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# KINETICS OF REACTION BETWEEN PHENOTHIAZINE DYE/METHYLENE GREEN AND PEROXYDISULPHATE ION IN PRESENCE OF BROMIDE ION

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**ABSTRACT:**

The rate of nuclear bromination was observed when the methylene green reacts with peroxydisulphate ion in presence of bromide ion. The reaction obeys zero order kinetics in the dye whereas first order kinetics in peroxodisulphate and bromide ion. The reaction was studied at various ionic strengths and temperatures to find out the effect of ionic strength on rate of nuclear bromination and energy of activation. The kinetics pertain to the rate determining stage of peroxydisulphate-bromide reaction. The study in different concentration of bromide and peroxydisulphate has shown that the rate constant increases by increasing the ionic strength and temperature of the system. The effect of ionic strength on the activation parameters was also studied.

## INTRODUCTION

Phenothiazine-5-ium-3,7-bis(dimethylamdno)-4-nitrochloride (M.G.) does not react rapidly with peroxydisulphate, but the depolarization occurs very easily in presence of bromide ion. The reaction shows sharp absorption band at wave length 658 am. The bromide- pm oxydisulphatc reaction (F. Uddin 1980) in presence of mineral acid follows according to following schemc

$$Br + S_2O_8^{-2} \rightleftharpoons BrS_2O_8^{-} \quad \text{(activatedcomplex)} \qquad (1)$$

$$BrS_2O_8^{-3} \longrightarrow BrSO_4^{-} + SO_4^{-2} \qquad (2)$$

$$BrSO_4^{-} + Br^{-} \longrightarrow Br + S_2O^{-2} \qquad (3)$$

The kinetics of reaction in presence of dye follows the same mechanism. The tesults indicate that the reaction in presence of acid follows the zero order kinetics to dye and first order kinetics in $S_2O_8^{-2}$ and $Br^{-}$each, both of these ion participates in the rate limiting step. The proposed mechanism is given as below:

$$S_2O_8^{-2} + Br^{-} \xrightarrow[\text{slow}]{H^+} BrSO_4 + HSO_4^{-} \qquad (4)$$

$$BrSO_4^{-} + Br^{-} \xrightarrow{\text{fast}} SO_4^{-2} + Br_2 \qquad (5)$$

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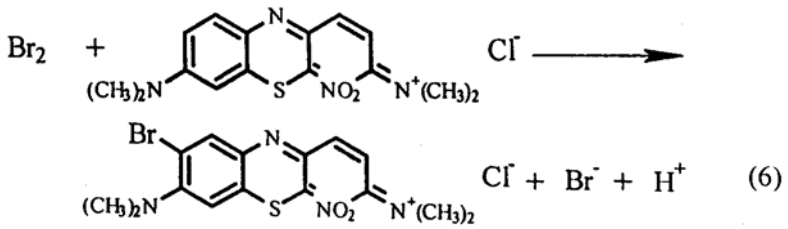


(6)

The experimental data for this reaction satisfies the following rate expression.

$$k_o = -d\,[M.G]\,/dt = k,\,[S_2O_8^{-2}]\,[Br^-] \qquad (7)$$

Where $k_\circ$ is specific rate constant of depolarization of dye and k, is the specific rate constant for the reaction between dye/methylene green and peroxydisulphate in the presence of bromide ion. The nuclear brominatlon, (P. V. Sub Rao, 1988) was observed when methyl orange interacts with persulphate in the presence of bromide ion. The effect of solvent on the reaction was also studied in various aqueous acetic acid mixtures. The effect of ionic strength and temperature on rate constant for a reactions such as bromoacetate-thiosulphate, (G. Corasaro, 1961) bromide-bromate, (F. Uddin, 1979) chloracetate-thiosulphate, (F. Uddin, 1985) dibromosuccinate-thiosulphate, (M. H., Bedford, 1934) and bromopropionate-thiosulphate, (F. Uddin, 1992, 1995) have been studied earlier.

In the present investigations the kinetics of reactions was studied in presence of thiazine dye. We considered it interesting to examine more thoroughly this reaction, to better clarify the mechanism and the effect of ionic strength on activation parameters.

## EXPERIMENTAL

All the chemicals employed were of analytical reagent grade. Double distilled water was used throughout the investigation. The wave length maxima of the Methylene green (M G) was found to be 658 run. Molar absorption co-efficient was found to be 28000 ($dm^3$/mol.cm). Kinetics were investigated at constant pH, which was maintained with sodiumbisulphate. The change in ionic strength was brought about by the addition of calculated volumes of potassium bromide and peroxydisulphate. The concentration of Methylene green (MG) and mineral acid were kept constant. i.e. $2.3 \times 10^{-5}$ moi.$dm^{-3}$ and 1.0 mol.$dm^{-3}$ respectively. The reaction was studied at various ionic strength i.e. 0.16-0.42 cool $dm^{-3}$ and at temperatures $30^0$, $35^0$, $40^0$, 45° and 50°C.

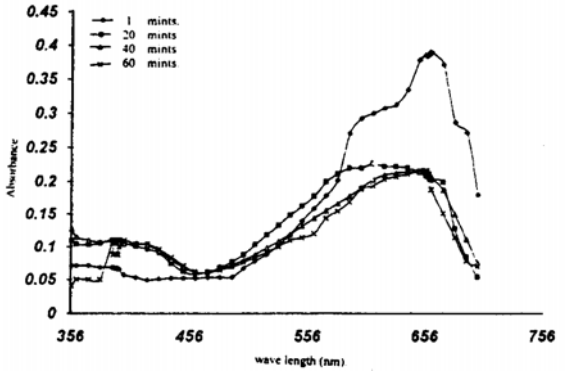


Fig. 1: Spectra of reaction mixture at different time intervals.

**Table-1**

**Rate measurements data at different time intervals**

$[M.G] = 2.3x10^{-5}$ mol.dm$^{-3}$; [Buffer] = 0.05 mol.dm$^{-3}$; [KBr] = 0.15 mol.dm$^{-3}$

$[K_2S_2O_8] = 0.017$ mol.dm$^{-3}$ ; $\mu$=0.201 mol.dm$^{-3}$ , Temperature = $40^0$C $\pm$ $0.1^0$ C

| Time $10^{-3}$s, | Abs. at λ 658 mn | Abs. at λ 393.5 nm | $10^6k_0$ (mol.dm$^{-3}$ s$^{-1}$) | $10^3$ $k_s$ (dm$^3$.mol$^{-1}$.s$^{-1}$) |
|---|---|---|---|---|
| 0.3 | 0.393 | 0.181 | | |
| 0.6 | 0.375 | 0.188 | | |
| 0.9 | 0.339 | 0.203 | | |
| 1.2 | 0.299 | 0.216 | | |
| 1.5 | 0.266 | 0.231 | | |
| 1.8 | 0.251 | 0.250 | | |
| 2.1 | 0.259 | 0.279 | 8.44 | 3.31 |
| 2.4 | 0.235 | 0.265 | | |
| 2.7 | 0.230 | 0.275 | | |
| 3.0 | 0.221 | 0.272 | | |
| 3.30 | 0.216 | 0.279 | | |
| 3.60 | 0.211 | 0.291 | | |
| 3.90 | 0.211 | 0.308 | | |
| 4.20 | 0.196 | 0.303 | | |
| 4.50 | 0.191 | 0.310 | | |

**Table –2**

**Influence of ionic strength on rate constant at $40^0$C.**

$[M.G] = 2.3x10^{-5}$ mol.dm$^{-3}$

| $\mu$ (mol. dm$^{-3}$) | [Br$^-$] (mol. dm$^{-3}$) | $10^2[S_2O_8^{-2}]$ (mol.dm$^{-3}$) | $10^5$ $k_0$ (mol.dm$^{-3}$ s$^{-1}$) | $10^3$ $k_s$ (dm$^3$ mol$^{-1}$.S$^{-1}$) |
|---|---|---|---|---|
| 0.16 | 0.114 | 1.60 | 0.175 | 0.96 |
| 0.20 | 0.15 | 1.70 | 0.844 | 3.31 |
| 0.29 | 0.23 | 2.0 | 2.00 | 4.36 |
| 0.32 | 0.257 | 2.1 | 2.96 | 5.50 |
| 0.42 | 0.357 | 2.24 | 5.40 | 6.76 |

**Table –3a**

**Rate measurements with respect to dye at various temperature and ionic strengths**

| Zero order rate constants $10^5$ $k_0$ (mol.dm$^{-3}$s$^{-1}$) at temperatures | | | | | |
|---|---|---|---|---|---|
| $\mu$ (mol.dm$^{-3}$) | $30^0$C | $35^0$C | $40^0$C | $45^0$C | $50^0$C |
| 0.16 | 0.113 | 0.161 | 0.175 | 0.366 | 0.450 |
| 0.20 | 0.56 | 0.644 | 0.844 | 0.925 | 1.13 |
| 0.29 | 1.21 | 1.56 | 2.00 | 2.20 | 3.11 |
| 0.32 | 1.67 | 2.05 | 2.96 | 3.17 | 4.18 |
| 0.42 | 2.95 | 3.41 | 5.40 | 6.06 | 7.81 |

**Table – 3b**
**Rate measurement with respect to KBr and $K_2S_2O_8$ at various temperature and ionic strengths**

| Rate constants $10^3$ $k_s$ ($dm^3$ $mol^{-1}.s^{-1}$) | | | | | |
|---|---|---|---|---|---|
| μ ($mol.dm^{-3}$) | $30^0$C | $35^0$C | $40^0$C | $45^0$C | $50^0$C |
| 0.16 | 0.621 | 0.885 | 0.963 | 2.00 | 2.47 |
| 0.20 | 2.20 | 2.51 | 3.31 | 3.63 | 4.46 |
| 0.29 | 2.63 | 3.39 | 4.36 | 4.79 | 6.76 |
| 0.32 | 3.10 | 3.80 | 5.50 | 5.88 | 7.76 |
| 0.42 | 3.70 | 4.27 | 6.76 | 7.58 | 9.77 |

**Table – 4**
**Activation parameters at $25^0$C**

| μ ($mol.dm^{-3}$) | Ea K.cal.$mol^{-1}$ | $H^{\#}$ K.cal.$mol^{-1}$ | $S^{\#}$ cal.$mol^{-1}$ | $G^{\#}$ K.cal.$mol^{-1}$ |
|---|---|---|---|---|
| 0.20 | 10.40 | 9.81 | -16.85 | 14.83 |
| 0.29 | 9.59 | 8.99 | -17.25 | 14.13 |
| 0.32 | 9.15 | 8.55 | -17.45 | 13.75 |
| 0.42 | 8.57 | 7.97 | -17.65 | 13.23 |

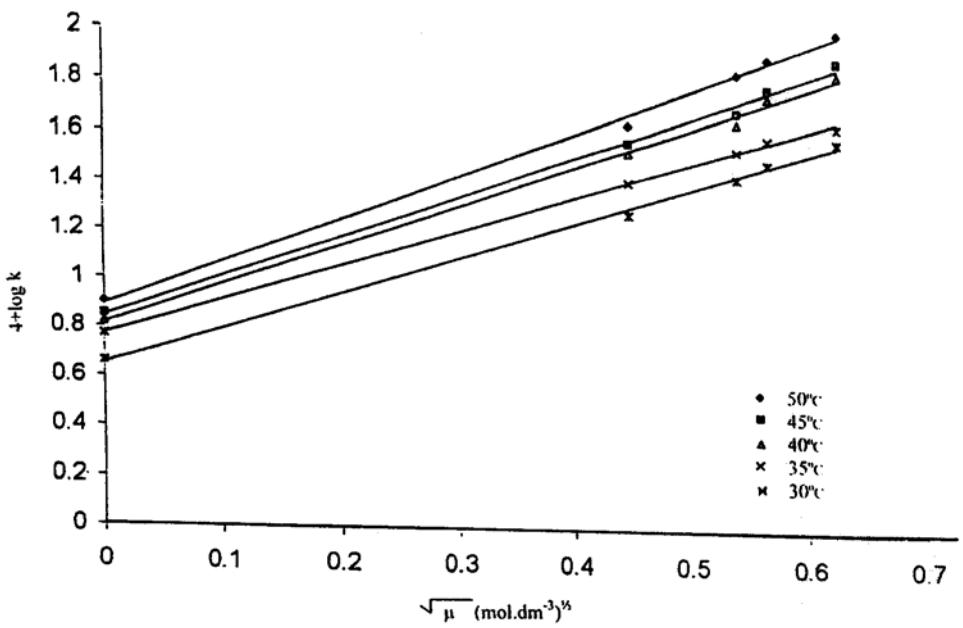


Fig. 2: log k vs √μ

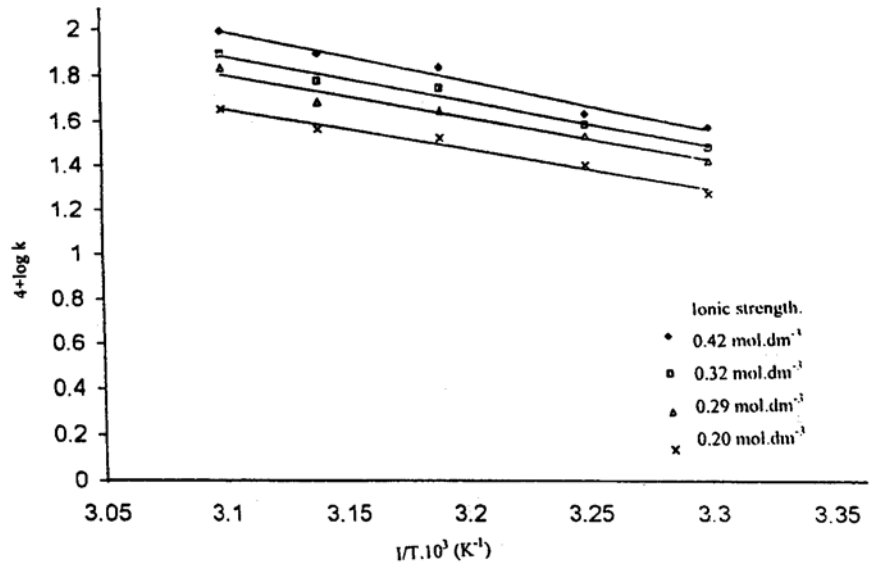


Fig. 3: log k vs $T^{-1}$

## RESULTS AND DISCUSSION

Absorption spectra: The spectra of reaction mixture at different time interval, is shown in fig.l. The maximum absorbance of reaction mixture at different time intervals is also shown at the wave length 650 to 660 nm. Which is due to the unreacted methylene green and them is continuous decrease in the value of absorbance at different time, while a new peak arises at wave length 390 to 400 nm which is due to the formation of bromine during the reaction.

The ionic strength of the reaction mixture was varied by increasing the concentration of bromide and peroxydisphate ions. While the concentrations of methylene green and acid kept constant throughout the experiments. The values of absorbencies at ionic strength 0.201 $mol.dm^{-3}$ and 40°C are summarized in Table I. A staight line with a negative slope was obtained when absorbace at k658 nm was plotted against time, zero order kinetics was followed with respect to methylene green.

The values of rate constant of the reaction at various ionic strength are tabulated in Table 2. The influence of ionic strength and temperature on specific rate constant is shown by Table 3.

According to the (Table 3) there is a gradual increase in the value of rate constant at particular temperature and ionic strength. The behavior was not acceptable when the reaction was studied at lower ionic strength there was an inverse relationship between the ionic strength. The abnormal behavior was supported by the observations made by king *et al*. Results in Table (3.b) show that the increase in ionic strength and temperature also increase the rate constant. This is in accordance with the Debye – Huckel-Bronsted (S. Glasstone, 1941) theory. The plot of log k vs square root of ionic strength fig. 2 is a straight line with a positive slope. The average value of $Z_ZA_Z$ calculated from the slope of the line was found to be 1.74. Where as the average value of $Z_ZA_Z$ from the Kilpatrick relation was determined as 1.93. Which is more closer to the theoretical value.

The values of energy of activation were calculated from the slope of Arrhenius plot. The representative plots are shown in fig. 3. The results of activation parameters presented in Table. 4 were obtained from usual relationships. (S. Glasston, 1941, A. Indelli, 1960) Variation of activation parameters with ionic strength (greater than 0.16 $mol.dm^{-3}$) follows the same pattern described earlier (F. Uddin, 1979, 1985, 1992, 1995, M. H., Bedford, 1934).

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