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SHORT COMMUNICATION

An efficient electrosynthesis of 2,4- and 2,6-diaminotoluenes

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1. Introduction

There is ongoing interest in the development of selective, mild and effective methods for the synthesis of aromatic amines due to their industrial importance. One convenient method is catalytic hydrogenation of the corresponding nitro compounds [1, 2]. In gas–solid heterogeneous catalysis, the hydrogenation reaction is often carried out at elevated temperatures in order to enhance the reactivity of a given catalyst. Under these conditions the selectivity is generally reduced.

The electroreduction of dinitrotoluene has been carried out in protic media under acidic, neutral and basic conditions [3] using an Ag electrode. The process was also carried out by indirect electrolysis in strongly acidic medium on a Pb cathode using the Ti^{3+}/Ti^{4+} redox couple as mediating system [4].

In this paper we report an efficient synthesis of 2,4- and 2,6-diaminotoluenes (DAT) in a basic aqueous methanolic solution using electrodes consisting of particles of Devarda copper [5, 6] or Raney nickel [5, 7, 8] embedded in a nickel matrix. With these electrodes, the reduction involves an electrocatalytic hydrogenation (ECH) process in which water functions as a convenient source of chemisorbed hydrogen [9].

The electrolysis is carried out at ambient temperature and poisoning of the catalyst by the diamine is minimized, and even suppressed, due to the fact that a negative potential is applied to the catalyst. Furthermore, the structure of the electrode ensures that the loss of catalytic activity of the Raney metal, due to the agglomeration of the particles [10, 11], is slowed down considerably [9].

2. Experimental details

The preparative electrolyses were carried out with a Princeton Applied Research (PAR) 173 potentiostat having both an Electrosynthesis Company (ESC) 640 digital coulometer and an ammeter connected in series within the auxiliary circuit. A two-compartment H-type cell having a Nafion 324 membrane as separator was used. The counterelectrode was a $5\,cm^2$ platinum plate. A saturated calomel electrode (SCE) was used as reference and was connected to the catholyte through a fritted glass disc positioned near the surface of the working electrode facing the counterelectrode. The Devarda copper [5, 6] and Raney nickel [5, 7, 8] working electrodes were prepared by co-deposition of Ni and of Cu particles of alloy dispersed in a nickel plating bath, on a stainless steel screen ($3 \times 4\,cm^2$). The content of alloy varied from 30 to 40% for the Devarda alloy and from 58 to 62% for the Raney nickel alloy.

The electrode was activated by leaching the deposited alloy in a 20% (Devarda copper) or a 30% (Raney nickel) aqueous solution of NaOH at 70° C for 7–8 h. The activated electrode was placed in the cell containing deaerated (N_2) 0.14 M sodium hydroxide solution in methanol : water 93 : 7 (by weight).

The potential was maintained at -1.4 V for 15 min (hydrogen evolution) then it was increased (~ -1.0 V) to the zero current point. The substrate was added in one portion. A rapid increase of current occurred. The electrolysis was followed by thin layer chromatography (TLC) on silica gel $60F_{254}$ (Merck) plates 0.25 mm thick, using chloroform : carbon tetrachloride : methanol (8 : 5 : 1) as eluent. The TLC spots were detected under a UV lamp.

The electrolysis was stopped when no more starting material was present in the electrolyte. The yields were determined by gas–liquid chromatography (GLC) using a DB-5 (dimethyldiphenylpolyxyloxane) fused silica capillary column (length: 30 m) at 130° C.

3. Results and discussion

The results of controlled potential electrolysis of 2,4- and 2,6-dinitrotoluenes (DNT) in basic medium at a Raney nickel or a Devarda copper cathode are reported in Table 1.

The potentials were fixed in the absence of the substrate, by increasing the potential to the zero current point from a cathodic value where hydrogen evolution was observed visually (see Section 2). Thus, they correspond more or less to the potential of formation of chemisorbed hydrogen on the electrode surface (see Equation 1) and this potential is roughly the same on a Devarda copper electrode and a Raney nickel electrode. Upon the addition of the substrate, the current increased suddenly, stabilized to a value corresponding to the current given in Table 1, and then decreased regularly as the substrate was reduced. The amount of electricity was equivalent to a 12-electron reduction of 2,4- or 2,6-dinitrotoluene to the corresponding diamine. The product yield and current efficiency are excellent with both the Raney nickel and the Devarda copper electrode.

A possible mechanism for these electrochemical reductions has been discussed in the case of nitrobenzene [9]. At the working potential of Table 1, the electroreduction of DNT should occur readily according to its half-wave potential $(E_{1/2})_1 = -0.68$ V against Hg pool on Hg electrode [12]. So the reduction

Table 1. Electrosynthesis of diaminotoluenes in basic medium at Raney Ni and Devarda copper cathodes. The concentration of starting material was 0.01 M

Medium	*Starting material*	*Cathode material*	*Zero current potential (V, against SCE)*	*Initial current (mA)*	*Chemical yield (%)*	*Current efficiency (%)*	*Cell voltage (V)*
0.14 M NaOH MeOH : H_2O 93 : 7	2,4-Dinitrotoluene	Devarda copper	−1.048	259	87–92	100	10–20
		Raney Ni	−0.992	157	87–92	100	10–20
	2,6-Dinitrotoluene	Devarda copper	−1.048	161	90–95	100	10–20
		Raney Ni	−1.00	90	90–95	100	10–20

of the first nitro group to the hydroxylamine may occur by a classical electronation–protonation (EP) mechanism. The second nitro group may also be reduced to the hydroxylamine by an EP mechanism $(E_{1/2})_{\mathrm{II}} = -0.88\,\mathrm{V}$ [12]. However, the conversion of the hydroxylamino groups to the amino groups must occur through an ECH mechanism [9]. But it is possible that, on these catalytic electrodes, the reduction of the nitro groups to the hydroxylamino groups also involves an ECH mechanism.

Thus the overall conversion of DNT to DAT may occur by an ECH mechanism summarized by Equations 1 to 4 where M is the surface of the electrode, M(H) represents chemisorbed hydrogen generated at the surface of the electrode by reduction of water (Equation 1), and M(DNT) and M(DAT) are the adsorbed starting material and product, respectively.

$$\mathrm{M} + \mathrm{H_2O} + e^- \longrightarrow \mathrm{M(H)_{ads}} + \mathrm{OH^-} \quad (1)$$

$$\mathrm{M} + \mathrm{DNT} \longrightarrow \mathrm{M(DNT)_{ads}} \quad (2)$$

$$\mathrm{M(DNT)} + 12\mathrm{M(H)} \longrightarrow \mathrm{M(DAT)} + 4\mathrm{H_2O} \quad (3)$$

$$\mathrm{M(DAT)} \longrightarrow \mathrm{M} + \mathrm{DAT} \quad (4)$$

4. Conclusion

We have shown that the electrochemical hydrogenation of 2,4- and 2,6-dinitrotoluenes to 2,4- and 2,6-diaminotoluenes in a basic medium is a very efficient process using Raney Ni or Devarda copper cathodes. The current efficiency is 100%, and thus higher than that obtained by indirect electrochemical reduction [4], and the chemical yield is also excellent (90–95%). The reduction involves an electrocatalytic hydrogenation process (Equations 1 to 4) at least for the hydrogenation of the hydroxylamino groups. The idea of using ECH for the reduction of dinitro compounds is interesting. This method could easily be extended to several other nitro compounds and may, therefore, be of considerable commercial interest.

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