

KINETICS AND MECHANISM OF DIAZO COUPLING. XXIII.*
 RELATION BETWEEN REACTIVITY OF SUBSTRATE
 AND VALUE OF REACTION CONSTANT ρ DURING COUPLING
 WITH SUBSTITUTED BENZENEDIAZONIUM IONS

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A relatively rough dependence with decreasing trend has been found when plotting $\log k$ of coupling reactions of various substrates with benzenediazonium ion against the respective ρ constants. Better dependences have been obtained when comparing the abovementioned values within sets of substrates having similar structure (*e.g.* anions of C-acids). The course of these dependences corresponds to the theoretically presumed shape of the whole curve.

During his studies on electrophilic aromatic substitution reactions, Brown¹ found that there was a quantitative relation between reactivity of electrophilic reagent, its selectivity and reaction constant (I).

$$\log (k_{p-\text{CH}_3}/k_{m-\text{CH}_3}) = \rho(\sigma_{p-\text{CH}_3}^+ - \sigma_{m-\text{CH}_3}^+) \quad (I)$$

The relation between the reaction constant value and reagent selectivity should have general validity. If we presume that the shape of the curve representing the dependence of potential energy on reaction coordinate does not substantially change with the change of selectivity², then the position of the activated complex as well as its structure approach to the reaction products eventually to the intermediate with the decreasing reactivity³. This results in a greater extent of breakage of the old bonds and formation of the new ones in activated complex. The greater the bond changes in the reaction centre are, the more significant is the influence of a substituent change (or, more generally, structure) of substrate on the reaction. And it is just the reaction constant ρ which represents a quantitative measure of sensitivity (susceptibility) of reaction to the substituent change.

The aim of this paper was to determine the extent of validity of the relation between reactivity and selectivity in the case of the coupling reactions studied by us.

During the last few years, we studied the influence of substitution of the benzenediazonium ion on the velocity of its reaction with a series of aromatic hydroxy and amino compounds and some anions of C-acids, too. These studies have now been completed by the determination of rate constants of the reaction of phenol and 2-naphthol with substituted benzenediazonium ions. Assuming that the NC bond

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formation between the substituted benzenediazonium ion and substrate is the rate-determining step (which is the case with all the reactions considered here), the value of ρ constant should be within the limits 0–5. The value 5 should correspond to such a reaction where the NC bond is completely formed. Its value was estimated on the one hand from the ρ constant of those coupling reactions the rate-determining step of which is the splitting off of the proton from the intermediate and, on the other hand, from the ρ constant of the equilibrium reaction⁴: $\text{XC}_6\text{H}_4\text{N}_2^+ + \text{CN}^- \rightleftharpoons \text{XC}_6\text{H}_4\text{—N=N—CN}$. The decreasing reactivity of the coupling component should be accompanied by increasing NC bond formation and, hence, by gradual increasing of ρ constant. The dependence of $\log k$ on the ρ constants should be represented by a curve which should approach to zero for the ρ constants of extremely rapid reactions and to 5 for very little reactive substrates. Shorter sections of this curve

TABLE I

ρ Constants of Reaction of Substituted Benzenediazonium Ions with Various Substrates and $\log k_0$ of Reaction of Benzenediazonium Ion with these Substrates
Temperature 20°C, ionic strength 0.3.

Substrate	Site	$\log k_0$	ρ	Ref.
Phenol	4	4.43	4.20	^a
4-Methylphenol	2	3.02	4.27	9
4-Methoxyphenol	2	4.50	4.09	9
1-Naphtholate	4	7.50	4.15	6
1-Hydroxynaphthalene-4-sulfonic acid	2	4.56	3.94	6
1-Naphthol (undissociated)	4	-1.90	4.80	11
2-Naphtholate	1	6.26	3.20	^a
2-Hydroxynaphthalene-6-sulfonic acid	1	4.76	3.18	7
1-Hydroxy-6-aminonaphthalene-3-sulfonic acid	5	2.25	4.04	10
1-Hydroxy-6-phenylaminonaphthalene-3-sulfonic acid	5	0.97	4.15	10
2-Aminonaphthalene-6-sulfonic acid	1	2.13	4.18	12
Acetone	α	9.50	1.89	5
ω -Methylglyoxal 4-methylhydrazone	α	7.50	2.62	13
ω -Methylglyoxal 4-nitrohydrazone	α	8.60	2.74	13
Nitroethane	α	5.12	2.88	14
Acetylacetone	α	5.11	3.45	15
Acetoacetanilide	α	6.80	3.06	8
Resorcinol dianion	4	9.80	3.10	16
3-Hydroxyphenolate	4	5.68	3.75	16
3-Methoxyphenolate	4	5.72	3.76	16
Resorcinol (undissociated)	4	-1.87	3.46	16

^a The present work.

should be replaceable by a straight line in the first approximation. The values of rate constants of the reaction with the unsubstituted benzenediazonium ion and the reaction constants found are given in Table I wherefrom it is obvious that the constant shows a decreasing trend with increasing reactivity of coupling component, but this relation is relatively rough.

E.g. the coupling rate constant of 1-naphthol differs from that of 1-hydroxy-6-phenylaminonaphthalene-3-sulfonic acid by 7 orders of magnitude, the respective reaction constants being practically the same. A far better dependence is obtained when only a certain group of substances is compared. This is especially obvious in the case of all the six anions of C-acids studied where a relatively good relation between $\log k_0$ and ρ constant was obtained (regression coefficient $r = 0.83$). The position of activating electron-donor substituent is decisive for classifying into a given group. From this point of view, all the aromatic substrates are classified as derivatives of 1-naphthol, 2-naphthol and substituted phenols. Position of the carbon atom, at which the reaction takes place, is far less significant. The same dependence holds for *p*-substituted phenols coupling at 2-position, as for those phenol derivatives which couple at 4-position. Undissociated resorcinol represents an exception, the reason of this deviation being not yet clear to us.

The lowest value of angular coefficient is encountered with the dependence of $\log k_0$ on ρ constants of the C-acids whose ρ values fall within the medium region. In the other groups it can be seen that the angular coefficients of the straight lines demarcated increase with increasing ρ constant value.

To sum up: it can be said that the expected dependence of $\log k_0$ on ρ constants is roughly fulfilled for this reaction type, but it is limited by a condition that only such substances are compared which belong to a group characterized by a certain substrate structure and position of activating substituent.

TABLE II

Dependence of Coupling Rate Constants of Substituted Benzenediazonium Ions with Phenol ($\log k$) and 2-Naphthol ($\log k'$) on σ Constants

Substituent	σ	$\log k$	$\log k'$	Substituent	σ	$\log k$	$\log k'$
4-OCH ₃	-0.40	—	5.030	4-Cl	0.20	5.250	6.940
4-CH ₃	-0.20	3.189	5.653	4-Cl	0.20	5.209	6.914
4-CH ₃	-0.20	3.732	5.643	3-Cl	0.39	6.025	7.485
3-CH ₃	-0.10	—	5.950	3-Cl	0.39	—	7.484
3-CH ₃	-0.10	—	5.893	3-NO ₂	0.70	7.446	8.550
H	0.00	4.350	6.353	3-NO ₂	0.70	7.372	8.515
H	0.00	4.294	6.296	3-NO ₂	0.70	7.425	—
H	0.00	4.400	—				

EXPERIMENTAL

Kinetic measurements of the coupling rate constants of 2-naphthol were carried out as follows: 2 ml (usually) of $5 \cdot 10^{-3}$ M diazonium salt stock solution was added to 500 ml buffer mixture having a ionic strength I 0.3 (adjusted by addition of potassium chloride) and 2-naphthol stock solution with stirring at 20°C in a thermostat. After definite time intervals, 25 ml samples of the reaction mixture were withdrawn with a pipette and added to 10 ml $5 \cdot 10^{-2}$ M resorcinol in 50 ml calibrated flasks (in the case of diazo compounds less reactive than 3-chlorobenzenediazonium ion) or to 10 ml $5 \cdot 10^{-3}$ M 1,8-dihydroxynaphthalene-3,6-disulfonic acid; then 5 ml alcohol was added, the mixture obtained was filtered and its extinction was measured by means of a VSU-2P spectrophotometer (Zeiss, Jena).

This rate constants were obtained graphically using the equation: $k't = -2.303 \log (E_t - E_\infty)$, where E_t and E_∞ are the extinctions of the samples at a time t and $t = \infty$ (final extinction of the reaction solution) respectively. The rate constants of the coupling with phenol were obtained in the same way. The results are given in Table II.

REFERENCES

1. Brown H. C. in the book: *Advances in Physical Organic Chemistry*, (V. Gold, Ed.), Vol. 1. Academic Press, New York 1963.
2. Evans M. G., Polanyi M.: *Trans. Faraday Soc.* 34, 11 (1938).
3. Hammond G. S.: *J. Am. Chem. Soc.* 77, 334 (1955).
4. Lewis E. S., Suhr H.: *Chem. Ber.* 92, 3043 (1959).
5. Macháček V., Macháčková O., Štěrba V.: *This Journal* 35, 2954 (1970).
6. Kropáčová H., Panchartek J., Štěrba V., Valter K.: *This Journal* 35, 3287 (1970).
7. Kaválek J., Panchartek J., Štěrba V.: *This Journal* 35, 3470 (1970).
8. Macháček V., Panchartek J., Štěrba V., Večeřa M.: *This Journal* 35, 844 (1970).
9. Dobáš I., Panchartek J., Štěrba V., Večeřa M.: *This Journal* 35, 1288 (1970).
10. Panchartek J., Štěrba V.: *This Journal* 34, 2971 (1969).
11. Štěrba V., Valter K.: *This Journal*, in press.
12. Zollinger H.: *Helv. Chim. Acta* 35, 1209 (1952).
13. Macháček V., Macháčková O., Štěrba V.: *This Journal* 36, 3187 (1971).
14. Macháček V., Panchartek J., Štěrba V., Tunka J.: *This Journal* 33, 3579 (1968).
15. Macháček V., Panchartek J., Štěrba V.: *This Journal* 35, 3410 (1970).
16. Macháčková O., Štěrba V., Valter K.: *This Journal*, in press.

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