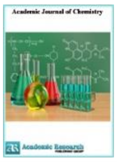

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Kinetics and Mechanism of the Reduction of Tartrazine by Nitrite Ion in Aqueous Acid Phase

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Abstract

Kinetics and mechanism of the reduction of tartrazine (TZ^+) by nitrite ion (NO_2^-) was conducted in aqueous acidic phase under pseudo-first order condition in excess of $[NO_2^-]$ at T = 28 ± 1°C, $[H^+] = 1 \times 10^{-4}$ mol/dm^3, $\lambda_{max} = 560$ nm and ionic strength I = 1.0 mol/dm^3 (NaCl). The stoichiometry of the reaction displayed 1:2 mole ratio for tartrazine and nitrite ion. The redox reaction was first order with respect to $[TZ^+]$ and first order with respect to $[NO_2^-]$. A second order rate constant was observed for the reaction. The rate also shows first order dependence on acid ion concentration. The overall reaction conforms to the rate law: $\frac{-d}{dt}[TZ^+] = a[H^+][TZ^+][NO_2^-]$ Where a = 6.7343 dm^6 mol^{-2} s^{-1}. The rate of reaction increased with increase in ionic strength. There was no positive polymerization in the reaction. The investigation of spectroscopic and Michaelis- Mentens plot studies did not indicate any complex formation. A plausible mechanism in support of an outer-sphere mechanism is proposed for the reaction.

Keywords: Kinetics; Tartrazine; Nitrite.

1. Introduction

Tartrazine is an organic salt, a trisodium salt of tartrazine acid. It is a synthetic lemon yellow azo dye used as food colourant [1]. Cubed or powdered chicken broth, pasta, frosting, macaroni and cheese, creamy orange cheeses, yogurt, butter and margarine; ice cream, many sodas, alcohol mixers and some beers etc are varieties of foods that contains tartrazine. Various types of medicines in liquid, capsule, pill, lotion, or gel forms, also contains tartrazine which gives yellow, orange or green hue for easy identification. Pharmaceutical products that contains tartrazine includes vitamins, antacids, cold medications (including cough drops and throat lozenges), lotions and prescription drugs. The European Food Safety Authority allows for tartrazine to be used in processed cheese, canned or bottled fruit or vegetables, processed fish or fishery products, wines and wine-based drinks [2].

Nitrite ion has a role as an antimicrobial food preservative, an antihypertensive agent, a food antioxidant, an antidote to cyanide poisoning. It is also used as a medication together with sodium thiosulphate to treat cyanide poisoning [3]. As a preservative, nitrite ion fights harmful bacteria in ham, salami and other processed and cured meats and also provides them with their pink colouration. However, under certain conditions in the human body, nitrite ion can damage cells and also morph into molecules that cause cancer [4]. Nitrite ion content is very low in vegetables [5] and very reactive in an acidic environment such as that of the stomach [6].

Hence knowledge of the kinetics that characterizes the reduction of tartrazine and nitrite ion is highly beneficial so as to enhance their applicability in the food and Pharmaceutical industries.

2. Material and Methods

2.1. Materials

Hydrochloric acid (36%, specific gravity 1.18) and sodium chloride were used respectively to investigate the effect of hydrogen ion concentration and to maintain the ionic strength of the medium. Stock solutions of tartrazine and sodium nitrite were prepared by dissolving known amounts of the reagents in distilled water and making up the solution to known volume. All reagents used were of 'Analar' grade and were used without further purification.

2.2. Stoichiometriy

The mole ratio technique was used to determine the stoichiometry of the reaction by keeping the concentration of tartrazine constant at 1×10^{-4} mol/dm^3 while that of nitrite ion was varied at $(1.0 - 10.0) \times 10^{-4}$ mol/dm^3, $[H^+] = 1 \times 10^{-4}$ mol/dm^3, I = 1.0 mol/dm^3, $\lambda_{max} = 560$ nm and at T = 28.0 ± 1°C The reacting mixtures were allowed to go to completion when the absorbance had attained zero values for a period of 36 hours. The point of inflection on the graph of absorbance versus concentration was used to calculate the mole ratio of the reaction.

2.3. Kinetic Measurements

All kinetic experiments were performed under pseudo-first order conditions with NO_2^- concentration at least 13 folds greater than that of the TZ^+. Pseudo-first order plots of log (A_t - A_∞) versus time t were made (where A_t and A_∞ are the absorbance at time, t and at the end of the reaction respectively). The pseudo-first order rate constant (k_1) were calculated from the slope of the graph. The second order rate constant (k_2) were obtained from k_1 as k_1/[NO_2^-]. The reaction rate was monitored on a Corning Colorimeter Model 252 at 28.0 ± 1°C, $[H^+] = 1 \times 10^{4}$ mol/dm^3 and I = 1.0 mol/dm^3 (NaCl). The results are represented in Table 1.

2.4. Acid Dependence Studies

Acid dependence rate constant was investigated in the range of 0.5 -3.5 × 10^{-4} mol/dm^3 hydrochloric acid, $[TZ^+] = 1.0 \times 10^{-5}$ mol/dm^3, $[NO_2^-] = 2.3 \times 10^{-4}$ mol/dm^3 and T = 28.0 ± 1.0 °C and I =1.0 mol/dm^3 (NaCl) while the concentration of all other parameters were kept constant. Graph of k_2 versus $[H^+]$ was plotted.

2.5. Effect of Ionic Strength

Ionic strength effect on reaction rate was studied in the range of (0.4 – 1.6) mol/dm^{-3} NaCl by keeping the concentration of all other parameters constant at $[H^+] = 1 \times 10^{-4}$ mol/dm^3, $[TZ^+] = 1.0 \times 10^{-5}$ mol/dm^3, $[NO_2^-] = 2.3 \times 10^{-4}$ mol/dm^3 and T = 28.0 ± 1.0 °C. Graph of log k_2 versus √½ was plotted (Figure 4).

2.6. Effect of Cation and Anion

The effect of cation and anion were studied as X = 1.4 × 10^{-4} – 2.4 × 10^{-4} mol/dm^3 (X = Li^+ and CO_3^{2-}) and the concentrations of other reactants were kept constant at $[H^+] = 1 \times 10^{-4}$ mol/dm^3, $[TZ^+] = 1.0 \times 10^{-5}$ mol/dm^3 , $[NO_2^-] = 2.3 \times 10^{-4}$ mol/dm^3 , T = 28.0 ± 1.0 °C. and ionic strength of 1.0 mol dm^3 (NaCl, Table 2).

2.7. Polymerization Studies

Acrylamide solution (2 ml) was added to the reacting mixture containing all the reactants in excess methanol. Acrylamide solution was also added to each of the reactants separately.

2.8. Intermediate Complex Formation

The electronic spectra of the reaction mixtures and that of tartrazine alone were compared within a range of 400 – 650 nm. Michaelis-Mentens plot of 1/k_1 versus 1/[NO_2^-] was achieved (Figure 5).

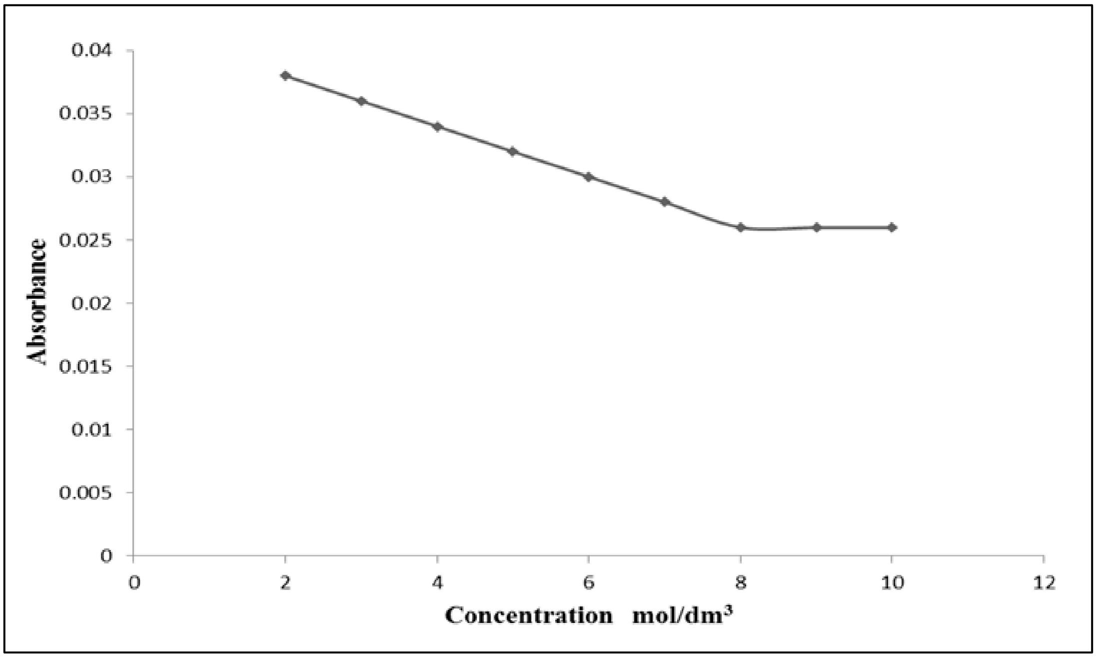
3. Results and Discussion

3.1. Stoichiometry

Stoichiometric study indicated 1: 2 mole ratios for TZ^+: NO_2^- (Figure 1). The overall rate equation is given as:

$$TZ^+ + 2NO_2^- + H^+ \longrightarrow \text{Product} \qquad (1)$$

Figure-1. Stoichiometry Plot for the reduction of TZ^+ by NO_2^- at $[TZ^+] = 1.0 \times 10^{-4}$ mol/dm^3, $[NO_2^-] = 1.0 \times 10^{-4}$ mol/dm^3 $[H^+] = 1.0 \times 10^{-4}$ mol/dm^3, I = 1.0 mol/dm^3, λ_{max} = 560 nm and T= 28 ± 1 °C



3.2. Kinetics

The pseudo-first order plot of log (A_t - A_∞) versus time (s) for this reaction was linear to about 90% of the reaction. The linearity of this plot indicates that the reaction is first order with respect to [TZ^+]. A plot of log k_1 vs. log [NO_2^-] was also linear with a slope of 0.99 (Figure 2) showing that the reaction is also first order with respect to [NO_2^-]. This is also buttressed by the constancy of k_2 values (Table 1). Thus, the reaction is second order at constant [H^+] and the rate equation for the reaction is:

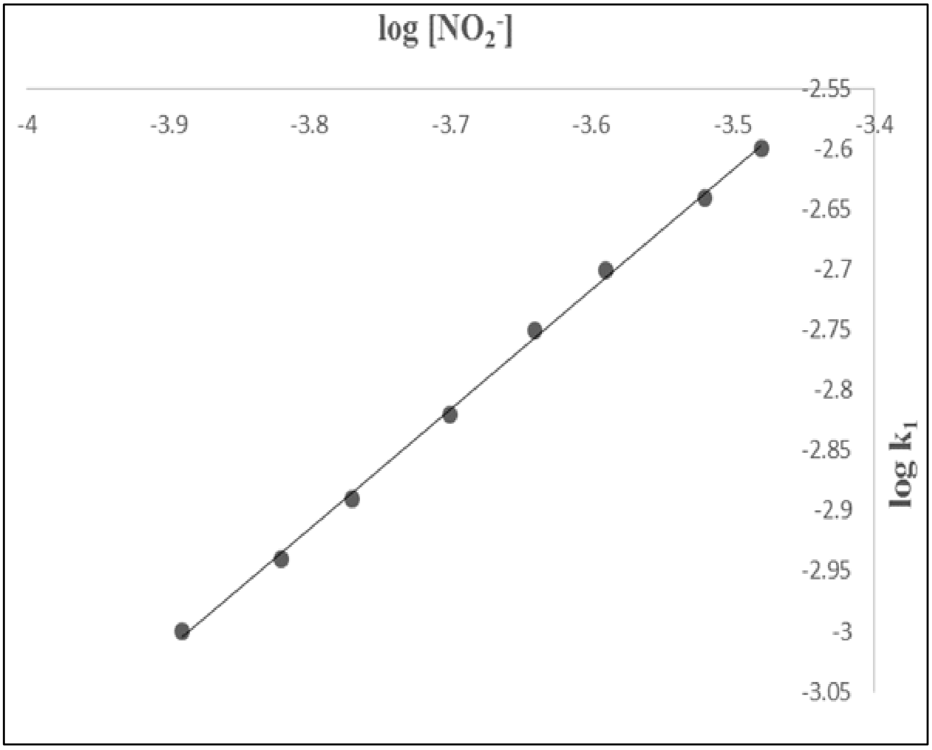
$$\frac{-d}{dt}[TZ^+] = k_2[TZ^+][NO_2^-] \qquad (2)$$

The order of one each for TZ^+ and NO_2^- concentration in the reaction conforms to results already reported by other authors regarding kinetic reactions involving nitrite ions and other oxidants [7-9].

Table-1. Pseudo-first Order Rate Constant and Second Order Rate Constant for the reduction of TZ^+ by NO_2^-. [TZ^+] = 1×10^{-5} mol dm^{-3}, [H^+] = 1× 10^{-4} mol dm^{-3}, I = 1.0 mol dm^{-3} (NaCl), T at 28 ±1°C, and λ_{max} = 560 nm

10^4[NO_2^-] mol/dm^3	10^4[H^+] mol/dm^3	I = 1.0 mol/dm^3	10^3 k_1 s^{-1}	k_2 dm^3 mol^{-1} s^{-1}
1.3	1.0	1.0	0.90	6.92
1.5	1.0	1.0	1.04	6.93
1.7	1.0	1.0	1.18	6.94
2.0	1.0	1.0	1.39	6.95
2.3	1.0	1.0	1.60	6.96
2.6	1.0	1.0	1.81	6.96
3.0	1.0	1.0	2.09	6.97
3.3	1.0	1.0	2.29	6.94
2.3	0.5	1.0	0.77	3.35
2.3	1.0	1.0	1.60	6.96
2.3	1.5	1.0	2.45	10.65
2.3	2.0	1.0	3.09	13.43
2.3	2.5	1.0	4.00	17.39
2.3	3.0	1.0	4.58	19.91
2.3	3.5	1.0	5.40	23.48
2.3	1.0	0.4	0.24	1.04
2.3	1.0	0.6	0.85	3.70
2.3	1.0	0.8	1.25	5.43
2.3	1.0	1.0	1.60	6.96
2.3	1.0	1.2	1.69	7.35
2.3	1.0	1.4	2.37	10.30
2.3	1.0	1.6	2.73	11.87

Figure-2. Plot of log k_2 versus [NO_2^-] for the Reduction of TZ^+ by NO_2^- at [TZ^+] = 1.0 ×10^{-5} mol/dm^3, [NO_2^-] = (1.3 – 3.3) ×10^{-4} mol/dm^3, [H^+] = 1.0 ×10^{-4} mol/dm^3, I = 1.0 mol/dm^3, λ_{max} = 560 nm and T= 28 ± 1 °C



3.3. Effect of Acid

From the result in Table 1, the rate constants of the reaction were found to increase with increase in $[H^+]$. The plot of k_2 versus $[H^+]$ was linear with no intercept (Figure 3). The nature of the rate constant is given as:

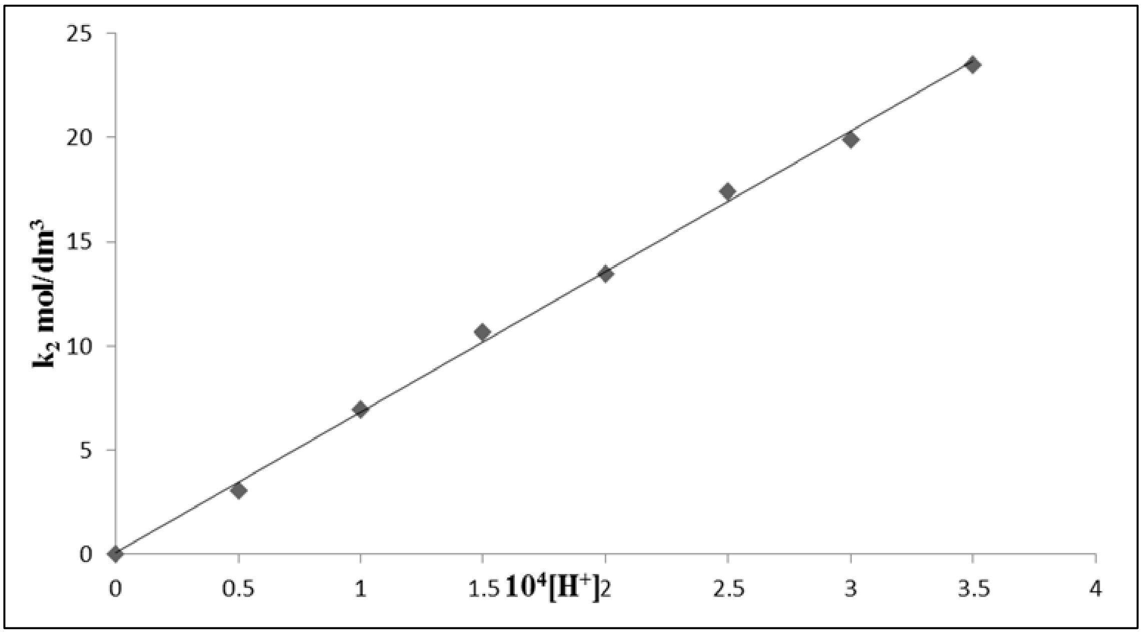
$$k_2 = a[H^+] \quad a = 6.7347\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{3}$$

Substituting equation (3) in equation (2), the rate of reaction becomes:

$$\frac{-d}{dt}[TZ^+] = a\,[H^+][TZ^+][NO_2^-] \tag{4}$$

The nature of $[H^+]$ dependence observed implies that there is a rapid equilibrium between protonated and unprotonated forms of the NO_2^- prior to the rate determining step and that only the protonated form is reactive Gupta [10]. Similar acid dependent has been reported by Babatunde [11] for reaction between parafuchsin and nitrite ion; also Chaudhuri, *et al.* [12] for the reduction of dioxomanganese complex by NO_2^- and by Iyun and Onu [13] for the reaction of rosaniline monchloride by nitrite ions in aqueous acidic media.

Figure-3. Plot of k_2 versus $[H^+]$ for the Reduction of TZ^+ by NO_2^- at $[TZ^+]$ = 1.0 ×10^{-5} mol/dm^3, $[NO_2^-]$ = 2.3 ×10^{-4} mol/dm^3, I = 1.0 mol/dm^3, λ_{max} = 560 nm and T= 28 ± 1 °C



3.4. Ionic Strength Effect

Ionic strength effect indicated that the rate of reaction increased with increase in the concentration of NaCl (Table 1). This conforms to a positive BrØnsted - Debye salt effect, implying that the activated complex is formed from either ions of like charges [14] or from charged or neutral reactants. A slope of 0.27 was obtained from the plot of k_1 against $\sqrt{}^{½}$ (Figure 4). Some other interactions may be taking place to describe the non-integral value for the products of the species at the transition state [15].

3.5. Effect of Added Ions

The rate of the reaction was observed to increase with increase in added Li^+ and CO_3^{2-}. Similar cation and anion catalysis has been reported by Umoru and Aliyu [16] for the reaction and mechanism of tartrazine and molybdate ion in hydrochloric acid.

3.6. Polymerization Studies

Added acrylamide solution to the reacting mixture and excess of methanol did not produce gelatinous precipitate. This indicates that the involvement of free radicals in the reaction is unlikely.

3.7. Intermediate Complex Formation

There was no shift of maximum absorbance from 560 nm for tartrazine. Plots of $1/k_1$ vs $1/[NO_2^-]$ gave a straight line which passed through the origin. (Fig.5), this further suggests the absence of formation of intermediate complex.

Figure-4. Plot of k_1 versus $\sqrt{½}$ for the Reduction of TZ^+ by NO_2^- at $[TZ^+]$ = 1.0 ×10^{-5} mol/dm^3, $[NO_2^-]$ = 2.3 ×10^{-4} mol/dm^3, $[H^+]$ = 1.0 ×10^{-4} mol/dm^3, I = 1.0 mol/dm^3, λ_{max} = 560 nm and T= 28 ± 1 °C

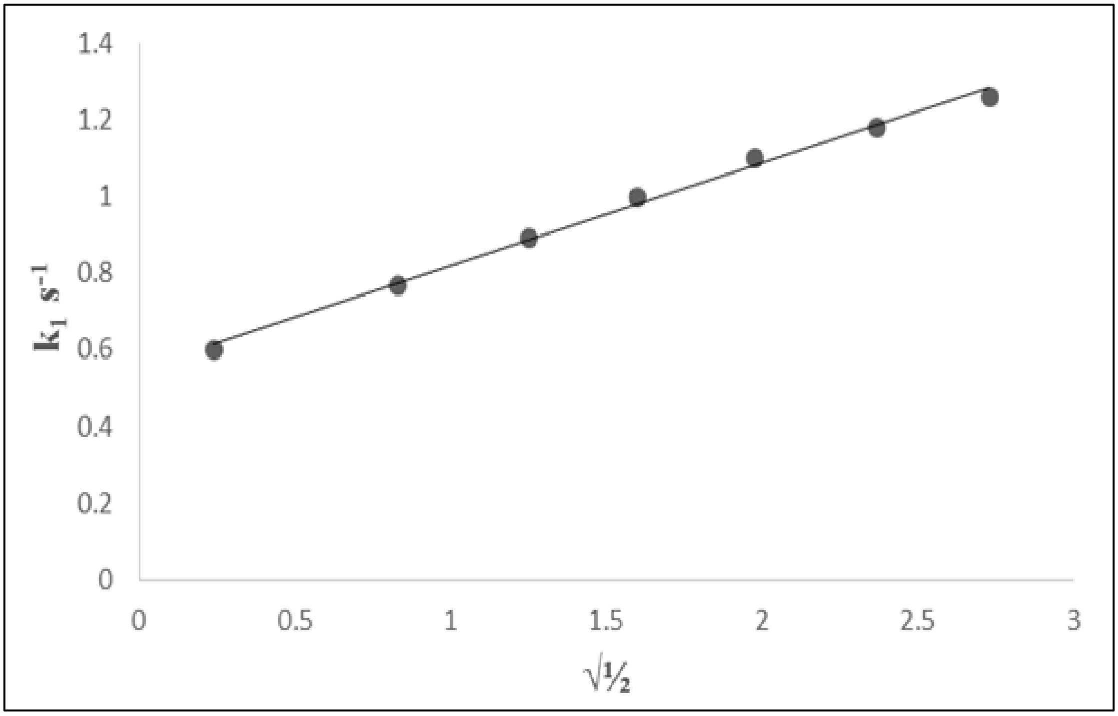


Figure-5. Plot of $1/k_1$ versus 1/[NO_2^-] for the Reduction of TZ^+ by NO_2^- at $[TZ^+]$ = 1.0 ×10^{-5} mol/dm^3, $[NO_2^-]$ = 1.3 – 3.3 ×10^{-4} mol/dm^3, $[H^+]$ = 1.0 × 10^{-4} mol/dm^3, I = 1.0 mol/dm^3 , λ_{max} = 560 nm and T= 28 ± 1 °C

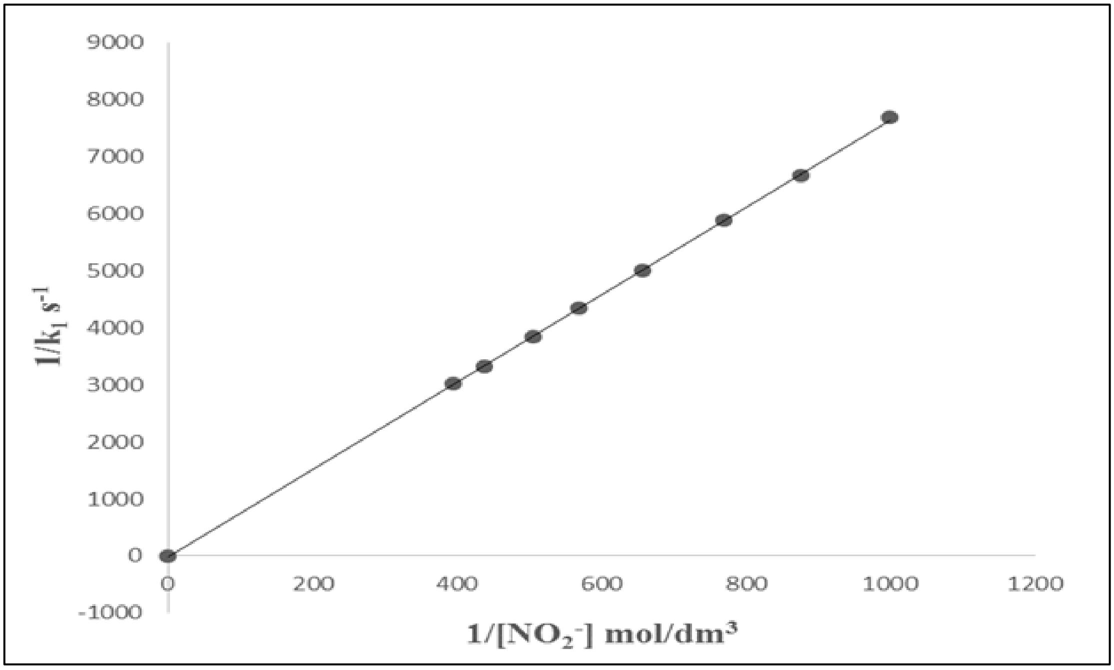


Table-2. Effect of Added Ions on the Second Order Rate Constants for Tartrazine and Nitrite Ion Reaction. [TZ^+] = 1 × 10^{-5} mol/dm^3, I = 1.0 mol/dm^3 (NaCl), [NO_2^-] = 2.3 × 10^{-4} mol/dm^3, T = 28 ± 1°C λ_{max} = 560 nm

X	10^4 [X] mol/dm^3	10^3 k_1 s^{-1}	k_2 dm^3 mol^{-1} s^{-1}
Li^+	1.4	1.01	4.39
	1.6	1.12	4.87
	1.8	1.29	5.61
	2.0	1.37	5.96
	2.2	1.57	6.83
	2.4	1.73	7.52
CO_3^{2-}	1.4	0.98	4.26
	1.6	1.13	4.91
	1.8	1.19	5.17
	2.0	1.31	5.69
	2.2	1.51	6.57
	2.4	1.63	7.09

4. Conclusion

The stoichiometry of the reaction displayed 1:2 mole ratio for tartrazine and nitrite ion. The redox reaction was first order with respect to $[TZ^+]$ and first order with respect to $[NO_2^-]$. A second order rate constant was observed for the reaction. The rate also shows first order dependence on acid ion concentration. This is an indication that in acidic environment, tartrazine and nitrite ions reacts effectively as such has no negative effects when ingested into the human stomach. The rate of reaction increased with increase in ionic strength. There was no positive polymerization in the reaction. The investigation of spectroscopic and Michaelis- Mentens plot studies did not indicate complex formation. An outer-sphere mechanism is proposed for the reaction.

5. Mechanism

Based on the evidences observed so far for the reactions between tartrazine and nitrite ion, an outer sphere mechanism has been proposed and the mechanism proposed below explains the experimental results:

$$NO_2^- + H^+ \overset{K_1}{\rightleftharpoons} \text{HONO} \tag{5}$$

$$\text{HONO} + H^+ \overset{k_1}{\rightleftharpoons} H_2ONO^+ \overset{k_2}{\rightleftharpoons} H_2O + :\overset{+}{N} = O \tag{6}$$

$$\overset{+}{TZ}^{+} + :N = O \overset{k_3}{\rightleftharpoons} [TZ//NO]^{2+} \tag{7}$$

$$[TZ//NO]^{2+} + NO_2^- \xrightarrow{k_4} [TZN]^{2+} + NO_3^- \tag{8}$$

$$\text{Rate} = k_4 [TZ//NO]^{2+} + NO_2^- \tag{9}$$

From equation 7

$$\frac{-d}{dt}[TZ//NO]^{2+} = k_3[TZ^+][:\overset{+}{N} = O] \tag{10}$$

Putting equation 10 in 9

$$\text{Rate} = k_4 k_3 [NO_2^-][TZ^+][:\overset{+}{N} = O] \tag{11}$$

From equation 5 & 6

$$[:\overset{+}{N} = O] = k_1 K_1 [NO_2^-][H^+] \tag{12}$$

Substituting equation 12 in 11

$$\text{Rate} = k_4 k_3 k_1 K_1 [H^+][NO_2^-][NO_2^-][TZ^+] \tag{13}$$

Therefore:

$$\text{Rate} = k[H^+][NO_2^-][NO_2^-][TZ^+] \tag{14}$$

Equation 14 conforms to the observed rate law in equation (4) where
$k = k_4 k_3 k_1 K_1 = a$

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