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Self-protonation mechanism in the electroreduction of hydroxyimines

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The electrochemical reduction mechanism of *N*-(*p*-hydroxybenzylidene)aniline, *N*-benzylidene-*p*-hydroxyaniline and of the corresponding methoxy derivatives has been investigated in DMF, by cyclic voltammetry, controlled potential electrolysis and coulometry. All the imines examined show two cathodic voltammetric peaks which correspond, for the methoxy derivatives, to two successive one-electron reduction steps while for the hydroxy substituted compounds they are attributable to the partial two-electron reduction of the substrate in the form of undissociated molecule and of its conjugate base. The latter stems from an intermolecular proton transfer from the substrate to its basic reduction intermediates, featuring a self-protonation mechanism. Kinetic analysis of the voltammetric results has allowed the electrode reduction mechanism to be fully characterized and the rate constant of the proton transfer rate-determining step to be evaluated.

The electrochemical reduction of Schiff bases has been widely studied, particularly in dipolar aprotic solvents,[1,2] since hydrolysis of imines is severely hampered in these media. The process involves hydrogenation of the C=N double bond, leading to the corresponding amine, although evidence of radical dimerisation [1d] and formation of dimeric diamines [2c] has also been reported. The overall two-electron process takes place in two successive one-electron steps or it gives rise to a single reduction wave, depending mainly on the proton-donor ability of the medium and on the basicity of the reduction intermediates. Stepwise reduction has been observed by voltammetric reduction of some aromatic Schiff bases in dimethylformamide (DMF),[1a,d,e,g] the first step being, at least partially, reversible, while the second one is irreversible, because of the fast proton transfer undergone by the very basic dianion. Owing to the intrinsic basicity of this class of compounds, the anion radical arising from the first electron transfer is often sufficiently basic to undergo proton transfer, even in dry DMF. Further reduction at the applied potential of the ensuing free radical gives rise to an overall two-electron process, according to the well known ECE mechanism. This appears to be the case, *e.g.*, with camphor [1c] and pinocamphone [1d] anils and with several substituted *N*-benzylidineanilines.[2c] It is worth noting, however, that with *N*-benzylideneanilines bearing a hydroxy group on either of the two phenyl rings, wave splitting is invariably observed,[1f,2c–e] which has been also attributed to stepwise reduction of the C=N bond.

It has been the aim of our investigation to show that the reduction pattern of OH substituted anils can be correctly interpreted on the grounds of a self-protonation mechanism involving proton transfer from the acidic parent compound to the electrogenerated bases. We report in this paper the results of the electrochemical reduction of the *p*-OH substituted anils **1a** and **2a** in DMF. For the sake of comparison the behaviour of the corresponding methoxy derivatives **1b** and **2b** has also been examined.

p-X–$C_6H_4CH{=}NC_6H_5$

X = OH **1a**
X = OCH_3 **1b**

p-Y–$C_6H_4N{=}CHC_6H_5$

Y = OH **2a**
Y = OCH_3 **2b**

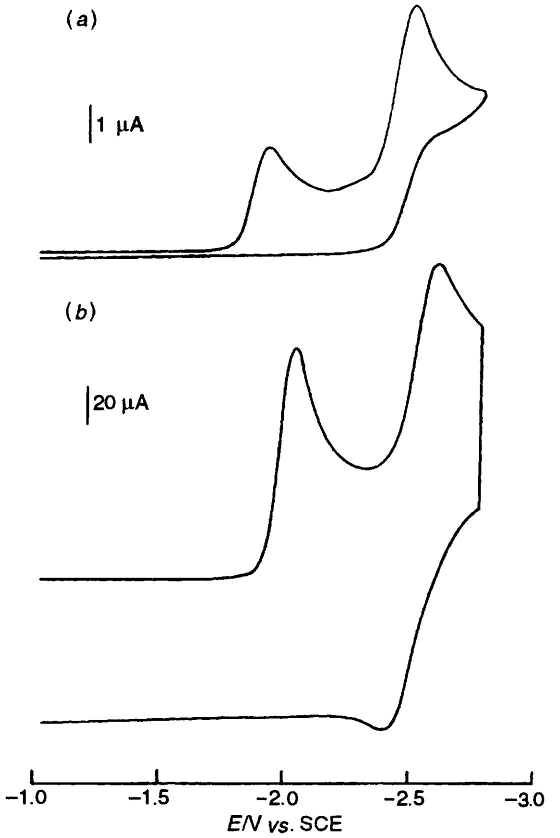

Fig. 1 Cyclic voltammograms of 0.93 mmol dm^{-3} **1a** in DMF + 0.1 mol dm^{-3} Bu_4NClO_4 at a Hg electrode at a sweep rate of (*a*) 0.2 V s^{-1} and (*b*) 400 V s^{-1}

Results and discussion

Cyclic voltammetry of **1a** in DMF + Bu_4NClO_4 (0.1 mol dm^{-3}) shows two reduction peaks (see Fig. 1) whose potential values are reported in Table 1. While the second peak, which is *ca.* double in height with respect to the first, becomes, at least partially, reversible increasing the potential sweep rate v, the first one shows no anodic partner up to 600 V s^{-1}. The first peak potential E_p^1 is shifted cathodically increasing v and anodically increasing the substrate concentration c, with slopes $\partial E_p^1/\partial \log v = -30$ mV and $\partial E_p^1/\partial \log c = 32$ mV, respectively. The width of the peak $\Delta E_{p/2}^1 = E_{p/2}^1 - E_p^1$ amounts to 81 mV, independently of v and c, in the whole range explored. However, the voltammetric pattern is strongly dependent upon the

Table 1 Voltammetric data of Schiff bases **1a**, **1b**, **2a** and **2b**[a]

Imine	c/mmol dm^{-3}	$-E_{pc}{}^{I}$/V	$-E_{pa}{}^{I}$/V	$-E^{oI}$/V	$-E_{pc}{}^{II}$/V
1a	0.93	1.939			2.511
1b	1.02	1.994	1.934	1.964	2.507
2a	1.01	1.902			2.349
2b	1.09	1.960	1.897	1.928	2.443

[a] Peak potentials referred to SCE were measured at $v = 0.5$ V s^{-1}.

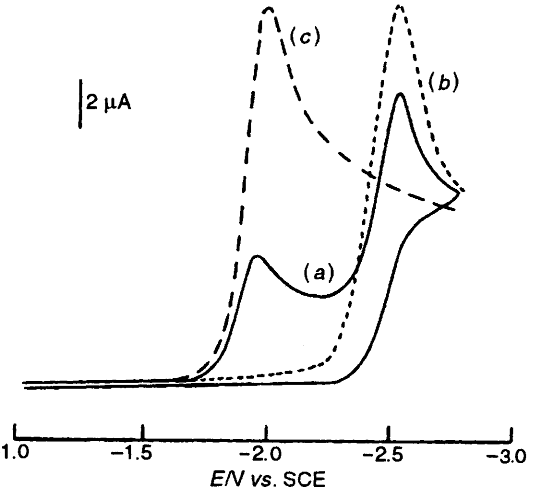

Fig. 2 Cyclic voltammograms of 6.3 mmol dm^{-3} **1a** in DMF + 0.1 mol dm^{-3} Bu_4NClO_4 at a Hg electrode at $v = 0.2$ V s^{-1}; (*a*) **1a** alone and after addition of either (*b*) 1 equiv. of Bu_4NOH or (*c*) 2 equiv. of CH_3CO_2H

composition of the medium. In fact, progressive addition of a strong base such as Bu_4NOH, causes a decrease of the first peak and an increase of the second, the first disappearing in the presence of 1 equivalent of base [see Fig. 2(*b*)]. This shows that the second peak is attributable to the reduction of the conjugate base of the substrate, which is the only form of the latter present in solution after addition of the strong base. On the contrary, addition of a relatively strong acid such as CH_3CO_2H, causes an increase of the first peak at the expense of the second, which eventually disappears. After addition of two equivalents of acid only the first peak is present, its peak current having increased threefold [see Fig. 2(*c*)].

Information about the stoichiometry of the electrode process occurring at the first voltammetric peak is provided by controlled potential coulometry. Exhaustive electrolysis carried out at −2.05 V requires 0.67 F mol^{-1}. At the end only the second peak is observable, its height having kept practically unchanged. HPLC analysis shows, however, that 2/3 of the substrate is still present, as conjugate base, in the electrolysed solution. Acidification of the latter with the stoichiometric amount of CH_3CO_2H restores the voltammetric pattern of **1a**, although both peaks are now reduced by *ca.* 33% with respect to their height before electrolysis. This outcome clearly shows that during electrolysis, which causes disappearance of the first peak, only 33% of the substrate has been reduced.

All the above results are compatible with the overall electrode reaction (1) according to which 67% of the substrate ROH

$$3ROH + 2e^- \longrightarrow RH_2OH + 2RO^- \qquad (1)$$

is transformed into its conjugate base RO^-, providing the protons necessary for the two-electron reduction of the remaining part to the corresponding amine RH_2OH (self-protonation reaction). In fact if the reduction is carried out directly in the presence of two equivalents of an exogenous proton donor stronger than the substrate, such as CH_3CO_2H, disappearance of the single peak present in these conditions requires 2 F mol^{-1} of **1a** and no trace of the substrate, not even as conjugate base, is found in the electrolysed solution. This is consistent with the overall two-electron reduction of the imine to the corresponding amine.

Controlled potential electrolysis and coulometry have also been performed directly at the potential of the second peak, where reduction of the conjugate base is expected to occur. Voltammetric curves recorded during electrolysis have shown that the latter causes, initially, a progressive decrease of the first peak, which disappears totally after the passage of 0.67 F mol^{-1} of **1a**. Only at this stage does the second peak start decreasing and eventually fades out, after the passage of *ca.* 2.2 F mol^{-1} of imine.

The voltammetric behaviour of imine **2a** is quite similar to that of **1a**. It shows two reduction peaks whose potential values are reported in Table 1. Only the second one, which is double in height with respect to the first, acquires a partial reversibility increasing v. The characteristics of the first peak are as follows: $\partial E_p{}^I/\partial \log v = -29$ mV; $\partial E_p{}^I/\partial \log c = 33$ mV and $E_{p/2}{}^I - E_p{}^I = 82$ mV. The effects of the acid–base properties of the medium on the voltammetric pattern of **2a**, as well as the effect of electrolysis carried out either at the first or at the second peak potential, are qualitatively and quantitatively similar to those illustrated above for the imine **1a**.

Substitution of the acidic proton of the OH moiety with a methyl group provides further support to the hypothesis of self-protonation in the reduction of imines **1a** and **2a**. In fact the voltammetric pattern of the resulting imines **1b** and **2b** differs appreciably from that of the OH substituted imines. Although two reduction peaks are observed also in this case (see Fig. 3, as an example and the potentials reported in Table 1), it is the first peak, rather than the second, to show reversible behaviour. The second peak is irreversible up to 600 V s^{-1}. Its peak potential varies with log v with a slope *ca.* −30 mV up to 1 V s^{-1} and *ca.* −55 mV for higher v values. This very simple voltammetric behaviour is quite similar to that of other aromatic Schiff bases bearing no acidic moieties and showing stepwise reduction.[1a,d,e,g] The anion radical arising from the first electron transfer is relatively stable while the very basic dianion produced in the second reduction step undergoes fast protonation by the medium. At low sweep rates ($v \leqslant 1$ V s^{-1}) the variation of the second peak potential is in fact characteristic of a fast electron transfer followed by a first- or pseudo-first-order decay of the reduction product. For higher v values, the higher slopes observed point to a slow, rate-determining electron transfer.

The two cathodic peaks shown by imines **1a** and **2a**, on the contrary, do not correspond to a stepwise reduction of such compounds but rather to the reduction of two forms of the same species, *i.e.* the undissociated hydroxyimine and its conjugate base. The sweep rate and concentration dependence of the first peak potential clearly indicate that its irreversibility is attributable to a fast follow-up reaction involving the electron transfer products. Considering the acidic properties of the substrate and the basicity of the reduction intermediates, the following mechanism can be proposed for the electrode process occurring at the first peak potentials.

$$ROH + e^- \rightleftharpoons ROH^{\bullet -} \qquad (2)$$

$$ROH^{\bullet -} + ROH \underset{k_{-p}}{\overset{k_p}{\rightleftharpoons}} RHOH^{\bullet} + RO^- \qquad (3)$$

$$RHOH^{\bullet} + e^- \rightleftharpoons RHOH^- \quad \text{and or} \qquad (4)$$

$$RHOH^{\bullet} + ROH^{\bullet -} \rightleftharpoons RHOH^- + ROH \qquad (5)$$

$$RHOH^- + ROH \rightleftharpoons RH_2OH + RO^- \qquad (6)$$

$$3ROH + 2e^- \longrightarrow RH_2OH + 2RO^- \qquad (1)$$

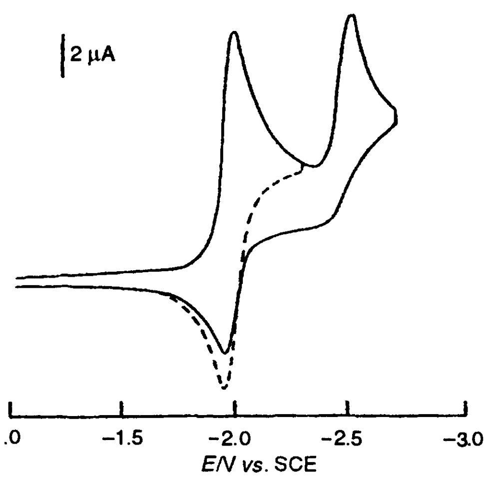

Fig. 3 Cyclic voltammogram of 0.96 mmol dm^{-3} **1b** in DMF + 0.1 mol dm^{-3} Bu_4NClO_4 at a Hg electrode at $v = 0.2$ V s^{-1}

According to this self-protonation pathway, which has been already shown to provide a good qualitative and quantitative account for the electrochemical reduction, in dipolar aprotic media, of organic molecules bearing acidic functions,[3] the anion radical from the first electron transfer reaction (2) undergoes proton transfer from the substrate. The ensuing neutral radical is reduced, either heterogeneously, at the applied potential, and/or homogeneously, to the anion $RHOH^-$ which is finally protonated by the substrate to the amine RH_2OH. This mechanism is in agreement with the overall electrode process involving the consumption of 2/3 F mol^{-1} of imine, 33% of which is transformed into the two-electron two-proton aminic reduction product while the remaining 67%, having provided the protons involved in the above reaction, is transformed into its conjugate base, reducible at the second peak potentials.

When an exogeneous proton donor, such as acetic acid, provides the protons involved in reactions (3) and (6), in place of the substrate, transformation of the latter into its conjugate base is hindered and its full two-electron reduction to amine at the first peak potentials is promoted, *i.e.* in the presence of acetic acid the first peak current increases threefold while the second peak disappears and the charge consumption during electrolysis varies from 0.67 to 2 F mol^{-1} of imine.

Addition of a strong base, such as Bu_4NOH, transforms the whole substrate into its conjugate base, with enhancement of the second peak and disappearance of the first one.

A detailed theoretical kinetic analysis of such a mechanism, under the conditions of linear sweep cyclic voltammetry, has been already reported.[3a] When the overall rate constant of the chemical processes associated with the fast electron transfer [reaction (2)] is large, within the timescale of the voltammetric experiment, the cathodic peak is chemically irreversible insofar as its anodic partner is totally absent in the whole sweep rate range featuring this situation. In these 'pure kinetic' conditions the peak current is scarcely dependent upon the rate of the process and information on kinetics and mechanism is rather provided by the peak potential dependence on experimental parameters such as potential sweep rate and substrate concentration. Simple expressions for the peak potential and useful diagnostic criteria are available when the overall process is kinetically controlled by a single step. Different kinetic forms are realized, depending on whether the second electron transfer occurs at the electrode or in solution and on the nature of the rate-determining step (rds).

A comparison of the experimental values of peak width and of slopes $\partial E_p/\partial \log v$ and $\partial E_p/\partial \log c$, reported above, with the theoretical values[3a] shows that an ECE_{rev} kinetic regime is clearly prevailing in the reduction of both imines **1a** and **2a**. This means that the electron transfer [reaction (2)] is fast, so that were it not for the follow-up reactions, the first peak would be reversible, as is, in fact, the first cathodic peak of the methoxy derivatives **1b** and **2b**. The above values also indicate that the second electron transfer takes place at the electrode and that the overall process is kinetically controlled by the first proton transfer step (3), characterised by the low value of the equilibrium constant $K_p = k_p/k_{-p}$. In spite of that, the process is continuously displaced to the right since the radical $RHOH^\bullet$ is withdrawn from the equilibrium by its electrode reduction reaction (4) yielding the anion $RHOH^-$, which undergoes further proton transfer from the substrate to form the final amine.

Determination of the rate constant k_p of the rds reaction (3) is feasible, in principle, through eqn. (7) featuring the dependence

$$E_p = E^\circ - 0.61(RT/F) + (RT/2F)\ln(RTck_p^2/k_{-p}/k_{-p}Fv) \quad (7)$$

of the peak potential from the experimental parameters, for the ECE_{rev} regime,[3a] where k_p^2/k_{-p} can be written as K_pk_p. E° is the standard potential of the first electron transfer, *i.e.* of the redox couple $ROH/ROH^{\bullet-}$. Unfortunately neither K_p nor E° are known. However, the value of k_p could be evaluated, at least as an order of magnitude, utilizing the E° value of the methoxy derivatives, for which reversibility of the first peak is easily obtained. It is well known, in fact, that the substituent effect of the –OH group on the standard potential of benzene derivatives differs from that of the $-OCH_3$ moiety by about 30 mV.[4] As to the value of K_p, it should be noted that, for the ECE_{rev} kinetic regime featuring the reduction mechanism of the imines **1a** and **2a**, $K_p = k_p/k_{-p} \ll 1$. Since k_p is expected to be rather high, as witnessed by the irreversibility of the first peak even at the highest v values, it can be safely assumed that k_{-p} is near its diffusional value, which amounts to 5×10^9 dm^3 mol^{-1} s^{-1} in DMF.[5] Substituting such a value for k_{-p} and the E° values of the corresponding methoxy derivatives reported in Table 1, k_p values of 5.9×10^7 and 5.4×10^7 dm^3 mol^{-1} s^{-1} can be calculated for imines **1a** and **2a**, respectively. Although approximate, for the reasons indicated, these values are rather high, as expected on the ground of voltammetric characteristics of the above imines.

It should be noted at this point that an alternative reaction path, leading to the overall stoichiometry in reaction (1), is the one based on a double proton transfer from the substrate to the dianion arising from disproportionation of the primary anion radical[3a] reaction (8). The possibility for this mechanism to

$$2ROH^{\bullet-} \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} ROH^{2-} + ROH \quad (8)$$

prevail depends on the value of the equilibrium constant $K_d = k_d/k_{-d}$, which is related to the difference $\Delta E^\circ = E_1^\circ - E_2^\circ$ between the standard potentials of the redox $ROH/ROH^{\bullet-}$ and $ROH^{\bullet-}/ROH^{2-}$, through the expression $RT\ln K_d = -nF\Delta E^\circ$. Although the above E° values are not measurable for imines **1a** and **2a**, a minimum value for ΔE° is provided by the difference between the potentials of the first and second peak of the corresponding methoxy derivatives. Utilizing the values reported in Table 1 it is easy to verify that $K_d \leqslant 7 \times 10^{-9}$. Even assuming for k_{-d} its diffusional value, the maximum value for k_d would result *ca.* 35 dm^3 mol^{-1} s^{-1}, corresponding to a half-life time for $ROH^{\bullet-}$ of *ca.* 30 s. This is clearly in contrast with the high reactivity of $ROH^{\bullet-}$, which decays so fast that the first peak of both hydroxyimines shows no reversibility even at $v = 600$ V s^{-1}. It can therefore be concluded that the mechanism based on disproportionation of $ROH^{\bullet-}$ can be safely neglected.

Let us finally consider the results of macroscale electrolysis performed directly at the second peak potential. As long as it is still present in its undissociated form (as witnessed by the persistence of the first peak in the voltammogram of the electrolysis solution), the substrate will undergo reduction at this potential with the same mechanism operating at the first peak. However, the conjugate base arising from the self-protonation steps [reactions (3) and (6)] can now undergo reduction reaction (9), yielding a dianion radical which, besides

$$\mathrm{RO^- - e^- \rightleftharpoons RO^{\cdot 2-}} \tag{9}$$

being a base, is a strong reducing agent. The latter is therefore expected to promote the electron transfer reaction (10) to ROH.

$$\mathrm{RO^{\cdot 2-} + ROH \rightleftharpoons RO^- + ROH^{\cdot -}} \tag{10}$$

Self-protonation of the resulting anion radical will then start the reaction sequence (3)–(6) which, summed up to reactions (9) and (10), leads to the overall reaction stoichiometry shown in reaction (1). It is also easy to verify that if the dianion radical from reaction (8) acts initially as a base, undergoing proton transfer from the substrate, a reaction sequence leading to the same overall stoichiometry as in reaction (1) will take place.[3b] This means that, as long as the substrate is still present, electrolysis gives the same effects, independently of the reduction potential. This is the reason why voltammograms recorded at various stages of electrolysis performed at the second peak potentials show that the second peak starts decreasing only when the first has completely disappeared.

Once the substrate has been totally transformed, after the passage of 0.67 F $\mathrm{mol^{-1}}$, the dianion radical from the electron transfer in reaction (9) will react with any proton donor present in the medium. Among the candidates, the hydroxyamine $\mathrm{RH_2OH}$ will presumably be the preferred one. However, besides adventitious water or any other acidic impurity, the background electrolyte is liable to release protons, through Hoffman elimination.[6] The overall electrode process at the potentials of the second peak can be summarized in the following way.

$$\mathrm{3ROH + 2e^- \longrightarrow RH_2OH + 2RO^-} \tag{1}$$

$$\mathrm{2RO^- + 4e^- + RH_2OH + 3HA \longrightarrow 3RH_2O^- + 3A^-} \tag{11}$$

$$\mathrm{ROH + 2e^- + HA \longrightarrow RH_2O^- + A^-} \tag{12}$$

Reaction (1) takes place as long as the substrate is still present while reaction (11) represents reduction of the conjugate base assisted by the hydroxyamine $\mathrm{RH_2OH}$ or by any other proton donor HA. The overall stoichiometry, reaction (12), is in agreement with the experimental results, showing that an amount of charge only slightly exceeding 2 F $\mathrm{mol^{-1}}$ is necessary for the exhaustive reduction of the substrate at the second peak potentials.

On the grounds of all the experimental results and of the kinetic analysis reported so far, it can be concluded that the two voltammetric peaks displayed by compounds **1a** and **2a** are fundamentally due to the same type of process, involving the two-electron reduction of the undissociated hydroxyimine and of its conjugate base to the corresponding aminic derivative.

Experimental

Dimethylformamide (C. Erba, RPE) was vacuum-distilled and stored in a dark bottle under a nitrogen atmosphere. $\mathrm{Bu_4NClO_4}$ (Fluka) was recrystallized twice from ethanol–water and dried at 60 °C under vacuum. Schiff bases were prepared by combining equimolar amounts of the suitable amines and aldehydes, and then refluxing in alcohol on a water bath for 2 h. After cooling, the precipitated product was collected and recrystallized twice from ethanol.

Electrochemical measurements were performed with an EG&G-PAR apparatus composed of a 273 A potentiostat and 175 universal programmer, and equipped with 310 Nicolet digital oscilloscope and an Amel 862A X-Y recorder. Voltammetric studies were performed using an Hg sphere as working electrode and a platinum wire as auxiliary electrode. The reference electrode was Ag/AgCl in DMF, but all potentials are referred to the saturated calomel electrode (SCE). Bulk electrolyses were performed using a mercury pool cathode. Analysis of the electrolyses products was mainly carried out with an HPLC Perkin-Elmer Series 4 liquid chromatograph, equipped with a UV detector and a reverse phase ODS2 column. The eluent was a water–acetonitrile mixture.

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