Oriental Journal of Chemistry Vol. **26**(2), 373-377 (2010)

Investigations into the kinetics and mechanism of Cr (VI) oxidation of hexamethylpararosalinine chloride in aqeuous acidic medium

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(Received: February 02, 2010; Accepted: April 28, 2010)

ABSTRACT

Investigations into the kinetics and mechanism of the redox reaction of hexamethylpararosalinine (HPR^+) and Cr (VI) were carried out in aqueous acidic medium, at a temperature of 31.0 ± 1°C; m = 0.50 mol dm^{-3} (NaCl), $[H^+] = 5.00 \times 10^{-3}$ mol dm^{-3} (HCl). The reaction displayed a stoichiometry of 1:1, first order dependence in both [dye] and [oxidant], dependence on acid concentrations (in the acid range used), negative salt effect, catalysed by added cations and anions and no evidence of intermediate complex formation. Rate equation for the reaction has been proposed as: $-d[MG^+]/dt = (a + b[H^+])[HPR^+][Cr_2O_7^{2-}]$ and the second order rate constant for the reaction was found to be $(11.96 \pm 0.13) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}. Log k_1 versus 1/D gave positive slope for the reaction. Based on the results obtained experimentally, the outer sphere mechanism is proposed for the reaction.

Key words: Kinetics, Mechanism, Catalysis, Salt effect, Cr (VI) oxidation.

INTRODUCTION

Hexamethylpararosalinine chloride (Crystal violet) is a triphenyltmethane dye that is antimicrobial [Chen and Day, 1974; Hall and Hamilton, 1982], mutagenic [Au *et al.*,1979; Thomas and MacPhee, 1984] and used to prevent fungal growth in poultry feed [Chen and Day, 1974; Hall and Hamilton, 19821]. It is used as a bacteriostatic agent in medical solutions [Bale, 1981; Safranek *et al.*,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 $N_3^{\cdot}$ and $OH^{\cdot}$ radicals [Chacaza *et al,*1976].

The dichromate ion, $Cr_2O_7^{2-}$, or Cr(IV) is a powerful oxidizing agent, oxidation reaction of which proceed through Cr(V) or Cr(VI) intermediates and the rate determining step may be the reduction of either intermediates (Nongkyrih and Mahanti, 1995; Medien, 2003; Mansoor and Shafi, 2009). In the reduction of Cr(IV), the lower stable state (+3) is attained by the transfer of three electrons, and it usually involves the transfer of no more than a pair of electrons in a single step. In a few cases, however, it has been reported where Cr (VI) appears to accept 3 electrons simultaneously (Edmonds *et al.,*1970; Hassan and Rocek, 1972, 1974)

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

EXPERIMENTAL

Preparation of reagents

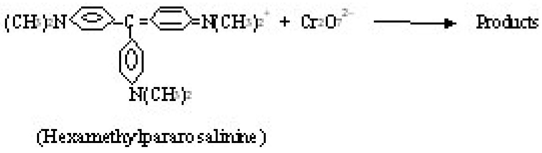
All chemicals and reagents used in the work were analar grade and were used without further purification. HCl was used to investigate the effect of H^+ on the reaction. $K_2Cr_2O_7$ was used as the oxidant. NaCl was used to maintain a constant ionic strength for each run. HPR^+, $Cr_2O_7^{2-}$ and the other solutions were prepared with distilled water.

The rate of reactions of the oxidant ($Cr_2O_7^{2-}$) and the reductant (HPR^+) were studied by monitoring the decrease in absorbance of the reductant at its λ_{max} (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 31.0 ± 1 °C, ionic strength of 0.50 mol dm^{-3} (NaCl) and $[H^+] = 5.00 \times 10^{-3}$ mol dm^{-3} (HCl). The pseudo-first order plots of log ($A_t - A_\infty$) against time were made and the slope of the plots gave the pseudo- first order rate constant, k_1. The second – order rate constants, k_2 , were determined from k_1 as $k_1/ [Cr_2O_7^{2-}]$.

RESULTS AND DISCUSSION

Stoichiometry

Stoichiometric studies show that one mole of dye is consumed by one mole of the oxidant, which is consistent with the equation below:



....(1)

Table 1 : Pseudo – first order and second order rate constants for the reaction of hexamethylpararosalinine and $Cr_2O_7^{2-}$. $[HPR^+] = 8.0 \times 10^{-5}$ mol dm^{-3}, λ = 530 nm; T= 31.0 ± 1 °C

10^2 $[Cr_2O_7^{2-}]$, mol dm^{-3}	10^4 $[H^+]$, mol dm^{-3}	μ, mol dm^{-3}	10^2k_1, min^{-1}	k_2, dm^3 mol^{-1} min^{-1}
2.63	50.00	0.50	1.49	0.57
3.00	50.00	0.50	1.69	0.56
3.38	50.00	0.50	1.89	0.56
3.75	50.00	0.50	2.10	0.56
4.13	50.00	0.50	2.31	0.56
4.50	50.00	0.50	2.49	0.55
5.25	50.00	0.50	2.93	0.56
3.75	5.00	0.50	0.60	0.16
3.75	10.00	0.50	0.79	0.21
3.75	40.00	0.50	1.82	0.49
3.75	50.00	0.50	2.12	0.57
3.75	60.00	0.50	2.57	0.69
3.75	80.00	0.50	3.24	0.86
3.75	90.00	0.50	3.63	0.97
3.75	50.00	0.30	2.90	0.77
3.75	50.00	0.40	2.50	0.56
3.75	50.00	0.60	2.00	0.53
3.75	50.00	0.70	1.50	0.40
3.75	50.00	0.80	1.40	0.37
3.75	50.00	0.90	1.30	0.36
3.75	50.00	1.00	1.20	0.32

Order of reaction

Plots of log log (A_t – $A_{¥}$) versus time obtained under pseudo-first order conditions were linear (A_t 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_1 , for the plots were obtained from the slope of the plots of log (A_t – $A_{¥}$) versus time. Order of reaction was obtained from the slope of the plots of log k_1 versus log [$Cr_2O_7^{2-}$], which was 1.03 ± 0.02, suggesting that the reaction is first order in [$Cr_2O_7^{2-}$], suggesting that the reaction is second order overall. The second order rate constants as determined from k_1/[$Cr_2O_7^{2-}$] were fairly constant (Table 1), the average being (0.55 ± .02) $dm^3\ mol^{-1}\ min^{-1}$. The rate law can therefore be represented by equation (2) below:

$$\frac{-d[MG]}{dt} = k_2\ [HPR^+][Cr_2O_7^{2-}] \qquad ...(2)$$

Table 2 : Effect of changes in the dielectric constant of the reaction medium for the reaction of hexamethylpararosalinine and $Cr_2O_7^{2-}$. [HPR^+] = 8.0 x 10^{-5} mole dm^{-3}; [$Cr_2O_7^{2-}$] = 3.75 x 10^{-2} mole dm^{-3}; [H^+] = 5.0 x 10^{-3} mole dm^{-3}; μ = 0.50 mole dm^{-3} ; λ = 530 nm; T = 31.0 ± 1°C

D	10^2k_1, s^{-1}	k_2, $dm^3\ mol^{-1}\ min^{-1}$
81.00	2.10	0.56
79.80	2.21	0.59
78.60	2.36	0.63
77.40	2.48	0.66
76.20	2.66	0.71
75.00	2.81	0.75
73.80	2.96	0.79
72.60	3.11	0.83
71.40	3.26	0.87

Table 3 : Rate data for the effect of added ions (Mg^{2+} and NO_3^-) on the rate of reaction of hexamethylpararosalinine and $Cr_2O_7^{2-}$. [HPR^+] = 8.0 x 10^{-5} x 10^{-3}mol dm^{-3}; [$Cr_2O_7^{2-}$] = 3.75 x 10^{-2} mol dm^{-3}; [H^+] = 5.0 x 10^{-3}mol dm^{-3}, μ = 0.50 mol dm^{-3}; ë = 530nm; T = 31.0 ± 1°C

Iron	10^3 [ion], mol dm^{-3}	10^2,k_1 s^{-1}	k_2, dm^3 $mol^{-1}\ s^{-1}$
Mg^{2+}	1.00	2.10	0.56
	20.00	1.99	0.53
	30.00	1.84	0.49
	40.00	1.76	0.47
	60.00	1.58	0.42
	80.00	1.46	0.39
	100.00	1.28	0.34
NO_3^-	1.00	2.10	0.56
	20.00	2.21	0.59
	30.00	2.40	0.64
	40.00	2.55	0.68
	60.00	2.66	0.71
	80.00	2.81	0.75
	100.00	2.93	0.78

Effect of acid

In the acid range used (1.00 x 10^{-4} d" [H^+]e" 1.00 × 10^{-2} mol dm^{-3}), rate of reaction increased with increase in [H^+].(Table 1). Plot of k_{H+} versus [H^+] is linear without an intercept. The H^+ dependent second order rate constant can thus be presented by equation (3) below

$$k_{H+} = a + b[H^+] \qquad ...(3)$$

where 'a' = 1.04 $dm^3\ mol^{-1}\ min^{-1}$ and 'b' = 0.12 $dm^6\ mol^{-2}\ min^{-1}$

In the range of [H^+] used, the overall rate equation is represented by equation (4) below:

$$\frac{-d[MG]}{dt} = (a+b)[H^+][HPR^+][Cr_2O_7^{2-}] \qquad ...(4)$$

Effect of ionic strength and medium dielectric constant

The rate of reaction was found to decrease with increase in ionic strength. The results are presented in Table 1.The rate of reactions also increased with increase in the percentage of acetone (increase in 1/D) (Table 2). These two observations suggest that the reactant ions in the rate determining step are oppositely charged.

Effect of added ions

Added Mg^{2+} and NO_3^- in the range 1×10–3 d” [M^{n+}] e” 1 x 10^{-1} mol dm^{-3} catalysed the reaction (Table 3).This is possibly due to coulombic bridging.

Test for intermediate complex

Michaelis – Menten plot of $1/k_1$ versus 1/ [$Cr_2O_7^{2-}$] gave a straight line passing through the origin ie. zero intercept, suggesting the absence of intermediate complex. Running the electronic spectrum of the reaction mixture after one minute of mixing between the wavelengths 480 – 680 nm, after which a similar run was carried out for the malachite green alone. From the spectra there was no significant shift in the λ_{max} further confirming the absence of intermediate complex.

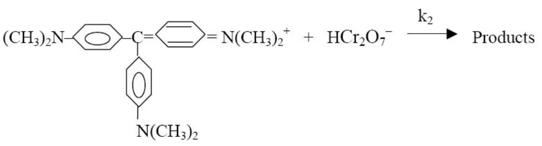
Test for free radicals

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 both the acid dependent and the acid independent pathways, suggesting that the protonated and the unprotonated species of the oxidant are the reactive species.

Possible mechanism consistent with above result is

$$Cr_2O_7^{2-} + H^+ \overset{K}{\rightleftharpoons} HCr_2O_7^- \quad ...(5)$$



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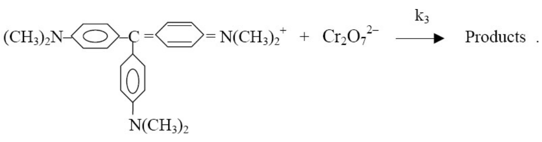

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$$Rate = k_2[HPR^+][HCr_2O_7^-] + k_3[HPR^+][Cr_2O_7^{2-}] \quad ...(8)$$

From equation (3),

$$[HCr_2O_7^-] = = K[Cr_2O_7^{2-}][H^+] \quad ...(9)$$

Putting equation (9) into equation (8) gives

$$Rate = K_2[HPR^+][HCr_2O_7^-] + k_3[HPR^+][Cr_2O_7^{2-}] \quad ...(10)$$

$$= (k_2K_1[H^+] + k_3)[HPR^+][Cr_2O_7^{2-}] \quad ...(11)$$

Equation (11) is consistent with equation (4) which is the observed rate law, where k_3 = ‘a’ = 1.98 dm^3 mol^{-1} s^{-1} and k_2K_1 = ‘b’ = 2.25 dm^6 mol^{-2} s^{-1}.

The negative Bronsted – Debye salt effect observed in the reaction of hexamethyl pararosalinine with $Cr_2O_7^{2-}$ indicates the interaction of reactants of opposite charges in the rate determining step (Sen *et al,* 1995). This assertion agrees with equations (6) and (7) in the proposed mechanism.

The Michaelis – Menten plot gave no intercept, suggesting the absence of intermediate complex formation. The spectra of the reaction mixture gave no significant shift from 530 nm .

The catalysis of added ions on the reaction rate is suggestive of the reaction proceeding through the outer – sphere mechanism (Pennington and Haim, 1967; Wilkins, 1974; Adegite *et al* 1977).

CONCLUSION

Based on the results obtained, it is evident that stoichiometric ratio for the HPR^+ – $Cr_2O_7^{2-}$ reaction was 1:1, The reaction is first order in both [HPR^+] and [$Cr_2O_7^{2-}$]. The rates of redox reaction showed positive dependence on changes in hydrogen ion concentration (in the acid range used). The negative salt effect displayed in the reaction and the effect of changes in the dielectric constant of the reaction medium on the rate constants suggests that species of opposite charges are reacting in the rate determining step. Lack of evidence of intermediate complex formation (from Michaelis- Menten plot analysis) and catalysis due to added ions strongly suggest that the reaction proceeded through the outer sphere pathway.

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