



Araştırma Makalesi / Research Article

THE ELECTROCHEMICAL BEHAVIOURS OF 4-(N, N- DIMETHYL AMINO) PHENYL PROPENAL AND DERIVATIVES

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ABSTRACT

4-(N, N- Dimethylamino) Phenyl Propenal and Derivatives have been studied over a wide pH range in aqueous and non-aqueous media using platinum foil electrode. Two reductions in acidic medium and one reduction in basic medium take place involving two electrons per reduction. In the first the C=C double bond is reduced, in the second the aldehyde group. In acid media, two-electron process is split into two one-electron steps. In alkaline media, when the rate of protonation of the radical anion formed in the uptake of the first electron decreases with increasing pH, the two electron reduction peak of 4-(N, N- Dimethyl amino) Phenyl propenal and derivatives decreases to one-electron peak, followed at -1.5V by another one-electron peak which corresponds to the radical anion reduction. In non-aqueous media, only one peak is seen. On the basis of linear and cyclic sweep voltammetry, coulometry, IR, Mass, and ¹H-NMR spectral studies and product identification a reaction mechanism are suggested to account for the reduction mechanism.

Keywords: Cyclic Voltammetry, Aminocinnamaldehyde, Aqueous and non-aqueous.

4-N, N- DİMETİL AMİNO FENİL PROPAN VE TÜREVLERİNİN ELEKTROKİMYASAL DAVRANIŞI

ÖZET

Geniş bir pH Aralığında 4- (N,N- Dimetilamino) fenil propanol ve türevlerinin sulu ve susuz ortamda platin elektrotla redüksiyonu incelendi. Asidik ortamda iki redüksiyon piki, bazik ortamda bir redüksiyon pili oluşmakta ve her redüksiyon reaksiyonuna iki elektron eşlik etmektedir. Önce -C=C- bağı indirgenir, sonra aldehit grubu indirgenir. İndirgenme asidik ortamda iki basamakta gerçekleşir her basamakta bir elektron alır. Alkali ortamda, pH değerinin artmasıyla ilk elektronu alan radikal anyonun protonlaşma hızı azalır. Radikal anyonun redüksiyonu -1.5 V da gerçekleşir. Susuz ortamda bir pik görülmektedir. Reaksiyon mekanizmaları siklik voltmetre, kulonmetre, IR, kütle ve proton NMR spektroskopisi verilerine göre açıklandı.

Anahtar Sözcükler: Siklik Voltametri, Aminosimaldehit, Sulu ve Susuz ortam.

1. INTRODUCTION

4-(N, N- Dimethylamino) Phenyl propenal and its derivatives are synthetic oxygen carriers and have the biological properties that are necessary to produce intermediate compounds in enzymatic reactions[1-3]. Examination of reductions of a number of α,β -unsaturated carbonyl compounds in

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dimethylformamide have been reported by Wawzonek and Gunderson[4], but the polarographic waves were predominantly used for analytical purpose[5-8]. Cinnamaldehyde has been investigated polarographically by Zuman[9-10] and coworkers in a wide pH range. According to Zuman, at pH \leq 10 the reaction mechanism of the -C=C- double bond is ECEC (E: electrochemical reduction or oxidation; C: chemical reduction or oxidation) (e, H⁺, e, H⁺), if pH \geq 10 then the reaction mechanism is EECC (e, e, H⁺, H⁺). In order that 4-(N, N- Dimethylamino) Phenyl Propenal and Derivatives obtained in present work acts as an oxygen carrier like cinnamaldehyde, its reduction potentials should be lower than the standard reduction potentials of oxygen in acidic and basic media (1.23 V, 0.4 V). When the reaction mechanism of 4-(N, N- Dimethyl amino) Phenyl Propenal and its derivatives is explained, it may constitute a model for understanding enzymatic reaction mechanisms.

1. (H₃C)₂N-C₆H₄-CH=CH-CHO 4-(N, N- Dimethyl amino) phenyl propenal
2. (H₃C)₂N- C₆H₄-CH=CH-CH=N₂OH 3-[4-N,N-Dimethylamino] phenyl propenal oksim
3. (H₃C)₂N- C₆H₄-CH=CH-CH=NC₆H₅OH 4-[3-(4-N,N-Dimethylamino)phenyl allylidene amino] phenol
4. (H₃C)₂N- C₆H₄-CH=CH-CH=NC₆H₅ COOH 4-[3-(4-N,N-Dimethylamino)phenyl allylidene amino] benzoic acid

2. EXPERIMENTAL

4-(N, N- Dimethylamino) Phenyl propenal and derivatives were prepared in Labarotuar and purified by distillation under reduced pressure. Their purity was checked by elemental analysis, spectral analysis and these compounds are given in the following Table 1.2.

Table 1. Elemental Analysis data of 4-(N, N- Dimethyl amino) Phenyl Propenal and Derivatives

Compound	Color	M.p(°C)	%C	%H	%N	%O
C ₁₁ H ₁₃ N ₂ O (1)	Yellow	133	75.35	7.46	8.02	9.17
C ₁₁ H ₁₄ N ₂ O (2)	White	138	69.43	7.39	14.71	8.47
C ₁₇ H ₁₈ N ₂ O (3)	Red-brown	142-143	76.05	6.88	10.45	6.62
C ₁₈ H ₁₈ N ₂ O ₂ (4)	Violet	125-126	73.47	6.12	9.52	10.89

Table 2. FT-IR Analysis 4-(N, N- Dimethyl amino) Phenyl Propenal and Derivatives

Compound	γ (C-H)N-Ar cm ⁻¹	γ (OH) cm ⁻¹	γ (C=O) cm ⁻¹	γ (C=N) cm ⁻¹	γ (C=C) aromatic cm ⁻¹	γ (C=C) aliphatic cm ⁻¹
C ₁₁ H ₁₃ N ₂ O (1)	816-978	2825	1676	1600-1676	1533	1140
C ₁₁ H ₁₄ N ₂ O (2)	527-816	3400	1676	1600-1676	1533-1383	1140
C ₁₇ H ₁₈ N ₂ O (3)	755	3420	-	1475	1565-1480	1150-1060
C ₁₈ H ₁₈ N ₂ O ₂ (4)	770	3412	1575	1498	1389-1250	1172-832

Stock solutions (0.01M) were prepared from weighed amounts of these compounds by dissolving in spectroscopic-grade ethanol. Over the range of pH 2-12, Britton-Robinson (B-R) buffers (0.04M) was used to control and stabilise the pH of the measuring solutions B-R buffer was prepared by dissolving 3.92g of 85% phosphoric acid, 2.40g of 96% acetic acid and 2.47g of boric acid in 1000 ml of distilled water. Buffer solutions at desired pH were prepared by mixing B-R solutions and aqueous potassium hydroxide (0.2M) or hydrochloric acid (0.2M) at different ratios. The pH buffer solutions varied between 1 and 13. The ionic strength was adjusted by addition of lithium chloride. The pH of the buffer solutions was measured by means of Mettler Delta-340 pH-meter with a general purpose glass electrode. Acetonitrile is used for cyclicvoltametric studies no aqueous medium. For cyclic voltammetry, 9-10ml of the supporting

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electrolyte and 0.2ml of the stock solution of the electro active species were mixed and de-aerated, yielding a final solution containing $2 \times 10^{-4} \text{M}$ electro active substances. The products of electrolysis and the products of the electrochemical reactions were identified by comparison of their properties with the expected products using Carlo-Erba 1106 elemental analyzer and mass spectrum #(FAB) and IR spectra A Mattson 1000.

Cyclic voltammetry and controlled potential electrolysis experiments were performed using a Wenking model P0S-73 connected a RW-11 X-Y Recorder. The standard three-electrode electrochemical cell was used. As the reference electrode, Ag, AgCl(s), Cl⁻ (sat.) is used in aqueous medium and Ag, AgBF₄(s), BF₄ (sat) is used in nonequeous. The working and auxiliary electrodes were made of platinum wire. Supporting electrolyte was not used in aqueous medium but tetrabutylammoniumtetrafluoroborat (TBABF₄) was used in no aqueous medium. All measurements were made under nitrogen atmosphere.

3. RESULTS AND DISCUSSION

In buffered aqueous solutions (pH=3.0- 7.2), and acetonitrile solution cyclic voltammetry scans of 4-(N, N- Dimethyl amino) Phenyl propenal are shown in Fig.1-2.

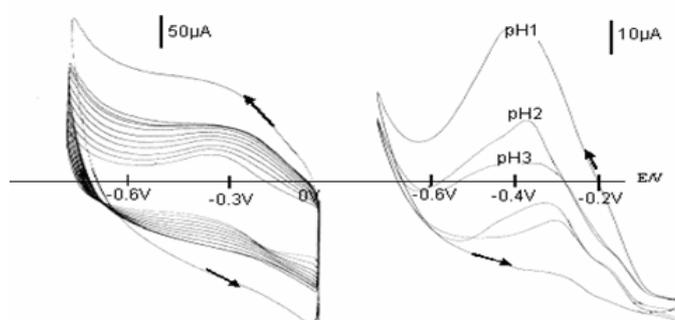


Figure 1. Multi-sweep cyclic voltammetry scan of 4-(N, N-Dimethyl amino) Phenyl Propenal in CH₃CN+ 0.1MTBATE, Scan rate: 100mVs^{-1} , 4-(N, N- Dimethyl amino) Phenyl Propenal $= 2 \times 10^{-4} \text{mol l}^{-1}$

Figure 2. Cyclic voltammetry scan of 4(N,N-Dimethyl amino) Phenyl Propenal in Britton-Robinson buffers (0.1m).pH-values: pH₁= 2.0; pH₂=5.0; pH₃=7.2 Scan rate: 100mVs^{-1} , 4-(N, N-Dimethyl amino) Phenyl Propenal $= 2 \times 10^{-4} \text{mol l}^{-1}$

In buffered solutions, the first peak splits in two peaks of practically equal height in solutions of high pH (Fig.2).The first two-electron step in the electroreduction of 4-(N, N-Dimethyl amino) Phenyl propenal results in the hydrogenation of the carbon-carbon double bond. In the higher pH-values, the second cathodic peak was observed at -0.5V vs Ag/AgCl [-0.751V vs. normal hydrogen electrode (NHE)] (Fig.2). This reduction process is followed at more negative potentials by the reduction of the aldehyde group. In acidic medium and acetonitrile solution, the only cathodic peak was observed at -0.5V , the corresponding anodic peak was observed (Fig.3.4).

At more negative potential, the second cathodic peak was not observed. These results indicated that this second peak was not pH dependent in the 3.0-9.0 pH range. Plots of \dot{i}_{p1a} vs. $v^{1/2}$ and $\dot{i}_{p1a}/v^{1/2}$ vs. v showed diffusion behaviour [11]. According to an overall scheme (1.2).

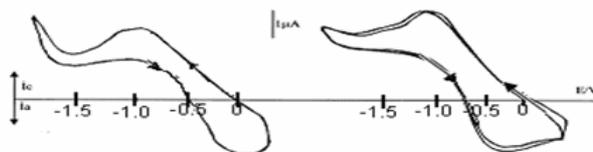
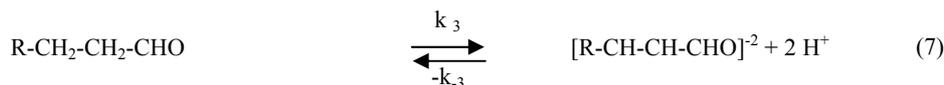
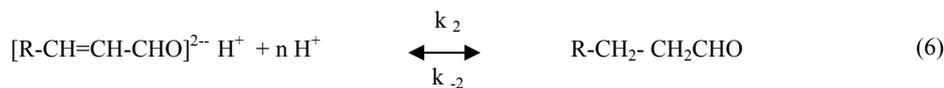
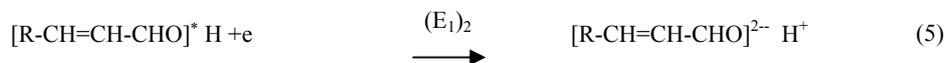
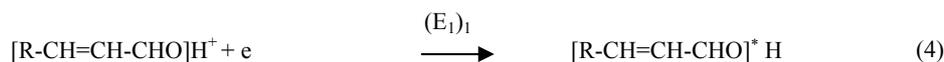
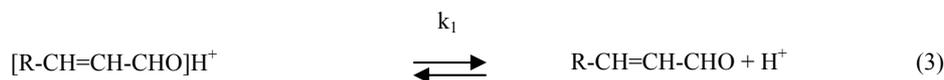


Figure 3. Cyclic voltammety scan of 3-[4- N,N-Dimethyl amino] phenyl Propenal oksim [2]. In acetonitrile (in NBu₄B₄ 0.1m). 3-[4-N, N-Dimethyl-lamino] Phenyl Propenal oksim] (2×10^{-4} mol/l). Scan rate: 100 mVs^{-1} .

Figure 4. Cyclic voltammety scan of 3-[4-N,N-Dimethyl amino] phenyl propenal oksim in Britton-Robinson buffers(0.1rr) pH₁=3.5 pH₂=5.5, Scan rate: 100 mVs^{-1} 3-[4-N, N-Dimethyl-lamino] phenyl Propenal oksim (2×10^{-4} mol/l).



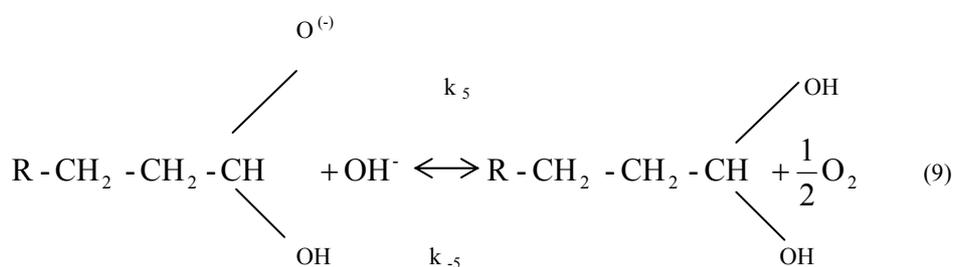
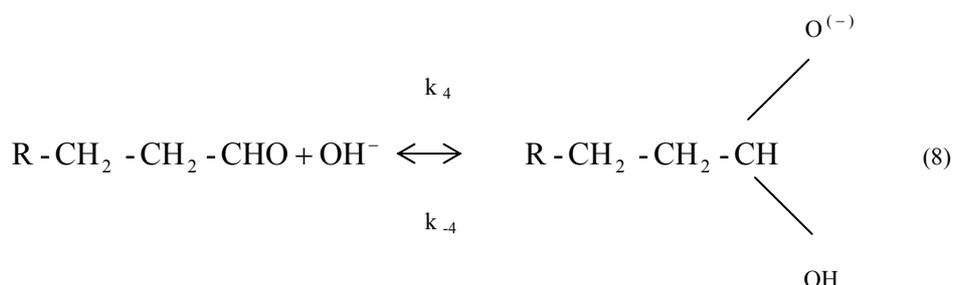
7.2 $> \text{pH} > 3.0$ the first reduction step can be split into a greater number of elementary steps. A more detailed reaction mechanism of these steps is given below. k^1 and k^2 values have also been determined by Irving-Rossotti potentiometric and PKAS-BEST computer methods.



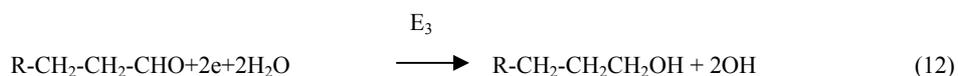
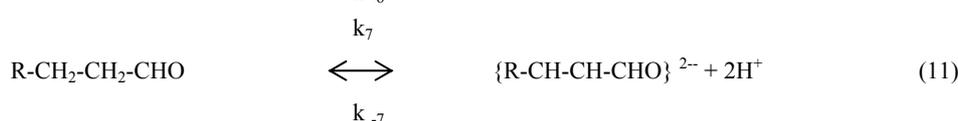
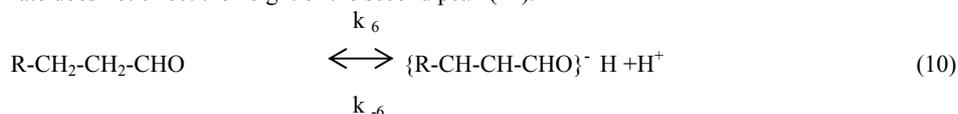
Because the rate of the protonation reaction (3) with the rate constant k^{-1} decreases with increasing pH, an increasing proportion of unprotonated aldehyde group is reduced at -0.5 V , the potential of the combined processes (4) and (6) at these pH-values does not apparently differ sufficiently from the potential of the unprotonated aldehyde corresponding to combined processes (4) and (7). Therefore it was not possible with aldehyde to observe formation of two peaks, since their ratio changes with pH.

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At pH<7 the rate of the establishment of equilibrium (3) can be considered as fast when compared with the increasing pH. At higher pH-values the rate of protonation of the radical anion with the rate constant k^{-1} decreases and is no more able to transform all the radical anion into radical. A decrease of the first peak is observed until at sufficiently high pH the contribution of reaction (3) can be neglected and the first peak reaches a value which corresponds to a one-electron reduction (4). According D. Barnes and P. Zuman[9-10], the reduction of this aldehyde in the reaction is limited by the rate of hydroxyl ions reactions (8) and (10).



The reduction of this aldehyde of 4-(N, N- Dimethyl amino) Phenyl propenal indicates that protonation reactions (10), (11) are fast when compared with dehydration reactions and their rate does not effect the height of the second peak (12).



An apparent non-additive is also observed in solutions containing 3 - [4-N, N-Dimethylamino] phenyl propenal oksim (Fig.4). At positive potentials the oxidized form of

aldehyde is adsorbed and prevents oxygen reduction. Only when is desorbed at $-1.2V$ an increase in the oxygen peak is observed. This behaviour formally resembles the reduction of oxygen in the presence of adsorbed 4-(N, N- Dimethyl amino) Phenyl propenal derivatives [12] (fig.4).

At $2.0 > pH > 4.5$ 3 - [4-N, N-Dimethylamino] phenyl propenal oksim three peaks at lower scan rates ($< 100 mVs^{-1}$) are observed. On increasing the scan rate the cv exhibits two peaks (fig.4). 4-[3-(4-N, N-Dimethylamino) phenyl allylidene amino] phenol give a two-step reduction. The diffusion current constant for one peak of 3-[4-N, N-Dimethylamino] phenyl propenal oksim indicates that one electron is involved. On increasing the scan rate, the second cathodic peak potential does not shift to more negative values. This peak [Fig.5.6 (1a-2a)] was not pH dependent in the 2.0-10.0 pH range. Plots of I_{p1} vs. $v^{1/2}$ and $I_{p1}/v^{1/2}$ vs. showed a diffusion behavior. The corresponding anodic peaks 1b and 2b appeared at $-0.48 V$ and $-0.75 V$. Ag/AgCl ($+0.519 V$ vs. NHE) was in the 2.0-10.0 pH range. At $pH > 11.0$, this peak was not observed [13] (Fig.6).

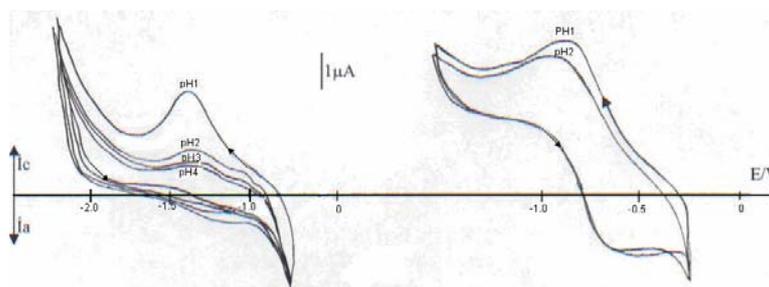


Figure 5. Cyclic voltammetry of 3-[4-N,N-Dimethylamino] phenyl Propenal oksim [$2 \times 10^{-4} mol/l$], $pH_1=8.0$ $pH_2=9.5$ $pH_3=10$ $pH_4=12$ (Britton-Robinson 0.1m); Scan rate: $50 mVs^{-1}$

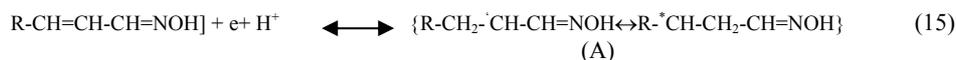
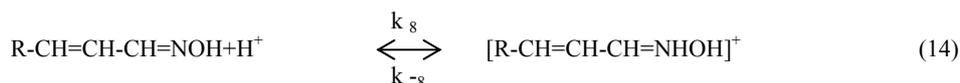
Figure 6. Cyclic voltammetry of 4-[3-(N, N - Dimethylamino) phenyl Allylidene amino] phenol [$2 \times 10^{-4} mol/l$], $pH_1=3.5$, $pH_2=6.5$ (Britton-Robinson 0.1m), Scan rate: $100 mVs^{-1}$

1st peak

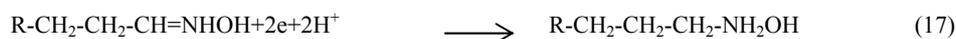


At higher pH values, the protonation rate is decreasing and the protonation rate constant value (k^7) is less than k^{-7} .

At $2.0 > pH > 5.0$, two separate one-electron peaks were observed.



2nd peak



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Between pH<7.0 and 9.0 at lower scan rates 100mVs⁻¹, 4-[3-(4-N, N-Dimethylamino) phenyl allylidene amino] benzoic acid exhibits three irreversibly cv peak (Eq.18-19) (fig.7.8). On increasing the scan rate, the cv peak tends to be irreversible. In weak alkaline solution, the prevailing electro active species is the cation and after anion.

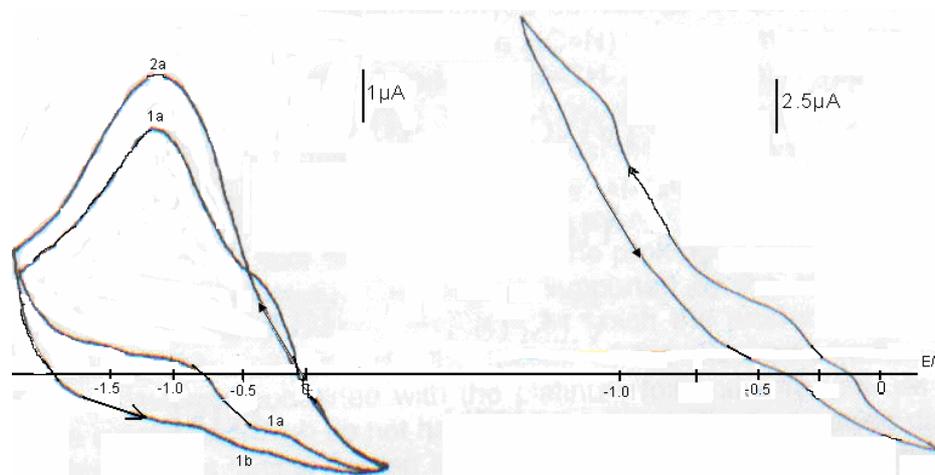
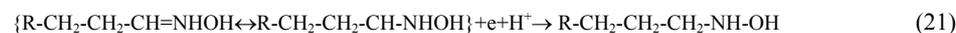
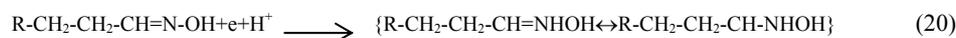
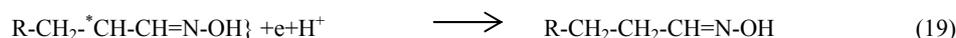


Figure 7. Cyclic voltammetry of 4-[3-(N,N-Dimethylamino)phenyl Allylidene amino] phenol. [2x10⁻⁴mol/l] p_{H1}=8.5, p_{H2}=10.0 (Britton-Robinson : 0.1M), Scan rate:100mVs⁻¹

Figure 8. Cyclic voltammetry scan of 4-[3-(4-N,N-Dimethylamino) phenyl Allylidene amino] benzoic acid. pH=3.0 (Britton-Robinson 0.1M), Scan rate:100mVs⁻¹



The reduction-oxidation potentials obtained from the cyclic voltammograms are showed in Table 3.

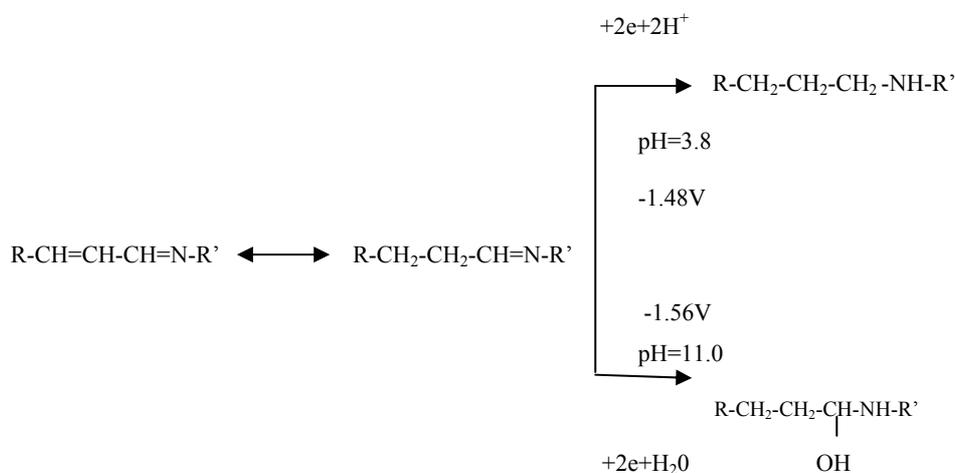
Electrolysis at the platinum foil electrode

To choose the potential, a current-voltage curve using a platinum foil (0.5cm²) was measured point by point. When the potential was applied to correspond to the limiting current of the first one-electron peak in acidic media, corresponded to a transfer of 0.75 electrons per molecule. In the IR analysis of the electrolysis products of 4-(N, N- Dimethyl amino) Phenyl propenal isolated with pH=3.8 and a reduction potential (-1.48 volts), the δ(C=N) band seem to be strong at 1630 cm⁻¹. The double-vibration band of -CH=CH- group within 1150-832cm⁻¹ disappears. During the reduction at pH=11.0 and -1.56volts, two alkane δ(-CH-) with medium vibration within 1384-

1461 cm^{-1} are observed, but a decrease of the carbonyl absorption band at 1700 cm^{-1} takes place (Fig.8-13). Mass spectrum has shown only polymer product which is viscous green-black oil. It is assumed that the polymerisation can not take place because of the prolonged time of contact of the primary products formed. This view is supported by the effects of pre-electrolysis time in single-sweep methods, in which the products formed at other potentials, can interact with the radicals at the electrode surface. All experimental evidence obtained with the platinum foil and wire indicate that with these electrodes which do not have a surface periodically renewed during the polarization, the radical formed in the first one-electron step can undergo complex interaction with components of the reaction mixture, in particular with the original compound and other radicals formed. Therefore, the product of electrolysis in solutions is the reactions mixture. According to these results, the reaction mechanism is proposed as follows:

Table 3. Voltammetric data for the cathodic and anodic process for the 4-(N, N- Dimethyl amino) Phenyl Propenal and Derivatives

Compound	Nonaqueous Media (CH ₃ CN)		pH=3.0		pH=7.0		pH=9.0	
	E _{p,c} (V)	E _{p,a} (V)	E _{p,c} (V)	E _{p,a} (V)	E _{p,c} (V)	E _{p,a} (V)	E _{p,c} (V)	E _{p,a} (V)
C ₁₁ H ₁₃ N ₀ (1)	-0.36	-0.30	-0.40	-0.30	-0.36	-0.15	-	-
	-	-	-	-	-0.40	-0.20	-0.56	-0.70
	-	-	-	-	-0.50	-0.30	-1.26	-1.32
C ₁₁ H ₁₄ N ₂ O (2)	-	-	-1.00	-0.50	-1.00	-1.20	-1.00	-1.10
	-	-	-1.20	-	-	-	-	-
	-1.20	-0.30	-1.35	-	-1.35	-1.40	-1.30	-1.35
C ₁₇ H ₁₈ N ₂ O (3)	-	-	-	-	-	-	-	-
	-	-	-0.90	-0.70	-0.65	-0.50	0.98	-0.80
	-1.28	-1.30	-1.10	-1.20	-1.00	-0.75	-1.28	-1.28
C ₁₈ H ₁₈ N ₂ O ₂ (4)	-	-	-0.25	-0.35	-	-	-	-
	-	-	-0.75	-	-0.76	-0.60	-1.05	-0.85
	-1.31	-1.33	-1.30	-	-1.46	-1.5	-1.50	-1.50



R: -N(CH₃)₂ C₆H₅ ; R': -OH, -C₆H₅OH, -C₆H₅COOH

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The products were believed to form as a result of the first peak which initially produced a red-black product, later green, which faded rapidly on exposure to air. The reaction mechanism which is proposed by Zuman[9-10] and co-workers for the first two electron reduction of 4-(N, N- Dimethyl amino) Phenyl propenal is also valid for the second two electron reduction mechanism. That is , if $\text{pH} < 10.0$, reaction mechanism is ECEC ($\text{e}, \text{H}^+, \text{e}, \text{H}^+$). If $\text{pH} > 10.0$, reaction mechanism is EECC ($\text{e}, \text{e}, \text{H}^+, \text{OH}^-$)[14].

4. CONCLUSION

Reduction potentials take more negative values as the molecular weights of the substitutes attached to the aldehyde group increase. On the other hand, in aqueous media, oxidation potentials is exchanged with pH, and stabilize at -1.5V . However, in non aqueous media, substitutes have no effect on the reduction potentials. In basic and acidic media, since standard potential of oxygen is greater than the oxidation and reduction potentials of 4-(N, N- Dimethyl amino) Phenyl propenal and its derivatives, oxygen will not decompose and therefore these compounds can be considered as synthetic oxygen carrier.

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