Electrochemical Reduction of 1-{[(4-Halophenyl)imino]methyl}-2-naphthols in Aprotic Media

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The electrochemical reduction of 1-{[(4-halophenyl)imino]methyl}-2-naphthols on graphite electrodes was studied using cyclic voltammetry, chronoamperometry, constant-potential coulometry and preparative constant-potential electrolysis techniques. The data revealed that the reduction on graphite was irreversible and followed an EC mechanism. The diffusion coefficients and the number of electrons transferred were determined using the chronoamperometric Cottrell slope and the ultramicro disc Pt-electrode steady-state current. The number of electrons was also determined by bulk electrolysis. The compounds were subjected to constant-potential preparative electrolysis and the electrolysis products were purified and identified by spectroscopic methods. Based on these findings, a mechanism for the electro-reduction process is proposed.

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Introduction

Schiff bases are used extensively as ligands in coordination chemistry.[1,2] Some Schiff bases have thermochromic and photochromic properties in their solid state.[3] They are also used as model systems for biological macromolecules and catalytic reactions.[4,5]

Although these have been numerous studies on 2-hydroxy-1-salicylaldehyde Schiff bases, the studies were made on Schiff bases prepared by using of 2-hydroxy-1-napthaldehyde and its reduction of carbonyl compounds both in aqueous and non-aqueous media. The electrode process, which was involved in the reduction of carbonyl compounds is understood known in substantial detail.[8] There have been relatively few studies concerning the electrochemical behavior of imines or Schiff bases in aprotic media.[9]

A number of studies have indicated that amines are products of the electrochemical reduction of imines in protic solvents.[10-12] Under aqueous conditions, the reduction has been shown to consist of two-electron, two-proton transfer, which converts the >C=N–linkage to a –CHNH– group.[13] However, the hydrolysis of the Schiff bases into the parent carbonyl compound complicates the situation in protic media. Hydrolysis is complete for all pH values, and is particularly fast in an acidic medium.

There are different mechanisms proposed in non-aqueous media where hydrolysis does not pose any problem. Scott and Jura[13] investigated the reduction of various azomethine compounds in dimethylformamide (DMF), and proposed the following mechanism:

$$\mathrm{ArCH{=}NAr' + e \rightleftharpoons Ar\bar{C}H{-}\dot{N}Ar'}\ \text{(first wave)},$$

$$\mathrm{Ar\bar{C}H{-}\dot{N}Ar' + e \longrightarrow Ar\bar{C}H{-}\bar{N}Ar'}\ \text{(second wave)},$$

$$\mathrm{Ar\bar{C}H{-}\bar{N}Ar' + 2BH \longrightarrow ArCH_2NHAr' + 2\bar{B}}\ \text{(chem. react.)}.$$

Kononenko *et al.*[14] claimed that the first wave observed in the electrochemical reduction of azomethine compounds in DMF was a two-electron irreversible transfer. Martinet *et al.*[15] supported Scot and Jura's[13] data in their study carried out on anils in non-aqueous media.

Andrieux *et al.*[16] in their cyclic voltammetric study carried out on various imines in acetonitrile and DMF medium claimed that the reduction was either a two-electron transfer resulting in a saturated amine, or two one-electron transfers leading to a dimerized product, depending on the compound and solvent employed. They stated that the reduction was irreversible in both cases. The first step in the reduction is assumed to involve an immonium cation derived from the attachment of a proton to the nitrogen atom of the >C=N– group. They considered that the only cause of irreversibility of benzaldehyde anil in linear sweep voltammetry is dimerization. The radical formed by protonation of the anion radical initially produced is either dimerized or reduced at the electrode easier than the imine, itself. This second trend is stronger than the first one. However, they observed dimerization, at least partially, in a less acidic medium in DMF.

Fry and Reed[17] investigated the reduction mechanism of different anils in DMF medium by using polarography, cyclic voltammetry, coulometry and preparative scale electrolysis. They observed a two-electron transfer irreversible reduction in both polarographic and cyclic voltammetric studies, and that the reduction took place with the formation of a radical anion in the first step, followed by rapid proton abstraction and second-electron transfer.

In studies carried out on various imines, the reduction potential was stated to be dependent on the size of the aromatic groups at either side of the C=N– group,[11,13] the types of

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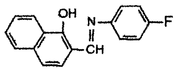
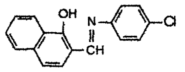
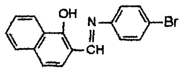
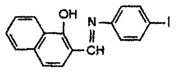
Table 1 Schiff bases investigated in this study

	Name	Structure	Melting point/°C
I	1-{[(4-Fluorophenyl)imino]-methyl}-2-naphthol		129
II	1-{[(4-Chlorophenyl)imino]-methyl}-2-naphthol		152
III	1-{[(4-Bromophenyl)imino]-methyl}-2-naphthol		164
IV	1-{[(4-Iodophenyl)imino]-methyl}-2-naphthol		171

All the structures given here are based on the assumption that the compounds are in the phenol imine form. *keto*-Amine and *keto*-enamine structures can be deduced there of.

substituents attached to the aromatic ring,[12,18,19] and intramolecular hydrogen bonds.[20,21] It was also claimed that the presence of electron withdrawing groups and hydrogen bonding facilitated the reduction.

Prasad *et al.*[22] found that *N*-(benzylidene)-2-aminopyrimidine was reduced with a two-electron transfer between pH 9.8 – 13.0, leading to *N*-(benzyl-2-aminopyrimidine). They also claimed that the protonation preceded the electronation in the reduction process, and that the whole process appeared to be diffusion-controlled and irreversible based on the voltammetric data.

In our previous work, the 1-{[(3-halophenyl)imino]methyl}-2-naphthol Schiff bases were synthesized and their structures and *keto-enol* tautomerism in protic and aprotic media were elucidated by using spectroscopic methods.[23] This study is concerned with an examination of their electrochemical behaviors. The synthesized Schiff bases were examined by the cyclic voltammetric, chronoamperometric and coulometric methods and the electroreduction products were investigated by using spectroscopic methods in order to determine the electrochemical mechanism.

Experimental

Apparatus

The melting points were determined on a Gallenkamp melting-points apparatus, and were not further corrected. Infrared spectra (KBr disc) were recorded on a Mattson 1000 FTIR spectrophotometer and reported in cm^{-1}; UV-visible spectra were measured on a Perkin-Elmer Lambda 2 Series recording spectrophotometer. Mass spectra were obtained using an Agilant GC-MSD and Micromass Platform 2 mass spectrometer operated at a 70 eV ionizing potential. ^1H and ^{13}C-NMR spectra were recorded on a Bruker DPX 400-MHz FT-NMR spectrometer operating at a proton frequency of 400.5 MHz and a carbon frequency of 100.7 MHz using $CDCl_3$ as a solvent and tetramethylsilane (TMS) internal standard.

Bulk electrolysis (BE), chronoamperometry (CA) and cyclic voltammetry on an ultramicro electrode were carried out on a BAS100B electrochemical analyzer equipped with a BAS100B cell stand and with a BAS100W.EXE data-processing program. Cyclic voltammograms on a graphite electrode were recorded on an EG&G Princeton Applied Research Model 362 Scanning Potantiostat with scan rates of between 5 and 500 mV s^{-1}. The IR drop was compensated. Constant-potential preparative electrolyses (CPE) were obtained on a PGZ 301 Dynamic-EIS Voltammetry, Radiometer Analytical Co., equipped with Volta lab 4.0 + PC Software.

All experiments, except for the CPE experiments, were carried out in an undivided conventional three-electrode cell with a working electrode and a platinum wire auxiliary electrode. An $Ag/AgNO_3$ (0.01 M)-CH_3CN electrode connected to the solution by a Luggin capillary was employed as a reference electrode. No correction for the junction potential was made. The working electrode for the electrochemical experiments, except for cyclic voltammetry on an ultramicro electrode and CPE, was a 3 mm diameter (0.071 cm^2) graphite disc (spectroscopic grade). Cyclic voltammograms on an ultramicro electrode were recorded with a 10 μm diameter platinum disc ultramicro electrode (Cypress Systems), and the CPE was performed with a 7 mm diameter (0.3848 cm^2) graphite electrode. The working electrodes were polished with 0.05 μm and 1 μm-size Al_2O_3 (Buehler). All measurements were run under a blanket of nitrogen. In order to remove the dissolved oxygen, the solutions were purged at room temperature with nitrogen saturated with the solvent for *ca.* 15 min, prior to each experiment.

The number of electrons was calculated from the amount of charge passed and the equivalent amount of the reduced BE product. Electrolysis was continued until the current dropped to about 1% of its initial value.

In order to ascertain the feasibility of an electrochemical synthesis of Schiff bases, different solvents and supporting electrolyte were tested, such as DMSO/Bu_4NF_4, $NaClO_4$; DMF/Et_4NBr, $NaClO_4$; CH_3CN/Bu_4NF_4 or $NaClO_4$. Solutions containing 20% (v/v) methanol in THF and Bu_4NBF_4 or Et_4NBr were also examined, but none of them gave a reduction peak in the potential range studied. For this reason, the solvent supporting electrolyte (SSE) was chosen as a solution of THF containing 20% (v/v) methanol and 0.1 M $NaClO_4$, which gave the best results in the appropriate potential range. The structure of the compounds obtained by electrochemical reduction was elucidated by using the IR, UV-vis, ^{13}C-NMR, ^1H-NMR and GC-MS techniques.

Reagents

Methanol and tetrahydrofuran (THF) were purchased from Merck and purified as described in the literature.[24] Sodium perchlorate ($NaClO_4$) was from Aldrich, and was used without further purification. 1-{[(4-Halophenyl)imino]methyl}-2-naphthols were prepared according to a method described elsewhere.[23] These compounds are listed in Table 1. The given melting points, relate to a reversible, true melting process. No decomposition was noticed.

Results and Discussion

Characterization of the electrode reaction

The cyclic voltammograms of compounds **I** – **IV** are shown in Fig. 1. All of the curves are initial scans on freshly cleaned graphite. As is evident on the voltammograms, the anodic half cycle does not have any peak; indicating that the concerned electroreductions are irreversible.

The peak current (i_p) and the current function $i_p/v^{1/2}C$ values were plotted against the scan rate in order to apply the Nicholson–Shain criteria to elucidate the reaction mechanism.[25] Plots of all the compounds are given in Figs. 2 and 3. The

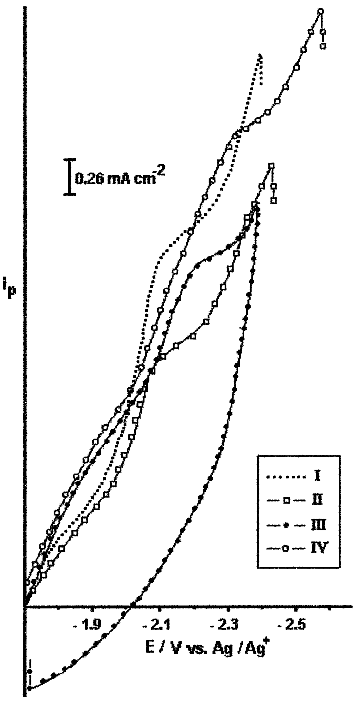


Fig. 1 Cyclic voltammograms of compounds **I** - **IV** (3 mM) for solutions containing 20% (v/v) methanol in THF (0.1 M $NaClO_4$) at a scan rate of 50 mV s^{-1} on a graphite electrode.

different plots in Fig. 2 are clearly straight lines; while in Fig. 3 the resulting plots are concave curves, whose slopes decrease towards higher scan rates. Figure 4 is a plot of the current against concentration. Both Figs. 2 and 4 gave linear plots for all of the compounds investigated. The Nicholson–Shain criteria state that the linear change of the current with the scan rate is an indication that the reaction is diffusion-controlled.[25]

The fact that the current function decreases exponentially towards higher scan rates is an indication that electron transfer is preceded by a chemical reaction. In the absence of chemical complications, this graph would be expected to be a nearly horizontal line. All of these points suggest that the overall reaction is irreversible and followed an EC mechanism.[26]

Ease of reduction decreases in the order of compounds **I** > **II** > **III** > **IV**, as can be seen from Fig. 1. This can be attributed to shifts in the reduction potential caused by changes in the halogen-substituted Ar groups attached to the iminic nitrogen. The reduction is facilitated by electron-withdrawing substituents attached to the phenyl ring. These results are in good agreement with a similar studied appearing in the literature.[11-13,18-21]

Determination of the number of electrons transferred and the diffusion coefficients

The numbers of electrons transferred (n) and diffusion coefficients (D) for compounds **I** - **IV** were simultaneously determined by using steady-state voltammetry at an ultramicro disc-electrode[27,28] and chronoamperometry at a graphite electrode. The two equations giving a Cottrell slope (S_{cott}) of the chronoamperometric i *vs.* $t^{-1/2}$ plots and the limiting steady state current (i_{ss}) at a ultramicrodisc electrode are:

$$S_{\mathrm{cott}} = \frac{nFAC^*D^{1/2}}{\pi^{1/2}}, \tag{1}$$

$$i_{\mathrm{ss}} = 4nFC^*Dr. \tag{2}$$

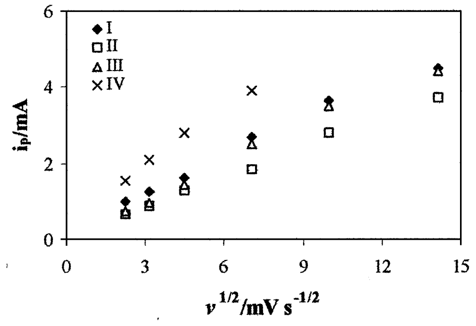


Fig. 2 Current changes for compounds **I** - **IV** (3 mM) with a scan rate for solutions containing 20% (v/v) methanol in THF (0.1 M $NaClO_4$) at a scan rate of 5 - 500 mV s^{-1} on a graphite electrode.

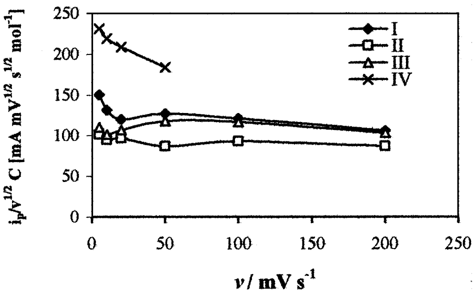


Fig. 3 Current function for compounds **I** - **IV** (3 mM) plotted against the scan rate for solutions containing 20% (v/v) methanol in THF (0.1 M $NaClO_4$) on a graphite electrode.

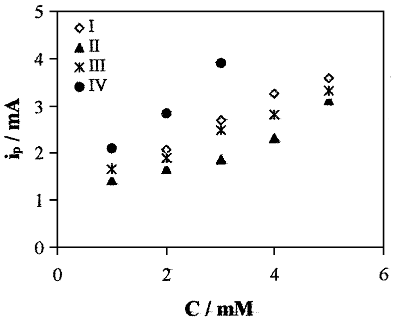


Fig. 4 Change with the concentration of the current for compounds **I** - **IV** in solutions containing 20% (v/v) methanol in THF (0.1 M $NaClO_4$) at a scan rate of 50 mV s^{-1} on a graphite electrode.

Combining these equations, one finds the number of electrons transferred to be

$$n = \frac{4\pi r S^2_{\mathrm{cott}}}{A^2FC^*i_{\mathrm{ss}}}. \tag{3}$$

Here, r is the radius of the ultramicro electrode, A is the area of the microelectrode, and all other symbols have their usual meaning.[27] In the chronoamperometric experiments, the potential was stepped from a value where there was no Faradaic current (about –100 mV) to a potential of –2300 mV, which is about 100 mV more cathodic than the first reduction peak for all of the compounds investigated. The electrochemically active area of the 3 mm graphite electrode was determined from the slope of the chronoamperometric i *vs.* $t^{-1/2}$ plot obtained with 5 mM solutions of ferrocene in 0.1 M $NaClO_4$-THF (containing

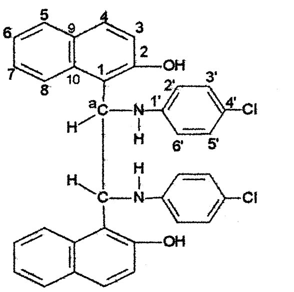
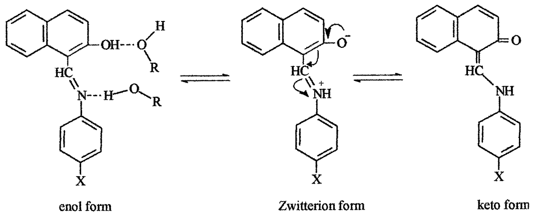


Fig. 5 The molecular structure of compound **II**.

Table 2 Diffusion coefficient, the amount of charge passed and the number of electrons transferred for compounds **I** – **IV** at 25°C

	Q^a/C (F mol^{-1})	D^b/cm^2 s^{-1} (± 0.02)	Electron transferred (n)/ eqiv. mol^{-1} (± 0.03)	
			n^c	n^d
I	0.875	3.00×10^{-5}	0.91	0.89
II	0.830	4.78×10^{-5}	0.72	0.71
III	0.855	3.30×10^{-5}	0.86	1.00
IV	0.697	5.89×10^{-5}	0.89	1.20

The concentration of the compound used was 3 mM.
a. Calculated from Bulk electrolysis.
b. Calculated from Cottrel slope (Eq. (1)).
c. Calculated from Bulk electrolysis.
d. Calculated from Eq. (3).



Scheme 1

20% methanol), and was found to be 0.80 ± 0.015 cm^2. The value of D for the ferrocene used in calculating this area was 4.8(± 0.1) × 10^{-6} cm^2 s^{-1}, and was obtained from the limiting current of steady-state voltammograms, assuming the true geometric area of a 10 μm diameter ultramicrodisc Pt electrode as the electroactive area, and employing Eq. (2). The value of n of the ferrocene-ferrocenium couple was taken to be 1. The experimental values of n and D for all compounds are given in Table 2.

The results of constant-potential coulometry obtained at each peak potential (Fig. 1) for the compounds **I** – **IV** are given in Table 2.

Controlled-potential preparative electrolyses and mechanism of the electrode reaction

Controlled-potential preparative electrolyses were carried out in a divided cell with a catholyte concentration of 40 mL of a 2.8×10^{-3} mol of **I** – **IV**. The anode was a Pt sheet. The anolyte was 20 mL of a SSE solution. The results are given in Table 3.

There were three products observed on thin-layer chromatography (TLC), but only one product was isolated after constant-potential preparative electrolysis. The mixture was evaporated to dryness in a rotary evaporator after electrolyses. The solid residue was triturated with diethyl ether several times, and the ether-soluble portion was subjected to preparative-TLC on silica gel 60PF$_{254}$ (Merck) plates using petroleum ether (40 – 60°C): ethyl acetate (3:1) as the eluent. The eluent was separated and evaporated to dryness. The crystals (mp compound **I**, 145 – 147°C; **II**, 90 – 92°C; **III**, 62 – 65°C and **IV**, 85 – 88°C) were analyzed using spectroscopic methods.

As a typical example, for the IR-spectrum of compound **I**, the following assignments were made: υ_{max} (KBr)/cm^{-1} 3470 (OH), 3425 (NH), 3065 – 3040 (CH arom.), 2910 – 2849 (CH aliphatic), 1575 (C=C arom.), 1427 (C-N), 1324 – 1078 (C-O).

The FT-IR-spectra of compounds **II** – **IV** are similar, except for the expected differences in the fingerprint region. In addition the characteristic broad band at the 3100 – 3000 cm^{-1} region corresponding to the intra-molecular hydrogen bonding and the bands between the 1700 – 1600 cm^{-1} region due to C=N and C=O stretching[23] were found to disappear.

The principal mass spectral peaks observed were as follows: Compound **I**: *m/z* (EI+ 6.124 e4) 533.0 [1.5%, $(M+1)^+$]; 437 [4.35, $(M–1(H)^+–C_6H_5F)^+$]; 342 (16, $C_{22}H_{18}N_2O_2^+$), 341 (30, $C_{22}H_{17}N_2O_2^+$), 325 (10, $C_{22}H_{15}NO_2^+$), 282 (38, $C_{22}H_{18}^+$), 281 (100, $C_{22}H_{17}^+$), 267 (9.7, $C_{17}H_{12}NOF^+$), 156 (4.1, $C_{11}H_8O^+$), 110 (3.2, $C_6H_5FN^+$), 95 (5.2, $C_6H_4F^+$).

Compound **II**: *m/z* (EI+ 5.73 e4) 566 (3.2%, $M^{+\cdot}$), 564 [3.4, $(M+2)^+$], 284 [8.6, $(M+2^{+\cdot}–C_{17}H_{13}NOCl)^+$], 282 [3.80, $(M^{+\cdot}–C_{17}H_{13}NOCl)^+$], 281 {[7.0, [$(M^{+\cdot}–C_{17}H_{13}NOCl)^+$–H]}; 263 (5.1, $C_{17}H_{10}NCl^+$), 227 (100, $C_{17}H_9N^+$), 170 (10.1 $C_{17}H_{12}NOCl^+$), 155 (7.4, $C_{11}H_7O^+$), 143 (32, $C_{10}H_7O^+$), 125 (11.94, $C_6H_5NCl^+$), 111 (24.52, $C_6H_4Cl^+$), 77 (9.2, $C_6H_5^+$).

Compound **III**: *m/z* (EI+ 5.57 e3) 652 [1.2%, $(M+4)^+$], 655.50 [0.8, $(M+2)^+$], 275 (3, $C_{18}H_{15}N_2O^+$), 184 (13, $C_{12}H_{10}NO^+$), 171 (100, $C_{11}H_9NO^+$), 155 (18, $C_{11}H_7O^+$), 138 (8, $C_{11}H_6^+$).

Compound **IV**: *m/z* (EI+ 1.18 e4) 748 (3.3%, $M^{+\cdot}$), 747 [1.2, $(M^{+\cdot}–1)$], 478 (3.4, $C_{24}H_{19}N_2OI^+$), 245 (25, $C_{17}H_{11}NO^+$), 208 (46.4, $C_{14}H_{12}N_2^+$), 207 (100, $C_{14}H_{11}N_2^+$), 170 (10, $C_{11}H_8ON^+$), 169 (11, $C_{11}H_7NO^+$), 153 (26, $C_{11}H_7N^+$), 152 (27, $C_{11}H_6N^+$), 143 (17, $C_{10}H_7O^+$).

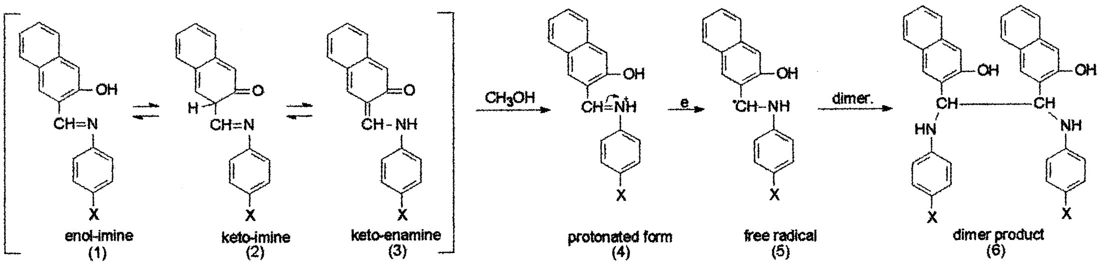
The molecular ion peaks corresponding to the dimerized product were observed in the MS spectra of all compounds. Further evidence for the identity of compounds **I** – **IV** came from ^{13}C-NMR (DEPT techniques) and ^{1}H-NMR data. As an example, ^{13}C-NMR data related to compound **II** are given below (The result were given as regards to Fig. 5): δ_C proton decoupled (100 MHz; [D$_6$] chloroform) 58.2 (C-a), 109.5 (C-1), 154.0 (C-2), 124.2 (C-3), 137.2 (C-4), 129.0 (C-5), 121.0 (C-6), 128.0 (C-7), 121.8 (C-8), 135.8 (C-9), 131.0 (C-10), 135.8 (C-1′), 124.6 (C-2′; C-6′), 137.3 (C-4′), 130.0 (C-3′; C-5′). δ_C DEPT 45, 90, 135 (100 MHz; [D$_6$] chloroform 58.2 (C-a), 124.2 (C-3), 137.2 (C-4), 129.0 (C-5), 121.0 (C-6), 128.0 (C-7), 121.8 (C-8), 124.6 (C-2′; C-6′), 130.0 (C-3′; C-5′).

^{13}C-NMR-DEPT results show that there are 11-methine protons [(DEPT-90 and DEPT-45) and no methylene proton (DEPT-135) and no methyl proton (DEPT-45 and DEPT-135)] in the structure. Moreover, the observation of 17 signals of the proton decoupled spectrum shows that the structure is a symmetrical dimer. ^{1}H-NMR data for compound **II** are: δ_H ppm (400 MHz; [D$_6$] chloroform; Me$_4$Si) 6.4 (2H, s, Ar-OH), 8.0 – 6.5 (20H, m, arom. protons); 3.0 – 4.0 (2H, d, aliph.-CH protons); 2.4 (2H, hump, NH protons).

The fact that the disappearance of the characteristic peaks located at δ9.2 (C=N-H) and δ15.2 (OH/NH) in the original ^{1}H-NMR spectra[23] of the compounds is another verification of dimeric formation.

Table 3 Constant-potential preparative electrolysis results for compounds **I** - **IV**

Compound	Electrolysis product/mol	*t*/min	Potential/V	*Q*/*C* (F mol^{-1})	Product yield, %	Current efficiency, %
I	1.09×10^{-3}	41.5	–2.25	199	38.9	73.0
II	8.90×10^{-4}	48.8	–2.20	180	31.8	66.0
III	9.87×10^{-4}	34.2	–2.30	195	35.3	72.0
IV	1.22×10^{-3}	40.0	–2.35	187	43.6	69.0



Scheme 2

It is known that 2-hydroxy Schiff bases interact with polar solvent molecules in protic media.[29-31] Here, the solvent molecules act as both proton donors and proton acceptors, and form a *keto* structure through a Zwitterion, as depicted in Scheme 1.[31] Starting from the CV data and this fact, the following pathway is proposed for the electrochemical reduction of Schiff bases (Scheme 2). The Schiff base is first protonated, and then reduced by taking an electron per molecule, finally giving the final product by radical-radical dimerization. Indeed, the spectroscopic evidence on the constant-potential preparative electrolysis products of compounds **I** - **IV** supports that these kinds of products do form.

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