

LETTERS
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Electrochemical Synthesis of Dimethylsulfone and Methanesulfonic Acid from Dimethylsulfoxide

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Dimethylsulfone (CH₃)₂SO₂ and methanesulfonic acid CH₃SO₃H can be used as solvents, catalysts of nitration, nitrosylation, etherification, acylation, and olefin polymerization as well as in chemical, electronic, and radio engineering industries, and for various drug manufactures.

The search for rational methods of petrochemical synthesis of organosulfur compounds is a problem of great practical importance.

Sulfones and sulfonic acids are synthesized by chemical and catalytic methods from sulfides, disulfides, thioalcohols, and other organosulfur compounds isolated from middle distillate fractions of sulfurous and sour oil.

Dimethylsulfone is synthesized by oxidation of dimethylsulfide or from dimethylsulfoxide in mild conditions and methanesulfonic acid is synthesized by strong oxidizers in more severe conditions. At the same time, there is no data on synthesis of methanesulfonic acid from dimethylsulfoxide.

Along with development of chemical methods, there are attempts to develop electrochemical methods for synthesis of organosulfur compounds. For example, the authors of [1] demonstrated that dimethylsulfide can electrochemically oxidized to dimethylsulfoxide with a good current efficiency.

The goal of this work is development of the methods for electrochemical synthesis of dimethylsulfone and methanesulfonic acid from dimethylsulfoxide.

Basing on the analysis of voltammetric studies carried out in aqueous and nonaqueous dimethylsulfoxide solutions in various modes, we found that dimethylsulfoxide is oxidized on platinum anode into two different products.

By preparative electrolysis of aqueous dimethylsulfoxide solutions of various concentrations in dia-

phragm-free electrolyzer with background electrolyte (sodium hydroxide) at current density from 0.01 to 0.02 A/cm² on platinum anode, we demonstrated formation of dimethylsulfone with the current efficiency of 92 to 94% [2].

The final product was isolated by solution concentrating (evaporating) and cooling with precipitation of dimethylsulfone crystals (melting point 110°C). The average current efficiency of dimethylsulfone was 92%.

Electrolysis of aqueous dimethylsulfoxide solutions at the current density from 0.1 to 0.2 A/cm² on smooth platinum with background aqueous sulfuric acid solutions produces dimethylsulfoxide in the anode section of diaphragm electrolyzer with the current efficiency over 90% [3]. Methanesulfonic acid is a strong acid with the melting point of 20°C, mixing with water and dissolving in polar organic solvents. The final product was isolated from the background electrolyte (sulfuric acid) by cooling and decantation.

Therefore, selecting the suitable current density and other conditions for electrolysis of dimethylsulfoxide solutions, we can synthesize two products: dimethylsulfone and methanesulfonic acid.

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