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Redox reactions of cobalt (III) complexes of -hydroxy acids by pyrazinium chloro chromate in the presence of Surfactant

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ABSTRACT

The kinetics of one electron transfer route seems to be unavailable for Pyrazinium Chloro Chromate (PyzCC) with cobalt (III) bound and unbound complexes of -hydroxy acids in surfactant medium. PyzCC oxidizes cobalt (III) bound and unbound -hydroxy acids. It rules out the synchronous C-C bond fission and electron transfer to cobalt (III) centre. Oxidation of above complexes increases with increase of temperature. With increase in surfactant concentration an increase in the rate is observed. The added Ammonium Lauryl sulphate (ALS) surfactant enhances the rate of oxidation of a reaction much more than without micelle. Similar trends have been observed in lactate, mandelato and glycolato CO (III) complexes.

Keywords: Pyrazinium Chloro Chromate, Ammanium lauryl sulphate.

ARTICLE INFO

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1. Introduction

Evolution 60 Thermo spectrophotometer has been employed to study the oxidation of -hydroxy acids such as mandelic acid, lactic acid, glycolic acid and their cobalt (III) complexes using Pyrazinium Chloro Chromate an oxidant in presence of surfactant. One equivalent oxidant like Cr (VI) induced electron transfer in pentaammine cobalt (III) complexes of hydroxyacids result in nearly 100% reduction at cobalt (1II) centre with synchronous carbon-carbon bond fission and decarboxylation. Such an electron

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transfer route seems to be unavailable for Pyrazinium Chloro Chromatein its reaction with cobalt (III) bound and unbound -hydroxy acids in micellar medium. Pyrazinium Chloro Chromate oxidize cobalt (III) bound and unbound -hydroxyacids to respective keto acid cobalt (III) complexes in Ammanium lauryl sulphate (ALS) and possibly the transition state is more electron deficient. Such a transition state can be envisaged only when the C-H bond fission occurs in the slow step with hydride ion transfer. [1-3]

The absence of formation of cobalt (II) rules out the synchronous C-C bond fission and electron transfer to cobalt (III). The thermodynamic parameters are in consistent with bimolecular reaction. The rate of PyzCC oxidation of cobalt (III) mandelato, lactato and glycolato complexes depends on the first power of PyzCC concentration. Similarly the reaction between PyzCC and unbound -hydroxy acid exhibits first order kinetics with respect to concentration of PyzCC of these three complexes lactato cobalt (III) complexes react faster than mandelato and glycolato complexes, where as in the unbound ligand similar trends follows. Oxidation is an important process in organic chemistry and introduction of new economic and effective reagents for oxidation under mild and conditions anhvdrous constitutes а standing challenge. oxidant is PvzCC is which nonhygroscopic, non-photosensitive, stable vellow orange solid which is freely soluble in water, acetic acid, N,N-dimethyl formamide. The little work has been done on PyzCC as oxidant in micellar medium. [4-5]

2. Materials and Methods

The surfactant used in the present work is Ammanium lauryl sulphate (ALS). [6-7] The surfactant is B.D.H, UK. (99%) ALS mandelic, lactic and glycolic acids from (SD Fine chemicals, India (95%) Pentaammine cobalt (III) complexes of _ hydroxyacids were prepared using Fan and Gould [8, 10]. Double distilled (deionised and CO₂ free) water was used as a solvent and HClO4 (E.Merck, India 95%) was standardized using standard Ammanium carbonate (BDH, AR) solution with methyl orange as an indicator. For the PyzCC oxidation of Co (III) complexes of -hydroxy acids and unbound ligands [11, 12]. The rate measurements were made at 31 \pm 0.2°C in 100% aqueous medium and temperature was controlled by electrically operated thermostat11. The volume of reaction mixture total in the spectrophotometric cell was kept as 2.5ml in each kinetic run. Evolution60 Thermo spectrophotometer fitted with recording and thermo stating arrangement was used to follow the rate of the reaction. Rate of these PyzCC oxidant with unbound ligand and cobalt (III) bound complexes were calculated from observed decrease in absorbance at 378 nm. The excess of the reductant was used in kinetic runs. It gives pseudo first order rate constant. It was determine from the International Journal of Chemistry and Pharmaceutical Sciences

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linear plot of the In A versus time. Reproducible result obtained giving good first order plot. The stoicheometric studies for the PyzCC oxidation of pentaammine cobalt (III) complexes of -hydroxy acid and unbound ligand in the presence of micelles were carried out at 31 ± 2 °C. It was observed that the cobalt (II) formation was negligibly small.

3. Results and Discussion

Kinetic study of the oxidation of pentaammine cobalt (III) complexes of -hydroxy acid by PyzCC in micellar medium dependence of rate on PyzCC concentration in micellar bound ligand. The rate of oxidation of lactato cobalt (III) complexes depends on PyzCC concentration, the specific rate calculated remains constant (Table 1) and Graph of logarithm of PyzCC concentration versus time Fig. 1 are linear. From the slope of these graphs, the calculated specific rate agrees with those obtained from integrated rate equation suggesting first order dependence on PyzCC concentration. The rate of oxidation of complexes is more in the presence of micelle and the rate calculated remains constant (Table 2 and Fig 2)

When the concentration of PyzCC is varied from 1.00 to 8.00×10^{-3} mol dm⁻³ at a fixed [cobalt (III)] and [HCIO4]. A specific rate remains constant. Then the of rate of disappearance of Cr (VI) is given by equation

$$-d [Cr (VI)] / dt = k [Cr (VI)] \dots (1)$$

At a particular PyzCC concentration with increases in mandelato/lactato/glycolato cobalt (1II) concentration in the range 1.00 to 8.00×10^{-3} mol dm⁻³ there is a proportional increases in the rate of oxidation (Table 3). The slope of nearly unity is obtained from a linear graph of logarithm. (Fig.3) of specific rate (k in s⁻¹) versus logarithm of Co (III) concentration in each case suggesting first order rate dependence of rate on [Co (III)].

Table – 1			
Time (Sec)	$10^{3}(a-x) \text{ mol dm}^{-3}$	$10^4 k_1 (s^{-1})$	
300	2.390	2.80	
600	2.205	2.74	
900	2.010	2.86	
1200	1.845	2.85	
1500	1.690	2.87	
1800	1.570	2.80	
2100	1.420	2.88	

 $[(NH_3)_5 Co^{III} - L]^{2+} = 2.00 X 10^{-2} mol dm^{-3}$ [HClO₄] = 1.00 mol dm⁻³ [PyzCC] = 2.00 X 10⁻³ mol dm⁻³ Temperature= 31± 0.2°C L=Lactic acid



Figure 1: Dependence of rate on first order kinetics

Table-2			
Time (Sec)	10 ³ (a-x)mol dm ⁻³	$10^4 k_1 (s^{-1})$	
300	2.579	3.910	
600	2.292	3.920	
900	2.036	3.930	
1200	1.807	3.940	
1500	1.602	3.950	
1800	1.371	4.162	
2100	1.260	3.970	

$$\begin{split} & [(NH_3)_5 \text{ Co}^{III} - L]^{2+} = 2.00 \text{ X } 10^{-2} \text{ mol } dm^{-3} \\ & [HCIO4] = 1.00 \text{ mol } dm^{-3} \\ & [PyzCC] = 2.00 \text{ X } 10^{-3} \text{ mol } dm^{-3} \\ & [Micelle] = 6.00 \text{ x } 10^{-4} \text{ mol } dm^{-3} \\ & \text{Temperature} = 31 \pm 0.2^{\circ}\text{C} \\ & L = Lactic \text{ acid} \end{split}$$



Figure 2: Dependence of rate on first order kinetics

Table 3			
[(NH ₃) ₅ Co ^{III} -L] ²⁺ 10 ² mol dm ⁻³	10 ⁴ .k ₁ s ⁻¹	10 ² .k2(dm3 mol ⁻¹ s ⁻¹⁾	
Lactato			
1.00	1.955	1.955	
2.00	3.910	1.960	
4.00	7.830	1.961	
6.00	11.700	1.940	
8.00	15.640	1.970	
Mandelato			
1.00	1.675	1.675	

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2.00	3.350	1.665
4.00	6.670	1.650
6.00	9.950	1.640
8.00	13.400	1.625
$[(NH_3)_5 Co^{III} - L]^{2+}10^2 mol dm^{-3}$	$10^{4}.k_{1} s^{-1}$	10 ² .k2(dm3 mol ⁻¹ s ⁻¹⁾
-		
Glycolato		
Glycolato 1.00	1.300	1.304
Glycolato 1.00 2.00	1.300 2.600	1.304 1.300
Glycolato 1.00 2.00 4.00	1.300 2.600 5.200	1.304 1.300 1.310
Glycolato 1.00 2.00 4.00 6.00	1.300 2.600 5.200 7.890	1.304 1.300 1.310 1.345

 $[PyzCC] = 2.00 X 10^{-3} mol dm^{-3}$ [Micelle] = 1.00 x 10⁻⁴ mol dm⁻³ [HClO4] = 1.00 mol dm⁻³

Temperature= $31 \pm 0.2^{\circ}$ C



Figure 3: Dependence of rate on [(NH3)5 CoIII –L] 2+ in ALS

Hence the rate law for the Cr (VI) oxidation of cobalt (III) bound of -hydroxy acids is given by equation 2.

-d [Cr (VI)]/dt = k2 [Cr (VI)] [Co (III)](2)

Dependence of rate on PyzCC concentration in micellar for -hydroxyacid

The rate of oxidation of lactic acid depends on PyzCC concentration. In any specific run the change in concentration of PyzCC, the specific rate calculated remains constant (Table 4) and graphs of logarithm of PyzCC concentration versus time are linear (Fig. 4). From the slope of these graphs, the specific rate calculated agrees with those obtained from integrated rate equation, suggesting first order dependence on PyzCC concentration. When concentration of PyzCC is varied from 1.00 to 4.00 x 10^{-3} moldm⁻³at a fixed [Co (III)] an [HClO4] specific rates remains constant. Then the rate of disappearance of Cr (VI) is given by equation 3. The rate of oxidation of alpha-hydroxy acid is more in the presence of micelle and the rate calculated remains constant (Table 5 and Fig 5)

 $-d [Cr (VI)/dt = K1 [Cr (VI)] \dots (3)$

Dependence of rate on the conc. of -hydroxyacid in ALS

The oxidation studies were carried out by varying initial [-hydroxy acid] in the range 1.00 to 8.00 $\times 10^{-3}$ mol dm⁻³ by keeping other variable constant. The near constancy in the k_2 values (Tables 6) and the slope of nearly unity is obtained from a linear graph of logarithm of specific rate $(k_1 \text{ in s}^{-1})$ verses logarithm of -hydroxy acid concentration in each case suggesting first order dependence of rate on [hydroxy acid] (Figs. 6). Hence the rate law for the Cr (VI) oxidation -hydroxy acid of is given below equation 4.

-d [Cr (VD1/dt =	k2 [Cr (VI)]] [- hvdroxy	v acidl	(4)
a loi ((1)] / ut =	\mathbb{K}_{2} [CI (\mathbb{I}])	IL IIJUIOA	, aciaj	(')

Table-4			
Time (Sec)	10 ³ (a-x) mol dm ⁻³	$10^4 k_1 (s^{-1})$	
300	2.078	1.900	
600	1.961	1.910	
900	1.850	1.920	
1200	1.744	1.930	
1500	1.645	1.950	
1800	1.542	1.970	
2100	1.462	1.940	

 $[Lactic acid] = 2.00 \text{ X } 10^{-2} \text{ mol dm}^{-3}$ $= 1.00 \text{ mol dm}^{-3}$ [HClO₄] [PyzCC] $= 2.00 \text{ X} 10^{-3} \text{ mol dm}^{-3}$ Temperature = $31 \pm 0.2^{\circ}$ C



Figure 4: Dependence of rate on first order kinetics

Table-5			
Time(Sec)	10 ³ (a-x) mol dm ⁻³	$10^4 k_1 (s^{-1})$	
300	2.059	2.200	
600	1.925	2.220	
900	1.797	2.240	
1200	1.677	2.260	
1500	1.565	2.270	
1800	1.462	2.270	
2100	1.361	2.280	

[Lactic acid] = 2.00 X 10-2 mol dm-3 $[HClO_4] = 1.00 \text{ mol dm}^{-3}$ [PyzCC] = 2.00 X 10-3 mol dm-3[Micelle] = $1.00 \times 10^{-4} \text{ mol dm}^{-3}$

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Temperature = $31 \pm 0.2^{\circ}$ C



Figure 5: Dependence of rate on first order kinetics

Table–6			
[- Hydroxy acid]. 10 ² (mol dm ⁻³)	$10^{4}.k1(s^{-1})$	$ \begin{array}{c} 10^{2} k_{2} \\ (dm^{3} mol^{-1} s^{-1}) \end{array} $	
Lactic acid			
1.00	1.110	1.110	
2.00	2.230	1.120	
4.00	4.400	1.085	
6.00	6.650	1.125	
8.00	8.800	1.075	
Mandelic acid			
1.00	0.950	0.950	
2.00	1.830	0.900	
4.00	3.600	0.988	
6.00	5.450	0.910	
8.00	7.250	0.925	
Glycolic acid			
1.00	0.707	0.707	
2.00	1.415	0.715	
4.00	2.820	0.705	
6.00	4.230	0.715	
8.00	5.680	0.735	

[Lactic acid] = 2.00 X 10-2 mol dm-3[Micelle] = $1.00 \times 10^{-4} \text{ mol dm}^{-3}$ [PyzCC] = 2.00 X 10-3 mol dm-3[HClO₄] $= 1.00 \text{ mol dm}^{-3}$ Temperature = $31 \pm 0.2^{\circ}$ C



Figure 6: Dependence of rate on [-Hydroxy acid] in ALS

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Comparison of rates on oxidation of pentaammine cobalt (III) complexes of both bound and unbound -hydroxy acid by PyzCC

Specific rate of the lactato complex is more compared to both the rates of oxidation of unbound ligand and mandelato complex deserves an explanation. The ligation of lactic acid to Co (III) centre has probably increased its reactivity towards PyzCC and this effect seems to be more specific for this ligand only. If the reaction proceeds through a preformed chromate ester, then the rate of C-H, fission will be enhanced, resulting in an increased rate of oxidation of lactato complex such a precursor complex may be sterically hindered in the case of mandelato and glycolato complexes.

4. Mechanism

Oxidation of pentaammine cobalt (III) complexes of both bound and unbound ligands in micellar medium. Thus, the kinetics of one electron transfer route seems to be unavailable for PyzCC with cobalt (III) bound and unbound complexes of -hydroxy acid in micellar medium, PyzCC oxidizes cobalt (III) bound and unbound -hydroxy acids. It rules out the synchronous C-C bond fission and electron transfer to cobalt (III) centre. Oxidation of above complexes increase with increase of temperature. With increase in micellar concentration an increase in the rate is observed. The added ALS micelle enhances the rate of oxidation of a reaction much more than the similar reaction without micelle. Similar trends has been observed in lactato and glycolato Co (III)



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