

Synthesis of (1-ethyl-2-phenyl-1,4-dihydroquinolin-4-yl)-(2,4,6-trimethylphenyl)-amine by Electrochemical Methods in Aprotic Media

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Abstract. The formation of (1-ethyl-2-phenyl-1,4-dihydroquinolin-4-yl)-(2,4,6-trimethylphenyl)-amine by the electro reduction of (1-ethyl-2-phenyl-1*H*-quinolin-4-ylidene)-(2,4,6-trimethylphenyl)-amine occurs through acceptance of two electrons accompanied by two successive peaks, each electron peak followed by a chemical reaction. The electrochemical reduction of (1-ethyl-2-phenyl-1*H*-quinolin-4-ylidene)-(2,4,6-trimethyl-phenyl)-amine was investigated in 0.1 M tetrabutylammoniumbromide in *N,N*-dimethylformamide at glassy carbon electrode using the technique of cyclic voltammetry at the room temperature (290K). In this medium the first peak was observed at -0.831 V (vs. $\text{Ag}|\text{Ag}^+$) at the glassy carbon electrode (GCE) surface, which is more stable and well defined as compared to the second peak. The diffusion coefficient (D) of investigated imine in the investigated solvent media has been calculated using the modified Randles-Sevcik equation. The electron transfer coefficient (α) of the reactant species has also been calculated. (doi: [10.5562/cca1855](https://doi.org/10.5562/cca1855))

Keywords: electroreduction, cyclic voltammetry, glassy carbon electrode (GCE), diffusion coefficient (D)

INTRODUCTION

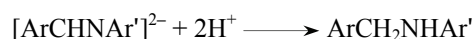
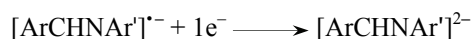
Imines are the class of most important and fundamental unsaturated organic compound with a $>\text{C}=\text{N}$ double bond as their characteristic chemical bond and are extensively present in natural products and many drugs. Since imines have many interesting biological activities and roles and can be converted into various very useful amines, they have received a much intense attention of chemists for a long time.^{1,2}

Imines are reduced by electrolysis without difficulty and some of the articles have indicated that the amines are the product of the reduction of imines in either protic or aprotic solvent. The first difficulty in the investigation of imines' reduction in aqueous media is contributed to its hydrolysis into the parent carbonyl compound.³⁻⁶

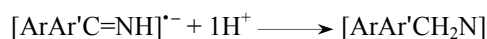
In a solvent having good proton donor capability, the initial reduction is assumed to occur via an immonium cation deriving from the addition of a proton to the nitrogen atom and is therefore more likely to be related to the reduction of the alkyl immonium salts rather than to the imine group itself. Studies in dimethylformamide give a more direct insight into the electrochemical properties of the $>\text{C}=\text{N}-$ group, for under the usual conditions, a pre-protonation step can be excluded in this

solvent. Another advantage of nonaqueous studies over that in aqueous media is the stability of the imines.⁷

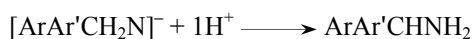
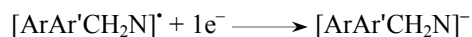
The electrochemical-electrochemical-chemical (EEC) mechanism is known to be applicable to the reduction of the aromatic imines in the low proton donor capability solvents, where two successive one electron wave are usually observed by the cyclic voltammetry experiments, and the first-step being reversible.^{8,9}



However, in a solvent with good proton donor capability and with unsaturated imine, a single two electron wave electrochemical-chemical-electrochemical (ECE) mechanism has been reported.^{10,11} The formed radical anion in the first step is rapidly protonated, resulting into a radical that will be easily reduced and finally protonated.



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Although the literature reveals the synthesis of amines using conventional methods, yet voltammetric methods are far better than the existing methods in the field with regards to their extra ordinary detection sensitivity, oligo determination capability, minimum detection limits, low cost, rapidity, accuracy, simplicity and non-destructive nature which have not been used for the said purpose.¹²⁻¹⁴

The electrochemical reduction mechanism of numerous aromatic imines at a glassy carbon electrode has been reported in aprotic media.¹⁵ On the other hand, relatively few studies have focused on the electrochemical behavior of heteroaromatic imines. In the present study, electro-reduction of (1-ethyl-2-phenyl-1,4-dihydroquinolin-4-yl)-(2,4,6-trimethylphenyl)-amine was studied at the GCE in N,N-dimethylformamide (DMF). Adsorption properties of imine on a GCE surface, the mechanism and the kinetics of the reduction were also investigated using cyclic voltammetry.

EXPERIMENTAL

Reagents

All the reagents used were of analytical grade. 2-phenylquinolin-1-ethyl-4-one was prepared according to reported method.¹⁶ Stock solution of imine (Q=NAr) were prepared at a concentration of 1×10^{-3} mol dm⁻³ in DMF. The supporting electrolyte of tetrabutylammonium bromide (TBAB) was purchased from SISCO Research laboratories Pvt. Ltd., and used without further purification.

Synthesis of (1-ethyl-2-phenyl-1*H*-quinolin-4-ylidene)-(2,4,6-trimethylphenyl)-amine

Imine (Q=NAr) was prepared according to the literature method.¹⁷ The general synthetic approach involved condensation of an equimolar mixture of corresponding 1-ethyl-2-phenyl-1*H*-quinolin-1-4-one (0.01 mol) and 2,4,6-Trimethylphenylamine (0.01 mol) in absolute ethanol in the presence of 2–3 drops of glacial acetic acid for 3–4 hours. On cooling, flakes separated out which were filtered and recrystallised from hot ethanol to give shining brightly coloured needles of (1-ethyl-2-phenyl-1*H*-quinolin-4-ylidene)-(2,4,6-trimethylphenyl)-amine (Q=NAr) in 70–80 % yield (scheme 1). Synthesized compounds were characterized by their IR and ¹H NMR studies.

¹H NMR Spectra

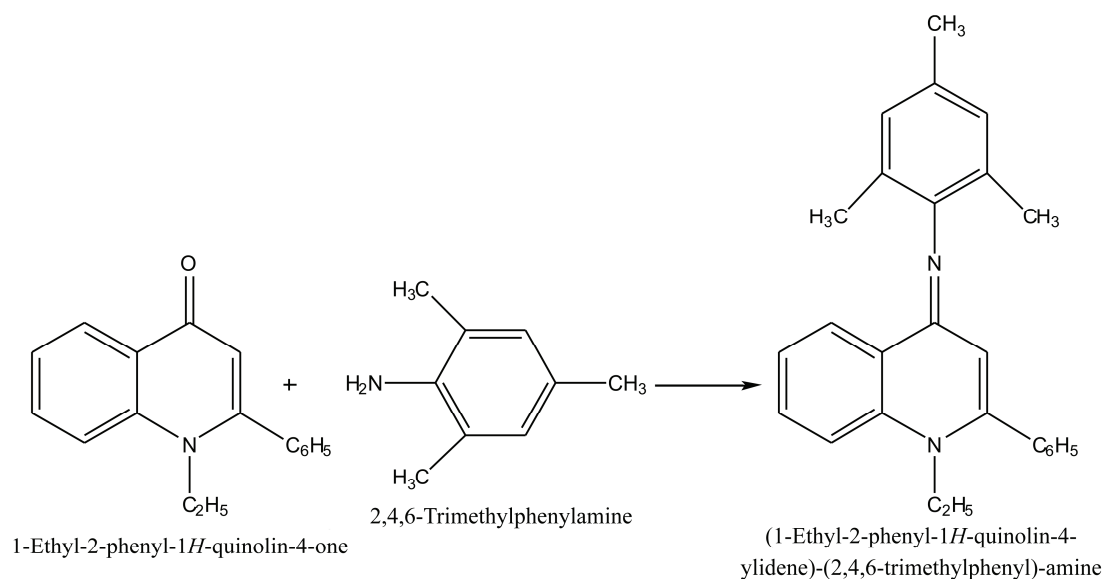
¹H NMR spectrum, δ /ppm: 1.29 (3H, t, CH₃), 4.50 (2H, q, CH₂), 6.33 (1H, s, H-3), 8.1 (1H, d, 5H), 7.0–7.2 (4H, m, H-6, H-7 and H-8), 7.4–7.8 (5H; m; H-2', H-3', H-4', H-5' and H-6'), 1.43 (9H, s, 3CH₃), 4.96 (2H; s; H-3'' and H-5'').

IR Spectra

IR spectra of (1-ethyl-2-phenyl-1*H*-quinolin-4-ylidene)-(2,4,6-trimethylphenyl)-amine is characterized by the disappearance of the (C=O) band of original compound 1-ethyl-2-phenyl-1*H*-quinolin-1-4-one in 1672 cm⁻¹ region. A band in 1634 cm⁻¹ region appear due to –N=C< bond. Free primary amino frequency of 2,4,6-trimethylphenylamine also disappeared in the IR spectra of product, confirming the formation of product.

Apparatus

The voltammetric measurements were carried out on an



Scheme 1.

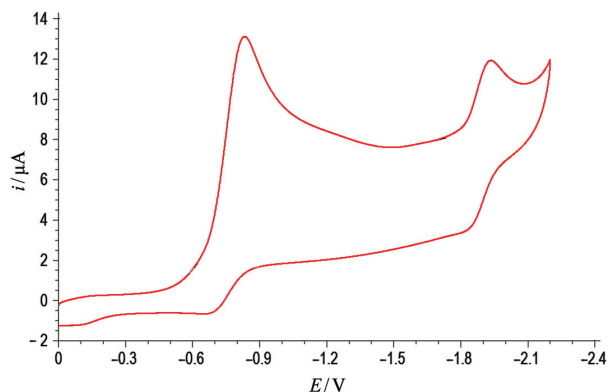


Figure 1. Cyclic Voltammogram of 1×10^{-3} M Q=NAr at Glassy Carbon Electrode (scan rate 20 mVs^{-1}).

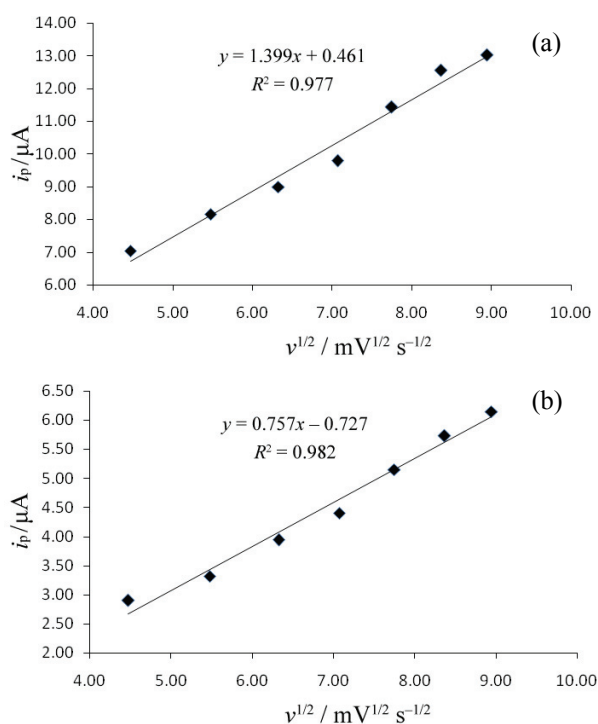


Figure 2. Plot of cathodic peak current (i_p) as a function of $v^{1/2}$ for 1st peak (a), plot of cathodic peak current (i_p) as a function of $v^{1/2}$ for 2nd peak (b).

electrochemical analyzer (CH Instruments, USA, Model CHI 1230), equipped with a 10 ml single compartment three-electrode glass cell. These systems were connected to a processor. All experiments were carried out in three-electrode system. Glassy carbon electrode (Part No. CHI 104) was used as the working electrode, a platinum wire as counter electrode and Ag|AgCl electrode as reference electrode. All solution used in the voltammetric system were deaerated with nitrogen for at least 15 min before executing the voltammetric experiments. All experiments were carried out at room temperature of 25 ± 1 °C. The GCE was polished using $0.3 \mu\text{m}$ Al_2O_3 before each experiment.

Sample Preparation

0.001 M stock solution of depolarizer *i.e.* (1-ethyl-2-phenyl-1*H*-quinolin-4-ylidene)-(2,4,6-trimethylphenyl)-amine was prepared by dissolving accurately weighed amount in purified DMF owing to low solubility of imine in water. More dilute solutions were prepared from the stock solution with supporting electrolyte *viz.* 0.1 M tetrabutylammoniumbromide (TBAB) solution in DMF just prior to analysis. The electrochemical measurements were then carried out.

Controlled Potential Electrolysis

Controlled-potential preparative electrolysis was carried out using H type cell separating the anode and cathode compartment by fine glass sinter. Other components of the cell assembly were as follows:

Cathode : Glassy Carbon Electrode

Catholyte : DMF + TBAB + (Q=NAr) compound

Total volume of catholyte : 100 ml

Anode : Pt sheet

Anolyte : DMF + TBAB

All measurements were carried out at controlled ambient temperature of 290 K. A magnetic stirrer was used for agitation. CPE experiment was carried out at potential of about 200 mV more negative than that obtained in CV experiment. The Ag|AgCl electrode which is used as a reference electrode was placed in the same compartment along with GCE. The electrolysis was carried out for 12 hrs for complete reduction of (1-ethyl-2-phenyl-1*H*-quinolin-4-ylidene)-(2,4,6-trimethylphenyl)-amine (Q=NAr). Reduction product was isolated and separated in column. To isolate the electrolysis product, DMF was distilled off in vacuo, the residue was shaken with dry ether and the supporting electrolyte was filtered off. The ethereal layer was evaporated and the residue thus obtained was purified by column chromatography on silica gel using ethyl acetate and hexane ($v(\text{eth.ac.}) : v(\text{hex.}) = 40 : 60$) as eluent. The reduced product was identified as (1-ethyl-2-phenyl-1,4-dihydroquinolin-4-yl)-(2,4,6-trimethylphenyl)-amine by IR and NMR spectra.

Analysis by Physico-chemical Methods

Analysis of product had been carried out by usual physico-chemical methods. Reduction of (1-ethyl-2-phenyl-1*H*-quinolin-4-ylidene)-(2,4,6-trimethylphenyl)-amine gives (1-ethyl-2-phenyl-1,4-dihydroquinolin-4-yl)-(2,4,6-trimethylphenyl)-amine (yield 76 %). The product was characterized by C, H analyzer and spectrophotometric techniques (IR and NMR).

The following observations were made:

- 1) A single clear spot on silica gel-G plate was obtained in iodine chamber, confirming that the product was a single compound and not a mixture.
- 2) The percentage of Carbon, Hydrogen and Nitrogen in the product was determined by Perkin Elmer elemental analysis.
- 3) IR spectra were recorded in KBr on a Shimadzu 400–50 infrared spectrophotometer (ν_{\max} in cm^{-1}).
- 4) ^1H NMR spectra were recorded on JEOL AL 300 ^1H NMR spectrophotometer using CDCl_3 as solvent and TMS as an internal standard (chemical shift in δ/ppm).

RESULTS AND DISCUSSION

Electroreduction of (1-ethyl-2-phenyl-1*H*-quinolin-4-ylidene)-(2,4,6-trimethylphenyl)-amine

From the results of the investigation it is inferred that the (1-ethyl-2-phenyl-1*H*-quinolin-4-ylidene)-(2,4,6-trimethylphenyl)-amine ($\text{Q}=\text{NAr}$) is electrochemically active in the potential range of -0.8 to -2.0 V. The cyclic voltammetric reduction of $\text{Q}=\text{NAr}$ in 0.1 M TBAB in DMF, at a glassy carbon cathode shows two cathodic peaks with $E_{p1} = -0.831$ V and $E_{p2} = -1.935$ V (Figure 1), with the intensity of the 1st peak being noticeably higher than that of the second one. Both peaks are irreversible at low scan rate values.

The first reduction wave, which corresponds to the initial addition of one electron to (1-ethyl-2-phenyl-1*H*-quinolin-4-ylidene)-(2,4,6-trimethylphenyl)-amine ($\text{Q}=\text{NAr}$) form the intermediate radical anion, is irreversible.

A study of effect of scan rate is made in order to evaluate the mechanism and the feasibility of electrochemical reactions involved at GCE in this medium. The relationship between the peak current (i_p) and the voltage scan rate (ν) is described by the modified Randles-Sevcik equation:¹⁸

$$i_p = 2.99 \times 10^5 n [\alpha n_a]^{1/2} ACD^{1/2} \nu^{1/2}$$

where, i_p is the peak current, α is the charge-transfer coefficient, n_a is the number of electron equivalents exchanged during the oxidation/reduction reversible process (electron stoichiometry), A/cm^2 is the active surface area of working electrode, $D/\text{cm}^2 \text{ s}^{-1}$ the diffusion coefficient, $C/\text{mol cm}^{-3}$ is the bulk concentration of the diffusing species, $\nu/\text{V s}^{-1}$ is the voltage scan rate, F is the faraday constant, R is the gas constant, and T/K is the absolute temperature.

In the present studies, the plot of the cathodic peak current (i_{pc}) was plotted against the square root of the scan rate ($\nu^{1/2}$) in order to apply the Nicholson-Shain

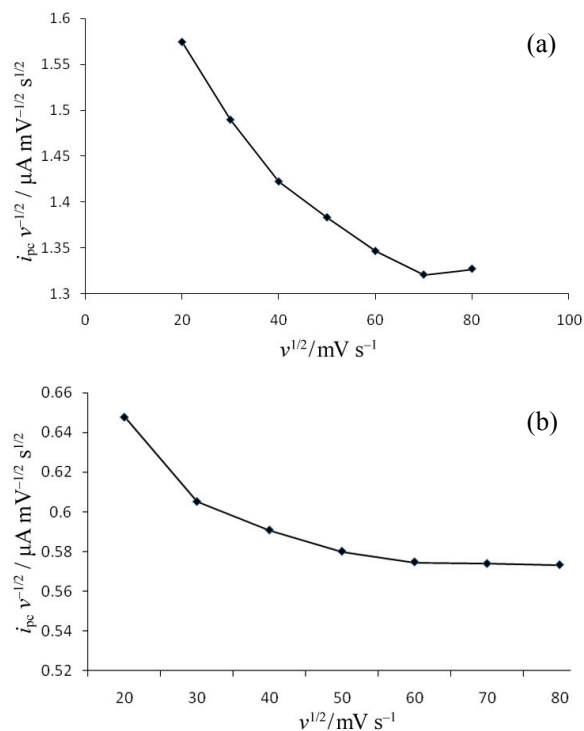


Figure 3. Dependence of $i_p/\nu^{1/2}$ vs. ν for 1×10^{-3} M $\text{Q}=\text{NAr}$ at glassy carbon electrode for 1st wave (a), dependence of $i_p/\nu^{1/2}$ vs ν for 1×10^{-3} M $\text{Q}=\text{NAr}$ at glassy carbon electrode for 2nd wave (b).

criteria to elucidate the reaction mechanism, for the 1st wave. The plot of peak current (i_{pc}) and square root of the scan rate ($\nu^{1/2}$) is clearly a straight line (Figure 2a). Nicholson-Shain criteria state that the linear change of the current with the scan rate is an indication that, the process was diffusion-controlled.^{19,20} But there appear a non zero intercept, this may be due to the electron transfer process complicated by the associated adsorption. The current function ($i_{pc}/\nu^{1/2}$) values were also plotted against the scan rate (Figure 3a). The current function ($i_{pc}/\nu^{1/2}$) decrease exponentially towards higher scan rate is an indication that the electron transfer is preceded by a chemical reaction. In the absence of chemical complication, this plot would be expected to be a nearly horizontal line. So the first electron transfer may be coupled to a fast chemical reaction which is very likely a protonation reaction by the tetrabutylammonium cation via Hofmann elimination²¹ or by residual proton impurities. All these fact suggest that the overall reaction in 1st step followed by an EC mechanism.

The second reduction wave which corresponds to the addition of one electron to the radical $[\text{QNHar}]^{\cdot}$ leading to the formation of the anion $[\text{QNHar}]^-$, was found to be electrochemically irreversible, with no anodic reversal current associated with it. The plot of the cathodic peak current (i_{pc}) plotted against the square root of the scan rate ($\nu^{1/2}$) and the current function

($i_{pc}/v^{1/2}$ C) values plotted against the scan rate are given in Figures 2b and 3b respectively. Furthermore, linear change of the current with the square root of scan rate and the ratio $i_{pc}/v^{1/2}$ decreases on increasing the scan rate. All the above evidence suggests that the irreversibility of the second wave is due to a moderately fast first-order reaction involving the product of the second electron-transfer.

The adsorptive character of the (1-ethyl-2-phenyl-1H-quinolin-4-ylidene)-(2,4,6-trimethylphenyl)-amine on the GCE was identified from the peak current's (i_p) dependence on the scan rate (v). Plots of $\log i_p$ vs. $\log v$ is a straight line and its slope is 0.57 and 0.66 for 1st and 2nd peak respectively, which is less than the theoretical value of 1.0 that is expected for an ideal reaction of surface species.

For 1st wave:

$$\log i_p = 0.574 \log v + 0.028, \quad R^2 = 0.976$$

and for the 2nd wave:

$$\log i_p = 0.669 \log v - 0.482, \quad R^2 = 0.991$$

The lower experimental slope than the theoretical one may be attributed to the partial involvement of the diffusive (1-ethyl-2-phenyl-1H-quinolin-4-ylidene)-(2,4,6-trimethylphenyl)-amine molecules in the electrode reaction of the adsorbed ones. The overall electrode process may thus be suggested as mainly diffusion-controlled with adsorption of the (1-ethyl-2-phenyl-1H-quinolin-4-ylidene)-(2,4,6-trimethylphenyl)-amine molecules at the electrode surface.

Estimation of an_a and Diffusion Coefficient D

The cathodic peak potential (E_{pc}) of the reduction peak was dependent on scan rate. The shift of peak potential was observed towards more negative values with the increase in scan rates which indicates a diffusion controlled irreversible nature of the system,²² where the peak potential is given by,

$$E_p = E^\circ - \left(\frac{RT}{an_a F} \right) \left[0.78 - \ln \frac{k^\circ}{D^{1/2}} + \ln \left(\frac{an_a F v}{RT} \right)^{1/2} \right]$$

where, a is the cathodic charge transfer coefficient, n_a is the number of electrons involved in the rate determining step, D the diffusion coefficient and k° is the standard rate constant of the electrochemical reaction. In the present work, the plot of E_{pc} vs. $\log v$ was linear having a correlation coefficient of 0.983 and 0.972 for 1st and 2nd peak respectively (Figures 4a and 4b) and this behavior was consistent with the EC nature of the reaction in

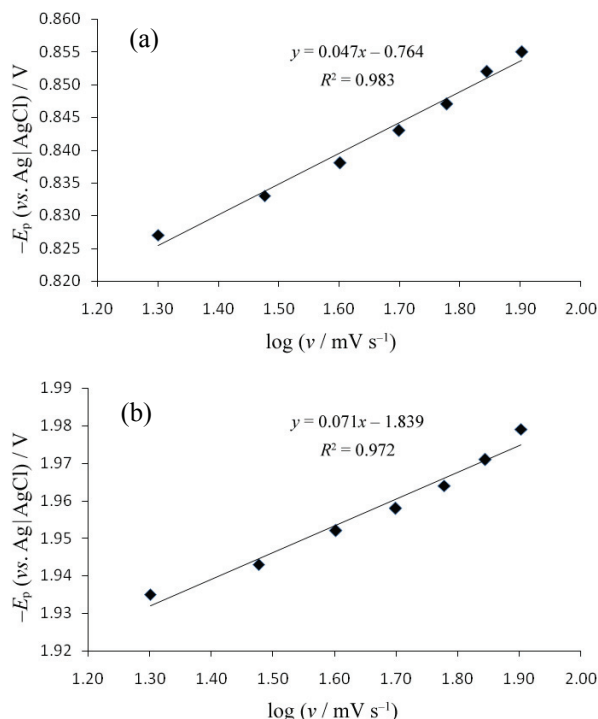


Figure 4. Plot of cathodic peak potential (E_p) as a function of $\log v$ for 1st peak (a), plot of cathodic peak potential (E_p) as a function of $\log v$ for 2nd peak (b).

which the electrode reaction is coupled with an irreversible follow-up chemical step.²³

The value of an_a is calculated from the slope of the plot between E_{pc} and $\log v$, the value of an_a is 0.678 and 0.583 for 1st and 2nd peak respectively. In most of irreversible case, a is the range from 0.30 to 0.70, thus the number of electrons transfer for each reduction step is most probably to be 1.

The D values for Q=NAr can be determined from the slope of i_{pc} vs $v^{1/2}$ plot, after careful substitution and unit analysis. The values of diffusion coefficients (D) are found to be $5.05 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $5.92 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for 1st and 2nd peak respectively.

Controlled Potential Electrolysis

CPE experiment were carried out in DMF containing 0.1 M tetrabutylammoniumbromide (TBAB) at potential about 200 mV more negative than the peak potential of irreversible reduction wave. The number of electron was calculated from the plot of amount of charge passes vs. $t^{1/2}$ and the value was found to be two. After electrolysis, the cell was disconnected from the circuit and the solvent was evaporated in vacuum. The residue was shaken with dry ether and the supporting electrolyte was filtered off. The ethereal layer was evaporated in turn. The resulting solid was identified.

C, H, N, Estimation Value

The observed values of the carbon, hydrogen and nitro-

gen, in the product, were 85.13 %, 6.97 %, 7.39 % respectively, as compared to their theoretical values, which are 85.24 %, 7.10 %, 7.65 % respectively, thus, confirming the product.

IR Spectra

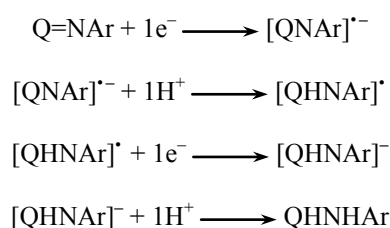
IR spectra of (1-ethyl-2-phenyl-1,4-dihydro-quinolin-4-yl)-(2,4,6-trimethylphenyl)-amine is characterized by the disappearance of the (C=N) band in 1623–1641 cm^{-1} region in comparison with that obtained for the original compound. A sharp peak was observed at 3345 cm^{-1} , which shows reduction of imine group into amine group.

NMR Spectra

^1H NMR spectrum, δ/ppm : 1.29 (3H, t, CH_3), 4.50 (2H, q, CH_2), 6.1 (1H, s, H-3), 4.51 (1H, t, 4-H), 10.3 (1H, s, NH), 6.5–6.7 (4H; m; H-5, H-6, H-7 and H-8), 7.2–7.5 (5H; m; H-2', H-3', H-4', H-5' and H-6'), 1.41 (9H, s, 3 CH_3), 5.73 (2H, s, H-3'' and H-5'').

Electrode Reaction Pathway

The result of cyclic voltammetry and controlled potential electrolysis suggest the consumption of two electron following the proton transfer reaction for reduction of the $-\text{CH}=\text{N}-$ centre to $-\text{CH}_2-\text{NH}-$. The data in the cyclic voltammetry results indicate that the reactant examined in this study ($\text{Q}=\text{NAr}$), is reduced in two discrete one electron transfer steps in DMF containing Bu_4NBr . After the first charge transfer, the protonation of the radical anion leads to a neutral radical whose charge is more favorable for the second electron transfer to occur. Therefore a second charge transfer occurred after protonation, leading to the saturation of carbon nitrogen double bond. Thus, the sequence of the electrode reaction pathway of the examined $\text{Q}=\text{NAr}$ at the glassy carbon electrode can be represented as follows:



CONCLUSION

The investigation have demonstrated that investigated $\text{Q}=\text{NAr}$ i.e. (2-phenyl-1H-quinolin-4-ylidene)-(2,4,6-trimethylphenyl)-amine has two reduction peak at glassy carbon electrode in DMF. On the basis of results obtained, the proposal of an electrode reaction mechanism pathway for $\text{Q}=\text{NAr}$ can conveniently be claimed

as EC mechanism. The electrochemical reduction occurs through acceptance of two electrons by successive one electron peak followed by chemical reaction. In order to test the validity of the proposed mechanism controlled-potential preparative electrolysis was carried out at the potential 200 mV more than the potential of the second peak for $\text{Q}=\text{NAr}$ and the reduction products were isolated and identified by spectroscopic methods.

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