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A Study of the Reaction Between Diazotized 2-Aminobenzenesulphonic Acid and 8-Amino-1-Naphthol-3,6-Disulphonic Acid

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ABSTRACT

The rate constants of the reaction between diazotized 2-aminobenzenesulphonic acid and 8-amino-1-naphthol-3,6-disulphonic acid were estimated approximately, using the reaction simulation program PPSSS, spectrophotometry and HPLC.

1 INTRODUCTION

The reaction between diazotized 2-aminobenzenesulphonic acid (**D**) and 8-amino-1-naphthol-3,6-disulphonic acid (**P**) is of similar type to that described in our previous reports.[1,2] In this present study it was not possible to prepare solutions of the individual monoazo and bisazo compounds, but it was possible to estimate the rate constants k_1, k_2 and k_3 using the procedure described elsewhere.[2]

2 RESULTS AND DISCUSSION

The sum of the rate constants ($k_1 + k_2$) was found to be $122 \mp 13{\cdot}3$ dm^2 mol^{-1} min^{-1} from spectrophotometric determinations in buffer solutions

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of pH 4 at 10°C. The ratio $[\mathbf{D}]_0/[\mathbf{P}]_0 \equiv n$ was kept at $n \leq 0{\cdot}5$ and the sum was determined graphically from the second order relationship:[2]

$$\ln \frac{(A_\infty - A_t)n}{A_\infty - A_t n} \text{ versus } t.$$

When n was 0·02, $(k_1 + k_2)$ was determined from the first order relationship:

$$\ln \frac{A_\infty - A_0}{A_\infty - A_t} \text{ versus } t$$

where A_∞, A_0 and A_t are absorbances at times infinity, zero and general time, respectively.

The ratio of the rate constants was estimated by HPLC to be $k_1/k_2 = 1{\cdot}95 \mp 0{\cdot}3\ \mathrm{dm^3\ mol^{-1}\ min^{-1}}$. Components **K**, **C**, **M** were the only anticipated products but two other red components (designated **X** and **Y**) were observed in the reaction solution. It was assumed that these were isomers of componds **K** and **C** formed by azo-coupling of the diazonium salt at positions *para* to the —NH_2 and —OH groups. The electronic spectra of **X** and **Y** were very similar. They were formed in the reaction liquor even at values $n > 2$, and it was therefore assumed they did not participate in any other reactions; no other blue disazo compound was observed. The ratio k_1/k_2 included only the formation of **K** and **C**; Lyčka and Jirman[3] and Freeman *et al.*[4] have suggested a possible origin of **X** and **Y**.

The rate constant k_3 (the formation of component **M**) was approximately estimated as $k_3 \simeq 1{\cdot}5\ \mathrm{dm^3\ mol^{-1}\ min^{-1}}$; since k_3 is smaller than k_1 and k_2, the reaction

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

proceeds slowly, and therefore decomposition of the diazonium salt could occur. Compound **K** was prepared by the reaction

$$\mathbf{P} + \mathbf{D} \xrightarrow{k_1} \mathbf{K}(\mathbf{X}).$$

At $n = 1$ and pH 3, only **K** and **X** were formed. This mixture was used to study the reaction

$$\mathbf{D} + \mathbf{K}(\mathbf{X}) \xrightarrow{k_3} \mathbf{M}.$$

At the pseudo-monomolecular level this is represented by eqn (1):

$$k_3 t[\mathbf{D}]_0 = \ln \frac{A_\infty - A_0}{A_\infty - A_t} \qquad (1)$$

The content of component **K** in solution at pH 3 was determined by

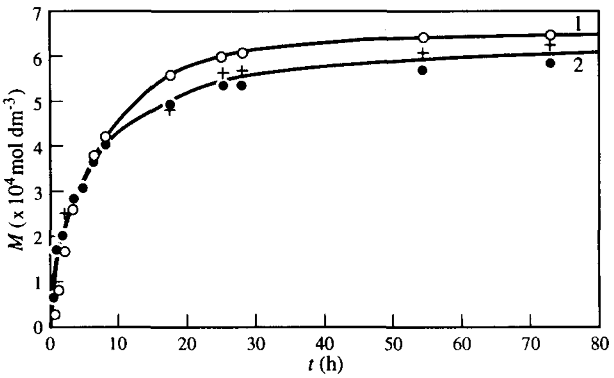


Fig. 1. Comparison between calculated and experimental data. Initial concentrations: $[\mathbf{D}]_0$ = 0·002 mol dm^{-3}; $[\mathbf{P}]_0$ = 0·001 mol dm^{-3}. Estimated experimentally: +, HPCL; ●, spectrophotometry (curve 2); k_1 = 80·65 dm^3 mol^{-1} min^{-1}; k_2 = 41·35 dm^3 mol^{-1} min^{-1}; k_3 = 1·5 dm^3 mol^{-1} min^{-1}. Computed: ○ (curve 1); k_1 = 76 dm^3 mol^{-1} min^{-1}; k_2 = 44 dm^3 mol^{-1} min^{-1}; k_3 = 3·5 dm^3 mol^{-1} min^{-1}.

HPLC with respect to the starting concentration $[\mathbf{P}]_0$, using the areas of the peaks for **K** and **X**.

The validity of the constants k_1, k_2 and k_3 was tested by computing the relationship between [**M**] and time, and comparing with experimental data; the simulation program PPSSS,[5] described in previous investigations, was employed.[1,2] The results are shown in Fig. 1. The computed values of **M** are in good agreement with experimental values up to a conversion of 60%; after this there is a difference, and the computed values of **M** indicate a higher level of conversion. It is concluded that this is probably due to the formation of components **X** and **Y**, which reduce the formation of the bisazo compound **M**.

For the reaction conditions:

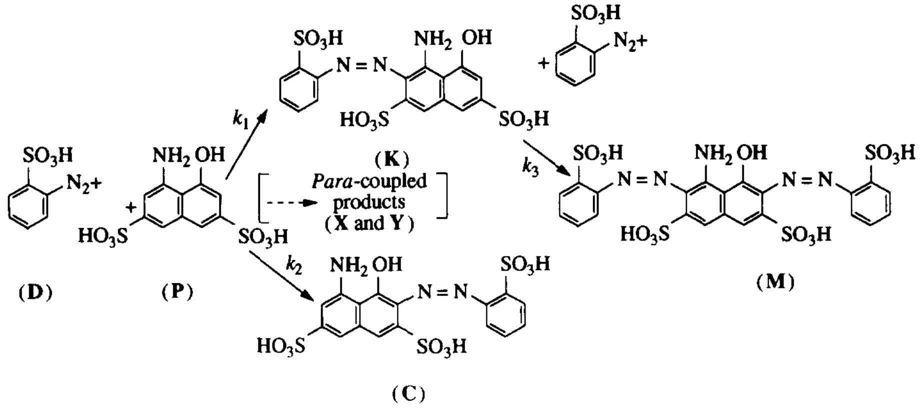
$[\mathbf{M}]_0 = [\mathbf{K}]_0 = [\mathbf{C}]_0 = 0$
$[\mathbf{P}]_0 = 0{\cdot}001$ mol dm^{-3}
$[\mathbf{D}]_0 = 0{\cdot}002$ mol dm^{-3}

the experimentally estimated rate constants were:

k_1 = 80·65 dm^3 mol^{-1} min^{-1}
k_2 = 41·35 dm^3 mol^{-1} min^{-1}
k_3 = 1·5 dm^3 mol^{-1} min^{-1}.

From the experimental relationship between $[\mathbf{A}]_\mathbf{M}$ and time, a relationship between [**M**] and time was determined using the PPSSS technique; the best fitted rate constants thus obtained were:

k_1 = 76 dm^3 mol^{-1} min^{-1}
k_2 = 44 dm^3 mol^{-1} min^{-1}
k_3 = 3·5 dm^3 mol^{-1} min^{-1}.



Scheme 1

3 EXPERIMENTAL

3.1 Chemicals

2-Aminobenzenesulphonic acid and 8-amino-1-naphthol-3,6-disulphonic acid were purified as described elsewhere;[6] adjustment of stock solutions, estimation of concentrations, and preparation of diazonium salts[6] and buffer solutions[1] were also described previously.

The standard solution of component **K** was prepared as follows: to a pH 3 buffer solution at 10°C was added 2 ml of a 0·015 mol dm^{-3} solution of **P** and 1·2 ml of a 0·025 mol dm^{-3} solution of component **D** with stirring; the ratio was $n \equiv [\mathbf{D}]_0/[\mathbf{P}]_0 = 1$. The reaction was complete after three days, the liquor containing component **C**, which does not take part in any further reactions.

3.2 Spectrophotometry

The formation of coloured products was checked using a Specol 11 spectrophotometer in buffer solution of pH 4 at 10°C. The absorbance values (A) were recorded at intervals at wavelengths λ 520 nm and λ 620 nm.

The sum of the rate constants ($k_1 + k_2$) was determined by adding 2 ml of a 0·0015 mol dm^{-3} solution of **P** to 25 ml of buffer solution (pH 4) at 10°C; 0·24 ml of a 0·0025 mol dm^{-3} solution of **D** was then added ($n = 0{\cdot}2$). The absorbance was monitored at 520 nm. Similar experiments were carried out at $n = 0{\cdot}02$ and 0·4, respectively. The values of $k_1 + k_2$ were determined according to the second order equation ($n = 0{\cdot}2$ or 0·4) and to the first order equation ($n = 0{\cdot}02$).

The rate constant k_3 was determined as follows. A solution of **K**

(2 ml, $C \simeq 0{\cdot}0008$ mol dm^{-3}) was added to 25 ml of buffer solution (pH 4); at time $t = 0$, 0·424 ml of a 0·025 mol dm^{-3} solution of **D** ($n = 7$) was injected and aliquots (1·5 ml) were taken at intervals, diluted with pH 4 buffer solution to 25 cm^3 and the absorbance measured at 620 nm. This procedure was repeated for $n \simeq 14$, 21 and 28. The values of k_3 were determined according to the first order equation.

3.3 HPLC

Samples of **K**, **C**, **X** and **Y** were analysed on a Varian 5020 chromatograph using Separon C18 as stationary phase, and a glass column 150 × 3 mm (5 μm).

The mobile phase was a mixture of 800 ml of 60% aq. methanol, and 200 ml of 0·1 mol dm^{-3} KH_2PO_4 and 0·1 mol dm^{-3} Na_2HPO_4. The flow rate was 0·5 ml min^{-1}, pressure 20 MPa, injection 3 μl, and detector Varian UV50 at λ 254 nm, 520 nm and 620 nm.

The ratio of the rate constants (k_1/k_2) was estimated as in Ref. 2. A 0·015 M solution of **P** (1 ml) was added to 25 ml of buffer solution (pH 4) at 10°C; 0·6 ml of a 0·025 mol cm^{-3} solution of **D** ($n = 0{\cdot}2$) was then added. The reaction was completed after 24 h and HPLC analysis was then carried out. The ratio of areas limited by the peaks corresponded to the ratio of the rate constants.

The content of components **K** and **X** in the standard solution at pH 3 was also estimated from the portions of areas under the peaks.

4 CONCLUSIONS

In this work, we have estimated the rate constants of the azo coupling reaction using 2-aminobenzenesulphonic acid as diazo component. The formation of the anticipated compounds **K** and **C** was also accompanied by the formation of other coloured components, **X** and **Y**, which are presumed to arise by azo coupling at the *para* position. The rate constants k_3 for the formation of **M** were determined only approximately.

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