JOURNAL OF APPLIED ELECTROCHEMISTRY **21** (1991) 799–804

The role of supporting electrolyte during the electrocatalytic hydrogenation of aromatic compounds

P. N. PINTAURO*, J. R. BONTHA

Department of Chemical Engineering, Tulane University, New Orleans, Louisiana 70118, USA

Received 16 October 1990; revised 18 February 1991

The electrocatalytic hydrogenation of benzene, aniline, and nitrobenzene was investigated at a Raney nickel powder cathode. The single phase electrolyte consisted of t-butanol, water, and a hydrotropic salt, either sodium or tetraethylammonium *p*-toluenesulphonate (TEATS). The hydrogenation of benzene was achieved only in the latter case; the only product detected was cyclohexane. The highest current efficiency (73%) was obtained at 50° C, 1.0 M benzene, 2.5 M TEATS, and at an apparent current density of $4.0\,\mathrm{mA\,cm^{-2}}$. Aniline was electrocatalytically hydrogenated to cyclohexylamine only in the presence of a quaternary ammonium ion supporting electrolyte (containing either Br^- or *p*-toluenesulphonate anions), with product current efficiencies of ~40%. When nitrobenzene was hydrogenated with a sodium *p*-toluenesulphonate supporting electrolyte, only nitro group reduction was observed. When the supporting electrolyte was TEATS, both nitro group reduction and aromatic ring hydrogenation occurred.

1. Introduction

Previous experimental studies have shown that low hydrogen overpotential electrocatalysts, such as Raney nickel and platinum or rhodium black, can effectively hydrogenate a variety of organic compounds, for example phenol to cyclohexanol [1], glucose to sorbitol [2, 3], dinitriles to diamines and/or aminonitriles [4, 5], and ketones and aldehydes to alcohols [6]. Similarly, flat sheet cathodes coated with Devarda copper or Raney nickel have been employed to hydrogenate nitroaromatics under potentiostatic conditions with high current efficiencies and near quantitative product yields [7, 8]. An electrocatalytic hydrogenation reaction uses a proton containing solvent (e.g. water) and electrical energy to generate hydrogen on a catalytically active metal surface. The overall hydrogenation reaction can be viewed as a two step process involving the electrochemical generation of atomic hydrogen on the catalytic cathode surface followed by the chemical combination of the surface hydrogen species with the organic substrate. An unwanted side reaction which consumes current but does not affect directly the yield of organic product is the generation of hydrogen gas on the catalyst surface.

Electrocatalytic hydrogenations can be carried out at temperatures and pressures which are more moderate than those employed in traditional chemical catalytic reaction schemes because the driving force for *in situ* hydrogen generation is the electric potential at the catalyst surface. For example, glucose has been electrocatalytically hydrogenated to sorbitol at atmospheric pressure and a temperature of ~60° C [2], whereas the corresponding chemical catalytic reaction requires high temperatures (80°–140° C) and high hydrogen gas pressures (20–140 atm) [10]. Similarly, benzene is hydrogenated via a chemical catalytic route using primarily Raney nickel catalyst at 300°–350° C and 20–30 atm pressure [11] but a series of preliminary benzene electrocatalytic hydrogenation experiments by Pintauro *et al.* [9] were carried out at 45°–65° C and 1 atmosphere pressure.

The electrochemical hydrogenation of aromatic compounds by conventional cathodic techniques is difficult and often requires complex solvent mixtures and high cathodic potentials. In 1973 Asahi Chemical Co. was awarded a patent for the cathodic reduction of benzene and other aromatic compounds to their dihydro products in a divided H-cell using a mercury cathode and an emulsion of water, organic reactant, and tetrabutylammonium bromide [12]. Coleman and Wagenknecht performed similar experiments in undivided batch and flow reactors with benzene, toluene, xylene, and naphthalene starting materials and an aqueous tetrabutylammonium hydroxide electrolyte [13]. In these experiments, the predominant product was the 1,4-dihydro derivative, with current efficiencies near 90%. When benzene was electrochemically reduced via solvated electrons on Pt in ethylenediamine saturated with LiCl, cyclohexadiene was produced in a divided cell [14], whereas cyclohexadiene and cyclohexane were synthesized in an undivided cell [15]. Pasquariello *et al.* reduced benzene to a mixture of cyclohexadiene, cyclohexene, and cyclohexane on Pt, Ag, and Pb cathodes using an ethanol/hexamethylphosphoramide (HMPA) solvent [16]. Benzene reduction current efficiencies as high as 91% were obtained when the elec-

---

* To whom all correspondence should be sent.

0021-891X/91 $03.00 + .12

trolytic solution contained 21% ethanol and 79% HMPA.

The direct electron transfer electrochemical reduction of nitroaromatic compounds has been studied extensively over the past 25 years. For the case of nitrobenzene, the reduction product is aniline and/or *p*-aminophenol at a low solution pH and N-coupled products such as azobenzene at high pH [17]. A limited number of studies have been carried out to investigate the electrocatalytic hydrogenation of nitroaromatics and aniline. Miller and Christensen electro-hydrogenated aniline at a Rh/C cathode in an aqueous 0.2 M H_2SO_4 electrolyte [1] and achieved a cyclohexylamine product yield of 73% after passing 12 faraday mol^{-1}. Chiba *et al.* [6] electrocatalytically hydrogenated a number of different nitroaromatic compounds (e.g., nitrobenzene and nitrotoluene) at a Raney nickel powder cathode using a methanol/sodium methoxide electrolyte. Nitro group reduction was observed at reasonably high current efficiencies; the synthesis of ring hydrogenated products was not reported. Belot *et al.* [7] and, more recently, Cyr *et al.* [8] have electrochemically hydrogenated nitrobenzene to aniline at a stainless steel cathode coated with either Devarda copper or Raney nickel. Using a mixture of methanol and water with either sodium acetate or KOH as the supporting electrolyte, nitrobenzene was reduced to aniline with high product yields (100%) and high current efficiencies (99%). These investigators did not observe benzene ring hydrogenation.

In the present study, the electrocatalytic hydrogenation of benzene, aniline, and nitrobenzene was studied using a divided H-cell reactor, a powdered Raney nickel cathode, and a single-phase electrolyte solution consisting of an alcohol/water mixture and a hydrotropic (McKee) salt supporting electrolyte. This work is an extension of a preliminary study by Pintauro *et al.* [9] which demonstrated that benzene could be electrocatalytically hydrogenated to cyclohexane using a Raney nickel powder cathode. The effects of electrolyte salt type and concentration, solvent composition, temperature, and initial reactant concentration on product yield and current efficiency were examined. A key element of the present study is the use of a hydrotropic salt supporting electrolyte. Hydrotropic salts such as the alkali, alkaline earth, or quaternary ammonium salts of the sulphonates of toluene and xylene have been shown to be particularly useful in organic electrochemical syntheses [18–21]. They are used to dissolve normally water-insoluble organic reactants in an aqueous reaction medium and also provide the ions needed for current conduction through the electrolyte.

2. Experimental details

All electrolyses were performed in a standard glass H-cell with a medium porosity sintered glass frit which separated the anode and cathode chambers. The anode was a graphite rod and the cathode was an uncompacted bed of Raney nickel powder (~0.4 cm in depth with a bed diameter of 4 cm) having an activity comparable to that of W-2 catalyst [22]. Electrical contact to the bed was provided by a nickel rod whose sides were coated with Teflon®. A schematic diagram of the H-cell is shown in Fig. 1. The nickel catalyst was prepared from 50/50 Ni/Al powder (Aldrich Chemical Co.) by a standard NaOH leaching technique [6]. Hydrogen produced and adsorbed on the nickel surface during catalyst activation was removed by soaking the powder in 100 ml of organic reactant for 18–24 h at 25° C.

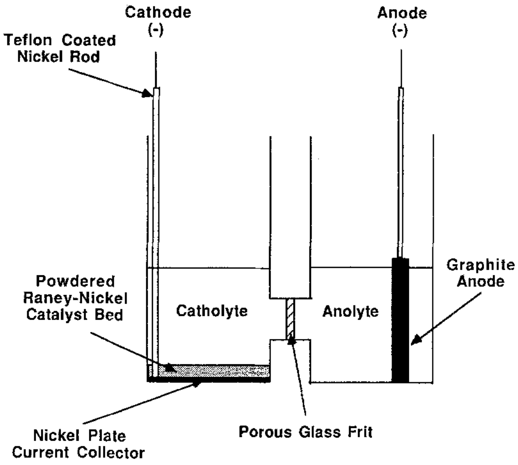

Fig. 1. A schematic diagram of the H-cell apparatus.

Electrolyte solutions were prepared from reagent-grade chemicals and deionized and distilled water. All reactions were carried out using a single-phase electrolyte solution which consisted of water, t-butanol co-solvent, reactant (either benzene, aniline, or nitrobenzene), and supporting electrolyte. For the benzene and nitrobenzene experiments, the supporting electrolyte was a hydrotropic salt, either tetraethylammonium *p*-toluenesulphonate, sodium *p*-toluenesulphonate, or mixtures thereof. For the case of aniline, which is more soluble than benzene in t-butanol/water mixtures, supporting electrolytes of tetraethylammonium *p*-toluenesulphonate, sodium *p*-toluenesulphonate, tetramethylammonium bromide, and tetraethylammonium bromide were employed.

In all benzene and aniline electrolyses, the total charge passed was sufficient to convert approximately 13% of initial reactant to a completely hydrogenated cyclohexyl product assuming 100% current efficiency (i.e., 0.78 faraday mol^{-1} of reactant). For the nitrobenzene hydrogenation experiments, sufficient charge was passed for 70% theoretical reduction of the nitro group and for the complete theoretical hydrogenation of both the nitro-group and aromatic ring. In a typical experiment, the anode and cathode compartments of the H-cell were each charged with 40 ml of electrolyte. All electrolyses were carried out under constant current conditions (50 mA total current which corresponds to a current density of 4.0 mA cm^{-2} of apparent cathode area) using a Hewlett-Packard Model 6294A d.c. power supply. The current was monitored on a Keithley Model 169 multimeter and the total charge was counted on a ESC Model 640 digital coulometer. Constant reaction temperature was achieved by immersing the H-cell in a water bath. For the benzene hydrogenation experiments, the anode and cathode compartments of the H-cell were fitted with dry ice/acetone Dewar condensers to minimize evaporative losses of benzene and its hydrogenation product(s) (condensers were not needed in the aniline and nitrobenzene electrolyses). Occasionally during an electrolysis the current was interrupted and the catholyte and Raney nickel powder were stirred. The catholyte pH was not controlled in the experiments; the initial pH was ~ 7.5 and the final pH was between 12 and 13. Due to the relative positions of the anode and cathode in the H-cell, a complex two-dimensional variation of the electric potential driving force (reaction distribution) exists in the nickel bed. Although Pintauro *et al.* [9] have reported the portential difference between the nickel bed and a reference electrode in the bulk catholyte during benzene hydrogenation (-1.03 V/SCE at 3.1 mA cm^{-2}), such measurements were not performed in the present study because they would yield little information regarding the potential distribution and its relationship to current efficiencies and product yields.

At the conclusion of an electrolysis, the catholyte was removed from the H-cell and the Raney nickel powder was washed with either toluene or N,N dimethylformamide to remove reactant and product(s) which may have adsorbed onto the catalyst surface. Initial and final samples of catholyte solution were analysed using a Perkin Elmer Sigma 115 gas chromatograph with a flame ionization detector. For benzene and its reduction products (1,3 and 1,4-cyclohexadiene, cyclohexene, and cyclohexane) a 20 metre column packed with 10% Carbowax on Supelcoport was employed. The GC was operated isothermally at 50° C with a nitrogen carrier gas flow rate of 30 ml min^{-1}. For aniline, nitrobenzene, and their reduction products a 20 meter GC column containing 2% Carbowax and 2% KOH on Carbopack was used with a nitrogen carrier gas flow rate of 50 ml min^{-1}. The column temperature was maintained constant at 70° C for 4 min after injection, then increased to 120° C at 10° C min^{-1} and held at 120° C for 5 min. In all analyses, products were identified by comparing the retention times with those of known commercial samples. The concentration of product(s) and reactant in the catholyte were determined by GC calibration with prepared standard solutions. GC errors were estimated to be $\pm 5\%$.

A comparison of the total charge passed in an electrolysis with the number of moles of product in the catholyte, as determined by GC analysis, was used to compute product current efficiencies. A mass balance calculation was also performed for each H-cell experiment, where the total moles of reactant and product(s) at the conclusion of an electrolysis was compared with the initial moles of reactant. During the preliminary aniline and nitrobenzene experiments, we found a tar-like polymerization product, similar to that described by Tomilov [23], on the carbon anode. This material eventually dislodged from the anode and penetrated into the glass frit of the H-cell, causing an undesirable increase in the cell voltage. This problem was circumvented by removing aniline and nitrobenzene reactants from the anode compartment of the H-cell. In these experiments, the mass balance and current efficiency results were corrected for reactant and products which diffused across the glass frit over the course of an electrolysis [24].

3. Results and discussion

3.1. *Benzene hydrogenation*

3.1.1. Supporting electrolyte and solvent effects. The initial benzene hydrogenation experiments focused on the choice of hydrotropic salt supporting electrolyte. Electrolyses were performed with tetraethylammonium *p*-toluenesulphonate (hereafter denoted as TEATS), sodium *p*-toluenesulphonate (SPTS), and mixtures of the two salts with a total supporting electrolyte concentration of 1.0 M. In these experiments the temperature was 50° C and the initial benzene concentration was 0.50 M. Two different solvents were employed: either a 50/50 or a 75/25 volume ratio t-butanol/water mixture.

Gas chromatography analysis of the final catholyte and the toluene washings of the nickel catalyst revealed that only cyclohexane was produced when benzene was electrocatalytically hydrogenated. Cyclohexene and cyclohexadiene were not detected in solution or on the catalyst surface. The absence of partially reduced products is consistent with the earlier finding of Pintauro *et al.* [9], who used both GC and NMR to confirm the presence of only cyclohexane product.

The effect of solvent and supporting electrolyte composition on cyclohexane current efficiency is shown in Fig. 2, where the abscissa is labeled as the mole fraction of TEATS in the mixed TEATS/SPTS electrolyte. The results show that the cation of the supporting electrolyte influences significantly the cyclohexane current efficiency. Although both SPTS

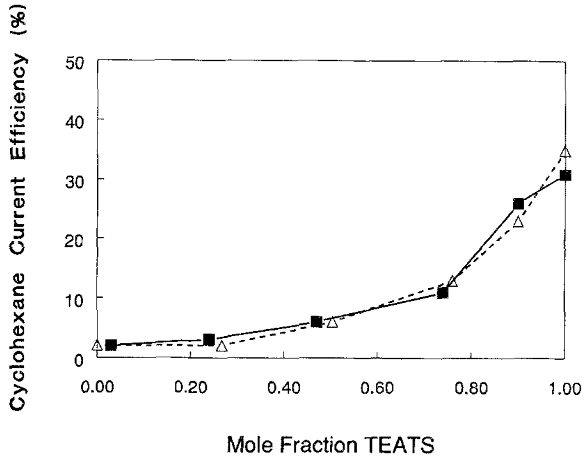

Fig. 2. The effect of hydrotropic salt composition on the current efficiency of cyclohexane synthesis ($T = 50$° C, current = 50 mA, initial benzene concentration = 0.5 M, total salt concentration = 1.0 M, charge passed = 0.78 faraday mol^{-1}). (■) 50/50 t-butanol/water solvent; (△) 75/25 t-butanol/water solvent.

and TEATS were effective for the complete solubilization of benzene in the alcohol/water solvent, essentially no cyclohexane was synthesized when the mole fraction of TEATS was less than ~0.28 (i.e., the mole fraction of SPTS was > 0.72). The cyclohexane current efficiency rose as the TEATS/SPTS concentration ratio was increased. This effect appears to be independent of the alcohol/water solvent composition. Current losses in these experiments have been attributed to hydrogen evolution. Mass balance computations at the conclusion of an electrolysis showed that nearly 100% of the initial reactant could be accounted for, based on the total moles of cyclohexane product and unreacted benzene in the cathode compartment of the H-cell.

The single cyclohexane product and the current efficiency trend in Fig. 2 can be explained by the presence of a quaternary ammonium ion film [25–27] on the Raney nickel surface. The presence of this film delays the onset of hydrogen gas evolution to higher overpotentials during direct electron transfer reductions by partially excluding water from the cathode surface [27, 28]. In the present study, we believe that benzene is solubilizing in the hydrophobic tetraethylammonium ion film and is remaining on the nickel surface for sufficiently long periods of time for it to react fully with six hydrogen atoms. We have seen, for example, large amounts of benzene and cyclohexane product on the catalyst surface at the conclusion of an experiment when the supporting electrolyte is TEATS. When the supporting electrolyte is sodium *p*-toluenesulphonate, hydrated sodium ions migrate to the electrode surface and the resulting hydrophilic ion/water layer effectively excludes benzene. Low surface concentrations of benzene and short benzene residence times on the cathode surface produce essentially no cyclohexane.

The effect of TEATS concentration on the cyclohexane current efficiency is shown in Fig. 3 for three different solvents: 50/50, 75/25, and 95/5 volume ratio t-butanol/water. In these experiments the solution temperature was 50° C and the initial benzene concentration was 0.50 M. It appears that a TEATS concentration of 0.33 M is insufficient for catalyst surface coverage, as evidenced by the low (14%) cyclohexane current efficiency. Above 2.0 M no discernable increase in current efficiency was observed, indicating near complete surface coverage by R_4N^+. The increase in current efficiency with TEATS concentration, in the 1.0–2.0 M range suggests that a higher bulk solution concentration of R_4N^+ is producing a more uniform organic film on the catalyst surface. Such a film is either solubilizing more benzene, thus improving the current efficiency of the hydrogenation reaction, or distributing electrogenerated adsorbed hydrogen more uniformly on the catalyst surface, thereby minimizing current losses by hydrogen gas evolution. The current efficiency results are essentially independent of solvent composition, indicating once again that quaternary ammonium ion effects are dominating the electrocatalytic hydrogenation reaction. Improvements in product current efficiency with increasing quaternary ammonium salt concentration have been reported previously by Coleman and Wagenknecht [13] during the electrochemical reduction of a benzene/water/tetrabutylammonium hydroxide emulsified electrolyte at a mercury cathode. In that study the current efficiency of cyclohexadiene product rose from 60% to 100% when the concentration of tetrabutylammonium salt was increased from 5 to 25 wt %.

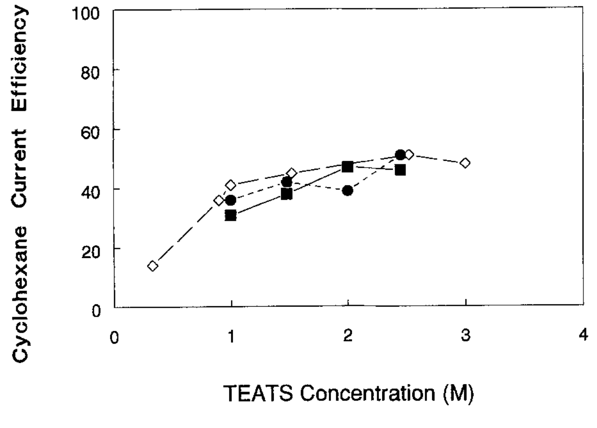

Fig. 3. The effect of tetraethylammonium *p*-toluenesulphonate (TEATS) concentration on the cyclohexane current efficiency (T = 50° C, current = 50 mA, initial benzene concentration = 0.5 M, charge passed = 0.78 faraday mol^{-1}). (◇) 95/5 t-butanol/water solvent; (●) 75/25 t-butanol/water solvent; (■) 50/50 t-butanol/water solvent.

3.1.2. Temperature effect. In order to study the effect of temperature on cyclohexane current efficiency, H-cell electrolyses were performed at four different temperatures ranging from 25° C to 59° C, with either a 50/50 or 75/25 volume ratio t-butanol/water solvent, a 2.5 M TEATS supporting electrolyte, and an initial benzene concentration of 0.50 M. These experiments showed that the cyclohexane current efficiency increased almost linearly from 16% to 51% as the reaction temperature was increased from 25° C to 59° C. Current efficiencies in the two different alcohol/water solvents were found to be essentially identical. The results suggest that elevated temperatures accelerate the reaction of adsorbed hydrogen with benzene to a greater extent than the adsorbed atomic hydrogen to hydrogen gas reaction.

3.1.3. Effect of initial benzene concentration. An increase in the bulk catholyte concentration of benzene should lead to an increase in the amount of benzene at the catalyst surface which, in turn, will increase the efficiency of hydrogen addition to the benzene ring. To test this hypothesis, H-cell electrocatalytic hydrogenation experiments were carried out with initial benzene concentrations ranging from 0.25 to 1.0 M. A single phase electrolyte was obtained for the entire concentration range by employing a 75/25 volume ratio t-butanol/water solvent containing 2.5 M TEATS. The total charge passed in each experiment was 1500 C, which represents a theoretical conversion (benzene to cyclohexane) ranging from 6.5% (at 1.0 M initial

Table 1. The effect of initial benzene concentration on the cyclohexane current efficiency. Conditions: T = 50° C, current = 50 mA, 2.5 M TEATS supporting electrolyte, 75/25 t-butanol/water solvent, charge passed = 1500 C.

Initial benzene concentration (M)	*Cyclohexane current efficiency (%)*
0.25	19
0.50	51
0.75	62
1.00	73

concentration) to 26% (for 0.25 M benzene). In all experiments the solution temperature and applied current were maintained constant at 50° C and 50 mA, respectively. As shown in Table 1, the cyclohexane current efficiency rose from 19% to 73% as the initial benzene concentration was increased from 0.25 to 1.0 M. This result is consistent with reaction rate data for the high temperature and pressure chemical catalytic hydrogenation of benzene [11]. It is also in qualitative agreement with the electrocatalytic glucose hydrogenation studies of Park *et al.* [3] who found dramatic increases in product (sorbitol) current efficiencies when the initial glucose reactant concentration was increased.

3.2. *Aniline and nitrobenzene hydrogenation*

These experiments were carried out to investigate functional group vs. aromatic ring hydrogenation in the divided H-cell. A series of seven electrocatalytic hydrogenation experiments with aniline starting material were performed first. Due to the higher solubility of aniline in water and alcohol/water solutions as compared to benzene (3.4 vol % in water at 20° C compared with 0.07 vol % at 22° C for benzene [29]), non-hydrotropic quaternary ammonium salts (tetramethylammonium bromide and tetraethylammonium bromide) as well as TEATS and SPTS were examined as the supporting electrolyte (at a concentration of 1.0 M). In all experiments the initial aniline concentration was 0.50 M, the applied current was 50 mA, and the temperature was 54° C. The results of these electrolyses are listed in Table 2.

In all experiments, the only product found in the catholyte and on the nickel catalyst was the completely hydrogenated ring compound cyclohexylamine. As was the case with benzene, partially hydrogenated products were not detected by GC analysis. The % closure on the mass balances, for the most part, were in the range of 94–100% and current losses were attributed solely to hydrogen gas evolution. The results in Table 2 show that the presence of a quaternary ammonium cation increases dramatically the current efficiency for hydrogenation (40% vs. ~20%). The cyclohexylamine current efficiency is independent of solvent composition, supporting electrolyte anion species, and the type of quaternary ammonium ion. Again, it appears that a quaternary ammonium ion film on the nickel catalyst surface is retaining aniline for a sufficiently long period of time for it to react fully with electro-generated hydrogen. The current efficiencies for hydrogen addition to aniline with SPTS are higher than those with benzene starting material (~20% vs. 1.5%) because aniline is more soluble in aqueous solutions, and has a somewhat greater affinity for the Na^+/H_2O region near the nickel surface.

Next, four nitrobenzene electrocatalytic hydrogenation experiments were carried out using a 50/50 volume ratio t-butanol/water solvent with either SPTS or TEATS supporting electrolyte at a concentration of 1.0 M. Electrolyses were continued until 70% theoretical conversion of nitrobenzene to aniline (4242 coulombs) and until ~ 100% theoretical conversion of the initial nitrobenzene to cyclohexylamine (12 600 coulombs). A charge balance calculation was made for each H-cell electrolysis, where the total coulombs necessary to synthesize the moles of organic products detected at the conclusion of an experiment was compared to the total charge passed, as noted by the coulometer. The charge consumed by electrochemical generation of hydrogen gas was determined by subtracting the coulombs consumed by organic product synthesis from the total charge passed. The results of these computations are listed in Table 3. Mass balances at the conclusion of an electrolysis were in the range of 95–102%. The charge balance of 103% in Exp. no. 1 is attributed to gas chromatography errors.

Table 2. Experimental mass balances and current efficiences for the electrocatalytic hydrogenation of aniline. Conditions: T = 54° C, current = 50 mA, charge passed = 0.78 faraday mol⁻¹.

Exp. run	*Supporting electrolyte*	*t-butanol/water solvent composition (vol/vol)*	*Closure of the Mass balance (%)*	*Cyclohexylamine current efficiency (%)*
1	TEATS	20/80	97	39
2	TMAB	20/80	94	42
3	TMAB	0/100	97	40
4	TEAB	20/80	98	39
5	TEAB	0/100	100	43
6	SPTS	20/80	100	24
7	SPTS	0/100	89	13

TEATS: tetraethylammonium *p*-toluenesulphonate
TMAB: tetramethylammonium bromide
TEAB: tetraethylammonium bromide
SPTS: sodium *p*-toluenesulphonate

Table 3. The electrocatalytic hydrogenation of nitrobenzene at a Raney nickel powder cathode. Conditions: $T = 50°$ C, current = 50 mA, 0.25 M initial nitrobenzene concentration.

Exp. run	*Supporting electrolyte*	*Charge passed (C)*	*Charge consumed (%)*		
			Nitrobenzene to aniline	*Aniline and nitrobenzene to cyclohexylamine*	*H_2 gas evolution*
1	TEATS	4242	73	30	–
2	TEATS	12062	40	27	33
3	SPTS	4241	48	4	48
4	SPTS	12592	41	4	55

The data in Table 3 show that both TEATS and SPTS were effective in hydrogenating nitrobenzene to aniline, although the efficiency of hydrogen addition is greater when quaternary ammonium ions are present. Thus, the presence of R_4N^+ is not a necessary condition for functional group hydrogenation. This finding is in agreement with the aromatic electrohydrogenation studies of Chiba and co-workers [6], Belot *et al.* [7], and Cyr *et al.* [8] who found functional group reduction but no ring hydrogenation with electrolytes of KOH, $NaOOCCH_3$, and acetic acid. When TEATS is present in solution, hydrogen adds to both the ring and nitro group. For Exp. run no. 1, these two reactions consumed all of the current. The cyclohexylamine current efficiency in Exp. runs no. 1 and 2 are lower than those listed in Table 2 because the concentration of aniline in the catholyte is low. Similarly, the drop in aniline current efficiency in Exp. run no. 2, as compared to Exp. run no. 1, is attributed to a lower average nitrobenzene concentration over the course of the longer electrolysis. As expected, essentially no charge was consumed for cyclohexylamine synthesis in Exp. runs no. 3 and 4.

Acknowledgement

This project was supported by a grant from the Custom Resins Division of Bemis Company, Inc.

References

[1] L. L. Miller and L. Christensen, *J. Org. Chem.* **43** (1978) 2059.

[2] K. Park, P. N. Pintauro, M. M. Baizer and K. Nobe, *J. Electrochem. Soc.* **132** (1985) 1850.

[3] *Idem., J. Appl. Electrochem.* **16** (986) 941.

[4] A. P. Tomilov, S. L. Kirilyus and I. P. Andriyanova, *Sov. Electrochem.* **8** (1972) 1050.

[5] Y. Song and P. N. Pintauro, *J. Appl. Electrochem.* **21** (1991) 21.

[6] T. Chiba, M. Okimoto, H. Nagai and T. Takata, *Bull. Chem. Soc. Jpn.* **56** (1983) 719.

[7] G. Belot, S. Desjardins and J. Lessard, *Tetrahedron Lett.* **25** (1984) 5347.

[8] A. Cyr, P. Huot, G. Belot and J. Lessard, *Electrochim. Acta* **35** (1990) 147.

[9] P. N. Pintauro, H. Phan, M. M. Baizer and K. Nobe, *AIChE Symposium Series No. 254* **83** (1987) 34.

[10] J. Wisniak, M. Hershkowitz and S. Stein, *Ind. Eng. Chem. Proc. Res. Dev.* **13** (1974) 232.

[11] H. W. Haines, *Ind. Eng. Chem.* **54** (1962) 23.

[12] T. Hatayama, US Patent 3 700 572 (24 Oct. 1973).

[13] J. P. Coleman and J. H. Wagenknecht, *J. Electrochem. Soc.* **128** (1981) 322.

[14] W. H. Sternberg, R. Markby and I. Vendor, *ibid.* **110** (1963) 425.

[15] A. R. Benkeser, E. M. Kaiser and R. F. Lambert, *J. Am. Chem. Soc.* **86** (1964) 5272.

[16] D. Pasquariello, J. Foise, R. Kershaw, G. Zoski, K. Dwight and A. Wold, *J. Phys. Chem.* **89** (1985) 1243.

[17] M. M. Baizer and H. Lund, '*Organic Electrochemistry*', 2nd ed., Marcel Dekker, New York, (1983) pp. 285–313.

[18] R. H. McKee, *Ind. Eng. Chem.* **38** (1946) 382.

[19] *Idem*, US Patent 1 932 908 (31 Oct. 1933).

[20] R. H. McKee and J. R. Heard, *Trans. Electrochem. Soc.* **65** (1934) 301.

[21] M. M. Baizer, *J. Electrochem. Soc.* **111** (1964) 215.

[22] R. Mozingo, 'Organic Syntheses', Coll. Vol. III. John Wiley, New York (1964) p. 181.

[23] A. P. Tomilov, S. G. Mairanovskii, M. Ya. Fioshin and V. A. Smirnov, 'Electrochemistry of Organic Compounds', Halsted Press, New York (1972) p. 351.

[24] J. Bontha, 'The Electrocatalytic Hydrogenation of Organic Compounds on Raney Nickel', M. S. Thesis, Tulane University (1990).

[25] T. C. Franklin and T. Jimbo, *J. Electrochem. Soc.* **134** (1987) 2169.

[26] M. M. Baizer and J. P. Petrovich, *ibid.* **114** (1967) 1023.

[27] F. Beck, *Angew. Chem. Int. Ed. Eng.* **11** (1972) 760.

[28] P. N. Pintauro, D. K. Johnson, K. Park, M. M. Baizer and K. Nobe, *J. Appl. Electrochem.* **14** (1984) 209.

[29] 'Chemical Engineer's Handbook', 6th Edition (edited by R. H. Perry and C. H. Chilton) Mc-Graw-Hill, New York (1987).