



**OXIDATION OF COBALT(III) COMPLEXES OF α -HYDROXY ACIDS BY
NICOTINIUM DI CHROMATE (NDC) IN THE PRESENCE OF
DIMETHYL DIOCTA DECYL AMMONIUM CHLORIDE (DDAC) -
A KINETIC AND MECHANISTIC STUDY**

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ABSTRACT

The kinetics of induced electron transfer reaction has been attempted presently with nicotinium dichromate (NDC) and pentaammine cobalt (III) complexes of α -hydroxy acid in the presence of micelles. The nicotinium dichromate (NDC) oxidizes cobalt (III) bound and unbound α -hydroxy acids. In nicotinium dichromate (NDC) induced electron transfer in the complex, the intermediate radical formed dissociates in a nearly synchronous C-C bond cleavage and the rest of it proceeding with C-H fission yielding cobalt (III) complex. With increase in surfactant (dimethyl dioctadecyl ammonium chloride) (DDAC) concentration, an increase in the rate was observed.

Key words: Nicotinium dichromate (NDC), Pentaammine cobalt (III) complexes, Dimethyl dioctadecyl ammonium chloride (DDAC).

INTRODUCTION

The oxidation of α -hydroxy acids such as mandelic acid, lactic acid, glycolic acid and their pentaammine cobalt (III) complexes using nicotinium dichromate (NDC) an oxidant has been carried out in presence of dimethyl dioctadecyl ammonium chloride (DDAC). The little work has been done on nicotinium dichromate (NDC) with pentaammine cobalt (III) complexes as oxidant in micellar media. The reaction between nicotinium dichromate (NDC) and unbound α -hydroxy acid exhibits second order kinetics with respect to concentration of nicotinium dichromate (NDC). A study of induced electron transfer reaction in Co(III)-L system by an external oxidant, whether an one electron transfer reaction takes place at the bound organic ligand gets oxidized, without disturbing cobalt (III) centre has been studied. Oxidation is an important process in organic chemistry and introduction of new economic and effective reagents for oxidation under mild and anhydrous conditions constitutes a standing challenge. The nicotinium di chromate (NDC) is oxidant, which is non-hygroscopic, non-photosensitive, and stable yellow solid, which is freely soluble in water, acetic acid, etc.

EXPERIMENTAL

Material and method

The surfactant used in the present work is dimethyl dioctadecyl ammonium chloride (DDAC). The

surfactants are purified by adopting earlier procedure. The chemicals dimethyl dioctadecyl ammonium chloride (DDAC) from (Bio Corporals 99%, Japan) mandelic, lactic and glycolic acids from (Karnataka Fine Chem., 97%, India) were purchased. Pentaammine cobalt (III) complexes of α -hydroxy acids were prepared using Fan and Gould. Double distilled (deionised and CO_2 free) water was used as a solvent and HClO_4 (E. Merck, India 95%) was standardized using standard sodium carbonate (BDH. AR) solution with methyl orange as an indicator. For nicotinium dichromate (NDC) oxidation of Co(III) complexes of bound and unbound ligands, the rate measurements were made at $33 \pm 0.2^\circ\text{C}$ in 100% aqueous medium. The temperature was controlled by electrically operated thermostat.

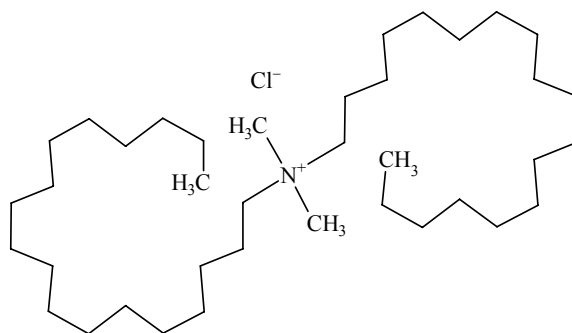
Preparation of nicotinium dichromate (NDC)

Nicotinium acid (7.38 g, 60 mL) was added to chromium trioxide CrO_3 (12 g, 120 mol), dissolved in water (12 mL at 0°C ice water bath) with vigorous stirring. After 15 min, acetone (100 mL at 0.5°C) was added to the resulting red orange suspension and the mixture was stirred at $0-5^\circ\text{C}$ for 15 min. The product was filtered off and washed with acetone (4×50 mL) and dichloromethane (25 mL) affording nicotinium dichromate (11 g) as yellow solid. M.P. 216°C .

Dimethyl dioctadecyl ammonium chloride (DDAC).

It is a cationic surfactant. Molecular formula: $\text{C}_{38}\text{H}_{80}\text{ClN}$. (Molecular weight 586.50). Dimethyl dioctadecyl ammonium chloride (DDAC), or distearyl dimethyl ammonium chloride, is a quaternary ammonium salt consisting of a nitrogen atom substituted with two methyl groups and two octadecyl groups. The long-chain hydrocarbon groups combined with the ionic nature of the amine group enables it to act as a surfactant or a detergent. In household products, it may be found as an ingredient in fabric softeners, cosmetics, and hair conditioners, in which it is added primarily for its antistatic effects. It is also used in organic synthesis as a phase transfer catalyst to increase reaction rates in a two-phase organic-water system.

Molecular structure



It's skin irritant and corrosive to eyes. Usually it not available is commercially as isolated compound, but as the main constituent of dihydrogenated tallow dimethyl ammonium chloride, that is a mixture of dialkyl dimethyl ammonium compounds with varying length carbon chains of C12 to C20. The pure compound caused moderate skin irritation and corrosive effects to eyes, based on rabbit studies.

RESULTS AND DISCUSSION

Kinetic study of the oxidation of pentaammine cobalt (III) complexes of α -hydroxy acid by nicotinium dichromate (NDC) in micellar medium and dependence of rate on nicotinium di chromate (NDC) concentration in micellar bound ligand has been studied. The rate of nicotinium di chromate (NDC) oxidation of pentaammine cobalt (III) complexes of α -hydroxy acids depends on NDC concentration, the specific rate calculated remains constant, and graph was linear. From the slope of these graphs, the calculated specific rate

agree with rate equation suggesting first order dependence on nicotinium di chromate (NDC) concentration. When the concentration of NDC was varied from 1.00 to 5.00×10^{-3} mol dm⁻³ at a fixed [Cobalt^(III)] and [HClO₄]. A specific rate remains constant. Then the rate of disappearance of Cr(VI) is given by Eq. (1).

$$-d[\text{Cr (VI)}] / dt = k_1[\text{Cr (VI)}] \quad \dots(1)$$

Dependence of rate on cobalt (III) concentration

The rate of NDC oxidation of [(NH₃)₅Co-L]²⁺ complexes of mandelic, lactic and glycolic acid, depends nearly on the first power of the concentration of Co(III) complexes. Graph of log k versus log [Co^(III)] are linear with slope nearly equal to one. Hence, the rate law for the Cr (VI) oxidation of cobalt (III) bound of α -hydroxy acids are given by Eq. (2).

$$-d[\text{Cr (VI)}] / dt = k_2[\text{Cr (VI)}][\text{Co(III)}] \quad \dots(2)$$

Dependence of rate on nicotinium dichromate (NDC) concentration in micellar for α -hydroxy acid

At a given initial concentration of NDC in micellar medium, the oxidation varies proportionately with the concentration of α -hydroxy acids and the rate of this reaction exhibits first order dependence on α -hydroxy acids concentration. Plot 3 of log k₁ versus (α -hydroxy acids) are linear with slope, nearly equal to one, indicating the order is with respect to α -hydroxy acids. Hence, the rate of disappearance of Cr (VI) is given by Eq. (3).

$$-d[\text{Cr (VI)}] / dt = k_2[\text{Cr (VI)}][\alpha\text{-Hydroxy acid}] \quad \dots(3)$$

Comparison of rates of oxidation of pentaammine cobalt (III) complexes of both bound and unbound α -hydroxy acids by NDC

The specific rate of the Co(III) lactato complex reacts faster than Co(III) mandelato and Co(III) glycolato complexes, because if the reaction proceeds through a performed bromated ester, then the rate of oxidation of C-H cleavage have been enhanced resulting in an increase in the rate of oxidation of Co(III) complex. Also chromate ester formation may be sterically hindered in the case of mandelato complex. The absence of such a steric retardation and enhanced acidity of methyl proton in the lactato complex may account for its greater reactivity. In this work, an induced electron transfer reaction has been attempted with NDC and pentaammine cobalt (III) complexes of α -hydroxy acid in the presence of micelle. The reaction exhibits second order kinetics and in the case of mandelato complex, the amount of cobalt (III) reduced corresponds to nearly initial concentration while nearly 70% of cobalt (III) is converted to keto acid cobalt (III) mandelato complex. The intermediate radical formed dissociated in a nearly synchronous manner with C-C bond cleavage only to the extent of 25% and rest of its proceeding with C-H fission giving keto acid, cobalt (III) complex. With increase in micelle concentration, an increase in the rate was observed. The dimethyl dioctadecyl ammonium chloride (DDAC) was added to enhanced the rate of oxidation. The same trends was observed in lactato and glycolato cobalt (III) complex.

Dependence of rate on the concentration of cobalt (III) bound α -hydroxy acids

At a particular NDC concentration with increasing mandelato/lactato/glycolato cobalt (III) concentration in the range 1.00×10^{-3} mol dm⁻³, there is a proportional increase in the rate of oxidation. The slopes of nearly unity is obtained from a linear graph of logarithm of specific rate (k₁ in s⁻¹) versus logarithm of cobalt (III) concentration in each case. It suggests first order dependence of rate law for the NDC oxidation of cobalt (III) bound α -hydroxy acids as given by Eq. (4).

$$-d[\text{Cr (VI)}] = k_2 [\text{Cr (VI)}] [\text{Co (III)}] \quad \dots(4)$$

$$[\text{NDC}] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{HClO}_4] = 1.00 \text{ mol dm}^{-3}$$

$$\text{Temperature} = 33 \pm 0.2^\circ\text{C}$$

Kinetic study of the oxidation of α -hydroxy acids by NDC

The kinetics of NDC reaction with α -hydroxy acids has been studied in the presence of $1.00 \text{ mol dm}^{-3} \text{ HClO}_4$ and in the absence of micelles at a temperature of $33 \pm 0.2^\circ\text{C}$.

Dependence of rate on nicotinium di chromate (NDC) concentration

Under identical conditions, NDC oxidations of unbound ligand mandelic acid has been studied to look in to the consequence of ligation with cobalt (III) centre. In any specific run, from the rate of disappearance of NDC, the specific rates calculated using integrated first order rate equations are constant.

Also graphs of logarithm of NDC concentration versus calculated, agree well with those calculated from integrated first order dependence on NDC oxidation of unbound α -hydroxy acids. Hence the rate law is given by Eq. (5).

$$-d[\text{Cr (VI)}]/dt = k_1[\text{Cr (VI)}] \quad \dots(5)$$

When the concentration of nicotinium di chromate (NDC) was varied from 1.00 to $5.00 \times 10^{-3} \text{ mol dm}^{-3}$, at a fixed α -hydroxy acids, $[\text{HClO}_4]$ and micellar concentration, the specific rates remain constant in keeping with the first dependence on nicotinium dichromate (NDC) concentration. Under identical conditions, the effect of changing unbound α -hydroxy acids concentration has been studied in the range of $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ with all the substrates in the absence of micellar medium. There is a monotonic increase in the rate of nicotinium dichromate (NDC) oxidation with unbound α -hydroxy acids with increasing concentration substrates.

Also a graph of logarithm of specific rate (k_1 in s^{-1}) versus logarithm of α -hydroxy acids concentration is linear with a slope nearly equal to unity, the rate law of nicotinium dichromate (NDC) oxidation of unbound α -hydroxy acids is similar to cobalt (III) bound ligands.

$$-d[\text{Cr (VI)}] = k_2 [\text{Cr (VI)}][\alpha\text{-hydroxy acid}] \quad \dots(6)$$

Earlier studies on induced electron transfer reaction involved mainly one equivalent oxidant, Ce (IV) and pentaammine cobalt (III) complexes, $[(\text{NH}_3)_5 \text{Co (III)-L}]^{2+}$ with bound ligands featuring conjugated fragments. In all these reactions, ultimately, reduction at cobalt (III) centre have been achieved due to the generation of a radical at the bound organic ligand by the one equivalent oxidant. But the percentage of cobalt (III) formed differed from reaction to reaction due to the partitioning of the reaction paths.

An induced electron transfer reaction has been attempted presently with nicotinium dichromate (NDC) and pentaammine cobalt (III) complexes of α -hydroxy acids in the presence of dimethyl dioctadecyl ammonium chloride (DDAC) medium and also in the absence of dimethyl dioctadecyl ammonium chloride (DDAC) medium. The reaction exhibits second order kinetics and in the case of mandelato complex, the amount of cobalt (III) reduced corresponding nearly 20 initial concentration and the amount of cobalt (II) PhCHO and CO_2 formed is nearly 20%. While nearly 75% of it is converted to keto acid cobalt (III)

complex, possibly Cr (VI) induced electron transfer in cobalt (III) mandelato complex, the intermediate radical formed dissociate in a synchronous manner with C-C bond cleavage only to the extent of 20%. The cobalt (III) bound α -hydroxy acid gets oxidized at higher rate than that of unbound ligand. With increasing dimethyl dioctadecyl ammonium chloride (DDAC) concentration, an increase in the rate was observed. Added dimethyl diocta decyl ammonium chloride (DDAC) enhances the rate of oxidation of reaction.

Similar trends has been observed in lactate and glycolato cobalt (III) complexes.

Table 1: Dimethyl dioctadecyl ammonium chloride (DDAC)

Time (sec)	$10^3 (a-x) \text{ mol dm}^{-3}$	$10^4 k_1 (\text{s}^{-1})$	$4 + \log (a-x)$
240	4.28	4.410	4.6314
480	3.49	4.421	4.5428
720	2.68	4.436	4.4281
960	1.91	4.447	4.2810
1200	1.58	4.453	4.1986
1440	1.23	4.462	4.0899
1680	1.13	4.474	4.0530
1920	0.81	4.482	3.9084
2160	0.69	4.490	3.8388

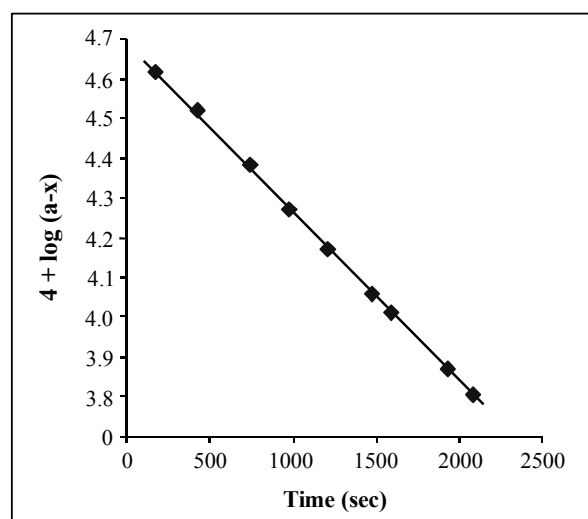


Fig. 1: First order dependence plots

Table 2: Dimethyl dioctadecyl ammonium chloride (DDAC)

$10^2 [(\text{NH}_3)_5\text{Co}^{(\text{III})} - \text{L}] \text{ mol dm}^{-3}$	$10^4 k_1 (\text{s}^{-1})$	$10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$4 + \log k_1$
L = Lactato			
1.00	3.36	3.36	4.5263
2.00	4.99	3.30	4.6981

Cont...

$10^2 [(NH_3)_5Co^{(III)}-L] \text{ mol dm}^{-3}$	$10^4 k_1 (\text{s}^{-1})$	$10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$4 + \log k_1$
3.00	7.15	3.39	4.8543
4.00	10.52	3.36	5.0220
5.00	15.45	3.37	5.1889
M = Mandelato			
1.00	2.84	2.84	4.4533
2.00	3.58	2.86	4.5538
3.00	4.88	2.84	4.6884
4.00	6.16	2.85	4.7895
5.00	7.88	2.85	4.8965
G = Glycolato			
1.00	1.91	1.90	4.2810
2.00	2.59	1.91	4.4132
3.00	3.50	1.93	4.5440
4.00	4.82	1.91	4.6830
5.00	6.66	1.93	4.8234

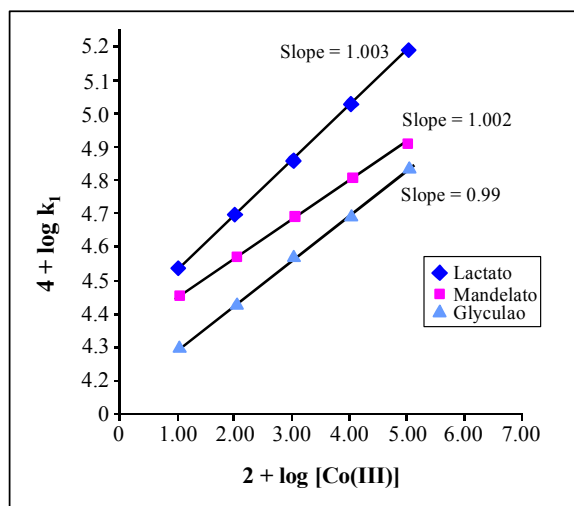


Fig. 2: Dependence of rate on $[Co^{(III)}]$ in dimethyl dioctadecyl ammonium chloride (DDAC)

Table 3: Dimethyl dioctadecyl ammonium chloride (DDAC)

Time (sec)	$10^3 (a-x) \text{ mol dm}^{-3}$	$10^4 k_1 (\text{s}^{-1})$	$4 + \log (a-x)$
240	1.26	2.651	4.1003
480	1.01	2.653	4.0043
720	0.79	2.644	3.8976
960	0.58	2.761	3.7634
1200	0.47	2.656	3.6720

Cont...

Time (sec)	$10^3 (a-x) \text{ mol dm}^{-3}$	$10^4 k_1 (\text{s}^{-1})$	$4 + \log (a-x)$
1440	0.36	2.666	3.5563
1680	0.27	2.673	3.4313
1920	0.20	2.682	3.3010
2160	0.16	2.689	3.2041

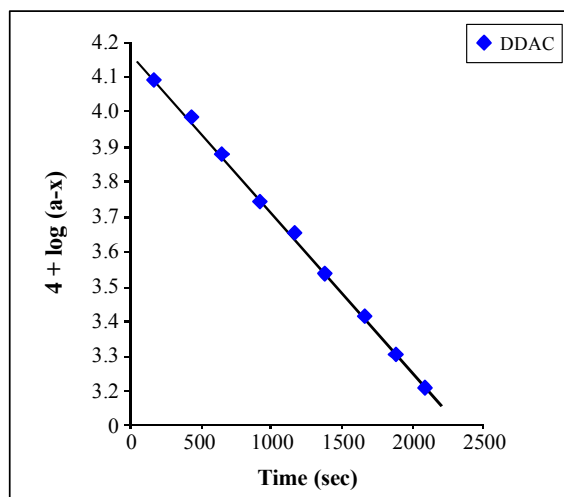


Fig. 3: First order dependence plots

Table 4: Dimethyl dioctadecyl ammonium chloride (DDAC)

$10^2 [(\text{NH}_3)_5\text{Co}^{(\text{III})} - \text{L}] \text{ mol dm}^{-3}$	$10^4 k_1 (\text{s}^{-1})$	$10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$4 + \log k_1$
L = Lactato			
1.00	1.24	1.24	4.0934
2.00	1.92	1.24	4.2833
3.00	2.68	1.24	4.4281
4.00	4.11	1.24	4.6138
5.00	6.36	1.24	4.8034
M = Mandelato			
1.00	0.97	0.97	3.9867
2.00	1.61	0.97	4.2060
3.00	2.10	0.97	4.3221
4.00	3.50	0.97	4.5440
5.00	5.38	0.97	4.7307
G = Glycolato			
1.00	0.52	0.52	3.7242
2.00	0.90	0.52	3.9542
3.00	1.23	0.52	4.0899
4.00	1.91	0.52	4.2810
5.00	3.03	0.52	4.4814

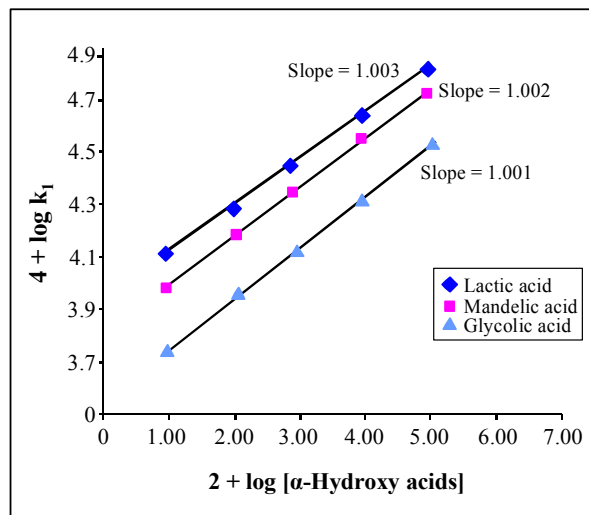


Fig. 4: Dependence of rate on [α-Hydroxyacids] in dimethyl dioctadecyl ammonium chloride (DDAC)

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