KINETICS AND MECHANISM OF DIAZO COUPLING. XXII.*
COUPLING OF BENZENEDIAZONIUM SALTS WITH N-METHYLANILINE

V.Beránek, H.Kořínková, P.Vetešník and M.Večeřa

Department of Organic Chemistry,
*Institute of Chemical Technology, Pardubice*

The title reaction was studied kinetically in 20% (by vol.) aqueous ethanol at 20°C and ionic strength 0·5. By an appropriate choice of medium and reactants concentrations the coupling at the activated p-carbon atom of N-methylaniline nucleus giving 3'- or 4'-substituted 4-methyl-aminoazobenzenes or coupling at the nitrogen of the methylamino group giving the respective diazoamino compounds could be studied separately. The experimental rate constants were correlated with Hammett σ substituent constants, and it was found that the reaction constants of the C- and N-couplings were the same practically ($\varrho_C = 3·98$; $\varrho_N = 3·94$), whereas the rate constant of N coupling was approximately 25 times greater than that of C-coupling.

During reactions of diazonium salts with aromatic amines the electrophilic diazonium cation can attack either the activated carbon atoms of the aromatic nucleus or the free electron pair of amino nitrogen. It depends on reaction conditions, substrate reactivity and structure, and electrophilic reagent reactivity whether the coupling will take place at the nitrogen or carbon atom. In the previous papers[1,2] we studied kinetically the coupling at the carbon atom of the aromatic nucleus only (N,N-dimethylaniline was used as the coupling component) or at the amino nitrogen atom only (aniline was used as the coupling component). In the present work we have chosen N-methyl-aniline as a substrate which makes it possible to study the C- and N-couplings simultaneously depending on the appropriate choice of reaction conditions (Scheme 1).

The influence of the initial acid–base equilibrium of the amine on the coupling reaction rate was elucidated by Wistar and Bartlett[3] and it was dealt with by us in previous papers[1,2], too.

In the present work we have studied the influence of substituents in the diazo component on its reactivity under various conditions making the formation of azo compound (C-coupling) or that of diazoamino compound (N-coupling) predominant, and we tried to evaluate the abovementioned scheme quantitatively. We have chosen 20% (by vol.) aqueous ethanol as medium, temperature 20°C, and ionic strength 0·5 in accord to the previous studies of this series[1,2].

Part XXI: This Journal **36**, 270 (1971).
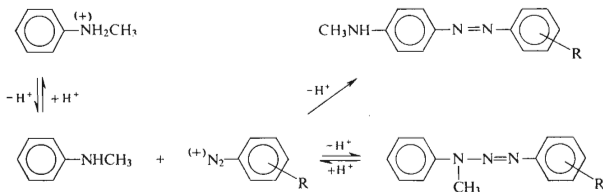
SCHEME 1

EXPERIMENTAL

Reagents

All the *meta* and *para* substituted anilines used were obtained from commercial samples or prepared by known methods. Recrystallization from aqueous ethanol or repeated vacuum distillation were used for their purification. Purity of the N-methylaniline used as coupling component was checked by means of gas–liquid chromatography (packing: Cellit 545 + 13% KOH + 8% Carbowax 20 M; grain 0·25—0·4 mm; temperature 125°C). By a comparation analysis it was found that the N-methylaniline contained less than 1% aniline and less than 0·5% N,N-dimethylaniline. Schäffer acid (2-hydroxynaphthalene-6-sulfonic acid) was obtained from a commercial sample by purification through a crystallization from aqueous solution. Various mixtures of disodium hydrogen phosphate and citric acid, or hydrochloric acid solutions of various concentrations[4] were used as buffers. Ionic strength of the solutions was adjusted at 0·5 by potassium chloride addition. Further an aqueous solution of 40 g/l borax was used. All the chemicals used were of p.a. purity grade. The solutions of monosubstituted benzenediazonium salts of various concentrations for the kinetic measurements were prepared according to the following general procedure: 1 equivalent of the amine was weighed into a calibrated flask, dissolved in 2·5 equivalents of 5M-HCl, and the solution was cooled at 0°C. Further, 1 equivalent of cold (0°C) 1M-NaNO₂ was added, and the mixture was let to stand for half an hour at 0°C. An eventual excess of nitrous acid was removed by an addition of amidosulfonic acid (potassium iodide–starch paper indicator). The volume was adjusted at 25 ml with 0°C cold water.

Determination of Ionization Constant of N-Methylaniline

For the purpose of the kinetic measurements and rate constants calculation, the pK_a of the coupling component (N-methylaniline) was determined spectrophotometrically[5] with the Unicam SP 800 apparatus under the conditions of the kinetic experiments (20% (by vol.) aqueous ethanol, ionic strength 0·5, temperature 20°C). The pH measurements were carried out using a Radiometer Copenhagen PHM 4c apparatus and a glass and saturated calomel electrodes. The value pK_a 5·08 ± 0·05 was found (analytical wavelength 285 nm).

Kinetics of C-Coupling of *m*- and *p*-Substituted Benzenediazonium Salts with N-Methylaniline

All the kinetic measurements were carried out in 20% (by vol.) aqueous ethanol at 20°C and ionic strength 0·5. The extinction of the azo dyestuff formed was followed continuously with the

use of the Unicam SP 800 spectrophotometer. 9 ml of the buffered N-methylaniline solution of a concentration $2.77 \cdot 10^{-2}$ mol/l in 20% (by vol.) aqueous ethanol was placed in a 3 cm sample cell. After tempering at 20°C, 5 microliters $5 \cdot 10^{-2}$M diazonium salt solution was injected using a Hamilton syringe which caused practically no change of the volume. The concentration of the diazo component in the reaction mixture was thus $2.77 \cdot 10^{-5}$ mol/l, that of N-methylaniline (coupling component) was $2.77 \cdot 10^{-2}$ mol/l. Spectra (dependence of the extinction on the wavelength) of the mixture were recorded at definite time intervals. The time intervals corresponding to definite values of the extinction at the wavelength of the long-wave absorption maximum of the azo compound formed were determined with the use of a stopwatch. In this way extinction, time and pH values were obtained wherefrom the rate constant of the pseudo-monomolecular reaction could be calculated, because a thousandfold excess of the coupling component was used in all the kinetic experiments. The pH value was adjusted individually for each of the diazo components used in such a way that the reaction proceeded at an optimum velocity suited for following the kinetic experiment by the abovementioned continuous method. The acidity values of reaction mixtures in the range not allowing the use of glass electrode measurement were determined titrimetrically. The pH measurement was carried out at the same temperature as the kinetic experiment. The results are presented in Table I and Fig. 1.

TABLE I

Rate Constants of C- and N-Coupling Reactions (k_C and k_N) of *m*- and *p*-Substituted Benzenediazonium Chlorides with N-Methylaniline in 20% (by vol.) Aqueous Ethanol at 20°C and Ionic Strength 0·5

Substituent	k_C $l\,mol^{-1}\,min^{-1}$	k_N $l\,mol^{-1}\,min^{-1}$	k_N/k_C
H	$5.25 \cdot 10^1$	$6.62 \cdot 10^2$	12·6
m-Cl	$1.20 \cdot 10^3$	$4.35 \cdot 10^4$	36·2
m-CN	$1.91 \cdot 10^4$	$3.32 \cdot 10^5$	17·4
m-F	$1.22 \cdot 10^3$	$3.89 \cdot 10^4$	31·8
m-Br	$0.99 \cdot 10^3$	$2.79 \cdot 10^4$	28·0
m-COCH$_3$	$7.03 \cdot 10^2$	$3.48 \cdot 10^4$	49·5
m-SO$_2$CH$_3$	$2.76 \cdot 10^4$	$3.09 \cdot 10^5$	11·2
m-CH$_3$	$2.90 \cdot 10^1$	$3.52 \cdot 10^2$	12·1
m-NO$_2$	$2.50 \cdot 10^4$	$6.78 \cdot 10^5$	27·1
p-NO$_2$	$4.54 \cdot 10^4$	$7.94 \cdot 10^5$	17·5
p-Cl	$2.78 \cdot 10^2$	$8.96 \cdot 10^3$	32·2
p-CN	$2.59 \cdot 10^4$	$4.56 \cdot 10^5$	17·6
p-F	$9.93 \cdot 10^1$	$7.63 \cdot 10^2$	7·7
p-Br	$3.33 \cdot 10^2$	$9.98 \cdot 10^3$	29·9
p-COCH$_3$	$1.70 \cdot 10^3$	$2.71 \cdot 10^4$	15·9
p-SO$_2$CH$_3$	$3.63 \cdot 10^4$	$4.40 \cdot 10^5$	12·1
p-CH$_3$	6·79	—	—

Kinetics of N-Coupling of *m*- and *p*-Substituted Benzenediazonium Salts with N-Methylaniline

The N-coupling reaction rate was measured with the use of a spectral method and discontinuous determination of the composition of samples withdrawn from the reaction mixture which is suitable for measurements of the more rapid reactions. The reactions were carried out in 20% (by vol.) aqueous ethanol at 20°C and ionic strength 0·5. 25 ml of a buffered coupling component solution of a concentration $1·2 . 10^{-4}$ mol/l was placed in a thermostated beaker equipped with a magnetic stirrer. Then 0·25 ml $1·2 . 10^{-2}$M diazo component solution was injected under vigorous stirring. At a definite time interval 50 ml Schäffer acid solution (concentration $2 . 10^{-2}$ mol/l) in borax aqueous solution (concentration 40 g/l) was added into the reaction mixture. The yet unreacted diazonium salt coupled with the Schäffer acid immediately, and the concentration of the azo dyestuff formed, which was measured spectrophotometrically, was directly proportional to the concentration of the unreacted diazonium salt in the reaction mixture. At least eight such experiments having various time intervals were carried out for evaluation of one rate constant. The diazonium salt decomposition in the reaction course was checked for every experiment series at the given pH: 0·25 ml of the diazonium salt solution was injected into 25 ml buffered coupling component solution; after a certain time the triazene formed was decomposed back to the diazonium salt and the respective amin by the addition of 3 ml 1M-HCl, and after about 5 minutes 50 ml Schäffer acid in borax solution was added. The decomposition of the diazonium salts was negligible in the time interval of the kinetic experiments in the given medium. The initial diazonium salt concentration was determined directly by injecting it into Schäffer acid and borax solution.
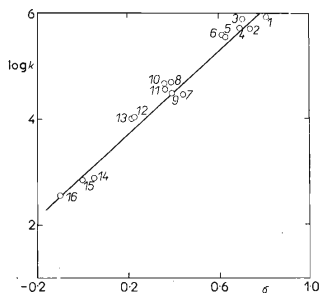

FIG. 1

The Hammett Correlation of C-Coupling Reaction of *m*- and *p*-Substituted Benzenediazonium Chlorides with N-Methylaniline in 20% (by vol.) Aqueous Ethanol at 20°C and Ionic Strength 0·5

1 p-NO$_2$; *2* p-SO$_2$CH$_3$; *3* m-NO$_2$; *4* p-CN; *5* m-SO$_2$CH$_3$; *6* m-CN; *7* p-COCH$_3$; *8* m-Cl; *9* m-Br; *10* m-F; *11* m-COCH$_3$; *12* p-Br; *13* p-Cl; *14* p-F; *15* H; *16* m-CH$_3$; *17* p-CH$_3$.
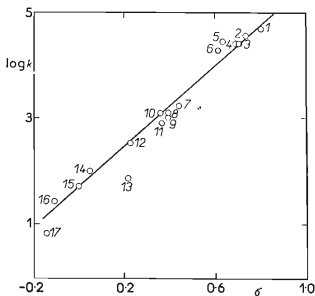

FIG. 2

The Hammett Correlation of N-Coupling Reaction of *m*- and *p*-Substituted Benzenediazonium Salts with N-Methylaniline in 20% (by vol.) Aqueous Ethanol at 20°C and Ionic Strength 0·5

For numbers see Fig. 1.

The reaction mixtures were transferred quantitatively from the beakers to 100 ml calibrated flasks, the volume was adjusted with water, and the extinction was measured at the long-wave absorption maximum of the azo dyestuff formed (λ 500 nm) using a Zeiss Jena VSU-1 apparatus. Such a pH value was chosen for each diazo component that the reaction proceeded at a well measurable velocity and the triazene formed did not decompose significantly. With the less reactive diazonium salts a fiftyfold excess of the coupling component was used. From the values experimentally found the N-coupling reaction rate constants were calculated according to the equations of pseudomonomolecular and bimolecular reactions. The results are summarized in Table I and Fig. 2.

RESULTS AND DISCUSSION

N-Methylaniline proved to be a very useful model coupling component for simultaneous study of C- and N-couplings. The substitution of the amino hydrogen by a methyl group excludes a tautomeric equilibrium of the triazene formed; such equilibrium complicates the interpretation of kinetic measurements of the triazenes prepared from primary amines. In addition to it, N-methylaniline is about 20 times more reactive than aniline which follows from a comparison of the rate constants of the respective coupling reactions with 3-nitrobenzenediazonium chloride: $3\cdot12 \cdot 10^4$ and $6\cdot78 \cdot 10^5$ l mol^{-1} min^{-1} respectively. The enhanced reactivity of N-methylaniline is caused by an electron density increase at nitrogen atom due to the inductive effect of the methyl group.

In order to be able to measure the C- and N-coupling kinetic, we had to follow the pH dependence of decomposition of some m- and p-substituted N-methyldiazoaminobenzenes. However, these decompositions have not been studied in detail, because the main purpose was to obtain some information about the dependence of decomposition (stability) of N-methyldiazoaminobenzene on pH and substitution. On the basis of this information the pH values were chosen for measurements of the C- and N-couplings of individual m- and p-substituted benzenediazonium salts.

The C-coupling was carried out at such pH values which prevented N-coupling. It was found that the coupling rate constants obtained for eight m-substituted and eight p-substituted benzenediazonium chlorides (including the unsubstituted benzenediazonium chloride) correlate with σ constants quite well, Eq. (1), $s_{yx} = 0\cdot16$, $r_{yx} = 0\cdot991$.

$$\log (k/k_0) = 3\cdot98\sigma_{m,p} . \tag{1b}$$

The pH values of N-coupling kinetics of N-methylaniline were chosen for individual m- and p-substituted benzenediazonium salts in such a way that: a) N-coupling proceeded at an optimum just measurable rate; b) no diazonium salt decomposition took place at the given pH, c) no reverse decomposition of the diazoamino compound formed took place.

With respect to the greater velocity of N-couplings, equimolecular concentrations of diazo and coupling components were used; with less reactive benzenediazonium

salts an 50 fold excess of the coupling component was adopted. The rate constants measured for eight m-substituted and seven p-substituted benzenediazonium chlorides (including the unsubstituted benzenediazonium chloride) are given in Table I and Fig. 2. The N-coupling of p-methylbenzenediazonium chloride could not be measured because the pH values necessary for this case were so high that a diazonium salt decomposition took place during the reaction which influenced the resulting rate constant. The expression (2) was obtained for correlation of logarithm of rate constants with the Hammett σ substituent constants $(s_{yx} = 0.17, r_{yx} = 0.989)$.

$$\log (k/k_0) = 3.94\sigma_{m,p}, \tag{2}$$

A comparison of the respective rate constants shows that the N-coupling is about $20-25$ times faster than the C-coupling in the case of N-methylaniline (Table I). Therefrom it follows that the amino nitrogen atom is activated towards electrophilic substitution much more than any carbon atom of the aromatic nucleus. In slightly acidic and neutral media the coupling takes place at the amino nitrogen whereas in strongly acidic medium the triazenes decompose and, therefore, the slower C-coupling predominates (Fig. 3). The influence of substituents in the diazo component on N- and C-coupling reaction rates is practically the same $(\varrho_C = 3.98; \varrho_N = 3.94)$. Electrophilic reactivity of diazonium ion, which is the reagent in coupling, is altered by substituents of the nucleus, being increased by electron-acceptor substituents and decreased by electron-donors. When comparing the reaction constants ϱ and rate constants k_0 of coupling reactions of diazonium salts with various coupling components (Table II), we can state that, whereas the range of the rate constants k_0 extends over many orders of magnitude, the reaction constants differ much less; the reaction selectivity is practically the same.

The present kinetic study makes it possible to support the empirical results obtained

FIG. 3

General Demarcation of C- and N-Coupling Ranges of m- and p-Substituted Benzenediazonium Chlorides with N-Methylaniline in 20% (by vol.) Aqueous Ethanol at 20°C with Respect to the pH Value of Medium

For numbers see Fig. 1.
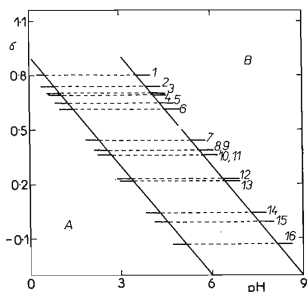
from the preparations of azo and triazene compounds theoretically and quantitatively and to estimate the appropriate reaction conditions for synthetic use of C- and N-coupling reactions (Fig. 3).

TABLE II

Reaction and Rate Constants of Coupling of Benzenediazonium Salts with Coupling Components

Coupling component	ϱ	k_0 1 mol^{-1} min^{-1}	ref.
N-Methylaniline[a] (C-coupling)	3·98	$5·25 . 10^1$	—[h]
N-Methylaniline[a] (N-coupling)	3·94	$6·62 . 10^2$	—[h]
N,N-Dimethylaniline[a]	3·84	$3·12 . 10^1$	1
Aniline[b] (N-coupling)	4·16	$7·17 . 10^0$	2
Nitroethane[c]	2·95	$2·97 . 10^2$	6
2-Hydroxynaphthalene-6-sulfonic acid[d]	3·45	$9·12 . 10^3$	7
Acetone[e]	1·89	$3·19 . 10^9$	11
Acetylacetone[e]	3·45	$1 20 . 10^5$	8
2-Amino-5-hydroxynaphthalene-7-sulfonic acid[f] (C_1-coupling)	4·04	$1·26 . 10^5$	9
2-Phenylamino-5-hydroxynaphthalene-7-sulfonic acid[f] (C_1-coupling)	4·15	$9·23 . 10^0$	9
1,8-Dihydroxynaphthalene-3,6-disulfonic acid[f] (C_2-coupling)	5·60	$6·02 . 10^2$	9
1-Hydroxy-8-acetylaminonaphthalene-3,6-disulfonic acid[f] (C_2-coupling)	5·30	$1·35 . 10^3$	9
2-Aminonaphthalene-6-sulfonic acid[g] (C_1-coupling)	4·26	$2·24 . 10^0$	10

[a] t 20°C, I 0·5, 20% (by vol.) aqueous ethanol; [b] t 0°C, I 0·5, water; [c] t 0·°C, I 0·6, water; [d] t 0°C, I 0·3, water; [e] t 20°C, I 0·1, water; [f] t 20°C, I 0·3, water; [g] t 20°C, I 0·3, water; [h] the present paper.

REFERENCES

1. Beránek V., Večeřa M.: This Journal *34*, 2753 (1969).
2. Beránek V., Večeřa M.: This Journal *35*, 3402 (1970).
3. Wistar R., Bartlett P. D.: J. Am. Chem. Soc. *63*, 413 (1941).
4. Schwabe K.: pH-*Meßtechnik*, p. 276. Steinkopf, Dresden 1963.
5. Serjeant E. P., Albert A.: *Ionization Constants of Acids and Bases.* Wiley, New York 1962.
6. Macháček V., Panchartek J., Štěrba V., Večeřa M.: This Journal *33*, 3154 (1968).
7. Panchartek J., Štěrba V., Vorlíček J., Večeřa M.: This Journal *33*, 894 (1968).
8. Macháček V., Panchartek J., Štěrba V.: This Journal *35*, 3410 (1970).
9. Panchartek J., Štěrba V.: This Journal *34*, 2971 (1969).
10. Zollinger H.: Helv. Chim. Acta *36*, 1730 (1953).
11. Macháček V., Macháčková O., Štěrba V.: This Journal *35*, 2954 (1970).

Translated by J. Panchartek.