

Electrochemical Amination of Isomeric Chloroanilines in Aqueous Solutions of Sulfuric Acid¹

Yu. A. Lisitsyn^a, * and A. V. Sukhov^a

^aKazan Federal University, Butlerov Chemical Institute, Kazan, 420008 Russia

*e-mail: Yuri.Lisitsyn@kpfu.ru

Received February 27, 2019; revised April 12, 2019; accepted July 17, 2019

Abstract—The processes of indirect cathodic amination of *para*, *ortho*, and *meta*-chloroanilines by means of the Ti(IV)–NH₂OH system in aqueous solutions of 9–17 M sulfuric acid are studied. The efficiency and regioselectivity of radical cation substitution increase with the increase in electrolyte acidity and temperature. Functionalization of *para*-chloroaniline in 17 M H₂SO₄ produces 4-chloro-1,3-phenylenediamine with the mass fraction of 99.7%. Its yield corresponding to the complete conversion of hydroxylamine is 91%. The only side product of amination is *para*-phenylenediamine.

Keywords: cathode, Ti(IV)/Ti(III) mediator system, hydroxylamine, amino radical cation, chloroanilines, radical cation aromatic substitution, chlorophenylenediamines

DOI: 10.1134/S1023193520050080

INTRODUCTION

Amination of aromatic substrates with the use of hydroxylamine and the Ti(IV)/Ti(III) mediator system produces the corresponding mono and/or diamino compounds [1, 2]. The isomeric composition and the yields of phenylenediamines depend on the sulfuric acid concentration and the nature of substituent in the aromatic ring. The latter factors probably determine the relative content of molecular associates ArNH₂ · HSO₄[−], ion pairs ArNH₃⁺, HSO₄[−], and cations ArNH₃⁺ in the catholyte [3–8]. In associates, the aromatic rings are activated with respect to electrophilic reagents. In ion pairs, due to the action of hydrosulfate ions, the effect of ammonium groups is limited by the field effect [9] and the rings are deactivated in the lesser extent than in cations. In associates and cations, the amino and ammonium groups, respectively, are responsible for orientation of substitution [10], whereas in ion pairs, it is the substituent which is the responsible, except for deactivated positions in the aromatic ring (in the C₆H₅NH₃⁺, HSO₄[−] ion pair, the *para*- and *meta*-positions are probably virtually equivalent for the attack of an amino radical cation).

Functionalization of anisole, a substrate activated with respect to amino radical cations, produces virtually the only substitution product—4-methoxy-1,3-

phenylenediamine [5], which allows its highly selective synthesis to be carried out from *para*- and *ortho*-anisidines [8]. At the same time, the amination of chlorobenzene, i.e., a deactivated compound, produces all isomeric chlorophenylenediamines except for 5-chloro-1,3-isomer [7]. This is explained by the fact that whereas anisidines in sulfuric acid solutions are in fact present only in the form of cations bound and partly unbound into ion pairs [3, 5, 8], the chloroanilines are present also as molecular associates [7], because the chlorine atom that pulls the electron density away from the ring in isomeric chloroanilinium makes easier the abstraction of a proton from the ammonium group by a sulfate ion.

Although the amination produces five isomeric chlorophenylenediamines, the analysis of their distribution as a function of sulfuric acid concentration [7] and the results of the trial electrolysis in the system Ti(IV)–NH₂OH–*n*-ClC₆H₄NH₂ [3] point to the possibility of selective synthesis of one isomer, namely, 4-chloro-1,3-phenylenediamine (4-Cl-1,3-PDA), which can be used, for example, in the synthesis of heat-resistant, fireproof, highly lasting fibers, films, and varnishes [11]. In this study we investigated the processes of amination of *para*, *ortho*, and *meta*-chloroanilines with the aim of finding the conditions that would favor the formation 4-Cl-1,3-PDA and obtaining the data that would confirm the correctness of interpretation of our earlier results on chlorobenzene amination [7].

¹ Published on the basis of materials of the XIX All-Russian Conference “Electrochemistry of Organic Compounds” (EKHOS-2018) (with international participation), Novocheerkassk, 2018.