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Electrosynthesis of lactic acid and 2,3-dimethyltartaric acid from pyruvic acid on lead cathode in aqueous medium

C. Martin, H. Huser, K. Servat and K. B. Kokoh*

LACCO 'Equipe Electrocatalyse'—UMR-CNRS 6503, University of Poitiers, Department of Chemistry,
40 Avenue du Recteur Pineau, 86022 Poitiers Cedex, France

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Abstract—Lactic and 2,3-dimethyltartaric acids have been synthesized from pyruvic acid by changing the nature of the supporting electrolyte and the electrode potential of lead cathode.

Electrocatalytic reduction of pyruvic acid (**1**) on lead electrode gives lactic acid (**2**) by hydrogenation of the carbonyl function (Fig. 1).

According to the nature of the electrolyte and the applied electrode potential, this reaction can compete with the production of 2,3-dimethyltartaric acid (**3**), which is due to an electropinacolization process (Fig. 2).

Various methods have been used to produce selectively **2** or **3** by the reduction of **1** and its derivatives. Hydrogenation product **2** is an useful intermediate in the biological sector, food and polymer industries.[1,2] In the literature, the carbonyl group has been transformed successfully by redox reduction to obtain **2** using sodium borohydride, C_2 symmetric diamines as chiral ligands and solutions of some cation perchlorates.[3–5] Up to 99% enantiomeric excess at 100% conversion was obtained. Compound **2** has also been synthesized from glucose by fermentative manufacture in the presence of externally added **1**.[6,7] Electroenzymatic route for producing **2** from **1** has been used extensively.[8–10] However, electrosynthesis of **3** from **1** in aqueous medium, which presents two asymmetric carbons, is very interesting in fundamental research to elucidate the distribution of the reaction products by diastereoselectivity. Indeed, in some cases,

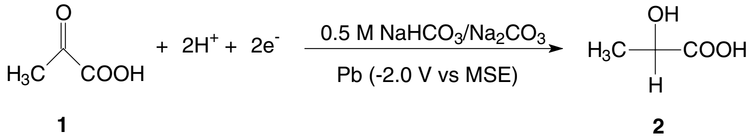

Figure 1. Electroreduction of pyruvic acid to lactic acid on lead cathode.

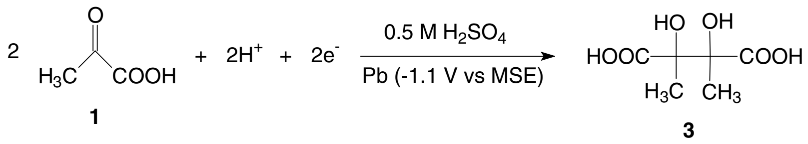

Figure 2. Electrohydrodimerization of pyruvic acid to 2,3-dimethyltartaric acid on lead cathode.

Keywords: Lead cathode; Electropinacolization; Pyruvic acid; Lactic acid; Dimethyltartaric acid.

* Corresponding author. Fax: +33 549 45 35 80; e-mail: boniface.kokoh@univ-poitiers.fr

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diastereo- and enantioselective pinacol coupling reaction of chiral α-ketoamides mediated by samarium diiodide (SmI_2) have afforded extremely high diastereoselectivities.[11,12] In 1958, the electrosynthesis of **3** was studied on Cu(Hg) in ammonia. The maximum yield obtained was close to 11%.[13] Negron-Mendoza et al. have described its production in one step from **1**, as raw material, using an ionizing radiation (γ-rays) as energy source. In these particular conditions, the best selectivity obtained was 73%.[14] Elsewhere, this carboxylic acid or its corresponding ester was synthesized using various organic substrates.[15–17] In this letter, we are interested in synthesizing **2** and **3** via the electrocatalytic reduction of **1**. In this connection, a key objective in the electrosynthesis is the development of the concepts and the methods of heterogeneous catalysis associated with those of interfacial electrochemistry. In aqueous medium, the electrocatalytic reduction of carbonyl compounds can lead mainly to the corresponding alcohol by hydrogenation and a pinacol by electrohydrodimerization.

Cyclic voltammetry was used to check the degree of purity of the reaction medium (0.5 M H_2SO_4 or 0.5 M $NaHCO_3/Na_2CO_3$) and that of the electrode. In sulfuric acid, an oxidation peak at $E = -0.8$ V versus $Hg/Hg_2SO_4/K_2SO_4$ satd (MSE: $E_{MSE} = 0.650$ V vs RHE at pH = 0) can be seen during the positive potential scan. This peak followed by a shoulder is attributed to $PbSO_4$ species, which desorb irreversibly from the electrode surface at $E = -1.05$ V versus MSE. A reduction wave of pyruvic acid begins in 0.5 H_2SO_4 at ca. −1.05 V versus MSE where $PbSO_4$ desorbs from the electrode surface. In carbonate buffer, the electrode surface is oxidized at −1.02 V versus MSE to $PbCO_3$ that were reduced reversibly during the negative potential sweep. In this medium, the reduction of pyruvic acid keeps the same shape, which starts at − 1.65 V versus MSE. Hydrogen evolution was observed at the lead cathode from −1.4 to −2.2 V versus MSE according to the nature of the supporting electrolyte. Therefore, the production of the latter should be competitive with that of **2** and **3** at more negative potentials (Fig. 3).

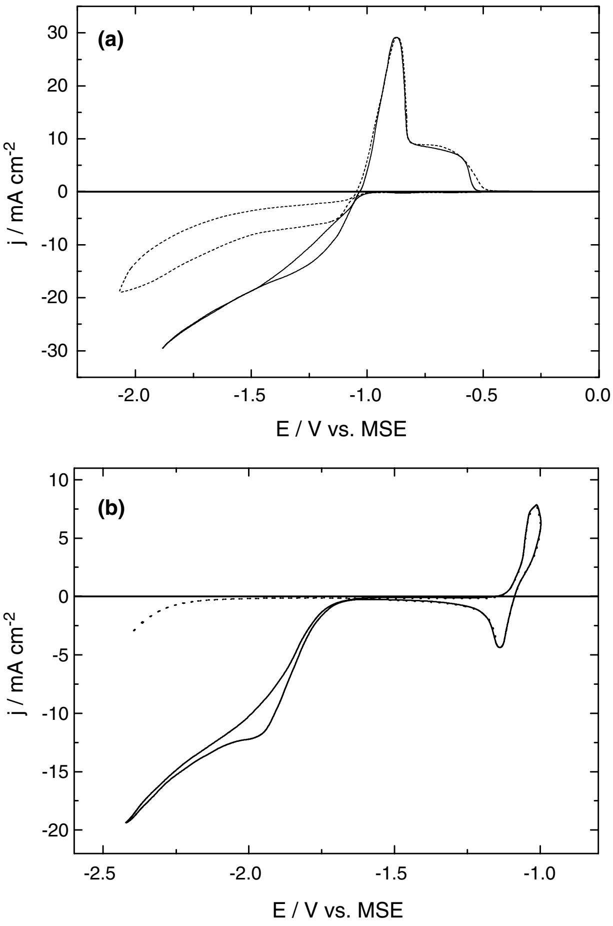

Figure 3. Voltammograms of Pb electrode recorded at 50 mV s^{-1}. (- - -) in different supporting electrolytes alone; (—) in the presence of 0.1 M of **1**. (a) 0.5 M H_2SO_4, (b) 0.5 M Na_2CO_3+0.5 M $NaHCO_3$.

In previous reports, a series of electrolyses of **1** were carried out at different fixed potentials on different cathodes materials and in various electrolytes. In sulfuric acid, we have studied the effects of the initial concentration of **1** and applied electrode potential on the distribution of the reaction products.[18] We have shown that **1** was mainly reduced to **2** in sulfuric acid medium on lead electrode when the initial concentration was about 0.1 M. Conversely, the electrohydrodimerization process was favoured when increasing the concentration of **1** and the electrode potential. In carbonate buffer, the selectivity towards **2** was higher in this medium and did not depend on the applied potential.[19] These results suggest that a high initial concentration of **1** favours the production of **3** as well as an increase of applied electrode potential. Moreover, concentrations less than/or ca. 0.1 M of **1** and potentials close to the hydrogen evolution promote the production of **2**. Based on this knowledge, various electrolyses[†] were performed on lead cathode. Firstly, **1** at two concentrations (0.1 and 0.5 M) was reduced at −2.0 V versus MSE in carbonate buffer in order to hydrogenate selectively to **2**. Other electrolyses were then performed in sulfuric acid where the formation of **3** at −1.1 V versus MSE was improved with initial concentrations of **1** higher than 0.5 M (Table 1).

According to our previous results, the best selectivity and the Faradaic yield of **2** ($\tau_{F2} = 91\%$ and $S_2 = 90\%$) were obtained in carbonate buffer with ca. 0.1 M of **1**.

In sulfuric medium, the increase of the initial concentration of **1** favoured the electrohydrodimerization to **3**. The conversion of **1** and the selectivity of **3** reach 84

[†] Electrochemical experiments were carried out in an undivided conventional three-electrode Pyrex cell (50 cm^3). Compound **1** was dissolved in aqueous supporting electrolyte (50 mL). The working electrode consisted of two lead plates having a geometric surface area of 32 cm^2. A 90% platinum/10% iridium perforated sheet and a saturated mercury/mercurous sulfate electrode (MSE) served as counter and reference electrodes, respectively. The electrolysis equipment was composed of a potentiostat (Wenking PGS 77) monitored by a microcomputer. The current intensity versus time was followed on a Kipp & Zonen BD 40 X-t recorder, and the quantity of electricity was measured directly by a coulometer (Wenking EVI 80).