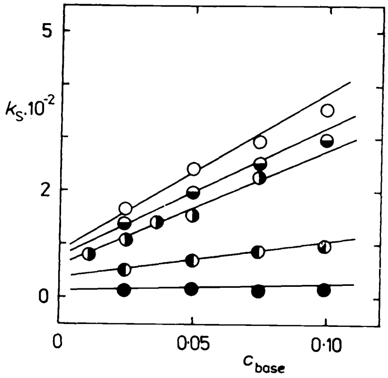


FIG. 3

The dependence of k_S (1 mol^{-1} s^{-1}) on the molar concentration of basic component of buffer for the reaction of methyl citrazinate (*VII*) with 4-methoxybenzenediazonium ion (*IXd*) in various buffers (○ 1 : 4, ◒ 1 : 1, ◑ 4 : 1 acetate; ◐ 1 : 1 ethoxyacetate; ● 1 : 1 chloroacetate) where α is the slope of the dependence of the rate constant k_S on the basic component of buffer, and k_B is the rate constant of the general-base-catalyzed reaction of diazonium ion with the anion of ester *VIII* (k_B is equal to the product of the equilibrium constant of formation of the intermediate and the rate constant of splitting off of the proton (Scheme 2)). For the buffers used Table III gives the k_B values calculated from the relation $k_B = \alpha/f$.

The situation is more complex in the azo coupling reaction with dianion and monoanion of citrazinic acid, since the k_S values found represent the sum of the rate constants of the reactions with dianion and monoanion (Eq. (*12*)):

$$\begin{aligned} k_S = k_{34S} + k_{5S} &= f^-(k_{34} + k_{34B}[B]) + f^{2-}(k_5 + k_{5B}[B]) = \\ &= k_{34ex} + \alpha^-[B] + k_{5ex} + \alpha^{2-}[B], \end{aligned} \qquad (12)$$

where f^- and f^{2-} are the fractions of monoanion and dianion in the mixture (Eqs (*5*) and (*6*)), α^- and α^{2-} are the slopes of dependences of the rate constant for the monoanion and dianion, respectively. If α^-/k_{34ex} were equal to α^{2-}/k_{5ex}, then k_{34B} would be equal to $\alpha k_{34}/k_{ex}$ and similarly k_{5B} would be equal to $\alpha k_5/k_{5ex}$, where α and k_{ex} are the values found experimentally for the individual buffer ratios (Table III). Table III also gives their ratios r whose values show that for a given buffer the r value decreases with increasing contribution of the pathway via dianion, i.e. the base catalysis is less significant in the reaction with dianion than in that with monoanion. In chloroacetate buffers the share of the rates of the buffer-noncatalyzed reaction pathways via dianion and monoanion (calculated from the f values and k_{34} and k_5, respectively) decreases from 5 for the most acidic buffer to 0·8. In the ethoxyacetate buffers the corresponding limits are 1 and 0·2. In the acetate and phosphate

TABLE III

The rate constants k_B (l^2 mol^{-2} s^{-1}) of the reactions of compounds *III*—*V* and *VII* with 4-methoxy derivative *IXd* catalyzed by the basic component of chloroacetate (1), ethoxyacetate (2), acetate (3), and dihydrogenphosphate (4) buffers

Buffer ($BH + B^-$)	k_B		
	VII	*III* + *IV*	*V*
1	689	114 (636)[a]	1 440
2	1 378	174 (960)[a]	2 040
3	3 074	—	5 560
4[b]	—	—	$7·2 . 10^4$

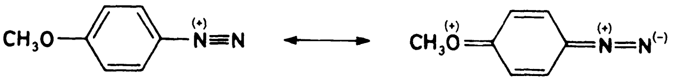
[a] Recalculated for the fraction of the anion *III*; [b] $BH = H_2PO_4^-$.

buffers the reactions go via the dianion except for acidic acetate buffers in which the share of the reaction pathway via the monoanion is less that 15% in the most acidic buffer. Using the relative shares of the reaction pathways in the given buffers and the r values of Table III we estimated the r values for both the individual pathways in the individual buffer types and calculated the k_B values for the reactions with the monoanions and dianions in the individual buffers (Table III).

The value of the Brønsted coefficient calculated from the dependence of log k_B on pK_a of the acidic component of buffer[12] is $\beta = 0{\cdot}35-0{\cdot}40$. In solutions of sodium hydroxide the k_S value increases linearly with OH^- ion concentration. The rate constant k_{OH} calculated from the dependence of k_S on the OH^- ion concentration is $(24{\cdot}6 \pm 1) \cdot 10^5\ l^2\ mol^{2-}\ s^{-1}$ and represents the rate constant of the hydroxyl-ion-catalyzed reaction of diazonium ions with dianion of citrazinic acid (Scheme 2; $B = OH^-$), the reaction of diazonium ion with trianion of citrazinic acid being very little likely.

The effect of substituents in benzenediazonium ion on the azo coupling rate was estimated in dilute hydrochloric acid solutions at the proton concentrations enabling application of the Specord UV VIS apparatus to the measurement. The dependence of log k_S on the proton concentration is presented in Fig. 4. From this dependence we read the average values of $\log (k/k_0)$, where k_0 is the rate constant for the non-substituted benzenediazonium ion.

In the *para*-substituted benzenediazonium ions *IXc*–*IXd* partial delocalization of electron pairs can take place such as e.g. in Eq. (*A*), and therefore Eq. (*13*) was adopted for the correlation of log k with the substituent constant[13] using



(*A*)

$$\log (k/k_0) = \varrho\sigma + r(\sigma^+ - \sigma) \qquad (13)$$

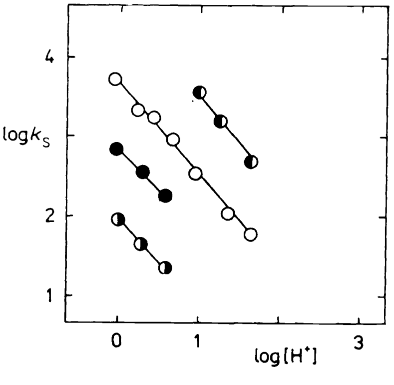


FIG. 4

The dependence of log k_S on log [H$^+$] for selected diazonium ions (○ benzendiazonium, ● 4-methylbenzenediazonium, ◐ 4-chlorobenzendiazonium, ◑ 4-methoxybenzenediazonium) the value of $r = 0{\cdot}26$ from ref.[14]. The value found for the reaction constant $\varrho = 4{\cdot}85 \pm 0{\cdot}15$ is substantially higher than that for usual azo coupling reactions in which the formation of intermediate is rate-limiting, and it approaches the ϱ values found for azo coupling reactions of 1-hydroxynaphthalene-3-sulfonic acid in which the splitting off of the proton from the intermediate is rate-limiting.

REFERENCES

1. Schwander H. R.: Dyes Pigments *3*, 133 (1982).
2. Cee A., Chmátal V., Vencl J., Dvořák J., Kuthan P.: Czech. 216 606; Chem. Abstr. *89*, 112 366 (1978).
3. Szele I., Zollinger H.: Top. Curr. Chem. *112*, 2 (1983).
4. Matrka M.: Chemie *10*, 635 (1958).
5. Pitha J.: Collect. Czech. Chem. Commun. *28*, 1408 (1963).
6. Crossley M. L., Kienle R. H., Benbrook C. H.: J. Am. Chem. Soc. *62*, 1400 (1940).
7. Štěrba V., Panchartek J.: *Kinetické metody při studiu reakcí organických sloučenin*, p. 66. SNTL, Prague 1985.
8. Cox R. A., Yates K.: Can. J. Chem. *59*, 2116 (1981).
9. Halle J. C., Terrier F., Schaal R.: Bull. Soc. Chim. Fr., II *1969*, 4569.
10. Exner O.: *Correlation Analysis of Chemical Data*. Plenum Press, New York 1988.
11. Zollinger H.: Helv. Chim. Acta *38*, 1597, 1617 (1955).
12. Ref.[7], p. 191.
13. Yukawa Y., Tsuno Y.: Bull. Chem. Soc. Jpn. *32*, 971 (1959).
14. Panchartek J., Štěrba V., Vorlíček J., Večeřa M.: Collect. Czech. Chem. Commun. *33*, 894 (1968).

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