

Study of the Reactions between Diazotized Aniline and 3-Aminobenzenesulphonic Acid with 8-Amino-1-Naphthol-3,6-Disulphonic Acid

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ABSTRACT

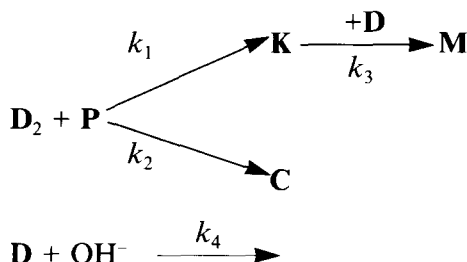
The rate constants of the two reaction systems involving the coupling of H-acid with diazotized aniline and 3-aminobenzenesulphonic acid were approximately estimated using spectrophotometry, HPLC and a simulation program (FEE, TU Brno, Dept. of Computers; PPSSS program).

1 INTRODUCTION

The reactions between diazotized sulpho-derivatives of aniline and 8-amino-1-naphthol-3,6-disulphonic acid (H-acid) (**P**) have been recently reported.^{1–4} We report here data on the reaction between diazotized 3-aminobenzenesulphonic acid (**D**₁) and component **P**. The reaction follows the general scheme as outlined in previous studies.^{2,3} Also investigated was the reaction between diazotized aniline (**D**₂) and (**P**), the reaction in this case being completed by reaction of diazotized aniline (**D**₂) with alkali. As shown on the next page, **K** is the product of monoazo coupling *ortho* to the NH₂ group and **C** that of coupling *ortho* to the OH group; **M** pertains to the disazo derivative.

As in a previous investigation,⁴ it was not possible to prepare solutions of the monoazo-compounds, precursors required for the direct determination of k_3 . Measurements were therefore made of the sum of the rate constants k_1 and k_2 , and their ratio.

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2 RESULTS AND DISCUSSION

2.1 Reaction $\text{P} + \text{D}_1$

The sum of the constants $k_1 + k_2$ was found spectrophotometrically to be $1541 \pm 73.5 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ in buffered solution of pH 4 and at $T = 10^\circ\text{C}$. When the ratio $[\text{D}_1]_0/[\text{P}]_0 \equiv n = 0.022$, the reaction is pseudomonomolecular, and the sum was determined from the first-order relationship

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

When the ratio was $n = 0.2$, the reaction is second-order, and the sum was determined from the relationship

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

In the above A_∞ , A_0 , A_t are absorbances at times infinity, zero and general time, respectively; absorbances were measured at $\lambda = 520 \text{ nm}$.

The ratio of the rate constants was estimated by HPLC to be $k_2/k_1 = 18.4 \pm 0.9 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$. In this estimation, we assumed that the absorption data of compounds **K** and **C** were very similar, and thus the ratio of areas limited by the peaks is the ratio of the rate constants.

The rate constant k_3 was determined to be $k_3 = 127.0 \pm 2.8 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ under the condition where $[\text{D}_1]_0/[\text{P}]_0 = 13.33$. The formation of **M** is pseudo-monomolecular and the system of differential equations previously described in Ref. 1 can then be solved.

If $(k_1 + k_2) \gg k_3$, then

$$\ln \frac{A_\infty - A_0}{A_\infty - A_t} = k_3 t [\text{D}_1]_0 \quad (1)$$

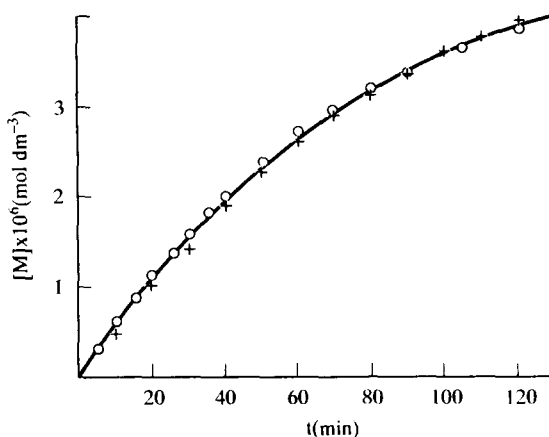


Fig. 1. Comparison of courses of computed (+) and experimental (O) data. Initial concentrations: $[P]_0 = 8.86 \cdot 10^{-5} \text{ mol dm}^{-3}$; $[D]_0 = 1.77 \cdot 10^{-4} \text{ mol dm}^{-3}$; $k_1 = 94 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$; $k_2 = 1455 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$; $k_3 = 137 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$.

where A_∞ , A_0 , A_t are absorbances at times infinity, zero and general time t , respectively; absorbances were measured at $\lambda = 620 \text{ nm}$.

The validity of the constants k_1 , k_2 , k_3 was tested using the simulation program PPSSS.⁵ Experimental data were obtained at $n = 2$; $[M]_\infty$ was computed using the PPSSS program and the constants k_1 , k_2 , k_3 , and absorbance coefficient and calculated values of $[M]$ were determined with respect to times t . Comparison of the courses of the computed and experimental values is shown in Fig. 1.

2.2 Reaction $P + D_2$

The sum of the constants ($k_1 + k_2$) was found to be $7.4 \pm 0.85 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$; conditions of the reactions were pH4 and $T = 10^\circ\text{C}$. The sum was determined from the first-order relationship ($n = 0.052$) and from the second-order relationship ($n = 0.2$).

The ratio of rate constants was estimated by HPLC, and a value of 15.9 ± 0.7 for k_2/k_1 was obtained.

The rate constant k_3 was determined spectrophotometrically and found to be $0.438 \pm 0.002 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$. The course of the reaction was pseudo-monomolecular ($n = 13.95$). We presumed the condition $(k_1 + k_2) \gg k_3$, and the value of k_3 was then calculated from eqn (1).

The rate constant k_2 was also determined by HPLC; the value was $6.75 \pm 0.35 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$, according to the equation at $n = 13.95$

$$\ln \frac{S_\infty}{S_\infty - S_t} = k_2 t [D_2]_0 \quad (2)$$

TABLE 1

Values of Reaction Constants k_1 , k_2 , k_3 ; **P** + **D**₁ Reaction. Calculated from Sum ($k_1 + k_2$) and Ratio k_2/k_1

	<i>Experiment</i>	<i>PPSSS program</i>
$k_1[\text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}]$	79.78 ± 7.49	94
$k_2[\text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}]$	1461 ± 80.88	1455
$k_3[\text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}]$	127.0 ± 2.8	137

TABLE 2

Values of Reaction Constants k_1 , k_2 , k_3 and k_4 ; **P** + **D**₂ Reaction

$k_1[\text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}]$	0.437 ± 0.050
$k_2[\text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}]$	6.75 ± 0.35
	6.96 ± 0.45^a
$k_3[\text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}]$	0.438 ± 0.002
$k_4[\text{h}^{-1}]$	$7.9 \cdot 10^{-3}$

^aCalculated from sum ($k_1 + k_2$) and ratio k_2/k_1 .

where S_∞ , S_t are the areas limited by the peaks at times infinity and general time.

2.3 Reaction **D**₂ + **OH**⁻

The rate constant k_4 was determined as $7.9 \cdot 10^{-3} \text{ h}^{-1}$. Component **D**₂ reacted in buffered solution at pH4 and $T = 10^\circ\text{C}$. The value of $[\text{D}_2]_t$ in solution was determined by fast reaction with 2-naphthol-6-sulphonic acid in buffered solution at pH 10. The decay of **D**₂ was first-order.

The validity of the constants k_1 , k_2 , k_3 , k_4 could not be proved by the PPSSS simulation program.⁵ The relationship $[\text{M}]$ versus t was not recorded since at wavelengths λ 620 nm and above, even component **C** absorbs slightly. Values of all the constants obtained are given in Tables 1 and 2.

3 EXPERIMENTAL

3.1 Chemicals

The components **P** and **D**₁ were purified as described in Ref. 6. Component **D**₂ was purified by distillation at atmospheric pressure and temperature 183–185°C. Adjustment of stock solutions, estimation of concentrations

and preparation of diazonium salts were described in Ref. 6. Buffer solutions were prepared as in Ref. 2.

3.2 Spectrophotometry

The formation of coloured products was monitored on a Specol 11 in buffer solution at pH 4 and $T = 10^\circ\text{C}$. The absorbance was checked at time intervals at wavelengths $\lambda = 520$ nm and 620 nm.

3.2.1 Reaction $P + D_1$

The sum of the rate constants ($k_1 + k_2$) was determined as follows: 1.5 cm^3 of a 0.015 M solution of P was added to 50 cm^3 buffer solution at pH 4 ($T = 10^\circ\text{C}$); 0.5 cm^3 of a 0.001 M solution of D_1 was then injected ($n = 0.022$) and the absorbance followed at 520 nm. This experiment was also carried out at $n = 0.2$, i.e. 75 cm^3 buffer solution was mixed with 3.33 cm^3 0.0015 M solution of P , and 1 cm^3 of a 0.001 M solution of D_1 was injected.

The rate constant k_3 was determined as follows: 0.5 cm^3 of a 0.0015 M solution of P was added to 25 cm^3 buffer solution (pH 4). 1.0 cm^3 of 0.01 M solution of D_1 was then injected ($n = 13.33$) and the absorbance measured at λ 620 nm at appropriate intervals.

3.2.2 Reaction $P + D_2$

The sum of the rate constants ($k_1 + k_2$) was determined as follows: 2 cm^3 of 0.015 M solution P was added to 25 cm^3 buffer solution (pH 4, $T = 10^\circ\text{C}$) and 1 cm^3 of a 0.001585 M solution of D_2 was injected. The red colour was monitored at λ 520 nm. The ratio used was $n = 0.052$. When the ratio was $n = 0.2$, the procedure used was as follows: 5 cm^3 of 0.0015 M solution P was added to 25 cm^3 of buffer solution, and 0.95 cm^3 of 0.001585 M solution of D_2 was then injected.

The rate constant k_3 was determined according to the first-order equation. The formation of component M was followed at λ 620 nm and $n = 13.95$, viz., 0.5 cm^3 0.015 of solution of P was mixed with 25 cm^3 buffer solution, and 2 cm^3 of 0.05229 M solution of D_2 was injected.

3.2.3 Reaction $D_2 + OH^-$

The rate constant k_4 was determined by reaction of D_2 with 2-naphthol-6-sulphonic acid. The procedure involved adding 1 cm^3 of 0.01585 M solution D_2 to 25 cm^3 buffer solution. Samples (1 cm^3) were taken at specific time intervals. Unreacted D_2 was estimated by reaction with 2-naphthol-6-sulphonic acid in buffer solution at pH 10. The absorbance of the coloured solution was measured at 482 nm.

3.3 HPLC analysis

The samples containing a mixture of components **K**, **C**, **M** (products of reactions **P** + **D**₁ and **P** + **D**₂) were analysed on a Varian 5020. The stationary phase was Separon C 18, glass column 150 × 3 mm, 5 μm. The mobile phase was a mixture of 60% methanol in water and 0.4 M Na₂SO₄ in a ratio of 1:9 (*S*₁). The second phase was 60% methanol in water and 0.1 M KH₂PO₄ with 0.1 M Na₂HPO₄. The ratio of the two solutions was 4:1 (*S*₂). The flow rate was 0.5 cm³ min⁻¹, pressure 20 MPa, injection 3 μl. The detector was a Varian UV 50, at λ 520 nm and 620 nm. The ratio *k*₂/*k*₁ was estimated as in Ref. 3.

3.3.1 Reaction **P** + **D**₁

1 cm³ of 0.015 M solution of **P** was added to 25 cm³ buffer solution. Four solutions of these concentrations were prepared. 0.6 cm³, 0.75 cm³, 0.9 cm³, 1.05 cm³ of 0.01 M solution of **D** were injected in each (*n* = 0.4; 0.5; 0.6; 0.7). Reactions were complete after 4 h and they were then analysed on the column with phase *S*₂.

3.3.2 Reaction **P** + **D**₂

1 cm³ of 0.015 M solution of **P** was mixed with 25 cm³ buffer solution; four solutions were again prepared, 0.379 cm³, 0.473 cm³, 0.567 cm³ and 0.662 cm³ 0.01585 M of solution **D**₂ was injected (*n* = 0.4; 0.5; 0.6; 0.7). Reactions were complete after two days and they were then analysed on a column with phase *S*₁.

The rate constant *k*₂ was estimated according to the following procedure: 1 cm³ of a 0.015 M solution of **P** was mixed with 25 cm³ buffer solution and then 4 cm³ 0.0523 M solution of **D**₂ was injected. Samples were taken at specific time intervals and analysed using phase *S*₁. The constant *k*₂ was determined according to eqn (2).

4 CONCLUSION

The rate constants of two reaction schemes were estimated. The first scheme was solved as in our previous studies, but in the second scheme, a further reaction occurs, viz., monomolecular decomposition of the diazonium salt of aniline in the reaction medium. The values of the rate constants were controlled by the simulation program PPSSS in the first scheme only. The second scheme ran slowly and we attempted to adjust the reaction solutions of high concentration. Absorption values at λ = 620 nm and *n* = 2 were affected by both the products **C** and **M**.

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