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Kinetics and mechanism of the redox reaction of toluidine blue and nitrite ions in aqueous acidic medium

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ABSTRACT

The kinetics of oxidation of Toluidine blue (hereafter referred to as TB^+) by nitrite ion have been studied in aqueous acidic medium under the pseudo-first order condition of excess $[NO_2^-]$ at 25 ±1°C, $[H^+] = 1 \times 10^{-2}$ mol dm^{-3} and ionic strength, I = 0.50 mol dm^{-3} (NaCl). The stoichiometry of the reaction was observed to be 3:1 mole ratio of toluidine blue to nitrite ions. The redox reaction follows second order kinetics at constant hydrogen ion concentration and the rate also shows first order dependence on hydrogen ion concentration. The overall reaction conforms to the rate law:

$$-\frac{d[TB^+]}{dt} = a\,[TB^+][NO_2^-][H^+] \quad \text{Where } a = 40.76\ \text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1}$$

A plausible mechanism has been proposed for this reaction.

Key words: Kinetics, Mechanisms, Toluidine blue, Nitrite ions.

INTRODUCTION

Toluidine blue is a dye belonging to the phenothiazine class same class as methylene blue and methylene green. Phenothiazines are important compounds in medicine and industry [1]. The dye can be used to treat methaemoglobinaemia [2]. The use of toluidine blue in this respect has been attributed to its electron donor –acceptor property [3, 4]. A literature survey shows that kinetics and mechanisms of the reduction of toluidine blue to its lueco compound have been reported [5-8]. However little has been reported on the oxidation of this dye [9].

Nitrite ion is a powerful oxidizing agent which has been used for centuries as a food preservative [10]. NO which is produced in the human body by a chemical reduction of nitrite is an essential regulator of numerous aspects of human physiology [11].

In this paper we report on the kinetics and mechanisms of the redox reaction of toluidine blue with nitrite ion.

MATERIALS AND METHODS

Materials: The reagents used were of analytical grade and were used as supplied. All solutions were made with distilled water, stock solutions of 1×10^{-3} mol dm^{-3}toluidine blue (BDH), 0.5 mol dm^{-3} sodium nitrite (BDH) and 2 mol dm^{-3} sodium chloride (M$B, used to maintain ionic strength constant) were prepared by dissolving 0.0077g in $25cm^3$ volumetric flask, 0.345g in $10cm^3$ volumetric flask and 5.8440g in $50cm^3$ volumetric flask respectively. Hydrochloric acid, which was used to investigate the effect of $[H^+]$ was standardized titrimetrically using standard solution of sodium bicarbonate. The λ_{max} = 600 nm was determined by measuring the absorbance of the solution of toluidine blue in the wavelength range 400-700nm.

Stoichiometry: The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method by keeping the concentration of the dye constant at 2.8×10^{-5}mol dm^{-3}, $[H^+] = 1 \times 10^{-2}$ mol dm^{-3}, I = 0.50 mol dm^{-3}, λ_{max} = 600nm, T = 25±1°C and $[NO_2^-]$ was varied from 0.10 -20.00 x 10^{-5} mol dm^{-3} . The absorbance of the reacting mixture was measured after the reaction had gone to completion over a period of 24 hours when the absorbance attained a steady value. A point of inflexion on the curve of absorbance versus mole ratio plot indicates the stoichiometry of the reaction [12].

Kinetic Measurements: The kinetics of the reaction was monitored using a Corning colorimeter Model 253 at 25±1°C, $[H^+] =1 \times 10^{-2}$ mol dm^{-3} and I=0.50 mol dm^{-3}. The progress of the reaction was monitored by following the decrease in absorbance of the dye at 600nm. All kinetic experiments were performed under pseudo-first order conditions with the concentration of the nitrite ions at least 1000- fold greater than that of the dye. The pseudo-first order plots of the log $(A_\infty - A_t)$ versus time t were made (where A_∞ and A_t are the absorbance at the end of the reaction and at time, t) and from the slope of the plots, the pseudo-first order rate constant (k_{obs}) was determined. The second order rate constant (k_1) was obtained from the relation:

$$k_1 = k_{obs}/ [NO_2^-] \qquad (1)$$

Effect of $[H^+]$ on the Reaction Rate: The effect of $[H^+]$ on the rate of the reaction was studied in the range of $1.0\times10^{-3} \leq [H^+] \geq 1.0\times10^{-1}$mol dm^{-3} while concentration of the dye and nitrite ion were kept constant at 2.80 $\times10^{-5}$ and 2.80 $\times10^{-3}$ mol dm^{-3} respectively at 25.0±1.0°C and I =0.50 mol dm^{-3}.

Effect of Ionic Strength: The effect of ionic strength on the rate of the reaction was investigated in the range of 0.20-1.00 mol dm^{-3} , while the concentration of other reactants were kept constant at 25±1°C. The results are presented in Table1.

Effect of Added Cation and Anion: The effect of added cation and anion were investigated for $[X] = 1.0 \times10^{-3}$ -100.0 $\times10^{-3}$ mol dm^{-3} (X =Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-) and the concentration of other reactants were kept constant at 25.±1°C and ionic strength of 0.50 mol dm^{-3}.

Test for Intermediate Complex: The spectra of the reaction mixture were obtained five and 15 minutes after the commencement of the reaction. These were compared with the spectra of the dye alone over a wavelength range of 400 -700 nm. Michaelis-Mentens plot of $1/k_{obs}$ versus $1/ [NO_2^-]$ was also made (Fig. 2).

Test for Free Radical: Acrylonitrile was added to the partially oxidized reaction mixture of toluidine blue and the nitrite ions in a large excess of methanol and to each of the reactants separately, and its effect noted.

RESULTS AND DISCUSSION

Stoichiometry and Product Analysis: A stoichiometric study showed that three mole of the dye was consumed by one mole of the nitrite ion. This comforms to the equation:

$$3TB^{+} + NO_2^{-} \xrightarrow{\qquad\qquad} \text{Products} \qquad (2)$$ A

ldehyde functional group was detected in the reaction products using Tollen's reagent [13].

Kinetics: The pseudo-first order of log (A_∞ -A_t) versus time, t for these reactions were linear for about 80% of the reaction. The linearity of these plots indicates that these reactions are first order with respect to [TB^+]. A plot of log k_{obs} versus log [NO_2^-] was linear with a slope of 0.995(Fig. 1), showing that the reaction is also first order with respect to [NO_2^-]. This is also supported by the constancy of k_1 values. Thus the reaction is second order at constant [H^+] and the rate equation for the reaction is:

$$-\frac{d[TB^+]}{dt} = k_1[TB^+][NO_2^-] \qquad (3)$$

where $k_1 = 3.62\times10^{-1}$ dm^3 mol^{-1}

similar observation was reported for the redox reaction toluidine blue [6,9] and reaction of nitrite ions with parafuchsin [14].

Effect of [H^+]: The rate constants of the reaction were found to increase with increase in [H^+], plot of log k_{obs} versus log [H^+] was linear with a slope of 1.003 (Fig. 2) suggesting the reaction to be first order with respect to [H^+]. Also the plot of k_1 versus [H^+] was linear with no intercept (Fig. 3). The nature of [H^+] dependence suggests that there is a rapid equilibrium between protonated and unprotonated form of nitrite ion prior to the rate-determining step, and that only the protonated form is reactive at the rate determining step [15]. The rate constant for the observed [H^+] dependence is given by:

$$k_1 = a[H^+] \qquad (4)$$

combining equation 3 and 4 gives

$$-\frac{d[TB^+]}{dt} = a[TB^+][NO_2^-][H^+] \qquad (5)$$

Where a = 40.76 dm^6 mol^{-2} s^{-1}

Similar acid dependence was observed in the reaction between toluidine blue and phenyl hydrazine [8] and parafuchsin and nitrite [14].

Effect of Ionic Strength: The reaction displayed a positive salt effect as the second order rate constants increased with increasing ionic strength according to Bronsted-Debye salt effect [16]. This suggests that the activated complex is formed from two ions of like charges like the protonated form of nitrite ion and TB^+. A plot of log k_1 versus $\sqrt{I}$ gave a straight line with a slope of 0.7 (Fig. 4). This suggests that some other interactions must be taking place to account for this non-integral value for the product of the charges of the reactant species at the transition state. Similar observation was reported in the reaction of nitrite [14].

Effect of Added anions: Addition of Ca^{2+}, Mg^{2+}, SO_4^{2-} and NO_3^- ions decreases the rate of the reaction. This observation is characteristic of reactions occurring via outer-sphere mechanistic pathway [14, 17]

Free Radical Test: The addition of acrylamide to the partially reacted mixture of the reactants followed by large excess of methanol did not lead to the formation of gelatinous precipitate .This suggests that free radicals might not likely be involved in this reaction [18], or that it reacts so quickly that this method cannot detect it.

Intermediate Complex Formation: The spectroscopic studies indicated no shift from the absorption maxima of 600 nm characteristic of TB^+.
This suggests that the formation of an intermediate complex during the reaction is very unlikely. Michaelis-Mentens plots of $1/k_{obs}$ versus $1/[NO_2^-]$ gave a straight line which passed through the origin (Fig.5). This further suggests the absence of intermediate complex formation of significant stability thereby supporting the operation of the outer-sphere mechanism [19] for this reaction.

On the basis of the result obtained, the following plausible mechanism is hereby proposed:

$$NO_2^- + H_2O \xrightleftharpoons{K_1} HONO + OH^- \qquad (6)$$

$$HONO + H^+ \xrightleftharpoons{K_2} H_2NO_2^+ \qquad (7)$$

$$H_2NO_2^+ \xrightleftharpoons{K_3} :N{=}O^+ + H_2O \qquad (8)$$

$$:N{=}O^+ + TB^+ \xrightarrow{k_4} [:N{=}O^+//TB^+] \qquad (9)$$

$$[TB//:N{=}O]^{2+} + 2TB^+ \xrightarrow{k_5} \text{Product s} \qquad (10)$$

$$H^+ + OH^- \xrightarrow{k_6} H_2O \qquad (11)$$

Equation 9 is the rate determining step. Hence:

$$\text{Rate} = k_4 [TB^+][:N{=}O^+] \qquad (12)$$

$$\text{But } [:N{=}O^+] = K_3 [H_2NO_2^+] \qquad (13)$$
$$[H_2NO_2^+] = K_2[HONO][H^+] \qquad (14)$$
$$[HONO] = K_1[NO_2^-] \qquad (15)$$

Substituting equations 13, 14 and 15 in 12 gives:

$$\text{Rate} = K_1K_2K_3\,k_4 [TB^+] [NO_2^-] [H^+] \qquad (14)$$

Therefore

$$\text{Rate} = k [TB^+] [NO_2^-] [H^+] \qquad (15)$$

Equation 15 is related to equation 5, and is consistent with the experimentally observed rate law. Where $k = K_1K_2k_3\,k_4 = a = 40.76$ $dm^3\ mol^{-2}\ s^{-1}$

Table 1: Pseudo-first order and second order rate constants for the reaction of toluidine blue and nitrite ions in aqueous HCl medium at $[TB^+] = 2.80 \times 10^{-5}$ mol dm^{-3}, T = 28±1°C, λ_{max}=600nm

$10^3[NO_2^-]$, mol dm^{-3}	$10^3[H^+]$, mol dm^{-3}	I, Mol dm^{-3}	10^3k_{obs}, s^{-1}	k_1, dm^3 mol^{-1} s^{-1}
1.87	10	0.5	0.68	0.36
2.80	10	0.5	0.99	0.35
3.73	10	0.5	1.35	0.36
4.67	10	0.5	1.70	0.36
5.60	10	0.5	2.02	0.36
6.52	10	0.5	2.50	0.38
7.47	10	0.5	2.60	0.35
9.33	10	0.5	3.32	0.36
11.20	10	0.5	4.10	0.37
2.80	1	0.5	8.00	0.03
2.80	10	0.5	9.80	0.35
2.80	20	0.5	2.21	0.79
2.80	30	0.5	3.19	1.14
2.80	50	0.5	5.07	3.01
2.80	100	0.5	7.60	4.52
2.80	10	0.2	0.66	0.24
2.80	10	0.3	0.82	0.29
2.80	10	0.4	0.90	0.32
2.80	10	0.5	1.01	0.36
2.80	10	0.6	1.17	0.42
2.80	10	0.7	1.26	0.45
2.80	10	0.8	1.31	0.47
2.80	10	1.0	1.47	0.53

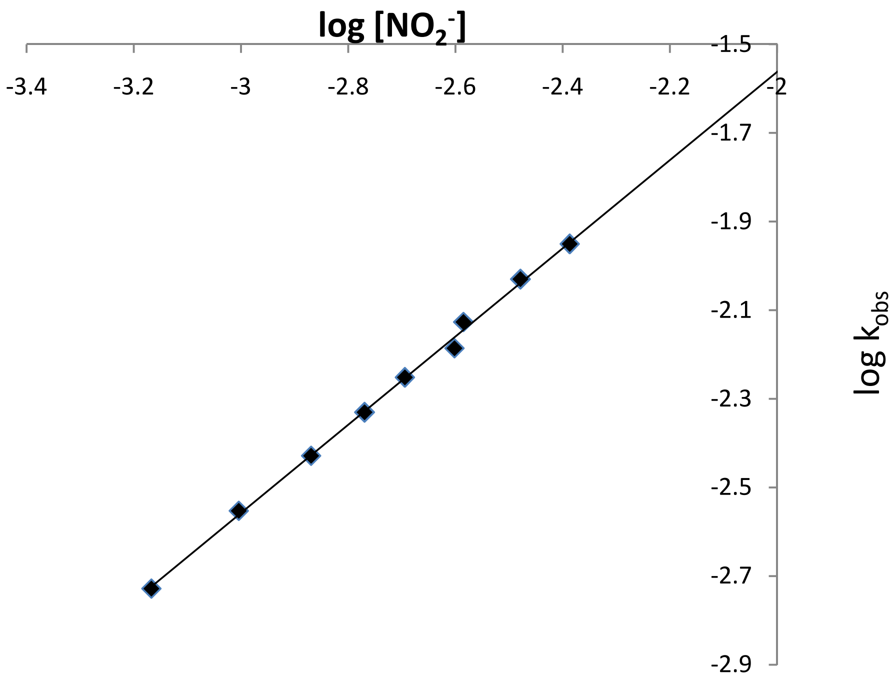

Figure 1: Plot of log k_{obs} versus log [NO_2^-] for the toluidine blue reaction with nitrite ion at [TB^+] 2.8×10^{-5} mol dm^{-3}, [H^+] = 1×10^{-2} mol dm^{-3}, I = 0.5 mol dm^{-3}, λ_{max} = 600nm and T = 25±1℃

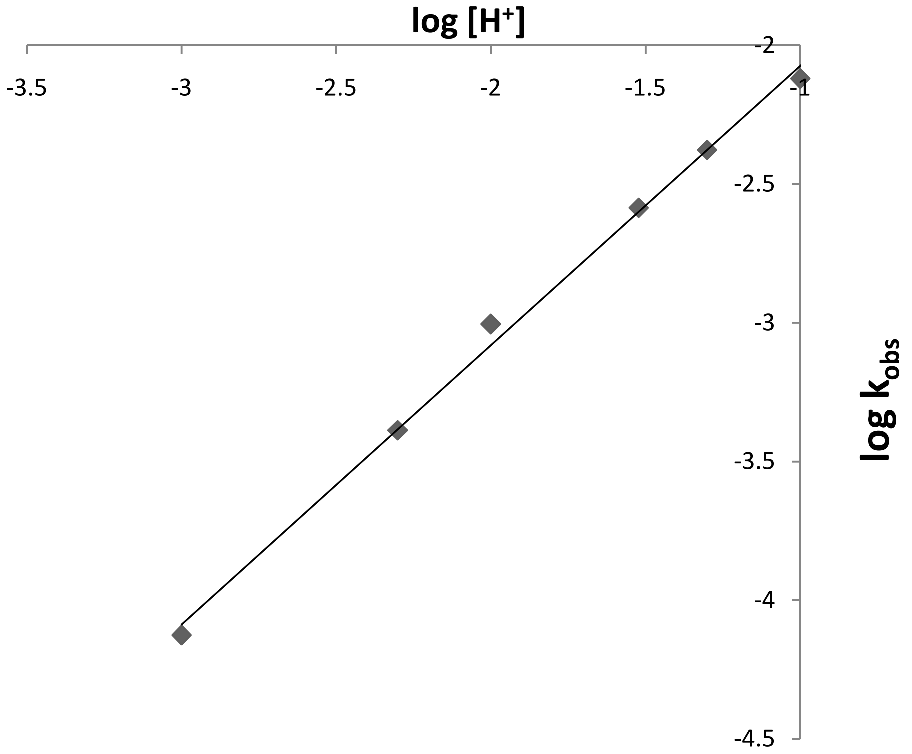

Figure 2: Plot of log k_{obs} versus log [H^+] for the toluidine blue reaction with nitrite ion at [TB^+] = 2.8×10^{-5}mol dm^{-3}, [NO_2^-] = 2.8×10^{-3} mol dm^{-3}, I = 0.5 mol dm^{-3} λ_{max} and T = 25 ± 1℃

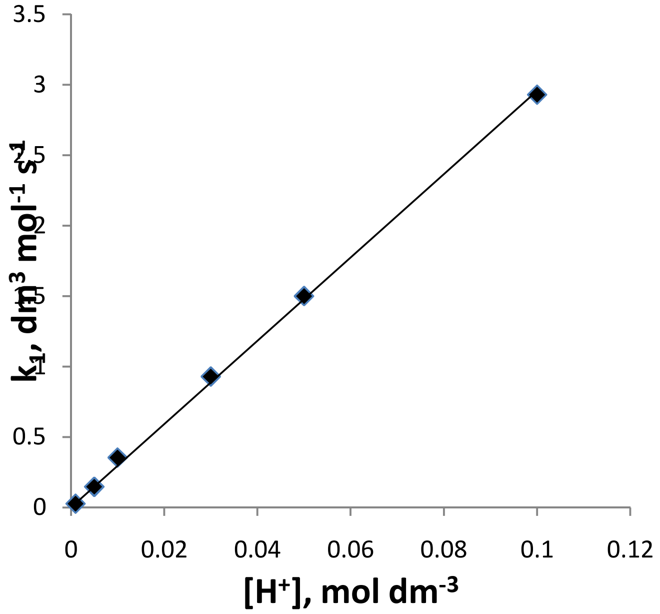

Figure 3: Plot of k_1 versus $[H^+]$ for the toluidine blue reaction with nitrite ion at $[TB^+]$ 2.8×10^{-5}mol dm^{-3}, $[NO_2^-] = 2.8\times10^{-3}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, λ_{max} = 600nm and T = 25 ± 1℃

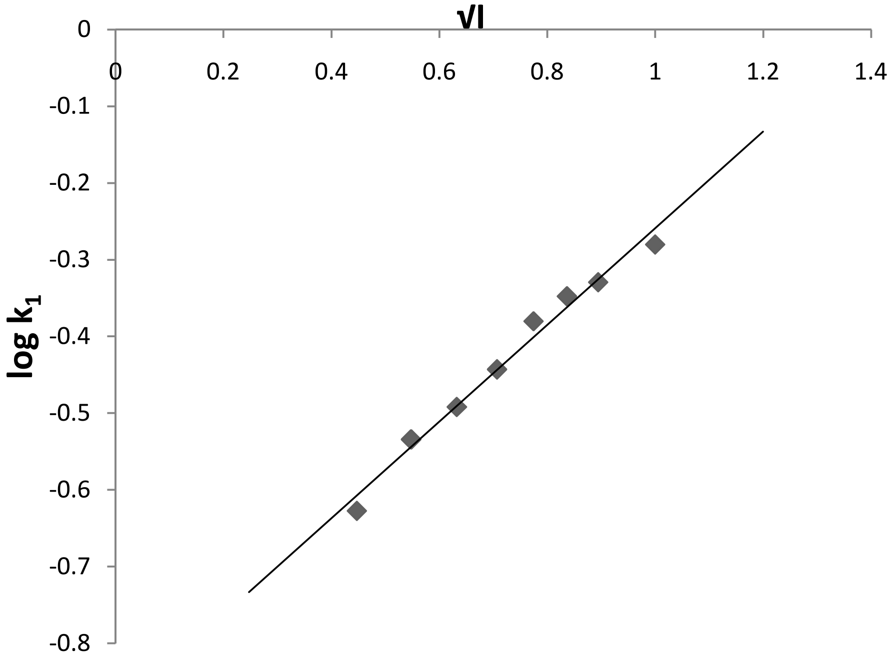

Figure 4: Plot of log k_1 versus √I for the toluidine blue reaction with nitrite ion at $[TB^+]$ 2.8×10^{-5}mol dm^{-3}, $[NO_2^-] = 2.8\times10^{-3}$ mol dm^{-3}, $[H^+] = 1\times10^{-2}$ mol dm^{-3}, λ_{max} = 600nm and T = 25 ± 1℃

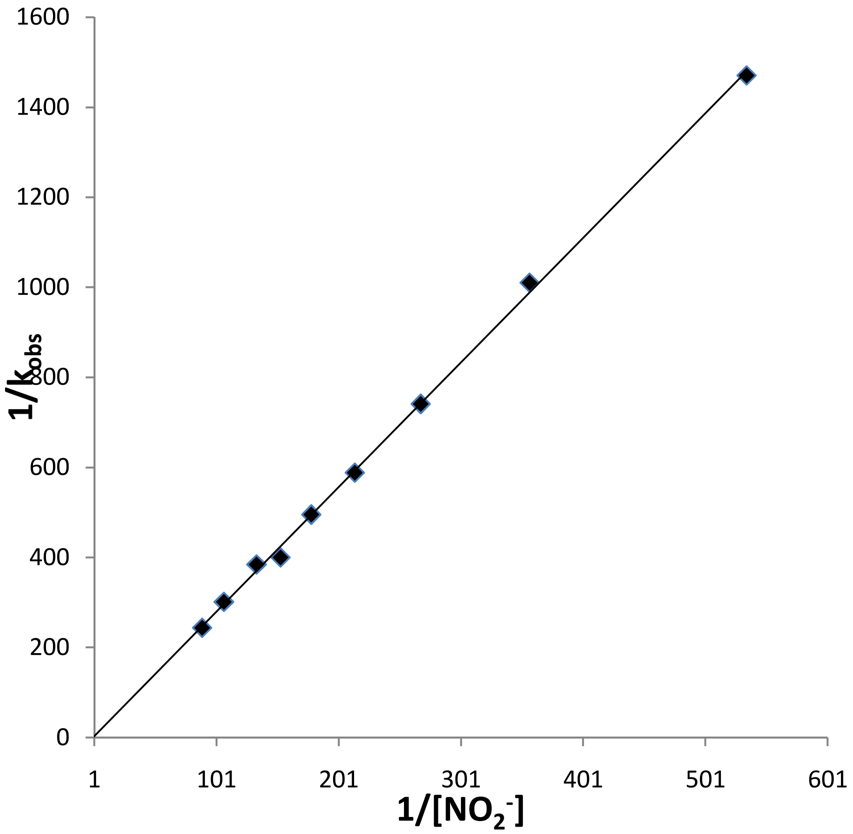

Figure 5: Michaelis-Menten's plot for the reaction of toluidine blue and nitrite ion at $[TB^+] = 2.80\times10^{-5}$ mol dm^{-3}, $[NO_2^-] = 2.80\times10^{-3}$ mol dm^{-3}, $[H^+] = 1.0\times10^{-2}$ mol dm^{-3}, I = 0.5 mol dm^{-3} and T = 25±1℃

CONCLUSION

The reaction is found to be second order overall at constant $[H^+]$. And the proposed reaction steps point to the outer sphere electron transfer process, considering the fact that addition of ions led to the inhibition of the reaction rates. When the absorbance's of the reaction mixture were measured as the reaction progresses, the λ_{max} of toluidine blue remained at 600nm, this is an indication of the absence of intermediate complex formation which would be as a result of a chemical bond between the reactants, thereby tempering with the electronic transition of the TB^+ by causing a distortion in the crystal field splitting , and hence a shift in the λ_{max} of TB^+ or appearance of a new peak which was hitherto absent. Also Michaelis-Menten plot of $1/k_{obs}$ against $1/[NO_2^-]$ passed through the origin. These points greatly favour the outer sphere mechanistic pathway for this reaction [17].

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