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Electrochemical reduction of ethylpicolinate: Competitive aspects of pyridine nucleus hydrogenation and ester reduction

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Electrolyses of ethylpicolinate in aqueous sulfuric acid solutions were performed on a lead cathode in galvanostatic mode. The reduction of the ester function was in competition with that of the pyridine nucleus. Study of the change in solution composition with time during electrolysis allowed evaluation of the influence of parameters such as acidity, current density, initial concentration of ethylpicolinate and temperature, on the competing formation of the different electrolysis products. Parameter values were chosen for synthesis of 2-hydroxymethylpyridine.

Keywords: *electrohydrogenation*, *electroreduction*, *ethylpicolinate*, *2-hydroxymethylpyridine*, *lead cathode*, *pyridine nucleus*

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1. Introduction

Some alcohols of aromatic heterocycles can be prepared by electrochemical reduction of the corresponding esters; this method of preparation is interesting when the esters are easily accessible raw materials [1–3]. Studies concerning the electroreduction of esters derived from pyridine were conducted by Ferles and Prystas at a lead cathode in sulfuric acid at 20 °C, without obtaining adequate selectivity [4]. Synthesis of 3-hydroxymethylpyridine by electroreduction at a zinc cathode of an ester derived from nicotinic acid was proposed by Tateyama *et al.* [5]. The mechanism of the electroreduction of esters derived from pyridine on a mercury cathode was studied by Iversen and Lund [6], and Nonaka *et al.* [7].

The reduction of 2-ethylpicolinate (**1**) to 2-hydroxymethylpyridine (**3**) is achieved with 2-formylpyridine (**2**) as an intermediate, in accordance with the following reactions, where Pyr designates the pyridinic group:

$$\mathrm{PyrCOOC_2H_5}(\mathbf{1}) + 2\,\mathrm{e}^- + 2\,\mathrm{H}^+ \rightarrow \mathrm{PyrCHO}(\mathbf{2}) + \mathrm{C_2H_5OH} \qquad (1)$$

$$\mathrm{PyrCHO}(\mathbf{2}) + 2\,\mathrm{e}^- + 2\,\mathrm{H}^+ \rightarrow \mathrm{PyrCH_2OH}(\mathbf{3}) \qquad (2)$$

The subsequent reduction of (**3**) to picoline (**4**) may also occur:

$$\mathrm{PyrCH_2OH}(\mathbf{3}) + 2\,\mathrm{e}^- + 2\,\mathrm{H}^+ \rightarrow \mathrm{PyrCH_3}(\mathbf{4}) + \mathrm{H_2O} \qquad (3)$$

Furthermore, the partial hydrolysis of (**1**) takes place:

$$\mathrm{PyrCOOC_2H_5}(\mathbf{1}) + \mathrm{H_2O} \rightarrow \mathrm{PyrCOOH}(\mathbf{5}) + \mathrm{C_2H_5OH} \qquad (4)$$

This produces picolinic acid (**5**); voltamperometric study of the latter shows an electrochemical behaviour close to that of (**1**) on a lead cathode [1]. The reduction of (**5**) leads to (**2**), followed by Reactions 2 and 3:

$$\mathrm{PyrCOOH}(\mathbf{5}) + 2\,\mathrm{e}^- + 2\,\mathrm{H}^+ \rightarrow \mathrm{PyrCHO}(\mathbf{2}) + \mathrm{H_2O} \qquad (5)$$

In parallel to the reduction of the ester function, electrohydrogenation of the pyridine nucleus of the different pyridinic derivatives present in the reactive medium may also occur. For instance, Ferles and Prystas obtained a mixture of picoline and pipecoline by electroreduction of (**1**), and the 1,2,3,6-tetrahydropicoline by electroreduction of (**4**) [4]. Other authors have observed that coloured polymers, able to catalyze proton reduction, are formed during the electroreduction of picolinic acid, mainly by electrohydrogenation of the nucleus of (**2**), in accordance with the following mechanism where Z indicates the side chain on a pyridine nucleus [8–12]:

$$\mathrm{ZPyr} + \mathrm{e}^- \rightarrow \mathrm{ZPyr}^{\circ-}$$

$$\mathrm{ZPyr}^{\circ-} + \mathrm{H}^+ \rightarrow \mathrm{ZPyrH}^{\circ}$$

$$\mathrm{ZPyrH}^{\circ} \rightarrow \mathrm{ZPyr} + \tfrac{1}{2}\mathrm{H_2}$$

$$\mathrm{ZPyrH}^{\circ} + \mathrm{ZPyrH}^{\circ} \rightarrow \mathrm{Z_2Pyr_2H_2}$$

Competition between the reduction of the side chain of an aromatic nucleus and that of the nucleus itself depends on the operating conditions. Electrohydrogenation of the nucleus is limited when the cathode has a high hydrogen overpotential [13, 14] and when the medium is strongly acidic [7, 15]. It also decreases in the case of a pyridine nucleus [15].

In this study electrolyses of aqueous solutions of (**1**) in sulfuric acid medium were performed under galvanostatic mode in a filter press reactor with a separator. The reduction of (**1**) to (**3**) was carried out on a lead cathode. The electrochemical behaviour of this electrode was studied using voltammetric techniques [1]: the electrode first underwent partial passivation and then steady passivation was reached during electrolysis. The change in the quantity of products and reagent during a preparative electrolysis leads to the optimum duration of the electrolysis giving the maximum quantity of (**3**). Study of the influence of parameters such as sulfuric acid concentration C_a, initial concentration C_1° of (**1**), temperature Θ and current density j allows selection of the optimum operating conditions giving alcohol (**3**).

2. Experimental details

The preparative electrolysis were performed in galvanostatic mode with a microflow cell (Electrocell AB; Sweden) and the electrolytic solutions were assayed by liquid phase chromatography (HPLC). Experimental details are given elsewhere [2] and [3]. The catholyte and the anolyte each had an initial volume of 150 cm^3. For electrolyses, periods varying from 3 to 12 h, no variation in these volumes was observed. The electrolyte flowrate in each loop was 12.8 $cm^3\ s^{-1}$. For the electrolyses in galvanostatic mode, j was chosen between 500 and 2800 A m^{-2}. These values were lower than the steady limiting value of the current densities obtained by voltamperometry, for concentrations C_1° of 0.24 and 1 mol dm^{-3} [3]. The sulfuric acid concentration C_a was between 1 and 9 mol dm^{-3}, and Θ between 20 and 80 °C.

The numbers of moles $n_i(t)$ of (**1**), (**2**), (**3**), (**4**) and (**5**) (i = 1, 2, 3, 4 and 5, respectively) at time t, were determined by HPLC and then represented as functions of the charge $Q(t)$ calculated by the ratio of the faraday number at t to the initial number n_1° of moles of (**1**), and expressed in faraday per mole. The parameter $Q(t)$ is more convenient than time as it can be easily compared to Q = 4 F mol^{-1}, the theoretical charge required for the complete reduction of (**1**) into (**3**).

Results of the electrolyses are discussed in terms of yield, selectivity, faradaic yield, molar balance, and conversion which are functions of time as defined below.

The product (i) yield R_i (i = 2, 3, 4) is defined as

$$R_i = n_i(t)/n_1^\circ$$

The selectivity S_3 in relation to the production of (**3**) is given as

$$S_3 = n_3(t)/[n_2(t) + n_3(t) + n_4(t)]$$

The faradaic yield R_f is calculated using

$$R_f = [2\,n_2(t) + 4\,n_3(t) + 6\,n_4(t)] \times F/Q(t)$$

The molar balance B is given as

$$B = [n_1(t) + n_2(t) + n_3(t) + n_4(t) + n_5(t)]/n_1^\circ$$

Bn_1° is the total mole number of reactant and products assayed by HPLC, and which have a nonhydrogenated pyridine nucleus.

For each electrolysis, the maximum yields in (**2**) and in (**3**) are denoted R_{2m} and R_{3m}, respectively. In a similar manner the value of the maximum selectivity with respect to (**3**) is denoted S_{3m}, and the charge values which correspond to the maximum concentration of (**2**), of (**3**), and to the maximum selectivity S_{3m} are, respectively, indicated Q_{2m}, Q_{3m}, Q'_{3m}. The appearance of (**4**) is not immediate after starting an electrolysis. In the range of concentrations studied, the appearance of (**4**) is arbitrarily defined when its concentration is equal to or greater than 0.005 mol dm^{-3}. The corresponding charge is indicated Q_4 and the corresponding values of B and R_f are indicated B_4 and R_{f4}, respectively.

3. Results and discussion

3.1. *Variation of the composition during an electrolysis*

Figure 1 shows the change in the number of moles $n_i(t)$ as a function of the charge $Q(t)$ during an electrolysis performed for j = 1071 A m^{-2}, C_1° = 0.24 mol dm^{-3}, C_a = 9 mol dm^{-3} and Θ = 50 °C. $n_2(t)$, $n_3(t)$ and $n_4(t)$ all pass through a maximum. Structures (**2**) and (**3**) are formed at the beginning of the electrolysis and Q_{3m} is slightly higher than Q_{2m}. (**4**) appears when Q_4 is close to Q_{2m} and Q_{3m}. It is possible to completely convert (**1**), and even (**2**), (**3**) and (**4**) by prolonging the electrolysis. B is close to 1 at the beginning of electrolysis and begins to decrease when $Q(t)$ is close to Q_4. As $n_5(t)$ decreases more slowly than $n_1(t)$, it seems that (**5**) is more difficult to reduce than (**1**). The preceding description also applies to electrolyses performed for other values of j, C_1°, C_a, and Θ in the ranges studied [2, 3, 16].

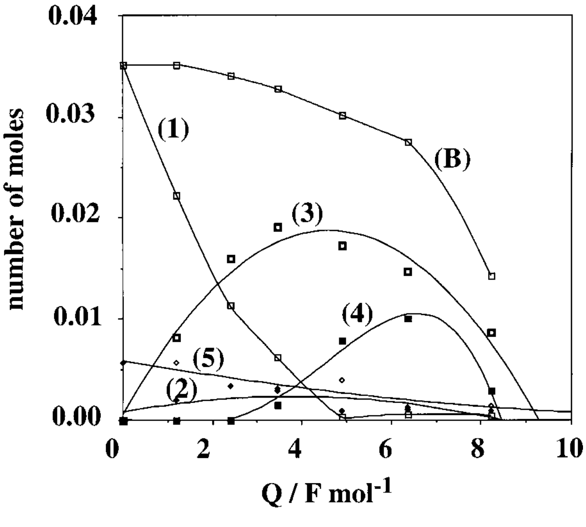

Fig. 1. Variation of the mole numbers as functions of the charge. C_1° = 0.24 mol dm^{-3}; j = 1071 A m^{-2}; Θ = 50 °C; C_a = 9 mol dm^{-3}; volume of the catholyte 150 cm^3; cathode area 14 cm^2; (1) ethylpicolinate (**1**); (2) 2-formylpyridine (**2**); (3) 2-hydroxymethylpyridine (**3**); (4) picoline (**4**); (5) picolinic acid (**5**); (B) $B \times n_1^\circ$: total mole number assayed by HPLC.

3.2. *Influence of parameters C_a, j, and C_l°*

3.2.1. Yield in 2-hydroxymethylpyridine. Figure 2 shows the change in R_3 as a function of $Q(t)$ for electrolyses performed at different acidity, at 50 °C, for $j = 571$ A m^{-2} and $C_l^\circ = 0.24$ mol dm^{-3}. All the curves show a maximum. R_{3m} and Q_{3m} increase respectively from 0.16 to 0.73 and from 2 to 5 F mol^{-1} when C_a increases from 1 to 9 mol dm^{-3}. The values of R_{3m} and Q_{3m} obtained for electrolyses performed at 50 °C with different values of j, C_a and C_l° are given in Table 1.

R_{3m} and Q_{3m} increase with acidity. A decrease in j causes R_{3m} to increase and has little influence on Q_{3m}. When $j = 1071$ A m^{-2} an increase in C_l° causes an increase in R_{3m}. In the studied range, the highest values of R_{3m} (0.77 and 0.73) are obtained when C_a is 7 and 9 mol dm^{-3} when $C_l^\circ = 0.24$ mol dm^{-3} and $j = 571$A m^{-2}. Q_{3m} is close to the theoretical value 4 F mol^{-1} for $C_a \geq 7$ mol dm^{-3}.

3.2.2. Yield in 2-formylpyridine. Figure 3 shows the change in R_2 as a function of $Q(t)$ for electrolyses performed at different acidities, at 50 °C, with $j = 571$ A m^{-2} and $C_l^\circ = 0.24$ mol dm^{-3}. Again all the curves show a maximum. R_{2m} decreases from 0.33 to 0.04 and Q_{2m} increases from 1.8 to 3.2 F mol^{-1} when C_a passes from 1 to 9 mol dm^{-3}. The values of R_{2m} and Q_{2m} obtained for electrolyses performed at 50 °C with different values of j, C_a and C_l° are given in Table 2.

R_{2m} decreases and Q_{2m} increases with increase in acidity. An increase in j causes an increase in R_{2m} and has little influence on Q_{2m}. In the studied range, the lowest values of R_{2m} (less than 0.1), are obtained when C_a is equal to 9 mol dm^{-3}. Tables 1 and 2 and Figs 2 and 3 show that R_{3m} is lower than R_{2m} when the acidity of the medium is low (1 mol dm^{-3}), and the contrary result is obtained when the acidity of the medium is high (9 mol dm^{-3}). These results show that (**2**) is reduced faster when the acidity increases and thus support the hypothesis of an acido-catalysed dehydration of (**6**) (which is the hydrate of (**2**), nonreducible), to (**2**) which is reducible [1, 3, 17–22]:

$$\mathrm{PyrCH(OH)_2(\mathbf{6}) \rightarrow PyrCHO(\mathbf{2}) + H_2O} \qquad (6)$$

As the hemiacetal (**7**), which is the intermediate formed by Reaction 7 during the reduction of (**1**) to (**2**) [23, 24], has a structure close to that of (**6**), it is

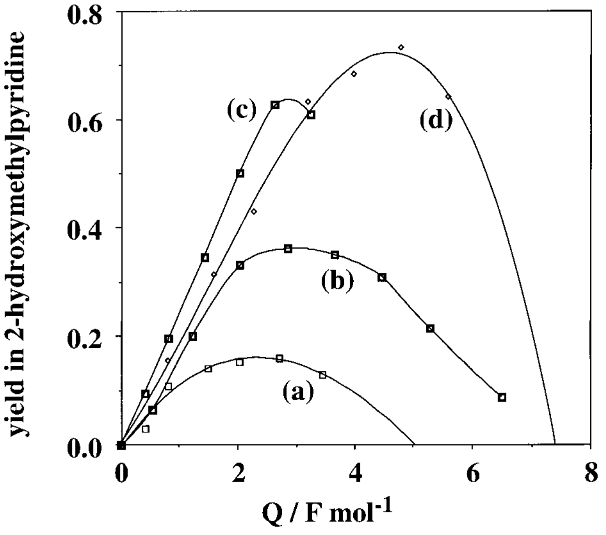

Fig. 2. Variation of the yield in 2-hydroxymethylpyridine R_3 as a function of the charge for different concentrations of sulfuric acid. $C_l^\circ = 0.24$ mol dm^{-3}; $j = 571$ A m^{-2}; $\Theta = 50$ °C. C_a: (a) 1, (b) 3, (c) 5 and (d) 9 mol dm^{-3}.

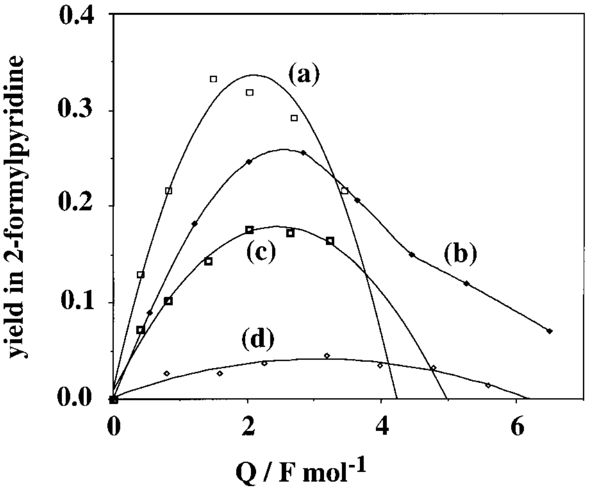

Fig. 3. Variation of the yield in 2-formylpyridine R_2 as a function of the charge for different concentrations of sulfuric acid. Same conditions and notation as Fig. 2.

Table 1. Maximum yield in 2-hydroxymethylpyridine R_{3m} and corresponding charge (Q_{3m} in F mol^{-1}) for different sets of ethylpicolinate and sulfuric acid concentrations and current densities ($\Theta = 50$ °C)

C_l° /mol dm^{-3}	j /A m^{-2}	C_a/mol dm^{-3}						
		1	*2*	*3*	*4*	*5*	*7*	*9*
0.24	571	0.16 (2.0)	0.2 (2.2)	0.37 (2.8)	0.44 (2.8)	0.62 (2.8)	0.77 (4.0)	0.73 (5.0)
0.24	1071			0.39 (2.3)		0.57 (3.3)	0.54 (4.0)	0.54 (3.8)
0.49	571					0.49 (2.5)	0.49 (3.7)	0.71 (3.3)
0.49	1071					0.50 (3.4)	0.59 (3.2)	0.71 (3.9)
0.98	1071			0.64 (2.6)		0.61 (2.5)		
0.98	1642			0.39 (3.5)		0.42 (3.5)		
0.98	2142			0.46 (2.0)		0.40 (3.2)		
0.98	2714			0.23 (3.0)				

Table 2. Maximum yield in 2-formylpyridine R_{2m} and corresponding charge (Q_{2m} in F mol^{-1}) for different sets of ethylpicolinate and sulfuric acid concentrations and current densities (Θ = 50 °C)

C_1° /mol dm^{-3}	j /A m^{-2}	C_a /mol dm^{-3}						
		1	*2*	*3*	*4*	*5*	*7*	*9*
0.24	571	0.33 (1.8)	0.29 (2.1)	0.26 (2.4)	0.22 (2.2)	0.18 (2.2)	0.14 (2.9)	0.04 (3.2)
0.24	1071			0.41 (2.5)		0.31 (2.5)	0.24 (3.0)	0.09 (2.2)
0.49	571					0.095 (2.0)	0.06 (2.6)	0.02 (3.2)
0.49	1071					0.2 (2.4)	0.12 (3.1)	0.07 (3.1)
0.98	1071			0.14 (2.3)		0.12 (2.5)		
0.98	1642			0.17 (2.5)		0.16 (2.5)		
0.98	2142			0.19 (2.5)		0.16 (2.6)		
0.98	2714			0.28 (2.2)				

likely that Reaction 8 is acido-catalysed, as is the dehydration (Reaction 6):

$$\mathrm{PyrCOOC_2H_5(\mathbf{1}) + 2\,e^- + 2\,H^+ \rightarrow PyrCHOHOC_2H_5} \quad (7)$$

$$\mathrm{PyrCHOHOC_2H_5(\mathbf{7}) \rightarrow PyrCHO(\mathbf{2}) + C_2H_5OH} \quad (8)$$

3.2.3. Selectivity with respect to 2-hydroxymethylpyridine. Figure 4 shows the evolution of S_3 as a function of $Q(t)$ for electrolyses performed at different acidities, at 50 °C, with j = 571 A m^{-2} and $C_1^\circ = 0.24$ mol dm^{-3}. All the curves present a maximum. S_{3m} and Q'_{3m} increase, respectively, from 0.37 to 0.97 and from 2 to 5 F mol^{-1} when C_a increases from 2 to 9 mol dm^{-3}. At the beginning of electrolysis, before the appearance of (**4**), S_3 increases: the ratio of the rate of reduction of (**2**) to (**3**) to the rate of reduction of (**1**) to (**2**) increases. Then, when the reduction of (**3**) to (**4**) takes place, S_3 decreases.

The values of S_{3m} and Q'_{3m} obtained for electrolyses performed at 50 °C with different values of j, C_a and C_1° are given in Table 3. S_{3m} and Q'_{3m} increase with acidity. Decrease of j causes S_{3m} to increase and has little influence on Q'_{3m}. An increase in C_1° induces an increase in S_{3m}. For j = 571 A m^{-2}, and for C_1° between 0.24 and 0.49 mol dm^{-3}, the highest value of S_{3m} (0.97) is obtained when C_a is 9 mol dm^{-3}. Q'_{3m} is generally close to Q_{3m} , but in the case where C_1° is high (0.98 mol dm^{-3}), S_3 begins to decrease from the beginning of electrolysis, or reaches a maximum value well before the maximum quantity of (**3**) is obtained.

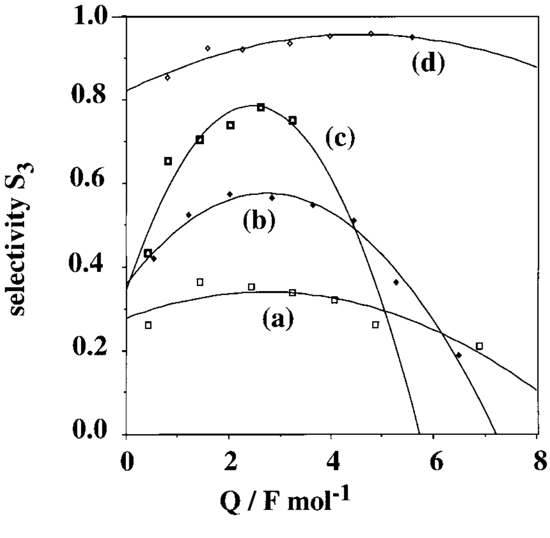

Fig. 4. Variation of the selectivity of 2-hydroxymethylpyridine S_3 as a function of the charge for different concentrations of sulfuric acid. $C_1^\circ = 0.24$ mol dm^{-3}; j = 571 A m^{-2}; Θ = 50 °C; C_a: (a) 2, (b) 3, (c) 5 and (d) 9 mol dm^{-3}.

3.2.4. Appearance of picoline. The appearance of (**4**), from the reduction of (**3**), is an important aspect of the electrolyses, since it must be avoided when the synthesis of (**3**) is desired. A voltamperometric study showed that (**3**) was less reducible than (**1**) and (**2**) on lead and that its reduction was almost indistinguishable from that of the reduction of the proton in a sulfuric acid medium [3]. The values of Q_4 obtained for the electrolyses performed at 50 °C with different values for j, C_a and C_1° are given in Table 4. Q_4 increases with acidity and with a decrease in C_1°. Tables 1, 2 and 4 show that Q_4, Q_{3m} and Q_{2m} are generally close, indicating that (**4**) appears when the maximum quantity of (**2**) or (**3**) is reached. During constant current electrolysis, the progressive consumption of (**1**) leads to a decrease in the cathode potential and to the possibility of reducing (**3**) into (**4**). This phenomenon is even more delayed as the imposed current density is weak, and the proton reduction is important because of the low pH.

3.2.5. Molar balance. The study of B as a function of $Q(t)$ for electrolyses performed at 50 °C under different values of j, C_a and C_1°, shows that B is generally close to 1 before obtaining the maximum quantity of (**2**) and the appearance of (**4**), which, as previously stated, are quite often close. Its value then falls noticeably. The electrolyses were stopped when (**1**) was completely converted. At the end of electrolysis, B can reach 0.4; $n_2(t)$ and $n_3(t)$ decrease and (**4**) is already formed. Figure 1 (curve B) shows the change in the total number of moles of the products assayed by HPLC.

The values of B_4 for electrolyses at 50 °C for different values for j, C_a and C_1° are given in Table 4. B_4 is close to 1 when C_a is 7 or 9 mol dm^{-3} (where

Table 3. Maximum selectivity in 2-hydroxymethylpyridine S_{3m} and corresponding charge (Q'_{3m} in F mol^{-1}) for different sets of ethylpicolinate and sulfuric acid concentrations and current densities (Θ = 50 °C)

C_1°/mol dm^{-3}	j /A m^{-2}	C_a /mol dm^{-3}						
		1	*2*	*3*	*4*	*5*	*7*	*9*
0.24	571	0.32 (2.7)	0.37 (2.0)	0.58 (2.2)	0.68 (2.2)	0.78 (3.0)	0.89 (4.5)	0.97 (5.0)
0.24	1071			0.49 (2.2)		0.63 (3.1)	0.66 (3.1)	0.84 (3.5)
0.49	571					0.84 (2.5)	0.93 (3.2)	0.97 (3.2)
0.49	1071					0.72 (3.5)	0.88 (4.5)	0.91 (4.0)
0.98	1071			0.76 (2.2)		0.85 (2.0)		
0.98	1642			no maximum		0.68 (2.6)		
0.98	2142			no maximum		no maximum		
0.98	2714			0.5 (4.0)				

Table 4. Charge value Q_4 in F mol^{-1}, molar balance (B_4) and faradaïc yield $R_{f,4}$, at picoline appearance, for different sets of ethylpicolinate and sulfuric acid concentrations and current densities (Θ = 50 °C)

C_1°/mol dm^{-3}	j /A m^{-2}	C_a /mol dm^{-3}						
		1	*2*	*3*	*4*	*5*	*7*	*9*
0.24	571	1.4 (0.66) *0.55*	1.9 (0.86) *0.78*	2.7 (0.81) *0.79*	2.7 (0.90) *0.98*	3.0 (0.88) *1*	4.2 (0.94) *0.75*	6.2 (0.68) *0.42*
0.24	1071			2.8 (0.87) *0.9*		2.8 (1.00) *1*	3.1 (1.00) *0.8*	3.1 (0.93) *0.8*
0.49	571					3.6 (0.63) *0.8*	3.6 (0.95) *0.8*	3.6 (0.80) *0.8*
0.49	1071					2.8 (0.86) *0.8*	3.2 (0.95) *0.85*	3.8 (0.95) *0.8*
0.98	1071			2.4 (0.74) *0.75*		2.7 (0.97) *0.99*		
0.98	1642			2.3 (0.73) *0.75*		2.7 (0.77) *0.74*		
0.98	2142			2.6 (0.61) *0.74*		2.7 (0.78) *0.75*		
0.98	2714			2.3 (0.60) *0.73*				

j = 1071 A m^{-2} in this last case) and lower than 1 for lower acidities, and when j or C_1° is high.

When B is less than 1, the reduction products of (**1**), other than (**2**), (**3**) and (**4**), appear: the dihydropicoline and the tetrahydropicoline, products of the electrohydrogenation of the pyridine nucleus, were detected by CPV analysis coupled with mass spectrometry [3]. Solid suspensions, in all probability consisting of insoluble polymers, appeared in the reactor and a thick viscous layer covered the cathode at low acidity. These deposits were not found at low pH. In slightly acid medium, B is less than 1 before the appearance of (**4**); the adsorption of the pyridine nucleus of the different derivatives onto the electrode favors the hydrogenation of the pyridine nucleus, compared to that of the side chain [8, 9, 25]. Under these conditions polymerization of the hydrogenated intermediate can occur.

3.2.6. Faradaic yield. The values of R_{f4} obtained for electrolyses performed at 50 °C at different j, C_a and C_1° are given in Table 4. When R_f is less than 1, proton reduction takes place together with the electrohydrogenation of the pyridine nucleus. These two reactions are in competition with the reduction of the side chain [10, 13, 14]. Table 4 (comparison of B_4 and R_{f4}) shows that at high acidity (C_a = 7 and 9 mol dm^{-3}), the proton reduction is favoured to the detriment of electrohydrogenation of the pyridine nucleus: B_4 is close to 1, while R_{f4} is less than 1. However, in the particular case where $C_a = 9$ mol dm^{-3}, $j = 571$ A m^{-2} and $C_1^\circ = 0.24$ mol dm^{-3}, B_4 and R_{f4} are both much lower than 1 and R_{f4} is less than B_4. In this last case, (**4**) appears long after the maximum of (**3**). This shows that proton reduction and electrohydrogenation of the pyridine nuclei are favoured with respect to the reduction of (**3**) into (**4**).

B_4 and R_{f4} have values lower than 1 and close to each other when the acidity is weaker ($1 \le C_a \le 3$ mol dm^{-3}), or when the current density is high ($1642 \le j \le 2714$ A m^{-2}), or again when C_1° is high ($C_1^\circ = 0.98$ mol dm^{-3}) in the studied range. This shows that the electrohydrogenation of the pyridine nucleus is favoured with respect to the reduction of (**3**) and (**4**), without any appreciable proton reduction. The formation of coloured polymers is favoured by a weak acid medium (C_a = 1 and 2 mol dm^{-3}), but also by a high value of C_1° (C_1° = 0.98 mol dm^{-3}).

3.2.7. Effect of feed method. To perform electrolyses involving higher quantities of reagent, it is planned to feed the catholyte over time, using additions of (**1**) before the appearance of (**4**). Maintaining sufficient concentration of (**1**) in the medium can limit the reduction of (**3**) into (**4**) as well as the electrohydrogenation. Three assays were performed for different values of experimental parameters j and Θ, with C_a equal to 3 mol dm^{-3}. The results are given in Table 5. At 50 °C a comparison of the two assays shows that the feeding technique using small consecutive additions gives a better yield in (**3**) than when using only one large addition. The values of B_4 and of R_f show that there is less electrohydrogenation in the second assay, for which the current density and the quantity of reducible matter at each time are lower. This feeding technique can thus be used for preparative electrolyses on a larger scale. Assay number 3 shows that an increase in temperature favors electrohydrogenation and the hydrolysis of (**1**) into (**5**). The influence of this parameter is examined below.

3.2.8. Choice of parameters C_a, j and C_1°. The neutralization of the reactive medium by a base at the end of electrolysis, with the aim of separating (**3**) and in the case of a highly concentrated acid medium, leads to the rejection of a very high quantity of sulfate. It is possible to compromise with an acidity of 3 mol dm^{-3}. To improve the performances of the synthesis of (**3**) from (**1**), it is desirable to operate with a low current density, but for economic reasons this can not be lower than 1071 A m^{-2}. Finally, a feeding technique over time into (**1**) is conceivable to perform electrolyses on a larger scale.

3.3. *Influence of temperature*

Electrolyses are performed at different temperatures in the conditions where $C_a = 3$ mol dm^{-3}, $j = 1071$ A m^{-2} and $C_1^\circ = 0.24$ or 0.98 mol dm^{-3}. Figure 5 shows the evolution of R_3 and of R_2 as a function of $Q(t)$ at 50 °C and at 80 °C, when $C_1^\circ = 0.24$ mol dm^{-3}. Other results are given in Table 6.

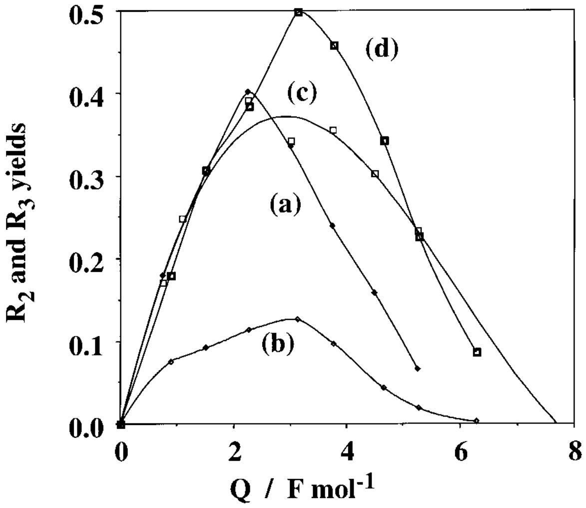

Fig. 5. Variation of the yield in 2-formylpyridine R_2 at $\Theta = 50$ °C (a), and at $\Theta = 80$ °C (b), and the yield in the 2-hydroxymethylpyridine R_3 at $\Theta = 50$ °C (c), and $\Theta = 80$ °C (d), as functions of the charge. $C_a = 3$ mol dm^{-3}; $C_1^\circ = 0.24$ mol dm^{-3}; $j = 1071$ A m^{-2}.

When Θ increases from 35 to 80 °C, R_{3m} and S_{3m} increase and R_{2m} decreases, whereas Q_{3m} and Q_{2m} increase while still remaining close. An increase in temperature accelerates the reaction (6) [1, 17–20] and consequently the reduction of (**2**) to (**3**). This shows that the reduction of (**1**) to (**2**), which depends upon the Reaction 8, is probably less accelerated than the reduction of (**2**) to (**3**) by an increase in temperature. At 20 °C these reactions are slow and limit the rate of reduction of (**1**).

The appearance of (**4**) precedes the maximum quantity of (**3**) at 20 °C ($Q_4 < Q_{3m}$): the reduction of (**3**) to (**4**) is favoured by a low temperature. When (**4**) appears at 20 °C, B_4 and R_{f4} equal 1. This means that the electrohydrogenation of the nucleus does not take place. From 35 to 80 °C, the more the temperature increases, the more the appearance of (**4**) is delayed; it coincides more or less with obtention of the maximum quantity of (**3**). At this time, B_4 is lower than 1 for temperatures from 50 to 80 °C and the more the temperature increases, the more R_{f4} decreases. An increase in temperature thus has the effect of accel-

Table 5. Electrolysis results with addition of ethylpicolinate (1)

(a): Addition of (**1**) at Q = 1.28 F mol^{-1}
(b): Addition of (**1**) at Q = 0.18 F mol^{-1} and then each 0.18 F mol^{-1}
(c): Addition of (**1**), respectively, at Q = 0.68; 1.35 and 2.13 F mol^{-1}

C_1° + addition /mol dm^{-3}	*0.98 + (1 × 0.98)* (a) run 1	*0.98 + (7 × 0.092)* (b) run 2	*0.24 + (3 × 0.24)* (c) run 3
Θ (°C)	50	50	80
j (A m^{-2})	1642	1071	1071
Q_4 (F mol^{-1})	1.84	1.83	3.59
R_3	0.28	0.36	0.46
R_2	0.08	0.08	0.03
R_5	0.034	0.085	0.20
R_f	0.78	0.87	0.52
B_4	0.53	0.76	0.69

Table 6. Temperature effect on electrolysis of ethylpicolinate

$C_a = 3$ mol dm^{-3}; $j = 1071$ A m^{-2}

C_1°/mol dm^{-3}	Θ /°C	$R_{3,max}$	Q_{3m}	$R_{2,max}$	Q_{2m}	$S_{3,max}$	Q'_{3m}	Q_4	B_4	$R_{f,4}$
0.24	20	0.1	1.8	0.2	1			0.7	1	1
	35	0.36	2.1	0.48	2.5	0.42	2.2	2.1	1	0.99
	50	0.39	2.3	0.41	2.5	0.49	2.2	2.8	0.87	0.90
	65	0.43	3.1	0.22	3.0	0.67	2.0	2.8	0.83	0.91
	80	0.50	3.1	0.13	3.2	0.78	2.6	2.9	0.94	0.78
0.98	50	0.64	2.6	0.15	2.3	0.76	2.2	2.4	0.74	0.75
	80	0.60	3.0	0.02	2.6	0.97	2.5	>4	<0.79	0.55

erating the electrohydrogenation of the pyridine nucleus (see also Table 5).

On the other hand, R_5 depends on the temperature: at 50 °C, R_5 is about 8% in the beginning of the electrolysis and about 4% at the end, whereas at 80 °C, R_5 is about 20% all over the electrolysis. There was practically no decrease in R_5 during the obtention of the maximum quantity of (**3**): (**5**) is less reducible than (**1**) [1].

It is thus necessary to compromise as regards the choice of temperature: a temperature increase improves the yield in (**3**) and delays the appearance of (**4**). But it favours the hydrolysis of (**1**) into (**5**), which is not very reducible, and the electrohydrogenation of the pyridine nuclei. The choice of 50 °C corresponds to this compromise.

4. Conclusion

This study shows that the sulfuric acid concentration, the current density, the initial ester concentration and the temperature influence the characteristics of the electrolyses of ethylpicolinate (**1**) in an aqueous sulfuric acid medium. The reduction of (**1**), which can be completely converted, successively leads to (**2**), (**3**) and (**4**). Electrohydrogenation of the pyridine nucleus of the derivatives present in the reactive medium occurs parallel to that of the ester function and leads to nonaromatized monocyclic or polycyclic derivatives. An increase in the acidity of the medium improves the yield in (**3**) and decreases the quantities of (**4**) and those of the electrohydrogenation nucleus products. However, a high sulfuric acid concentration set the problem of its regeneration. A concentration of 3 mol dm^{-3} appears to be an acceptable value. A low current density and a low quantity of (**1**) limit the electrohydrogenation, but for economic reasons it may be necessary to use a higher current density, for instance equal to or greater than 1000 A m^{-2}, and successive feedings into (**1**) during electrolysis. A high temperature increases the maximum quantity of (**3**) obtained during electrolysis and limits its reduction into (**4**). But it also accelerates the electrohydrogenation of the nucleus and favors the hydrolysis of (**1**) into (**5**), which is less reducible than (**1**). The value of 50 °C appears to be acceptable.

The study of the influence of the medium acidity and of the temperature shows the essential role of nonreducible intermediates, such as hemiacetal (**7**) and the hydrate (**6**): their transformation into (**2**) is accelerated by an acid catalysis and by a temperature increase.

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