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Electrochemical preparation of Co(III) acetate and its application in organic syntheses

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The Co(III) acetate in acetic acid medium containing alkali metal acetate can be generated electrochemically in a divided cell with an efficiency of 92%. This solution can be used effectively for acetylation of aromatic hydrocarbons.

Key words: Electrochemical oxidation, cobalt(III) acetate preparation, synthesis of acetylated organic compounds

INTRODUCTION

The Co(III) is a versatile oxidant under acidic conditions whose formal potential can be varied due to its strong complexation property. This behaviour has led its utility in indirect electrosyntheses [1-4]. The literature on preparation and application of Co(III) acetate is exhaustive, but however, no practical method is available. In this study we report the electrochemical oxidation of Co(II) to Co(III) in acetic acid sodium acetate medium at graphite electrode. Table I gives the effect of various parameters on generation/regeneration of Co(III) acetate.

TABLE-I: Cell parameters for the generation of Co(III) from Co(II) acetate tetrahydrate (0.2M) in 1M sodium acetate trihydrate at graphite anodes (10 × 3.5) cm^2 at a constant c.d. of 42 $mA.cm^{-2}$

	Acetic acid concentration	Undivided cell		Divided cell (H-type)		Divided cell porous pot separator		After 1st regeneration Yield of Co^{3+} %	After 2nd regeneration Yield of Co^{3+} %
		Cell voltage (V)	Yield of Co^{3+} %	Cell voltage (V)	Yield of Co^{3+} %	Cell voltage (V)	Yield of Co^{3+} %		
I	25% CH_3COOH + 75% H_2O	3.5	29	15.0	54	4.5	51	-	-
II	50% CH_3COOH + 50% H_2O	5.0	32	17.5	58	6.0	54	-	-
III	75% CH_3COOH + 25% H_2O	6.0	40	22.5	62.5	8.0	58	54	56
IV	100% glacial acetic acid (A)	9.0	50	28.5	68	10.0	65	62	61
B.	" + Co(II) (0.1M)					8.0	40		
C.	" + Co(II) (0.3M)					11.0	70		
D.	" + Co(II) (0.5M)					11.0	81		
E.	" + Co(II) (0.5M) (anhydrous)					14.0	92		

RESULTS AND DISCUSSION

The study reveals that the Faradaic yield of Co(III) increases with the decrease in water content of the system and under nearly anhydrous condition, the efficiency of oxidation is 92%. It has been observed that higher concentration of depolarizer increases the current efficiency of the system, but the concentration greater than 0.2M of Co(II) leads to the precipitation of Co(III) acetate eventually due to the formation of dimeric and trimeric species. Due to higher cell voltages it was not found practical to study the regeneration of spent oxidant under anhydrous conditions. From practical point of view, 89% glacial acetic acid containing 0.2M Co(II) and 1M sodium acetate was a highly suitable medium. The study on current density on oxidation suggests that lower current densities are highly favourable but from space- time-yield point of view the c.d. of 42mA.cm^{-2} was found to be more suitable in this parallel plate type of reactor. At higher c.d. 750 mA.cm^{-2} the current efficiencies fall obviously due to the oxidation of water which leads to the formation of very many oxygenated products causing the decomposition of electrolyte itself. However, no attempt has been made to quantify these findings.

An attempt has also been made to study the effect of temperature, concentration of toluene, Co(III) and synergetic effect of various anions like Cl^-, Br^-, ClO_4^- and So_4^{--} on acetylation reaction of toluene to benzyl acet The best results were obtained at 360K at ambient press in presence of 1% KBr. Among all these synerg anions the Br^- does not interfere in regeneration of sp oxidant. The efficiency of acetylation reaction was 9 The reaction can be written as:

$$ArCH_3 + Co(III) \longrightarrow [ArCH_3]^+ \longrightarrow ArCH_2 + H^+ + Co$$

$$ArCH_2 \underset{-Co(II)}{\overset{+Co(III)}{\longrightarrow}} ArCH_2^+ \overset{HOAC}{\longrightarrow} ArCH_2OAC + H^+$$

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