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THE ELECTROCHEMICAL REDUCTION OF *o*-NITROTOLUENE TO *o*-TOLIDINE—I. COULOMETRY AT CONTROLLED POTENTIAL; PRODUCTION ASPECTS

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Abstract—*o*-Tolidine formed by reduction of *o*-nitrotoluene is used for production of azo-dyestuffs being important pigments for textiles. At the moment, nitrotoluene is reduced to *o*-hydrazotoluene by zinc dust after which hydrazotoluene is rearranged into tolidine.

Environmental reasons forced us to seek an alternative in the electrochemical route for tolidine production. On the basis of voltammograms, controlled-potential electrolyses were carried out for nitrotoluene in alkaline ethanol-water solutions and in alkaline aqueous solutions containing McKee salt and for azoxytoluene in alkaline and acidic ethanol-water solutions as well as in acidic aqueous solutions containing McKee salt in acid.

It has been found that production of tolidine has to take place in at least two steps, namely in alkaline solutions for the reduction of nitrotoluene to azoxytoluene and in acidic solution for the reduction of azoxytoluene to hydrazotoluene which is then directly rearranged into tolidine.

To obtain a high chemical yield and current efficiency for azoxytoluene formation in ethanol-water media the reduction has to be carried out at high nitrotoluene concentrations. For Pt, Ag, Au, Cr, Fe and graphite cathodes a chemical yield of almost 100 per cent was reached at nitrotoluene concentrations higher than about 0.20 M. At concentrations lower than 0.025 M many by-products were formed.

The production of tolidine from azoxytoluene can be carried out either in one step in acidic media or in two steps in which case the first occurs in alkaline solution and the second in acidic solution. In the latter case the chemical yield for hydrazotoluene from azoxytoluene is also 100 per cent and a high current efficiency is also attainable. The chemical yield of the rearrangement of hydrazotoluene strongly depends on the nature and pH of the solution and temperature; a chemical yield of about 80 per cent is, however, obtainable in practice.

The chemical yield for tolidine formation from azoxytoluene in acidic media containing McKee acid and salt is about 87% with a current efficiency of about 40 per cent. This production route is preferred.

1. INTRODUCTION

The electrochemical reduction of *o*-nitrotoluene (nitrotoluene) to *o*-tolidine (tolidine) has been investigated owing to the use of tolidine as an intermediate for production of azo-dyestuffs being important pigments of textiles[1].

An electrochemical production method may be attractive for both economical and environmental reasons. Tolidine is formed from 2, 2' dimethylhydrazobenzene (*o*-hydrazotoluene or hydrazotoluene) by the benzidine rearrangement which occurs only in acidic media[2]. The reduction of nitrotoluene to 2, 2' dimethylazoxybenzene (*o*-azoxytoluene or azoxytoluene) however, must take place in alkaline media[3]; further reduction to hydrazotoluene can be performed both in alkaline and acidic media. Consequently, at least two separate operations are needed for production of tolidine from nitrotoluene. Hitherto, in the industrial production of tolidine nitrotoluene is reduced to hydrazotoluene by zinc dust in two separate batch operations and following that, again in a batch operation, hydrazotoluene is rearranged into tolidine.

Most experimental results, however, have been obtained[3, 4] on the reduction of nitrobenzene. Reaction schemes for the reduction of nitrobenzene are proposed[3, 5] and it is to be expected that

nitrotoluene behaves like nitrobenzene. The first stable reduction product of the nitro compound is the azoxy compound. Further reduction of the azoxy compound depends on experimental conditions[3]. The first step is carried out in an alkaline emulsion, an alkaline aqueous alcohol solution or in alkaline solution of Na- or K-salts of organic acids, such as toluenesulphonic acid. Hence, nitrobenzene can be reduced to azoxybenzene with a chemical yield of 95% and to hydrazobenzene with a yield of 90 per cent[6].

The presence of the methyl group in the benzene ring of nitrotoluene retards the formation of azoxytoluene and enhances the formation of *o*-tolidine (tolidine)[7].

For the reduction of nitrotoluene in a solution of Na-K-xylene sulphonate, the hydrazotoluene yield decreases strongly with increasing current density and increases with increasing free alkali concentration; the toluidine yield, however, rises from 5 to 23 per cent at a cathodic current density increase from 10 to 30 mA/cm²[8]. A hydrazotoluene yield of about 90 per cent and a current efficiency of also about 90 per cent are attainable[8]. Batch electrolyses[8] were carried out under constant current conditions in which the current was decreased stepwise. The electrochemical formation of hydrazotoluene starts as soon as the concentration of nitrotoluene has reached a low value, depending on cathode potential and cathode

material. Research has shown[3, 5, 8] that the hydrazo compound can not be produced electrochemically in one continuous electrolytic process. A continuous process for the production of toluidine would stand a good chance of competing economically with the chemical production processes[4]. In order to prove this possibility the reduction of nitrotoluene to azoxytoluene in alkaline solution and of azoxytoluene in both alkaline and acidic media was investigated. Only in the latter case the rearrangement of hydrazotoluene occurs in the electrolytic cell. This means that a separate rearrangement operation can be omitted.

2. EXPERIMENTAL

2.1. Controlled-potential electrolysis

A cross-section of the electrolytic cell used for the reduction of azoxytoluene is shown in Fig. 1. The thermostated cell was divided by a cation-exchange membrane (Naphion 425) into a cathodic and an anodic compartment.

Under the circumstances indicated below, solid reduction products were separated during electrolysis from the catholyte in large amounts. To prevent crystals adhering to the cathode, a sessile cathode of 33 cm² was placed about 3 cm above the bottom of the cathodic compartment (Fig. 1). A platinum foil of 20 cm² served as the anode.

The nitrotoluene was reduced in an almost identical cell; only position and surface area of the cathode were different: the cathode with a surface area of 44 cm² served as the bottom of the cell.

Fig. 1. Electrolytic cell.

Preliminary experiments showed that an acidic anolyte must be used to avoid a strong increase in ohmic resistance of the anolyte during electrolysis. Mostly, a 2 M H₂SO₄ solution served as the catholyte, circulated at a rate of about 5 cm³/min.

During electrolysis, the catholyte, mostly 500 cm³, was agitated by a propeller-type stirrer (5 rev/s). The catholyte was sampled with a syringe; if the catholyte contained small droplets or particles in not too large amounts, the stirring was more vigorous during sampling, so that representative samples were obtained. The solid reduction products were filtered off after electrolysis, washed with ethanol and dried in air. They were then analysed with a liquid chromatograph together with the filtrate of the catholyte and the washing liquid of the solid products and the cell.

In many experiments the pH of the catholyte was kept constant by using a titrator (Radiometer TTT2) and an autoburette (Radiometer ABU 13).

All the electrolyses were carried out at a controlled cathode potential. The potential between cathode and reference electrode (a saturated calomel electrode) was adjusted with a potentiostat (Wenking type 70 HPS). (NH₄)₂SO₄ was used as the supporting electrolyte in an agar bridge except for some experiments in which azoxytoluene was reduced in acidic media. In these cases the sodium salt of the organic acid present in the catholyte was used.

2.2. Analysis

Liquid chromatography with *uv* detection was used to analyse both the catholyte samples and the solid products formed. A separation column (length 14–20 cm, *id* 0.4 cm) packed with 5 μm adsorbent Lichrosorb SI 100 or Lichrosorb SI 60 was used. Further details: eluent pumping rate at 20°C: 0.6–1.0 cm³/min; eluent: a mixture of iso-octane, dichloromethane and ethanol (or isopropanol); LC 3 *uv* detector (Pye Unicam) at a fixed wave length, *viz* 254 nm.

The volumetric ratio of these solvents was about 660:40:1 for the determination of nitrotoluene, azotoluene, azoxytoluene, hydrazotoluene, nitrosotoluene and toluenehydroxylamine; it was about 20:5:1 for the determination of toluidine and related compounds. The degassed samples (10–20 μl) were injected with a syringe injection device. All pure test substances (with the exception of diphenylene) were available for identification and calibration. The extinction coefficient for diphenylene was obtained from the ratio of the chemical yield of toluidine and diphenylene, *viz* R_{toluidine}/R_{diphenylene} is 8.0, for a rearrangement of hydrazotoluene carried out as described[9, 10]. In addition, the *ir* spectra and the melting points of the solid reduction products were determined for their identification.

3. RESULTS AND DISCUSSION

3.1. Reduction of nitrotoluene in alkaline ethanol-water media

It was found that in alkaline solutions with 0.4–1.0 M NaOH nitrotoluene can be reduced to the

rather stable products azoxytoluene, azotoluene and hydrazotoluene. Moreover, when the analysis was carried out directly after sampling, the unstable nitrosotoluene was also detected. Besides these products mentioned, it was found, however, that still other products that are difficult to identify were formed. For instance, in a separate experiment it was chromatographically found that nitrosotoluene reacts with ethanol and/or nitrotoluene to a stable compound which was also present in the catholyte at the end of a nitrotoluene electrolysis. The formation of toluene-hydroxylamine as an intermediate could not be established.

In contrast to literature[8] formation of *o*-toluidine (toluidine) by nitrotoluene reduction in an alkaline ethanol-water solution was not observed. Löb[11] has found that nitrotoluene in alkaline ethanol-aqueous solution can be reduced almost quantitatively to azotoluene or hydrazotoluene, depending on the type of electrolysis. In Figure 2 a characteristic plot at constant cathode potential for the concentrations of nitrotoluene, azoxytoluene, azotoluene, hydrazotoluene and nitrosotoluene are given as a function of the time electrolysis. This plot shows that after $t = 4$ h both the nitrotoluene and the azoxytoluene concentrations decrease, whereas the hydrazotoluene concentration increases and the azotoluene and nitrosotoluene concentrations increase up to a fixed value and then remain constant. During the first four hours of electrolysis, nitrotoluene is almost completely reduced to azoxytoluene. From the results shown in Fig. 2 it must be concluded that the concentration of nitrotoluene strongly affects the ratio of the quantities of the reduction products.

To verify this conclusion, the starting concentrations of nitrotoluene were varied.

3.1.1. Low nitrotoluene concentration (< 0.1 M). A typical relation between the nitrotoluene and the azoxytoluene concentration during electrolysis is plotted in Fig. 3. The slope of the curve in Fig. 3 shows that the chemical yield $R_{\text{azoxytoluene}}$ decreases with decreasing nitrotoluene concentration; it was about 80 per cent at a nitrotoluene concentration of about 20 mM (Fig. 3). In these experiments only the concentration of nitrotoluene and that of azoxytoluene were deter-

mined. The effect of the cathode potential on the chemical yield is shown in Fig. 4.

3.1.2. High nitrotoluene concentration (< 0.5 M). The potential-controlled electrolysis was started at a nitrotoluene concentration of about 0.5 M and finished at about 0.05 M for Pt, Ag, Au, Cr, Fe and pyrolytic graphite as cathode material. A characteristic result of Pt is given in Fig. 5. During the first six hours of the electrolysis the current density remained practically constant at 35 mA/cm². The current efficiency for the reduction of nitrotoluene was about 85 per cent with the exception of the first quarter. For all other cathode materials mentioned, nitrotoluene can almost be quantitatively reduced to azoxytoluene with a high current efficiency; the cathode potential was, of course, adapted to the material used.

3.2. Reduction of nitrotoluene in alkaline water media

The reduction of nitrotoluene was carried out with a platinum as well as a stainless steel cathode at 60°C in an aqueous solution containing 2.5 M sodium xylenesulphonate, 0.4 M NaOH and initially 0.4 M nitrotoluene. The final nitrotoluene concentration was 0.26 M for the platinum and 0.20 M for the stainless steel cathode. It was found that for the platinum cathode at $E = -1300$ mV and an average current density of about 70 mA/cm², the chemical yield for azoxytoluene is 88 per cent and that for azotoluene 1 per cent.

For the stainless steel cathode at $E = -1800$ mV and an average current density of about 100 mA/cm², the chemical yield for azoxytoluene is 77 per cent and that for azotoluene 6 per cent. The current efficiency for the azoxytoluene formation was, respectively, 63 per cent and 44 per cent. Moreover, small quantities of unknown compounds were formed, in particular, when the stainless steel cathode was used. The formation of toluidine, however, was practically negligible.

McKee *et al.* have already investigated the nitrotoluene reduction in alkaline aqueous solutions containing a high concentration of NaK-xylenesulphonate. They found that the final reduction products are hydrazotoluene and toluidine and that

Fig. 2. The concentration of nitrotoluene and of each of its reduction products are plotted vs the time of electrolysis for a lead cathode at 1050 mV and 50°C in an ethanol solution containing 0.4 M NaOH and 0.84 M H₂O.

Fig. 3. The concentration of nitrotoluene is plotted vs the concentration of azoxytoluene for a platinum cathode at -1150 mV and 50°C in an ethanol solution containing 0.4 M NaOH and 0.84 M H_2O .

Fig. 4. The chemical yield for azoxytoluene is plotted vs the cathode potential for a platinum cathode at 50°C in an ethanol solution containing 0.4 M NaOH and 0.84 M H_2O .

the chemical yield ratio $R_{\text{hydrazotoluene}}/R_{\text{toluidine}}$ increases with increasing NaOH concentration and decreases with increasing current density. For a bronze cathode at which the added nitrotoluene was always completely reduced, a maximum $R_{\text{toluidine}}$ of about 25 per cent was obtained.

3.3. Reduction of azoxytoluene in alkaline ethanol-water media

In agreement with the literature[3] it was found that only azotoluene and hydrazotoluene are formed during reduction of azoxytoluene in alkaline solution.

A characteristic result of an azoxytoluene electrolysis is shown in Fig. 6. In this figure the concentration of azoxytoluene, azotoluene and of hydrazotoluene are plotted vs the quantity of charge passed through the cell for an ethanol-water solution containing 1 M NaOH. During the electrolysis the azotoluene concentration remained practically constant. From Fig. 6 it can be deduced that hydrazotoluene can be formed from azoxytoluene with a chemical yield of practically 100 per cent. Moreover, the overall current efficiency was about 77 per cent. Experiments with NaOH concentrations of 0.4 and 2 M gave almost the same results.

3.4. Reduction of azoxytoluene in acidic ethanol-water media

Azoxybenzene shows a single 4-electron polarographic wave over the pH range 2–12 and, moreover, azobenzene is easier to reduce than azoxybenzene[12]. It appeared that besides toluidine only 3,3'-dimethyl-2,4'-diaminodiphenyl (diphenylene) in a well determinable quantity is formed. The toluidine was isolated from the catholyte and identified by means of liquid chromatography and infrared spectroscopy and by determination of melting point; diphenylene by means of liquid chromatography alone. This result agrees with those of the rearrangement experiments of Lukashevich[10], who found that the following compounds with two phenyl groups are formed: toluidine, diphenylene and *o*-semidine. The last-named compound is only formed to about 0.7 per cent.

Electrolyses were carried out at 60°C and with various cathode materials, viz Pt, Au, Fe, Pb, stainless steel 316 and pyrolytic graphite in ethanol-water mixtures (9:1) acidified with H_2SO_4 so that the pH was between 0.6 and 3.4. During these electrolyses the current strongly decreased and the cathode was covered, partly to completely, with a layer of probably toluidine sulphate. In some cases this layer was peeled off periodically. This is affected by stirring, H_2SO_4 concentration and ethanol content of the catholyte.

Fig. 5. The concentration of nitrotoluene is plotted vs the concentrations of azoxytoluene, azotoluene and hydrazotoluene and vs the sum of the concentration of these reduction products for a platinum cathode at -1150 mV and at 50°C in an ethanol solution containing 0.4 M NaOH and 1.1 M H_2O .

Fig. 6. The concentration of azoxytoluene and its reduction products are plotted *vs* the quantity of charge passed through the electrolytic cell for a stainless steel cathode at -2000 mV *vs sce* and 60°C and in an ethanol solution containing 0.84 M H_2O and 1.0 M NaOH .

This layer strongly blocked the electrochemical process. Therefore only benzene-sulphonic acid and toluene-sulphonic acid were used in the subsequent experiments. A characteristic result is shown in Fig. 7, where the concentrations of azoxytoluene, tolidine and diphenylene are plotted *vs* the charge Q passed through. The pH of the catholyte was kept constant by automatic titration with a 4 M benzenesulphonic acid solution. Figure 7 shows a linear decrease of the azoxytoluene concentration and a linear increase of the tolidine and of the diphenylene concentration. The chemical yield of tolidine, R_{tolidine} , is 63 per cent, that for diphenylene, $R_{\text{diphenylene}}$ 16 per cent, with $R_{\text{tolidine}}/R_{\text{diphenylene}}$ it is 4.0.

The low total chemical yield of tolidine and diphenylene, *viz* 79 per cent, is due to losses of azoxytoluene by evaporation and to the formation of a number of by-products, as shown chromatographically; their identification did not occur. It must be stressed that *o*-tolidine was only found when the azoxytoluene contains some nitrotoluene. In Table 1 the results of some azoxytoluene electrolyses are

summarized. The initial concentration of azoxytoluene was about 0.2 M, the ethanol-water ratio of the catholyte was $9:1$, a stainless steel 316 sheet of 33 cm^2 was used as the cathode and the cathode potential was -700 or -800 mV *vs sce*. In most of the experiments only the catholyte was analysed at the end of the electrolysis and, moreover, only R_{tolidine} was determined.

3.5. Reduction of azoxytoluene in acidic water media

The solubility of azoxytoluene in aqueous solutions, containing McKee and inorganic acids and salts, is low. These solutions are only useful for industrial production of tolidine when azoxytoluene added to these solutions has been emulsified.

At the beginning of the 5.5 h-electrolysis at -1300 mV and 60°C the catholyte contained 1 M sodium toluene sulphonate, 0.1 M toluene sulphonic acid and 46.5 mmol azoxytoluene. The pH of the catholyte was kept at 1.56 by automatic titration with 4 M toluene sulphonic acids. The current remained

Fig. 7. The concentrations of azoxytoluene and its reduction products are plotted *vs* the quantity of charge passed through the electrolytic cell for a stainless steel cathode of 33 cm^2 at -700 mV *vs sce* and 60°C in an ethanol-water solution of $9:1$ ratio containing 0.5 M benzenesulphonic acid ($\text{pH} = 0.65$) and at the start of electrolysis 0.095 M azoxytoluene. The current decrease from 1.1 to 0.9 A during the electrolysis.

Table 1. Tolidine and diphenylene yield and their ratio for reduction of azoxytoluene in acidic solution

sulphonic acid		temperature, °C	R_{tolidine} , %	$R_{\text{diphenylene}}$, %	$R_{\text{tolidine}}/R_{\text{diphenylene}}$
type	concentration, M				
benzene	0.5	40	65		
benzene	0.5	60	63	11	4.0
benzene	0.5	75	57		
benzene	1.0	60	61		
benzene	2.0	60	55		
p-toluene	0.5	60	65		

practically 1 A during the first 4 h and decreased to 0.25 A. A solid salt was separated during electrolysis.

It was found that, besides azoxytoluene the catholyte now contained only two adequately determinable reduction products, viz tolidine and diphenylene. The separated solid product obtained after cooling to 25°C consisted of azoxytoluene and tolidine toluene-sulphonate. The analyses showed that the catholyte and separated salt together contained 12.6 mmol azoxytoluene, 23.3 mmol tolidine and 0.84 mmol diphenylene. Taking into account the sampling during the electrolysis and the addition of titrant it was calculated that the chemical yield of tolidine was 87 per cent and the ratio $R_{\text{tolidine}}/R_{\text{diphenylene}}$ was 28. The current efficiency for tolidine was about 40 per cent.

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