

ORIGINAL ARTICLE

**PYRIDINIUM BROMO CHROMATE(PBC) OXIDATION OF COBALT (III) COMPLEXES OF
-HYDROXY ACIDS**

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ABSTRACT

Pyridiniumbromochromate (PBC) oxidation of pentaammine cobalt(III) complexes of mandelic, lactic and glycolic acids have been studied in the presence of $0.40 \text{ mol dm}^{-3} \text{HClO}_4$. The rate of oxidation shows first order kinetics each in Co(III) complex and (PBC). Various thermodynamic parameters have been evaluated. The stoichiometry of reaction of pyridiniumbromochromate with $[\text{Co}(\text{NH}_3)_5\text{L}]^{2+}$ complexes of -hydroxy acids yield Co(II) and a carbonyl compound to the extent of 13%. The other product of the reaction, phenylglyoxal cobalt(III) complex, is obtained in 87% yield by a two electron oxidation.

.Keywords Pyridiniumbromochromate (PBC), induced electron transfer, pentaamminecobalt(III) complex

1.INTRODUCTION

The oxidation of aldehydes, organic sulfides and alcohols by pyridiniumbromochromate has been the subject of an intensive investigation by Banerji and Co-workers¹⁻⁴. Pyridiniumbromochromate is a mild and selective oxidant that has been used in the oxidation of a number of organic compounds⁵. Hydroxy acids can be oxidized, either like alcohols⁶ yielding corresponding oxoacids. The induced electron – transfer reactions, in which a Co(III) –bound organic ligand suffers a net two-electron oxidation initiated by an external oxidant such as Ce(IV), yielding a carbon radical intermediate, have been studied in detail by Taube and Coworkers⁷. The cation radical formed subsequently undergoes an intramolecular second one-electron transfer, resulting in the reduction at the cobalt (III) center without altering the carbon skeleton of the ligand⁸. The present work concern the highly reactive oxidant pyridiniumbromochromate oxidation of pentaamminecobalt(III) complex of mandelic, lactic and glycolic acids in aqueous medium.

2.MATERIALS AND METHODS

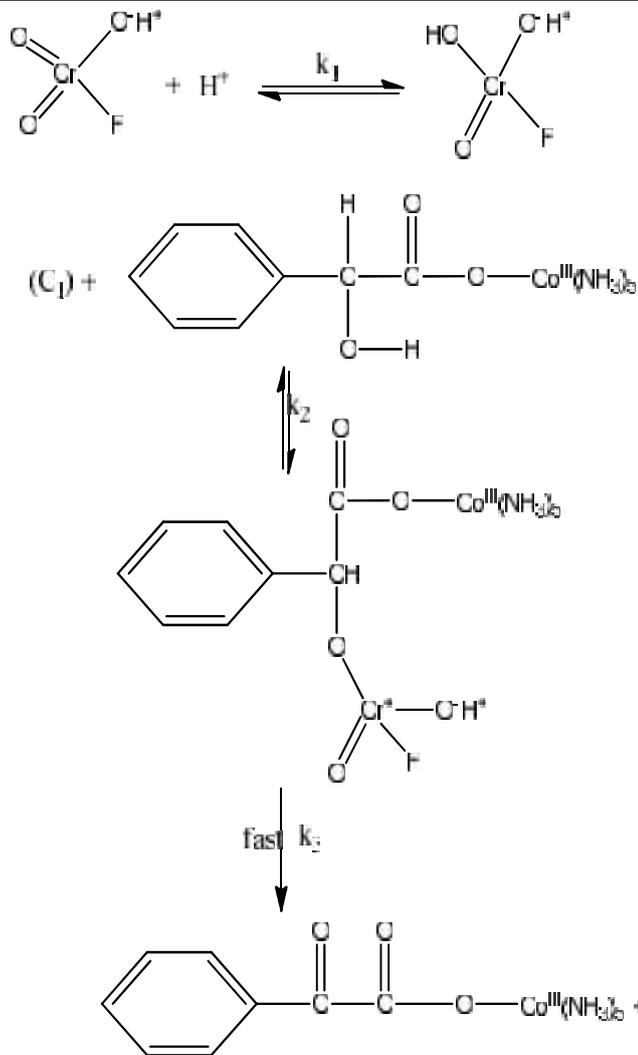
The pentaamminecobalt(III) complex of -hydroxy acids were prepared as their perchlorates following the procedure

of Fan and Gould⁹. Mandelic, lactic and glycolic acids (Aldrich) used were of extra pure variety and physical constants agreed with literature values. The pyridiniumbromochromate(PBC) was prepared by the reported method¹⁰ and its purity checked by Iodometric method. Cobalt analysis⁹ of these complexes are in agreement with the assigned structures.

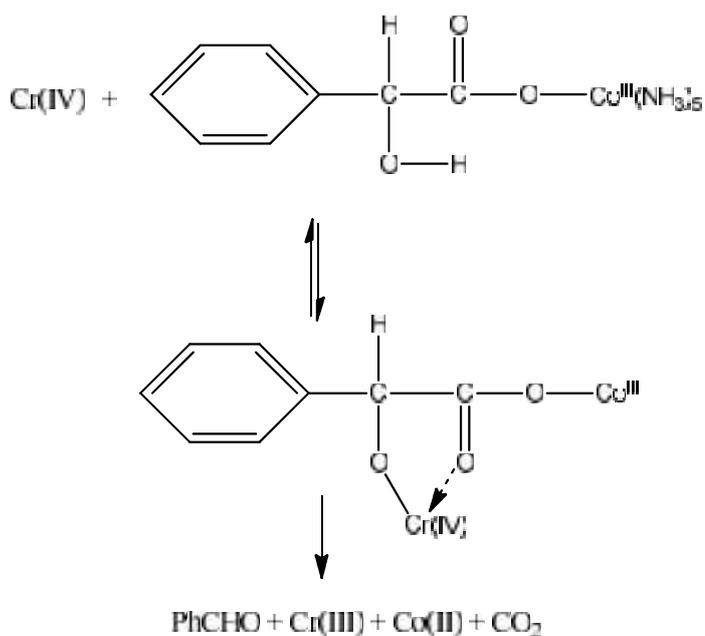
Product analysis

Kinetic studies on the pyridiniumbromochromate of pentaamminecobalt(III) complex of -hydroxy acids has been made in aqueous perchloric acids medium under pseudo-first oxidation by maintaining a large excess the Co(III) complex over oxidant Co^{II} was estimated after 9 half lives of reaction in the results of excess of PBC, by dilution 10-fold with conc. HCl, allowing evaluation of chlorine to cease, and then measuring the absorbance at 692 nm ($\epsilon=560$). This corresponded to nearly 13% of the initial concentration of the cobalt (III) complex. Absorbance with blank solutions containing PBC were also measured to apply suitable correction which came to less than 2% of the absorbance done to the chlorocomplex of Co^{II} . The other products of the oxidation involving $(\text{NH}_3)_5\text{Co}^{\text{III}}$ -mandelate or $(\text{NH}_3)_5\text{Co}^{\text{III}}$ -lactate or $(\text{NH}_3)_5\text{Co}^{\text{III}}$ -glycolate as the reactants, was found to be $(\text{NH}_3)_5\text{Co}^{\text{III}}$ -phenylglyoxalate or $(\text{NH}_3)_5\text{Co}^{\text{III}}$ -pyruvate respectively. After the reactions were complete, the reaction mixtures were neutralized to pH = 6.0 by the addition of a

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Scheme-1



Scheme-2

4.CONCLUSION

Induced electron transfer reaction has been attempted presently with Pyridiniumbromochromate (PBC) and pentaammine cobalt(III) complexes of α -hydroxy acids like Mandelic, lactic and glycolic acids in perchloric acid medium. The reaction exhibits second order kinetics and in the case of mandelato complex. The amount of cobalt(III) reduced corresponds to nearly 13% of initial concentration and amount of cobalt(II), PhCHO and CO_2 formed is nearly 13%. In all the cases, ligation of cobalt(III) center reduces the rate of PBC oxidation of ligands due to the electrostatic influence of cobalt(III) center.

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