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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

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