

SHORT COMMUNICATION

Indirect reduction of *o*- and *m*-nitrobenzoic acids at a Ti/ceramic TiO₂ cathode

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1. Introduction

The Ti/ ceramic TiO₂ cathode was used successfully for the catalytic reduction (indirect) of several compounds such as 5-nitrosalicylic acid [1], isomeric nitroanilines [2,3], isomeric chloronitrobenzenes [4], 1-nitroso 2-naphthol [5] and maleic acid [6] to the corresponding amines, diamines or to succinic acid, in earlier studies. The Ti⁴⁺/Ti³⁺ redox species at the electrode was responsible for the catalytic reduction. In continuation of the above work, the results of galvanostatic electrolysis data on the reduction of *o*- and *m*-nitrobenzoic acids (*o*-NBA and *m*-NBA) to the corresponding aminobenzoic acids (*o*-ABA and *m*-ABA) are reported. Also reported, are cyclic voltammetric studies.

o-Aminobenzoic acid (anthranilic acid) is usually made from phthalic anhydride via sodium phthalate. Oxidative decarboxylation, carried out using sodium hypochlorite solution at 60–100 °C followed by acidification, yields 88% of *o*-ABA. Other synthetic routes include the amination of *o*-chlorobenzoic acid and the reduction of *o*-NBA. *m*-ABA is prepared by the reduction of *m*-NBA [7].

Electrolytic reduction of *o*- and *m*-NBA in a divided cell (porous diaphragm) with Pb anode and Sn, Pb, Cu, graphite or amalgamated cathode (catholyte:HCl 0.58–4.46 N; Anolyte 15% H₂SO₄) in the current density range 2–14 A dm⁻² at 30–50 °C (for *o*-NBA) and 40–60 °C (for *m*-NBA) yields *o*- and *m*-ABA in 92–98% depending on the conditions [8]. Reduction of *o*- and *m*-NBA in 30% H₂SO₄ at Cu cathode and Pb anode yields a mixture of *o*-ABA (*m*-ABA) and 5-hydroxyanthranilic acid (5-aminosalicylic acid) [9].

Electrolytic reduction of *o*-NBA at a controlled potential of –0.9 V against SCE at a silver cathode in HCl–KCl at pH 1 in 30% EtOH at 20 °C yields *o*-ABA and that of *m*-NBA at a potential of –0.75 V against SCE in 1N H₂SO₄ in 15% EtOH below 15 °C yields *m*-ABA. However, at higher temperature and higher acid strength (50% H₂SO₄; 100 °C for *o*-NBA and 2N H₂SO₄; 95 °C for *m*-NBA) at potentials of –0.1 V and –0.3 V, 2,5-NH₂OHC₆H₃COOH and 3,6-NH₂OHC₆H₃COOH are formed respectively [10].

o-ABA (vitamin L₁) enhances milk production in cows. It serves as an intermediate for making dyes, tranquilizers and antiphlogistics, and as odorant for toiletries [11] and as an ascaricide in swine [7]. *m*-ABA is used as a dye intermediate [11].

2. Experimental details

Details of the electrode preparation method and the cells employed for galvanostatic and cyclic voltammetric studies are as reported earlier [1–4,12]. The electrolysis of the nitrobenzoic acids was carried out as reported for the other nitro compounds [1–4]. The quantity of electricity consumed was 6 faraday mol⁻¹ of the corresponding NBA. At the completion of electrolysis, the products, namely the corresponding amine sulphates that separated, were isolated and converted to the corresponding amines and were characterized by their melting points and i.r. spectra. The amine in solution, at the end of electrolysis, was estimated by diazotization [13]. An experiment was also carried out with 40 g of *m*-NBA in 5.64 M H₂SO₄ solution at 80 °C by passing a charge corresponding to 4 faraday mol⁻¹ of *m*-NBA.

3. Results and discussion**3.1. Galvanostatic studies**

The results of galvanostatic reduction of *o*-NBA and *m*-NBA at the Ti/ceramic TiO₂ cathode in 50% ethanolic solution containing 1.88 M H₂SO₄ at different cathode current densities (and also in 5.64 M H₂SO₄ solution at 80 °C in the case of *m*-NBA) are summarized in Table 1. It can be seen that the yield of *o*-ABA as well as that of *m*-ABA is maximum at a current density of 5 A dm⁻². At lower current density, the potential for the reduction of the nitro compound is not reached and, at higher current density, there is competitive hydrogen evolution, thereby reducing the yield of the aminobenzoic acids. The current efficiency lies in the range 87 to 95.3% and is low at high current density due to competing hydrogen evolution. Hence, an optimum current density of 5 A dm⁻² is ideal for obtaining maximum yield of both *o*-ABA and *m*-ABA, as observed also for the reduction of most other compounds at this cathode [2–6].

For the reduction of *m*-NBA in 5.64 M H₂SO₄ solution at 80 °C, it was found that on passing 4 faraday mol⁻¹, only *m*-ABA was formed and not the rearranged product, namely, 5-aminosalicylic acid (5-ASA). (A higher acid strength and temperature as above, would result in 5-ASA as the product if the corresponding hydroxylamine is formed as an intermediate during the reduction of the *m*-NBA,

Table 1. Galvanostatic reduction of *o*- and *m*-nitrobenzoic acids at a Ti/ceramic TiO₂ cathode in 50% ethanolic solution containing H₂SO₄

Educt	Wt /g	T /°C	H ₂ SO ₄ /M	c.d. /A dm ⁻²	i /A	c.v. /V	Wt. of amine A/g	B/g	Yield /%	CE /%
<i>o</i> -NBA	50	35	1.88	3	5.0	3.5	13.0	18.5	76.8	91.0
<i>o</i> -NBA	50	35	1.88	5	8.4	5.0	18.0	18.3	88.5	91.5
<i>m</i> -NBA	50	35	1.88	3	5.0	3.5	22.6	14.8	91.2	92.6
<i>m</i> -NBA	50	35	1.88	5	8.4	5.0	15.2	23.7	94.9	95.3
<i>m</i> -NBA	50	35	1.88	7	11.8	8.0	22.6	10.0	79.5	81.0
<i>m</i> -NBA	40	80	5.64	5	8.8	2.5	24.0	6.1	91.8	92.7

c.d. = current density; *i* = cell current; c.v. = cell voltage; CE = current efficiency

A = amine neutralized from the amine sulfate that separated at the end of electrolysis

B = amine in solution at the end of electrolysis

analogous to *p*-aminophenol being observed as the exclusive product in the reduction of nitrobenzene at higher acid strength and temperature [14].) However, the absence of such a rearranged product suggests that the electrode catalyses further reduction of the hydroxylamine formed during the reduction of *m*-NBA. In the above solution, when extra current was passed (6 faraday mol⁻¹ of *m*-NBA), the yield of *m*-ABA was increased to 91.8% (Table 1). A reduction in the yield and current efficiency for amine formation at 80 °C at an acid strength of 5.64 M as compared to that at 35 °C, at an acid strength of 1.88 M, is due to the side reaction involving resin formation under the conditions employed for the former.

The *o*- and *m*-aminobenzoic acids isolated as above, melted at 145 °C and 178 °C, respectively, in accordance with literature data [11]. The i.r. spectra of these compounds matched with those of the corresponding aminobenzoic acids [15] with the -NH₂ stretch observed at 2941 cm⁻¹ and the C=O stretch at 1639 cm⁻¹.

3.2. Cyclic voltammetric studies

The behaviour of the Ti/ceramic TiO₂ strip cathode in 50% ethanolic solution containing 1 M H₂SO₄ at a sweep rate of 0.2 V s⁻¹ is shown in Fig. 1. The cathodic peak appears at -0.57 V and the anodic peak at -0.52 V. These peaks are attributed to the following

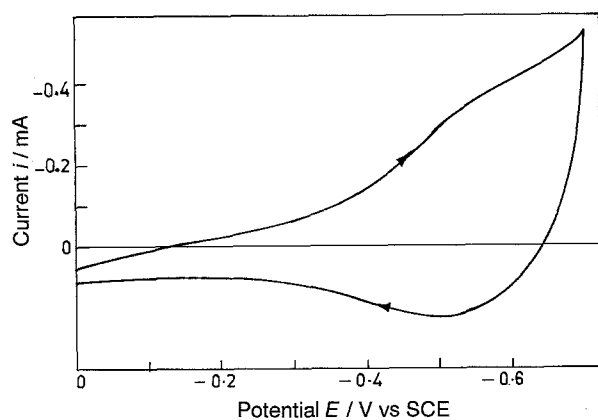
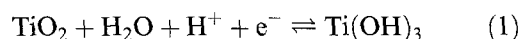
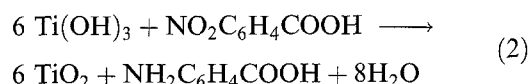


Fig. 1. The behaviour of Ti/ceramic TiO₂ strip cathode in 50% ethanolic solution containing 1 M H₂SO₄. Sweep rate: 0.2 V s⁻¹

redox reaction, as also discussed in earlier communications [1-5]:



The cyclic voltammograms for the reduction of *o*- and *m*-nitrobenzoic acids ($C = 1 \times 10^{-2}$ M) at this cathode in 50% ethanolic solution containing 1 M H₂SO₄, at a sweep rate of 0.2 V s⁻¹ are shown in Fig. 2(a) and (b), respectively. It can be seen that with the addition of the corresponding nitro compounds (comparing Fig. 2(a) and (b)), the cathodic peak height is increased with simultaneous disappearance of the anodic peak, indicating heterogeneous redox catalysis, i.e. the electrogenerated Ti³⁺ brings about the reduction of the nitro compound chemically and, during this process, the Ti⁴⁺ species is regenerated as shown below:



The above general reaction holds good for heterogeneous catalytic reduction of all the nitro compounds studied earlier [1-6], by the Ti⁴⁺/Ti³⁺ redox species. A fast reaction between the Ti³⁺ and the nitro compound is indicated by the fact that even in the time scale of low sweep rates such as 0.005 V s⁻¹, the increase in cathodic peak height with the disappearance of the anodic peak is seen.

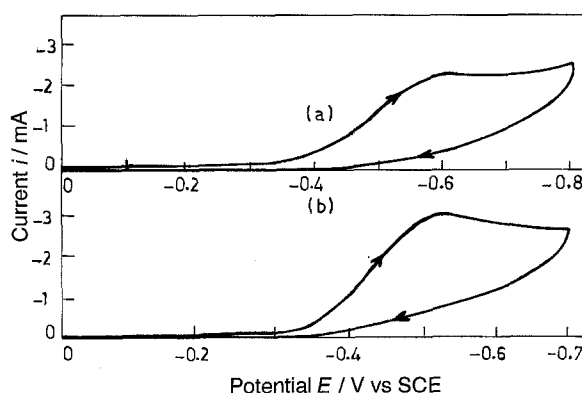


Fig. 2. Reduction of *o*- and *m*-nitrobenzoic acids (1×10^{-2} M) at the Ti/ceramic TiO₂ cathode in 50% ethanolic solution containing 1 M H₂SO₄. Sweep rate: 0.2 V s⁻¹.

The reduction potentials for the nitro compounds at the Ti/ceramic TiO₂ cathode vary in the range -0.45 to -0.55 V, depending on the sweep rate and position of the nitro group. *o*-NBA is reduced less easily compared to *m*-NBA possibly due to the steric effect of the *o*-carboxyl group.

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