COUPLING KINETICS OF BENZENEDIAZONIUM IONS WITH 2,6-DIOXO-3-(*p*-SUBSTITUTED PHENYLHYDRAZONO)-1,2,3,6-TETRAHYDROPYRIDINE-4-CARBOXYLIC ACID

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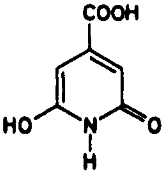
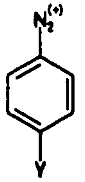
The kinetics have been measured of the reactions of 4-nitro-, 4-chloro-, and 4-methoxybenzenediazonium ions with substituted phenylazo derivatives of citrazinic acid in buffer solutions, and the pK_a values of the corresponding monoazo and bisazo compounds have been estimated. The reactions of 4-nitrobenzenediazonium ion with 4-chloro- and 4-methoxyphenylazo derivatives and of 4-chlorobenzenediazonium ion with 4-methoxyphenylazo derivative were accompanied by a partial replacement of the substituted phenylazo group by the 4-nitro- and 4-chlorophenylazo groups, respectively. The reactions of 4-chloro- and 4-methoxybenzenediazonium ions are subject to general base catalysis, the rate-limiting step consisting in the splitting off of the proton from the tetrahedral intermediate; with 4-nitrobenzenediazonium ion the reaction rate is limited by the formation of the tetrahedral intermediate.

Our previous paper[1] dealt with the coupling kinetics of 4-methoxybenzenediazonium ion with citrazinic acid (*I*) in dilute solutions of hydrochloric acid and in chloroacetate, ethoxyacetate, acetate, and dihydrogenphosphate buffers. The reaction is subject to general base catalysis, i.e. the rate-limiting step consists in the splitting off of the proton from the tetrahedral intermediate. Also estimated were the coupling rate constants with substituted benzenediazonium ions; the high value of the constant $\rho = 4.85$ confirms the mechanism suggested.

The aim of the present work was to study the azo coupling kinetics of 4-methoxy- (*IIa*), 4-chloro- (*IIb*), and 4-nitrobenzenediazonium (*IIc*) ions with 2,6-dioxo-3-(4-methoxyphenylhydrazono)- (*IIIa*), 2,6-dioxo-3-(4-chlorophenylhydrazono)- (*IIIb*), and 2,6-dioxo-3-(4-nitrophenylhydrazono)-1,2,3,6-tetrahydropyridine-4-carboxylic acid (*IIIc*), respectively, (which were formed by azo coupling reactions of the respective benzenediazonium ions with citrazinic acid) to give the corresponding 2,6-dioxo-5-(4-methoxyphenylazo)- (*VIa*), 2,6-dioxo-5-(4-chlorophenylazo)- (*VIb*), and 2,6-dioxo-5-(4-nitrophenylazo)-3-(4-nitrophenylhydrazono)-1,2,3,6-tetrahydropyridine-4-carboxylic (*VIc*) acids. Another aim was to estimate the pK_a values of the mono- and bisazo compounds prepared and to compare them with the pK_a value of citrazinic acid.



I



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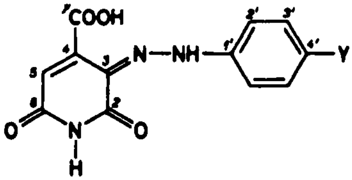


III

In formulae *II* and *III*: *a*, Y = OCH_3; *b*, Y = Cl; *c*, Y = NO_2

EXPERIMENTAL

Reagents

Citrazinic acid (compound (*I*), VCHZ Synthesia Semtín) was purified by a known procedure[1]. Also the preparation of solutions of substituted benzenediazonium salts for kinetic measurements was described in the previous communication[1]. The buffers were prepared from redistilled water and chemicals of p.a. purity grade. The pH values of the solutions were determined with the help of an MV 870 apparatus (VEB Praecitronic, Germany) using a combined glass and silver chloride electrode at 25 °C. The ^1H and ^{13}C NMR spectra were measured with a Bruker AM 400 apparatus at 400.13 MHz (^1H) and 100.61 MHz (^{13}C) in hexadeuteriodimethyl sulfoxide at 25 °C. The chemical shifts are referenced to the solvent signal $\delta(^1H)$ 2.55, $\delta(^{13}C)$ 39.6 (Table I). The electronic spectra were measured with a Zeiss-Specord UV-VIS apparatus.

Preparation of Monoazo Compounds *IIIa* – *IIIc*

A solution prepared from 40 mmol substituted aniline and 44 ml 2.5 M-HCl (3.5 M-HCl for 4-nitroaniline) was cooled to 0 to −5 °C and treated with a solution of 40 mmol sodium nitrite in 16 ml water. The solution of diazonium salt obtained was filtered with charcoal and treated with 40 ml 1 M CH_3COONa (60 ml for 4-nitrobenzenediazonium salt), whereupon it was added with stirring to a solution of 6.35 g (40 mmol) citrazinic acid in 60 ml 1 M-NaOH. The mixture was stirred for another 1 h, and the dyestuff was collected by filtration, washed with water, and dried in air.

Preparation of Bisazo Compounds *VIa* – *VIf*

The diazonium salt solution prepared in the same way as above was added to a solution of 2.95 g (19 mmol) citrazinic acid in 120 ml 1 M-Na_2CO_3 (165 ml for 4-nitrobenzenediazonium salt). The reaction mixture was stirred 1.5 h, whereafter the dyestuff was collected by filtration, washed with water, and dried in air.

Both the monoazo and bisazo compounds were purified by dissolving 0.5 g of the substance in 40 ml 0.1 M-NaOH, filtering with charcoal, and pouring into 55 ml 0.1 M-HCl at ca 60 °C (65 ml 0.1 M-HCl for the bisazo compounds). After 2 – 5 h, the crystalline solid was collected by filtration, washed with water, and dried in air. The purity was verified by ascending TLC (Silufol; propanol–ammonia 2 : 1). The physi-

TABLE I

Chemical shifts $\delta(^{1}H)$ and $\delta(^{13}C)$ of monoazo compounds *IIIa* – *IIIc* in dimethyl sulfoxide-d_6 at 25 °C (for denotation see formula *III* on p. 1916)

Denotation H/C	*IIIa*		*IIIb*		*IIIc*	
	$^{1}H^{a}$	$^{13}C^{a}$	^{1}H	^{13}C	^{1}H	^{13}C
2^{b}	–	163.5	–	163.5	–	163.5
3	–	120.5	–	122.0	–	124.4
4	–	146.1	–	145.7	–	145.3
5	6.16	113.6	6.26	115.5	6.36	117.5
6^{b}	–	161.7	–	161.5	–	161.3
7	–	166.0	–	165.7	–	165.4
1'	–	134.9	–	140.5	–	147.0
2'	7.43	117.7	7.45	117.7	7.63	116.1
3'	7.00	115.0	7.45	129.4	8.26	125.5
4'	–	157.6	–	129.3	–	143.6
NH	14.21	–	13.98	–	13.96	–

[a] $\delta(OCH_3) = 3.76$ (^{1}H) / 55.5 (^{13}C); [b] the assignment of signals can be reversed.

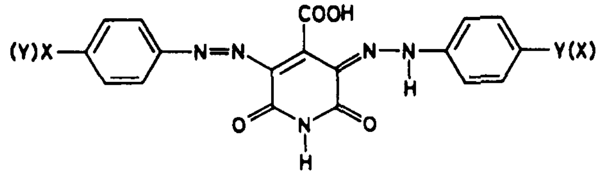
TABLE II

Properties of monoazo compounds *IIIa* – *IIIc* and bisazo compounds *VIa* – *VIf*

Compound	R_F	$\lambda_{max}{}^{a}$ nm	ε l mol^{-1} cm^{-1}	Calculated/Found		
				% C	% N	% H
IIIa	0.48	452	33 700	54.00	14.50	3.80
				54.30	14.80	3.52
IIIb	0.59	432	34 400	49.20	14.34	2.73
				49.20	14.25	2.62
IIIc	0.45	437	46 400	47.40	18.40	2.63
				47.66	18.80	2.60
VIa	0.52	518	36 300	–	–	–
VIb	0.76	488	35 000	–	–	–
VIc	0.65	479	33 300	–	–	–

[a] Measured in acetate buffer 1 : 1.

cal properties, elemental analyses, and R_F values of the mono- and bisazo compounds prepared are given in Table II. For the kinetic experiments and for pK_a measurements we prepared 10^{-2} mol l^{-1} solutions of the monoazo compounds and 5 . 10^{-3} mol l^{-1} solutions of bisazo compounds in 0.01 M borax. The measurements were carried out at 25 °C at the ionic strength of 0.5 mol l^{-1} (adjusted by addition of potassium chloride) in the following buffers: acetate, $CH_3COOH : CH_3COONa$ = 4:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:4; phosphate, $HPO_4^{2-} : H_2PO_4^-$ = 3:1, 2:1, 1:1, 1:2, 1:3; glycinamide, $NH_2CH_2CONH_2.HCl : NH_2CH_2CONH_2$ = 7:1, 5:3, 3:1, 1:1, 1:3, 3:5, 1:7; borax, $HBO_2 : BO_2^-$ = 3:1.5, 3:1, 1:1, 3:5, 3:7.5.



VI

	a	*b*	*c*	*d*	*e*	*f*
X	OCH_3	Cl	NO_2	OCH_3	OCH_3	Cl
Y	OCH_3	Cl	NO_2	Cl	NO_2	NO_2

Estimation of pK_a

The spectra of solutions of monoazo compounds were measured in the borax buffers, phosphate buffer (the spectra of monoanions *IVa* – *IVc*), and in 0.01 M-NaOH (the spectra of dianions *Va* – *Vc*) in the wavelength interval of 350 – 600 nm. Similarly measured were the spectra of the bisazo compounds in acetate buffer (the spectra of monoanions *VIIa* – *VIIf*), in 0.01 M-NaOH and 0.1 M borax (for the nitro derivative *VIc*) (the spectra of dianions *VIIIa* – *VIIIf*) and in phosphate (for the nitro derivative *VIc*), glycinamide (methoxy derivative *VIa*), and in both phosphate and glycinamide buffers (the chloro derivative *VIb*). In all the cases the spectra showed well-developed isosbestic points. At a chosen wavelength the absorbances were measured in buffer solutions, and the pK_a values (Table III) were calculated from Eq. (*1*),

$$pK_a = \log I + pH, \qquad (1)$$

where $\log I = (A_S - A) / (A - A_{SH})$, and A_{SH}, A_S , and A are the absorbances of the monoanion, dianion and in the buffer solutions, respectively.

Kinetic Measurements

A 10 ml calibrated flask was charged with the necessary amount of buffer (see Table IV), potassium chloride solution and redistilled water. The solution was temperated at 25 °C, and the calculated amount of diazonium salt solution was added thereto. The final volume of the mixture was 10 ml. Using a pipette, 2 ml of the solution was transferred from the flask into a 1 cm quartz cell, and 10 to 16 μl 5 . 10^{-3} mol l^{-1} monoazo compound solution was injected to it at the time t = 0, whereafter the absorbance changes were monitored at a chosen wavelength (Table IV). The rest of the solution in the calibrated flask was used for pH estimation. The rate constants k_{obs} were calculated from Eq. (2) or determined by the Guggenheim method[2] (for slow reactions).

$$k_{obs} = (1 / t) \ln (A_{\infty} - A_t) + \text{const.} \qquad (2)$$

RESULTS AND DISCUSSION

pKa Values

The pK_a values of the mono- and bisazo compounds investigated are presented in Table III. The phenylazo group present as a substituent increases, by its polar effect, the acidity of carboxylic group. The K_a value of the bisazo compound *VIa* is higher than that of the monoazo compound *IIIa* by one order of magnitude, the difference being as high as two orders in the case of the bisazo compound *VIc*. The pK_a value of citrazinic acid (formation of the dianion) is 4.4; the polar effect of arylazo group should lower this value (according to the analogy with the difference between mono- and bisazo compounds) by 1 – 2 orders of magnitude, and – on the other hand – formation of hydrogen bond should cause an increase by 2 – 3 orders of magnitude, hence the pK_a value of the monoazo compounds should be 5.5 – 6.5. In reality, the pK_a values are in the interval of 8.93 – 9.16, i.e. higher by ca three units than the above estimate, which is obviously due to formation of a very stable hydrazone form (the ^{1}H NMR spectra of all three monoazo compounds *IIIa* – *IIIc* exhibit signals corresponding to the pure hydrazone forms). The pK_a difference between the 4-methoxy (*IIIa*) and 4-nitro (*IIIc*) derivatives of monoazo compounds is 0.23, whereas the difference ΔpK_a of mono- and bisazo compounds for 4-nitro derivatives *IIIc* and *VIc* (1.89) and 4-methoxy derivatives *IIIa* and *VIa* (0.71) is 1.18, i.e. more than a four-fold, in spite of the fact that the substituent on the second phenylazo group is much more remote from the N–H group.

TABLE III

pK_a values of monoazo compounds *IIIa* – *IIIc* and bisazo compounds *VIa* – *VIf* measured in aqueous solutions at 25 °C at λ_{anal} (nm) and wavelengths of isosbestic point λ_{iso} (nm)

Compound	λ_{anal}	λ_{iso}	pK_a
I	–	–	4.40
IIIa	450.0	416.0	9.16
IIIb	435.0	463.0	9.10
IIIc	440.0	465.0	8.93
VIa	408.0	490.0	8.45
VIb	400.0	448.3	7.60
VIc	555.5	510.0	7.04

TABLE IV

Rate constants k_2 ($l\ mol^{-1}\ s^{-1}$), k_B ($l^2\ mol^{-2}\ s^{-1}$), and values of their ratios $r = k_B / k_2$ for coupling reactions of benzenediazonium ions *IIa* – *IIc* with monoazo compounds *IIIa* – *IIIc* in aqueous solutions of borax (1), phosphate (2), and acetate (3) buffers at 25 °C

Diazonium ion	Buffer	*IIIa*				*IIIb*				*IIIc*			
		k_2	k_B	r	λ	k_2	k_B	r	λ	k_2	k_B	r	λ
IIa	1	2.15 (± 0.15)	37 (± 2)	17.2	520.0	0.69 (± 0.03)	9.0 (± 0.8)	13	500.0	0.044 (± 0.008)	0.44 (± 0.09)	10	555.5
	2	2.50 (± 0.30)	62 (± 4)	24.8	550.0	–	–	–	–	–	–	–	–
IIb	1	–	–	–	–	213 (± 20)	800 (± 100)	3.8	500.0	19 (± 2)	90 (± 20)	4.7	540.0
	2	1 970[a] (± 100)	16 000 (± 800)	8.1	510.2	215 (± 15)	1 700 (± 200)	7.9	510.2	–	–	–	–
IIc	1	–	–	–	–	–	–	–	–	940 (± 15)	–	–	540.0
	2	–	–	–	–	12 000[b] (± 900)	–	–	500.0	925 (± 30)	–	–	500.0
	3	90 000[c] (± 7 000)	–	–	530.0	13 000[b] (± 800)	–	–	500.0	–	–	–	–

[a] k_{ex} = 1 480 ± 180; [b] k_{ex} = 8 400 ± 900; [c] k_{ex} = 90 000 ± 7 000 ($l\ mol^{-1}\ s^{-1}$).

The pK_a difference of 1.18 corresponds to the ρ constant of ca 1, which roughly agrees with the reaction constants ρ found with substituted 1-phenylazo-2-naphthols[3] (1.44) existing predominantly in the hydrazone forms, and with 2-hydroxy-5-methylazobenzene[4] (1.22) measured in 50% methanol. This means that the ρ value of the monoazo derivatives is low (about 0.25).

The Coupling Kinetics

The coupling kinetics of substituted benzenediazonium ions *IIa* – *IIc* with substituted azo derivatives of citrazinic acid *IIIa* – *IIIc* was studied in acetate, phosphate, and borax buffers. In all the cases an at least ten-fold excess of the diazonium salt was used, hence the reaction was kinetically of pseudo-first order.

The coupling reaction described by Scheme 1 obeys the kinetic equation (*3*), where $k_2 = k_1k_2^0 / (k_{-1} + k_2^0)$ is the rate constant of noncatalyzed and/or water-catalyzed reaction ($\mathrm{l\,mol^{-1}\,s^{-1}}$), $k_B = k_1k_2^B[B]/(k_{-1} + k_2^B[B])$ is the rate constant of the reaction catalyzed by the basic buffer component B ($\mathrm{l^2\,mol^{-2}\,s^{-1}}$).

$$v = \mathrm{d[product]}/\mathrm{d}t = (k_2 + k_B[B])\,[\mathrm{ArN_2^+}]\,[\text{azo compound}^{2-}] =$$

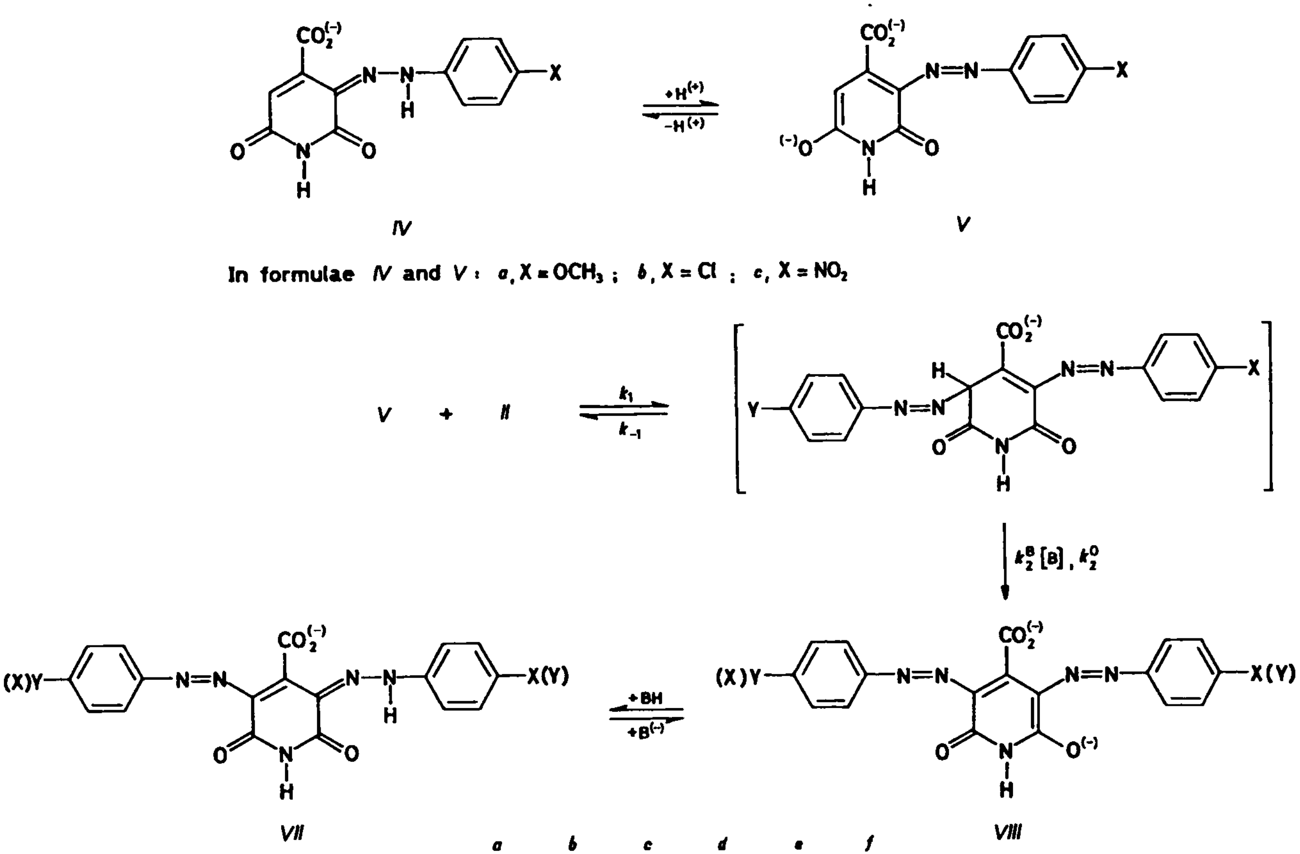
$$= (k_2 + k_B[B])\,(K_a / (K_a + a_{H^+}))\,c_{\text{azo compounds}} =$$

$$= k_S\,[\mathrm{ArN_2^+}]\,c_{\text{azo compounds}} = k_{obs}\,c_{\text{azo compounds}} \qquad (3)$$

In the reactions of methoxybenzenediazonium ion *IIa* with the dianions of monoazo compounds *Va* – *Vc* the time dependence of absorbance increase was exponential in all the cases, and the A_∞ value (found after 7 – 8 half-lives) did not change with time any more.

In the reactions of chlorobenzenediazonium ion *IIb* with chlorophenylazo derivative *IIIb* of citrazinic acid and, to a lesser extent, of nitrobenzenediazonium ion *IIc* with nitrophenylazo derivative *IIIc* the maximum absorbance was attained after ca 4 – 5 half-lives, whereafter a roughly linear decrease was observed. This decrease was substantially faster in borax buffers than in acetate buffers, and its rate increased with the buffer concentration. The decrease is probably due to the radical decomposition of substituted benzenediazohydroxide and subsequent attack of the azo compound by the radicals formed. For the calculation of k_{obs} the corrected A_∞ values were obtained by extrapolation from the practically linear decrease of absorbance to the corresponding time t.

The reactions of nitrobenzenediazonium ion *IIc* with chloro *IIIb* and methoxyphenylazo *IIIa* derivatives and of chlorobenzenediazonium ion *IIb* with methoxy derivative *IIIa* proceeded kinetically in two steps. In the reaction of nitrobenzenediazonium ion *IIc* with methoxy derivative *IIIa* the rate of the second step was



In formulae *IV* and *V*: *a*, X = OCH_3 ; *b*, X = Cl ; *c*, X = NO_2

	a	*b*	*c*	*d*	*e*	*f*
X	OCH_3	Cl	NO_2	OCH_3	OCH_3	Cl
Y	OCH_3	Cl	NO_2	Cl	NO_2	NO_2

SCHEME 1

lower by ca two orders of magnitude, hence the two reactions could be followed separately (one in acetate buffer and the other in phosphate buffers).

In the reaction of nitrobenzenediazonium ion *IIc* with the chloro derivative *IIIb* the second step was ca 35× slower: when the first step was practically finished, there took place an only slight, practically linear increase of absorbance, hence the corrected A_∞ values were obtained by linear extrapolation to the corresponding time.

With chlorobenzenediazonium ion *IIb* and methoxy derivative *IIIa* the difference between the rate constants was still smaller, hence the two rate constants had to be evaluated by the method used for a system of two consecutive competitive reactions[2].

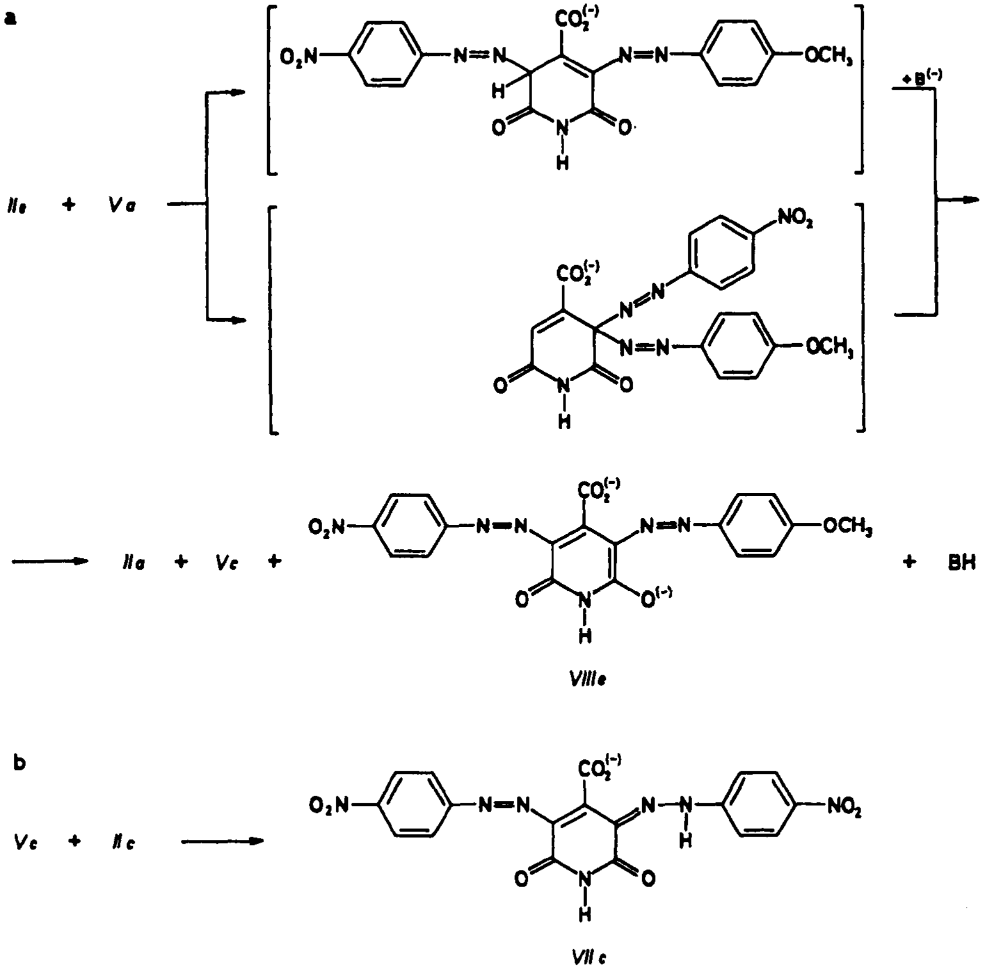
When evaluating the rate constants of the second step we found that in the reaction of nitrobenzenediazonium ion *IIc* with the methoxy (*IIIa*) and chloro (*IIIb*) derivatives the k_{obs} value is the same in both cases and practically identical with the rate constant of reaction of nitrobenzenediazonium ion *IIc* with the nitro derivative *IIIc*. Similarly, with chlorobenzenediazonium ion *IIb* the rate constant of the second step was comparable with that of the reaction of chlorobenzenediazonium ion *IIb* with chloro derivative *IIIb*. Therefrom it follows that the first step involves the formation of bisazo compound and – simultaneously – replacement of the substituted phenylazo group of the original azo compound by the more reactive nitro *IIIc* or chlorophenylazo *IIIb* group (Scheme 2). The overall rate constant k_{tot} of the first step is given by Eq. (*4*), where k_{coup} is the rate constant of formation of the bisazo derivative and k_{ex} is the rate constant of exchange of one phenylazo group for the other.

$$k_{tot} = k_{coup} + k_{ex} \qquad (4)$$

In order to confirm this substitution reaction, we compared the spectrum of the reaction mixture formed in the reaction of nitrobenzenediazonium ion *IIc* with methoxyphenylazo derivative *IIIa* in acetate buffer (where only the first step takes place, i.e. the simultaneous formation of the "mixed" bisazo compound *VIIIe* and replacement of methoxyphenylazo group by nitrophenylazo group) with the spectra of the reaction mixtures obtained from the reactions of benzenediazonium ion *IIa* with nitrophenylazo derivative *IIIc* (Fig. 1). The two spectra would be identical if the reaction of methoxybenzenediazonium ion with the nitrophenylazo derivative proceeded to 50%. This means that in the first reaction step the formation of bisazo derivative and the replacement of methoxyphenylazo group by nitrophenylazo group proceed at the same rate.

The next step consisted in verification of formation of 4-methoxybenzenediazonium ion (*IIa*) in the reaction. For this purpose, citrazinic acid was added after the reaction was finished with application of ca 0.9 equivalents of 4-nitrobenzenediazonium ion (*IIc*) in a reaction mixture containing acetate buffer. The plot of absorbance change had the same shape and the same λ_{max} as the 4-methoxyphenylazo derivative *IIIa*, and the calculated percentage of replacement reaction (55%) is – within experimental error – the same as that in the first method. This method was adopted with a modification for estimation of relative proportion of the replacement reaction in the first step for the remaining two cases. In the reaction of 4-nitrobenzenediazonium ion (*IIc*) with 4-chlorophenylazo derivative *IIIb* the replacement of 4-chlorophenylazo group by 4-nitrophenylazo group proceeded to 40% and in the reaction of 4-nitrophenylazo derivative *IIIc* with 4-chlorobenzenediazonium ion (*IIb*) it makes 43%.

The rate constants k_{obs} (and k_S) with 4-methoxy- and 4-chlorobenzenediazonium ions increased with increasing concentration of the basic buffer component (for a given buffer ratio). The dependence was linear in all the cases (Fig. 2).



SCHEME 2

$$k_S = y_0 + \alpha[B] \tag{5}$$

$$k_2 = y_0\,[1 + (a_{H^+}/K_a)] \text{ and } k_B = \alpha\,[1 + (a_{H^+}/K_a)] \tag{6}$$

In all the cases the ratio r of the slope α of the given dependence to the intercept y_0 at the y axis ($r = \alpha/y_0$) was substantially greater for 4-methoxy derivative *IIIa* than for 4-chloro derivative *IIIb* (Table IV), but it was at least one order smaller than that in the reaction of 4-methoxybenzenediazonium ion (*IIa*) with citrazinic acid (*I*) in the same buffer. With 4-nitrobenzenediazonium ion (*IIc*), either no increase of k_S with the basic buffer component concentration was observed or a small increase of k_S (in phosphate buffers) was caused by the pH increase connected with increasing buffer concentration. Therefrom it can be concluded that in the case of 4-methoxy- and 4-chlorobenzenediazonium ions the rate-limiting step consists in splitting off of the proton by the basic buffer component (k_2^B) and/or by water (k_2^0) like in the reactions with citrazinic acid. According to these results, with the 4-nitro derivative *IIIc*, where no base catalysis was proved, the rate-limiting step probably consists in the reaction of diazonium ion with the dianion of monoazo compound ($k_2 = k_1$).

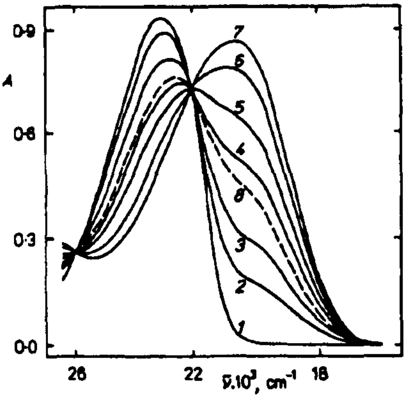


Fig. 1
Spectral record (acetate buffer 1:1) of the products formed from monoazo compound *IIIc* ($c_0 = 3 \cdot 10^{-5}$ mol l^{-1}) and benzenediazonium ion *IIa* in borax buffer at 25 °C after 2, 4, 9, 14, 24, and 60 min (curves *2* – *7*). Spectral record of reaction product from monoazo compound *IIIa* ($c_0 = 3 \cdot 10^{-5}$ mol l^{-1}) and benzenediazonium ion *IIc* in acetate buffer 1 : 1 (curve *8*). Spectrum of monoazo compound *IIIc* in acetate buffer 1 : 1 (curve *1*)

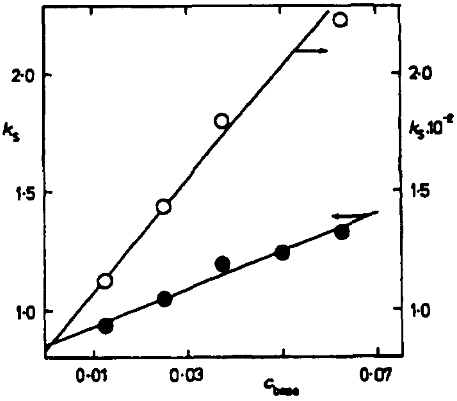


Fig. 2
Dependence of rate constant k_S (l mol^{-1} s^{-1}; Eq. (*5*)) on the base concentration in phosphate buffer for the reactions of *IIa* + *Va* (○) and *IIb* + *Vb* (●)

Table IV presents the values of k_2, k_B, k_{ex}, and $r = \alpha/y_0$ (or $r = k_B/k_2$) for the individual buffer types. In the cases of simultaneous replacement of azo group the k_2 values were calculated with the presumption that base catalysis did not operate in the replacement reaction.

Figure 3 presents the dependence of $\log k_2$ on the σ constants for the reactions of substituted benzenediazonium ions *IIa* – *IIc* with the individual phenylazo derivatives *IIIa* – *IIIc*, and Fig. 4 gives the same dependence for the reactions of substituted phenylazo derivatives with 4-chloro- (*IIb*), 4-methoxy- (*IIa*), and 4-nitrobenzenediazonium (*IIc*) ions. In the first case we used[7] Eq. (*7*) and in the second case Eq. (*8*).

$$\log k / k_0 = \rho \, [\sigma + 0.26 \, (\sigma^+ - \sigma)] \qquad (7)$$

$$\log k / k_0 = \rho \, \sigma \qquad (8)$$

With all the three monoazo compounds *IIIa* – *IIIc* the dependence is nonlinear (Fig. 3) and a considerable break is observed in it; the slope calculated from the values for 4-methoxy- (*IIa*) and 4-chlorobenzenediazonium (*IIb*) ions is $\rho = 4.6$ like in the reactions with citrazinic acid (*I*) in accordance with the fact that the rate-limiting step is the splitting off of the proton from the intermediate. The subsequent abrupt decrease in slope to the value of 3.1 is typical of a change in the rate-limiting step – in accordance with the above statement that no base catalysis was observed in the reaction with 4-nitrobenzenediazonium ion (*IIc*). The rate-limiting splitting off of the proton from the

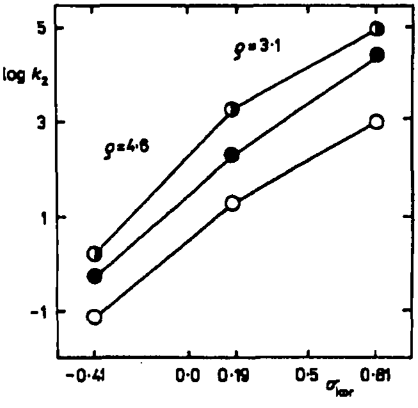


Fig. 3

Dependence of $\log k_2$ (Eq. (*6*)) on $\sigma_p + 0.26(\sigma_p^- - \sigma_p)$ for reactions of substituted benzenediazonium ions *IIa* – *IIc* with dianions of monoazo compounds *Va* (○), *Vb* (●) and *Vc* (◑)

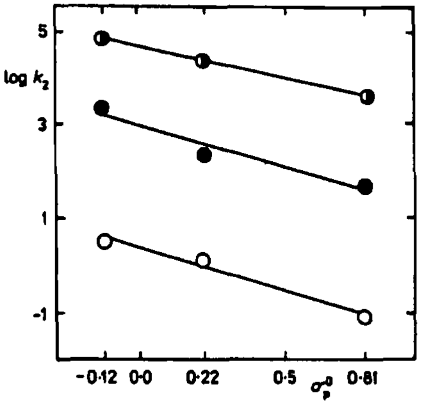


Fig. 4

Dependence of $\log k_2$ (Eq. (*6*)) on σ_p^0 constants for reactions of dianions of monoazo compounds *Va* – *Vc* with substituted benzenediazonium ions *IIa* (○), *IIb* (●) and *IIc* (◑)

tetrahedral intermediate which was observed in the coupling reactions with 4-hydroxynaphthalene-2-sulfonic acid and 7-hydroxynaphthalene-1-sulfonic acid was explained by steric effect of the adjacent sulfonic acid group[6]. In our case the formation of bisazo compound should be sterically affected by the adjacent COO^- group even more markedly than the formation of monoazo compound, however, the base catalysis is much weaker with 4-methoxy- (*IIa*) and 4-chlorobenzenediazonium (*IIb*) ions and is completely absent with 4-nitrobenzenediazonium ion (*IIc*). This result suggests that polar effect of the substituted phenylazo group which is introduced becomes decisive in this case. The stronger electron-attracting this group is, the more acidic is the proton in C–H bond and the more easily it is split off. At the same time also the energy needed for reverse splitting off of the diazonium group is increased, hence there is a change in the rate-limiting step with the 4-nitro derivative *IIIc*. The polar effect of substituted phenylazo group in the monoazo derivatives probably also causes much weaker operation of base catalysis in this case than in the coupling reaction of citrazinic acid[6].

In the reactions of the individual substituted benzenediazonium ions *IIa* – *IIc* with the series of three monoazo dyestuffs *IIIa* – *IIIc* (Fig. 4) the values of slopes of dependences of $\log k_2$ on σ_p^0 constants are similar although the reaction of 4-nitrobenzenediazonium ion (*IIc*) has a different rate-limiting step. The values of ρ constants are in the range of 2 ± 0.2.

The substituent in phenylazo group has the greatest effect on the stability of the intermediate. The more the structure of the activated complex differs from that of the intermediate, the weaker is the effect of substituent on its stability (as expressed by the ρ constant). The comparable values of ρ constants of the reactions of dianions of compounds *Va* – *Vc* with the diazonium ions *IIa* – *IIc* suggest that the distances between the activated complexes of rate-limiting steps and the corresponding intermediate (at the reaction coordinate) are comparable.

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