

SUBSTITUENT EFFECTS ON THE ELECTROCHEMICAL OXIDATION OF ANILINES IN AQUEOUS MEDIUM AT PLATINUM ANODE

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ABSTRACT

Anodic oxidation on selective anilines has been carried out at platinum electrode in aqueous protic medium. Depending on the substituents present, benzidine, hydroxyaniline, diphenylamine, hydrazobenzene and azobenzene derivatives have been identified by chromatography and ^1H NMR. Probable mechanisms for the anodic transformations are suggested. The credibility of the mechanism has been established by substituent effects.

Key words : Electrochemical oxidation, Substituted anilines, Protic medium, Platinum

INTRODUCTION

Studies on the electrochemical oxidation of aliphatic amines in non-aqueous and aqueous alkaline media have been reported in earlier literature^{1–3}. Preliminary works on the anodic processes of anilines are observed to be accompanied by hydrolysis, ring substitution and multiple coupling^{4,5}. Only a very few investigations on the mechanistic aspects have been conceived^{6,7}. Further, substituent effects and decomposition pathways for electrochemical processes on anilines are observed to be incomplete⁸.

The present work probes the anodic behavior of anilines at platinum electrode in the vicinity of both; the electron donating and withdrawing groups. Anilines, substituted with o-OH, p-OH, o-Cl, o-NO₂, p-NO₂ and m-NO₂ are chosen, in order to ascertain both electronic and steric effects on the proposed mechanism.

EXPERIMENTAL

Materials – Aniline (Nice) and o-toluidine (s. d. fine) were purified by steam distillation; p-toluidine and o-chloroaniline (Burgoyne) by ordinary distillation. m-nitroaniline (Riedel) is distilled with methanol⁹. o- and p-nitroanilines (Viosojuz, USSR) were used as such. Pretreated platinum strips were used as the electrodes.

Electrolysis – The preparative electrochemical oxidation was carried out galvanostatically in a divided H-cell. The working electrode potentials were measured as cell voltages. Current-voltage studies were performed with 0.05 M sulfuric acid solution and 0.01 M

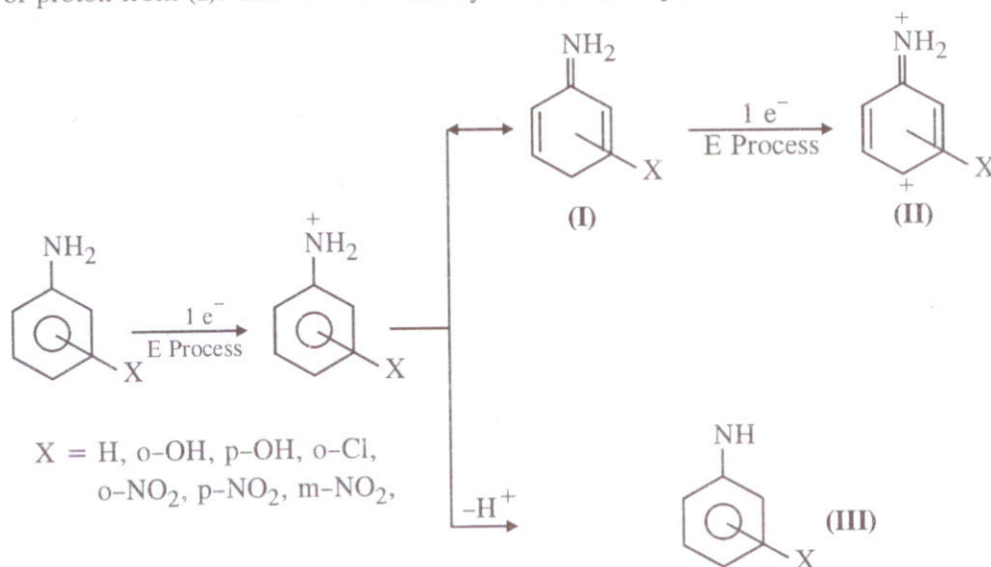
solutions of anilines, under identical conditions. For preparative electrolyses, assuming a 3-electron process, calculated quantities of current were passed, through 0.01 M acidic solutions of anilines.

Product analysis – The common observation in almost all the systems is that black, green or dark brown water-soluble dye material has been formed alongwith other products. The product mixtures, after ether extraction were analyzed chromatographically using silica gel-G (Acme) coated plates. Quantitative separation of various products was affected with TLC. The products were characterized by chemicals tests and with ^1H NMR (Bruker – 200 MHz) spectral studies.

RESULTS AND DISCUSSION

All the anodic processes have been performed just below the decomposition potential of the solvent. The oxidation has been assumed to occur both at the aromatic nucleus and at the nitrogenous side chain, leading to the formation of appropriate products – derivatives of benzidine, hydroxyaniline, diphenylamine, hydrazobenzene and azobenzene. The initial oxidation occurs at basic nitrogen. Subsequent electron relay may lead to ring oxidation. Consequently the products are to be formed through three different intermediates.

The mechanistic pathway envisages the generation of cation radical intermediate (I) with the subsequent formation of a dication (II). Such a proposal is very much supported by earlier reports like ESR spectral studies^{10,11}, tafel data¹² and gamma irradiation¹³ in similar systems. Such two closely spaced 1-electron steps, especially in amines of conjugated diene systems have already been established¹⁴. The formation of radical intermediate (II) occurs through a loss of proton from (I). This is in conformity with earlier reports on radical initiations for the



Cation Radical Mechanism

$$\text{H}_2\text{N}^+=\text{C}_6\text{H}_4\text{X} + \text{X-C}_6\text{H}_4=\text{NH}_2^+ \xrightarrow[\text{C Process}]{-2\text{H}^+} \text{H}_2\text{N-C}_6\text{H}_4\text{X-C}_6\text{H}_4\text{NH}_2$$

(I) (II) (IV)

The dication intermediate formed by two 1-electron oxidative steps, leads to hydroxyanilines and diphenylamine derivatives. The attack of solvent water on the ring charge, results ultimately in hydroxy derivative (V) by an EC route.

The scheme illustrates the C process and subsequent reactions of 2-substituted benzaldehyde derivatives.

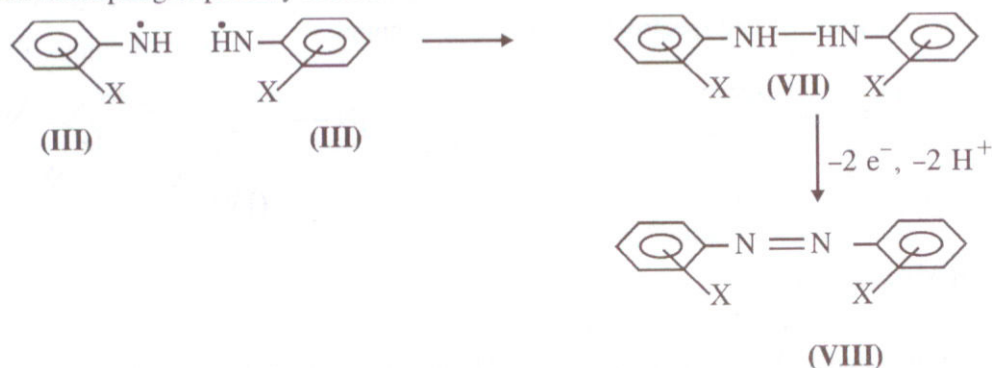
 Top reaction: A 2-substituted benzaldehyde derivative (II) reacts with water (H₂O) via the C process to form a 2-substituted benzamide derivative (V). The intermediate steps show the formation of a hemiacetal-like structure followed by a rearrangement.

 Bottom reaction: A 2-substituted benzaldehyde derivative (II) reacts with a 2-substituted imine derivative (II) to form a 2,2'-disubstituted diphenylamine derivative (VI). The reaction proceeds via a protonated intermediate, followed by deprotonation (-H⁺) to yield the final product (VI).

All the three EC mechanistic proposals are supported individually by earlier reports on similar systems^{18,20}.

Radical Mechanism

The radical intermediate (III) has to undergo coupling leading to hydrazobenzene derivative (VII). Further 2-electron oxidation and subsequent loss of protons results in azobenzene derivative (VIII). Similar reports on 3-electron ECE processes are found in the oxidative coupling of primary amines²¹⁻²³.



The loss of proton in acid medium can well be justified by the availability of a number of compounds including the parent aniline, in the anolyte. It is substantiated by the observation that a part of the unreacted substrate is invariably identified in the developed chromatogram. This is the common observation in the electrode processes involving anilines¹. Alternatively the protons eliminated in various steps may also drift towards the cathode and get reduced to liberate hydrogen.

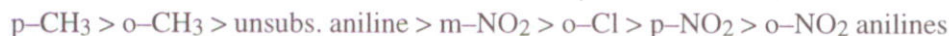
Substituent Effects – The comparative yields of the various products are based on the comparative stabilities of the intermediates. With aniline as the standard, this substituent study brings an indirect evidence and credibility to the proposed mechanism.

The yields of benzidine or semidine derivatives, which are the products of cation radical (I) are observed in the following decreasing order



$o\text{-NO}_2$ and $p\text{-NO}_2$ groups stabilize the cation radical (I) by resonance greatly than $o\text{-Cl}$ group by the residual field effect. $m\text{-NO}_2$ group highly destabilizes the positive charge on the amino group. On the contrary, the methyl substituents stabilize any ionic intermediate by hyperconjugation. Also the + I effect favors further oxidation to generate dication (II) rather than allowing the radical to dimerize.

Similarly the order in the yields of hydroxy derivatives is observed to be in accordance with the decreasing stabilities of corresponding dications (II).

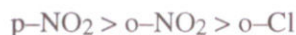


Further, the attack by stronger nucleophile, viz., water, is more pronounced than by the parent aniline.

The dication of unsubstituted aniline is stabilized by (2 + 1) resonance structures. In cases of methyl-substituted anilines, in addition to these resonance structures, stabilization may be enhanced by (3 + 1) hyperconjugative structures. The well pronounced – M and – I effects destabilize (II) in *m*-NO₂ and *o*-Cl anilines, respectively. When –NO₂ is at ortho or para, its reinforced – M and – I effects destabilize the positive charge in (II), to a very large extent.

The substrate, a weaker nucleophile can attack only the less stabilized dication, due to its enhanced reactivity. Thus the above order is almost reversed in the formation of diphenylamine derivatives.

The formation of azobenzenes through radical intermediates is favored in *o*-NO₂, *p*-NO₂ and *o*-Cl anilines in the following order



The above order can very well be understood by considering the ease of forming the radical (III) from cation radical (I). Obviously the *o*- and *p*-NO₂ groups, by their – M and – I effects herald the loss of proton from cation centre. But the opposing – I and + M effects of chlorine influence the loss of proton slightly to a lower level.

As *m*-nitro group is in conjugation, rendering the lone pair on amino nitrogen non-available, further oxidation of hydrazobenzene is hindered.

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