

A Study of the Kinetic and Mechanism of Electrochemical Reduction for Para Nitro Phenol, 2,4- Di Nitro Phenol , 2,4,6-Tri Nitro Phenol in HCL(0.5M) Medium

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Abstract

In this study, the voltammetric behavior of 4-nitrophenol, 2,4-nitrophenol and 2,4,6-tri nitro phenol in acidic medium was investigated by cyclic voltammetry at glassy carbon electrode. The reduction of the para nitro phenol ($2.10^{-4}M$) in the presence of HCL (0.5M) as supporting electrolyte reveals one irreversible peak while the reduction of the 2,4-di nitro phenol shows two irreversible current peaks and the reduction of the 2,4,6- tri nitro phenol gives three irreversible current peaks to produce the derivatives amines as the final products

Keywords: Polarography, Cyclic voltammetry, Glassy carbon electrode (GCE), 4-nitro phenol, 2,4-di nitro phenol , 2,4,6 tri nitro phenol

1. Introduction:

Para nitro phenol is important intermediate in the production of fungicides, dyes, pesticides, pharmaceuticals and explosives [1]. 2,4-dinitrophenol (24DNP) has been utilized for a number of different applications including

The manufacture, wood preservatives, and photographic developers [2], [3]. While 2,4,6- tri Nitro phenol (PA) is importance in dye industries, pharmaceuticals, and chemical laboratories [4]. The easy electrochemical reduction of nitro groups at the systems with conjugated double bonds permits very sensitive determinations of a number of biologically active organic nitro compounds.

The nitro compounds one of the best electrophores as regards to both ease of reduction and versatility of derived products. [5] Numerous investigations have been made on the reduction of para nitro phenol ,2,4-di nitro phenol , 2,4,6- tri nitro phenol in a wide ranges of pH (2-10) [2],[6], [7]. The cyclic voltammetric behavior of para nitro phenol, 2,4- di nitro phenol ,2,4,6- tri nitro phenol in the presence of HCL (0.5M) as supporting electrolyte was studied for the first time in this study.

In this work, the electrochemical technique such as voltammetry is used, because it is inexpensive and sensitive.

Also the Carbon electrode is used, and that due to their low background current, wide potential, low cost and suitability for various sensing and detection applications.

The aim of this work is study the kinetic and mechanism of electrochemical reduction for Para nitro phenol, 2,4- di nitro phenol ,2,4,6- tri nitro phenol in acidic medium and the effect of scan rate .

1.1. Materials and Methods:

Para nitro phenol 99%, 2-4 di nitro phenol 99%, 2-4-6 tri-nitro phenol 99% were purchased from Merck Laboratories. All the chemicals used in the experiments were of analytical grade and used without further purification the water utilized in all studies was double distilled and deionized.

The polarograms were obtained with ampere-metric station model (Amel 443). A three-electrode cell, with an Ag/AgCl reference electrode and a platinum counter electrode. The glassy carbon electrode was used as working electrode.

1.1.1 Experimental Procedure:

The general procedure for obtaining polarograms was as follows:

Para nitro phenol ($2.10^{-4}M$), 2,4- di nitro phenol ($2.10^{-4}M$), 2,4,6- tri nitro phenol ($2.10^{-4}M$) were prepared by weighing suitable amounts of these compounds and dissolving them in ethanol (5 ml) Then the solutions were transferred to volumetric flask (100-ml) and diluted to the mark using distilled water that contains (HCl) (0.5 M) At first, 25 ml of each solution prepared was put into the polarographic cell. Then the solutions were purged with nitrogen for 5 min.

The polarograms were recorded by applying a negative going scan over the potential range from 0 to -1800 mV. The obtained polarograms were used for further calculations. All measurements were made at $25^{\circ}C$.

Results and discussion:

1.2 Voltammetric behavior of the para nitro phenol

The cyclic voltammograms of the reduction of the para nitro phenol (2.10^{-4} M) in the presence of HCL (0.5M) as supporting electrolyte the result is show in figure(1). On the initial negative going scan, it can be noticed the cathodic Current peak increased starting for the potential value of -340 mV. The cathodic current continued to rise until

The limiting current appeared at -622mV, while there was no any peak appeared on the return-going scan as show in the fig. (1). the cathodic current peak represented the reduction of para nitro phenol to para hydroxy aminophenol and subsequently para aminophenol as indicated in the equation (1).

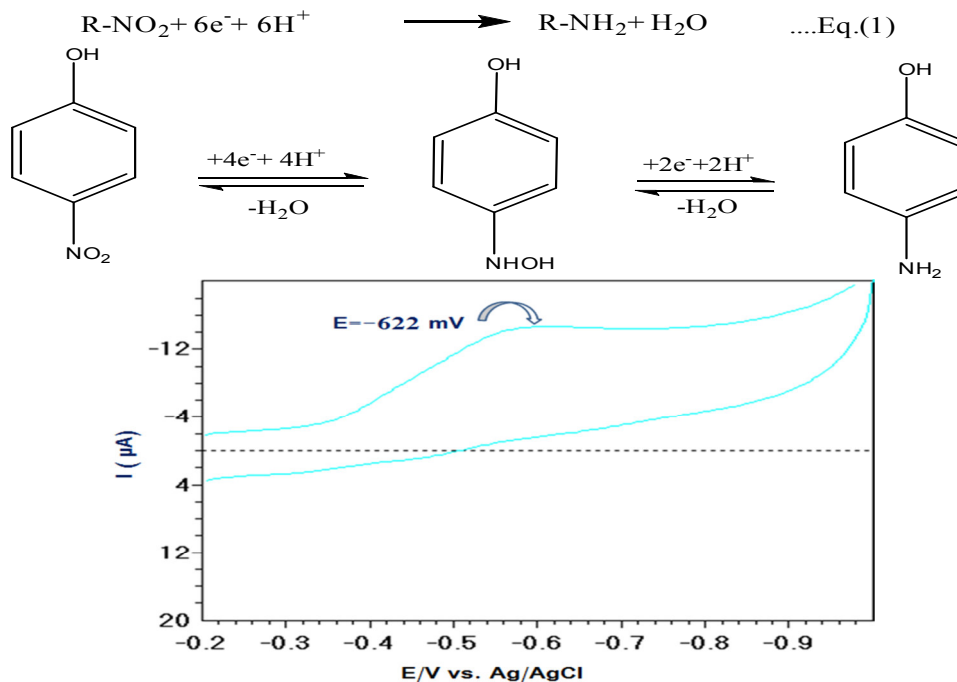


Fig. 1. cyclic voltammograms at (GCE) cathode of (2.10^{-4} M) para nitro phenol In 0.5 M HCl media Scan Rate: 50 mV/ s

2.2. Effect of Scan Rate on the reduction of para nitro phenol:

The effect of scan rate was studied on the cyclic voltammetric behavior of par nitro phenol and investigated over the range from 60 to 100 mV/s. A plot of peak height vs. the square root of scan ($v^{1/2}$) was found to be linear for all the peaks studied indicating the diffusional process as show in fig. (1a).

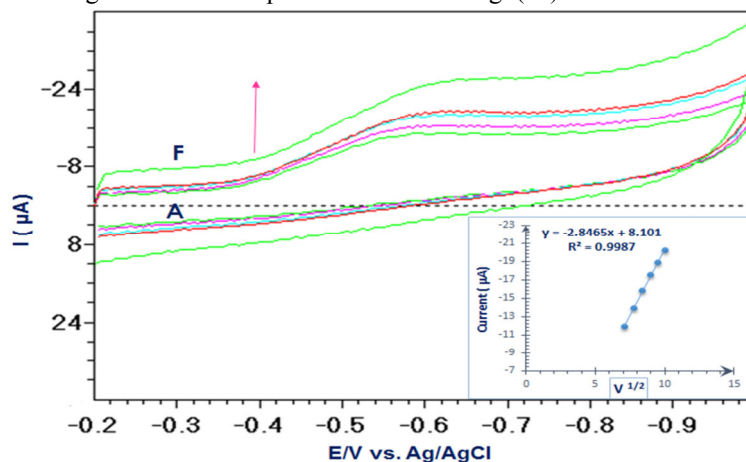


Fig. (1a). Cyclic voltammograms of the para nitro phenol in 0.5M HCl solution at different scan rates, and a plot of I_p as a function of ($v^{1/2}$)

3.2 Voltammetric behavior of the 2,4- di nitro phenol:

The cyclic voltammograms of the 2,4-di nitro phenol (2.10^{-4} M) in the presence of HCL (0.5M) as supporting

electrolyte the result is show in figure(2). On the initial negative going scan, it can be noticed two prominent cathodic current peaks appeared. This cathodic current increased steeply starting at the potential values at -0.2 mV for the first peak and at -0.4mV for the second peak. The cathodic currents continued to rise until the limiting currents appeared at -277.4 mV and at -560 mV while there was no any peak appeared in the return scan. In this case, of reduction, the experimental results show that the first cathodic current peak Includes 10 electrons

Resulting from the reduction of the nitro group at the para site to amine. In addition, the second nitro group to hydroxy aminophenol. The second cathodic current peak includes two electrons resulting follow up reduction the hydroxy aminophenol which formed in the initial peak to amine as indicated in the equation (2).

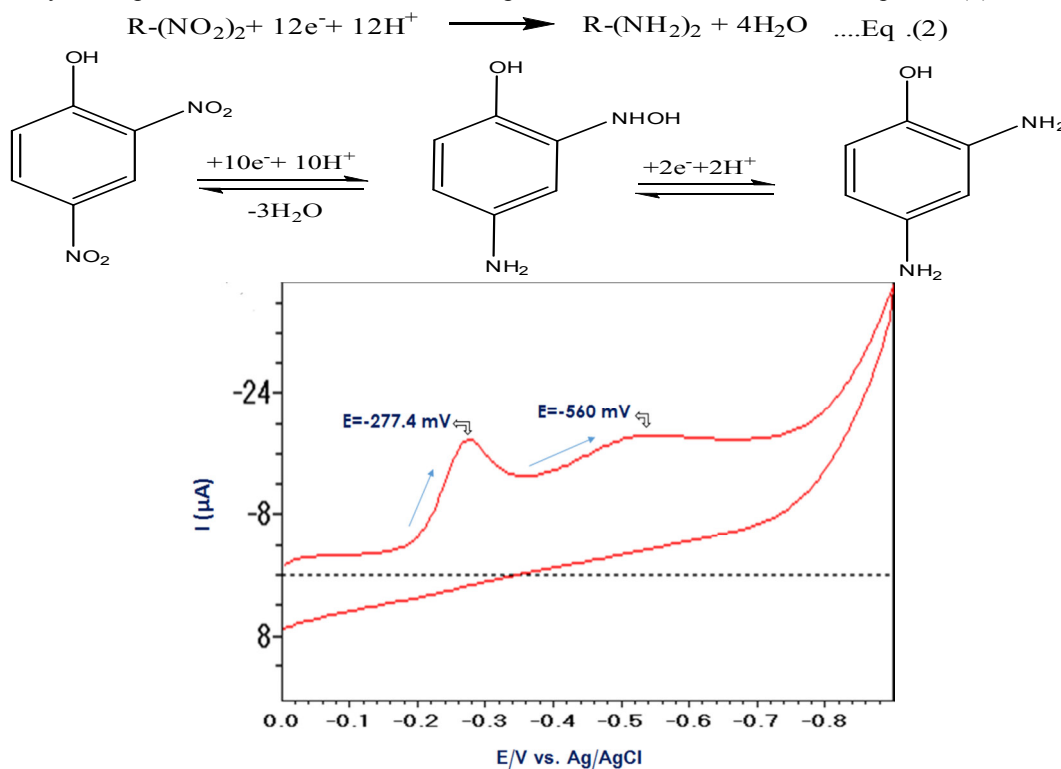


Fig. 2. Cyclic voltammograms at (GCE) cathode of (2.10^{-4} M) 2,4-di pnitro phenol In 0.5 M HCl media, scan rate: 50 mV/ s

4.2. Effect of Scan Rate on the reduction of 2,4- di nitro phenol:

The effect of scan rate was studied on the cyclic voltammetric behavior of 2,4- di nitro phenol and investigated over the range of 60 to 100 mV/s . A plot of peak height vs. the square root of scan ($v^{1/2}$) was found to be linear for all the peaks studied indicating a diffusional process as show in fig. (2a).

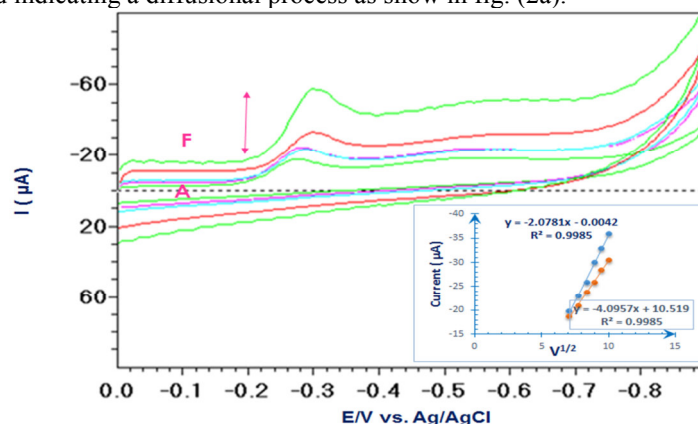


Fig.(2a). Cyclic voltammograms of the 2,4-di nitro phenol in 0.5M HCl solution at different scan rates, and a plot of I_p as a function of ($v^{1/2}$)

5.2. Voltammetric behavior of the 2,4,6- tri nitro phenol:

The cyclic voltammograms of the 2,4,6-tri nitro phenol ($2 \cdot 10^{-4}$ M) in the presence of HCL (0.5 M) as supporting electrolyte the result is show in figure (3). On the initial negative going scan, it can be noticed three prominent cathodic current peaks appeared. The cathodic current increased steeply starting at the potential values at -0.01 mV for the first peak at -0.2 mV, for the second peak and at -440mV for the third peak. The cathodic currents continued to rise until the limiting currents appeared at -130.1 mV, at -277.1 mV and at -653.2 mV respectively, while there was no any peak appeared. On the return scan. In this case, of reduction, the experimental results Show that the

First cathodic current peaks at -130.1mV includes 10 electrons resulting from the reduction of the nitro group at the para site to amine and the other Nitro group to hydroxyl aminophenol. The second cathodic current peak at -277.1mV includes six electrons Resulting follow up reduction the hydroxyl aminophenol which formed in the Initial peak to Amine and the reduction of the third nitro group to hydroxy aminophenol. The third cathodic current peak

At -653.2mV includes two electrons resulting follow up reduction the hydroxy aminophenol, which formed in the second peak to amine as, indicated in the equation (3).

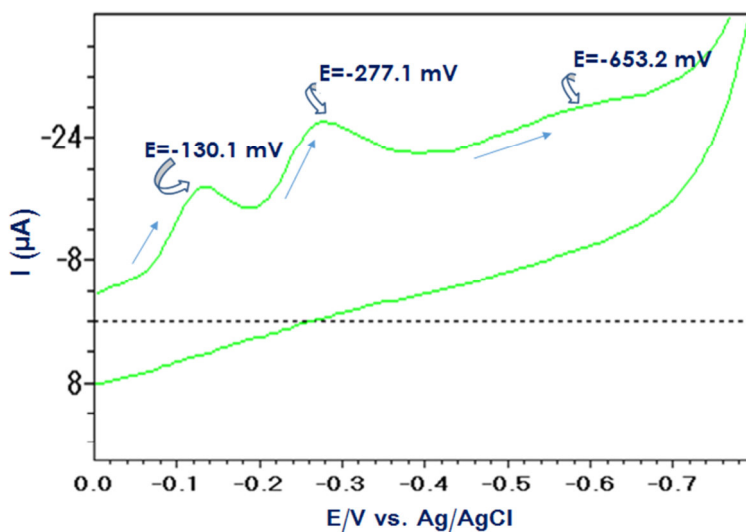
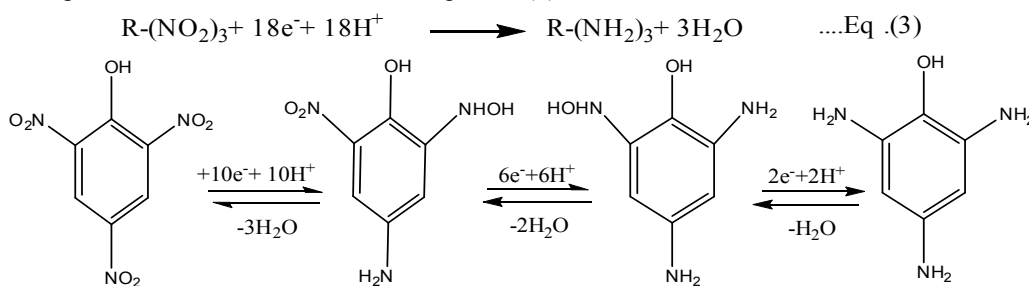


Fig. (3). cyclic voltammograms at (GCE) cathode of ($2 \cdot 10^{-4}$ M) 2,4,6-tri nitro phenol in 0.5 M HCl media Scan rate: 50 mV/ s

6.2. Effect of Scan Rate on the reduction of 2,4- di nitro phenol:

The effect of scan rate was studied on the cyclic voltammetric behavior of 2,4- di nitro phenol and investigated over the range of 60 to 100 mV/s. A plot of peak height vs. the square root of scan ($v^{1/2}$) was found to be linear for all the peaks studied indicating a diffusional process as show in fig.(3a).

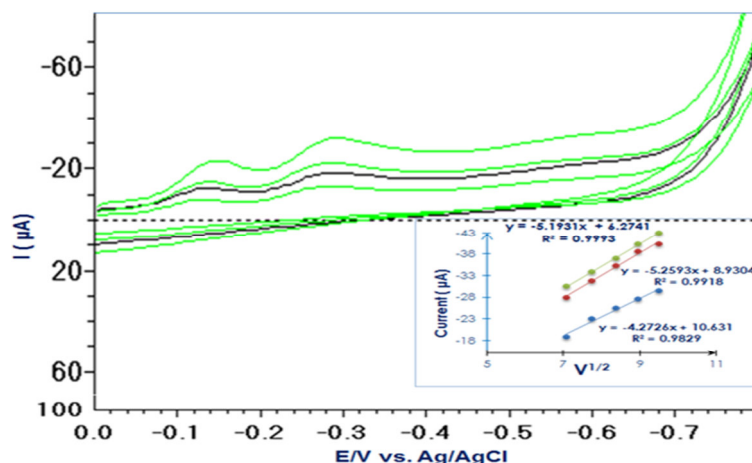


Fig. (3a). Cyclic voltammograms of the 2,4,6-tri nitro phenol in 0.5M HCl solution at different scan rates, and a plot of I_p as a function of $(v^{1/2})$

3. Conclusion

This study showed the mechanism of reduction of the para nitro phenol, 2,4-di nitro phenol and 2,4,6 –tri nitro phenol in acidic medium at (GC) electrode . The kinetics of the reduction process of para nitro phenol, 2,4-DNP and 2,4,6- tri nitro phenol studied by (cv) indicated that the reduction process is diffusional Controlled.

The experimental results showed, that the method is highly reliable, accurate and very efficient to produce the derivatives amine.

References

- 1- Sousa.c, Nascimento.C, Barek.J,2015, Differential Pulse Voltammetric Determination of 4-Nitrophenol Using a Glassy Carbon Electrode: Comparative Study between Cathodic and Anodic Quantification, International Journal of ELECTROCHEMICAL SCIENCE,10,PP:7261-7274.
- 2- Honeychurch.k,(2016), Development of an Electrochemical Assay for the Illegal “Fat Burner” 2,4-dinitrophenol and Its Potential Application in Forensic and Biomedical Analysis , Advances in Analytical Chemistry, 6(2), PP. 41-48.
- 3- Song.Y , Wang.Y,Feng.j,(2013), Electrochemical Behavior of 2, 4-Dinitrophenol , at Multi-Walled Carbon Nanotube-Modified Glassy Carbon Electrode and Its Application , Int. J. Electrochem. Sci, (8),PP. 2229 – 2237.
- 4- Mukherjee.S, Gole.B, Bar.A, (2013),Fluorescent Tris-Imidazolium Sensors for Picric Acid Explosive , The Journal of Organic Chemistry ,(78), PP.1306–1310
- 5- Gupta .S, (2017), A Comparative Electrochemical Behaviour Study of p-nitrophenol Using GC and Pt Electrode , IRA-International Journal of Applied Sciences , 6(3) , PP.94-105
- 6- El Mhammedi.M, Chtaini.A,2009, Electrochemical determination of *para*-nitrophenol at apatite-modified carbon paste electrode: Application in river water samples, paste electrode: Application in river water samples,(163),PP.323-328
- 7- Salles.M,2012 Development of an enzymeless electroanalytical method for the indirect detection of creatinine in urine samples , Sensors and Actuators B: Chemical, (173),PP.847-851
- 8- Schoonman.J, Picken.S, Burtica.G, Electrochemical Determination of 2,4-Dinitrophenol from Aqueous Solution at Expanded Graphite – Carbon Nanofiber – Epoxy Composite Electrode, Chemical Bulletin of “Politehnica”, 54(68),PP.61-65 .