

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

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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.

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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.<sup>1,2</sup> In the literature,

the carbonyl group has been transformed successfully by redox reduction to obtain **2** using sodium borohydride, C<sub>2</sub> symmetric diamines as chiral ligands and solutions of some cation perchlorates.<sup>3–5</sup> 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**.<sup>6,7</sup> Electroenzymatic route for producing **2** from **1** has been used extensively.<sup>8–10</sup> However, electro-synthesis 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,

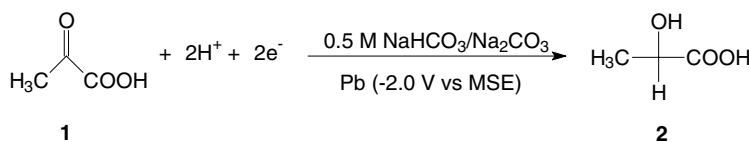


Figure 1. Electroreduction of pyruvic acid to lactic acid on lead cathode.

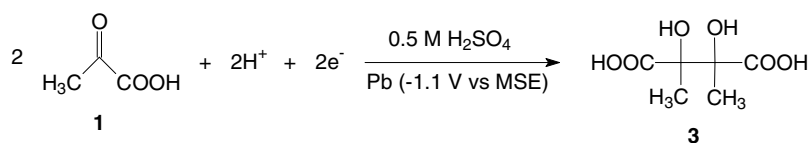


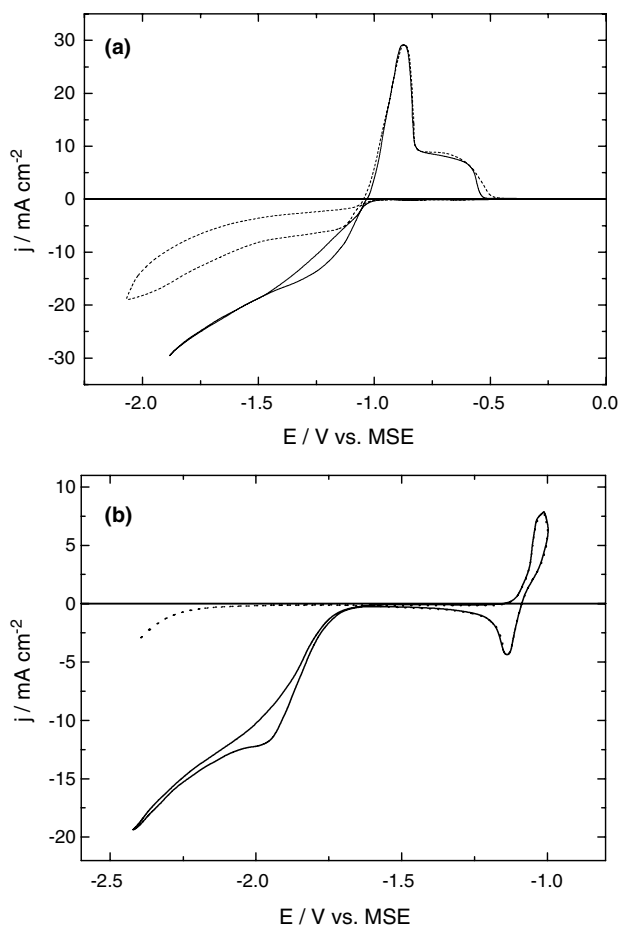
Figure 2. Electrohydrodimerization of pyruvic acid to 2,3-dimethyltartaric acid on lead cathode.

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

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diastereo- and enantioselective pinacol coupling reaction of chiral  $\alpha$ -ketoamides mediated by samarium diiodide ( $\text{SmI}_2$ ) have afforded extremely high diastereoselectivities.<sup>11,12</sup> In 1958, the electrosynthesis of **3** was studied on  $\text{Cu}(\text{Hg})$  in ammonia. The maximum yield obtained was close to 11%.<sup>13</sup> Negron-Mendoza et al. have described its production in one step from **1**, as raw material, using an ionizing radiation ( $\gamma$ -rays) as energy source. In these particular conditions, the best selectivity obtained was 73%.<sup>14</sup> Elsewhere, this carboxylic acid or its corresponding ester was synthesized using various organic substrates.<sup>15–17</sup> 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  $\text{H}_2\text{SO}_4$  or 0.5 M  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ ) and that of the electrode. In sulfuric acid, an oxidation peak at  $E = -0.8$  V versus  $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$  satd (MSE:  $E_{\text{MSE}} = 0.650$  V vs



**Figure 3.** Voltammograms of Pb electrode recorded at  $50 \text{ mV s}^{-1}$ . (---) in different supporting electrolytes alone; (—) in the presence of 0.1 M of **1**. (a) 0.5 M  $\text{H}_2\text{SO}_4$ , (b) 0.5 M  $\text{Na}_2\text{CO}_3 + 0.5$  M  $\text{NaHCO}_3$ .

RHE at  $\text{pH} = 0$ ) can be seen during the positive potential scan. This peak followed by a shoulder is attributed to  $\text{PbSO}_4$  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  $\text{H}_2\text{SO}_4$  at ca.  $-1.05$  V versus MSE where  $\text{PbSO}_4$  desorbs from the electrode surface. In carbonate buffer, the electrode surface is oxidized at  $-1.02$  V versus MSE to  $\text{PbCO}_3$  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).

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.<sup>18</sup> 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.<sup>19</sup> 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<sup>†</sup> 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** ( $\tau_{\text{F}2} = 91\%$  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

<sup>†</sup>Electrochemical experiments were carried out in an undivided conventional three-electrode Pyrex cell ( $50 \text{ cm}^3$ ). Compound **1** was dissolved in aqueous supporting electrolyte (50 mL). The working electrode consisted of two lead plates having a geometric surface area of  $32 \text{ cm}^2$ . 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).

**Table 1.** Electrocatalytic reduction of **1** on lead cathode in various electrolytes

Electrolyte	Potential (V vs MSE)	Initial concentration of <b>1</b> (M)	$X_1$ (%)	$S_2$ (%)	$\tau_{F2}$ (%)	$S_3$ (%)	$\tau_{F3}$ (%)	$n_{exp}$
0.5 M NaHCO <sub>3</sub> /Na <sub>2</sub> CO <sub>3</sub>	−2.0	0.09	92	90	91	—	—	2.96
		0.5	88	64	65	—	—	2.75
0.5 M H <sub>2</sub> SO <sub>4</sub>	−1.1	0.125	78	—	—	41	14	2.95
		0.3	79	—	—	54	23	2.19
		0.9	76	—	—	56	26	2.17
		1.7	84	—	—	69	33	2.05

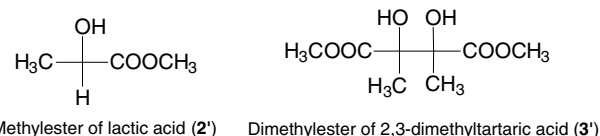
$X$ : yield of **1** ( $X$  (%) =  $\frac{C_0 - C_t}{C_0} \times 100$ );  $\tau_{Fi}$ : Faradaic yield ( $\tau_{Fi} = \frac{nFiC_i}{Q_{exp}}$ );  $S_{ii}$ : selectivity ( $S_{ii}$  (%) =  $\frac{1}{v_i} \times \frac{C_{ii}}{C_0 - C_t} \times 100$ ),  $n_{exp} = \frac{Q_{exp}}{F(C_0 - C_t)v}$ , where  $C_0$  is the initial concentration of **1**;  $C_t$  is its concentration at the time  $t$ ;  $C_{ii}$  is the concentration of the considered reaction product;  $n$  is the number of electrons,  $v_i$ , the stoichiometric number of the reaction product and  $v$  corresponds to the volume of solution,  $n_{exp}$  is the experimental number of electrons.

and 69%, respectively, on lead and at −1.1 V versus MSE.

Moreover, up to 2 M, no reduction of **1** is observed, which is probably due to the saturation of the lead surface by adsorbed molecules of **1**.

Analyses of the electrolyzed solutions by HPLC<sup>‡</sup> allowed to determine **2** and **3**. A chemical step of esterification is necessary to separate and isolate the reaction products. However, the aqueous electrolyte was removed at the end of electrolysis to recover dry organic compounds free from inorganic ions. The esterified corresponding products were separated by flash chromatography and then identified spectroscopically by GC–MS–MS,<sup>§</sup> ESI–MS high resolution,<sup>¶</sup> <sup>1</sup>H and <sup>13</sup>C NMR.<sup>||</sup> Compounds **2'** and **3'**<sup>20,21</sup> (Fig. 4) were obtained as the major products in different proportions according to the suitable electrolyte. The yields of isolated products **2'** (at −2.0 V vs MSE, in carbonate buffer with ca. 0.1 M of **1**) and **3'** (at −1.1 V vs MSE, in sulfuric acid with ca. 1.7 M of **1**) are 76% and 29%, respectively. Other side products, which were probably issued from the reduction of the carboxylic group of **1** were detected in small amounts.

It can also be noticed that **3'** exists in two different configurations **3'a** and **3'b** (racemic and meso forms), which were separated successfully but not yet assigned.

**Figure 4.**

In conclusion, we have shown that the electrocatalytic reduction of **1** on Pb cathode favours the selectivity of **2** or **3** by changing the nature of the supporting electrolyte and by utilizing a suitable initial concentration of **1**. This electropinacolization enlarges the scope of the synthesis of **3** at room temperature in aqueous medium.

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<sup>‡</sup> Analysis of the composition mixture was carried out by HPLC, which consisted of a pump (Knauer Pump 64) and two detectors settled online (UV Applied Biosystems 785A and refractometer Shodex RI-71). The partition was performed on a HPX-87H (300 mm × 7.8 mm, BioRad, 3.33 mM H<sub>2</sub>SO<sub>4</sub> in water, 0.6 mL min<sup>−1</sup>) and the quantitative analyses were carried out using the so-called 'external standard' method. According to the used medium as supporting electrolyte, an ionic exchange resin was necessary to neutralize it (for the sulfuric acid solution: Amberlite IRA-900 Cl and for the alkaline solutions: Amberlite IRA-400 Na). The aqueous solutions of the electrolyzed products, free from inorganic ions, were removed at 50 °C under vacuum, and then dissolved in methanol (10 cm<sup>3</sup>) for esterification using 2,2-dimethoxypropane (1 cm<sup>3</sup>). The separation was performed on silica gel 15–40 μm (Silica Gel 60 from Sigma) with ethyl acetate/petroleum ether (60:40) as eluent.

<sup>§</sup> The different reaction products were identified by GC–MS–MS (EI: 70 eV, Cl/NH<sub>3</sub> and Cl/CH<sub>4</sub>: 100 eV, 1200L Varian).

<sup>¶</sup> ESI high resolution: positive mode at 60 °C in methanol with spray voltage: 4 kV, ZabSpec TOF Micromass.

<sup>||</sup> <sup>1</sup>H and <sup>13</sup>C NMR: 300 MHz, CDCl<sub>3</sub>, WP 200 SY Bruker spectrometer.

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20. Compound **2'**: ESI-MS high resolution,  $[M+Na]^+$  = 127.0373 (127.0371 calcd).  $^1H$  NMR (300 MHz,  $CDCl_3$ ),  $\delta$ : 4.33 (1H, q,  $J$  9.01,  $H_2$ ); 3.77 (3H, s,  $OCH_3$ ); 1.42 (3H, d,  $J$  6.00,  $H_3$ ).  $^{13}C$  NMR (300 MHz,  $CDCl_3$ ),  $\delta$ : 176.19 ( $C_1$ ); 66.51 ( $C_2$ ); 52.55 ( $OCH_3$ ); 20.25 ( $C_3$ ).
21. Compound **3'a**: ESI-MS high resolution,  $[M+Na]^+$  = 229.0689 (229.0688 calcd).  $^1H$  NMR (300 MHz,  $CDCl_3$ ),  $\delta$ : 3.83 (6H, s,  $OCH_3$ ); 1.52 (6H, s,  $CH_3$ ).  $^{13}C$  NMR (300 MHz,  $CDCl_3$ ),  $\delta$ : 175.26 ( $C_1$ ); 78.98 ( $C_2$ ); 53.12 ( $OCH_3$ ); 20.47 ( $CH_3$ ). Compound **3'b**:  $[M+Na]^+$  = 229.0689 (229.0688 calcd).  $^1H$  NMR (300 MHz,  $CDCl_3$ ),  $\delta$ : 3.76 (6H, s,  $OCH_3$ ); 1.48 (6H, s,  $CH_3$ ).  $^{13}C$  NMR (300 MHz,  $CDCl_3$ ),  $\delta$ : 174.71 ( $C_1$ ); 78.82 ( $C_2$ ); 53.00 ( $OCH_3$ ); 20.30 ( $CH_3$ ).