

Synthesis of maleic and malic acids by electrochemical reaction of furfural with hydrogen peroxide

© Vladimir V. Poskonin, and Mikhail M. Yakovlev

Department of Chemistry, Kuban State Technological University, Moskovskaya St., 2, Krasnodar, 350072, Russia. Phone: +7 (918) 345-04-95. E-mail: vposkonin@mail.ru

*Supervising author; †Corresponding author

Keywords: furfural, hydrogen peroxide, anodic oxidation, maleic acid, malic acid, syntheses.

Abstract

The electrochemical reaction of furfural with aqueous hydrogen peroxide leads to the predominant formation of carboxylic acids, 5-hydroxy-2(5H)-furanone and 2(5H)-furanone. Among the carboxylic acids formed, the most interesting are malic and maleic acids. The yield of which depends on the reagents ratio, current strength, type and amount of the background electrolyte. The conditions under which the greatest yields of these products are achieved are found. It was found that malic acid, along with 5-hydroxy-2(5H)-furanone and 2(5H)-furanone, is the main product of the reaction of furfural with aqueous H₂O₂ under anodic oxidation. Its preparative synthesis with 24% yield was carried out at the molar ratio of furfural, H₂O₂ and LiClO₄ as a background electrolyte equal to 1 : 1.6 : (0.1-0.2), and a current of 0.03 A at 50 °C. The yield of maleic acid increases with increasing acidity of the medium and increasing the initial content of H₂O₂ in the reaction medium, while its greatest yield is observed in the solution of chloric acid. At a molar ratio of furfural, H₂O₂ and HClO₄, equal to 1 : 5.5 : 0.01, and a current strength of 0.01 A at 50 °C, its preparative yield reaches 41%. The results obtained suggest that maleic acid is mainly a product of oxidation of the tautomeric form of 5-hydroxy-2(5H)-furanone – *cis*-β-formylacrylic acid, while malic acid can be formed from 2(5H)-furanone and maleic acid. The scheme of maleic and malic acids formation in the studied conditions is proposed.

References

- [1] L.A. Badovskaya, V.V. Poskonin. Influence of acid-base properties of the medium on reactions in the "furfural – H₂O₂ – H₂O" system in the presence and absence of VOSO₄. *Journal of General Chemistry*. **2014**. Vol.84. No.6. P.952-959. (russian)
- [2] L.A. Badovskaya, V.V. Poskonin, L.V. Povarova. Синтез функциональных производных фурана окислением фуранов и формилфуранов пероксидом водорода. *Russian Chemical Bulletin*. **2017**. No.4. P.593-599. (russian)
- [3] L.A. Badovskaya, V.V. Poskonin. Influence of the metal nature on catalytic reactions in the system "furfural – H₂O₂ – H₂O – salt of d-metal V or VI groups" in acidic media. *Kinetics and Catalysis*. **2015**. Vol.56. No.2. P.172-181. (russian)
- [4] S. Bern, Hans J. Schäfer, H. Jürgen, M. Yoshihiro, F. Toshio. Encyclopedia of Electrochemistry. Organic Electrochemistry. Münster, Yokohama: Institut für Organische Chemie. *Tokyo Institute of Technology*. **2009**. 641p.
- [5] Brockman K. Electrochemistry of organic compounds. *Leningrad: ONTI Khimteoret*. **1947**. P.30-31. (russian)
- [6] Patent of England 253877. Oxidation of furfural by direct current. K. Tompson, H.A. Tor. Declared 20.03.36. Published 27.08.36.
- [7] Copyright certificate 40972 USSR. Preparation of maleic and succinic acids. D.A. Deribas, B.V. Shvartsberg, V.V. Iliinskiy. *Published: Bulletin of inventions*. **1935**. No.1. (russian)
- [8] N. Hellstrom, K. Svensk, I. Tid. Anodic electrochemical oxidation of furfural. *Electrochim Acta*. **1948**. No.60. P.214-218.
- [9] V.A. Smirnov, V.I. Milman, O.B. Krayanskiy. Electrochemical oxidation of furfural. *Electrochemistry*. **1971**. Vol.6. No.7. P.830-834. (russian)

- [10] V.I. Milman, V.A. Zverev, V.A. Smirnov, M.S. Klebanov. The influence of homogeneous catalysts for electrochemical synthesis of β -formylacrylic acid. *Electrochemistry*. **1978**. Vol.17. No.10. P.1555-1558. (russian)
- [11] Copyright certificate. 412176 USSR. A method of β -formylacrylic acid preparation. V.A. Smirnov, V.I. Milman, O.B. Krayanskiy. *Published: Bulletin of inventions*. **1978**. No.3. (russian)
- [12] V.L. Kornienko, G.A. Kolyagin. Indirect oxidation of organic substances by oxygen reduction intermediates. *Electrochemistry*. **2003**. Vol.39. No.12. P.1462-1470. (russian)
- [13] V.V. Poskonin, M.M. Yakovlev. On some features of the reaction of furfural with hydrogen peroxide under electrolysis on separated graphite electrodes. *Almanac of Modern Science and Education*. **2008**. No.5(12). P.101-102. (russian)
- [14] M.M. Yakovlev, V.V. Poskonin. On the composition of the main products of furfural electrochemical transformation in an aqueous solution of hydrogen peroxide. *Almanac of Modern Science and Education*. **2009**. No.5(24). P.189-190. (russian)
- [15] M.M. Yakovlev, V.V. Poskonin. The reaction of the furfural with the aqueous hydrogen peroxide under conditions of anodic synthesis. *News Universities. North Caucasus region. Natural science*. **2010**. No.5(159). P.60-64. (russian)
- [16] M.M. Yakovlev, V.V. Poskonin. Synthesis of 2(5H)-furanone and 5-hydroxy-2(5H)- in the system "furfural-hydrogen peroxide-anolite" under the action of direct electric current. *Fundamental Research*. **2011**. No.8. Part.1. P.207-210. (russian)
- [17] V.A. Rabinovich, Z.Ya. Khavin. Brief chemical reference book. Ed. 3rd, Rev. ed. by Potekhin A.A., Efimov A.I. *Leningrad: Khimiya*. **1991**. 432p. (russian)