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LETTERS TO THE EDITOR

Efficiency of Radical-Cation Amination of Aromatic Compounds in Sulfuric Acid Solutions

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One of the reasons why the M^{n+}–NH_2OH system, where M^{n+} is a transition metal ion (one-electron reducer), has not found application in chemical synthesis of primary amines is that deprotonated aminyl radicals are very fast reduced to ammonia [scheme (1)].

$$\dot{N}H_2 + M^{n+} \xrightarrow{H^+} NH_3 + M^{(n+1)+}. \qquad (1)$$

Despite long-standing efforts [1–4] at aminating unsaturated and aromatic substrates in aqueous and aqueous-organic media with amine cations [Eq. (2)], the hydroxylamine-based yields of amination products still remain relatively low.

$$\dot{N}H_2 + H^+ \rightleftarrows \overset{\cdot+}{N}H_3. \qquad (2)$$

In the present work we used the example of the Ti(IV)–NH_2OH–C_6H_6 system to show that ammonia formation can be suppressed by using electrochemical radical-cation amination; thus we synthesized aniline and isomeric phenylenediamines with a total hydroxylamine-based yield of about 100%.

The amination of benzene was performed in an electrochemical cell equipped with a reflux condenser, a thermostating shell, and a ceramic diaphragm between the cathodic and anodic compartments. The object of electrolysis was a highly dispersed emulsion of 5 ml of the aromatic substrate in 25 ml of a catholyte, specifically, 11 M aqueous H_2SO_4 containing 0.1 M Ti(IV) sulfate, 0.2 M NH_2OH or 5 M CH_3CO_2H (electrolyte 1), or 5.5 M CH_3CN (electrolyte 2). The reaction temperatures in electrolytes 1 and 2 were 60 and 50°C, respectively. Titanium(III) ions were generated on a platinum cathode at a current density of 2 mA/cm^2. The quantity of electricity (Q), passed through the electrolyte, was varied from 5 to 482.4°C.

After the electrochemical process had been complete, the catholyte was cooled, made weakly acidic by treatment with aqueous sodium hydroxide, and neutralized with $NaHCO_3$. The amination products were extracted with chloroform and analyzed by chromatography on a Chrom-4 gas chromatograph with a flame-ionization detector. The temperature of the glass column [2500 × 3 mm, 5% XE-60 na Chromaton N-AW-DMCS (0.160–0.200 mm)] was 150°C, carrier gas helium.

The highest efficiency of the radical-cation amination is observed at low Q values, when the concentration of Ti(III) ions in the solution is low and, consequently, reaction (1) is slow. Benzene amination in sulfuric acid media occurs by a chain mechanism [5, 6], and the total current yields (one electron per one hydroxylamine molecule) in electrolytes 1 and 2 are hundreds percent. Thus, for example, on passing 10 C of electricity through the electrolytes, the yields of amination products are higher than 900 and 1200%, respectively.

Upon completion of the electrolyses accomplished with passing the quantity of electricity theoretically required for complete consumption of hydroxylamine in a one-electron process (Q_t 482.4 C), electrolytes 1 and 2 have a stable violet color characteristic of Ti(III) solutions. These solutions are decolorized by addition of hydroxylamine, which implies complete conversion of the latter in the electrochemical processes (the fact that the cathodic potential and the yields of amines depend on Q suggests that the amination of benzene in catholytes 1 and 2 is largely complete on the consumption of ~80 and 60% of Q_t). Consequently, the overall current yield of aniline and isomeric phenylenediamines in the electrosyntesis with the consumption of Q_t simply the total yield of amines with respect to hydroxylamine. In our experiments, the hydroxylamine-based yields of benzene amination products were 95.6% in the first solution and 99.6% in the second.

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