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Cathodic reduction of 4-nitroso-*N*,*N*-dimethylaniline at various electrode materials

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Abstract

This study is concerned with the cathodic reduction of 4-nitroso-*N*,*N*-dimethylaniline to 4-amino-*N*,*N*-dimethylaniline in 1.0 M HCl and 1.0 M H_2SO_4 containing 10% MeOH. The effect of cathode material, supporting electrolyte, electroactive compound concentration, temperature and current density in the electrochemical synthesis of 4-amino-*N*,*N*-dimethylaniline were investigated. The best cathode material was tin, which gave a selectivity of 92.7% with a current yield of 90.3% at a current density of 6 mA cm^{-2}. The final electrolysis product was obtained as its respective HCl and H_2SO_4 salts and their structures were elucidated using spectrochemical techniques.

1. Introduction

4-amino-*N*,*N*-dimethylaniline (4-ADMA) and its derivatives are important in the dye and photography industries. The revolutionary colour developing process [1] in the photographic industry is based upon the oxidative coupling reaction of 4-ADMA and its derivatives, which results in the development of colours such as cyanine blue, magenda red and yellow. The basic reactions are as follows:

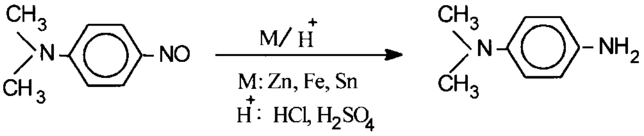
$$\text{Silver salt (AgX) exposed to light} + \text{Developer} \rightarrow \text{Oxidized developer} \quad (1)$$

$$\text{Oxidized developer} + \text{Coupler} \rightarrow \text{Dye} \quad (2)$$

4-ADMA and its derivatives are used in the determination of the activity of enzymes and sulfur in proteins [2, 3], the determination of peroxide [4], the amount of air and free and total chlorine content in water [5] and as corrosion inhibitors in the polymer industry [6].

The free base 4-ADMA is an unstable compound with a melting point of 38 °C and a boiling point of 262 °C [7]. It is easily oxidized with oxygen in air with normal light at ambient temperature. This is why it is prepared as sulfate, HCl or oxalate salts.

This compound was first synthesized by Erdmann in 1894, by the reduction of 4-nitroso-*N*,*N*-dimethylaniline (4-NDMA) at room temperature in HCl medium [8]. He proposed the following reaction scheme for this process:

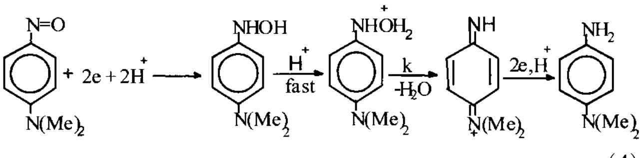


(3)

This strategy was also employed in other studies [9–15]. The corresponding amines of various nitroso compounds, as well as other alkyl-nitrosodimethylanilines, were obtained by reducing them with Pd–C catalyst in the presence of $NaBH_4$ [16, 17]. Manda and Shigeru obtained 4-ADMA.HCl with a yield of 83% by the reduction of 4-NDMA.HCl with metals such as Ca, Mg and Al [18].

The most comprehensive study, which constitutes the basis of synthetic methods for 4-ADMA and its other substituted derivatives, was carried out in the Kodak laboratories [19].

The mechanism concerning the synthesis of 4-ADMA by the reduction of 4-NDMA was first outlined by Holleck and Schindles [20]. Leedy and Adams stated that the reduction took place by an ECE mechanism and proposed the following scheme [21]:



(4)

Manda and Shimura investigated the parameters effecting the reduction mechanism under constant current conditions [22]. The best results were obtained by Cu and Ni cathodes using 10% H_2SO_4 supporting electrolyte and a current density of 0.005 A dm^{-2}.

In a patented study, carried out in Japan [23] on the reduction of 4-NDMA to 4-ADMA in 10% H_2SO_4 using Cu, Ni, steel, monel, Fe, Pb, Pt and C electrodes, the best results were obtained on Cu and steel electrodes.

2. Experimental details

The cathode materials used were Cu (99.9%, Johnson Mathey Co.) Pb (99.99%, Aldrich), Ti (99.7%, Aldrich), Sn (99.99%, Aldrich), Cu(Hg) and carbon cloth. The metal electrodes were in cylindrical form 13 × 10 cm^2 in size. Electrical contact was made with a Cu wire.

The carbon cloth electrode was prepared by covering a cylindrical glass support with carbon cloth. The electrical contact was obtained by fixing a Cu wire to the cloth and immersing it in mercury. The anode material used throughout the experiments was a Pb rod.

The supporting electrolyte was 1.0 M HCl and H_2SO_4 solutions containing 10% MeOH. All the solutions were prepared with doubly distilled water with conductivity of $1/12.4 \times 10^{-6}\ \Omega^{-1}$.

The amalgamated copper and Ti/TiO_2 were prepared according to the literature [24–26].

Since the nitroso compounds are not stable, the HCl salt of 4-nitroso-*N*,*N*-dimethylaniline (4-NDMA.HCl) was used in the study as an electroactive agent. This compound was synthesized and purified according to the literature procedure [7] m.p. 175–177 °C (lit. [7] mp 177 °C); ν_{max} (KBr)/cm^{-1} 3000–2250 (Broad, splitted ammonium band) 1540–1500, (—C=C— backbone stretching neighbouring to —N=O group), 1380–1340 (—N=O asymmetric vibration) 850–810 (—N=O bending); λ/nm 232 (0.461), 243 (0.407), 253 (0.341), 265 (0.252), 274 (0.271), 286 (0.202), 357 (0.318). This salt dissolved completely at conditions where the supporting electrolyte/MeOH ratio was 100/10. The solution became cloudy when the amount of MeOH was increased. The preparative electrolysis was carried out in a cell equipped with a cooling jacket.

All the electrolyses were carried out at constant temperature of 25 ± 0.05 °C and a current density of 3–19 mA cm^{-2}.

3. Results and discussion

3.1. *Effect of various electrolysis parameters*

The results indicated that (Table 1) the yield of 4-ADMA changes, according to the cathode material employed, in the following order: Sn > Cu(Hg) > Ti/TiO_2 > carboncloth > Pb > Cu. The prime factors effecting this order are hydrogen overvoltage, catalytic effect (for Ti/TiO_2 electrode), the catalytic reduction of Sn^{2+} ions formed in the solution in acidic media the case of Sn and the adverse effect of $PbSO_4$ formed in H_2SO_4 medium for the Pb electrode. The difficulty in evaluating the results obtained for the various electrode materials with respect to certain variables is obvious.

Table 1. Effect of cathode material in the electrolysis of 4-NDMA.HCl. Catholyte: 220 mL, temperature: 25 °C, concentration of 4-NDMA.HCl: 2.0 g (0.01071 mol), $Q = 4134$ C (4 F mol^{-1}), $i = 6$ mA cm^{-2}

Electrode material	Selectivity /%	Conversion /%	Derivative product yield /%	c.e /%
Cu	87.4	70	53.2	61.2
Sn	92.7	97	80.5	90.3
Pb	75.3	85	57.4	64.0
Carbon cloth	75.3	90	61.3	67.8
Ti/TiO_2	89.1	80	63.2	71.3
Cu(Hg)	89.7	95	73.6	85.3

The results obtained at current densities in the range 3–19 mA cm^{-2} are given in Table 2 and indicate that the best yield was obtained at a current density of 6 mA cm^{-2}.

The electrolyses carried out by changing amount of electroactive compound between 1.0 g (0.0053 mol) and 5.0 g (0.0267 mol) revealed that the best yield was obtained when the amount, was 2.0 g (0.0107 mol). At amounts higher than this, the product and the current yield decreased. This can be attributed to the increase in the amount of side products (resinous compounds) as a result of the reaction between the reduced compound on the electrode surface and the nitroso compound (Table 3).

The current and product yields decreased in electrolyses at elevated temperatures (Table 4). This is due to the instability of the nitroso compounds. The decrease in product yield at temperatures below room temperature, on the other hand, can be attributed to the decrease in solubility and diffusion rate of the electroactive compound.

The effect of acids such as HCl and H_2SO_4 on the product yield are shown in Table 5. It is seen that the use of H_2SO_4 gave much better results.

Table 2. Effect of current density in the electrolysis of 4-NDMA.HCl, cf. Table 1, cathode: Sn

Current density /mA cm^{-2}	c.e /%	Derivative product yield /%	Mass loss in electrode /g
3	70.0	61.7	0.24
6	90.3	80.5	0.49
9	79.0	70.8	0.53
12	61.2	56.3	0.44
15	59.6	50.5	0.45
19	57.8	48.4	0.29

Table 3. Effect of concentration of electroactive compound in the electrolysis of 4-NDMA.HCl, cf. Table 1, cathode: Sn

Amount of electroactive compound/g	Q /C (4 F mol^{-1})	c.e /%	Derivative product yield/%	Mass loss in electrode /g
1.0 (0.0053 mol)	2067	67.7	59.7	0.16
2.0 (0.0107 mol)	4134	90.3	80.5	0.49
3.0 (0.0160 mol)	6203	72.0	61.8	0.54
4.0 (0.0214 mol)	8271	68.5	60.3	0.48
5.0 (0.0267 mol)	10339	65.0	57.3	0.10

In studies carried out with a Sn electrode it was observed that the mass loss increased between 6 and 9 mA cm^{-2} and remained constant thereafter (Table 2). The fact that the mass loss is small at low current densities can be explained by the lower dissolution of the metal at these values. The dissolution of the metal increases with increasing current density. However, the resinous compounds formed at the surface causes the formation of a protective film, which prevents excessive dissolution of the electrode. It can be concluded that there is an optimum equilibrium condition at current densities outside these values. The mass loss was observed to be higher in HCl than in H_2SO_4. This is due to the higher dissolution of this metal in this acid (Table 5).

3.2. *Product isolation and the analytical aspects*

The products could not be isolated by classical separation methods due to the fact that the electrolyses were carried out in aqueous media, and sulfate and HCl salts of the product were highly soluble in water. The amount of product formed was determined by uv spectroscopy. Also the solid derivative of the product was prepared after each electrolysis and compared with the uv data.

The sulfate salt of 4-ADMA in 10% MeOH containing 1.0 M H_2SO_4 solution was prepared as follows: (i) the solution was neutralized with NH_3 (pH 7.0–8.0) to separate the free base; (ii) Since the solubility of free base in water is close to that in organic solvents it was continuously extracted with $CHCl_3$; (iii) The solution obtained after the continuous extraction procedure was dried over K_2CO_3 and $CHCl_3$ was evaporated to give the free base (m.p. 36–38 °C lit., [7] m.p. 38 °C); ν_{max} (KBr)/cm^{-1} 3330–3220 (Ar–NH_2, primer amine peaks, two peaks), 2980, 2950, 2850, 2810, 2775, 1610, 1510, 1425, 1335, 1270, 1205, 1150, 1050, 945, 835, 820, 685, 620, 450; λ/nm 226 (0.430), 238 (0.309), 253 (0.146), 283 (0.233), 359 (0.183); M.S (ES+ 1.51 e6) M/z 137.2 $(M+1)^+$ 75.96% 12.2 (12.66) and 65.3 (17.72); (iv) the free base was dissolved in absolute methanol and precipitated as a sulfate salt with oleum, filtered out and dried over K_2CO_3 in a dessicator. It was then recrystallised from absolute methanol (m.p. 230–235 °C (decomp.) lit., [19] m.p. >235 °C); found C, 52.25, H, 6.92, N, 14.83, S, 8.27, O, 18.56, $C_{16}H_{26}N_4O_4S$ requires C, 51.87, H, 7.00, N, 15.13, S, 8.64, O, 17.29; ν_{max} (KBr)/cm^{-1} 3300–2680 (broad, single band, primer amine salt) 2582, 2560, 1610, 1510, 1500, 1450, 1350, 1230, 1210, 1150, 1135, 1050, 900, 800, 550, 400; λ/nm 238 (0.376), 265 (0.438), 302 (0.837), 414 (0.156), 548 (0.059); M.S (ES+ 1,51 e6) M/z $(M+1)^+$ 137.2 75.95% 122.2 (12.66) and 65.3 (17.72)].

Table 4. Effect of temperature upon the product yield in the electrolysis of 4-NDMA.HCl, cf. Table 1, cathode: Sn

Temperature /°C	c.e /%	Derivative product yield /%	Mass loss in electrode /g
10	65.3	59.2	0.11
25	90.3	80.5	0.49
40	64.2	53.8	0.65
60	52.6	46.2	0.88

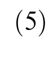
Table 5. Effect of acid in the electrolysis of 4-NDMA.HCl, cf. Table 1, cathode: Sn

Acid	Product yield /%	Derivative product yield /%	Mass loss in electrode /g
1.0 M H_2SO_4	90.3	80.5	0.49
1.0 M HCl	64.3	59.5	1.32

The HCl salt of 4-ADMA was prepared using the same procedure followed in the preparation of the sulfate salt (i)–(iii). Then half the organic phase was evaporated and the HCl salt was precipitated by passing HCl vapor through a Kipps apparatus [7]. The gray–white salt obtained was recrystallized from absolute methanol [(m.p. 215–220 °C (decomp.) lit., [17] 198–200 °C (for mono salt)]; found C, 46.57, H, 6.53, N, 13.30 $C_8H_{14}Cl_2N_2$ requires C, 45.90, H, 6.69, N, 13.39; ν_{max} (KBr)/cm^{-1} 3254–2740 (broad, single band, amine salt) 260–2565, 2450, 2000 (NH_4^+ overtone) 1550, 1510, 1465, 1425, 1310, 1285, 1185, 1150, 1120, 980, 950, 860, 780, 680, 480; M.S (ES+ 8.19 e4) M/z $(M+1)^+$ 136.9 30.3% 121.8 base peak, 100) 107.2 (20.25) 106.4 (15.19); λ/nm 222 (0.460), 234 (0.285), 266 (0.228), 296 (0.354), 516 (0.014), 552 (0.015).

λ/nm (The electrolysis solution with HCl supporting electrolyte) 226 (0.489), 241 (0.403), 265 (0.294), 297 (0.545), 435 (0.092), 550 (0.032); λ/nm (The electrolysis solution with H_2SO_4 electrolyte) 231 (0.421), 251 (0.193), 263 (0.160), 278 (0.265), 306 (0.384), 373 (0.007), 515 (0.009), 548 (0.010), 593 (0.004).

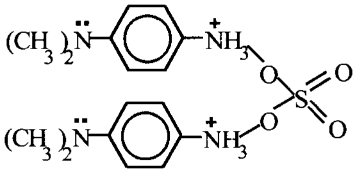
The benzoate derivative of the product of each electrolysis was prepared according to literature [16], yields were determined and compared with the u.v. data of the electrolysis product (Tables 1–4). The corresponding reaction is as follows:



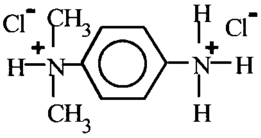
(5)

The raw product obtain was recrystalised from ethanol (m.p. 228–230 °C lit., [16] m.p. 226 °C); ν_{max} (KBr)/cm^{-1} 3330–3060 (—NH— stretching), 2810–2790 (—N(CH$_3$)$_2$—) 1660 (—NHC=O).

There was a band at 3335–3325 cm^{-1} in the i.r spectra of free base characteristic of primer amines, which was observed to disappear in the spectra of sulfate salt and replaced with a very broad and intensive band located in the 3000–2400 cm^{-1} region. This shift in frequency is due to the formation of hydrogen bonds and the broadening caused by hydrogen bonding decreases the splitting of the band [27]. The structure of the sulfate salt is proposed as follows, taking the steric effect of the tertiary amine group (—N(CH$_3$)$_2$—) and the size of the sulfate ion into account:



Similarly the fact that the disappearance of the bands at 3335–3325 cm^{-1}, the absence of bands at 2760–2860 cm^{-1} due to C—N stretching in the ir spectra of the related salts together with u.v., ms and elemental analysis data of HCl salt lead us to conclude the following structure:



The LC–MS spectra of the electrolysis solution with H$_2$SO$_4$, supporting electrolyte the sulfate salt prepared from the product obtained from it and the free base were compared with each other. In all these three spectra the molecular ion peak was observed to be replaced by a $(M+1)^+$ peak. This shows that the molecular ion peak ($M^{+\bullet}$) in neutral molecules containing heteroatoms such as N, O and S are replaced by the peak $(M+1)^+$ formed by proton transfer [27]. The electrolysis data obtained in HCl and H$_2$SO$_4$ media revealed that 4-ADMA is in the form of 4-ADMA.2HCl and 4-ADMA.1/2 H$_2$SO$_4$, respectively.

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