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Research Article

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Kinetic study on induced electron transfer reaction in pentaammine cobalt(III) complexes of α-hydroxy acids by nicotinium dichromate (NDC) in micellar medium

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ABSTRACT

Nicotinium DiChromate (NDC) oxidation of pentaamminecobalt(III)complexes of α-hydroxy acids in micellar medium yielding nearly 100% of carbonyl compounds are ultimate products. The decrease in UV-visible absorbance at l=502 nm for Co(III) complex corresponds to nearly 100% of the initial absorbance. The stoichiometry of unbound ligand and cobalt(III) complex is accounting for about 100% reduction at the cobalt(III) centre. The kinetic and stoichiometric results have been accounted by a suitable mechanism.

Keywords: Nicotinium DiChromate(NDC), Pentaamminecobalt(III) complexes, Induced electron transfer reaction, ALS, Dimethyl Diocta decyl Ammonium Chloride (DDAC).

INTRODUCTION

Nicotinium DiChromate (NDC) is an efficient reagent for oxidation of primary and secondary alcohols to carbonyl compounds. A large class of organic compounds were oxidized by NDC has been reported1-5. Since induced electron transfer in pentaamminecobalt(III) complexes of α-hydroxy acids with various oxidants have been studied6-11. The extent of NDC oxidation of pentaamminecobalt(III) complexes of α-hydroxy acids in micellar medium as an oxidis able hydroxyl group is separated from carboxyl bound to Co(III) centre by a saturated fragment namely C-C bond12. The cation radical is formed due to the oxidation of hydroxyl group by NDC is nearly in a synchronous fashion of electron transfer resulting in a C-C, O-H bonds scission and reduction at cobalt(III) center.

EXPERIMENTAL SECTION

1.1. Preparation of Nicotinium Dichromate.(NDC).

Nicotinium acid (7.38g , 60ml) was added to Chromium trioxide CrO3 (12g, 120 mol), dissolved in water (12ml at 0ºC ice water bath) with vigorous stirring. After 15 min Acetone (100ml at 0.5º C) was added to the resulting red orange suspension and the mixture was stirred at 0º C --- 5º C for 15 min. The Product was filtered off end washed with Acetone (4×50ml) and Dichloromethane (25 ml) affording Nicotinium dichromate (11g) as usage yellow solid. M.P.217 ºC. α-Hydroxy acids employed as ligands. The monomeric cobalt(III) complexes of α-hydroxy acids were prepared as their perchlorates by the method of Fan and Gould 13.

1.2. Kinetic measurements

The tris (α-hydroxo) complex; $(NH_3)_3$ Co $(OH)_3$ Co $(NH_3)_3$ $(ClO_4)_3$ (triol) has been prepared by the procedure of Siebert and Co workers 14,15. And unbound ligands in the presence of micelles were carried out at 32±0.2 0C in an electrically operated thermostat bath. The concentrations of unreacted NDC was determined iodometrically. The disappearance of Co(III) was followed spectrophotometrically by following the decrease in absorbance at 470 nm. (For the monomeric Co(III) complex). Ionic strength was maintained by the addition of suitable quantities of $NaClO_4$. The specific rates estimated from the optical density measurements agree with the values from the volumetric procedure within ±7% curiously, the change in absorbance observed at 470 nm Co(III) complexes of α-hydroxy acids corresponds to nearly 100% of the initial concentration of Co(III), while the change in optical density at 374 nm for NDC corresponds to nearly 100% of [Co(III)] initial .Co(II) was estimated after completion of reaction, by diluting the reaction mixture 10-fold with concentrated HCl, Allowing the evolution of chlorine gas to cease and then measuring the absorbance of yellow Nicotinium complex of Co(II) at 660 nm (e =560 dm3 mol-1cm-1)16,17. The amount of Co(II) estimated in all these cases corresponds to nearly 100% of [Co(II)]initial. After 48 h, the product was extracted with diethyl ether and analyzed iodometrically for the amount of benzaldehyde formed was determined by measuring absorbance at 229 nm [e=11,400 dm3 mol-1 cm-1]18,19. The yield of benzaldehyde in all these cases was nearly 100% [Co(III)] initial Table 1 & 2.

Table: 1. Stoichiometric data for NDC oxidation of Co(III) bound and unbound α –hydroxy acids in presence of Ammonium Lauryl Sulfate (ALS) at 32 ± 0.2 °C

$[HClO_4]$ = 1.00 mol dm^{-3}.
[ALS] = $1.00x10^{-4}$ mol dm^{-3}.
Temperature = 32 ±0.2°C

10^3[Compound] mol dm^{-3}	10^2 [NDC] $_{initial}$ mol dm^{-3}	10^2 [NDC] $_{Final}$ mol dm^{-3}	$\Delta 10^3$ [NDC] mol dm^{-3}	[Compound] : Δ [NDC]
Mandelic acid				
4.0	2.0	1.60	4.0	1.00 : 1.00
5.0	2.0	1.55	4.5	1.00 : 0.90
6.0	3.0	2.42	5.8	1.00 : 0.98
Lactic acid				
4.0	2.0	1.60	3.9	1.00 : 0.97
5.0	2.0	1.51	4.9	1.00 : 0.98
6.0	3.0	2.40	6.0	1.00 : 1.00
Glycolic acid				
4.0	2.0	1.60	4.0	1.00 : 1.00
5.0	2.0	1.50	5.0	1.00 : 1.00
6.0	3.0	2.42	5.8	1.00 : 0.96
Co^{III} Mandelato				
4.0	2.0	1.75	3.9	1.00 : 0.92
5.0	2.0	1.71	4.2	1.00 : 0.98
6.0	3.0	2.42	6.1	1.00 : 1.00
Co^{III} - Lactato				
4.0	2.0	1.63	4.0	1.00 : 0.97
5.0	2.0	1.74	4.2	1.00 : 1.00
6.0	3.0	2.42	6.1	1.00 : 1.02
Co^{III} -Glycolato				
3.0	1.0	0.91	0.89	1.00 : 0.89
3.5	2.0	0.82	0.88	1.00 : 0.88
4.0	2.0	1.60	4.00	1.00 : 1.00

Table: 2. Stoichiometric data for NDC oxidation of Co(III) bound and unbound α –hydroxy acids in presence of Dimethyl Diocta decyl Ammonium Chloride (DDAC) at 32 ± 0.2 °C

[$HClO_4$] = 1.00 mol dm⁻³.
[DDAC] = 1.00x10⁻⁴ mol dm⁻³.
Temperature = 32 ± 0.2ºC.

10^3[Compound] mol dm^{-3}	10^2 [NDC] $_{initial}$ mol dm^{-3}	10^2 [NDC] $_{Final}$ mol dm^{-3}	Δ10^3 [NDC] mol dm^{-3}	[Compound] : Δ [NDC]
Mandelic acid				
4.0	2.0	1.59	3.92	1.00 : 1.03
5.0	2.0	1.54	4.38	1.00 : 0.88
6.0	3.0	2.41	5.72	1.00 : 0.96
Lactic acid				
4.0	2.0	1.61	3.91	1.00 : 0.99
5.0	2.0	1.53	4.92	1.00 : 1.00
6.0	3.0	2.40	6.00	1.00 : 0.98
Glycolic acid				
4.0	2.0	1.63	4.02	1.00 : 1.07
5.0	2.0	1.50	5.00	1.00 : 1.00
6.0	3.0	2.43	5.81	1.00 : 0.96
Co^{III} - Mandelato				
4.0	2.0	1.74	3.88	1.00 : 0.90
5.0	2.0	1.70	4.18	1.00 : 0.94
6.0	3.0	2.42	6.10	1.00 : 1.00
Co^{III} - Lactato				
4.0	2.0	1.62	3.99	1.00 : 0.96
5.0	2.0	1.73	4.18	1.00 : 0.99
6.0	3.0	2.40	6.00	1.00 : 1.00
Co^{III} - Glycolato				
3.0	1.0	0.90	0.88	1.00 : 0.86
3.5	2.0	0.83	0.87	1.00 : 0.82
4.0	2.0	1.58	3.98	1.00 : 0.90

After neutralization of the reaction mixture with sodium bicarbonate, the pH of the aqueous layer was adjusted to about 6.0 and the aqueous layer was separated by filtration in the case of both free ligands and corresponding complexes. On evaporation of water under reduced pressure, the product separated and the percentage yield was calculated. Though the yield of cobalt(II) was 100%, the estimation of cobalt(II), Cr(V) and carbonyl compounds were quantitative, In both the cases the IR spectra of the product agreed with IR spectra of authentic samples.

RESULTS AND DISCUSSION

Table 3 summarizes the kinetic data for the NDC oxidation of free α -hydroxy acids with 1N $HClO_4$ in presence of anionic and cationic micelles at 32±0.2 0C. The reaction exhibits total second order dependence on [Cobalt(III)] as well as [α-hydroxy acids]. Based on the oxidation of NDC with α-hydroxy acids the following rate law has been deduced.

Rate=k[α-hydroxy acid] [NDC]

Table 4 lists the formation constants for NDC co-complexes of α-hydroxy acid along with the specific rates. Such complex formation seems to be absent when the carboxyl and it is tied up by Co(III) and the reaction between NDC and Co(III) complexes of α-hydroxy acids exhibit uncomplicated second order kinetics.

From a comparison, the specific rates for NDC oxidation of the respective Co(III)complexes and the dimeric cobalt(III) glyoxalato complex, one can infer that the oxidation rates of α-hydroxy acids are not significantly affected by complex formation. This may be due to the point of attack lies away from the Co(III) centre so that its electrostatic influence is less felt. There is, however a considerable change in the specific rate of NDC oxidation of the Co(III) keto acid complex as the two Co(III) centers can exert greater electrostatic influence over the reacting centre. This suggests that NDC attacks the O-H centre in the slow step of the reaction, leading to ligand oxidation takes place. The rate of the reaction is increased by the addition of both Ammonium Lauryl Sulfate (ALS) and Dimethyl Diocta decyl Ammonium Chloride (DDAC). A plot of specific rate constant versus micellar concentration is sigmoidal in shape the catalytic effect is more Dimethyl Diocta decyl Ammonium Chloride (DDAC) than Ammonium Lauryl Sulfate (ALS).

The specific rate of the lactato complex is more when compared to both the rate of unbound ligand and mandelato complex is due to the ligation of lactic acid to cobalt(III) centre has probably increased its reactivity towards NDC and this effect seems to be more specific for this ligands only. In NMR spectrum of lactato complex the alpha methine proton has undergone considerable downfield shift compared to the alpha C-H proton of the unbound ligand [d C-H=1.62 ppm in lactic acid and d=C-H 2.19 ppm in lactato complex where as d= C-H 4.62 ppm in mandelic acid d=C-H=3.73 ppm in the respective complex]. Suggesting an increase in acidic nature of methine proton of lactic acid is due to ligation to metal centre. If the reaction proceeds through a performed chromate ester, then the rate of alpha C-H will been hanced, resulting in an increased rate of oxidation of lactato complex such a precursor complex may be satirically hindered in the case of mandelato and glycolato complexes.

The stoichiometric results indicate that for 1 mole of cobalt(III) complex, about 0.65 mole of NDC is consumed, whereas with the unbound ligands for 1 mole of a-hydroxy acids about0.92 mole of NDC is consumed (Table 3 & 4). The stoichiometric results coupled with kinetic data and product analysis can be accounted for by the following the reaction Scheme 1.

Table: 3. First order rate constants for NDC oxidation of α -hydroxy acids at 32 ± 0.2°C

[NDC] = 2.00×10^{-3} mol dm^{-3}.
[$HClO_4$] = 1.00 mol dm^{-3}.
[ALS] = 1.00×10^{-4} mol dm^{-3}.
[DDAC] = 1.00×10^{-4} mol dm^{-3}.
Temperature = 32 ± 0.2°C.

10^2[α-hydroxy acids] mol dm^{-3}	10^4 k_1 S^{-1} ALS	10^2 k_2 dm^{-3} mol S^{-1} ALS	10^4 k_1 S^{-1} DDAC	10^2 k_2 dm^{-3} mol S^{-1} DDAC
Lactic acid				
1.00	3.33	4.5224	3.24	4.5105
2.00	4.42	4.5220	3.99	4.1500
3.00	5.54	4.5220	5.15	4.1499
4.00	8.12	4.5200	5.97	4.1500
5.00	15.05	4.5180	8.06	4.1500
Mandelic acid				
1.00	2.20	4.3924	2.17	4.3364
2.00	3.01	4.3922	2.69	4.3360
3.00	3.69	4.3920	3.24	4.3360
4.00	5.14	4.3920	4.61	4.3358
5.00	6.98	4.3920	5.54	4.3368
Glycolic acid				
1.00	1.66	4.315	1.58	4.1986
2.00	2.07	4.314	1.90	4.1980
3.00	2.59	4.315	2.81	4.1980
4.00	3.24	4.314	3.34	4.1979
5.00	4.15	4.314	3.91	4.1980

The reaction scheme proposes that NDC oxidizes OH center of the cobalt(III) bound α-hydroxy n acids at a rate of comparable to that of the unbound ligand and there is 100%reduction at the cobalt(III) centre, forms a chromate ester with cobalt(III) glyoxalato complex which can decompose in a slow step, proceeds through C-C bond fission leading to the formation of cobalt(II), carbonyl compounds and carbon dioxide. As 1 mole of cobalt(III) glyoxalato complex consumes 0.65 mole of NDC yielding nearly 100% of Co(II)and 100% carbonyl compounds. Similarly 1 mole of unbound α-hydroxy acid consumes nearly 0.92 mole of NDC, yielding 100% of carbonyl products and CO2.

Scheme – I

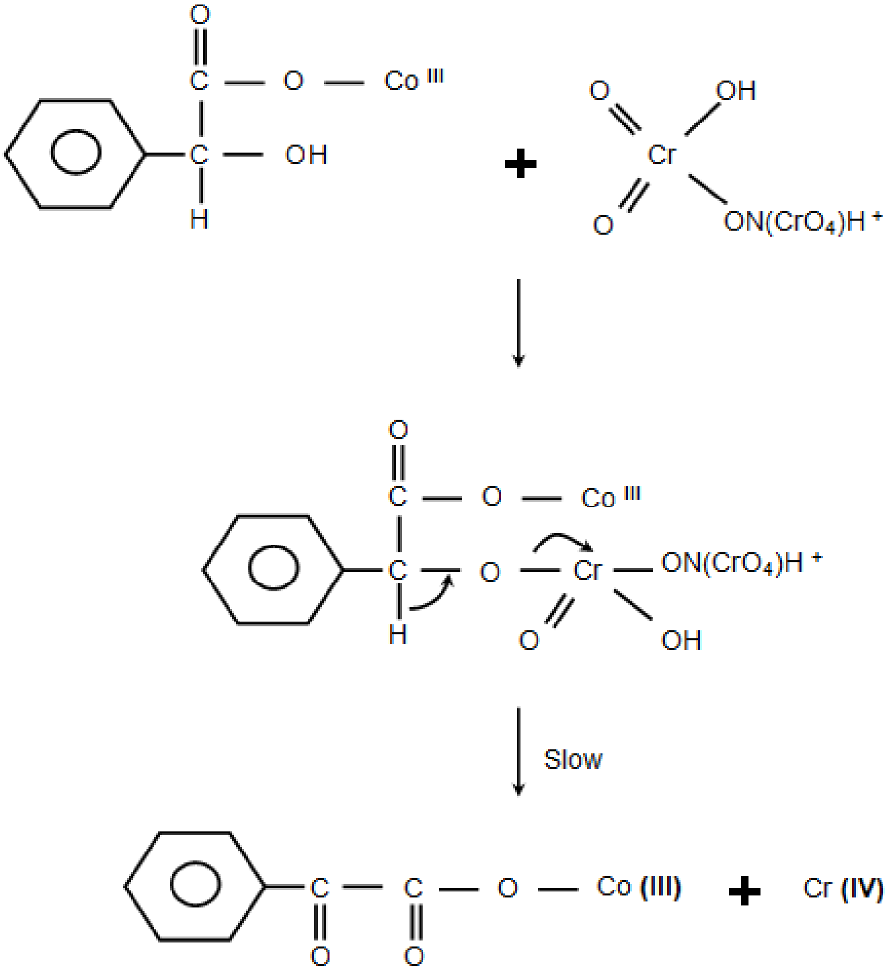
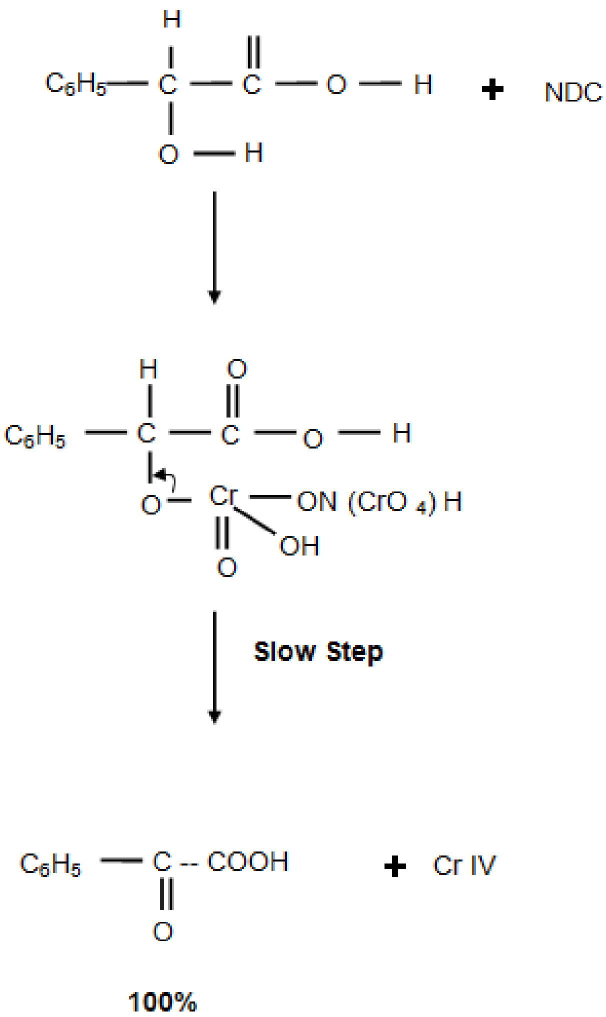


Table: 4. First order rate constants for NDC oxidation of Co(III) complexes of α-hydroxy acids at 32 ± 0.2 °C

[NDC] = 2.00×10^{-3} mol dm^{-3}.
[$HClO_4$] = 1.00 mol dm^{-3}.
[ALS] = 1.00×10^{-4} mol dm^{-3}.
[DDAC] = 1.00×10^{-4} mol dm^{-3}.
Temperature = 32 ±0.2°C.

$10^3[(NH_3)_5Co(III)L]$ mol dm^{-3}	10^4 k$_1$ S^{-1} ALS	10^2 k$_2$ dm^{-3} mol S^{-1} ALS	10^4 k$_1$ S^{-1} DDAC	10^2 k$_2$ dm^{-3} mol S^{-1} DDAC
L = Lactato				
1.00	1.02	4.0086	0.96	3.9822
2.00	1.68	4.0084	1.43	3.9820
3.00	2.69	4.0084	2.33	3.9820
4.00	3.66	4.0082	2.66	3.9821
5.00	5.62	4.0084	4.20	3.9820
L = Mandelato				
1.00	0.67	3.8260	0.72	3.8573
2.00	0.85	3.8258	0.91	3.8570
3.00	1.33	3.8259	1.36	3.8572
4.00	2.10	3.8258	1.93	3.8571
5.00	3.17	3.8258	2.76	3.8571
L = Glycolato				
1.00	0.42	3.6232	0.49	3.6901
2.00	0.64	3.6233	0.69	3.6903
3.00	0.88	3.6230	0.93	3.6903
4.00	1.92	3.6230	1.46	3.6902
5.00	2.43	3.6230	2.41	3.6903

Scheme - II



Nicotinium dichromate forms a chromate ester with CO(III) mandelato complex which can decompose in a slow step leading to the formation of the keto acid complex and Cr(IV). The absence of formation of co(II) rules out the synchromous C-C bond fission and electron transfer to Co(III). The oxidation of cobalt(III) complexes of α-hydroxy acids by Nicotinium dichromate proceeds mainly through C-H bond fission. The mechanism of NDC oxidation of Cobalt (III) lactato, glycolato, mandlic, lactic and glycolic acids will be similar to the one proposed for the Cobalt(III) mandelato complex.

CONCLUSION

It has been found that the rate of oxidation of Co(III) complexes of unbound and bound moieties are enhanced more in the presence of Dimethyl Diocta decyl Ammonium Chloride (DDAC) when compared to the Ammonium Lauryl Sulfate (ALS). The micelles act as a positive catalyst in the present study.

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