

KINETICS AND MECHANISM OF DIAZO COUPLING. XXIV.*
 COUPLING KINETICS OF BENZENEDIAZONIUM IONS
 WITH RESORCINOL AND ITS O-METHYL DERIVATIVES

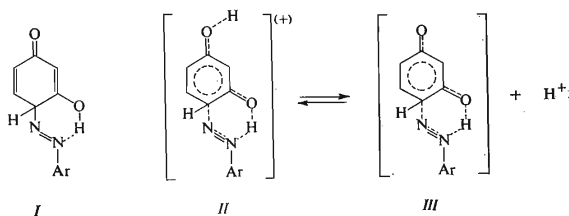
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Undissociated resorcinol reacts with substituted benzenediazonium ions in water more slowly than resorcinol monoanion by about 7.5 orders of magnitude, whereas the respective dianion is more reactive by about 4.5 orders of magnitude. Although the anion of 3-methoxyphenol reacts practically at the same rate as the resorcinol monoanion, 3-methoxyphenol reacts with substituted benzene diazonium ions about 2–3 times more slowly than 1,3-dimethoxybenzene and about 20 times more slowly than resorcinol. The differences found have been explained, on the one hand by different influence of the activating groups, and on the other hand, by the so called "levelling effect" of O^- groups mainly. The rate constants of the reaction of substituted benzenediazonium ions with resorcinol, 3-methoxyphenol, and their anions have been correlated with the Hammett equation.

In the papers^{1,2} the activating influence of O^- , OH and OR groups at the 1-position of naphthalene on the reaction rate with substituted benzenediazonium ions was compared.



The aim of the present paper is to carry out a similar comparison for such instances when there is another one activating group of the same type present in the molecule. A comparison of the previous results with the present ones should supply some

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information about the magnitude of the so called "levelling effect" of one strongly activating group on the action of another activating group. Resorcinol and its O-methyl derivatives were chosen as a model. These compounds have the both groups in the so called alternating position, so that both can make themselves felt by their inductive as well as resonance effects during the reaction. Phenol can be supposed to be the first member of this series, being a derivative with hydrogen at *m*-position.

Coupling kinetics of resorcinol with several substituted benzenediazonium ions were studied by Conant and Peterson³ and, by Elofson and coworkers⁴. They found that the angular coefficients of the dependence of $\log k$ on pH attained a value higher than unity at higher pH values, and they explained this fact by a simultaneous coupling with resorcinol dianion. They did not, however, determine the respective rate constant of the reaction with the dianion.

EXPERIMENTAL

A commercial sample of resorcinol was used. 3-Methoxyphenol was prepared by methylation of resorcinol with dimethyl sulphate in alkaline medium⁵. The reaction mixture was extracted with benzene (removal of 1,3-dimethoxybenzene), and the oil separated on acidification was extracted with benzene. The organic layer was then washed with water several times to remove resorcinol, benzene was distilled off, and the residue was purified by distillation⁶ (b.p. 244°C).

1,3-Dimethoxybenzene: 5.5 g (0.05 mol) resorcinol was dissolved in 250 ml ether containing about 4.5 g (0.11 mol) diazomethane. The solution was left to stand overnight at the room temperature. Ether was distilled off after repeated washing with diluted sodium hydroxide. The residue was dissolved in about 30 ml 70% aqueous methanol, and, after addition of 3 g sodium dithionite, the mixture was heated at 60°C 20 minutes (removal of eventual coupling product of diazomethane with resorcinol). After cooling, acidification and dilution with water, the oil separated was extracted with benzene, organic layer was washed with water and benzene was distilled off. The remaining 1,3-dimethoxybenzene was then purified by distillation⁷ (b.p. 214 to 215°C). The yield was about 2.5 g. The solutions for kinetic measurements were prepared in a similar way as in the previous work². The other chemicals used were commercial samples of p.a. purity grade.

4-(4'-Chlorophenylazo)- and 4-(phenylazo)-3-methoxyphenol: 2.5 g (0.02 mol) 3-methoxyphenol was dissolved in 500 ml solution of 10 g sodium acetate and 2 ml conc. acetic acid. 10 ml 1M diazonium salt solution was added dropwise into this mixture with stirring at 5°C. After 30 minutes, the amorphous dyestuff was extracted with benzene, the organic layer was concentrated and chromatographed through a small column filled with silica gel. The by-products were removed by benzene elution, and the main product was eluted with acetone and, after evaporating the solvent, crystallized from aqueous methanol. For 4-phenylazo-3-methoxyphenol $C_{13}H_{12}N_2O_2$ (228.2) calculated: 68.40% C, 5.30% H, 12.26% N; found: 68.10% C, 5.50% H, 12.27% N; m.p. 140°C. For 4-(4'-chlorophenylazo)-3-methoxyphenol $C_{13}H_{11}N_2O_2Cl$ (262.7) calculated: 59.45% C, 4.22% H, 10.67% N; found: 59.30% C, 4.32% H, 10.65% N; m.p. 105–106°C. Proton NMR spectra were measured with the use of a Tesla BS-487 A apparatus at $26 \pm 2^\circ C$ in $CDCl_3$ with hexamethyldisiloxane as the internal standard.

Kinetic Measurements

Direct measurements of extinction of the azo dyestuff formed. This method was used for the measurement of kinetics of the coupling of resorcinol with the diazo compounds less reactive than 3-nitrobenzenediazonium chloride. Usually, 1 ml $1 \cdot 10^{-4}$ M diazonium salt solution was added into the tempered solution of the substrate in buffer or diluted mineral acid located in a 50 ml calibrated flask; a part of the solution was transferred into a 3 cm quartz cell placed in the thermostated cellholder of a VSU-2 P spectrophotometer (Zeiss, Jena), and the time dependence of the extinction was followed at a wavelength corresponding to λ_{\max} of the azo dyestuff formed. The reaction was followed up to 2–3 half-lives. The rate constant was obtained graphically by plotting $\log E$ vs time according to Eq. (1)

$$k't = -2.303 \log (E_{\infty} - E_t) + C_1, \quad (1)$$

where E_t and E_{∞} are the extinction of the solution at a time t and that of the final solution respectively.

Measurements of diazonium compound decrease. This method had to be adopted in the cases of the polysubstituted diazonium ions which gave sparingly soluble dyestuffs. Aqueous diazonium salt solution was added to the stirred reaction solution located in a thermostat at 20°C, and, at regular time intervals, 5 ml samples were withdrawn with a pipette and added into 10 ml 10^{-2} M 1,8-dihydroxynaphthalene-3,6-disulfonic acid in 50 ml calibrated flask, 10 ml ethanol was added to each sample and the volume was adjusted with distilled water. The extinction measurements were carried out at λ_{\max} 510 nm. The rate constants were determined graphically again,

$$k't = -2.303 \log (E_t - E_{\infty}) + C_2 \quad (2)$$

Eq. (2) being used. From the experimental rate constants and the known concentration of substrate, the bimolecular rate constants $k_1 - k_{v1}$ were computed relating to the reaction of a certain benzenediazonium ion with resorcinol, its mono- and dianion, 3-methoxyphenol, its anion, and 1,3-dimethoxybenzene respectively. The same indices have been used for the respective dissociation constants.

Competing reaction with 2-hydroxynaphthalene-6-sulfonic acid. 0.5 ml $5 \cdot 10^{-4}$ M diazonium salt solution was injected rapidly from a syringe into a solution of 25 ml 0.1 M borax, the calculated amount of 0.1 M hydrochloric acid (pH 8.35), 2.5 ml 10^{-3} M resorcinol and 10–20 ml 10^{-2} M 2-hydroxynaphthalene-6-sulfonic acid under stirring at 20°C. After five minutes, 2 ml 4 M acetic acid was added, and the extinction was measured at 475–505 nm. The ratio of rate constants relating to analytical concentrations of the substrates was calculated from Eq. (3) where [R]

$$k_{NS}/k_R = ([R]/[NS]) ((E - E_R)/(E_{NS} - E)) \quad (3)$$

and [NS] are the concentrations of resorcinol and 2-hydroxynaphthalene-6-sulfonic acid respectively, and the ratio of extinction differences gives the ratio of the reaction products of the respective benzenediazonium ion with 2-hydroxynaphthalene-6-sulfonic acid and resorcinol. The rate constants were calculated from the rate constant ratio (k_R/k_{NS}) obtained from Eq. (3) and on the basis of the constant k_{NS} calculated from the Hammett equation (4) where 3.18 is the ρ constant of

$$\log k_R = \log (k_R/k_{NS}) + \log k_{NS} = \log (k_R/k_{NS}) + 3.18\sigma + C_3 \quad (4)$$

the coupling reaction of substituted benzenediazonium ions with 2-hydroxynaphthalene-6-sulfonic

acid⁸ and the σ constants refer to the substituent in benzenediazonium ion. The value of C_3 constant was calculated from the same equation, when the coupling rate constant of 4-methoxybenzenediazonium ion with resorcinol dianion (obtained directly under the same conditions as in the competing reactions) was used for k_R . The mixtures of solution of borax, boric acid, Na_2HPO_4 - KH_2PO_4 , sodium acetate-acetic acid, boric acid-sodium citrate, Na_2SO_4 - KHSO_4 were used as buffers. The constant ionic strength $I = 0.1$ was adjusted by addition of potassium chloride.

RESULTS AND DISCUSSION

The coupling kinetics of resorcinol with the substituted benzenediazonium ions was studied in the acidity range $\text{H}_0 - 0.9$ to pH 8.6. In strongly acid region the reaction was followed with benzenediazonium ion and its more reactive substitution derivatives, whereas 4-methoxy- and 4-methylbenzenediazonium ions were used for the kinetic measurements at higher pH values. The reaction was 1. order both in diazonium ion and resorcinol in the whole range studied and in all cases. As an at least eightfold excess of resorcinol was used, the reaction took the pseudomonomolecular course. The respective 4-phenylazoresorcinol derivative was the only product detected in all cases.

In acid medium the increase of H_0 value from about -0.3 to -0.9 caused a reaction rate decrease of about 10% only. This small change is obviously due to the influence of medium on the activity coefficients of the starting substances and activated complex. The reaction of the substituted benzenediazonium ions with the undissociated resorcinol is practically the only reaction to be considered in this medium. The influence of decreasing acidity of medium on the reaction rate was studied in detail in the case of 3-nitrobenzenediazonium ion. Decreasing proton concentration from pH 0.3 results in a gradual increase of the rate constant. This is caused by the fact that resorcinol monoanion makes itself felt in the reaction to a gradually increasing extent, so that the experimental rate constant is given by Eq. (5).

$$k'/[\text{R}] = k_1 + k_{11}K_1/[\text{H}^+]. \quad (5)$$

The coupling rates of 3-nitrobenzenediazonium ion with resorcinol and its anion are equal at pH 1.3. In the pH range 2.5-5.5 the dependence of $\log k$ on pH is linear with all the benzenediazonium ions studied, the angular coefficient being unity, which correspond to the reaction of resorcinol monoanion. From the experimental values the rate constants of reactions of the substituted benzenediazonium ions were calculated (Table I).

The dependence of $\log k$ on pH deviates from linearity, the rate constant being increased more rapidly up to pH 7.5, when the linear dependence is restored, the angular coefficient being, however, 2 (Fig. 1). At pH > 8 the rate constant increases more slowly than it should increase according to the abovementioned linear dependence, which is caused by the fact that the concentration of undissociated resorcinol

cannot be considered to be constant, so that the dianion concentration does not increase with the square of $[\text{OH}^-]$. From the values obtained experimentally, the coupling rate constant of 4-methoxy- and 4-methylbenzenediazonium ion with

TABLE I

Dependence of Coupling Rate Constants ($1 \text{ mol}^{-1} \text{ min}^{-1}$) of Substituted Benzenediazonium Ions with Resorcinol, 3-Methoxyphenol and their Anions on σ Constants (water, 20°C , $1/0.1$)

Experimental error is maximum $\pm 15\%$ for resorcinol dianion and maximum $\pm 10\%$ for the other substrates.

Substituent	$\sum\sigma^a$	Resorcinol			3-Methoxyphenol	
		k_I	k_{II}	k_{III}	k_{IV}	k_V
4-OCH ₃	-0.40	—	$1.39 \cdot 10^4$	$3.80 \cdot 10^8$	—	$1.66 \cdot 10^4$
4-CH ₃	-0.20	—	$5.06 \cdot 10^4$	$1.78 \cdot 10^9$	—	$9.32 \cdot 10^4$
3-CH ₃	-0.10	—	—	$3.73 \cdot 10^9$	—	—
H	0.00	$1.35 \cdot 10^{-2}$	$3.52 \cdot 10^5$	$7.42 \cdot 10^9$	—	$3.65 \cdot 10^5$
4-Cl	0.20	$7.88 \cdot 10^{-2}$	$2.32 \cdot 10^6$	$2.75 \cdot 10^{10}$	—	$2.89 \cdot 10^6$
3-Cl	0.39	$3.63 \cdot 10^{-1}$	$9.72 \cdot 10^6$	$6.02 \cdot 10^{10}$	—	$1.55 \cdot 10^7$
2-Cl	0.44	$4.69 \cdot 10^{-1}$	—	—	—	—
3-NO ₂	0.70	3.47	$1.92 \cdot 10^8$	$1.70 \cdot 10^{11}$	1.58	$2.0 \cdot 10^8$
3,5-di-Cl	0.78	4.62	—	—	1.33	—
2,4,6-tri-Cl	1.08	$4.47 \cdot 10^1$	—	—	$1.26 \cdot 10^1$	—
2-Cl-4-NO ₂	1.24	$1.05 \cdot 10^2$	—	—	$3.47 \cdot 10^1$	—
2,6-di-Cl-4-NO ₂	1.68	$2.77 \cdot 10^3$	—	—	$7.52 \cdot 10^2$	—

^a Most values of σ constants see ref.¹⁴, the values of *p*-Cl, *p*-CH₃ and *p*-OCH₃ were modified according to ref.¹⁵. The value of $\sigma_{0-\text{Cl}}$ was read from the correlation of coupling rate constants of monosubstituted benzenediazonium ions with undissociated resorcinol.

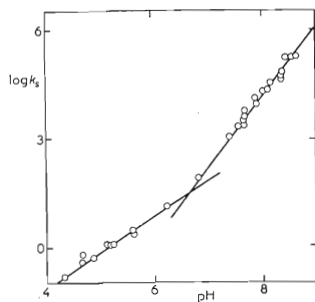


FIG. 1

Dependence of Logarithm of Stoichiometric Rate Constant of Coupling of 4-Methoxybenzenediazonium Ion with Resorcinol on pH

Water, 20°C , ionic strength $I = 0.1$.

resorcinol dianion ($\text{pH} > 7.5$) was calculated using Eq. (6) where K_{II} is the dissociation

$$\log k_{III} = \log(k'/[R]) + \text{p}K_I + \text{p}K_{II} - \text{pH} + \log(K_I + [H^+]) \quad (6)$$

constant of resorcinol to the second degree. The reaction of the other more reactive benzenediazonium ions was too rapid under the conditions used, so that the rate constants could be obtained only with difficulties in this way or were inaccessible. Therefore, the rate constants k_R (equivalent to the term $k'/[R]$ in Eq. (6)) were obtained by the method of competing reactions. A method similar to that used for resorcinol and its monoanion was adopted for rate constant determination of the reactions of substituted benzenediazonium ions with 3-methoxyphenol and its anion (Table I). In the case of the undissociated 3-methoxyphenol the coupling rates of nitrobenzenediazonium and more reactive diazonium ions were measured. The less reactive reagents could not be used because of the low solubility of 3-methoxyphenol. Both the undissociated 4-methoxyphenol and its anion give two coupling products. 4-Phenylazo derivative is the predominating product (70–80% according to visual estimate) as it was ascertained on the basis of NMR spectra. The coupling site was determined by comparison of spectra of 4-phenylazo- and 4-(4'-chlorophenylazo)-resorcinol with those of 4-phenylazo- and 4-(4'-chlorophenylazo)-3-methoxyphenol. As the derivatives of resorcinol were slightly soluble, it was possible to identify only the OH proton in *o*-position to the azo group at -3.90 and -3.45τ . On the contrary, the 3-methoxyphenol derivatives showed no singlet of OH proton in the range -4 to -3τ , wherefrom it follows that the coupling took place at the *o*-position to the methoxy group. The coupling kinetics of 1,3-dimethoxybenzene were measured only with the two most reactive benzenediazonium ions because of low solubility and low reactivity. The reaction was again 1. order in both the diazonium ion and 1,3-dimethoxybenzene. The results are given in Table I. The reaction product was uniform in the both cases. On the basis of analogy with the coupling products of resorcinol and 3-methoxyphenol, we supposed that the coupling took place at position 4.

In order to be able to compare the results obtained with those of kinetic studies of coupling of 1-naphthol and 1-methoxynaphthalene, the coupling rate constants of 2-chloro-4-nitrobenzenediazonium ion with resorcinol, 3-methoxyphenol and 1,3-dimethoxybenzene were determined in 32% (by vol.) acetic acid. The results are given in Table II. When studying the coupling kinetics of substituted benzenediazonium ions with 1-naphthol¹ and 1-methoxynaphthalene² we found that the difference in rate constants of coupling of 1-naphthol and 1-naphtholate ion was about 8 orders of magnitude and 1-methoxynaphthalene reacted slower than undissociated 1-naphthol by about 2 orders of magnitude. Table II summarizes the $\log k$ values of the reactions of benzenediazonium ion resp. 3-nitro- and 2-chloro-4-nitrobenzenediazonium ions with 1,3-disubstituted benzene derivatives having H, OH, OR or O⁻ group at position 3. The difference between the coupling rate constants of resorcinol

mono- and dianion is about 4.5 orders of magnitude, whereas, in the case of 1-naphthol¹ and 2-hydroxynaphthalene-6-sulfonic acid⁸, the corresponding difference is about 8 orders of magnitude. This large decrease of the reactivity difference is caused obviously by the so called "levelling effect" of the O⁻ group already present at position 1. Mesomeric influence of the O⁻ group in position 3 does not make itself felt in activated complex to such a degree as *e.g.* in the case of 1-naphthol or 2-hydroxynaphthalene-6-sulfonic acid, because the negatively charged oxygen atom at position 1 supplies electrons to the reaction site, too. The "levelling effect" of O⁻ group is still more obvious when comparing the rate constants of the reaction of 3-methoxyphenolate ion. In this case the both anions react practically at the same speed, although the hydroxy derivative reacted more rapidly than the methoxy derivative by about 2 orders of magnitude in the case of both the coupling of 1-hydroxy-resp. 1-methoxynaphthalene¹ and the bromination of phenol and anisol¹³. The higher reactivity of the hydroxy derivative is explained by a partial splitting of the OH bond in the activated complex and, consequently, greater significance of mesomeric effect of oxygen^{9,10}. In the intermediate formed the OH bond is obviously completely split, so that the intermediate has the structure of an unsaturated cyclic ketone (*e.g.* bromocyclohexadienone in the case of the bromination of phenol). The structure of the intermediate formed in coupling of resorcinol monoanion is represented by formula I (see p. 1851) which means that the OH bond splitting did not practically occur;

TABLE II

Comparison of Rate Constants (1 mol⁻¹ min⁻¹) of Substrates with Various Benzenediazonium Ions

A Unsubstituted benzenediazonium ion; B 3-nitrobenzenediazonium ion; C 2-chloro-4-nitrobenzenediazonium ion. All in water; D 2-chloro-4-nitrobenzenediazonium ion in 32% (by vol.) acetic acid.

Substrate	A	B	C	D
Phenolate anion ¹²	2.77 · 10 ⁴	2.35 · 10 ⁷	—	—
Resorcinol (<i>k_I</i>)	1.35 · 10 ⁻²	3.47	1.05 · 10 ²	9.32 · 10 ²
Resorcinol monoanion (<i>k_{II}</i>)	3.52 · 10 ⁵	1.92 · 10 ⁸	—	—
Resorcinol dianion (<i>k_{III}</i>)	7.42 · 10 ⁹	1.70 · 10 ^{11a}	—	—
3-Methoxyphenol (<i>k_{IV}</i>)	—	1.58	3.47 · 10 ¹	5.62 · 10 ¹
3-Methoxyphenolate anion (<i>k_V</i>)	3.65 · 10 ⁵	2.09 · 10 ⁸	—	—
1,3-Dimethoxybenzene (<i>k_{VI}</i>)	—	—	5.75	6.30
1-Naphthol ²	—	2.82 · 10 ¹	1.15 · 10 ³	9.54 · 10 ²
1-Naphtholate anion ¹	2.63 · 10 ⁷	2.24 · 10 ¹⁰	1.48 · 10 ^{11a}	—
1-Methoxynaphthalene ²	—	—	—	1.38 · 10 ¹

^a The value is misrepresented by a diffusion-controlled course of the reaction.

probably for this reason the effects of OH and OCH₃ groups are comparable. The lower significance of the mesomeric effect of OH and OCH₃ groups in this case is also supported by the difference between the rate constants of resorcinol monoanion and 3-methoxyphenolate ion and that of phenolate ion being less than 1.5 orders of magnitude. In the second column of Table II the reactivity of 3-hydroxy- resp. 3-methoxyphenol is compared with that of the respective anions. The difference is about 7.5 and 8 orders of magnitude in the case of 3-hydroxy and 2-methoxy derivatives respectively which is practically the same difference as that found with 1-naphthol and 2-hydroxynaphthalene-6-sulfonic acid. This is another piece of evidence for the "levelling effect" of OCH₃ resp. OH group being far smaller than that of O⁻ group.

Table II further presents the changes of rate constants caused by gradual substitution of OH groups by OCH₃ groups. Such a substitution of one OH group of resorcinol by OCH₃ group causes a threefold decrease of the reaction rate in diluted sulphuric acid, the substitution of the second group being accompanied by a sixfold decrease. This is substantially less than in the case of 1-hydroxy- and 1-methoxynaphthalenes. The rate of the reaction carried out in 32% acetic acid decreased sixteen and nine times on substitution of the first and second OH group by OCH₃ group respectively. This means that, in the same medium, the substitution of the both OH groups by OCH₃ groups had the same effect as the substitution of 1-naphthol by 1-methoxynaphthalene. The results obtained suggest that, in contrast to the reaction with resorcinol monoanion, a substantial splitting of OH bonds occurs in the activated complex in this case, and hence, the mesomeric effect of OH group is increased. The considerable change of the rate constant ratio, which accompanies the change of solvent (water-32% acetic acid), is caused mainly by about eightfold acceleration of the reaction with resorcinol. Such a large change was quite unexpected, especially because the reaction rate of 1-naphthol was practically the same in both the media. One of the decisive reasons is probably the fact that the solubility of 1-naphthol is strongly increased on changing the solvent from water to 32% acetic acid, and, hence, its activity coefficient strongly decreases, whereas resorcinol behaves contrariwise.

The influence of substituents of benzenediazonium cation on the reaction rate was evaluated quantitatively with the use of the Hammett equation. Only the rate constants of monosubstituted benzenediazonium ions were used in the correlation. Eqs (7), (8), (9) and (10) were obtained for undissociated resorcinol, resorcinol monoanion, resorcinol dianion and 3-methoxyphenolate ion respectively.

$$\log k_{\text{I}} = (3.45 \pm 0.055) \sigma - (1.87 \pm 0.047), \quad (7)$$

$$\log k_{\text{II}} = (3.76 \pm 0.030) \sigma - (5.57 \pm 0.02); \quad r = 0.9995, \quad (8)$$

$$\log k_{\text{III}} = (3.12 \pm 0.10) \sigma - (9.87 \pm 0.18); \quad r = 0.995, \quad (9)$$

$$\log k_{\text{IV}} = (3.74 \pm 0.03) \sigma - (5.71 \pm 0.02); \quad J = 0.9995. \quad (10)$$

In the case of the undissociated resorcinol and 3-methoxyphenol the rate constants of polysubstituted benzenediazonium ions were correlated with $\sum\sigma$, too. In these cases, too, linear dependences were obtained but the ρ constants were substantially smaller than those of monosubstituted diazonium ions ($\rho \approx 2.95$ and 3.1 for resorcinol and 3-methoxyphenol respectively). We observed a similar decrease of ρ constant connected with polysubstituted benzenediazonium ions^{2,5}.

The both monoanions have practically the same ρ constant which is in accord with practically the same reactivity of the both substrates¹¹. The very low value of ρ constant of undissociated resorcinol was rather surprising. We have no satisfactory explanation for this fact. The dependence of $\log k$ of the coupling of resorcinol dianion is given in Fig. 2. The first four points of the least reactive benzenediazonium ions lie on a straight line having a slope of 3.12 . The relatively low value of this ρ constant stands in accord with high reactivity of resorcinol dianion^{11,12} again.

The last three substituted benzenediazonium ions deviate gradually more and more from the straight line. This deviation is obviously due to a gradual change to a diffusion-controlled rate-determining step, as it was the case with coupling reaction of polysubstituted benzenediazonium ions with 1-naphtholate ion.

If we know the rate constants of reactions of a reagent with a substrate both in its undissociated and dissociated forms, we can calculate the dissociation constant of the activated complex of the reaction of the neutral substrate according to Eq. (11) (ref.¹³) where pK_{HS} is the pK_A value of the substrate and k_{HS} and k_A are the rate constants of the reactions of the undissociated and dissociated substrate respectively.

$$pK_A = pK_{HS} + \log(k_{HS}/k_S). \quad (11)$$

In the case of reactions of substituted benzenediazonium ions, the constant calculated

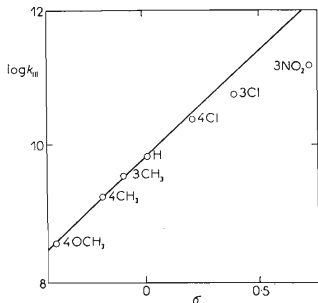


FIG. 2

Hammett Correlation of Logarithms of Coupling Rate Constants of Substituted Benzenediazonium Ions with Resorcinol Dianion
Water, 20°C, ionic strength $I = 0.1$.

relates to the reaction (A) where the structures II and III represent the activated complexes of reactions of a substituted benzenediazonium ion with resorcinol and its monoanion respectively. The pK_A value calculated for the activated complex II of the reaction of resorcinol with 4-chlorobenzenediazonium ion is 1.73. For the sake of comparison we give the respective value of the reaction of the same diazonium ion with 1-naphthol. *viz.* -0.03. The high value of these dissociation constants, as compared to those of starting hydroxy compounds, is caused by the positive charge formed at substrate nucleus by the reaction with benzenediazonium ion. The structure of the activated complex² lies at the boundary between an aromatic hydroxy compound and a protonated ketone, and therefore, the pK_A lies between pK_A 's of the both compounds.

The pK_A value of the activated complex III formed from 4-chlorobenzenediazonium ion and resorcinol monoanion is 7.14 which is by about 6 units lower than pK_A of the complex II, whereas the difference between pK_{A1} and pK_{A2} of resorcinol is only 2. The large decrease of acidity is caused, first of all, by that the positive charge at the benzene nucleus, which was the main driving power of splitting off of the first proton, is nullified due to conjugation with the electron pair of oxygen atom. A hydrogen bond to the nitrogen atom of the azo group may make itself felt to a lesser extent, too.

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