

LARGE AMPLITUDE PULSED VOLTAMMETRY OF 4-CHLOROANILINE

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The electrochemical oxidation of 4-chloro and 4-bromoaniline were studied in un-buffered dimethylformamide (DMF) medium. By combined application of conventional and fast voltammetry (100 kV s⁻¹ range), the primary radical cation intermediates, formed by the one electron oxidation of each 4-haloaniline were characterized. The overall reaction path involves a dimerization via an N-C bond formation and de-halogenation at the para position. A detailed mechanistic study demonstrates that this proceeds through a fast reversible deprotonation of the primary radical cation followed by the subsequent N-C bond formation between the resulting radical and its parent radical cation which is the rate-determining step of the sequence (e-p-RRC kinetic sequence). The effect of a relatively strong, but weakly nucleophilic base, 2,6-lutidine, was also studied and confirmed the involvement of the fast deprotonation pre-equilibrium. The fast voltammetric experiments, were simulated and the apparent rate constants. For the overall deprotonation dimerization sequence obtained from peak potential shift analysis were confirmed (Amatore *et al* 1999).

The anodic oxidation of 4-chloroaniline (**I**) was studied by a potentiodynamic method on smooth platinum electrodes. The current potential curves showed only one oxidation maximum. The shapes of the curves did not change with the concentration of **I** or of the H⁺ nor with temperature. Only the value of the current density maxima varied. The peak potential moved to more positive values with the increase of the H⁺ concentration. In all cases the order of reaction was < 1, indicating a radical mechanism (Branzoi *et al* 1982).

The oxidation of 2,4,6-tribromoaniline (**I**) in MeCN (containing LiClO₄, H₂O and sometimes MgO to N-(2,4,6-tribromophenyl)-3,5-dibromo-*p*-benzoquinonediimine (**II**) and 2,2',4,4',6,6'-hexabromoazobenzene (**III**) in various proportions. Addition of MgO or lutidine increases the proportion of (**III**) formed. The nature of the initial stage of the anodic oxidation was discussed, and that of a redox system,

appearing at a potential less than that required for the oxidation of (**I**), was shown (Cauquis *et al* 1969).

The electrochemical oxidation of 2,4-dibromo-6-methylaniline and 4-bromo-2,6-dimethylaniline in aqueous sulfuric acid solutions at concentrations higher than 1.9 mol/dm³, at a platinum electrode, has been studied by rotating disk electrode, cyclic voltammetry (CV) and controlled-potential electrolysis. A single oxidation process (**1a**) was found for 2,4-dibromo-6-methylaniline up to 5.0 mol/dm³ acid once whereupon it displays second oxidation process (**2a**). The *p*-benzoquinone 2,3-dibromo-6-methyl-2,5-cyclohexadiene-1,4-dione was obtained as the final product of process (**1a**). For 4-bromo-2,6-dimethylaniline, however, two different oxidation processes were always found, depending on the acid medium. In solutions of acid concentration lower than 3.0 mol/dm³ the first process (**1b**) was followed by process, corresponding to the oxidation higher acid concentration both processes overlap, the composite process being observed as well as the second oxidation process. The final product of process is the dimer 4-(4'-bromo-2',6'-dimethylphenylimino)-2,6-dimethyl-2,5-cyclohexadiene-1-one. The CV results showed that this methylaniline and then the final para-benzoquinone obtained after exhaustive electrolysis proceeded from its hydrolytic degradation. The reaction mechanism and limiting steps were suggested. The role of protonation acid hydrolysis in the oxidation was described (Arias *et al* 1990).

The electrochemical oxidation of the 2,4-dibromoaniline in aqueous H₂SO₄ at concentrations > 1.0 mol/dm³, at a platinum electrode, was studied by using a rotating-disk electrode, cyclic voltammetry and controlled potential electrolysis. A single oxidation process was found at acid concentrations < 6.5 mol/dm³. At higher acid concentration, a second oxidation process was also observed ≤ 12.0 mol/dm³ acid concentration, whereupon, it overlapped with the first process. Both processes were controlled either by diffusion or by adsorption depending on the tested medium. The electroactive species of the first process was always monoprotonated form (Ar-NH₃)⁺. This specie oxidized in a 2-electron step to form the (Ar-NH₃)³⁺ cation. Deprotonation of this cation and subsequent hydrolysis of the generating species gave the corresponding *p*-benzoquinonimine, which further hydrolyzed to bromo-*p*-benzoquinone. Two additional redox pairs obtained in cyclic voltammograms were ascribed to the reduction equal of the two last compounds. After long electrolysis times, the bromo-*p*-benzoquinone was hydrated to the 3-bromo-1,2,4-benzenetriol and a new additional redox pair found in cyclic voltammograms following electrolysis experiments was attributed to the oxidation equal of this product. The loss of two protons from the benzene ring of the (Ar-NH₃)³⁺ cation

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produced the electroactive species of the second process, which was bielectronically oxidized. Under diffusion control, both processes were irreversible and the corresponding initial 2-electron transfer is the ratedetermining step (Arias and Brillas 1985).

The electrochemical oxidation of 4-chloro, 2, 4-dichloro and 2,4,6-trichloroanilines was investigated in acetonitrile solution. Based on the experimental results, it can be stated that the mechanism introduced (Bacon and Adams 1968) describing the voltammetric oxidation of 4-substituted aniline derivatives in acidic aqueous media in the main electrochemical oxidation route in acetonitrile as well. It was shown, that in the cases of 4-chloro and 2,4-dichloroanilines, the substituent in the para position was not only eliminated at the electrochemically initiated dimerization step, but it was oxidized to chlorine, which substitutes the free ortho position of the starting chloroaniline. As a consequence of that oxidized form of chlorinated 4-amino-diphenylamines was formed also besides chlorinated anilines. 2-Amino-4, 5-dichloro-diphenylamine had been found as a product of oxidation at the oxidation of 4-chloroaniline. This can be explained by dimerization of 4-chloroaniline at the ortho position by the one electron oxidized substrate. In the case of both monomer compounds, the role of 'head-to-head' 2, 4, 6-trichloroaniline, because the rejected chloride ion can be oxidized only to chlorine.

The oxidation products prepared by controlled potential electrolysis (CPC, were isolated and identified by different techniques (GC-ECD, GC-MS and ES-MS: gas chromatography,

mass spectrometry and electrospray mass spectrometry). Cyclic voltammograms of the chloroaniline type substrates and *n*-tetrabutylammonium chloride have been recorded before and after the CPC electrolysis, and were also used for product identification (Kadar *et al* 2001). Haloaminobenzenes continue to be the focus of the research (Freccero *et al* 2003). Recently, their electrochemistry was reviewed (Haque 2003).

In this paper large amplitude pulse voltammetric experiments suggest that the oxidation of 4-chloroaniline involves the

Table 1
Characteristics of large amplitude pulse voltammograms of 4-chloroaniline

No.	Rest potential V	Sweep rate mVs^{-1}	Drop time S	$E_{1/2}$ V	i_1 μA
1	-0.2	5	2	0.806	24.50
2	-0.2	5	2	0.809	24.50
3	-0.2	5	2	0.809	25.00
4	-0.2	2	5	0.814	25.50
5	0.1	2	5	0.814	25.00
6	0.0	2	5	0.816	25.75
7	-0.1	2	5	0.824	25.75
8	-0.2	2	5	0.822	27.50

Concentration of 4-chloroaniline: 0.2 mmol/dm^3 . Concentration of buffer: 0.2 mol/dm^3 , pH 6.34.

Carbon paste electrode. All potentials vs. Ag/AgCl,Cl^-

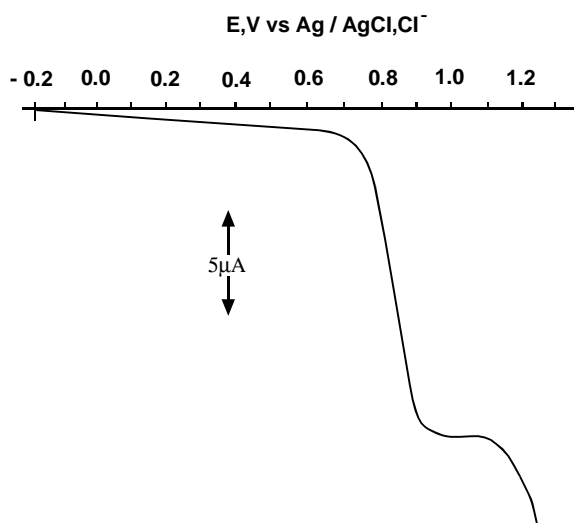


Fig 1. Large amplitude pulse voltammogram of $2 \times 10^{-4} \text{ mol/dm}^3$ 4-chloroaniline at carbon paste electrode in $2 \times 10^{-1} \text{ mol/dm}^3$ phosphate buffer pH 6.34, Sweep rate 5 mVs^{-1} . Drop time 2 s, Rest potential -0.2 V, (Table 1), No.1.

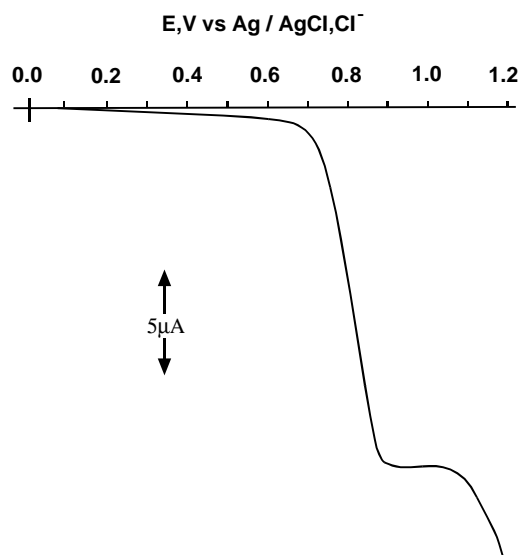


Fig 2. Large amplitude pulse voltammogram of $2 \times 10^{-4} \text{ mol/dm}^3$ 4-chloroaniline at carbon paste electrode in $2 \times 10^{-1} \text{ mol/dm}^3$ phosphate buffer pH 6.34, Sweep rate 2 mVs^{-1} , Drop time 5 s, Rest potential -0.1 V, (Table 1) No.4.

elimination of one electron as the initial oxidation reaction at the carbon paste anode.

Large amplitude pulse voltammetry of 4-chloroaniline.

(i) *Chemicals.* 4-Chloroaniline was obtained from a local supplier (E-Merck). Other chemicals were reagent grade or better and were used as received.

(ii) *Preparation of buffer.* Buffer solution for the pH 6.34 was adjusted to an ionic strength of 0.20 by addition of the required amount of sodium chloride. The buffer solution used for electrochemical experiments at the pH 6.34, phosphate buffer (0.2 mol/dm^3) (Rusling *et al* 1993). pH was noted by using a digital pH meter and combination glass electrode.

Solutions of 4-chloroaniline were prepared by dissolving the compound in buffer of pH 6.34, so that the final concentration of 4-chloroaniline was $2 \times 10^{-4} \text{ mol/dm}^3$. Purified nitrogen was bubbled through the solution for five to ten minutes to remove oxygen and nitrogen atmosphere was maintained above solutions during voltammetry.

(iii) *Carbon paste electrode.* The carbon paste electrode (CPE) was a disk of area 0.12 cm^2 surrounded by a Teflon collar of diameter 0.3 cm. The carbon paste was prepared from fisher ACS grade Graphite powder, Grade No. 38, and nujol as described in literature (Adams 1969). The surface of this electrode was renewed before each scan.

(a) *Counter electrode.* A platinum wire was used as a counter electrode.

(b) *Reference electrode.* Silver-silver chloride, chloride electrode.

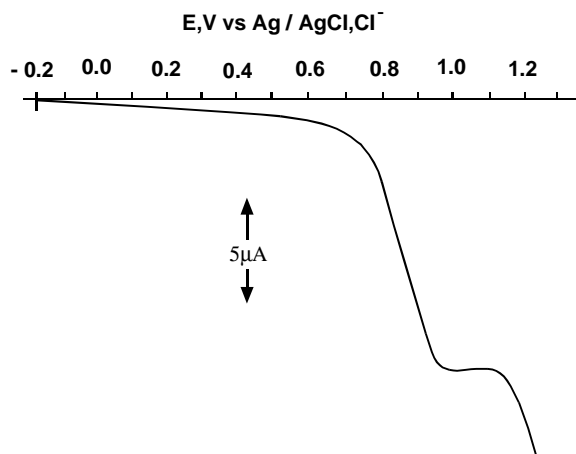


Fig 3. Large amplitude pulse voltammogram of $2 \times 10^{-4} \text{ mol/dm}^3$ 4-chloroaniline at carbon paste electrode in $2 \times 10^{-1} \text{ mol/dm}^3$ phosphate buffer pH 6.34, Sweep rate 2 m Vs^{-1} , Drop time 5 s, Rest potential 0.0 V, (Table 1) No.6.

A low resistance silver-silver chloride saturated KCl, reference electrode was used for experiments in the aqueous system (Sawyer *et al* 1995).

Voltammetry in three electrode cell was done using conventional electrochemical instrumentation (Haque 1986, 1988, 1990 and 1993).

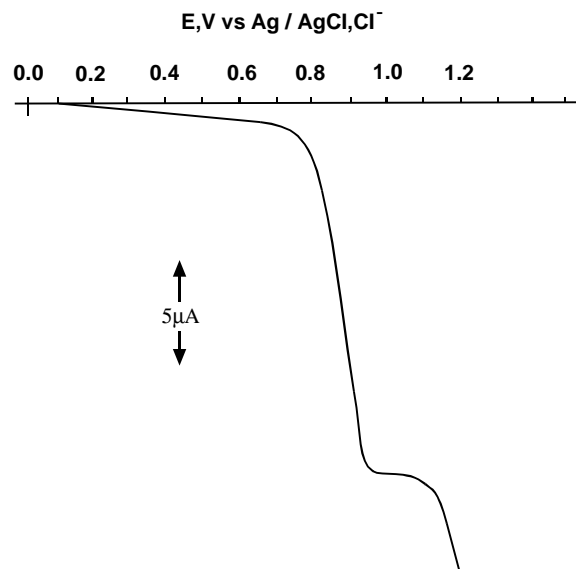


Fig 4. Large amplitude pulse voltammogram of $2 \times 10^{-4} \text{ mol/dm}^3$ 4-chloroaniline at carbon paste electrode in $2 \times 10^{-1} \text{ mol/dm}^3$ phosphate buffer pH 6.34, Sweep rate 2 m Vs^{-1} , Drop time 5 s, Rest potential 0.1 V, (Table 1) No.7.

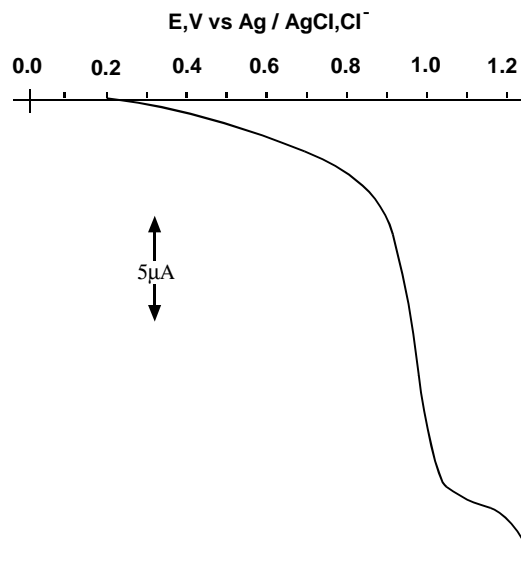


Fig 5. Large amplitude pulse voltammogram of $2 \times 10^{-4} \text{ mol/dm}^3$ 4-chloroaniline at carbon paste electrode in $2 \times 10^{-1} \text{ mol/dm}^3$ phosphate buffer pH 6.34, Sweep rate 2 m Vs^{-1} , Drop time 5 s, Rest potential 0.2 V, (Table 1) No.8.

The experiments indicate that the oxidation of 4-chloroaniline involves the elimination of one electron as the initial oxidation reaction at the carbon anode.

The experiments were performed by varying the values of rest potential, drop-time and sweep rate in large amplitude pulse voltammetry.

Under the conditions of Fig 1, half wave potential came out to be 0.806 V and i_1 (plateau current) was 24.50 μA . This experiment was repeated; the reproducibility was found to be good as given in Table 1, last column, runs 2 and 3.

The experiments were performed at carbon paste electrode; the concentration of buffer was 0.2 mol/dm³ (phosphate buffer) and the concentration of 4-chloroaniline was 0.2 mmol/dm³. Other experiments were performed by changing the rest potential or initial potential, Fig 2.

The sweep rate and drop-time in Fig 2 are 2mVs⁻¹ and 5s, at the rest potentials - 0.2V, run 4 and 0.1V, run 5, respectively. The half wave potential showed a small increase and the value of the limiting (plateau) current was nearly unchanged, (Table 1).

Fig 3 shows that when the value of rest potential is kept at 0.0 V, run 6, the value of half wave potential is 0.816 V and the value of the limiting current was slightly higher at 27.75 μA . Fig 4 and 5 show the effect of rest potential on half wave potential and limiting current, run 7 and 8 in Table 1.

Table 1 summarizes the values of half wave potentials and limiting currents. The reasonably constant value of limiting current in the last column of Table 1 shows that 4-chloroaniline can be used as a standard for one-electron oxidation reactions involving aromatic amines.

One electron oxidation of anilines initially results in the formation of aniline radical cations. The reaction can be represented as:



The cation thus formed undergoes rapid followup reactions. Mostly the oxidized form of the dimer is formed ultimately.

Our experiments show that the oxidation of 4-chloroaniline involves loss of one electron in the initial oxidation step at carbon paste electrode. This is in conformity with investigations by others, and also that the 4-halo substituted aromatic amines show principally the same reactions both in aqueous (Bacon and Adams 1968) and non-aqueous media (Kadar *et al* 2001).

Key words: Pulse voltammetry, Bond formation, Electro-dimerization.

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