REDOX KINETICS AND MECHANISM OF THE REACTION OF HEXAMETHYLPARAROSALININE^HLORIDE AND NITRITE IONS IN ACID MEDIUM

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Abstract

The redox kinetics of the reaction of hexamethylpararosalinine chloride (HPR) was studied in aqueous acidic I medium. All measurements were carried out at £',,,, =* 530 nm; [If]* = 5 x 10^3*mol dm* (HNOJ; ionic strength, u = I-* 0.50 *mol dm' (NaNOJ and temperature* = 32 ± 1°C. *The stoichiometry as obtained by the mole ratio method was in (he ratio of 1:2* (HPJR$^+$: *NOJ. The order of the reaction was observed to be first order with respect to both [NO* J *and* |HPR*J; *second order overall. The rate law was thus predicted as Rate = k*$_2$*[HPR*][NOJ, where* fc$_2$ *is the second order | rate constant for the reaction and was calculated to be 0.37dm*^{3} *mol*^{1} *min*^{1}. *Add was observed to catalyze the reaction I cottjorming to the rate equation d\HPR]/dt = (a[tf])[HPR*][NOJ where '«' is the slope obtained from theplotof | kut versus /H*/ and was found to be 3.04 dm*^{6} *mof min*^{1}. *Michaelis Menten plot showed an intercept indicating the i presence of an intermediate complex. Based on the results obtained experimentally, the inner sphere mechanism is $ proposed for the* HPR* *NO*$_2$*reaction and a plausible mechanismjbr the reaction is proposed.*

Keywords: Kinetics, mechanism, catalysis, salt effect, intermediate

INTRODUCTION

Hexamethylpararosaline chloride (Crystal violet) is a triphenyltmethane dye that is antimicrobial (Chen & Day, 1974; Hall & Hamilton, 1982), mutagenic (Au *et al*, 1979; Thomas & MacPhee, 1984) and used to prevent fungal growth in poultry feed (Chen & Day, 1974; Hall & Hamilton, 1982). It : is used as a bacteriostatic agent in medical solutions [Bale, 1981; Safranek, 1981], to treat skin infections by *staphylococcus aureus* (Ryan,1992; Saji *et al.*, 1995). It has been reported to undergo electrochemical oxidation in liquid sulphur dioxide [Hall *et al.*, 1966], oxidation with N,' and OH' radicals (Bhasikuttan *etal*, 1995).

Nitrite ions can act as an oxidizing or reducing agent depending on the substrate. When they act as the latter, they are oxidized to nitrates. Oxidation of nitrites to nitrates by hypochlorite ions in aqueous basic solutions has been reported (Cachaza *et al.*, 1976). It has been reported that nitrite ions are common contaminants of natural waters (Cachaza *et al*, 1976), present in high concentrations in human saliva as peroxydase catalysed oxidation of human salivary nitrite to nitrate was observed (Takahama *et al.*, 2003) and also oxidises intracorpuscular haemoglobin to oxyhaemoglobin, itself been reduced to nitric acid (Metcalf,1962).

This work is carried out to obtain relevant kinetic data which would give an idea on the conditions bestsuitableforthereactionsof hexamethylpararosalinine chloride and oxidizing agents such as nitrite ions and the mechanisms for such reactions. The knowledge would be very beneficial to toxicologists and workers in the drug and dye industries, as well as to those involved in its handling when used for staining purposes.

MATERIALS AND METHOD

Preparation of Reagents

All chemicals and reagents used in the work were analar grade and were used without further purification. HNO_3 was used to investigate the effect of hydrogen ion concentration on the reaction, $NaNO_2$ was used as the oxidant and NaNOj was used to maintain a constant ionic strength for each run. Hexamethylpararosalinine chloride, the oxidant and the other solutions were prepared with distilled water.

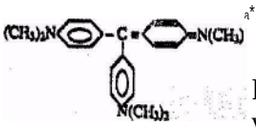
The rate of reactions of the oxidant (NOj) and the reductant (HPR$^+$) were studied by'monitoring the decrease in absorbance of the reductant at its 1,^ (530 nm) using Seward digital biomedical colorimeter. All kinetic measurements were carried

out under pseudo-first order conditions with oxidant concentrations at least 50 fold in excess of the reductant concentration at temperature of 32 ± 1 °C, ionic strength of 0.50 mol dm^3($NaNO_3$) and [H*] - 5 x 10^j mol dm^j (HNO_3). The pseudo-first order plots of log (A,. A*) against time were made and the slope of the plots gave the pseudo- first order rate constant, X. The second order rate constants, kj, were determined from kj ask,/ [NoJ.

RESULTS AND DISCUSSION

Stoichiometry

Stoichiometric studies show that one mole of dye is consumed by two moles of the oxidant (Figure 1) which is consistent with the equation below:



$_n$* + SNOT Product .,,, ...d)

Order of Reaction

Plots of log log (A, A,) versus time obtained under pseudo-first order conditions were linear for about 100% of the reactions (A, and A, are the absorbances of the complex at time 't' and at the end of the reaction respectively), suggesting that the reaction is first order with respect to [HPR*]. Pseudo-first order rate constants, k, , for the plots were obtained from the slope of the plots of log (A, A») versus time. Order of reaction in [NOJ was obtained from the slope of the plot of log k, versus log [NOJ, which was 1.13 ± 0.02 (Figure 2), suggesting that the reaction is first order in [NOJ, meaning that the reaction is second order overall. The second order rate constants for the reactions, k, , calculated from kj/ [NOJ were fairly constant and reported in Table 1 and the average was found to be 0.37 dm^3 mol^{-1} min^{-1} . The rate law can therefore be represented by equation (2) below: -d[HPR*] - fcJHPR^+][NOJ .....(2)

dt.

Effect of acid

In the acid range used (1.00 x 10* = [H> 1.00 x 10^2 mol dm^5), rate of reaction increased with increase in [H*](Table 1). Plot of k_{H+} versus [H^+] is linear without an intercept and with a slope of 3.04 dm^3 mol^2 min^1 (Figure 4.) The H* dependent second order rate constant can thus be presented by equation (3) below:

k_{Ht} = apT] ....,.....(3)

Order of reaction with respect to [H*] is obtained from the slope of the plot of log kj versus log [H^+] and was obtained as 0.98 (Figure 3), suggesting a first order in [H*].

In the range of [H*] used, the overall fate equation is represented by equation (4) below: -d[HPR*]/dt - a[KT][HPR^+][NOJ .....(4)

Effect of changes in the ionic strength of reaction medium on rate of reaction

The rate of reaction was affected by changes in the ionic strength of the reaction medium (Table 1). Plot of log k, versus vji gave a positive slope (Figure 5). This observation suggests that the reactant ions in the rate determining step are of the same charge.

Test for intermediate complex

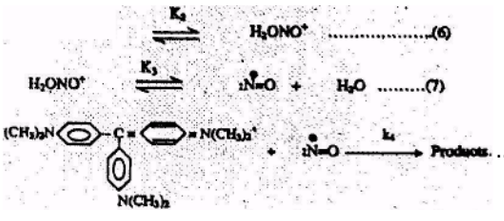
Michaelis Menten plot of 1/k, versus I/ [NOJ gave a straight line with an intercept (Figure 6), suggesting the presence of an intermediate complex.

Testf or free radicals

Addition of acrylamide (0.001- 0.015 M) solution to partially oxidized reaction mixture with addition of excess methanol gave no gel indicative of the absence of free radicals in the reaction mixture.

The acid dependence in this system showed only the acid dependent pathway, suggesting that the protonated species of the oxidant is the only reactive species. Possible mechanism consistent with above result k

NO," + MONO>>• OH". ..(5)



Oir

Rota « MHPRll?N-0| ....OH

But (:N=O) . K,[HiONCn ....(11)

«nd [HjONO'J = Ki[HONO][l-n ....<1J>

also. [MONO] * K,[NOjT .....(13)

It follows lhal[?N=»O) - KoiyHONOKH*] .....(14)

-KjKjKiPKVIHI .....(15)

Substituting equation (IS) into equation (10). we tuive equation (16):

Rate = MCjK:K, [HPRIWOniH*) .....(16)

Equation (1 6) conforms to the observed nie law in equation (4), who* '•' • k4K_3K_2K, * 3.04 dm" *taof' f'*

The positive suit *dim* observed: for the rent-lion (Hawed UK interaction of like chargei in the activated complex. "Hilt agrees will) equation (8) in *the* reaction Khcu.

Table 1: Pseudo – first order and second order rate constants for the reaction of hexamthylpararosalinine chloride and NO_2^-. $[HPR^+] = 1.25 \times 10^{-4}$ mol dm^{-3}; $\lambda = 530$ nm; Temp. 32 ± 1 °C

10^2 $[NO_2^-]$, dm^3 mol^{-1}	10^3 $[H^+]$, dm^3 mol^{-1}	μ dm^3 mol^{-1}	10^2k_1, min	k_2, dm^3 mol^{-1} min
1.95	5.0	0.50	0.73	0.37
2.34	5.0	0.50	0.88	0.38
2.73	5.0	0.50	1.02	0.37
3.12	5.0	0.50	1.16	0.37
3.51	5.0	0.50	1.31	0.37
3.90	5.0	0.50	1.46	0.37
4.28	5.0	0.50	1.61	0.38
4.68	5.0	0.50	1.76	0.38
3.90	0.5	0.50	0.16	0.04
3.90	2.0	0.50	0.60	0.15
3.90	3.0	0.50	0.87	0.22
3.90	5.0	0.50	1.46	0.37
3.90	6.0	0.50	1.81	0.46
3.90	8.0	0.50	2.18	0.56
3.90	10.0	0.50	2.94	0.75
3.90	5.0	0.10	0.82	0.21
3.90	5.0	0.30	1.21	0.31
3.90	5.0	0.40	1.33	0.34
3.90	5.0	0.50	1.44	0.37
3.90	5.0	0.60	1.56	0.40
3.90	5.0	0.70	1.60	0.41
3.90	5.0	0.80	1.72	0.44

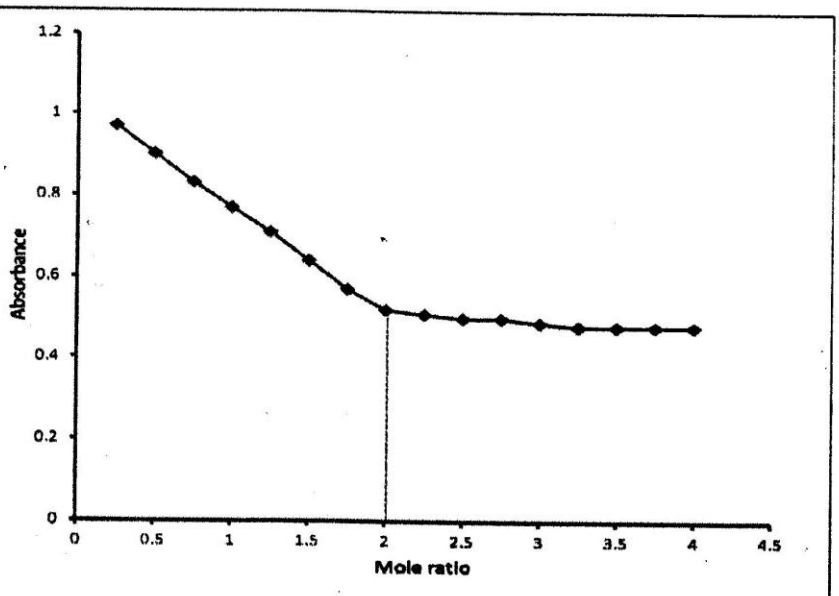


Figure 1 : Plot of Absorbance against mole ratio for the reaction of hexamethylpararosalinine Chloride and NO_2^-. [HPR^+] = 1.25 x 10^{-4} mol dm^{-3} ; [NO_2^-]= (3.13 - 43.75) x 10^{-5} mol dm^{-3}; [H+] = 5.0 x 10^{-3} mol dm^{-3}; μ = 0.50 mol dm^{-3}; λ = 530 nm; Temp. 32 ± 1 °C

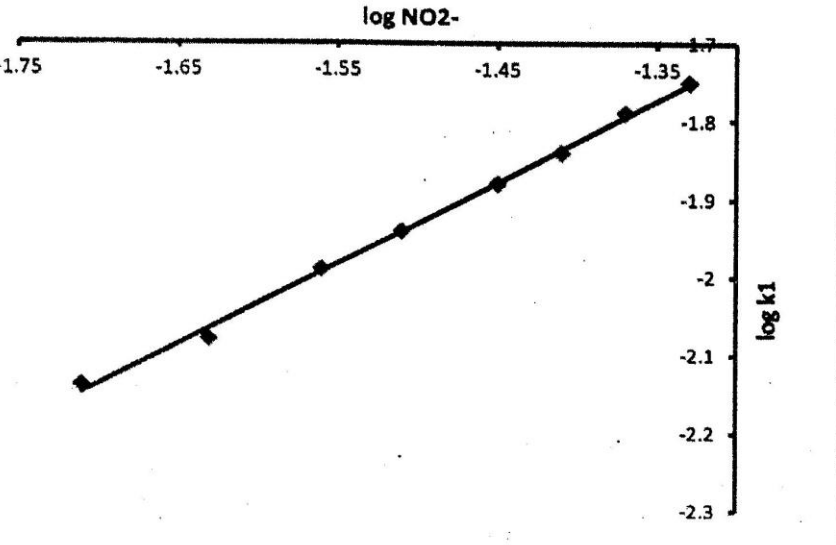


Figure 2.0 : Plot of log k1 against log [NO_2^-] for the reaction of hexamethylpararosalinine chloride and NO_2^-. [HPR^+] = 1.25 x 10^{-4} mol dm^{-3} ; [NO_2^-]= (1.95 - 4.68) x 10^{-2} mol dm^{-3}; [H+] = 5.0 x 10^{-3} mol dm^{-3}; μ = 0.50 mol dm^{-3}; λ = 530 nm; Temp. 32 ± 1 °

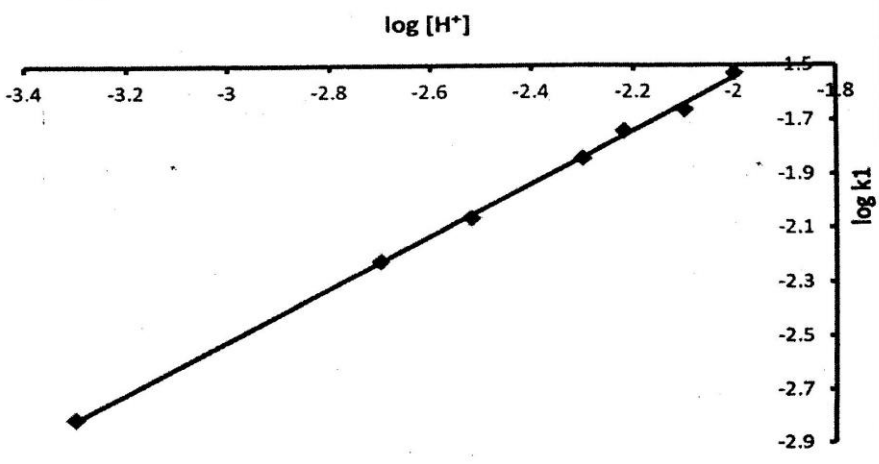


Figure 3 : Plot of log k1 against log [H⁺] for the reaction of hexamethyl pararosalinine chloride and NO_2^- [HPR⁺] = 1.25 x 10^{-4} mol dm^{-3} ; [NO_2^-]= 3.90 x 10^{-2} mol dm^{-3}; [H+] = (5.0 - 100.0) x 10^{-3} mol dm^{-3}; μ = 0.50 mol dm^{-3}; λ = 530 nm; Temp. 32 ± 1 °

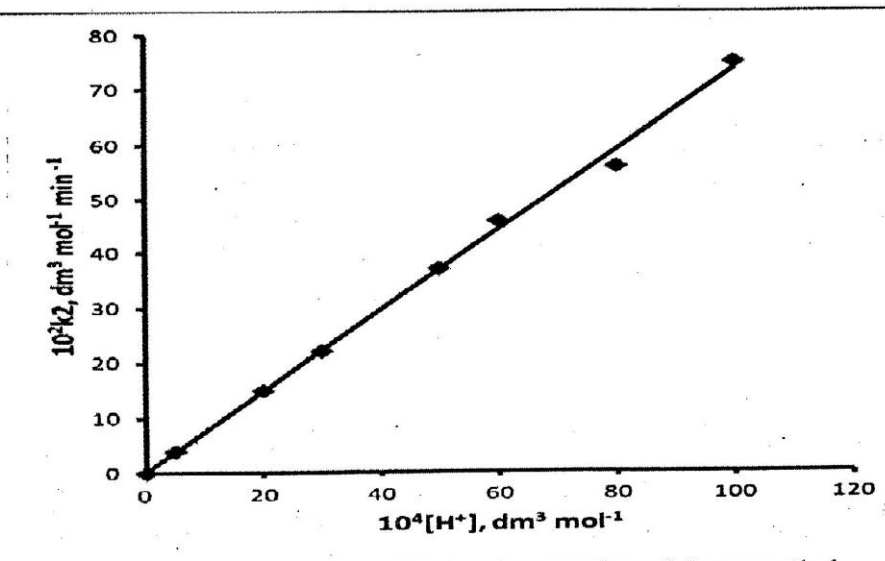


Figure 4 : Plot of kH+ against [H⁺] for the reaction of hexamethyl pararosalinine chloride and NO_2^- [HPR⁺] = 1.25 x 10^{-4} mol dm^{-3} ; [NO_2^-]= 3.90 x 10^{-2} mol dm^{-3}; [H+] = (5.0 - 100.0) x 10^{-3} mol dm^{-3}; μ = 0.50 mol dm^{-3}; λ = 530 nm; Temp. 32 ± 1 °

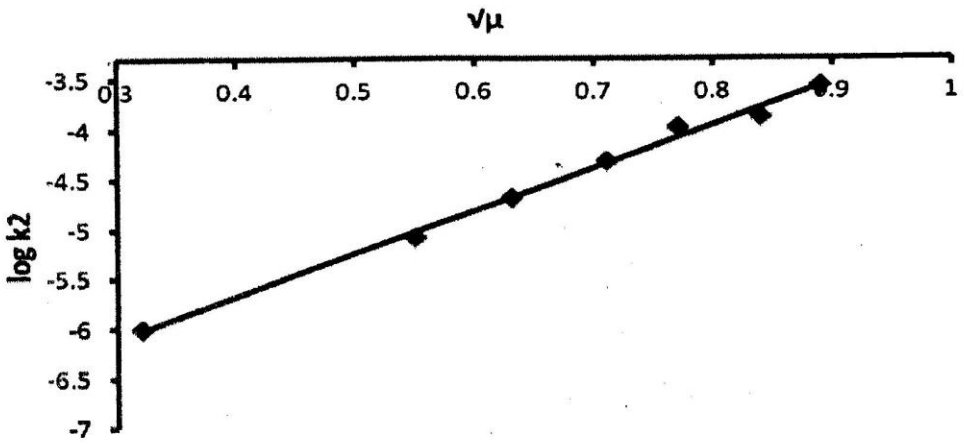


Figure 5 : Plot of log k2 against √μ for the reaction of hexamethyl pararosalinine chloride and NO_2^- [HPR^+] = 1.25×10^{-4} mol dm^{-3} ; [NO_2^-]= 3.90×10^{-2} mol dm^{-3}; [H+] = 5.0×10^{-3} mol dm^{-3}; μ = 0.10 - 0.80 mol dm^{-3}; λ = 530 nm; Temp. 32 ± 1 °

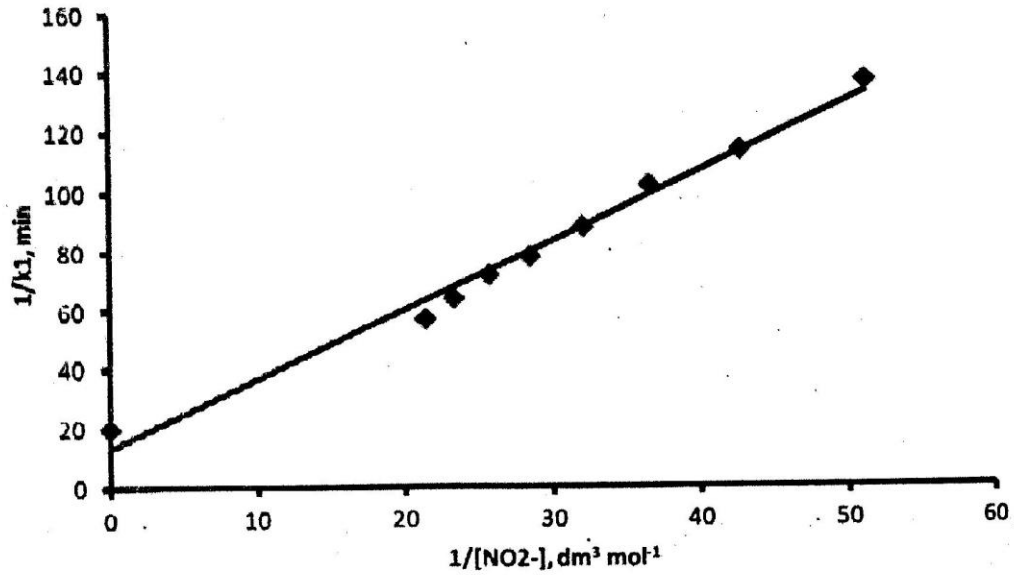


Figure 6: Michaelis - Menten Plot for the reaction of hexamethyl pararosalinine chloride and NO_2^-. [HPR^+] = 1.25×10^{-4} mol dm^{-3} ; [NO_2^-]= (1.95 - 4.68) x 10^{-2} mol dm^{-3}; [H+] = 5.0×10^{-3} mol dm^{-3}; μ = 0.50 mol dm^{-3}; λ = 530 nm; Temp. 32 ± 1 °

Equation (16) conforms to the observed rate law in equation (4), where 'a[1] =

kjg^K, = 3.04 dm" mof s'[1]

The positive salt effect observed for the reaction showed the interaction of like charges in the activated complex. This agrees with equation (3) in the reaction scheme.

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