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RESEARCH ARTICLE

COMPARATIVE ELECTROCHEMICAL STUDIES OF o- , m- and p- TOLUIDINE

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ABSTRACT

Electrochemical oxidation of methoxy substituted aniline (toluidine) has been done on both gold and platinum electrode cyclic voltametrically. The results were compared in different supporting electrolytes such as KCl, KNO_3, H_2SO_4, HCl, etc. Effect of pH was observed on electrochemical oxidation of o- , m- & p- toluidine at gold and platinum electrode. During various scan single oxidation peak during first forward scan with no corresponding cathodic peak obtained while a new anodic cathodic couple peak appears in subsequent scan obtained. Kinetic parameters like heterogeneous rate constant, transfer co-efficient and diffusion co-efficient were also calculated. Micro quantities of toluidine by linear sweep voltammetry and hydrodynamic voltammetry were also determined.

INTRODUCTION

Toluidines are methyl substituted aromatic amines and contribute among the degradation products of azo dyes. Three isomers of toluidine are found according to the position of methyl ($-CH_3$) group i.e o, p and m toulidines. Toluidines are used in manufacturing of various dyes and other organic chemicals; o-isomer is used in textiles printing and making colours fast to acids, p-isomer is also used as a reagent for lignin, nitrile phloroglucinol [1]. Literature survey reveals that most of the electrochemical oxidation studies of toluidines has been done on any one or two isomers generally in non-aqueous media.

Due to the presence of electron donating methyl group the isomeric toluidines are more easily oxidised than the parent aniline. Lord and Rogers [2] polarographically studied some aromatic amines like aniline, o- toluidine and m- toluidine and reported that the formal potentials obtained polarographically for these organic compounds agreed well with the critical oxidation potential obtained chemically. Aniline and p-toluidine were analysed by oxidation at a rotating platinum electrode by Beilis [3]. Polarographic oxidation data were collected for aniline, substituted anilines, azobenzene and hydrazobenzenes at rotating platinum electrode by Wawzonek and Mc Intyre [4]. Study of anodic oxidation of a series of p-substituted anilines in aqueous media by Bacon and Adams [5] revealed a common pattern of p- group elimination and head to tail coupling to give 4'- substituted 4 -amino diphenylamine. Optically transparent electrodes were used by Kuwana and Strojek [6] to study the kinetics and mechanism of o- toluidine oxidation wherein the intermediate formed was identified as a dimer species. A graphite electrode has also been used to study toluidines [7]. p-Thiocyano-o-toluidine was shown to be the major product when o- toluidine was oxidised in water, ethanol, HCl, NH_4 SCN by Helwig and Patent [8] and also by Malnikov *et al* [9]. They also showed that 3- methyl 4-thiocyano -aniline was the dominant product of m- toluidine oxidation in presence of ammonium thiocyanide solution. These studies were carried out a carbon anode .2- Amino -6-methylbenzothiazole is formed during oxidation of p-toluidine in ethanol, thiocyanide and HCl acid medium [10], at a carbon anode. However when the oxidation of p- toluidine was carried out in ethanol, KOH medium at iron anode , p,p'- azotoluene and 5- amino -2-methyl -p- quinone -bis- p- tolyimide are the main product [11]. Rosaniline is formed when a mixture of aniline, p- toluidine and o-toluidine were oxidised in sulphuric acid medimu at platinum anode [12]. Anodic oxidation pathways of diphenylamines system in aqueous acidic solution at platinum button electrode were studied by Donald *et al* [13]. Cyclic voltammetry of o- toluidine has been studied at GCE in aqueous medium by Rao *et al* [14]. The oxidative dimerisation reaction of N, N- dimethyl - p- toluidine in acetonitrile was studied by cyclic voltammetry using micro disc electrode by Neil and co-workers [15]. Literature survey reveals that most of the studies on electrochemical oxidation of toluidines have been done in non-aqueous solvent specially (acetonitrile). In case of aqueous medium the most studied supporting

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electrolyte has been sulphuric acid. As far as working electrode is concern earlier studies were on polarography using mercury electrode and later on Adms[5] group have used platinum electrde. Moreover, it is surprising thatsystematic electrochemical studies of all the three isomers have not been repoted. In present studies a detailed systematic investigations on electro chemical behaviour of all the three isomers at different pH and in a number of supporting electrolytes at two different working electrodes viz platinum and gold electrode have been reported.

MATERIALS AND METHODS

Cyclic voltammograms were recorded with electrochemical analyzer CV–27, from Bioanalytical System Inc. (BAS), West Lafayette, USA in combination with a Series–100, Omnigraphic X–Y recorder, Houston Instruments, Austin (USA) and a cell stand C–1 (BAS, USA) served the purpose of electrochemical cell. The instrument is easy to use, versatile reliable and has broad applicability. It can perform various electrochemical techniques like linear sweep voltammetry, cyclic voltammetry, chronoamperometry, chronocouloumetry, potentiometry, amperometry and stripping voltammetry. Instrument is designed to perform electrochemical techniques in which the potential of the working electrode is controlled and the resulting current is measured. It offers a potential range + 5.0 to – 5.0 volt (V) and scan rate ranging from 0.0001 Vs^{-1} to Vs^{-1} and current gain ranging from 0.002 mA/V to 10 mA/V. A X–Y recorder Houston, Bausch & Lomb is connected to series to the CV–27 voltammograph. The solid electrodes used as working electrode are:-

1. Platinum Electrode (PtE)
2. Gold Electrode (AuE)

Both supplied from Bioanalytical system Inc. (BAS), USA. These electrodes are disk of highly pure electrode materials (viz. gold or platinum) embedded in CTFE plastic rod having geometric area of 1.76 x 10^{-2} Cm^{2}. Pretreatment of solid electrode surface was made by micropolishing before measurement using diamond lapping compound 1μm (Kemet, Kent, U.K.) and finally with 0.05 μm α–alumina powder on a fabric pad attached to glass plates then thoroughly rinsed by deionized water. These electrodes are found to be very useful due to their high mechanical stability, low polarity, good conductivity, inertness and usefulness over a wide potential region.

Silver–Silver chloride (Ag/AgCl) supplied by Bioanalytical systems Inc. USA was used as a reference electrode. All the potential reported in this study were measured with respect to this electrode. A platinum wire, fused to the top of the electrochemical cell served as an auxiliary electrode. A digital pH – mV temperature meter (Model PH 206) from Lutron Instrument, Taiwan was used to measure the pH values of experimental solutions.

During experiment deoxygenation and inert atmosphere is maintained by passing the Nitrogen (N_2) gas over the solution (blanket mode) using BAS C–1A cell stand. Reagents used throughout the present investigation were of analytically pure grade (AR). ; o– and p- toluidine from SD Fine Chemicals, India; *m*–toluidine from Sisco Chem, India. Acetic buffer was prepared by adding requisite amount of 0.5M sodium acetate and 0.25M acetic acid to get a buffer in the pH range of 3 to 7. A great care was taken while handling these aromatic amines. Eye, skin and clothing contacts were also avoided by wearing gloves and glasses, while preparing the solutions, inhalation of compounds was avoided by wearing a mask.

RESULTS AND DISCUSSIONS

Cyclic voltammetric studies at Platinum and Gold electrode: Using different supporting electrolytes

Electro chemical oxidation of toluidine (o-, m-, p-: isomer) at platinum and gold electrode has been studied in detail. Preliminary cyclic voltammetric (CV) studies were carried out in different supporting electrolytes as listed below:

0.1 M HCl	0.1 M H_2SO_4	Acetate buffer (pH 3 to 7)
0.1 M KCl	0.1 M potassium hydrogen pthalate (pH 4.05)	0.1 M KNO_3

For this set of experiments the conditions were as follows- initial potential is fixed as 0.0volts and final potential as 1.2 volts vs Ag/AgCl electrode scan rate is 100 mVs-1 and concentration of the analyte as 1mM.

In general during the electrochemical oxidation of toluidine in aqueous medium containing minimum amount of methanol for solubility purpose (10% in p-toluidine, 20% in o-toluidine and 30% in m-toluidine) at platinum and gold electrode, CV studies reveals a anodic peak during anodic scan without corresponding cathodic peak during reverse scan.

However, in the subsequent scan a small anodic and cathodic peak (product couple peak) have appeared during anodic and cathodic scan respectively. Cyclic voltammetric characteristics of main oxidation peak and product couple peak of o-toluidine is included in table 1.

Electrochemical behaviour of o-toluidine shows one oxidation peak at potential range between 0.83 V to 1.6 V vs Ag/AgCl and a couple peak where cathodic peak varies from 0.24 to 0.60 V and anodic peak 0.33 V to 0.50 V vs Ag-AgCl range in all medium at Pt and gold Electrode. In cash of KCl supporting electrolyte no couple peak was obtained at gold Electrode.

Electro Chemical behaviour of p-toluidine at PtE shows two-oxidation peak and no couple peak except potassium hydrogen pthalate and H_2SO_4. On the other hand p-toluidine at gold electrode shows one oxidation peak in KCl media and acetate buffer (pH3) and two oxidation peaks are obtained in potassium hydrogen pthalate. No couple peak is obtained in all the media.

Electrochemical behaviour of m-toluidine shows resemblance with o-toluidine here we get one oxidation peak and a couple peak at both Pt and gold electrode.

Table 1 Cyclic voltammetric characterstics of o-Toluidine in diffrent supporting electrolyte and at different working Electrode

Concentration: 1mM Reference Electrode: Ag/AgCl Scan rate:100mVs^{-1}

Supporting electrolyte	**Oxidation peak**		**Product couple peak**				**ΔEp (mV)**	**Ipa/Ipc**
	Epa (V)	**Ipa (μA)**	**Cathodic**		**Anodic**			
			Epc (V)	**Ipc (μA)**	**Epa (V)**	**Ipa (μA)**		
Platinum Electrode								
0.1 M KCl	0.86	22.5	0.26	5.5	0.33	5.5	70	1.0
0.1M K NO_3	0.86	21.5	0.24	5.5	0.33	5.5	90	1.0
0.1M PHP* .	0.83	24.5	0.28	10	0.36	7.5	80	0.8
0.1M HCl	1.00	30.0	0.45	3.5	0.50	4.0	50	1.1
0.1 H_2SO_4	0.97	19.0	0.45	2.5	0.50	2.5	50	1.0
0.2 M AB$^{\#.}$	0.83	33.5	0.24	7.0	0.36	5.0	120	0.7
Gold Electrode								
0.1 M KCl	0.87	21.5	-	-	-	-	-	-
0.1M K NO_3	0.90	27.5	0.26	6.5	0.34	7.5	80	1.1
0.1M PHP* .	0.87	22.0	0.29	8.5	0.35	7.5	60	0.9
0.1M HCl	0.95	35.5	0.60	6.0	0.50	4.5	100	0.8
0.1 H_2SO_4	0.91	18.0	0.40	2.0	0.45	2.5	50	1.2
0.2 M AB$^{\#.}$	0.84	27.5	0.28	8.0	0.35	5.0	70	0.6

0.2 M AB$^{\#---}$ Acetate Buffer (pH 3)
0.1M PHP*-- Potassium Hydrogen Pthalate (pH4)

Some of the notable features of these cyclic voltammetric studies are as follows:-

1. Cyclic voltammogram with well-defined irreversible anodic peaks were obtained in all supporting electrolyte under study. The peak potential is in the range of +0.8 Volt to +1.0 volt vs Ag / AgCl electrode for all the three isomers under study employing PtE as well as gold electrode.
2. During reverse cathodic scan no cathodic peak corresponding to main anodic peak.
3. ***Couple peak :*** At more negative potential a small cathodic peak with corresponding anodic peak during anodic scan was observed- In the potential range +0.20 Volt to +0.60 Volt vs Ag / AgCl electrode was observed at PtE as well as gold electrode. This product couple peak appears well defined in case of o- and m- toluidine in all the supporting electrolyte viz. 0.1M KCl, 0.1 M $KNO_{3,}$ 0.1M HCl, 0.1M $H_2SO_{4,}$ 0.2M Acetate buffer (pH3) and 0.1M Potassium hydrogen phalate (pH4). In case p- toluidine main oxidation peak is well defined as in other two isomers, however the product couple peak was not observed in most of the supporting electrolyte except in 0.1 M H_2SO_4 and 0.1 M Potassium hydrogen phalate (pH4) where small couple peak at much cathodic potential was revealed.
4. ***Mechanism of electrochemical oxidation of toluidines:*** In general electrochemical oxidation of all the three isomers showed a irreversible anodic peak (A) and one reversible product couple peak (BB') in the potential available with gold and Pt electrode, 0.0 Volt to +1.2 Volts Ag / AgCl electrode. This suggest following mechanism.

    1. ***Peak A:*** Toluidines under go a primary one electron oxidation to form cation radicals.
    2. ***Couple peak BB':*** These cation radicals then under goes fast head to tail coupling reaction, giving rise to formation of substituted 4-amino- diphenylamine (substituted -4-ADA).

The substituted 4-ADA is much more easily oxidized then toluidine itself and therefore their peak appears at more positive potential as compared to that of single irreversible peak.

Cyclic voltammogram with well-defined anodic peak were obtained at all the pH ranging from 3 to 7 employing acetate buffer at PtE and gold electrode.

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