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Abstract

Full Text

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Electrochemical Oxidation of β-Picoline

A number of studies have shown that picolines are readily oxidized electrochemically, with formation of the corresponding aldehydes (^{1},^{2}) and pyridinecarboxylic acids (^{1}-^{4}), as well as products of oxidation of the pyridine ring (^{2}). In the literature, however, there are no data on the influence of the electrolyte composition and electrolysis conditions on the yield of individual products. The present communication sets forth the results of a study of the process of electrochemical oxidation of β-picoline.

The starting β-picoline was extracted from an aqueous solution of the picoline fraction (b.p. 138–144°) in the form of the sparingly soluble complex salt $CuSO_4 \cdot 5H_2O \cdot C_6H_7N$ (^{5}), which was then decomposed with caustic soda. Further purification of β-picoline by threefold freezing out gave a product of ~99% purity.

Fig. 1. Influence of the amount of electricity passed through the electrolyte on the yield of nicotinic acid by current (1) and by substance (2)

Preliminary experiments established that β-picoline can be oxidized electrochemically only in an acidic medium on anodes of platinum and of lead previously coated with a layer of dioxide. On a lead anode, the oxidation of β-picoline proceeded with a considerably higher current yield than on a platinum one; therefore the subsequent experiments were carried out only with a lead anode in an electrolyzer with a porous ceramic diaphragm. Into the anode compartment, of capacity ~50 cm^3, β-picoline in sulfuric-acid solution was introduced. The lead cathode was placed inside a diaphragm cup containing a dilute solution of sulfuric acid. The anode surface was 2 dm^2. After electrolysis was complete, the anolyte was filtered from the sludge, neutralized with soda, then acidified with acetic acid to pH 4–4.5 and heated on a boiling water bath. Copper sulfate or acetate was added to the hot solution, and heating on the bath was continued for several more hours. The precipitated copper nicotinate was filtered off and dried.

The influence of the amount of electricity passed through the electrolyte, the current density, the temperature, additions of salts of polyvalent metals (Mn and Cr), and the concentrations of β-picoline and sulfuric acid on the yield of nicotinic acid by current and by substance was studied. In separate experiments the total current consumption for the oxidation of organic substances was also determined by comparing the volumes of oxygen evolved over equal intervals of time in a gas coulometer and in an electrolyzer containing a sulfuric-acid solution of β-picoline. Comparison of the results of these experiments with the yields of nicotinic acid obtained under the same conditions makes it possible

determine the rate of the side oxidation processes occurring at the anode.

Figure 1 shows the effect of the amount of electricity Q passed through the electrolyte* on the yield of nicotinic acid by current and by substance. The experiments were carried out under the following conditions: temperature 40°, anodic current density 10 A/dm^2; anolyte—a solution of 1 M/l β-picoline in 7 N sulfuric acid. As follows from the curves, the nicotinic acid formed

Table 1

Nicotinic acid yield (in percent)

Q, %	Yield	Temperature of the anolyte, °C	Temperature of the anolyte, °C	Temperature of the anolyte, °C	Temperature of the anolyte, °C	Temperature of the anolyte, °C
		20	30	40	60	80
100	By current and by substance	39		41	38	35
150	By current	30	35	37	28	25
150	By substance	45	53	54	42	37
200	By current	24	27	27	23	17

200	By substance	48	54	54	47	35

Table 2

Nicotinic acid yield (in percent)
(β-picoline concentration 1 M/l, temperature 40°, current density 5 A/dm^2)

Q, %	Yield	Conc. of sulfuric acid, N	Conc. of sulfuric acid, N	Conc. of sulfuric acid, N	Conc. of sulfuric acid, N	Conc. of sulfuric acid, N
		3	7	11.5	17	25
100	By current and by substance	36	41	48	51	34
150	By current	31	37	42	43	22
150	By substance	57	54	63	65	33
200	By current	25	27	27	29	17
200	By substance	51	54	55	59	34

as a result of the oxidation of β-picoline is rather readily oxidized further. However, the oxidation process of β-picoline proceeds at a considerably higher rate. This was also confirmed by specially performed experiments on the electrooxidation of nicotinic acid. The increase, observed at the beginning of electrolysis, in the current yield of nicotinic acid indicates the formation of unstable intermediate products of the oxidation of β-picoline to nicotinic acid, for example pyridine-3-aldehyde.

Table 3

Nicotinic acid yield (in percent)
(temperature 40°, current density 5 A/dm^2)

Q, %	Yield	Concentration of β-picoline, M/l	Concentration of β-picoline, M/l	Concentration of β-picoline, M/l
		1	1.7	3.5
		Concentration of sulfuric acid, N	Concentration of sulfuric acid, N	Concentration of sulfuric acid, N
		17	15.5	13
100	By current and by substance	51	55	49
150	By current	43	43	38
150	By substance	65	65	57
200	By current	29	29	22
200	By substance	59	59	44

Changing the anodic current density within the range from 1 to 10 A/dm^2 had almost no effect on the yield of nicotinic acid. Only at small values of Q (50-100%) did the yield decrease somewhat with increasing current density. The introduction into the anolyte of small amounts of Mn^{++} and Cr^{+++} likewise produced no noticeable effect.

The effect of temperature (Table 1) was studied in the electrolyte of the composition indicated above at a current density of 5 A/dm^2. The decrease in product yield with increasing temperature is apparently connected with an increase in the relative weight of side reactions at high temperature, since the total current consumption for all oxidation processes changed almost not at all with increasing temperature (92% at 20° and 97% at 80°). An analogous phenomenon was also observed in studying the influence of electrolyte acidity (Table 2): here there is a noticeable change in the yield of nicotinic acid with increasing acidity at a constant total rate of oxidation of the organic substances.

The maximum yield of nicotinic acid can be obtained over a fairly wide range of anolyte acidity, from 11 to 17 N. Increas— the acidity of the anolyte during electrolysis due to electromigration is proportional to the amount of electricity passed; therefore, in experiments with a variable concentration of β-picoline, the initial concentration of sulfuric acid was chosen so that the average acidity during electrolysis was approximately the same in all experiments and did not go beyond the values corresponding to the maximum yield of nicotinic acid (Table 3).

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* For $Q = 100\%$, the amount of electricity equal to $6F$ per 1 mole of β-picoline was taken.

It should be noted that the yield of nicotinic acid with respect to substance was calculated for the entire initial β-picoline, i.e., in most cases it was somewhat underestimated, since at $Q = 100$ or 150% the anolyte after electrolysis still contained a certain amount of unoxidized β-picoline. The latter can be regenerated when the process is carried out on a larger scale.

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Note: Figure translations are in progress. See original paper for figures.