# KINETICS OF THE REDUCTION OF ROSANILINE HYDROCHLORIDE WITH SULPHITE ION IN AQUEOUS PERCHLORIC ACID.

### J. F. IYUN and O. A. PETERS

## ABSTRACT

The kinetics of the reduction of rosaniline hydrochloride (RH) in perchloric acid has been investigated under pseudo-first order condition of an excess $[SO_3^{2-}]$ at ionic strength of 1.0 mol $dm^{-3}$ ($CH_3COONa$), T = 30 $\pm 0.1\,^\circ$ C and $\lambda_{max}$ = 540nm. The stoichiometry of the reaction was observed to be 1:1 in terms of mole ratio of RH and $SO_3^{2-}$ ions consumed. The rate of reaction increased with increase in ionic strength. The rate law is found to be of the form.

$$-\frac{d}{dt}[RH] = (\,a + b\,[H^+]^{-1}\,)\,[RH]$$

where a $=0.30 \times 10^{-2}$ mol $dm^{-3}$ $min^{-1}$ and b= $70.58 \times 10^{-2}$ mol $dm^{-3}$ $min^{-1}$ and a pH range of 1.0 $\leq [H^+] \leq$ 3.5 $\times 10^{-4}$ mol $dm^{-3}$. The results from kinetics studies and spectroscopy investigations did not implicate complex formation. A plausible mechanism is proposed for the reaction.
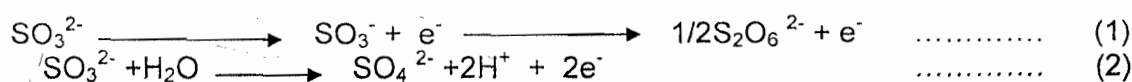
KEY WORDS:- Rosaniline hydrochloride, sulphite, kinetics and mechanism.

INTRODUCTION

The sulphite ion has been reported to be a powerful reductant ( Russel and Yost,1944,Davies et al 1969, Veprek-Siska et al 1966,Dennis et al 1963, Murray 1968, Haight et al 1965 ). The ion has been known to reduce metal ions and other oxidants by a variety of mechanism and with varying stoichiometry(Higginson and Marsall,1957)
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These reactions have from investigations proved that the stoichiometry and products of the reaction allow a distinction to be made between one and two equivalent oxidizing agent as shown by equations 1 and 2, the products being dithionate and sulphate ions respectively(Higginson and Marshall,1957,Davies et al 1969, Veprek-Siska et al 1966)

$$SO_3^{2-} \longrightarrow SO_3^- + e^- \longrightarrow 1/2S_2O_6^{2-} + e^- \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^- \quad \ldots\ldots\ldots\ldots \quad (2)$$

Rosaniline hydrochloride, (basic fuchsin or basic violet) is a biological stain and an important histochemical reagent used in plant and animals histology (Fig.1)(Lawal,1997)
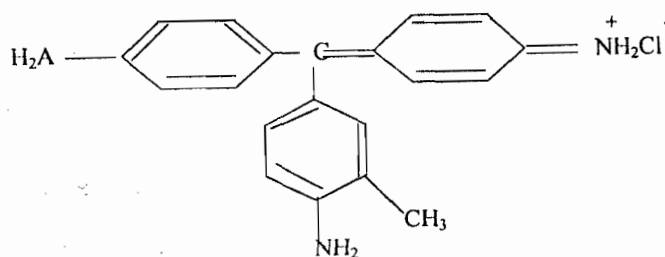


FIGURE 1: - Rosaniline Hydrochloride (Basic Fuchsin)

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When this dye is reduced with sulphite or sulphurous acid, a type of leuco- fuchsin is produced which is known as Schiff's reagent. This is often employed by chemists and biologists as indicator for detecting the presence of aldehydes(Conn,1961). In view of the importance of Schiff's reagent (fuchsin-sulphurous acid) in histochemistry, the redox reaction of this stain with sulphite ion has been investigated.

## EXPERIMENTAL

### Materials and reagents

Rosaniline hydrochloride (basic fuchsin) microscopic grade (BDH) was prepared and characterized as described (Culling,1963) Perchloric acid was employed to investigate the effect of hydrogen ions on the rate of the reaction while sodium ethanoate was employed as a buffer to maintain a constant ionic strength. Sodium sulphite and all other chemicals were used without further purification.

### Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. Solutions containing a known concentration of the dye and varying concentrations of $Na_2SO_3$ were reacted at $[H^+] = 2 \times 10^{-4}$ mol $dm^{-3}$ and ionic strength of 1.0 mol $dm^{-3}$ ($CH_3COONa$) and the absorbance were measured at $\lambda_{max}$540nm after reactions had gone to completion. The stoichiometry was evaluated from the plot of the absorbance versus different volumes of $Na_2SO_3$.

The determination of stoichiometry confirmed the overall reaction to be

$$RH + SO_3^{2-} + H_2O \longrightarrow Product + SO_4^{2-}$$
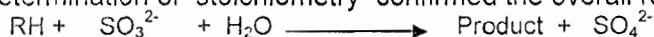
### Kinetic Studies

All kinetic runs were performed under pseudo-first order conditions with the concentration of sulphite ions at least 20 fold in excess of the dye concentration. The rate of reaction was monitored by following the rate of decrease in the absorbance of the dye at $\lambda_{max}$ 540nm on the colorimeter 252 Model.

Pseudo-first order rate constants were obtained from the slope of the plots of $\log(A_t-A_\infty)$ versus time where $A_t$ and $A_\infty$ are absorbances of the reaction mixture at a specific time and at the end of the reaction respectively. The temperature was kept constant at $30 \pm 0.1°C$ for all kinetic runs at $[H^+] = 2 \times 10^{-4}$ mol $dm^{-3}$ and ionic strength of 1.0 mol $dm^{-3}$.($CH_3COONa$) unless otherwise stated.
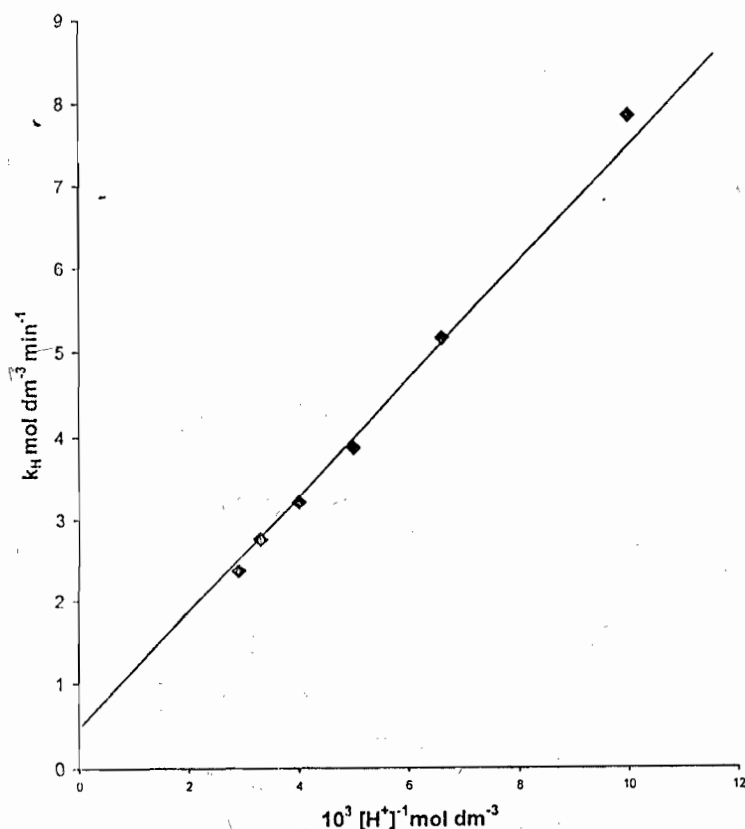


Fig 2:- Plot of $k_H$ vs $[H^+]^{-1}$ for the reaction of Rosaniline hydrochloride and sulphite ions.

## Acid Dependence Studies

The effect of acid on the rate of reaction was investigated by keeping all other conditions constant while varying the concentration of perchloric acid in the range $1.0 \leq [H^+] \leq 3.5 \times 10^{-4}$ mol dm$^{-3}$ at [RH] = 10$^{-6}$ mol dm$^{-3}$, [SO$_3^{2-}$] 50 x 10$^{-6}$ mol dm$^{-3}$, Ionic strength of I = 1.0 mol dm$^{-3}$ (CH$_3$COONa) and T= 30.0 $\pm$ 0.1°C. The results are presented in Table 1. Plot of $K_H$ Versus [H$^+$]$^{-1}$ was made (Fig.2)

## Effect of Ionic Strength

The effect of ionic strength on the rate of the reaction was studied over the range of $0.20 \leq I \leq 1.60$ mol dm$^{-3}$ (CH$_3$COONa) while the concentration of the other reactions were kept constant. The results are presented in Table 1. Plot of $k_o$ Vs $\sqrt{I}$ was made (fig1.3)
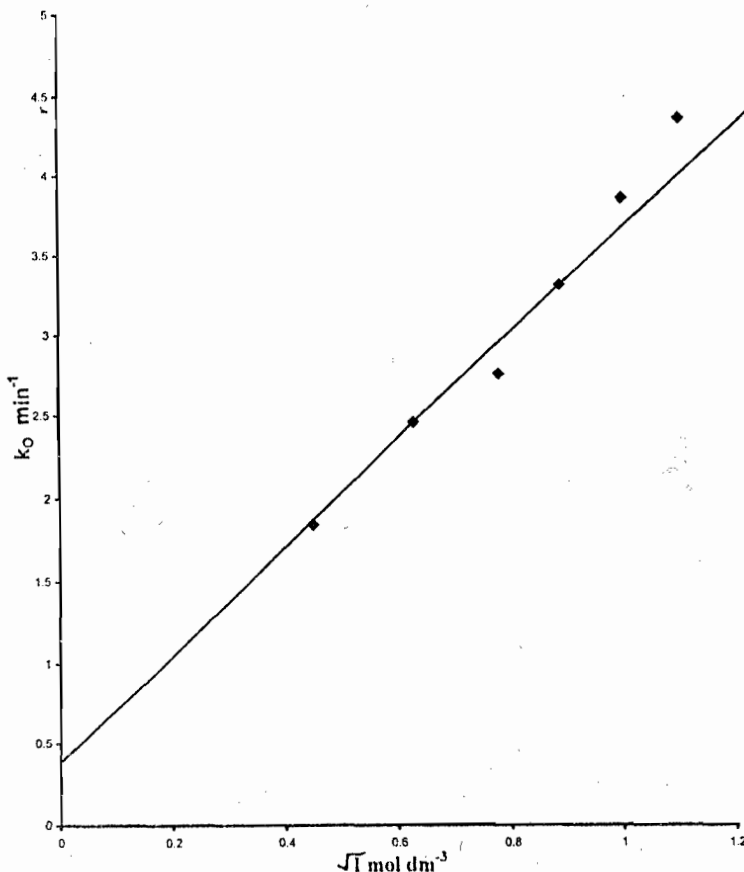


Fig 3:-Plot of $k_o$ against $\sqrt{I}$ for the reduction of rosaniline hydrochloride and sulphite ions.

## Test for Intermediate Complex Formation
The spectrum of the reaction mixture and that of the dye alone were compared within 400-600nm.

## Test for Free Radicals
Acrylamide was added to the partially oxidized reaction mixtures of the dye and SO$_3^{2-}$ion at [H$^+$] = 2 x 10$^{-4}$ mol dm$^{-3}$ and ionic strength of 1.0 mol dm$^{-3}$ (CH$_3$COONa) in a large excess of methanol and to each of the reactants separately.

## RESULTS AND DISCUSSION.

**Stoichiometry**: - The results of the spectrophotometric titration indicate a 1:1 stoichiometry. The overall reaction is given by equation (3)

$$RH \; + \; SO_3^{2-} \; + H_2O \longrightarrow Products \; + \; SO_4^{2-} \qquad \ldots\ldots\ldots\ldots \qquad (3)$$

This 1:1 stoichiometry is similar to those reported for the redox reaction of the dye with Chlorite(Iyun and Onu 1999)and Nitrite ions(Iyun and Onu 1998).

**Kinetic :-**The pseudo-first order plots for the reaction are linear for more than 95% of the extent of the reaction indicating that it is first order dependence on [RH].The observed pseudo-first order rate constant ($k_o$)evaluated from the slopes of pseudo –first order plots were constant irrespective of the concentration of the sulphite ions.(Table 1).Thus, over the range of $2.0 \, i^L \, [SO_3^{2-}] \, i^L 9.0 \times 10^{-5}$ mol dm$^{-3}$ at [H$^+$] = $2.0 \times 10^{-4}$ mol dm$^{-3}$(CH$_3$COONa), this suggests that the rate is zero order in [SO$_3^{2-}$]. The zero-order dependence observed in this study is not common in reactions of SO$_3^{2-}$ ions but non-linear dependence of the rate constants on [SO$_3^{2-}$] has been reported by Berglund and Elding 1995 therefore, the rate of the reaction can be written as

$$-\frac{d}{dt}[RH] \quad = \quad k_o[RH]$$

where $k_o = (3.78 \pm 0.03) \times 10^{-2}$min$^{-1}$.

**Effect of Acid:-**

Table 1 shows that the rate was inversely affected by [H$^+$].This pattern of acid dependence observed in this study is similar to those reported for oxy- anion reactions especially that of sulphite ions by Iyun and Lawal 1997). This inverse acid pathway, shows that there is a pre-equilibrium step before the rate determining step in which a proton is lost. Plot of $k_o$ versus [H$^+$]$^{-1}$ was linear with an intercept (Fig 2). The acid dependence rate constant can then be represented by equation 4.

$$k_o = a + b[H+]^{-1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Therefore the overall equation within the acid range investigated is given as

$$-\frac{d}{dt}[RH] \quad = \quad ( \, a + b[H^+]^{-1} \, )[RH]$$

Where a = $0.30 \times 10^{-2}$ min$^{-1}$ and b = $70.58 \times 10^{-2}$ min$^{-1}$

**Effect of Ionic Strength :-**

The rate constant is dependent on ionic strength as shown in Table 1 thus indicating a positive salt effect (Bronsted – 1922)

A plot of $k_o$ vs $\sqrt{I}$ gave a slope of 0.58 (Figure 3). The slope indicates that some other interactions must be taking place to account for this non-integral value for the product species at the transition state. And the reaction involves two like charges most probably negative charges. Addition of acrylamide to the partially oxidized reaction mixture of SO$_3^{2-}$ and the dye showed gel-formation on addition of excess methanol, indicating the presence of free radical.

Table 1
PSEUDO FIRST ORDER RATE CONSTANTS FOR THE REDUCTION OF ROSANILINE
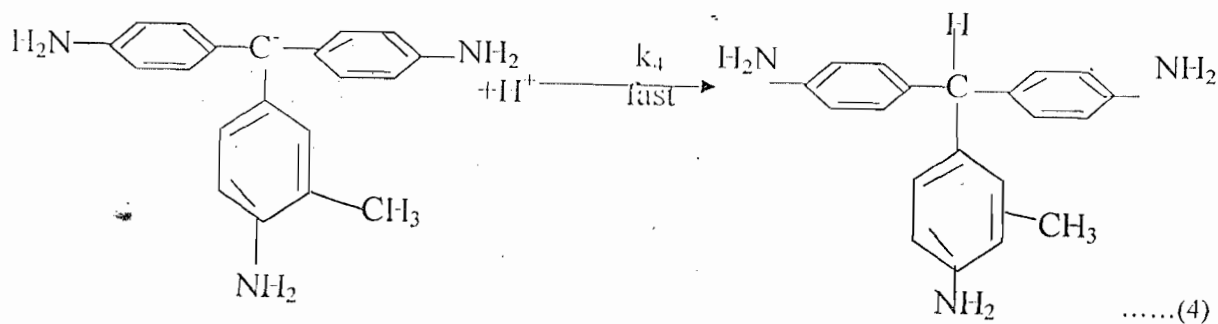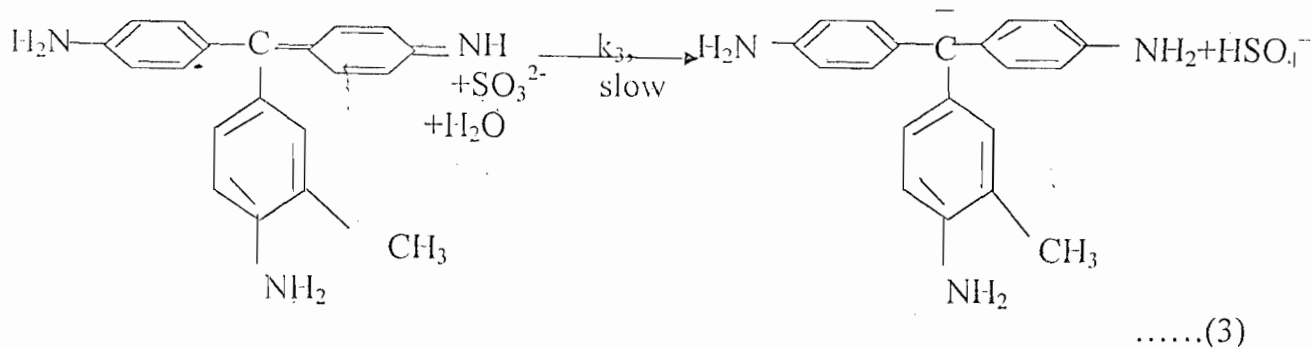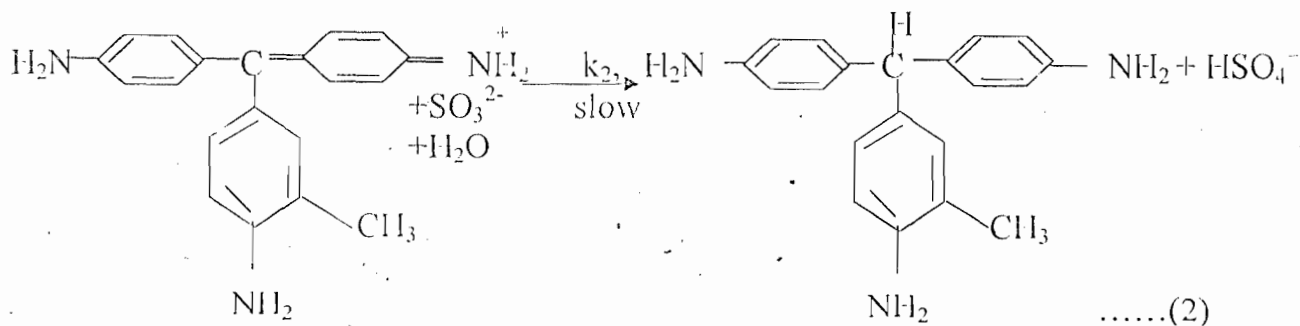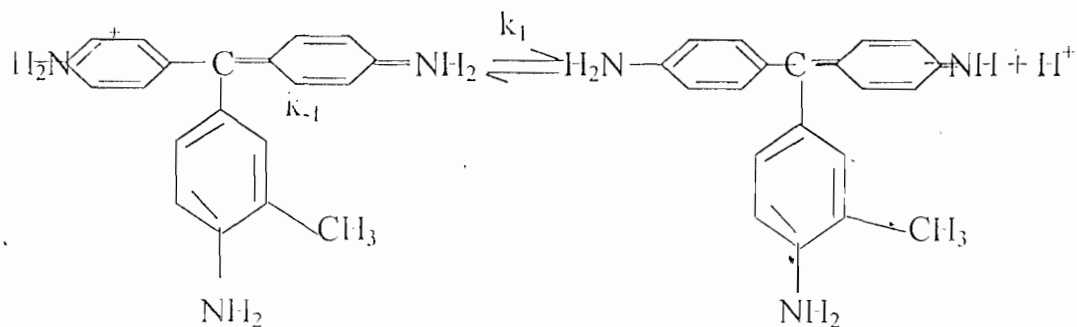HYDROCHLORIDE WITH SULPHITE IONS.

[RH] = $1 \times 10^{-6}$ mol dm$^{-3}$, T = 30 1°C, $\lambda$ max= 540 nm.

| $10^6$ [SO$_3^{2-}$], mol dm$^{-1}$ | $10^4$[H$^+$] mol dm$^{-1}$ | I(CH$_3$COONa), mol dm$^{-1}$ | $10^2$ $k_o$ min$^{-1}$ |
|---|---|---|---|
| 20 | 2 | 1.0 | 3.92 |
| 30 | 2 | 1.0 | 3.69 |
| 40 | 2 | 1.0 | 3.80 |
| 50 | 2 | 1.0 | 3.87 |
| 60 | 2 | 1.0 | 3.99 |
| 70 | 2 | 1.0 | 3.84 |
| 80 | 2 | 1.0 | 3.69 |
| 90 | 2 | 1.0 | 3.46 |
| 50 | 1.0 | 1.0 | 7.86 |
| 50 | 1.5 | 1.0 | 5.16 |
| 50 | 2.0 | 1.0 | 3.87 |
| 50 | 2.5 | 1.0 | 3.22 |
| 50 | 3.0 | 1.0 | 2.76 |
| 50 | 3.5 | 1.0 | 2.37 |
| 50 | 2 | 0.2 | 1.84 |
| 50 | 2 | 0.4 | 2.46 |
| 50 | 2 | 0.6 | 2.76 |
| 50 | 2 | 0.8 | 3.32 |
| 50 | 2 | 1.0 | 3.87 |
| 50 | 2 | 1.2 | 4.38 |

The presence of free radical is common feature of the dye reacting with any sulphurous compound.

Results from spectroscopic studies indicate no significant shift from the absorption maxima of $\lambda_{max}$ 540nm but a slight enhancement of absorbance that is very short lived.

The obtained rate constant is independent of $[SO_3^{-2}]$ therefore Michaelis-Menten's plot is not important and the enhancement of the absorbance may be due to formation of ion-pair.

## Reaction Mechanism.

Based on the evidence from the rate law and stoichiometry, the reaction of RH with $SO_3^{2-}$ is probably occurring as proposed below



i.e. $RH^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R + H^+$ .....(1)



.....(2)



.....(3)



.....(4)

$$2HSO_4^- \longrightarrow 2SO_4^{2-} + 2H^+ \qquad \dots\dots(5)$$

$$\text{Rate} = k_2[RH^+] + k_3[R] \qquad \dots\dots(6)$$

From equation 1

$$K = \frac{[R][H^+]}{[RH]} \qquad \dots\dots(7)$$

Therefore

$$[R] = \frac{K[RH^+]}{[H^+]} \qquad \dots\dots(8)$$

Substitute equation 8 in 6

$$\text{Rate} = k_2[RH^+] + \frac{k_3 K[RH^+]}{[H^+]}$$
$$= k_2[RH^+] + k_3 K[RH^+][H^+]^{-1}$$
$$= (k_2 + k_3 K[H^+]^{-1})[RH^+]$$

This equation is similar to the rate equation i.e

$$(a + b[H^+]^{-1})[RH^+]$$

Where $k_2 = a$ and $k_3 K = b$.

The proposed mechanism was determined considering (a) rate law which is independent on the $[SO_3^{2-}]$ ions (b.) the rate of the reaction is inversely dependent on the $[H^+]$. The rate equation is derived as discussed above. Absence of spectrophotometric evidence of intermediate complex formation suggests that a precursor complex is probably not formed prior to electron transfer step.

## CONCLUSION

The (1:1) stoichiometry has been proposed for the reaction
The reaction involve two independent pathways both directly dependent on acid and inversely dependent on acid, the evidence for intermediate formation was neither detected nor identified by the spectroscopic method.

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