
SHORT
COMMUNICATIONS

Electrosynthesis of Anisidines in Aqueous Sulfuric and Acetic Acids

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Abstract—The influence of the concentrations of acetic and sulfuric acids on the efficiency of anisole amination by means of hydroxylamine and Ti(IV)/Ti(III) mediator was studied. *Ortho*- and *para*-anisidines were obtained with the total yields of about 79% by current and hydroxylamine.

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The indirect cathode amination of aromatic compounds with the Ti(IV)–hydroxylamine system in 0.5–7 M aqueous solutions of sulfuric acid gave the corresponding monoamine isomers [1, 2]. However, in the functionalization of substrates with low solubilities in water, the current efficiency was only slightly higher than 10% even after incomplete conversion of NH_2OH [3]. The major reason for this was the disappearance of main part of the aminyl radicals caused by their interaction with titanium(III) ions [1, 2].

In this work, the amination of anisole was used to show that the rate of the formation (competing with substitution) of ammonia (ammonium) can be substantially decreased by the introduction of acetic acid (AcOH) into the sulfuric acid electrolyte; acetic acid is fairly inert with respect to amino radical intermediates [4].

The amination of anisole was performed in a glass electrochemical cell, in which the cathode and anode spaces were separated by a ceramic diaphragm. An aqueous solution containing 0.2 M NH_2OH , 0.1 M Ti(IV), and the required concentrations of H_2SO_4 and AcOH served as a catholyte. The electrolysis of argon-deaerated high-dispersity emulsion of anisole (5 ml, 0.046 mol) in catholyte (25 ml) was performed at 40°C and a current density on a mercury cathode of 2 mA/cm². As in [3, 5], the amount of electricity passed during electrolysis was generally 250 C.

After electrolysis, the catholyte was diluted with water to a ~1 M concentration of H_2SO_4 and neutralized by successively treating it with saturated aqueous solution of NaOH and NaHCO_3 . The anisole amination products were extracted with chloroform and analyzed on a Chrom-4 chromatograph. For qualitative analysis, we used flame ionization and heat conduction detec-

tors, and phases XE-60, SE-30, and OV-17. Quantitative analysis of anisidines was performed using a flame ionization detector and a glass column with length 2500 mm and inside diameter 3 mm (5% XE-60 on Chromaton N-AW (0.160–0.200 mm)). The column temperature was 150°C; the carrier gas (helium) flow rate was 15 ml/min.

The amination of anisole in 1.5 M H_2SO_4 showed that the presence of small amounts of AcOH in the catholyte led to a decrease rather than increase in the efficiency of substitution. The dependence of the current efficiency of anisidine formation on the content of the organic solvent was minimum in a 10 M solution. However, using AcOH concentrations higher than 12 M was restricted by the solubility of Ti(IV) complexes in aqueous–organic catholytes. We found that the problem of complex solubility was absent in more acid aqueous–organic media. Taking into account this and the character of the dependence of the yield of anisidines on the molar ratio of $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ [5], we performed preliminary electrolyses of the Ti(IV)– NH_2OH –anisole system in 6 and 9 M H_2SO_4 containing maximum possible concentrations of CH_3COOH (11 and 7.6 M, respectively).

The products of anisole amination in these electrolytes were *ortho*- and *para*-anisidines (*para* : *ortho* ~ 1.8). The highest total current efficiency of amino compounds formation was obtained in 6 M H_2SO_4 ; because of the chain mechanism of electrochemical amination [1, 2], the yield of anisidines was 152%. When electrolysis was performed by passing the amount of electricity necessary for the complete exhaustion of hydroxylamine in a one-electron process (482.4 C) through the electrolyte, the catholyte acquired a violet coloration characteristic of Ti(III)-containing solutions. The addition of hydroxylaminium sulfate to the sample taken

from the catholyte volume caused solution decolorization, which was evidence of the complete conversion of NH_2OH . The current yield of anisidines (79%) corresponded to that of hydroxylamine.

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