

Kinetics of Reduction of Maxilon Blue-SG by Sulfide Ion: Kinetic Salt Effect in Elucidation of Reaction Mechanism

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Abstract:The reaction between Maxilon blue (MB^+) and the sulfide ion is an ideal kinetic experiment in order to show the dependence of the reaction rate on the concentrations of reactants, ionic strength and temperature. By using excess concentrations of sulfide, the reaction or the disappearance of MB^+ was monitored spectrophotometrically and kinetically at 654 nm by measuring the decrease in absorbance of MB^+ . The indicator reaction follows pseudo-first-order kinetics. Specifically, the reduction of MB^+ with S^{2-} ion in the presence of Se(IV) in an phosphate buffer medium, pH=6.5 was studied. The rate law for this system was found to be $rate_i = k_{cat}[MB^+][S^{2-}]^3[Se(IV)] + k_{uncat}[MB^+][S^{2-}]^3$ with values of $k_{cat}=0.150 s^{-1}$ and $k_{uncat}=0.122 s^{-1}$ with an ionic strength of 0.05M KNO_3 . The values of activation energies for the Se(IV)-catalysed and uncatalysed reactions were found to be 18.43 And 18.70 kcal.mol⁻¹, respectively. The experiments with varying ionic strength demonstrate how kinetic salt effect can be used to predict the nature of charged species involved in the rate-determining step in the absence and presence of Se(IV). On the basis of the reaction orders and kinetic salt effect, the reaction mechanism is suggested with and without catalyst.

Keywords: Maxilon blue-SG, initial rate method, catalysed-reaction, spectrophotometry.

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1. Introduction

Maxilon blue-SG is a cationic oxazine derivative dyestuff which can be dissolved in water. It is easily reduced to the colorless hydrogenated molecule by a variety of reductive reagents. An ideal chemical system for study of reaction kinetics

should be easy to handle, simple in procedure, and suitable to probe into the details involving the reaction mechanism. In these respects, the reduction reaction of Maxilon Blue (MB⁺) with sulfide ion is ideal and informative for researchers to identify the species present in the rate-limiting step.

The appearance of the dyestuff during the reaction gives a qualitative view point about reaction rate and thus reaction kinetics can be followed with relative ease. The reaction is slow enough to allow thermostating of reaction mixtures during the kinetic measurements and fast enough to carry out a kinetic run in about 15 min. The primary kinetic salt effect exhibited by the reaction can be used to understand the nature of the reacting species that forms activated complex [1-3].

1.1 Theory

In aqueous solutions, ionic strength plays an important role on the reaction rate. It can be studied by varying the concentration of an inert electrolyte. The rate limiting step is the formation of the intermediate. The intermediate is assumed to be in equilibrium with the ionic reactants:



Any change in the ionic strength of the reaction mixture shifts the direction of the equilibrium in equation (1) depending on the charge of the intermediate. Reacting ions of the same sign will give rise to a highly charged, and highly solvated products, TS*. The process of solvation is accompanied with a large decrease in entropy and an increase in the rate of formation of the transition state.

The Bronsted equation for dilute aqueous solutions at 25°C is given as,

$$\log k/k_0 = 1.02z_1z_2\mu^{1/2} \quad (2)$$

$$\log k = \log k_0 + 1.02 z_1z_2\mu^{1/2} \quad (3)$$

The term k is the rate constant in salt solution and k₀ is the rate constant in water, C_i and z_i are the concentration and charge of the ith ion respectively. The ionic strength, μ of the solution is defined as,

$$\mu = 1/2\sum_i C_i z_i^2 \quad (4)$$

A plot of log k versus μ^{1/2} is a linear curve. Bronsted relation predicts that the rate constant increases with increasing ionic strength if the reacting ions have the same charge.

The rate constant decreases with increasing ionic strength if the reacting ions are oppositely charged. This behaviour is known as the primary salt effect [4].

2. Experimental

2.1 Reagents

Double distilled water and analytical reagent grade chemicals were used throughout the experiments.

A solution of 6.95×10^{-5} M Maxilon Blue-SG (MB^+) was prepared by dissolving 0.0250 g MB^+ (Sigma) in water and diluting to 100 mL in a 100 mL volumetric flask.

Standard sodium selenite solution, 500 mg.L^{-1} was prepared by dissolving 0.5102 g dry Na_2SeO_3 (Sigma) in water and diluting to 1 L in a volumetric flask. This solution was standardized iodometrically. Working solutions were prepared by diluting the stock solution in the suitable proportions with water.

Stock sodium sulfide solution (0.100 M) was prepared by dissolving 2.4020 g $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (Merck) in water and diluting to 100 mL in a volumetric flask. This solution must be prepared daily and standardized iodometrically if required. Working solutions were again prepared by diluting in suitable proportions with water.

Buffer solution (0.5M, pH=6.5) was prepared by dissolving 1.4530 g $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ and 6.5275 g $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (Merck) in water and diluting to 100 mL in a volumetric flask.

Potassium nitrate solution, 3.0 M was prepared by dissolving the appropriate amount of potassium nitrate (Merck) in a 100 mL volumetric flask and diluting to the mark with water.

All glassware were cleaned with detergent solution, rinsed with tap water, soaked in dilute HNO_3 solution (%2(v/v)), rinsed with water and dried.

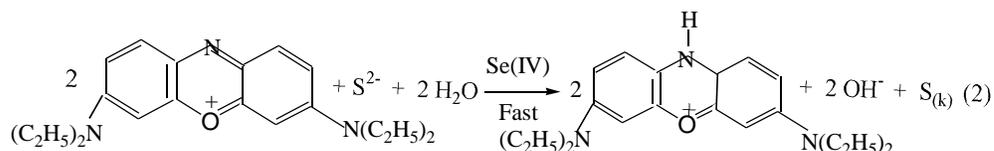
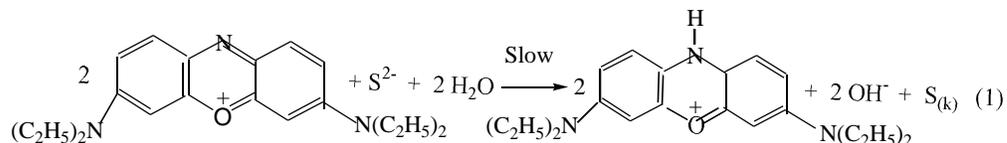
2.2 Apparatus

In this study, A Shimadzu Model UV-Visible 1601PC Spectrophotometer equipped with 1.0 cm quartz cell was used. This spectrophotometer has a 2 nm band width in 190-1100 nm wavelength range and ± 0.2 nm wavelength accuracy. TCC-140A temperature controlled cell holder was attached to this instrument for absorbance measurements. A Grant LTG-6G Model Thermostat bath (operating in -20 and 100°C

temperature range) was used to control the reaction temperature with $\pm 0.1^\circ\text{C}$ accuracy. A stopwatch was also used for recording the reaction time if necessary.

2.3 Experimental Procedure

Maxilon Blue-SG is reduced in a slow rate with sulfide ion at 25°C . The catalysed- and uncatalysed reactions between Maxilon blue and sulfide ion is described in the presence of trace amounts of selenium in form Se(IV) as follows:



Initially, the spectrum of the reaction mixture containing 2.0 mL 0.5M, pH=6.5 phosphate buffer, 0.5 mL %0.01(w/v) MB^+ and 0.5 mL 0.1M $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and 7.0 mL of water was scanned repetitively at 2 min intervals. Kinetic runs were pursued by measuring absorbance of a mixture of thermostated solutions as a function of time at regular 10 or 15 s intervals up to 15 min. Under the pseudo-first order conditions (in the presence of excess sulfide and low $[\text{MB}^+]$), rate constants for the catalysed- and uncatalysed reaction was directly calculated from the slope of the experimental absorbance versus time curve (by taking into consideration the slope of the linear part of initial rate curve, that is absorbance-time curve; that is $dA/dt = k_{\text{uncat}}$ or k_{cat} under the initial rate condition).

2.3.1 Kinetic Measurements

Initially, the spectrum of the reaction mixture without catalyst was scanned repetitively at 2 min intervals. The repetitive scanning is necessary to determine the absorption maximum to assess the approximate speed of the reaction, and to detect the peak shifts, if there is.

MB⁺ has an absorbance peak at wavelength of 654 nm (λ_{\max}) with molar absorptivity $\epsilon=4.01 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ (in a concentration range of 1.94×10^{-5} - $5.56 \times 10^{-6} \text{ M MB}^+$).

Kinetic runs were pursued by measuring absorbance of the catalysed- and uncatalysed-reaction systems at thermostatic conditions as a function of time at regular intervals (10- or 15-s) up to 15 min. Under the initial rate conditions the rate constants of both the catalysed- and uncatalysed-reaction rates were directly determined from the gradient of the plot ($\tan\theta=dA/dt$).

The requisite ionic strength of the medium is maintained by adding appropriate volumes of 3.0M KNO₃ solution. The indicator reaction is initiated by adding sulfide solution.

2.3.2 Data Analysis

According to the Lambert-Beer law (3), the absorbance (A) of a dilute solution is proportional to its concentration, C and path length, l:

$$A = \epsilon_{\max} \cdot C \cdot l \quad (3)$$

Under the studying conditions, the MB⁺ concentrations obey the Lambert-Beer law. In the presence of excess sulfide and low [MB⁺], the reaction is first order with respect to MB⁺ (pseudo-first order indeed). For a pseudo-first order reaction, log A-t or log [MB⁺]-t should be linear with a slope of $-k'/2.303$ (equation 4). Here k' is a pseudo-first order rate constant. Thus, rate constants can be calculated from the slope of the plot.

$$\log A = (-k'/2.303) \cdot t + C \quad (4)$$

Under the pseudo-first order conditions, a linear plot of log A or log ΔA versus time indicates the first-order dependence of rate on MB⁺ and the slope of the log [S²⁻] versus log k' plot will be equal to the order of reaction with respect to sulfide ion [4].

2.3.4 Kinetic Parameters

In the presence of excess sulfide and low indicator concentration, reaction is first order with respect to MB⁺ ($\Delta A_0=k_{\text{uncat}}' \cdot [\text{MB}^+] \cdot t$ or $\Delta A_C=k_{\text{cat}}' \cdot [\text{Se(IV)}] \cdot t$). For the pseudo-first order reaction, the slope of linear curve in linear concentration range gives the reaction rate constant ($\Delta A/\Delta t =k_{\text{cat}}$ or k_{uncat}).

Under the pseudo-first order conditions, linear graph of the absorbance change against time (ΔA_0 or ΔA_C) will give the first-order dependence of rate on MB⁺ and slope of log[S²⁻] versus log k' will give the order of reaction with respect to sulfide ion. Rate

constants were obtained by using a mixture containing 2 mL 0.5M, pH=6.5 phosphate buffer, 0.5 mL %0.01 (w/v) Maxilon blue for the uncatalysed reaction and 2 mL 0.5M, pH=6.5 phosphate buffer, 0.5 mL %0.01(w/v) Maxilon blue, 0.5 mL 2.0 $\mu\text{g}\cdot\text{mL}^{-1}$ Se(IV) for the catalysed-reaction between 3.0×10^{-3} - 8.0×10^{-3} M S^{2-} concentration without salt effect. Average rate constants are shown for the uncatalysed- and catalysed reaction in Table.1.

Table.1 Pseudo-First Order Rate Constants of the Uncatalysed- and Catalysed Reactions for Different Sulfide Concentrations Without Salt Effect

[S ²⁻]/ mM	Uncatalysed reaction		Catalysed reaction	
	Initial absorbance	k _{uncat} /s ⁻¹	Initial absorbance	k _{cat} /s ⁻¹
3	0.6055	0.0129	0.6262	0.0178
4	0.5926	0.0285	0.6060	0.0391
5	0.5874	0.0568	0.5499	0.0578
6	0.5852	0.0990	0.5298	0.1039
7	0.5601	0.1346	0.5172	0.1498
8	0.5547	0.1844	0.5010	0.2084
	Average k _{uncat} =0.086		Average k _{cat} =0.096	

Similar rate constants were also obtained by using the same procedures and solutions but with a fixed ionic strength of 0.05M at 30.0±0.1°C. These rate constants are shown for the uncatalysed- and catalysed reaction in ionic strength environment of $\mu=0.05\text{M}$ in Table.2.

Table.2 Pseudo-First Order Rate Constants of the Uncatalysed- and Catalysed Reactions for Different Sulfide Concentrations with a Ionic Strength of $\mu=0.05\text{M}$

[S ²⁻]/ mM	Uncatalysed reaction		Catalysed reaction	
	Initial absorbance	k _{uncat} /s ⁻¹	Initial absorbance	k _{cat} /s ⁻¹
3	0.6034	0.0126	0.5728	0.0171
4	0.5973	0.0355	0.5586	0.0491
5	0.5613	0.0848	0.5457	0.0960
6	0.5427	0.1349	0.5124	0.1806
7	0.5253	0.2131	0.4950	0.2394
8	0.5145	0.2505	0.4462	0.3171
	Average k _{uncat} =0.122		Average k _{cat} =0.145	

A plot of $\ln [S^{2-}]$ versus $\ln k$ has given a linear curve that its slope gives the reaction order (b) with respect to sulfide and its intercept also gives the second-order rate constant ($\ln k'$). Under the initial rate conditions (that is, in the presence of excess sulfide concentration), the rate constants and the reaction orders of both the uncatalysed- and catalysed-reactions were determined from the plots of $\ln [S^{2-}]-\ln k'$.

By using regression analysis, the reaction orders with respect to sulfide and pseudo-second order rate constants were found to be $b=2.775$ and $k'=8.46 \times 10^{-6} \text{ s}^{-1}$ for the uncatalysed-reaction; $b'=2.495$ and $k''=2.83 \times 10^{-5} \text{ s}^{-1}$ for the catalysed-reaction without inert salt effect in Figure.1.

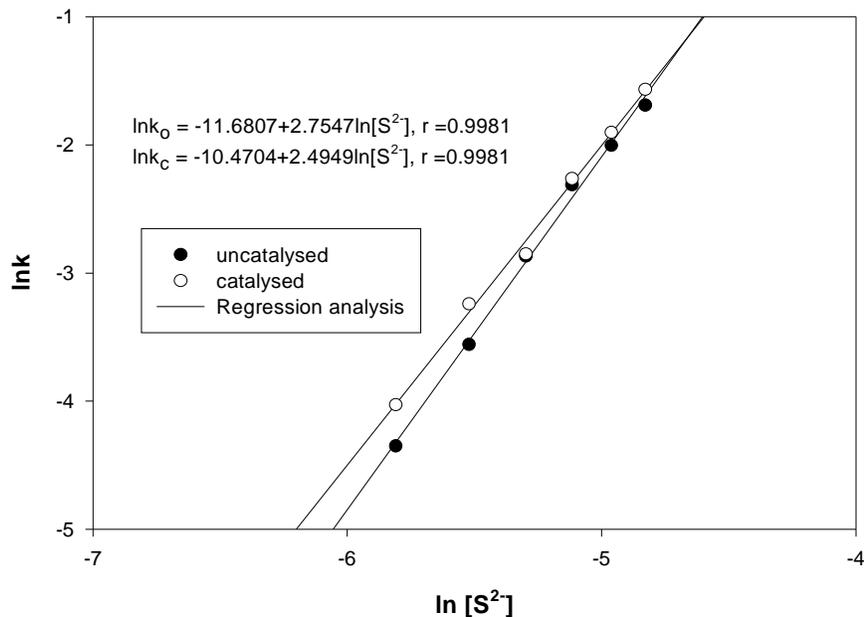


Figure.1 The Change of Rate Constants of the Uncatylsed- and Catalysed Reaction with Sulfide Concentration without Inert Salt Effect

Additionally, the reaction orders with respect to sulfide and pseudo-second order rate constants were also found to be $b=3.125$ and $k'=9.15 \times 10^{-7} \text{ s}^{-1}$ for the uncatylsed-reaction; $b'=2.997$ and $k''=1.42 \times 10^{-6} \text{ s}^{-1}$ for the catalysed-reaction in an ionic strength environment of $\mu=0.05\text{M}$ in Figure.2.

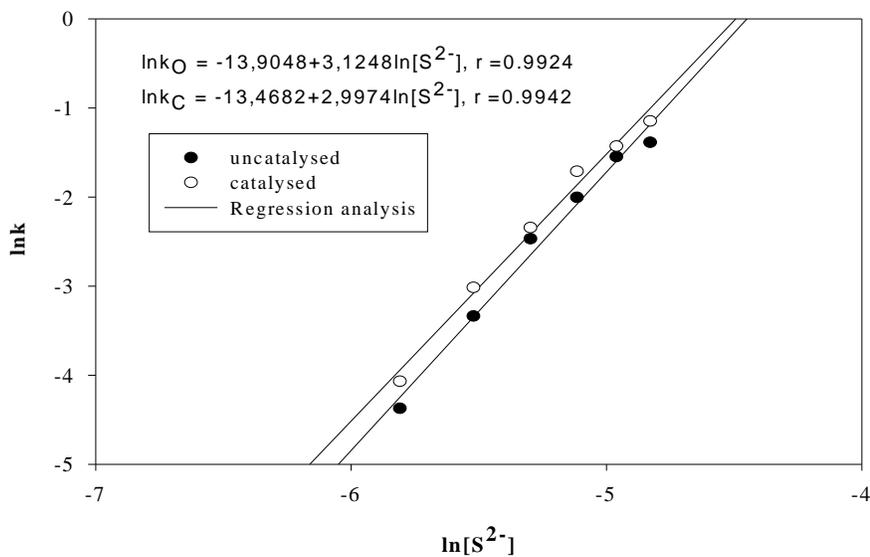


Figure.2 The Changes of Rate Constants for Uncatalysed- and Catalysed Reactions with Sulfide Concentration in an Ionic Strength Environment of 0.05M

The activation energies were determined by making the measurements in different temperatures between 5-30°C according to the method described below (in the initial rate condition, that is $\Delta A_0 = k_{\text{uncat}} \cdot [\text{MB}^+]$ or $\Delta A_C = k_{\text{cat}} \cdot [\text{MB}^+][\text{Se(IV)}]$) by the absorbance changes of the uncatalysed- and catalysed-reaction with time of the first 4.0 min are taken equivalence to rate constants.

The activation energies of the uncatalysed- and catalysed reaction were calculated from slope of plots of $\ln k - 1/T$ by taking into consideration Arrhenius equation, $k = A \cdot e^{-E_a/RT}$ or the natural logarithm of this equation, $\ln k = \ln A - E_a/RT$ in Figure.3.

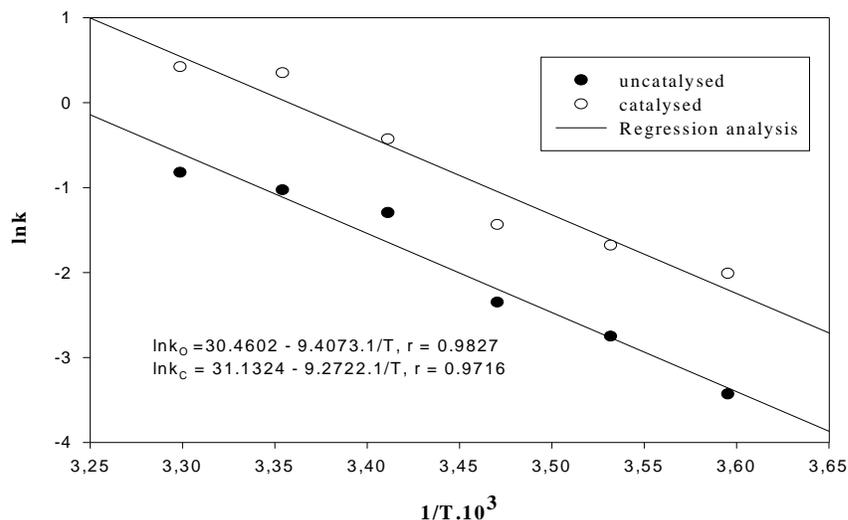


Figure.3 The Changes of Rate Constants for Uncatalysed- and Catalysed Reactions with Reverse of Temperature

Activation energies were found as $E_{a,\text{uncat}} = 18.70$ and $E_{a,\text{cat}} = 18.43 \text{ kcal.mol}^{-1}$ at fixed reactants and catalyst concentrations for the uncatalysed- and catalysed reactions respectively.

Also, collision numbers for the uncatalysed- and catalysed reactions were found from the intercept of $\ln k - 1/T$ plots ($\ln A$) as $A_{\text{uncat}} = 1.69 \times 10^{13}$ and $A_{\text{cat}} = 3.32 \times 10^{13}$ respectively.

2.3.5 Investigation of Kinetic Salt Effect

Ionic strength (μ) variation generally gives rise to two types of effects on chemical reaction rates which is known as primary and secondary salt effects.

Primary salt effect arises on the basis of the different types of reactants present in the rate-determining step. Reactions between two pair of ions of like charge are usually accelerated by increasing ionic strength because the highly charged activated complex favorably interacts with the denser ionic environment.

A reverse trend is observed in the case of reactions between two oppositely charged species. The rates of reactions between two uncharged molecules or between an ion and a molecule are usually only slightly affected by the addition of salts.

The secondary salt effect arises due to the presence of acid-base equilibrium prior to the rate-determining step (or the secondary salt effect states salt effect on the acid-base equilibrium prior to the rate-determining step). It is indirect the effect of this on the indicator reaction rate.

When primary and secondary salt effects are operative in the same direction, either significant acceleration or significant inhibition is observed. However, a negligible effect is observed if primary and secondary salt effects are operative in opposite directions.

The primary salt effect can be studied by varying initial concentrations of potassium nitrate at fixed concentrations of MB^+ , sulfide ion and the other experimental variables. Ionic strength can be varied between 0.01-0.05 M by adding appropriate volumes of KNO_3 solution. A plot of $\log k'$ versus $\mu^{1/2}$ is linear with a slope of $1.02z_Az_B$. The sign of the slope indicates whether the species present in the rate determining step have like or unlike charges, and the magnitude gives the product of charges on the species.

Under the optimum conditions, the change of absorbance with time ($A=f(t)$) was pursued by as a function of time at regular intervals (10- or 15-s) up to 10 min for the uncatalysed- and catalysed reaction mixtures.

The rate constants (from slope of the initial rate curves, $dA/dt=k_{\text{uncat}}$ or k_{cat}) were directly determined from linear absorbance-time region. This A-t curves were repeated three times and the averages of their slopes were taken into consideration for both the uncatalysed- and catalysed reaction systems.

It is known that the slopes of linear $\ln k'-\mu^{1/2}$ curves have been an equal to $1.02z_Az_B$ value for the uncatalysed- and catalysed reaction in Figure.4.

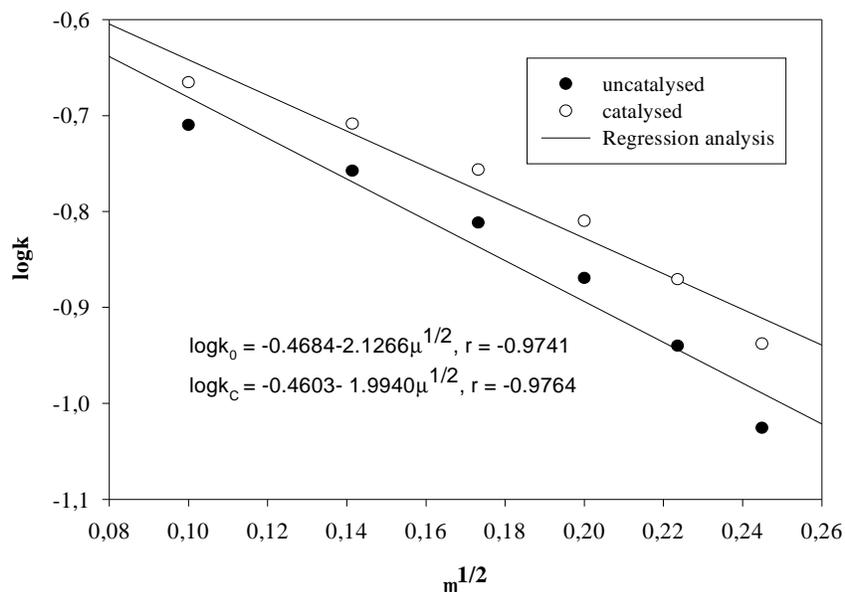


Figure.4 The Changes of Rate Constants for Uncatalysed- and Catalysed Reactions with Square Root of Ionic Strength of Environment

The sign of the slope indicates whether the species present in the rate-determining step have like or unlike charges, and the magnitude also gives the product of charges on the species.

Under the initial rate conditions, the product of charges on the species present in the rate-determining step were established from plots of $\log k'-\mu^{1/2}$ as $(z_A.z_B)_0=-2.127$ and $(z_A.z_B)_C=-1.994$ for the uncatalysed- and catalysed reaction systems, respectively. The approximately equal to the product of charges $(z_A.z_B)$ each other and a negative slope for the uncatalysed- and catalysed reaction indicate that negative salt effect (inhibitory effect) comes true. At the same time, a negative slope of a plot of $\log k'-\mu^{1/2}$ ($1.02z_Az_B$) shows that species involved in the rate-determining step have oppositely charges. The intercept of $\log k'-\mu^{1/2}$ linear curve also gives a limiting value of the rate constant in which ionic strength tends to zero.

The limiting-rate constants were determined as $k_0=0.340$ and $k_0'=0.346$ for the uncatalysed- and catalysed reaction system.

3. Results And Discussion

In this study, the primary salt effect on the indicator reaction was investigated to understand the nature of reactant species involved in the formation of activated complex in the rate-determining step.

In the presence of excess sulfide and low MB^+ , in each kinetic run the plot of $\log A-t$ or $\Delta A-t$ was linear for the first 4.0 min. The data were directly analyzed using the initial rate method. The pseudo-first order rate constants obtained by using this method are $k_{\text{uncat}}=0.122$ and $k_{\text{cat}}=0.150 \text{ s}^{-1}$; and $k_{\text{uncat}}=0.086$ and $k_{\text{cat}}=0.096 \text{ s}^{-1}$ with and without 0.05M KNO_3 for uncatalysed- and catalysed-reactions, respectively. Since ionic strength influences the reaction rate between charged species significantly, ionic strength (μ) was maintained constant during the variation of sulfide ion concentration.

The activation energies obtained by using $\ln k-1/T$ plots are $E_{a,\text{uncat}}=18.70$ and $E_{a,\text{cat}}=18.43 \text{ kcal.mol}^{-1}$ for the uncatalysed- and catalysed reactions respectively. Table.1 and 2 summarize the rate constants for different concentrations of sulfide ion with and without salt effect. The plot of $\log [S^{2-}]-\log k'$ was linear with a slope equal to 3.12 and 3.00, suggesting a third-order dependence with respect to sulfide for the uncatalysed- and catalysed reaction. The experimental third-order rate constants are $k'=9.15 \times 10^{-7}$ and $k''=1.42 \times 10^{-6} \text{ s}^{-1}$ respectively. The ionic strength was also studied between 0.01 and 0.05M at fixed concentrations of MB^+ and sulfide. Figure.4 illustrates a linear plot of $\log k'$ versus $\mu^{1/2}$ whose slope is approximately -2 for both the uncatalysed- and catalysed reaction. In addition, the limiting values of the rate constant in which ionic strength tends to zero were calculated from the $\log k'$ versus $\mu^{1/2}$ linear plots as $k_0=0.340$ and $k_0'=0.346$ for the uncatalysed- and catalysed reaction.

The observed negative salt effect, and a first-order and third-order dependence of the reaction rate on the reactants (with respect to MB^+ and sulfide ions respectively) suggests that the rate-determining step involves one molecular ion of MB^+ and three ion of S^{2-} . Thus, the rate-determining step of the reaction is a nucleophilic attack of sulfide (S^{2-}) or selenosulfide ($[SeS]^{2-}$) ion on MB^+ . The activated complex subsequently hydrolyses to HMB (or HMB^+) and elemental sulphur (and/or selenium a part from

elemental sulphur). During the reaction, MB^+ is reduced to colorless hydrogenated molecule form of Maxilon blue (HMB^+ or HMB) either through two one-electron reduction step or by a two-electron transfer step. Our experimental results are essentially in agreement with the mechanism originally proposed on the literature [5-9].

Thus, the $MB^+ - S^{2-}$ or $MB^+ - S^{2-} - Se(IV)$ reaction system can best explain the application of the kinetic salt effect in predicting the species present in the rate-determining step and in elucidating reaction mechanism:



Activated complex



Activated complex



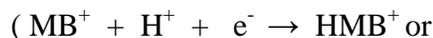
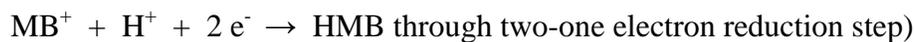
The rate equations can be written in the absence and presence of catalyst respectively as follows:

$$R_{\text{uncat}} = k_{\text{uncat}}[MB^+][S^{2-}]^3$$

$$R_{\text{cat}} = k_{\text{cat}}[MB^+][S^{2-}]^3[Se(IV)]$$

The rate law for the total reaction can also be rewritten as follows:

$$R_{\text{total}} = k_{\text{cat}}[MB^+][S^{2-}]^3[Se(IV)] + k_{\text{uncat}}[MB^+][S^{2-}]^3$$



Also, the results of this study indicate that $MB^+ - S^{2-}$ reaction system can successfully used for the determination of trace amounts of selenium (in form $Se(IV)$) by the catalytic-spectrophotometric method. In addition, the results of this study can also be used for the determination of selenium with a detection limit of $0.205 \text{ ngSe(IV)/mL}$ in a concentration range of $0.004-0.2 \mu\text{g.mL}^{-1}$ by kinetic spectrophotometric method.

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