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An efficient method for the electrochemical preparation of Co(III) acetate

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The electrochemical oxidation of Co^{2+} to Co^{3+} in acetic acid medium has been effectively and efficiently carried out in a divided cell at a graphite electrode with a current efficiency of 92% using a porous pot as separator. Using Co^{3+} acetate, oxidation of toluene to benzyl acetate was successfully carried out.

1. Introduction

Co^{3+} is a versatile oxidant whose oxidation potential varies considerably due to its strong complex formation tendency and it has found ready applications in indirect electrosynthesis, particularly for the oxidation/acetylation of side chains of an aromatic ring [1–4]. Oxidation involving cobaltic acetate is highly susceptible to the medium of the reaction and the organic substrate [5–9].

The preparation of cobaltic acetate by chemical methods and its application have been previously reported (10, 11). However, studies on the electrochemical preparation of cobaltic acetate have been limited [12–14]. It has been reported that electrolysis of aqueous solution containing cobaltous acetate and potassium acetate at a platinum electrode yields $(HOAc)_4Co(OH)_2Co(AcOH)_4^{4+}$ whereas in glacial acetic acid medium the monomeric $Co(OAc)_3$ and trimeric $Co_3(OAc)_9$ are formed. The ozonization of cobaltous acetate in glacial acetic acid has been reported to give $Co_2(OAc)_4(HOAc)$ [15]. This indicates that the formation of a bridged hydroxyl complex by an electrochemical method can be avoided and may find more use in synthetic/analytical chemistry.

This report describes an inexpensive method for the electrochemical preparation of cobaltic acetate in acetic acid medium in a divided and undivided cell at a graphite electrode and its application for the preparation of benzyl acetate from toluene and electrochemical regeneration of the spent oxidant.

2. Experimental details

The laboratory scale experiments were carried out in an undivided and in a divided cell. The experiments in a divided cell were carried out either by using an H-cell separated by a G-3 glass frit or using a porous pot as a diaphragm. The experiments with the undivided cell were carried out in a tall beaker. In all the experiments graphite electrodes were used (anode area = $35\,cm^2$; cathode area = $16.5\,cm^2$). The experimental data were collected by varying the concentration of cobaltous acetate tetrahydrate, anhydrous sodium acetate and glacial acetic acid and the anodic current density. The current efficiency of the system was calculated by taking into account the total current passed over a given time and the yield of Co^{3+}.

The polarization and cyclic voltammetric studies were carried out on a Tacussel bipad potentiostat coupled with a PAR programmer 175 using a three compartment cell at either platinum or polished graphite electrodes ($0.25\,cm^2$). All potentials were measured against a saturated calomel electrode (SCE).

All the chemicals used were of BDH/Lobachemie AnalaR grade. Toluene was used after double distillation and was free from other alkyl substituted benzenes.

The u.v.-visible spectra (electronic spectra) of Co^{3+} acetate generated was recorded using a Hitachi U-3400 spectrophotometer.

2.1. *Oxidation of toluene*

The oxidation of toluene by Co(III) was carried out at 90° C under constant stirring with a magnetic stirrer for 2 h in a three necked flask fitted with a reflux condenser, a dropping funnel and a thermometer. The completion of the reaction was indicated by the green solution turning violet.

3. Results and discussion

In the present study on the oxidation of Co(II) to Co(III) acetate, it has been observed that the divided cell gives better current efficiency for Co(III) generation at the graphite anode. In an undivided cell, Co(II) is reduced to cobalt and deposited as a bright thin layer on the cathode.

3.1. *Preparation of Co(III)*

Figure 1 shows the effect of acetic acid concentration on the yield of Co(III) acetate in an undivided cell as well as in an H-cell. The results indicate that the efficiency of Co(III) generation increases with increase

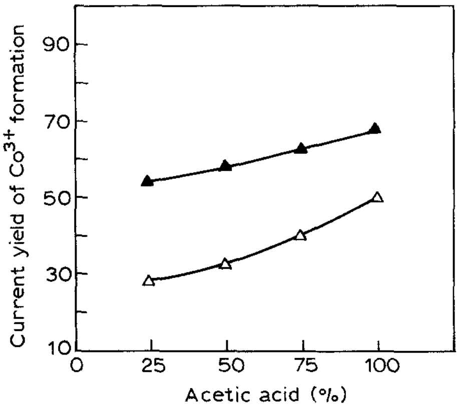

Fig. 1. Effect of acetic acid concentration on the electro-chemical generation of cobaltic acetate. (△) Undivided cell; (▲) divided cell.

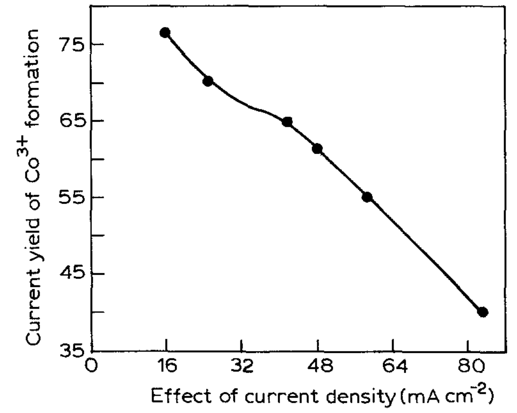

Fig. 2. Effect of anode current density on the electro-chemical generation of cobaltic acetate.

in concentration of acetic acid. The variation of current density (c.d.) with yields of Co(III) generated (Fig. 2) indicates that lower current densities are favourable, therefore the electrogeneration of Co(III) acetate was carried out at a current density of 42 mA cm^{-2}. Though the primary anodic reaction is the oxidation of Co(II) to Co(III), at higher anodic current densities, *viz.* 100 mA cm^{-2}, the current efficiency falls due to side reactions such as the oxidation of acetate ion to CO_2.

The effect of the concentration of Co(II) acetate on the electrochemical generation of Co(III) acetate was investigated by keeping other parameters constant (Fig. 3). It has found that the current efficiency (c.e.) is 40% at 0.1 M, 62.5% at 0.2 M and 81% at 0.5 M concentration of Co(II) acetate. The observation reveals that at concentrations above 0.2 M, the precipitation of Co(III) acetate begins due to the formation of polymeric cobaltic acetate [14], which prevents the galvanostatic electrolysis due to increase in cell voltage. Therefore, to obtain a homogeneous solution a 0.2 M concentration of Co(II) was used.

Table I gives the comparative study using divided and undivided cells for Co(III) formation in the presence of varying amounts of acetic acid. The results reveal that during regeneration of spent oxidant the current efficiency falls from 65 to 62%. This fall in efficiency may be attributed to adsorption of organic impurities on electrode surface.

Figure 4 shows the graph of Faradaic efficiency of generation of Co(III) acetate in a divided cell at different concentrations of acetic acid. It can be seen that on passing two Faradays of charge, the yields lie between 84 and 86% whereas on passing 1 Faraday of charge, the yield lies between 54 and 68%. The possible inference is that Co(III) acetate dimer (insoluble) is precipitated at the anode surface and thus limits diffusion of Co(II) to the anode surface. The observation reveals that Co(III) acetate dimer formation can be checked by lowering the acetic acid concentration. The lowering of acetic acid concentration, however, adversely affects the stability of Co(III) as has been observed by keeping electro generated Co(III) acetate in 25% acetic acid solution, which completely turns to Co(II) in 160 h under ambient laboratory conditions. In contrast, the solution of Co(III) acetate electro generated in glacial acetic acid is quite stable for practical purposes, thus the initial Co(III) concentration of 65% reduces to 55% after storing for two months, therefore Co(III) preparation/regeneration was preferred in this medium.

Table 1. Cell parameters for the generation of Co(III) from Co(II) acetate tetrahydrate (0.2 M) *in* 1 M. *Sodium acetate trihydrate at a graphite anode* (10 *cm* × 3.5 *cm*) *at a constant current density of* 42 *mA* cm^{-2}.

		Undivided cell		Divided cell (H-type)		Divided cell using porous pot as separator		After 1st regeneration	After 2nd regeneration
		Cell voltage (V)	Formation of Co^{3+} (%)	Cell voltage (V)	Formation of Co^{3+} (%)	Cell voltage (V)	Formation of Co^{3+} (%)	Formation of Co^{3+} (%)	(%)
I	25% CH_3COOH + 75% H_2O	3.5	29	10.5	54	4.5	51	–	–
II	50% CH_3COOH + 50% H_2O	5.0	32	17.5	58	6.0	54	–	–
III	75% CH_3 COOH + 25% H_2O	6.0	40	22.5	62.5	8.0	58	54	56
IV	100% glacial acetic acid containing	9.0	50	28.5	68	10.0	65	62	61
	(a) Co(II) (0.1 M)	–	–	–	–	8.0	40	–	–
	(b) Co(II) (0.3 M)	–	–	–	–	11.0	70	–	–
	(c) Co(II) (0.5 M)	–	–	–	–	11.0	81	–	–
	(d) Co(II) (0.5 M) (anhydrous)	–	–	–	–	14.0	92	–	–

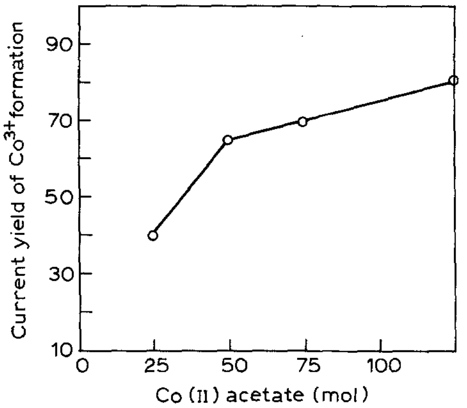

Fig. 3. Effect of concentration of Co(II) acetate on the electrochemical generation of Co(III) acetate.

3.2. *Cyclic voltammetry*

The cyclic voltammetric study using platinum, glassy carbon and finely polished graphite working electrodes reveals very interesting features. In all the experiments the cyclic voltammograms were recorded in the range 0.0 to 1.45 V with respect to SCE at variable scan rates from 10 to 200 mV s^{-1} (Fig. 5). In the forward scan, an anodic peak at 1.15 V appears corresponding to the oxidation of Co^{2+} to Co^{3+}. In the reverse scan no peak was observed. This highly irreversible behaviour is essentially due to the formation of polymeric cobaltic acetate species [14].

3.3. *Analysis*

Co^{3+} was determined iodometrically and spectrophotometrically. The spectrophotometric determination were carried out at 622 nm, where the maximum absorption for Co^{3+} occurs. The difference in results by these two methods was not more than 1.2%. The concentration of Co(III) ion was verified by direct potentiometric titration using platinum foil as indicator electrode. The toluene oxidation products were analysed by GLC after extraction with toluene. No trace of any aldehyde or benzoic acid was found.

3.4. *Oxidation of toluene*

The oxidation of toluene (0.06 M) by cobaltic acetate (0.125 M) in the presence of 1% potassium bromide at 90° C afforded 92% benzyl acetate and 0.5% phenyl propionic acid. Thus oxidation proceeds by the loss of a proton from the alkyl group attached to the aromatic ring. The reaction leading to the formation of benzylacetate can be written as follows:

$$\mathrm{ArMe + Co(III) \longrightarrow (ArMe)^{+\cdot} + Co(II)} \quad (1)$$

$$\mathrm{(ArMe)^{+\cdot} \longrightarrow ArCH_2^{\cdot} + H^+} \quad (2)$$

$$\mathrm{ArCH_2^{\cdot} + Co(III) \longrightarrow ArCH_2^+ + Co(II)} \quad (3)$$

$$\mathrm{ArCH_2^+ + HOAc \longrightarrow ArCH_2OAc + H^+} \quad (4)$$

The mechanism of formation of 1-phenylpropionic acid may be by way of oxidative decomposition of acetic acid by Co(III) which gives rise to carbon centred free radicals. Thus the reaction can be written:

$$\mathrm{Co(III)\,(OAc)_3 \longrightarrow Co(II)\,(OAc)_2 + CH_3COO^{\cdot}} \quad (5)$$

$$\mathrm{CH_3COO^{\cdot} \longrightarrow CH_3^{\cdot} + CO_2} \quad (6)$$

$$\mathrm{CH_3^{\cdot} + HOAc \longrightarrow CH_4 + {}^{\cdot}CH_2COOH} \quad (7)$$

This $^{\cdot}CH_2COOH$ can react with $^{\cdot}CH_2Ar$ to give Ar CH_2CH_2COOH. This type of reaction has also been reported using Mn(III) acetate [16].

The effect on the acetylation reaction of toluene to

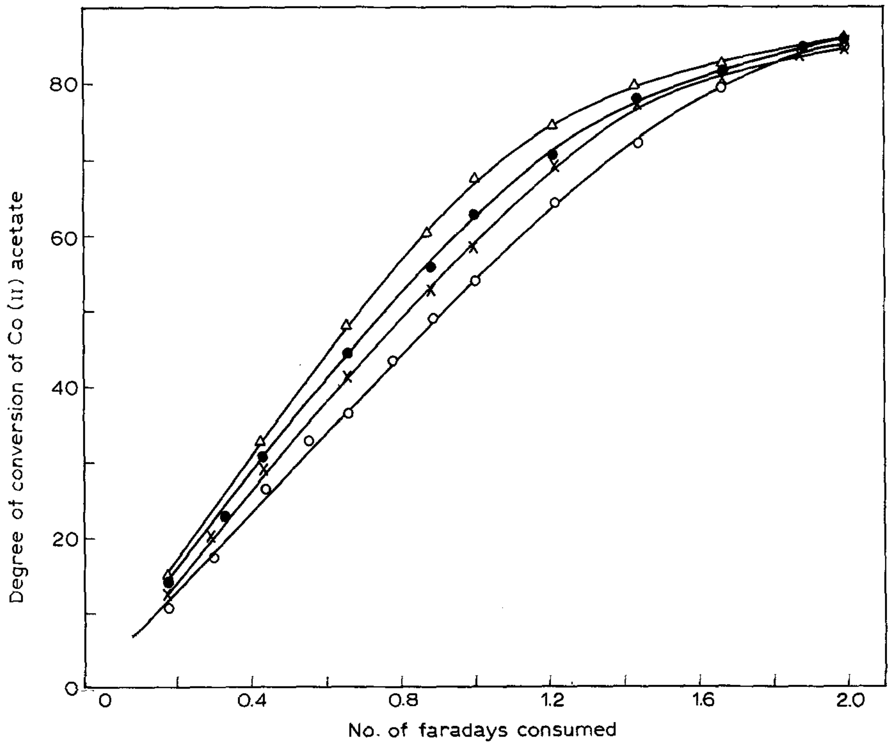

Fig. 4. Degree of conversion of Co(II) acetate to Co(III) acetate at various acetic acid concentrations: (○) 25% CH_3COOH; (×) 50% CH_3COOH; (●) 75% CH_3COOH; (△) 100% glacial acetic acid.

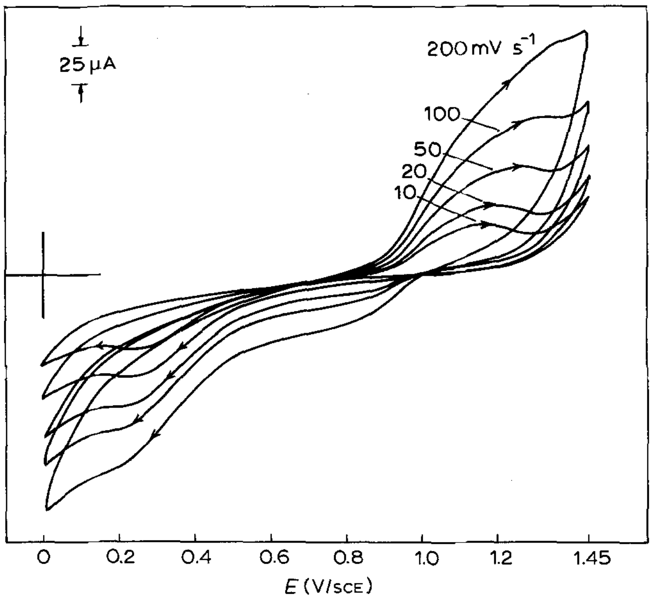

Fig. 5. Cyclic voltammogram of Co(III) acetate (generated in glacial acetic acid) at a Pt electrode (0.25 cm^2) at different scan rates against SCE.

benzyl acetate of various anions such as Cl^-, Br^-, ClO_4^-, SO_4^{2-} and PO_4^{3-} were studied. The best synergetic effect was observed on Br^- which does not interfere in the regeneration of Co(III).

The presence of bromide ion (1% KBr) has been found to considerably enhance the reaction rate. It has been reported by Kamiya [17] that $Br^\cdot$ is the chain carrying species and the reaction can be written as

$$Co(III) + Br^- \longrightarrow Co(II) + Br^\cdot \qquad (8)$$

$$Br^\cdot + ArMe \longrightarrow ArCH_2^\cdot + HBr \qquad (9)$$

The aryl radicals thus formed react with Co(III) as depicted in Equation 3 to yield $ArCH_2^+$ which reacts with acetic acid in the absence of oxygen to give an ester, Equation 4. The Co(II) thus obtained during the course of the reaction can be reoxidized to Co(III) acetate electrochemically.

4. Conclusion

The present study indicates that Co(III) can be prepared electrochemically in acetic acid medium using graphite electrodes with high current efficiency and can be used usefully for the oxidation of aliphatic side chains on an aromatic nucleus.

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