# Kinetics of Coupling of Diazotized Sulfanilamid with 1-Naphthylamine

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### Abstract

In this study, the coupling kinetics of sulfanilamid diazonium salt with 1-naphthylamine has been studied by spectrophotometric method. In the experiments conducted at constant temperature, 25°C, pH has been varied between 2.2-3.4, reactant concentration between  $1.25 \times 10^{-5} - 5 \times 10^{-5}$  M, and ionic strength between 0.1-1 M. The reaction has been confirmed to be of second-order and rate constants and the dissociation constant of 1-naphthylamine have been calculated. © 1993 John Wiley & Sons, Inc.

### Introduction

In addition to its polluting effect,  $NO_x$  forms photochemical smog with ozone and even in very low concentration it acts as a catalysis in the oxidation of  $SO_2$  to  $H_2SO_4$ . Although there are various  $NO_x$  analysis methods, the commonly used is the Gries–Saltzman method which is based on the measurement of the absorbance of red–purple colored azo dye formed by coupling of sulfanilic acid diazonium salt with 1-naphthylamine at 550 nm [1–3]. It is believed that this method is not very accurate for very low  $NO_x$  concentration measurement. When sulfanilamid is used instead of sulfanilic acid the speed of the reaction increases and it is pointed out that sulfanilamid is more suitable when compared with sulfanilic acid [4]. The determination of  $NO_2^-$  ion in water is also accomplished similarly by this method with sulfanilamid [5].

Meanwhile, some constraints have to be imposed on the conditions used in this analysis; it was observed that the absorbance of the dye solution decreases after a certain period of time, which is function of  $NO_2^{-}$  concentration and pH. This decrease in absorbance is due to the precipitation of the azo-dye formed and restricts the applicability of this method. So, the kinetics of the coupling reaction of sulfanilamid diazo salt with 1-naphthylamine, as well as the precipitation kinetics of the azo dye, need to be studied in detail in order to establish clearly the experimental conditions of the analysis.

### **Material and Method**

All chemicals were of analytical grade (Fluka). HCl + phtalate buffer system was used for ensuring constant pH in reaction medium. In adjusting ionic strength. NaNO<sub>3</sub> was used as inert electrolyte.

International Journal of Chemical Kinetics, Vol. 25, 881–889 (1993) © 1993 John Wiley & Sons, Inc. CCC 0538-8066/93/110881-09 Solutions of diazonium salt and 1-naphthylamine were freshly prepared daily for each experiment; buffered 0.01 M stock solution of sulfanilamid was prepared, which was diluted to required concentrations with buffer solution and cooled in an ice-water bath to 2-4 °C. A buffered solution of NaNO<sub>2</sub> (4% excess) was then added dropwise while mixing the solution gently. The diazotization was permitted to continue at this temperature for half an hour. Then, excess nitrile was destroyed by adding urea.

The reaction was followed by monitoring the absorbance of azo dye product at the kinetic mode of SHIMADZU UV160A spectrophotometer with 1 cm optic length, quartz, thermostated cuvettes. The reaction temperature was held constant at  $25 \pm 0.1^{\circ}$ C in all experiments. For pH measurements EIL 7050 pHmeter and Ingold glass electrode were used.

Spectrums of the reaction medium were also obtained at definite time intervals for each pH value and reactant concentration considered in this study. A typical situation is shown in Figure 1. The greatest change in absorbance was observed at wavelengths between 515-520 nm at various parameters values. So, all the runs were carried out at 519 nm. A typical run was carried as follows: Initially 1.5 cm<sup>3</sup> 1-naphthylamine solution was put into the cuvette, then 1.5 cm<sup>3</sup> diazo salt solution was poured into the cuvette with a fast delivery pipette and the reaction was started immediately.

Reactants were used in equi-molar concentrations, in the range 1.25  $10^{-5}-5.10^{-5}$  M, pH was varied between 2.2-3.4.



Wavelenghts (nm)

Figure 1. The spectrum of the reaction medium at selected times (pH = 2.2,  $M = 5.10^{-5}$ ).

## **Kinetics and Mechanism of Coupling Reaction**

The overall coupling reaction is as follows:



The mechanism of the coupling can be represented by means of a fourreactions scheme, as follows (6.7):

(1) 
$$D + A \xrightarrow{} B \xrightarrow{A} S_1$$
  
 $C \xrightarrow{A} S_2$ 

Where D represents diazonium salt, A: 1-naphthylamine, B: p-substitued azo dye, C: o-substituted azo dye, and  $S_1, S_2$ : disubstituted dyes.

The coupling occurs preferentially in the p-position; the amounts of o-substitued dye and of two disubstitued diazo dyes are negligible, as found by thin layer chromatographic analysis of product dye. So, kinetic equation is derived according to one-reaction scheme.

The coupling reaction proceeds over a  $\sigma$ -complex according to  $S_E^2$  mechanism:

(2) 
$$\operatorname{ArN}_{2}^{+}\operatorname{ArNH}_{2} \xrightarrow[k_{2}]{k_{2}} \sigma\text{-complex } \xrightarrow[OH^{-}]{k_{3}} B + H_{2}O$$

The reaction of  $\sigma$ -complex with OH<sup>-</sup> is second-order with respect to both reactants, which is the rate controlling step (8,9). If pseudo-steadystate approximation is assumed for the  $\sigma$ -complex and when the following equilibrium reactions are taken into consideration;

$$(3a) A + H_2O \iff AH^+ + OH$$

(3b) 
$$H_2O \rightleftharpoons H^+ + OH^-$$

The rate equation is derived as

$$(4) r_B = k[D][A_t]$$

where  $A_t$  is total amine concentration and k is given as

(5) 
$$k = \frac{k_1 \cdot k_2 \cdot K_W}{(k_2[\mathrm{H}^+] + k_3 \cdot K_W) \left(1 + \frac{K_B}{K_W} \cdot [\mathrm{H}^+]\right)}$$

 $K_B$  is the base dissociation constant of 1-Naphthylamine,  $(8.4 \times 10^{-11} \text{ at } 25^{\circ}\text{C})$  and  $K_W$  is the ionization constant of water  $(1.01 \times 10^{-14} \text{ at } 25^{\circ}\text{C})$ .

If reactants are in equi-molar concentrations, by integration of eq. (4), the following is obtained;

(6) 
$$\frac{[B]}{[A_o - B]} = A_o kt$$

where  $A_o$  is the initial reactant concentration. On the other hand, if Lambert-Beer law is applied:

(7) 
$$Abs = \varepsilon[B]$$

eq. (6) may be arranged properly to give

(8) 
$$\frac{1}{\text{Abs}} = \frac{1}{\varepsilon A_o} + \frac{1}{\varepsilon A_o^2 k} \left(\frac{1}{t}\right)$$

On the other hand, if eq. (5) is rearranged suitably:

(9) 
$$\frac{1}{k} = \frac{1}{k_1} + \left[\frac{k_2 + k_2 K_B}{k_1 k_3 \cdot K_W}\right] [\mathrm{H}^+] + \left[\frac{k_2 \cdot K_B}{k_1 k_3 K_W^2}\right] [\mathrm{H}^+]^2$$

eq. (9) is obtained which is a polynomer of second-order with respect to  $\rm H^+$  concentration.

### **Experimental Results and Discussion**

The same absorbance-time curves were obtained for ionic strengths 0.2 and 1.0 M, at pH 3.4, reactant concentration  $1.25 \ 10^{-5}$  M. Thus, it is concluded that ionic strength has no effect on reaction kinetics. This result is consistent with the fact that the reaction occurs between an ion (diazonium) and a neutral molecule (1-naphthylamine).

The effect of pH on reaction rate was investigated in the range 2.2-3.4 with 0.2 intervals of pH; this range contains the pH (approx. 2.5) applied in the analytical method. Furthermore, for pH < 2, the reaction is too slow, while for pH > 3.5 the rate is too fast to follow with the manual mixing method and also the precipitation of the dye occurs prematurely.

The effect of reactant concentration was studied at three values; 5 imes $10^{-5}$ ,  $2.5 \times 10^{-5}$ , and  $1.25 \times 10^{-5}$  M. Typical absorbance-time curves are shown in Figure 2a and 2b for a low (1.25 imes 10<sup>-5</sup> M) and for a high (5 imes $10^{-5}$  M) reactant concentration. For concentrations greater than 1.25 imes $10^{-5}$  M, absorbance-time curves show a maximum point; for  $t < t_{max}$ , the solution is clear while for  $t > t_{max}$  the precipitation of the azo dye occurs, which is the cause in decrease of absorbance.  $t_{max}$  is function of both pH and reactant concentration; for example,  $t_{max}$  increases from 240 s to 750 s, by decreasing pH from 3.4 to 2.4, for  $5 \times 10^{-5}$  M reactant concentration. On the other hand, at constant pH 3.4,  $t_{max}$  increases from 240 s to 640 s, if reactant concentration is decreased from  $5 \times 10^{-5}$  to  $2.5 \times 10^{-5}$  M. Thus, the first period may be used to obtain the chemical kinetic law, while the second period may be evaluated to investigate the kinetics of precipitation of the azo dye. Typical linear curves of  $Abs^{-1}$  vs.  $t^{-1}$  obtained in the first periods are shown in Figure 3 at constant pH 2.41, for various reactant concentrations, and in Figure 4 for various pH at constant reactant



Figure 2. (a) Typical absorbance-time curve),  $M = 1.25 \ 10^{-5}$ , pH = 2.41. (b) Typical absorbance-time curve,  $M = 5.10^{-5}$ , pH = 2.41.

concentration 1.25  $10^{-5}$  M. Almost 20 data was used for calculating the slopes (a) and intercepts (b) of these curves in linear regression analysis which gave  $R^2$  values greater than 0.995. Then, by means of eq. (8). the constant k and  $\varepsilon$  were calculated as

(10a) 
$$k = \frac{a}{bA_{c}}$$

and

(10b) 
$$\varepsilon' = \frac{1}{bA_o}$$

By noting that  $\varepsilon' = \varepsilon.l$ , where l is optic path (1 cm), extinction coefficients,  $\varepsilon$ , were calculated with mean value of 195350 ± 7350 dm<sup>2</sup> mol<sup>-1</sup>, which agrees well with the measured value, 193600 dm<sup>2</sup> mol<sup>-1</sup>. On the



Figure 3. Curves of Abs<sup>1-</sup> vs.  $t^{1-}$  various reactant concentration, (pH = 3.2).

other hand, the rate constant k is shown as function of pH in Figure 5. In order to test the validity of eq. (9) and to calculate other kinetic parameters, one must know true H<sup>+</sup> concentrations. As the ionic strength, I, was smaller than 0.1, the following relation was used to calculate true H<sup>+</sup>



Figure 4. Curves of Abs<sup>1-</sup> vs.  $t^{1-}$  at different pH values (reactant concentration =  $5 \times 10^{-5}$  M).



Figure 5. Rate constant  $k_1$  as function of pH.

concentrations:

(11) 
$$\log[H^+] = -pH + \frac{0.5\sqrt{I}}{1+\sqrt{I}}$$

In Figure 6, 1/k values was shown as function of  $[H^+]$ . The following parameter values were obtained by means of regression analysis;

(12) 
$$k_1 = 11242 \pm 781 \text{ s}^{-1}$$

If the values given in the literature are used for  $K_B$  and  $K_W$ ,  $k_2/k_3$  is calculated as  $1.12 \times 10^{-12} \pm 7.8 \times 10^{-14}$ .

On the other hand, both  $K_B$  and  $k_2/k_3$  may be calculated by means of eq. (9). Thus, the following values are obtained:

(13) 
$$\frac{k_2}{k_3} = 1.26 \times 10^{-12} \pm 7.8 \times 10^{-14} \, (\mathrm{dm^3 \ mol^{-1} \ s^{-1}/dm^3 \ mol^{-1} \ s^{-1})}$$

and

(14) 
$$K_B = 7.32 \times 10^{-11}$$
.

This value of  $K_B$  is close to  $8.4 \times 10^{-11}$  which is given in the literature (10).

### Conclusion

In this study, the kinetics of the coupling reaction of sulfanilamid diazonium salt with 1-naphthylamine was studied spectrophotometrically.



Figure 6. The relation between 1/k and  $[H^+]$ .

For reaction concentrations greater than  $1.25 \ 10^{-5}$  M, absorbance-time curves show two periods separated by a maximum points which corresponds to the beginning of precipitation of the azo dye product. The time to reach this maximum point is function of pH and azo dye concentration. High pH accelerates the reaction rate but decreases also the time to reach the precipitation of the dye which has lower solubility at high pH, as it possesses a basic solvatizing NH<sub>2</sub> group. Two examples may be given here; for pH = 2.4 and  $[NO_2^{-1}] = 5 \times 10^{-5}$  M,  $t_{max} \approx 750$  s, and from eq. (6), the maximum conversion which can be obtained at these conditions is 86.7%, and on the other hand, for pH = 3.2 and  $[NO_2^{-1}] = 0.2510^{-5}$  M;  $t_{max} \approx 520$  s, and maximum conversion is 95%, which means that, at these conditions, the method will predict the NO<sub>2</sub><sup>-</sup> concentration with limited accuracy. Absorbance-time data in the first period was used to obtain kinetic parameters as follows:

$$k_1 = 11242 \pm 781 \text{ s}^{-1}$$
  
 $\frac{k_2}{k_3} = 1.26 \times 10^{-12} \pm 7.8 \times 10^{-14}$ 

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