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KINETICS OF BROMINATION OF SAFRANINE BY PEROXYDISULPHATE ION IN PRESENCE OF BROMIDE ION

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SUMMARY

Kinetics of brominaiton safranine by peroxydisulphate ion in presence of bromide on has been investigated at various temperatures and ionic strengths. The rate followed first order kinetics in peroxy disulphate and bromide ion each, and zero order kinetics in safranine. A linear relation was obtained for the variation of logarithm of rate constant (log k) with the square root of ionic strength of the media (μ). The rate constants for the rate controlling step were evaluated and interpreted as a function of ionic strengths and temperatures. The values of activation parameters were also computed.

INTRODUCTION

The kinetics of ionic reactions have been widely studied by many cu-workers (F. Uddin, 1975, 1985, 1995). These reactions show a remarkable similarity in the kinetics behaviour, effect of ionic strength on rate constant and on activation parameters. Majority of such reactions were shown to be very specific and more dependent upon the nature and ionic strength of the reacting species. The kinetics of some ionic reactions were also studied in presence of dye (RV. Subb Rao., 1988, K., Tennakone, 1987, P., Sevick., 1991, J.R., Sutter, 1990). The mechanism and rate law of such reactions were determined, which showed that the rate of decolourization of dye was equal to the rate constant of ionic species. Moreover such reaction was reported to be enhanced by the increase in presence of non-aqueous solvent (P.V., Subb Rao, 1988).

The present investigation reveals the study of kinetics of oxidation of safranine and peroxydisulphate ion in presence of bromide ion. The reaction was studied as a function of ionic strength at various temperatures.

EXPERIMENTAL

All the chemicals used were of Analar grade. Double distilled water was used throughout the investigations.

Preliminary Experiments:

The spectra of the safranine was recorded on a Shimadzu CV-VIS spectrophotometer UV-160A (a microcomputer-controlled double-beam recording spectrophotometer). Safranine showed a maxima at the wavelength 493 nm with molar extinction coefficient 3.98x 10^3 dm^3 mol^{-1} cm^1.

Kinetic Procedure:

The kinetic study was made in aqueous sulphuric acid medium. The course of the reaction was followed by measuring the absorbance of unreacted safranine. The rates were measured at various ionic strengths ranging 0.13 to 0.325 mol.dm^3 and temperatures 30 to 50°C. The concentration of safranine were kept constant throughout the measurements, while the ionic strength was varied by changing the concentration of peroxydisulphate and bromide ion. 0.05

mol.dm^{-3} sodium bisulphate buffer was used to maintain the ionic strength of the system. The rate constants were calculated from the average of duplicate determinations. The values of specific rate constants were compiled in tables 1 and 2.

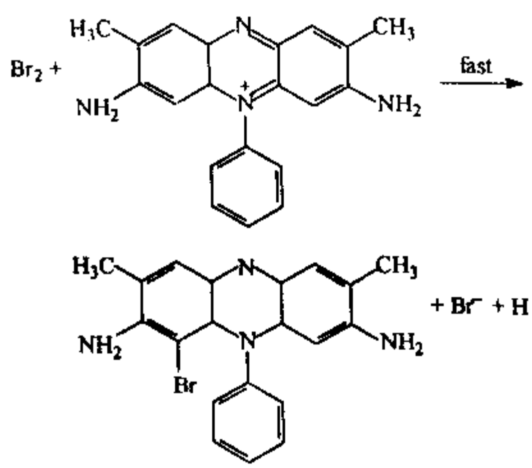
RESULTS AND DISCUSSION

Safranine (phenazinium-3, 7-diamino-2,8-dimethyl chloride) was used to observe the kinetics of reaction.

In acidic medium peroxydisulphate ion behaves as an oxidizing agent and oxidizes bromide ions to molecular bromine (P.V., Subb Rao, 1988, F., Uddin, 1980, S., Subhan, 1980). The liberated bromine was used to brominate the safranine, according to the following mechanism.

$$S_2O_8^{-2} + Br^- \xrightarrow{slow} BrSO_4^- + HSO_4^- \quad (1)$$

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



(3)

Proposed rate law is given as:

$$-\frac{d[S]}{dt} = k_o = K_S\left[S_2O_8^{-2}\right]\left[Br^-\right] \quad (4)$$

The rate of decolorization of safranine *Oc*) should be equal to the rate constant of peroxidisulphate and bromide on (K_s). Since zero order kinetics was observed in safranine, it will not participate in rate determining step and reaction obeys first order Kinetics in S,CR[1] and Br . Since they participates in rate determining step the specific rate constant K, were calculated from the relation.

Table 1
Influence of ionic strength on rate constant at 40°C.
[Safranine] = 1.0x10^{-4} mol.dm^{-3}

μ (mol.dm^{-3})	[Br$^-$] (mol.dm^{-3})	10^2 [$S_2O_8^{-2}$]	$10^5.k_o$ (mol.dm^{-3}.s^{-1})	10^3. ks (dm^3.mol^{-1}.s^{-1})
0.130	0.10	1.00	0.37	3.70
0.215	0.16	1.6	1.07	3.98
0.260	0.200	2.00	1.66	4.16
0.303	0.233	2.33	2.35	4.36
0.325	0.30	2.00	2.77	4.40

Table 2a
Rate measurements with respect to dye at various temperatures and ionic strengths.

Ionic strength μ (mol.dm^{-3})	Zero order rate constant 10^5 k_o (mol.dm^{-3} s^{-1}) at temperatures				
	30°C	35°C	40°C	45°C	50°C
0.130	0.295	0.33	0.37	0.426	0.467
0.215	0.854	0.95	1.07	1.230	1.350
0.260	1.320	1.49	1.66	1.890	2.090
0.303	1.860	2.10	2.35	2.710	2.960
0.325	2.120	2.37	2.77	2.890	3.370

Table 2b
Rate measurements with respect to KBr and $K_2S_2O_8$ at various temperatures and ionic strengths.

μ (mol.dm^{-3})	Rate constant 10^3 k_o (mol.dm^{-3} s^{-1}) at temperatures				
	30°C	35°C	40°C	45°C	50°C
0.130	• 2.95	3.30	3.70	4.26	4.67
0.215	3.16	3.55	3.78	4.57	5.00
0.260	3.30	3.70	4.16	4.73	5.20
0.303	3.46	3.89	4.36	5.00	5.50
0.325	3.55	3.95	4.40	4.80	5.60

$$K_s = K_o / [S_2O_8^{-2}] [Br^-] \qquad (5)$$

Where k_o values were calculated from the slopes of linear plot observed between absorbance and time.

The data in Table 1, shows that the rate of oxidation increases with the increase in the ionic strength of the media. Calculated values of 2"^{d} order rate constant presented in table 2 also shows the same variation. The plots of log k vs $\sqrt{\mu}$ and $\sqrt{\mu}/1 + \sqrt{\mu}$ shows linear relation as shown in figures 1 and 2 respectively. The slopes of the lines d log k/d $\sqrt{\mu}$ and d log k/d $\sqrt{\mu}/1 + \sqrt{\mu}$ were used to calculate the value of Z_A Z_B. The average values of Z_A Z_B comes out to be 0.92 and 1.6 respectively (Table 3).

Therefore Kilpatrick's relation is a better approximation for the determination of values of Z_A Z_B

Effect of Temperature:

The results led to the conclusion that rate of reaction increases with temperature, plot of log k versus T^1 is linear and is shown in Fig. 3. The activation energy $E_a^{\#}$ was calculated from the slope i.e. d log k/d (1/T). $\Delta H^{\#}$, ΔG and $\Delta S^{\#}$ values were calculated from usual relationships (S., Glasstone, A., 1941, Indeili, 1960) and tabulated in table 4.

It is found that energy of activation enthalpy of activation ($\Delta H^{\#`}$) and free energy of activations ($\Delta G^{\#`}$) decreased with increase in ionic strength of the media. These results are in accordance with the theory (S., Glasstone, 1941, A., Indeili, 1960).

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Table 3

Evaluation of $Z_A Z_B$ from slopes

Temperature (°C)	Debye Huckle plot	Kilpatrick plot
30	0.97	1.40
35	0.96	1.44
40	0.80	1.60
45	0.94	1.58
50	0.93	1.74
Average	0.92	1.6

Table 4

Activation parameters at 25°C

μ (mol.dm^{-3})	E_a (K.J.mol^{-1})	$\Delta H^{\neq}$ (K.J.mol^{-1})	$\Delta S^{\neq}$ (J.deg^{-1}mol^{-1})	$\Delta G^{\neq}$ (K.J.mol^{-1})
0.130	34.5	31.9	-222.5	98.2
0.215	30.6	28.1	-222.5	94.4
0.260	26.8	24.3	-222.5	90.6
0.303	22.9	20.4	-222.5	86.7
0.325	21.1	18.6	-222.5	84.9

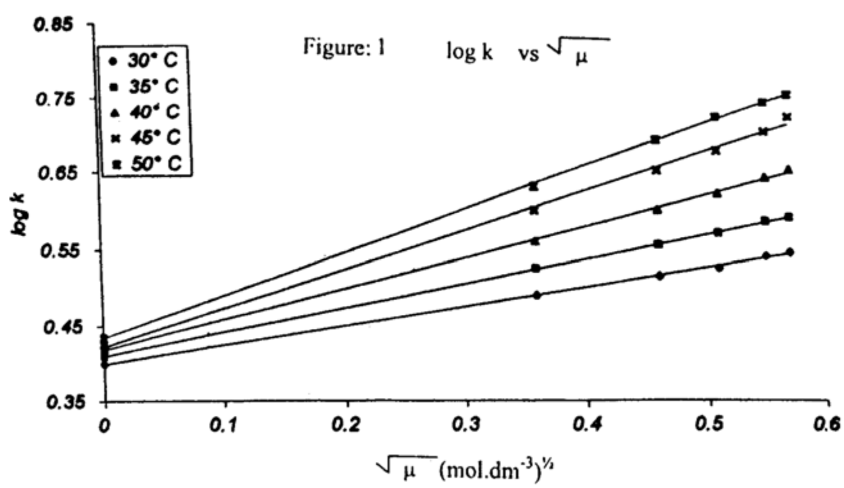


figure: 2 log k vs $\sqrt{\mu}/1+\sqrt{\mu}$

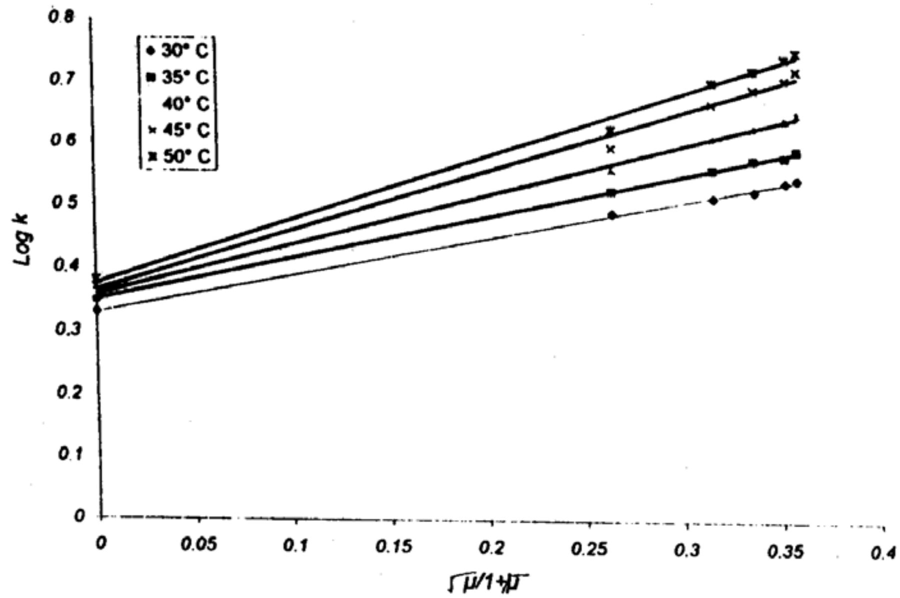
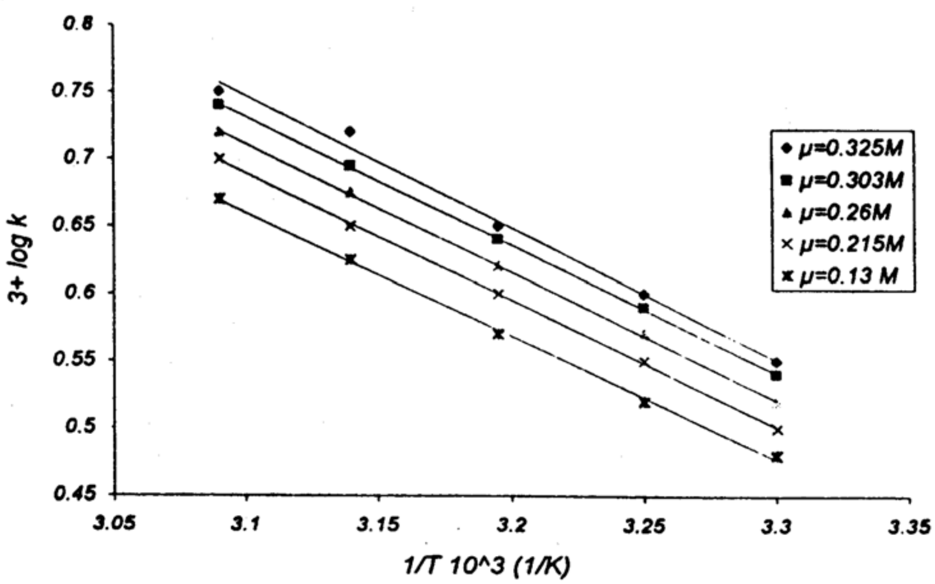


figure: 3 log k vs I/T



REFERENCES

A. Indelli and E.S. Amis, J. *Am. Chem. Soc.,* 82, 332-338 (1960).
F. Uddin and M.G. Ahmed, *Pak. J. Sci. Ind. Res.,* 22, 17 (1979).
F. Uddin and I. Hussain, Nigarian *J. Sc. Tech., 3(2),* 80-84 (1985).
F. Uddin and Z. Khalid, *Egypt. J Chem.,* 38(1), 15-26 (1995).
F. Uddin and G. Ahmed, *Gazz. Chim. Ital.,* 110, 593 (1980).
J.R. Sutter and W. Spencer, *J. Phy. Chem.,* 94, 4116-4119 (1990).
K. Tennakone, S. Wickramanayke and M.U. Gunasekara, J. Chem. Soc., *Faraday Trans.* 1, 83(8), 2553-2558 (1987).
M.S. Suhhan, *Rev. Roam. Chim.,* 25, 851 (1980).
P.V. Subb Rao, K. Ramakrishna and G.V. Saradamba, *J. Ind. Chem. Soc,* **LXV**. 329-332 (1988)
P. Sevickand Dunford, H.B.. *J Phy Chem.,* 95, 2411-2415 (1991).
S. Glasstone, K.T. Laidler and H. Eyring, McGraw Hill Book Co., New York, pp. 196 (1941).