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BRIEF COMMUNICATIONS

Electrocatalytic Synthesis of Isonipecotic Acid

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Abstract—An electrocatalytic synthesis of isonipecotic acid was carried out by cathodic reduction of isonicotinic acid in a membrane electrolyzer on a copper cathode activated with Raney nickel in an alkaline medium under mild conditions.

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Isonipecotic acid (INPA), 4-piperidinecarboxylic acid, is an important intermediate product in synthesis of biologically active compounds for medicine and veterinary, in particular, it is used for preparing Aceclydine.

It is known [1] that cathodic reduction of heterocyclic compounds, among them pyridine, in an acid medium allows preparation of dihydro derivatives and dimeric products.

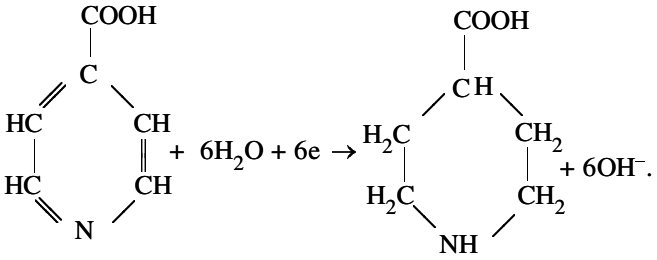
It was reported [2] that, in cathodic reduction of isonicotinic acid anilide in alkaline media on a mercury cathode at controllable potential, this substance is quantitatively converted to its dihydro derivative.

In this study we developed a procedure for exhaustive cathodic reduction of isonicotinic acid (INA).

The cathodic reduction of isonicotinic acid was studied in aqueous alkali on a cathode activated with powdered Raney nickel. An electrolyzer of membrane type was equipped with a nickel anode and a flat horizontal copper cathode. The powdered catalyst was fixed on the cathode surface with a permanent magnet.

15–40 wt % aqueous alkalis were used as anolytes, and 3–10 wt % aqueous alkalis as catholytes. The INA concentration was varied within 5–15%. The catholyte and anolyte were stirred with a mechanical stirrer (50–100 rpm). The catalyst amount on the cathode surface was 5–15 g cm^{-2}. In the course of cathodic reduction, the temperature in the electrolyzer was in the range 20–35°C.

We found that the optimal conditions for cathodic reduction of isonicotinic acid were as follows: initial INA concentration 5–10 wt %, initial sodium hydroxide concentration 5–6 wt % in catholyte and 20–25 wt % in anolyte, temperature 20–30°C, and catalyst content on the cathode surface 8–10 g cm^{-2}. Taking into account that INPA is difficultly separated from INA, in our experiments we ensured quantitative cathodic reduction of INA by passing the electricity in the amount exceeding the calculated value (6 F per mol INA) by 65–70%. The maximal current efficiency for INPA was 60%. We established that cathodic reduction of INA proceeds by the following scheme:



The target product was isolated in the form of INPA hydrochloride which was used in further organic syntheses.

EXPERIMENTAL

Isonicotinic acid, sodium hydroxide, and hydrochloric acid were of the reagent grade.

Electrolyses were performed in a glass cylinder with a lid holding a nickel anode incorporated into a ceramic diaphragm. A hollow copper disk connected to a voltage source was used as a cathode. The electrolyzer was equipped also with a mechanical stirrer and a connecting tube for removing gaseous electrolysis products [3].

The cathodic chamber was loaded with 5% aqueous NaOH (170 cm^3), INA (8.5 g), and Raney nickel (2 g), and the anodic chamber, with 40 cm^3 of 20% aqueous NaOH. The electrolysis was carried out with mild stirring (60 rpm) at 25–30 °C at a current strength of 5 A and a cathodic current density of 8.3 A dm^{-3} (per geometric surface area) for 4.1 h up to completion of hydrogen uptake. After completion of the electrolysis, the catholyte was treated with hydrochloric acid to convert INPA to its poorly soluble hydrochloride derivative. The resulting suspension was cooled and filtered, and the white precipitate of the final product was washed with cold water and dried. Yield of INPA hydrochloride 11.3 g.

Found, %: C 42.80, N 8.29, Cl 21.95.
$C_6H_{12}NCl$.
Calculated, %: C 43.77, N 8.50, Cl 21.55.

The amount of electricity passed through the electrolyzer was 20.5 A h, which exceeds the calculated value by a factor of 1.7. The INPA chemical yield and the corresponding current efficiency were 99 and 60%, respectively.

CONCLUSION

An electrocatalytic synthesis of isonipecotic acid was carried by cathodic reduction of isonicotinic acid on a copper cathode activated with Raney nickel in aqueous alkali with quantitative yield and 60% current efficiency.

REFERENCES

1. Shchennikova, M.K. and Korshunov, I.A., *Zh. Fiz. Khim.*, 1948, vol. 22, pp. 504–508.
2. Lund, H., *Acta Chem. Scand.*, 1963, vol. 17, pp. 2325–2340.
3. Osadchenko, I.M. and Tomilov, A.P., *Elektrokhimiya*, 1997, vol. 33, no. 6, pp. 729–730.