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LETTERS TO THE EDITOR

Selectivity of Electrochemical Amination of Anisole in Water Solutions of H_2SO_4

Yu. A. Lisitsyn and A. V. Sukhov

A.M. Butlerov Chemical Institute of Kazan (Privolzhskiy) Federal University,
ul. Kremlevskaya 18, Kazan, Tatarstan, 420008 Russia
e-mail: Yuri.Lisitsyn@kpfu.ru

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Electrochemical amination of anisole by Ti(IV)/Ti(III) mediator system and hydroxylamine in water solutions of sulfuric acid with the concentration more than 6 M gives isomeric anisidines and a series of higher boiling amino compounds [1].

We have found that the above-mentioned non-identified products [1] are isomeric methoxyphenylenediamines. After evaluation of effect of the sulfuric acid concentration on the degree, selectivity, and efficiency of amino radical cation substitution, the principal possibility of selective synthesis of 4-methoxy-1,3-phenylenediamine was revealed.

During amination of anisole in 8-15 M sulfuric acid solutions with the consumption of the amount of electricity theoretically necessary for the complete conversion of NH_2OH in the process with the expenditure of one electron per its molecule the main products of substitution are *orto*-, *para*-anisidines, and 4-methoxy-1,3-phenylenediamine. *meta*-Anisidine and 4-methoxy-1,2-phenylenediamine are found in insignificant amounts.

Dependences of yields by current of anisidines as well as of 4-methoxy-1,3-phenylenediamine on the concentration of acid passes through the maxima at 14 and 10 M of sulfuric acid, respectively. At 8, 10, 12, 14, and 15 M of sulfuric acid yields of monoamines are 8.0, 13.1, 21.6, 26.4, and 14.3%, and the diamine yields are 31.0, 46.1, 37.1, 3.3 and 1.9%. Considering the composition of products the increase in the total efficiency of electrochemical process with the increase in the sulfuric acid concentration up to 12 M may be attributed to the increase in the solubility of aromatic substrate in catholyte, and also the concentrations of *para*-anisidinium and the associates of *para*-anisidine protonated or unprtonated at the methoxy group with the basic components of the electrolyte [2, 3], mainly with the hydrosulfate ion [4]. The decrease in the total yield of amino compounds in more acidic solutions originates probably from the processes of protonation and sulfonation of anisole and the formation of diprotonated anisidines (evidently *para*-anisidine dication as well as dications of isomeric phenylenediamines [3] practically do not react with electrophylic amino radical cation). The occurrence of the protonation is suggested, in particular, by the dependence of isomeric composition of anisidines on the concentration of acid. In particular, whereas in 10 M sulfuric acid the content of *para*- and *meta*-anisidines is 60.8 and 0.2%, in 15 M sulfuric acid it is 86.3 and 0.8% respectively.

After completion of electrolysis catholytes with 10 and 12 M sulfuric acid content were light and dark violet respectively. The presence of coloration characteristic of Ti(III) solution and its disappearance after addition of hydroxylamine sulfate to a sample of catholyte shows that in the media with the concentration of acid 10 and more mol/l complete conversion of NH_2OH is observed. In the experiments carried out under these conditions using the theoretically necessary amount of electricity yields of amino compounds with respect to current and the source of amino radical intermediates coincide.

Note specially that the results of functionalyzation of anisole obtained in this work point to the possibility of the directed synthesis of 4-methoxy-1,3-phenylenediamine from *para*-anisidine, and of highly selective functionalization of monosubstituted anilines containing *orhto*-, *para*-orienting substituents in the position 4.

The amination of $C_6H_5OCH_3$ was carried out at 40°C in the three-electrode glass electrochemical cell equipped with a jacket for temperature control, reflux condenser, and ceramic diaphragm separating the cathode and the anode areas.

Catholyte, 25 ml, contained 0.1 M of Ti(IV), 0.2 M of NH_2OH, and water solution of sulfuric acid of the given concentration. Amount of added anisole was 5 ml. Emulsion of aromatic substrate in 8–12 M sulfuric acid or its solution in 14 and 15 M sulfuric acid was deaerated with argon and exposed to electrolysis.

In the amination of anisole IPC-ProMF potentiostate was used. Current density on platinum cathode (8.2 cm^2) was 2 mA cm^{-2}, amount of electricity 482.4 C. Reproducibility of values of cathode potential in the course of experiment was provided by pre-electrolysis washing of electrode with acetone and water, and the subsequent anode-cathode polarization at the current ±5 A in the sulfuric acid solution of the concentration under study. Control and automatic registration of potential measured relative to the silver chloride electrode was carried out by a Keithley 2000/E multimeter and a computer coupled with the potentiostate. Electrode from platinated platinum was used as an anode, and the role of anolyte was played by water solution of sulfuric acid with the concentration equal to the concentration of catholyte acid.

After the completion of electrolysis the emulsion or the solution of anisole in catholyte was diluted with cold water to the concentration of sulfuric acid about 1.5 M, alkalinized to the weakly acidic reaction with saturated water solution of sodium hydroxide, and neutralized with sodium bicarbonate. The products of amination of anisole were extracted with chloroform.

The quantitative analysis of aromatic mono- and diaminocompounds was carried out by a Chromateck-Krystall 5000.2 chromatograph with the flame ionization detector. Temperature of CP-Sil 8 CB capillary column ($60\ m\times0.25\ mm\times0.25\mu$) was 160°C, pressure of carrier gas (helium) was 200 kPa. For the confirmation of qualitative composition of products of electrolysis Chrom-5 chromatograph with the flame ionization detector and glass columns ($3.5\ m\times3\ mm$) filled with XE-60 and OV-17 phases was also used.

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