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Kinetics of the Azo Coupling Reaction Used in the Synthesis of Ostazin Yellow HR

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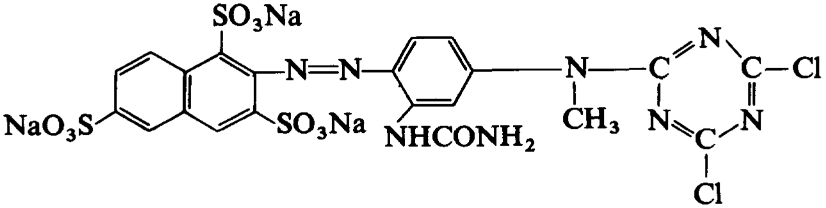
ABSTRACT

The azo coupling reaction between diazotized 2-naphthylamine-3,6,8-trisulphonic acid and 3-aminophenylurea was studied. The reaction proceeds together with decomposition of the diazonium salt. The rate constants of both reactions were estimated potentiometrically. A theoretical relationship of the azo coupling reaction product and time was calculated, and compared with the experimentally observed data.

1 INTRODUCTION

Diazotized 2-naphthylamine-3,6,8-trisulphonic acid [D] reacts with 3-aminophenylurea [P] in mildly acidic solution; the principal product is used in the further synthesis of Ostazin Yellow HR (C.I. Reactive Orange 12).



The azo coupling reaction proceeds together with decomposition of component [D] and other side reactions, i.e.

$$D + P \xrightarrow{k_1} B \qquad (1)$$

$$D + OH^- \xrightarrow{k_2}$$

in which B denotes the main product and also all other coloured components produced in the reaction.

The kinetic differential equations for Scheme 1:

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

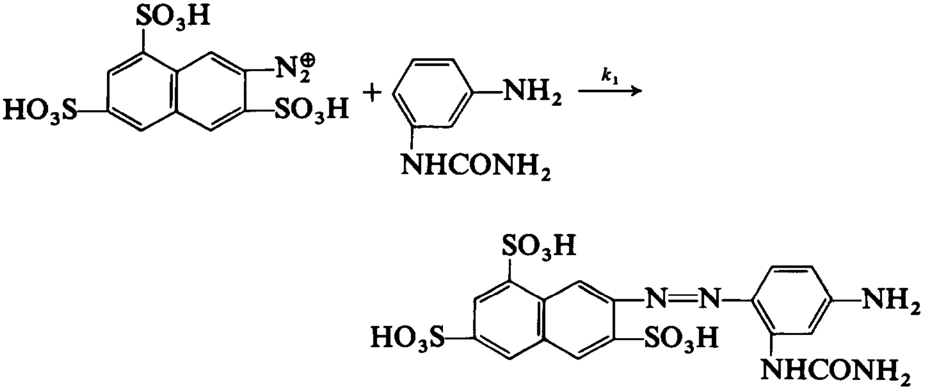
$$\frac{d[P]}{dt} = -k_1[D][P]$$

$$\frac{d[B]}{dt} = k_1[D][P]$$

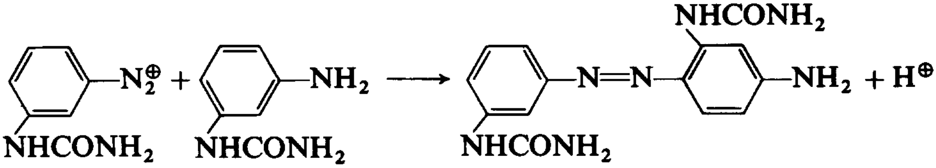
are not soluble in the 'closed formula' concentration–time relationship. However, it is possible to determine the rate constant k_2 by determination of [D] in solution in the absence of [P]. Estimation of k_1, using the method of currentless curves potential–time,[1] and also spectrophotometrically, was effected with only minor error. It is possible to use computing methods for the determination of component [B] (vs. time) and to compare these values with those experimentally recorded.

2 RESULTS AND DISCUSSION

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



In addition to the principal product, both the *o*-isomer and the bis-azo derivative were formed. Azoamino compounds were also formed, these then reverting to 2-naphthylamine-3,6,8-trisulphonic acid (NATSK) and nitrous acid, the latter then reacting with [P], giving a diazonium salt which undergoes further azo coupling with [P]:



All these coloured compounds are recorded as [B]. The rate constant k_1 has many errors and only the determined rate constant k_2 is a true value. The determined constants k_1 are shown in Tables 1 and 2.

In buffered solution of pH 5·6 and at 5°C the reaction was 1st order; it was assumed that an intermediate was initially formed, which then decomposed slowly to the dye.

The concentrations of B were calculated (Scheme 1) at a known value of $k_2(1{\cdot}85 \times 10^{-5}\ \mathrm{s}^{-1})$, and k_1 determined (Tables 1 and 2) at pH 5·6 and 25°C. Numerical calculations were computed using the Runge–Kutta–Merson method with a modified program.[2] The initial values $[\mathrm{P}]_{t=0}$ and $[\mathrm{D}]_{t=0}$ were regarded as equal, and [B] values were transformed to the absorbance A (with known absorption coefficient), and the A–time relationship compared with the experimental data (see Fig. 1). The best rate constants were: $k_2 = 1{\cdot}83 \times 10^{-5}\ \mathrm{s}^{-1}$; $k_1 = 49\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$.

TABLE 1

Potentiometrically Determined Rate Constant k_1 ($\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$) $[\mathrm{P}]_{t=0} = 2 \times 10^{-3}$ M

T (°C)	*5*	*15*	*25*
pH 4·6	6·35 ∓ 0·48	14·33 ∓ 0·38	21·99 ∓ 3·17
pH 5·6	14·89 ∓ 0·37	24·38 ∓ 0·39	49·48 ∓ 1·32

TABLE 2

Spectrophotometrically Observed Rate Constant k_1 ($\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$) $[\mathrm{D}]_{t=0} = [\mathrm{P}]_{t=0} = 3 \times 10^{-3}\ \mathrm{mol\ dm}^{-3}$

T (°C)	*5*	*15*	*25*
pH 3·6	2·20 ∓ 0·10	4·18 ∓ 0·08	6·85 ∓ 0·24
pH 4·6	8·56 ∓ 0·36	15·77 ∓ 0·79	24·33 ∓ 0·06
pH 5·6	(4·46 ∓ 0·21) × $10^{-4}\ \mathrm{s}^{-1}$	29·58 ∓ 0·42	44·16 ∓ 0·45

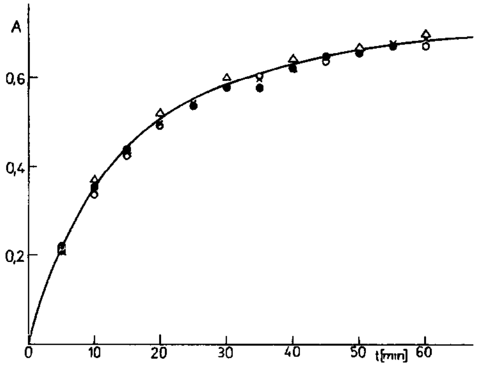


Fig. 1. Relationship between A and time: ●, ○, ×, reproduction of measurement; Δ, the best fitted calculated values of A.

3 EXPERIMENTAL

3.1 Chemicals

Compound [P] (technical grade, VCHZ Pardubice–Rybitví) was recrystallized from water (charcoal) and precipitated as the hydrochloride by addition of HCl.

2-Naphthylamine-3,6,8-trisulphonic acid (NATSK) (reagent grade, VCHZ Pardubice-Rybitví) was dissolved in hot distilled water and filtered through activated carbon. After cooling, crystals of NATSK were obtained. The NATSK solutions were analysed potentiometrically after diazotization with sodium nitrite.

Other chemicals used were of reagent grade (Lachema, Brno).

3.1.1 Buffer solution

Buffer solutions of pH 3·6, 4·6, 5·6 and 10·0 were prepared as in Ref. 3.

3.1.2 Preparation of diazonium salt

Solutions (0·001M and 0·025M) of NATSK in 0·5M hydrochloric acid were diazotized with sodium nitrite (1·5 molar excess) for 30 min at 5°C; excess nitrite was removed by addition of sulphamic acid. The diazotized solutions were prepared one day prior to measurement.

3.2 Apparatus

Potential–time curves were recorded on an apparatus described previously.[1] A ground gold rotating electrode[4] was used as indicator electrode and a saturated calomel electrode with a salt bridge was used as reference. The approximate value of the rate constant k_1 (production of [B]) was determined as in Ref. 5; other azo coupling reactions have been similarly studied.[3,6–8]

The formation of [B] was followed spectrophotometrically at λ 460 nm.

The decrease of [D] (determination of k_2) was also followed spectrophotometrically. The unreacted component D was estimated by reaction with 2-naphthol-6-sulphonic acid in buffered solution at pH 10; the dyestuff was determined at λ 494 nm.

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