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LETTERS TO THE EDITOR

Indirect Cathode Amination of Anisole in Dilute Sulfuric Acid and Acetonitrile Solutions

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Electrochemical cation-radical amination of aromatic compounds poorly soluble in water and activated towards electrophilic reagents, in particular, anisole, is carried out in dilute sulfuric acid containing an organic solvent inert with respect to the amino radical intermediates [1–4], e.g., acetonitrile [1] or acetic acid [2, 3], in a concentration close to the maximum possible. In the electrolysis performed under these conditions with full theoretical conversion of NH_2OH with the use of one electron per its molecule, the total efficiency of aromatic monoamino compounds on the current corresponds to their yield relative to the source of amino radicals.

In this work we show that the amination of anisole to form the isomeric anisidines can be performed with a fairly high yield relative to hydroxylamine under the milder conditions than those used in [1]: at a lower H_2SO_4 concentration and temperatures.

The highest total yield of anisidines (78%) was obtained by the electrolysis of the anisole emulsion in 6 M H_2SO_4 and 11.6 M CH_3CN at 40°C in an electrochemical cell having a mercury cathode of 12.3 cm^2 area [1]. Since the working electrode area in the cell we used was 11 cm^2 and the efficiency of the target electrochemical process depended on the concentrations of oxidized and reduced forms of the Ti(IV)/Ti(III) mediator system [4], we initially duplicated the abovementioned electrolysis. The yield of anisidines relative to hydroxylamine was 80%. The increase in the amination efficiency with a decrease in the cathode area is connected with a decrease in the rate of the competitive reduction of aminyl radicals to ammonia due to the lower rate of the cathode generation of Ti(III) at the same current density.

Taking into account the data on the conductivity of the sulfuric acid solutions [5], as well as the influence of temperature on the results of the anisole amination in solution of acetic acid and 4 M H_2SO_4 [3], we carried out the electrolyses of Ti(IV)–NH_2OH–$C_6H_5OCH_3$ system in an electrolyte containing 4 M H_2SO_4 and 14.1 M CH_3CN at 30, 25, 20, and 15°C. In this case, in contrast to the experiment performed in 6 M H_2SO_4 a solution of anisole in the catholyte rather then emulsion was subjected to the electrolysis.

Total yields of the isomeric anisidines (2 *para*/*ortho* ~ 3.9) formed at the mentioned temperatures are 79.6, 81.1, 84.2, and 82.3%, respectively, not inferior to that obtained in 6 M H_2SO_4 solution at 40°C. Hence, from an economy point of view, the electrosynthesis of aromatic monoamino compounds from substrates, which are poorly soluble in water, it is apparently desirable to perform it under the conditions we have found: at room temperature in 4 M H_2SO_4 solution contained the maximal possible concentration of CH_3CN.

The amination of aromatic substrate was performed in a glass electrochemical cell having a jacket for the temperature control and ceramic diaphragm that separated the cathode and anode chambers. The catholyte (25 ml) containing 0.1 M of Ti(IV), 0.2 M of NH_2OH, 4 or 6 M of H_2SO_4, 14.1 or 11.6 M of CH_3CN, and a small amount of water was introduced with the Ti(IV) solution and was added to achieve the volume of 25 ml after the dissolution of the system components. The volume of anisole added to the catholyte was 5 ml. The electrolysis of anisole as a solution in 4 M H_2SO_4 deaerated with argon or as a highly dispersed emulsion in 6 M H_2SO_4 was performed at the cathode current density of 2 mA cm^{-2} and the quantity of consumed electricity 482.4 C.

When the electrolysis was complete, the catholyte was diluted with cold water to a concentration of H_2SO_4 1–1.5 M, alkalinized to the slightly acidic reaction with a saturated NaOH aqueous solution, and neutralized with $NaHCO_3$.

The quantitative analysis of the isomeric anisidines (their qualitative composition has been established earlier [1, 6]) was performed on a Chrom-5 chromatograph equipped with a flame ionization detector. The temperature of the glass column [2500× 3 mm, 5% XE-60 on Chromaton N-AW-DMCS (0.160–0.200 mm)] was 150°C, the rate of the carrier gas (helium) was 15 ml min^{-1}.

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