

ELECTROCHEMICAL STUDIES OF TOLUIDINES WITH SPECIAL REFERENCE TO EFFECT OF pH, SCAN RATE

KUMBHAT SUNITA* SHARMA RICHA¹ SAHAY MANISHA²

*Professor, Jai Narain Vyas University, Jodhpur (Raj.), INDIA

¹ Assistant Professor, S. S. Jain Subodh P.G. (Autonomous) College Jaipur (Raj.), 302004, India, E-mail: dr.richa25@gmail.com

² S. S. Jain Subodh P.G. (Autonomous) College Jaipur (Raj.), 302004, India.

ABSTRACT

Electrochemical oxidation of methyl substituted aniline (toluidine) has been done on both gold and platinum electrode cyclic voltammetrically. The results were compared in different supporting electrolytes such as KCl, KNO₃, H₂SO₄, HCl, etc. Effect of pH was observed on electrochemical oxidation of o-, m- & p- toluidine at gold and platinum electrode. Effect of pH was carried out in acetate buffer ranging from pH 3 to 7. Effect of scan rate was observed in acetate buffer at pH 3, scan rate ranging from 20 mVs⁻¹ to 300 mVs⁻¹.

Key words: o-,m- and p- toluidines; cyclic voltammetrically; gold electrode; platinum electrode.

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 (-CH₃) group i.e o, p and m toluidines. 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, NH₄ SCN by Helwig and Patent [8] and also by Malnikov et al [9]. They also showed that 3- methyl 4- thiocyno -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 medium 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 electrolyte has been sulphuric acid. As far as working electrode is concern earlier studies were on polarography using mercury electrode and later on Adams [5] group have used platinum electrode. Moreover, it is surprising that systematic electrochemical studies of all the three isomers have not been reported. 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, chronocoulometry, 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:-

- a) Platinum Electrode (PtE)
- b) 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 $1.76 \times 10^{-2} \text{ Cm}^2$. Pretreatment of solid electrode surface was made by micropolishing before measurement using diamond lapping compound $1\mu\text{m}$ (Kemet, Kent, U.K.) and finally with $0.05 \mu\text{m}$ 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:

Effect of pH: To observe the effect of change of pH on electrochemical oxidation behaviour of toluidines at PtE and gold electrode acetate buffer (pH 3 to 7) was undertaken as supporting electrode. It was found from the observation that the peak current and peak shapes were good in acidic media. As we increase the pH the current starts decreasing and peak shapes were changed. The couple peaks were obtained only in more acidic solution i.e. at pH= 3. After pH= 3 the couple peak starts diminish. Table 1 includes the cyclic voltammetric characteristics.

Table 1
Cyclic voltammetric Characteristics of o-toluidine at different pH and at different working electrode
Concentration : 1mM Reference electrode : Ag-AgCl Scan rate: 100 mVs⁻¹

pH	Oxidation peak		Product couple peak				ΔE_p (mV)	I _{pa} /I _{pc}
	E _{pa} (V)	I _{pa} (μA)	Cathodic		Anodic			
			E _{pc} (V)	I _{pc} (μA)	E _{pa} (V)	I _{pa} (μA)		
Platinum Electrode								
3	0.83	33.5	0.24	7.0	0.36	5.0	120	0.71
4	0.80	23.5	Diminish	-	-	-	-	-
5	0.76	19.5	-	-	-	-	-	-
6	0.76	19.5	-	-	-	-	-	-
7	0.76	20.0	-	-	-	-	-	-
Gold Electrode								
3	0.84	27.5	0.28	8.0	0.35	5.0	120	0.62
4	0.79	20.5	0.21	5.0	0.32	3.0	110	0.60
5	0.76	18.0	-	-	-	-	-	-
6	0.76	15.5	-	-	-	-	-	-
7	0.77	15.5	-	-	-	-	-	-

Effect of Scan Rate: Effect of variation of scan rate on CV characteristics of toluidine has been observed at varying scan rate ranging from 20 mVs^{-1} to 300 mVs^{-1} . In general one oxidation peak and one couple peak is observed except p-toluidene where we get only oxidation peak. With increase in the scan rate, the peak potential of oxidation peak and the anodic peak shift towards more positive potential but in case of cathodic peak, the peak potential shifts towards less positive potential. The peak current increases with increase in the scan rate. CV characteristics at different scan rate for o- isomers at PtE is included in table 2.

Table 2

Cyclic voltammetric characteristics of o-Toluidines at different scan rate in acetate buffer at Paltinum electrode.

Concentration: 1mM Reference electrode: Ag-AgCl Scan rate: 100mVs⁻¹

Scan rate	Oxidation peak		Product couple peak				ΔE_p (mV)	I _{pa} /I _{pc}
	E _{pa} (V)	I _{pa} (μ A)	Cathodic		Anodic			
			E _{pc} (V)	I _{pc} (μ A)	E _{pa} (V)	I _{pa} (μ A)		
o-toluidine								
20	0.96	7.5	0.44	1.5	0.49	-	50	-
40	0.98	10.0	0.44	2.5	0.49	-	50	-
60	0.99	12.5	0.44	2.5	0.50	3.0	0	1.2
80	1.0	14.0	0.43	3.5	0.50	3.0	70	0.9
100	1.0	16.0	0.43	5.0	0.50	3.0	70	0.6
150	1.1	20.5	0.43	7.5	0.50	4.5	70	0.6
200	1.2	24.0	0.42	8.5	0.50	5.5	80	0.6
300	1.3	27.5	0.41	9.0	0.50	5.5	90	0.6

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

- 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.
- During reverse cathodic scan no cathodic peak corresponding to main anodic peak.
- 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 KNO₃, 0.1M HCl, 0.1M H₂SO₄, 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 H₂SO₄ and 0.1 M Potassium hydrogen phalate (pH4) where small couple peak at much cathodic potential was revealed.
- 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.
- pH greatly influence the characteristic of cyclic voltammogram; the product couple peak was observed only at pH3 for o- and m- isomer. For p- toluidine no product peak was seemed under potential range +0.0 Volt to +1.2 Volt vs Ag / AgCl electrode. The observations were consistent with both the working electrode under study.
- Peak potential shift of the main oxidation peak was near about approximately 70 mV, 110 mV and 210 mV towards more negative potential for a five unit change of pH, at scan rate of 100 mVs⁻¹ for o-, m- and p- toluidine respectively.
- Peak current was found to be highest at pH 3 employing acetate buffer as supporting electrolyte at Pt and gold electrode.
- On varying the scan arte in the range 20 to 300 mVs⁻¹ anodic peak current increases. The peak current of product couple peak also increases on increasing scan rate. A linear relationship was observed between peak current and square root of scan rate, showing diffusion controlled process.

References

- The Merck Index, Susan Budavari(Ed), Maryadele J. O'Neil (Asso.Ed), Ann Smith(Asst.Ed), Patricia E Heckelman (Editorial Asst.), 11th edition, centennial edition, Published by MERK and Co., Inc Rahway. N.J. USA, 1989
- S.S.Lord and L.B.Rogers, Anal.Chem., 26(1954)284
- I.Yu.Beilis, Lab.Dalo(1964)723
- S.Wawzonek and T.W.McIntyre, J.Electrochem. Soc.,114(1967)1025.
- J.Bacon and R.N.Adams, J.Am.Chem.Soc.,90(1968)6590.
- T.Kuwana and J.W.Strojek, Transaction Faraday Soc.,45(1968)134.
- J.C.Suatoni, R.E.Snyder and R.O.Clark,Anal.Chem., 33(1961)1894.
- U.S.Patent and E.L.Halwig Chem.Abstr.,25(1931)5355.
- N.N.Melnikov, S.I. Sklyarenko and E.M. Cherkasova,J.Gen.Chem.USSR,9(1939)1891.
- N.N. Melnikov and E.M. Cherkasova,J.Gen.Chem.USSR,14(1944)113
- R. Christeller,"Organische Elektrochemie" by F. Fichter., p.120, Steinhof, Dresden, 1942.
- A.Z.Voigt, Angew. Chem., 7(1894) 106.



13. Anodic oxidation pathways of aromatic amines.IV, Diphenylamine System in Aqueous Acid Solution, Donald.W.Leedy and R.N.Adams,J.Am.Chem.Soc.92:6,(1970) 1646.
14. Diffusion coefficient and Heterogeneous rate constant of some aromatic amines in aqueous medium, S.Usha Rao. Sunita Kumbhat and R.C.Kapoor, SAEST. 22, no. 3 (1987).
15. The electro-oxidation of N,N-dimethyl-p-toluidine in acetonitrile: a microdisk Voltammetric study, Neil V.Rees, Oleksiy V.Klymenko, Richard G Compton, Munetaka Oyama, J.Electroanal.Chem. 531(2002) 33-42.