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A Study of the Kinetics of the Azo Coupling Reaction Used in the Synthesis of C.I. Reactive Orange 4

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ABSTRACT

*The azo coupling reaction between diazotized 2-naphthylamino-1,5-disulphonic acid and the condensation product of 2,4,6-trichloro-1,3,5-triazine with 5-hydroxy-2(*N*-methyl)naphthylamino-7-sulphonic acid was studied. In addition to the azo coupling, decomposition of the diazonium salt, and also dimerization of the coupling components occurs. The rate constants of all the reactions were estimated spectrophotometrically and potentiometrically. The relationship between the concentration of dye and time was estimated using a computer and these functions were compared with experimental data. For the best fitting curves, rate constants of dye formation were estimated.*

1 INTRODUCTION

The azo coupling reaction between diazotized 2-naphthylamine-1,5-disulphonic acid (D) and the condensation product of 2,4,6-trichloro-1,3,5-triazine with 5-hydroxy-2-(*N*-methyl)naphthylamine-7-sulphonic acid (P) proceeds together with other reactions, viz. (a) decomposition of the diazonium salt in mild alkaline solution, and (b) dimerization of the component (P).

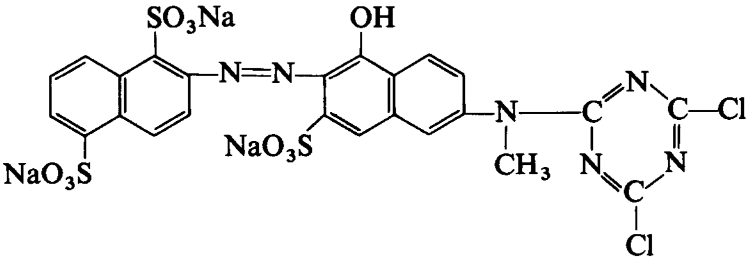
The overall scheme can be represented as follows:

$$\mathrm{D} + \mathrm{P} \xrightarrow{k_1} \mathrm{B} \tag{1}$$

$$\mathrm{D} + \mathrm{OH}^- \xrightarrow{k_2} \tag{2}$$

$$\mathrm{P} + \mathrm{P} \xrightarrow{k_3} \tag{3}$$

In the above, B is used to denote the resultant dyestuff, i.e. Ostazin Orange S2R (C.I. Reactive Orange 4),



The differential kinetic equations for this scheme, viz.

$$\frac{\mathrm{d[D]}}{\mathrm{d}t} = - k_1[\mathrm{P}][\mathrm{D}] - k_2[\mathrm{D}]$$

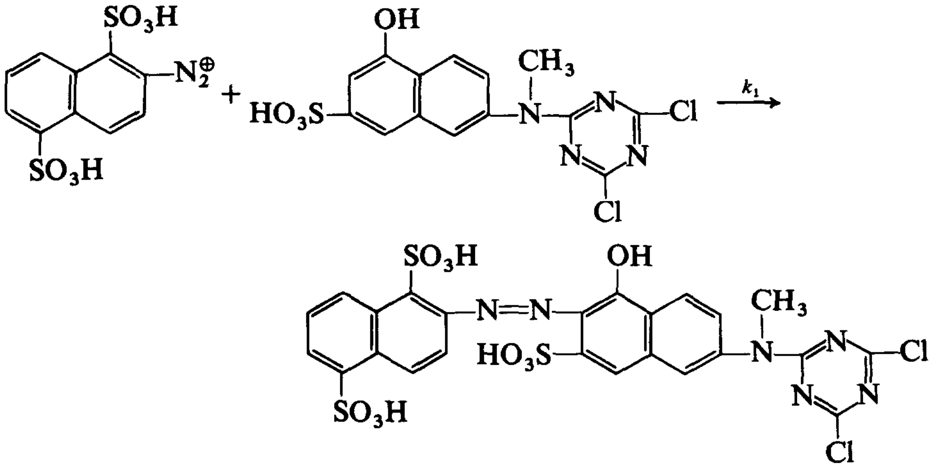
$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = - k_1[\mathrm{P}][\mathrm{D}] - k_3[\mathrm{P}]^2$$

$$\frac{\mathrm{d[B]}}{\mathrm{d}t} = - k_1[\mathrm{P}][\mathrm{D}]$$

are not soluble using a closed concentration–time relationship. However, it is possible to determine the rate constants k_2 and k_3, when following [D]–t and [P]–t separately in the reaction solution. Spectrophotometric monitoring of the [B]–t relationship does not give an accurate value for k_1, and the relationship does not give a linear plot (1st or 2nd order). The deviation is due to the additional reactions (with k_2 and k_3). The [B]–t relationship is an ascending curve reaching value $[\mathrm{B}]_{t=\infty}$ and this value depends on the rate constants k_1, k_2 and k_3 and on the initial concentrations $[\mathrm{P}]_{t=0}$ and $[\mathrm{D}]_{t=0}$. Application of the method of currentless curves of potential–time[1-4] does not give the correct value either. A theoretical relationship between [B]–t and parameters k_1, k_2 and k_3 was obtained using a computer, and comparison was made between the experimental and the calculated data.

2 RESULTS AND DISCUSSION

The azo coupling reaction of D with compound P is a 2nd order reaction:



The decomposition of D in buffer at pH 8 was a 1st order reaction, resulting in the formation of by-products of a non-reactive character. Decomposition was faster in the phosphate buffer than in the borate buffer. The values of the rate constants are given in Table 1.

Reaction (3) of P in buffer pH 8 (borate and phosphate) was a 2nd order reaction. The product did not undergo further azo coupling reactions, and therefore was assumed to be a dimer (P_2).

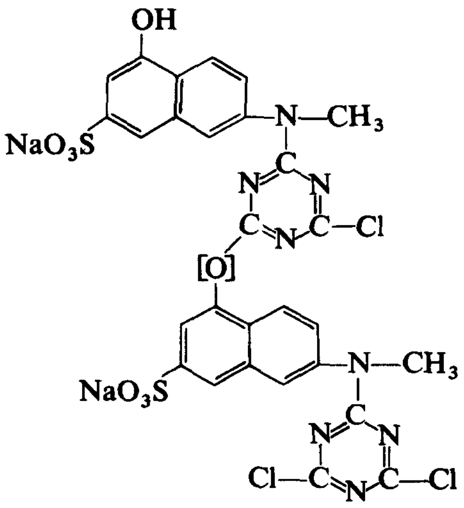


TABLE 1
Decomposition of D

pH	*T (°C)*	k_2 (s^{-1})	$[D]_{t=0}$ ($mol\ dm^{-3}$)
8 (Borate)	5	$1{\cdot}130 \times 10^{-5}$	$3{\cdot}29 \times 10^{-4}$
8 (Phosphate)	5	$9{\cdot}800 \times 10^{-5}$	$3{\cdot}29 \times 10^{-4}$
8 (Borate)	25	$1{\cdot}015 \times 10^{-4}$	$3{\cdot}29 \times 10^{-4}$
8 (Phosphate)	25	$7{\cdot}180 \times 10^{-4}$	$3{\cdot}29 \times 10^{-4}$

TABLE 2
Decrease in Concentration of P

pH	*T (°C)*	k_3 ($dm^3\ mol^{-1}\ s^{-1}$)	$[P]_{t=0}$ ($mol\ dm^{-3}$)
8 (Borate)	5	0·12–0·15	$8{\cdot}39 \times 10^{-4}$
8 (Phosphate)	5	0·12–0·176	$8{\cdot}39 \times 10^{-4}$
8 (Borate)	25	0·56	$8{\cdot}39 \times 10^{-4}$
8 (Phosphate)	25	0·56	$8{\cdot}39 \times 10^{-4}$

The values of the rate constants are quoted in Table 2.

Solution of the differential equations (1)–(3) was carried out using a computer, at fixed initial concentrations and rate constants. Values of [B] as a function of time were computed using the Runge–Kutta–Merson method.[1]

The calculated relationships [B]–t were compared with the experimental ones, at pH 8 (both buffers) and 25°C. Comparative data between experimental and computed functions are given in Table 3. Figures 1 and 2 compare the experimental and computed curves.

The experimentally estimated rate constants k_2 and k_3 were in agreement with the calculated values. Estimation of the approximate value of k_1 was derived using the method of currentless potential–time curves.

The final concentration of component B (degree of conversion)

TABLE 3
Experimental and Computed Rate Constants (pH 8, 25°C)

	k_1 ($dm^3\ mol^{-1}\ s^{-1}$)	k_2 (s^{-1})	k_2 ($dm^3\ mol^{-1}\ s^{-1}$)
Borate buffer (experimental)	17·0	$1{\cdot}01 \times 10^{-4}$	0·56
Borate buffer (computed)	12·0	$1{\cdot}01 \times 10^{-4}$	0·57
Phosphate buffer (experimental)	15·6	$7{\cdot}16 \times 10^{-4}$	0·56
Phosphate buffer (computed)	27·0	$7{\cdot}10 \times 10^{-4}$	0·57

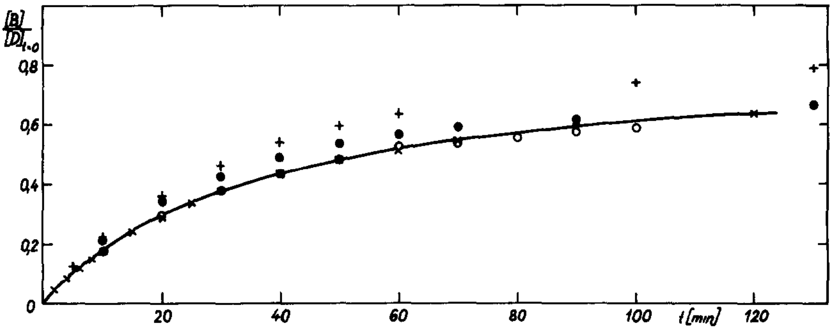


Fig. 1. The calculated functions $[B]/[D]_{t=0}$ versus time; borate buffer pH 8, $T = 25°C$, $[D]_{t=0} = [P]_{t=0} = 3{\cdot}21 \times 10^{-5}$ mol dm^3. ○, $k_1 = 12$ dm^3 mol^{-1} s^{-1}; $k_2 = 1{\cdot}01 \times 10^{-4}$ s^{-1}; $k_3 = 0{\cdot}57$ dm^3 mol^{-1} s^{-1}; ×, experiment; ●, $k_1 = 15$ dm^3 mol^{-1} s^{-1}; $k_2 = 1{\cdot}01 \times 10^{-4}$ s^{-1}; $k_3 = 0{\cdot}57$ dm^3 mol^{-1} s^{-1}; +, $k_1 = 15$ dm^3 mol^{-1} s^{-1}; $k_2 = 0$; $k_3 = 0$.

depends on the initial concentrations of components $[D]_{t=0}$ and $[P]_{t=0}$. Results are shown in Table 4.

From Table 4 it can be assumed that, with increase in the concentrations of P and D, reactions (1) and (3) are accelerated; and that they are of 2nd order. Reaction (2) is of 1st order and is, therefore less accelerated.

3 EXPERIMENTAL

3.1 Chemicals

2-Naphthylamino-1,5-disulphonic acid (technical grade) was twice recrystallized from hot water (charcoal). The coupling component was pre-

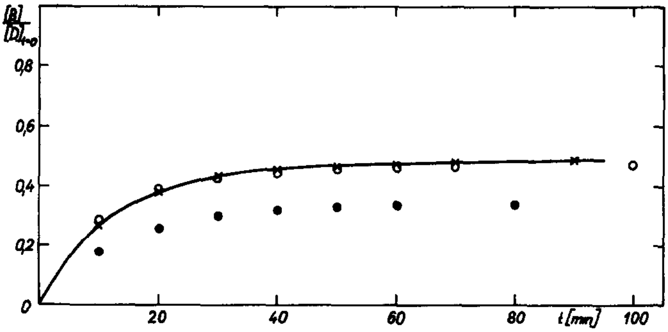


Fig. 2. The calculated functions $[B]/[D]_{t=0}$ versus time; phosphate buffer pH 8, $T = 25°C$, ○, $k_1 = 27$ dm^3 mol^{-1} s^{-1}; $k_2 = 0{\cdot}000\ 7$ s^{-1}; $k_3 = 0{\cdot}57$ dm^3 mol^{-1} s^{-1}; ×, experiment; ●, $k_1 = 15{\cdot}6$ dm^3 mol^{-1} s^{-1}; $k_2 = 0{\cdot}000\ 718$ s^{-1}; $k_3 = 0{\cdot}56$ dm^3 mol^{-1} s^{-1}.

TABLE 4

$[D]_{t=0} = [P]_{t=0}$ (*mol dm^{-3}*)	*$[B]_{t\to\infty}$* (*mol dm^{-3}*)	*Conversion* (%)
0·6	0·563	93·83
0·06	0·056 3	93·83
0·006	0·005 629	93·829
0·000 84	$7{\cdot}84 \times 10^{-4}$	93·57
$3{\cdot}21 \times 10^{-5}$	$2{\cdot}28 \times 10^{-5}$	71·02

pared as follows: to 0·125 mol of 2,4,6-trichloro-1,3,5-triazine in ice-cold water was added over 1 h a solution of 0·1 mol 5-hydroxy-2(*N*-methyl)naphthylamine-7-sulphonic acid maintaining a maximum temperature of 5°C and pH of 3–4. The suspension was stirred and then diluted with cold water to a concentration of 0·05 M. This stock solution was then stored at 5°C for 1 week and then used for the experiments; its strength was determined potentiometrically with diazotized sulphanilic acid at pH 5,[2,3] using a ground gold rotation electrode.

Borate buffer (pH 8, ionic strength $I = 1$), phosphate buffer pH 8 ($I = 1$) were prepared as described in Ref. 4.

3.1.1 Preparation of diazonium salts

Solutions (0·01 M and 0·001 M) of 2-naphthylamino-1,5-disulphonic acid in 0, 5 M HCl were diazotized with $NaNO_2$ (1·5 molar excess) at 5°C. After 30 min, excess of nitrite was removed by addition of urea.

3.2 Apparatus

Potential–time curves were recorded on equipment previously described.[2] A ground gold rotating electrode[3] served as indicator and a saturated calomel electrode was used as the reference. The approximate rate constant (k_1) of the coupling reaction (1) was determined by the method of currentless potential–time.[5] Using this method, the constants were estimated.[4–6] The rate constant k_2 of reaction (2) was determined spectrophotometrically. Decomposition of the diazonium salt in the absence of compound P resulted in the formation of slightly coloured non-reactive components. The concentration of unreacted diazonium salt was estimated by reaction with 2-naphthol-6-sulphonic acid in buffer solution at pH 10. Absorbance was measured at 490 nm. The rate constant k_3 of reaction (3) was also estimated spectrophotometrically. Unreacted coupling component P reacted with diazotized sulphanilic acid in the absence of the diazonium salt D.

The formation of compound B was monitored spectrophotometrically; the diazonium salt D was reacted with the coupling component P in a 1:1 molar ratio.

REFERENCES

1. Timar, J. & Tockstein, A., *Sci. Papers, VŠCHT Pardubice*, **52** (1988) 115.
2. Tockstein, A. & Matušek, M., *Coll. Czech. Chem. Commun.*, **32** (1967) 3089.
3. VUOS, Parbubice-Rybitli, Czech. Patent 183 365 (1975).
4. Dlask, V., *Coll. Czech. Chem. Commun.*, **49** (1984) 1262.
5. Tockstein, A. & Skopal, F., *Coll. Czech. Chem. Commun.*, **48** (1983) 1358.
6. Velich, V., Dlask, V. & Růžička, K., *Dyes and Pigments*, **6** (1985) 445.
7. Růžička, K., Smékal, O., Velich, V. & Dlask, V., *Chemický Průmysl*, **35/60** (1985) 630.