

Electrochemical Amination. Synthesis of Aniline in Aqueous–Acetonitrile Solutions of Sulfuric Acid

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Abstract—The process of indirect cathodic amination of benzene is studied in aqueous media containing 4–10 M H₂SO₄ and, accordingly, 13.8–7.1 M CH₃CN. At 50°C, electrolysis in the system of Ti(IV)–NH₂OH–C₆H₆ results in formation of aniline and also small amounts of isomeric phenylenediamines and diphenyl. The current efficiency of aniline is maximum in the catholyte containing 8 M H₂SO₄ and 9.4 M CH₃CN. Under these conditions, full conversion of hydroxylamine is observed; the 80% current efficiency of aniline corresponds to the efficiency of the amino radical source and its mass fraction among the products of electrolysis exceeds 97%.

Keywords: cathode, Ti(IV)/Ti(III) mediator system, hydroxylamine, amino cation–radical, benzene, cation–radical aromatic substitution, aniline

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