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A Study of the Reaction between Diazotized 2-Amino-1,4-Benzenedisulphonic Acid and 8-Amino-1-Naphthol-3,6-Disulphonic Acid. Part II

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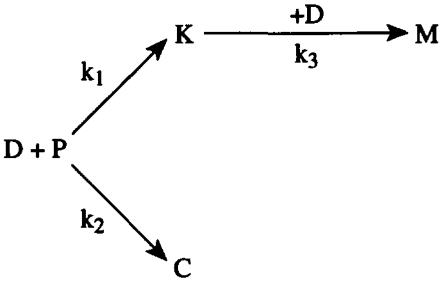
ABSTRACT

Spectrophotometry and HPLC were used for the determination of the rate constants for the azo coupling reactions of the schemes suggested. The content of colored components in the reaction solution was also determined; the results corresponded to the calculated data reported in Part I of this investigation.

1 INTRODUCTION

The reaction between diazotized 2-amino-1,4-benzenedisulphonic acid (**D**) and 8-amino-1-naphthol-3,6-disulphonic acid (**P**) can be represented by Scheme 1:



Scheme 1

in which **K** is the required product; the azo coupling reaction is directed by the —NH_2 group; **C** is an undesirable product resulting from azo coupling being directed by the —OH group; **M** is the bis-azo compound, also undesirable, and k_1, k_2 and k_3 are the relevant rate constants.

The mono-azo compound **K** is subsequently reacted with the diazonium salt of the condensation product of *m*-phenylenediaminosulphonic acid and 2,4,6-trichloro-1,3,5-triazine to give the dyestuff Ostazin Blue S2G. The content of components **K**, **C** and **M** in the reaction medium depends on the rate constants k_1, k_2 and k_3 and on the initial concentrations $[\mathbf{P}]_0$ and $[\mathbf{D}]_0$. We attempted to study this scheme using spectrophotometry and HPLC. An additional aim was to determine the quantity of **K**, **C** and **M** in the final reaction liquor and to compare the results with those evaluated in Part I of this investigation.

2 RESULTS AND DISCUSSION

Chromatography on silica gel plates showed that the component **K** was formed at pH 2 and that $[\mathbf{D}]_0/[\mathbf{P}]_0 \equiv n = 1$; the reaction is therefore:

$$\mathrm{P+D} \xrightarrow{k_1} \mathrm{K}$$

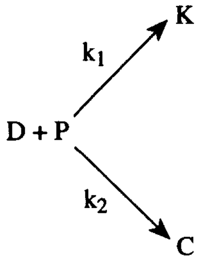
Scheme 2

At pH 4, three products (**K**, **C** and **M**) were present in the reaction mixture, i.e. as shown in Scheme 1. Two products (**K** and **C**) were formed when n was in the interval (0·1; 0·4). Thus,

(a) we were able to prepare a solution containing component **K** at pH 2 and at 10°C; this solution was used to study the reaction

$$\mathrm{D+K} \xrightarrow{k_3} \mathrm{M}$$

(b) when $n < 0{\cdot}4$, it was possible to determine the sum $(k_1 + k_2)$, i.e. only part of Scheme 1 was operative:



Scheme 3

(c) the value of k_3 was much smaller in comparison to k_1 and k_2; the presence of **M** was observed for $n > 0{\cdot}6$.

It was confirmed spectrophotometrically that the diazonium salt (**D**) was stable at pH 4 and at 10°C.

The sum $(k_1 + k_2)$ was estimated from the second-order kinetic equation:

$$(1 - n)(k_1 + k_2) \,.\, \mathbf{t} \,.\, [\mathbf{P}]_0 = \ln n - \ln \frac{(A_\infty - A_t) \,.\, n}{(A_\infty - A_t n)} \tag{1}$$

at $n = 0{\cdot}3$, $0{\cdot}2$ and $0{\cdot}1$.

When $n = 0{\cdot}03$ (pseudo-monomolecular reaction) eqn (1) can be transformed into:

$$(k_1 + k_2) = \frac{1}{[\mathbf{P}]_0 t} \ln \frac{(A_\infty - A_0)}{A_\infty - A_t} \tag{2}$$

where A_0 denotes the absorbance of the solution at time $t = 0$; A_t denotes the absorbance of the solution at a specific time; and A_∞ denotes the absorbance of the solution at time $t \to \infty$. Measurements were made at wavelength 526 nm.

The rate constant k_3 (second-order kinetic equation) was determined by following the absorbance of **M** at λ 626 nm and at $n = 0{\cdot}1$ and $n = 1$. At this wavelength only component **M** absorbed; at λ 526 nm all three components absorbed.

The coefficients of absorption were determined from the relationship of components **K** and **M** on the concentration of **K** and **M** at 526 nm and 626 nm; values are denoted as $\varepsilon_{\mathbf{M}}^{526}$; $\varepsilon_{\mathbf{M}}^{626}$; $\varepsilon_{\mathbf{K}}^{526}$, respectively.

High power liquid chromatography

A linear relationship between the area limited by the peaks and the concentration of **K** was found. The mixture **K** + **C** gave two peaks; the area pertinent to **K**, i.e. $[\mathbf{K}]_\infty$, was estimated. The value $[\mathbf{C}]_\infty$ was calculated from the equation $[\mathbf{K}]_\infty + [\mathbf{C}]_\infty = [\mathbf{D}]_0$.

$$\frac{[\mathbf{C}]_\infty}{[\mathbf{K}]_\infty} = \frac{k_2}{k_1}$$

The ratio, i.e. the ratio of areas, was also calculated; $\varepsilon_{\mathbf{C}}^{526}$ was calculated from the relationship for the total absorbance at λ 526 nm, denoted as $A_{\mathbf{K+C}}^{526}$:

$$A_{\mathbf{K+C}}^{526} = \varepsilon_{\mathbf{K}}^{526} \,.\, 1 \,.\, [\mathbf{K}]_\infty + \varepsilon_{\mathbf{C}}^{526} \,.\, 1 \,.\, [\mathbf{C}]_\infty \tag{3}$$

Values $[\mathbf{K}]_\infty$, $[\mathbf{C}]_\infty$ and $[\mathbf{M}]_\infty$ in any reaction solution were then estimated from the following relationships:

$$A_{\mathbf{K+C+M}}^{526} = \varepsilon_{\mathbf{K}}^{526} \,.\, 1 \,.\, [\mathbf{K}]_\infty + \varepsilon_{\mathbf{C}}^{526} \,.\, 1 \,.\, [\mathbf{C}]_\infty + \varepsilon_{\mathbf{M}}^{526} \,.\, 1 \,.\, [\mathbf{M}]_\infty \tag{4}$$

$$[\mathbf{D}]_0 = [\mathbf{K}]_\infty + [\mathbf{C}]_\infty + 2[\mathbf{M}]_\infty \tag{5}$$

TABLE 1

Percentage Content of **K**, **C** and **M** in the Reaction Solution at pH = 4, t = 10°C, $[\mathbf{D}]_0 = [\mathbf{P}]_0$

[D]₀ (mol dm⁻³)	***K**%*	***C**%*	***M**%*
2·58 × 10^{-5}	76·09 ∓ 0·76	15·28 ∓ 1·63	4·08 ∓ 0·12
2·08 × 10^{-5}	76·37 ∓ 0·46	15·18 ∓ 0·34	4·43 ∓ 0·25
1·83 × 10^{-5}	76·33 ∓ 0·63	14·05 ∓ 0·07	4·53 ∓ 0·66
1·57 × 10^{-5}	75·84 ∓ 0·13	15·83 ∓ 0·40	4·16 ∓ 0·13
1·32 × 10^{-5}	75·83 ∓ 0·91	15·29 ∓ 0·10	4·53 ∓ 0·38
1·06 × 10^{-5}	76·04 ∓ 0·35	15·65 ∓ 1·65	4·32 ∓ 0·40

The values $[\mathbf{K}]_\infty$, $[\mathbf{C}]_\infty$ and $[\mathbf{M}]_\infty$ divided by $[\mathbf{P}]_0$ gave the percentage content in the reaction solution; the results are shown in Table 1.

The content of **K**, **C** and **M** in the reaction solution was also determined by HPLC; the results are shown in Table 2.

The rate constants k_1, k_2 and k_3 were then determined as in Ref. 1, viz:

$k_1 = 55{\cdot}54\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$
$k_2 = 11{\cdot}22\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$
$k_3 = 1{\cdot}58\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$

Absorbance coefficients were calculated as follows:

$\varepsilon_{\mathbf{K}}^{526} = 25\,337\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$
$\varepsilon_{\mathbf{C}}^{526} = 16\,750\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$
$\varepsilon_{\mathbf{M}}^{526} = 20\,400\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$
$\varepsilon_{\mathbf{M}}^{626} = 32\,500\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$

Mean values of the percentage content were calculated from these results, and were in agreement with the calculated data reported in Table 5 of Part I.[1]

TABLE 2

Percentage Content of **K**, **C** and **M** under the same conditions as in Table 1

[D]₀ (mol dm⁻³)	***K**%*	***C**%*	***M**%*
7·05 × 10^{-4}	77·23 ∓ 0·64	18·92 ∓ 0·62	4·45 ∓ 0·29
6·34 × 10^{-4}	79·72 ∓ 0·34	18·54 ∓ 0·00	4·38 ∓ 0·15
5·13 × 10^{-4}	77·60 ∓ 0·00	18·25 ∓ 0·04	4·37 ∓ 0·48
4·64 × 10^{-4}	75·53 ∓ 0·96	18·25 ∓ 0·30	4·46 ∓ 0·13
3·90 × 10^{-4}	76·75 ∓ 1·12	18·97 ∓ 0·56	4·13 ∓ 0·05
2·63 × 10^{-4}	77·42 ∓ 2·13	18·16 ∓ 1·36	4·59 ∓ 0·30

3 EXPERIMENTAL

3.1 General

2-Amino-1,4-benzenedisulphonic acid (ADSK) and 8-amino-1-naphthol-3,6-disulphonic acid were purified as described previously in Ref. 2. The purity of both chemicals was checked potentiometrically by diazotization with 0·1 M sodium nitrite.

Solutions of the diazonium salts (**D**) were prepared as reported previously.[2] Buffer solutions were prepared as follows:

pH 2: 28·27 g citric acid monohydrate in 1 dm^3 distilled water.
pH 3: 90·58 ml acetic acid and 29·52 g sodium acetate in 1 dm^3 distilled water.

All pH values were checked using a pH-meter.

Component **K** was prepared as follows: to 25 ml buffer solution pH 2 (10°C) was added 10 ml (0·015 M, $f = 0·9004$) solution of **P** and 2·87 ml (0·05 M, $f = 0·9404$) solution of **D**. This mixture was kept in a refrigerator at 10°C; the reaction was complete after 5 days, there being no further change in the absorbance of the solution.

Component **M** was prepared similarly, viz. to 25 ml of buffer solution pH 4 (10°C) was added 12 ml of a solution of **K** (pH 2, $c = 3·56 \times 10^{-3}$ M) and 0·91 ml (0·05 M) solution of **D** ($f = 0·9404$). The solution was kept in a refrigerator at 10°C; reaction was complete after 3 days.

3.2 Spectrophotometry

The formation of colored components in the azo coupling reactions was monitored using a Hewlett-Packard HP 8950 UV/VIS; absorbance vs wavelength plots were made at various time intervals in buffer solution (pH 4) at 10°C.

For observation of the formation of component **K** (deep purple color): 0·5 ml solution of **P** ($c = 0·0015$ M, $f = 0·9004$) was added to 25 ml of a solution of pH 2 buffer at 10°C; 0·658 ml of a 0·001 M solution of **D** ($f = 1·025$) was rapidly added. Plots of A vs λ were recorded. The plot at time $t \rightarrow \infty$ was also registered; the ratio $[\mathbf{D}]_0/[\mathbf{P}]_0 \equiv n$ was 1.

For observation of the formation of component **M** (blue colored): 0·2 ml of a solution of **K** (pH 2, $c = 1·52 \times 10^{-3}$ M) was placed into 25 ml of pH 4 buffer solution ($t = 10$°C). A solution of **D** (0·3 ml, $1·0 \times 10^{-3}$ M, $f = 1·025$) was then added rapidly and A vs λ plots recorded. The parameter n was 0·1 or 1.

The formation of components **K** and **C** (deep purple and red, respectively) was observed as follows: 0·5 ml of a 0·0013 M solution of **P** (f = 0·962) was added to 25 ml of pH 4 buffer solution at 10°C. A solution of **D** (0·001 M, f = 1·0025) was added such that the parameters n were 0·03; 0·01; 0·2; 0·3; plots of A vs λ were recorded and also the plots for $t \rightarrow \infty$.

The stability of **D** was monitored at pH 2 and pH 4, at 10°C; 1 ml of a 0·01 M solution of **D** was added to 25 ml of buffer solution. Samples (1 ml) were taken at specific time intervals. Unreacted **D** was estimated by reaction with 2-naphthol-6-sulphonic acid in buffer solution at pH 10. The absorbance of the colored solution was measured at 482 nm.

3.3 High power liquid chromatography measurements

The mixture of **K**, **C** and **M** in the reaction solution was separated using a column (Tessek Ltd, Praha, Czechoslovakia) filled with Separon SGX, C18, 7 μm, CGS 3 × 150 mm. The flow was 1 ml/min and the mobile phase was 0·7 M Na_2SO_4 in distilled water. The detection was carried out using UV–VIS Detector LCD 2563 with filter at λ 546 nm.

3.4 Chromatography on silica gel

The formation of colored components was observed using this technique. The mixture was separated on silica gel plates, using propanol and 5% $KHCO_3$ (1 : 2).

4 CONCLUSION

The results of solving the differential kinetic equations were compared with the experimentally used concentrations at time infinity. A good agreement was observed and it can be assumed that the proposed reaction scheme is coincident with the actual reaction, i.e. the procedure for the estimation of parameters is also correct. The applicability of the language of simulation (PPSSS) was also confirmed. Advantages of this language are its simplicity and speed of calculations. It is anticipated that the method can be used for the solution of more complicated reaction schemes, and data pertinent to this will be reported later.

REFERENCES

1. Plocek, J. & Dlask, V., *Dyes and Pigments* **26** (1994) 307.
2. Dlask, V., *Coll. Czech. Chem. Commun.*, **49** (1984) 162.