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A Study of the Reaction between Diazotized 4-Aminobenzenesulphonic Acid and 8-Amino-1-naphthol-3,6-disulphonic Acid. Part 1

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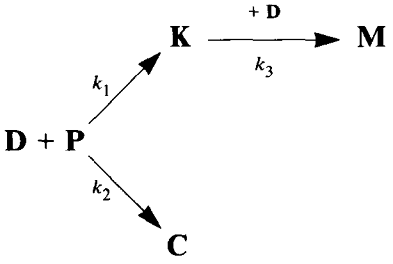
ABSTRACT

Approximate estimations have been made for the rate constants of the reaction system used in the synthesis of the disazo dye Ryvalon Blue 2GM. The methods used involved spectrophotometry, HPLC and the reaction simulation program PPSSS.

INTRODUCTION

The reaction between diazotized 4-aminobenzenesulphonic acid (**D**) and 8-amino-1-naphthol-3,6-disulphonic acid (**P**) follows Scheme 1 (cf. previous studies.[1,2])



Scheme 1

The intermediate product **K** is the component used in the production of the disazo dyestuff Ryvalon Blue 2GM (CI Reactive Blue 194). Unlike an earlier investigation, it was not possible in this case to prepare a solution of the monoazocompound **K**, which is the initial component required for the determination of the rate constant k_3. It was possible, however, to determine the sum of the rate constants ($k_1 + k_2$) and their ratio k_1/k_2, and also to monitor the concentrations of **M**, **K**, and **C**. The aim of this work was:

(a) to determine the sum ($k_1 + k_2$) by using spectrophotometry;
(b) to estimate approximately the ratio k_1/k_2 using HPLC;
(c) to monitor the relationship between the concentration of **M** and time using spectrophotometry, and
(d) on the basis of these results, to compute k_1, k_2 and k_3 using the simulation program PPSSS.[3]

RESULTS AND DISCUSSION

(a) The sum of rate constants ($k_1 + k_2$) was determined to be 1200 ± 40 dm^3 mol^{-1} min^{-1}.
(b) The ratio of the rate constants was estimated to be $k_2/k_1 \approx 2{\cdot}5$.
(c) The relationship between [M] and time was determined spectrophotometrically at initial conditions $[\mathbf{D}]_0 = [\mathbf{P}]_0 = 9{\cdot}24 \times 10^{-5}$ mol dm^{-3}. The value of $[\mathbf{M}]_{t=\infty}$ was $5{\cdot}2 \times 10^{-6}$ mol dm^{-3}.

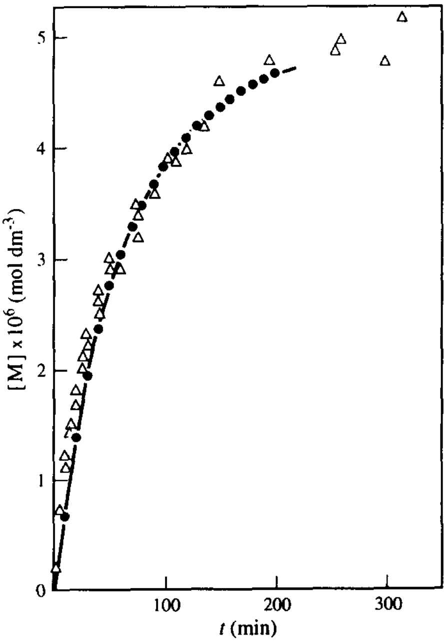


Fig. 1. Comparison of courses of computed (●) and experimental (△) data. Initial concentrations: $[\mathbf{D}]_0 = [\mathbf{P}]_0 = 9{\cdot}24 \times 10^{-5}$ mol dm^{-3}, $k_1 = 343 \pm 11$ dm^3 mol^{-1} min^{-1}; $k_2 = 857 \pm 11$ dm^3 mol^{-1} min^{-1}; $k_3 = 137{\cdot}5$ dm^3 mol^{-1} min^{-1}.

TABLE 1

Determination of Rate Constant k_3

Initial concentration (INT 4 = INT 5) = 0·0000924

k_1	k_2	k_3	*M*	*K*	*C*	*D*	*P*	
UNI 1	UNI 2	UNI 3	INT 1	INT 2	INT 3	INT 4	INT 5	CRIT
343	857	100	$4{\cdot}74 \times 10^{-6}$	$2{\cdot}10 \times 10^{-5}$	$6{\cdot}3 \times 10^{-5}$	$1{\cdot}78 \times 10^{-21}$	$4{\cdot}24 \times 10^{-6}$	$-1{\cdot}92 \times 10^{-6}$
		160	$5{\cdot}66 \times 10^{-6}$	$1{\cdot}91 \times 10^{-5}$	$6{\cdot}19 \times 10^{-5}$	$3{\cdot}77 \times 10^{-27}$	$5{\cdot}66 \times 10^{-6}$	$0{\cdot}92 \times 10^{-6}$
		130	$4{\cdot}49 \times 10^{-6}$	$2{\cdot}0 \times 10^{-5}$	$6{\cdot}24 \times 10^{-5}$	$1{\cdot}83 \times 10^{-24}$	$4{\cdot}99 \times 10^{-6}$	$-0{\cdot}42 \times 10^{-6}$
		145	$5{\cdot}34 \times 10^{-6}$	$1{\cdot}95 \times 10^{-5}$	$6{\cdot}22 \times 10^{-5}$	$7{\cdot}69 \times 10^{-26}$	$5{\cdot}34 \times 10^{-6}$	$0{\cdot}28 \times 10^{-6}$
		137·5	$5{\cdot}17 \times 10^{-6}$	$1{\cdot}98 \times 10^{-5}$	$6{\cdot}23 \times 10^{-5}$	$3{\cdot}68 \times 10^{-25}$	$5{\cdot}17 \times 10^{-6}$	$0{\cdot}06 \times 10^{-6}$

(d) The rate constant k_3 was evaluated using computing techniques involving PPSSS[3] and the model 'DLASK 2'.[1] The system of differential kinetic equations was solved as in ref. (1). The rate constant k was determined on the basis of criterion:

$$\text{CRIT} = /[\text{M}]_{t\to 0} - 5{\cdot}2 \times 10^{-6}/ + /[\text{P}]_{t\to\infty} - 5{\cdot}2 \times 10^{-6}/ \to 0$$

where $5{\cdot}2 \times 10^{-6}$ is the value of [M] and [P] at infinite time. The system was solved using the half-interval method (Table 1); the calculation was complete within 90 min.

Figure 1 shows the relationship between [M] and time as computed and also as determined experimentally. It is apparent that there is good correspondence between the computed and experimental data.

EXPERIMENTAL

Chemicals

1-Aminobenzenesulphonic acid and 8-amino-1-naphthol-3,6-disulphonic acid (**P**) were purified as in ref. 4. The diazonium salt (**D**) was prepared according to the same reference. The buffer solutions used were:

pH 1·4: 2·25 g glycine, 1·54 cm^3 of 85% H_3PO_4, 100 cm^3 distilled water.
pH 4: 90·58 cm^3 acetic acid, 29·52 g sodium acetate in 1 dm^3 distilled water.

The standard solution of component **M** was prepared as follows. To 25 cm^3 buffer solution pH 1·4 was added 1 cm^3 of a 0·016 mol dm^{-3} solution of **P** and 6·6 cm^3 of a 0·025 mol dm^{-3} solution of **D**; the molar ratio $[\text{D}]_0/[\text{P}]_0$ was 10. Reaction was commenced at $t = 0$ and 0°C in a refrigerator, and was complete after 5 days. The mixture contained the component **D** and also its decomposition product. The solution conformed with Lambert–Beer's Law.

The standard solution of component **K** was prepared as follows. To 25 cm^3 of buffer solution pH 1·4 was added 2 cm^3 of a 0·0165 mol dm^{-3} solution of **P** and 0·132 cm^3 of a 0·025 mol dm^{-3} solution of **D**. Reaction conditions were the same as above; the molar ratio $[\text{D}]_0/[\text{P}]_0$ was 0·1. The mixture contained component **P** and also conformed to Lambert–Beer's law.

Spectrophotometry

The coloured products of the azo-coupling reactions were monitored using a Hewlett–Packard HP 8950 UV/VIS. Absorbance (A) and wavelengths (λ) were determined at various time intervals in buffer solutions of pH 4 and at 10°C.

The sum of the rate constants ($k_1 + k_2$) was determined as follows. A 2 cm^3 sample of a 0·0015 mol dm^{-3} solution of **P** was added to 25 cm^3 of a buffered solution at pH 4 and at 10°C. Then 0·24 cm^3 of a 0·00125 mol dm^{-3} of solution **D** was added and plots of A against λ made. The ratio $[\mathbf{D}]_0/[\mathbf{P}]_0$ was 0·1. The formation of **K** and **C** followed first order kinetics and the sum ($k_1 + k_2$) was determined from the plots using the relationship:[2]

$$\ln \frac{(A_\infty - A_t)\,0{\cdot}1}{A_\infty - 0{\cdot}1A_t} \text{ versus } t$$

The absorbance was read at λ520 nm.

Formation of [M] in relation to reaction time

A 2 cm^3 sample of a 0·0015 mol dm^{-3} solution of **P** was added to 25 cm^3 of a buffered solution at pH 4 and 10°C. Then 2·4 cm^3 of a 0·00125 mol dm^{-3} solution of **D** was added and the absorbance measured over various time intervals at λ 620 nm (component **M** only absorbs at this wavelength). The concentrations of **M** in solution were determined from Lambert–Beer's law.

HPLC analysis

The samples, containing an unknown mixture of **M**, **K**, **C**, were analysed by HPLC (Varian 5020). The stationary phase was Separon SGX C18, glass column 150 × 3 mm (i.d.), 5 μm. The mobile phase was a variable mixture of 0·2 M Na_2SO_4 (solvent A) and methanol + H_2O, 6 : 4 (solvent B). The gradient programme used was from 5% B to 40% B linearly for 15 min; flowrate 0·5 ml min^{-1}. The detector used was a Varian UV 50, at wavelengths of 254, 520 and 620 nm, respectively.

Mixtures with initial concentrations $[\mathbf{P}]_0 = 7{\cdot}55 \times 10^{-4}$ mol dm^{-3} and $[\mathbf{D}]_0 = 7{\cdot}55 \times 10^{-5}$ mol dm^{-3} (dyes **K** and **C** only) were analysed. Because dyes **K** and **C** are isomers it is assumed that their absorption data are very similar. The ratio of areas limited by the peaks is the ratio of the rate constants.

CONCLUSIONS

Estimation of all three rate constants in the reaction scheme has been demonstrated avoiding the isolation and analysis of the dyes and adjustments of their solutions. Two estimated rate constants of the system were used for the computing process and the third one was calculated. The experimental course of the concentration of one of the products was compared with computed data. The results corresponded very well and it can be concluded that the assumptions used are valid.

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