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Electrolytic equipment for reductions in liquid ammonia

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We have developed static and circulating electrolytic equipment for liquid ammonia (or low molecular weight amines) to perform reductions of compounds bearing at least one reducible group. The equipment contains undivided electrochemical cells including consumable magnesium anodes. Birch and Bouveault-Blanc reductions are performed with substrate weight percents up to 10%. A circulating electrolytic cell working at room temperature is described which may be adaptable to large scale production.

1. Introduction

When electrochemical processes are performed in undivided cells the problems due to separators are avoided, and the scaling up of the process is simplified. If an unreactive anode (gold, platinum, carbon, stainless steel) is used, the main disadvantage of such cells is that they cannot be used to reduce acidic compounds: in such a case, the process corresponds to the solvent decomposition ($2NH_3 \rightarrow N_2 + 3H_2$). In some cases of non-acidic compounds, the reduction product may be oxidized at the anode.

We have overcome this problem by using a magnesium consumable anode [1, 2]. In a medium containing an alkali metal halide (MX) or an alkali metal tetrafluoroborate (MBF_4) as supporting electrolyte, the anodic reaction corresponds to the oxidation of magnesium into a non-electroactive salt.

$$Mg + 2X^- \longrightarrow MgX_2\downarrow + 2e^-$$

or

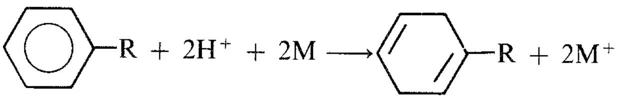
$$Mg + 2BF_4^- \longrightarrow Mg(BF_4)_2 + 2e^-$$

Therefore, the cathodic and anodic reactions can be carried out in the same compartment.

This type of cell has been tested to perform Birch and Bouveault-Blanc dissolving metal reductions. A static cell has been used to prove that such an electrolytic process can work efficiently. Circulating cells (one at −33° C and the other at +20° C) are the first attempts in the scaling up of the process.

2. Theory

Birch reductions classically proceed by means of an alkali metal M (sodium, potassium or lithium) dissolved in liquid ammonia in the presence of a proton donor (ethyl, isopropyl or t-butylalcohol) [3–6]:



where R = H, alkyl, NR′₂, OR′, OH. . . .

If the R substituent bears an acidic proton, this acidic proton is reduced before the ring. With electron withdrawing substituents, the 1-4 dihydrogeno compound is obtained [5].

Birch reactions can also be performed in solvents such as low weight amines; electrochemical procedures are described in methylamine [7, 8] and ethylendiamine [9].

Bouveault–Blanc reductions usually proceed by means of sodium dissolved in ethanol [10, 11]. In the case of difficult reductions, ammonia, with a small amount of an alcohol as proton donor, is the preferred solvent [12]:

$$RCO_2R' + 4H^+ + 4M$$
$$\longrightarrow RCH_2OH + R'OH + 4M^+$$

This reaction can also be performed using $AlLiH_4$.

Our purpose is to carry out these reactions in liquid ammonia by an electrolytic procedure. Liquid ammonia has been chosen as the solvent because it is the most general solvent for these reactions; it is especially convenient for difficult reductions [13].

The principle of our process consists in generating solvated electrons electrochemically; once formed, the solvated electrons reduce the substrate [14–16]. Solvated electrons, which can be obtained by dissolving alkali metals, M, in liquid ammonia ($M \xrightarrow{NH_3} (e^-, NH_3, M^+)$) can also be electrogenerated in the presence of a supporting electrolyte (alkali metal halide, MX), using an unreactive cathode, provided that the medium does not contain any reducible species:

$$e^- + M^+ \xrightarrow{NH_3} (e^-, NH_3, M^+)$$

In the presence of a consumable magnesium anode, the process is:

$$2MX + Mg \xrightarrow{NH_3} MgX_2\downarrow + 2(e^-, NH_3, M^+)$$

The solvated electrons, which are stable under these conditions, can diffuse into the solution and be used as reducing agents in Birch or Bouveault–Blanc

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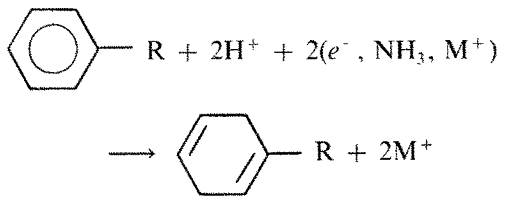
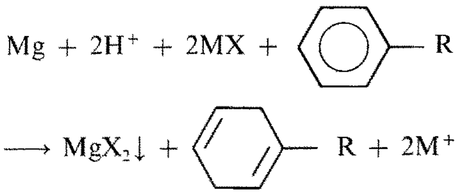
reductions:



$$RCO_2R' + 4H^+ + 4(e^-, NH_3, M^+) \longrightarrow RCH_2OH + R'OH + 4M^+$$

(Electrolysis balance:



$$2Mg + 4H^+ + 4MX + RCO_2R' \longrightarrow 2MgX_2\downarrow + RCH_2OH + 4M^+ + R'OH)$$

Since M^+ is not consumed by the reaction, the supporting electrolyte can be used in less than stoichiometric amounts. If there are no more free X^- in the medium, the conjugate base of the proton donor takes their place.

To illustrate these reactions, some substrates were chosen because of their pharmaceutical interest: 1-naphthol and phenyl glycine (Birch reductions), ethylcyclopropylcarboxylate and diethyl sebacate (Bouveault–Blanc reactions). In the case of ethyl cyclopropyl carboxylate, instead of cyclopropyl carbinol, 4,5-octane diol is obtained.

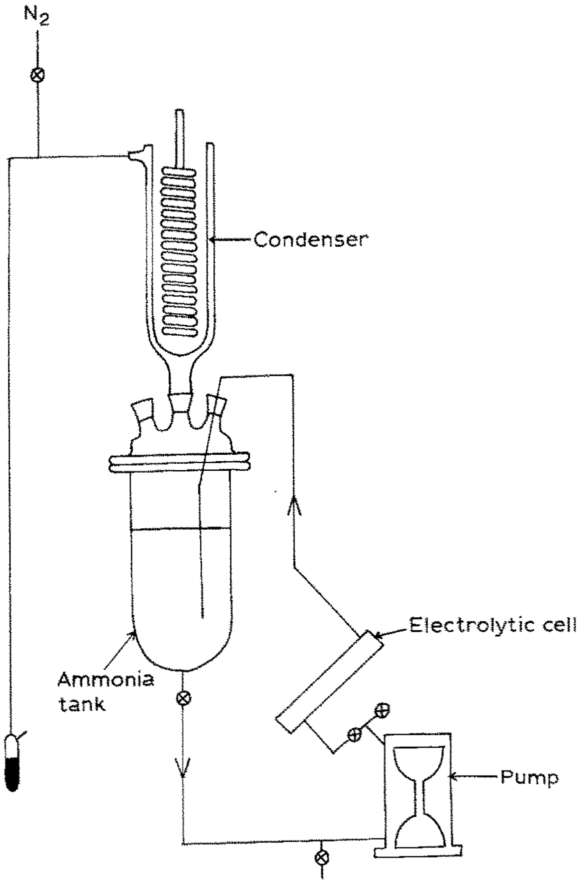


Fig. 1. Circulating electrolytic device for low temperature.

3. Experimental details

3.1. *Static electrolytic cell*

The electrolytic cell was a glass reactor equipped with a condenser cooled by acetone whose temperature was maintained at −75° C by a cryocooler (Huber, Bioblock Scientific).

The anode was a 2.5 cm diameter Mg rod (Weber Métaux) with a surface area of approximately 63 cm^2 at the beginning of the electrolysis. The cathode was usually a perforated Al sheet (Le Métal Deployé), which surrounded 75% of the anode surface. A Mg rod or a stainless steel grid were also used as cathodes. The distance between anode and cathode was about 1 cm.

The solution was stirred with a magnetic stirrer. All the connections were made in glass (or Teflon for the parts which did not contact the solution).

Ammonia was condensed at low pressure ($p = 10^{-2}$ mm Hg) using a vacuum line connected to the top of the condenser. The volume of ammonia was usually between 100 and 300 ml. The solvent temperature was about −33° C and the pressure about 10^5 Pa.

3.2. *Circulating electrolytic apparatus for low temperature operation*

The experimental set up shown in Fig. 1 comprises:

(i) a 2 dm^3 tank (equipped with the same cooling device as in 3.1);

(ii) a 50 ml cylindric electrolytic cell made of Duralumin (Fig. 2). The anode was the same as in 3.1. The cathode was the cell body (125 cm^2 surface area);

(iii) a Nordele membrane pump (M2 Wilden) driven by a pneumatic motor. The pump was always located before the electrolytic cell. Its dead volume was about 0.8 dm^3; and

(iv) four valves.

The cell, the pump and the connections were insulated, in order to minimize thermal exchange.

Ammonia was directly decanted from a pressurized ammonia bottle into the tank. The solvent temperature was about −33° C for a 10^5 Pa pressure.

3.3. *Circulating electrolytic apparatus for room temperature operation*

The principle of the room temperature cell is the same as for the low temperature cell (3.2) except all the parts were made of stainless steel (316 L). The device shown in Fig. 3 comprises:

(i) a 1.8 dm^3 jacketed ammonia tank and a mechanical stirrer;

(ii) a high pressure pump to introduce the reactants into the tank (there were also other inlets in the tank);

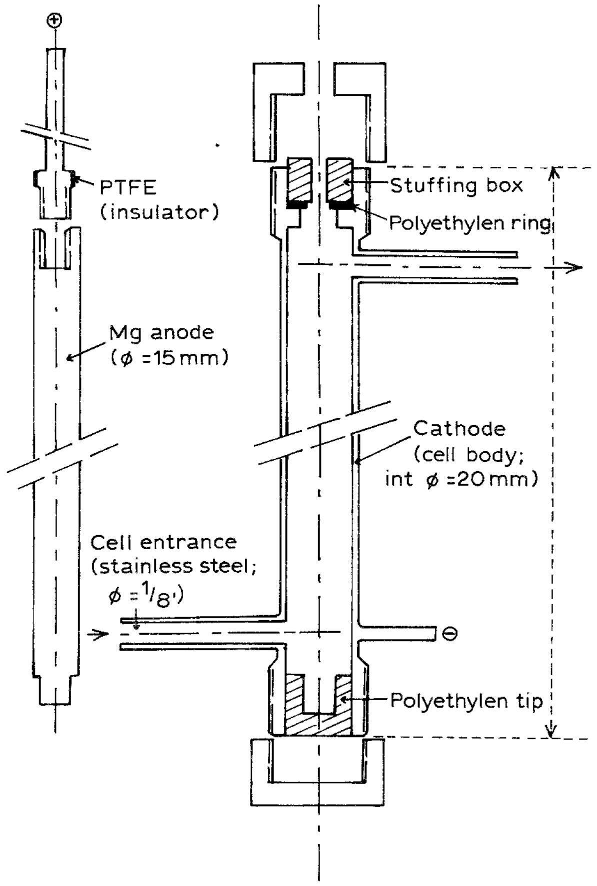


Fig. 2. Cylindrical circulating electrolytic cell.

(iii) the same electrolytic cell as in 3.2 except that it was made of stainless steel;

(iv) a centrifugal pump (Micropump) driven by a pressurized air motor (flow rate: $20\,m^3\,h^{-1}$ for a back pressure of 4×10^5 Pa).

(v) a thick glass observation tube;

(vi) a safety valve set at 15×10^5 Pa;

(vii) a manometer (Bourdon);

(viii) a decompression valve; and

(ix) a nitrogen compression valve.

The apparatus works satisfactorily with a solvent volume between 0.7 and $1\,dm^3$, 50 g of substrate and 75 g of supporting electrolyte. Under these conditions, for a temperature of 20° C, the pressure is about 10^6 Pa.

We have tested another device, based on the same principle in the Société Nationale des Poudres et Explosifs (SNPE) which differs by the electrolytic cell (Fig. 4). The cathode is an aluminium sheet which coats the inside of the bodycell. The anode is made of blocks of magnesium; as the reaction proceeds in the bottom of the cell (V-shape), when magnesium is consumed, the blocks go down, so that the surface and the volume of the anode do not change during the electrolysis. This device works satisfactorily for a solvent volume about $2\,dm^3$.

3.4. *Chemicals and apparatus*

All the chemicals (electrolytes, proton donors, substrates) were commercially available and used without further purification. Tetrahydrofuran was distilled before use under an inert atmosphere in the presence of sodium napthalenide.

The electrolyses were carried out at a constant current using a stabilized power supply (EDL, 20 V, 1.2 A, Sodilec). Potentiometric and coulometric measurements were carried out respectively with a recorder (*x*, *t*) (EPL, Tacussel) and an integrator (IG5-N, Tacussel).

Identification of the reaction products was performed with a Varian EM 390 90 MHz NMR spectrometer.

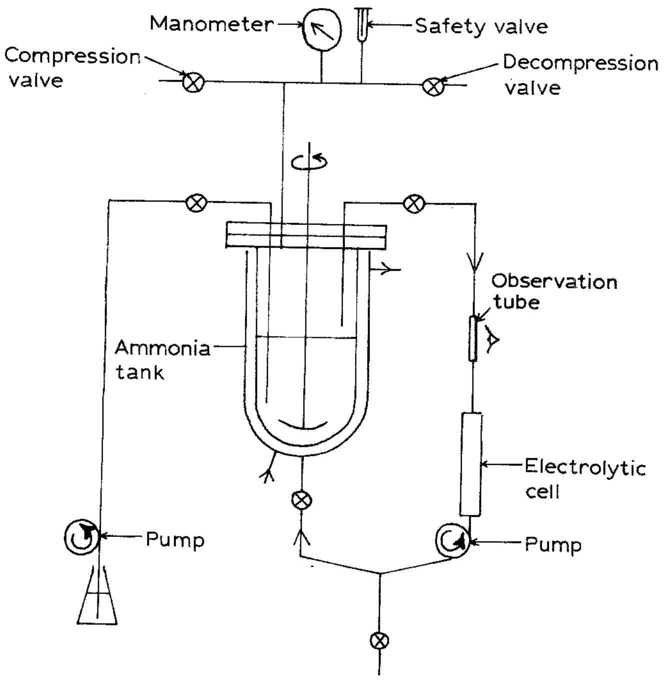


Fig. 3. Circulating electrolytic device for room temperature.

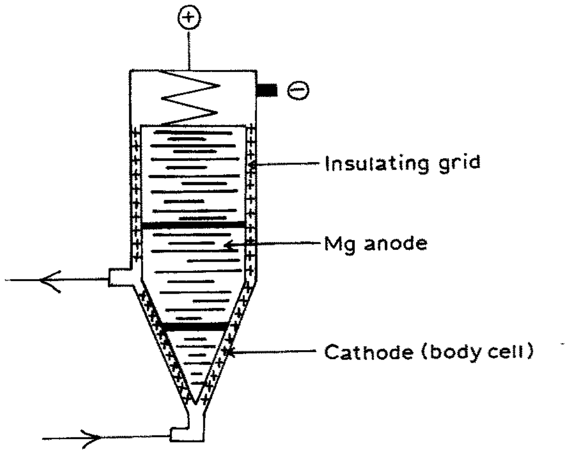


Fig. 4. SNPE circulating electrolytic cell.

3.5. *Experimental procedure*

The electrolyte (NaCl, $NaBF_4$, KBr, LiCl, $LiO(CO)CH_3$, $LiBF_4$), the proton donor (H_2O, CH_3CH_2OH, CH_3–$CHOH$–CH_3, $(CH_3)_3COH$), and the substrate were successively introduced in the cell containing 0.1 to 2 dm^3 ammonia. The electrolysis was performed by setting a constant current intensity between the electrodes. An electric charge larger than the stoichiometric amount which is necessary to reduce the substrate was passed through the circuit. The electrolysis was stopped once a blue colour due to free solvated electrons appeared in the solution. The ecess of solvated electrons was neutralized with NH_4Cl.

When the ammonia was evaporated, the solid residue was hydrolyzed by a HCl solution to pH 6.5. This precipitated the reaction products while leaving the magnesium salts in solution. The reaction products were then filtered and dried in a dessicator containing P_2O_5.

In the case of phenylglycine, the reaction product (2,5-dihydrophenylglycine) could not be separated from the starting product.

4. Electrochemical preparation of free solvated electrons solutions in the static cell

As free electrons are easier to oxidize than magnesium, the amount of free electrons present in the solution is less than what is expected with a 100% electrical yield. This amount depends on the geometry of the cell (3.1), especially the distance between the electrodes, and the amount of supporting electrolyte present in the solution.

4.1. *Influence of the distance between the electrodes*

In the course of the constant current electrolyses, if the distance between the electrodes increases, the voltage, the Joule effect and ammonia vaporization increase too. If the distance between the electrodes decreases, a larger percentage of free electrons generated at the cathode is oxidized at the anode. A 1 cm distance has been adopted as a compromise for the static cell and 0.5–0.3 cm for the circulating cells.

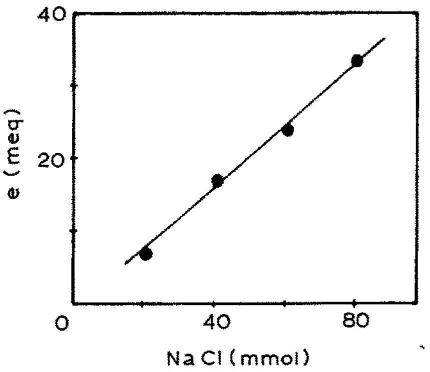


Fig. 5. Amount of solvated electrons as a function of the amount of supporting electrolyte.

4.2. *Influence of the amount of supporting electrolyte*

In a solution of 150 ml ammonia containing a given amount of supporting electrolyte (20–80 m mol), 0.1 Faraday is passed (I = 1 A, Al cathode); the concentration of free solvated electrons obtained is then determined by titration with ammonium chloride till the disappearance of the blue colour (see [13], pp. 39–55):

$$\underset{\text{blue}}{(e^-, NH_3, Na^+)} + NH_4^+ \longrightarrow \underset{\text{colourless}}{Na^+ + 2NH_3 + \tfrac{1}{2}H_2}$$

The results are reported in Fig. 5. The amount of solvated electrons is proportional to the amount of supporting electrolyte. The slope of the line is about 0.4, which means that 40% of the supporting electrolyte can be converted into solvated electrons.

4.3. *Voltage between the electrodes during the preparation*

We have represented in Fig. 6 the voltage between the electrodes as a function of the charge which is passed through a solution of 150 ml ammonia containing 80 m mol NaCl (I = 1 A, Al cathode). The curve can be divided into three parts:

Part I, which is very short, here the voltage decreases quickly, this corresponds to the cleaning of the electrodes;

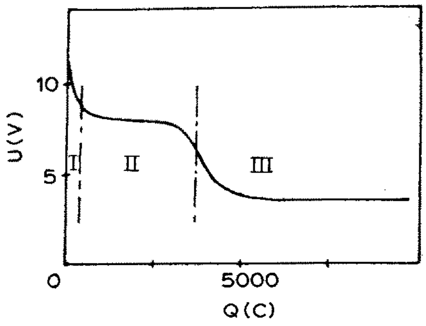
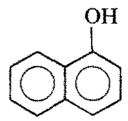
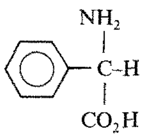
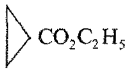
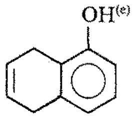
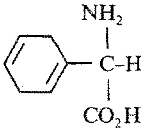
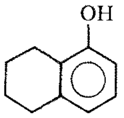


Fig. 6. Voltage between the electrodes as a function of the electric charge passed through the circuit.

Table 1. Results obtained with the static cell ($T = -33°C$)

Ammonia amount	*210 g (300 ml)*		*140 g (200 ml)*			*140 g*	*140 g*	
Starting material							$CO_2C_2H_5(CH_2)_8CO_2C_2H_5$	
	1	2	3	4	5	6	7	8
(m mol)	149	175(d)	80	33(d)	4.6	63	20	54(d)
(%)(a)	(11)	(13)	(8.6)	(3.6)	(0.5)	(3)	(3.7)	(10)
Electrolyte	NaCl	$NaBF_4$	LiCl	$LiBF_4$	$LiBF_4$	NaCl	NaCl	$NaBF_4$
(m mol)	479	100	353	37.3	22.4	120	85	246
(%)(a)	(13.5)	(5)	(10.7)	(2.5)	(1.5)	(5)	(3.6)	(19.3)
Proton donor	H_2O		tert-butOH			EtOH	iso-propOH	
(m mol)	500	555	319	118	21.3	154	92	262
(%)(a)	(4.3)	(4.8)	(16.9)	(6.2)	(1.1)	(5.1)	(3.9)	(11.2)
I (A)	1	1	0.1	1	2	1	0.2	1
U (V)	5	5	20	4	4	4	20	11
Product					$CH_3\text{-}(CH_2)_2CHOH)_2$		$HO(CH_2)_{10}OH$	
Q(b)								
theoretical	3		3			5	8	
experimental	3.3	3.3	8	3.5	6	5	9.2	10.6
Chemical yield(c) (%)	93	93	70	75 [19]	95	78(f)	95	92

(a) weight percetange of the solvent in parenthesis.
(b) Faradays of substrate involved per mole.
(c) determined by NMR.
(d) introduced in 20 ml THF
(e) by product



(f) recrystallized product.

Part II, here the voltage does not change. The anodic reaction corresponds to the solvent oxidation. The solvated electrons are generated and accumulated in the solution. The electric charge passed in part II corresponds to the amount of solvated electrons in solution.

Part III, here the voltage is constant and less than in part II: the electrons generated at the cathode are oxidized at the anode.

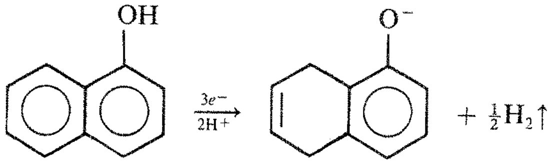
Such a behaviour has also been observed using LiCl, $LiBF_4$ or KBr as supporting electrolytes and Mg or stainless steel cathodes.

5. Results obtained with the static cell

The static cell has been tested with two examples of Birch reductions of acidic compounds (1-naphthol, phenylglycine) and monester or diester Bouveault-Blanc reactions (ethyl cyclopropyl carboxylate or diethyl sebacate).

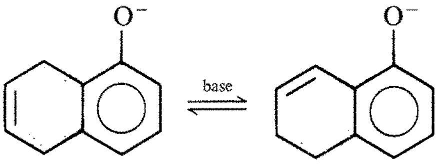
The most significant experiments are reported in Table 1.

5.1. *Reduction of 1-naphthol*

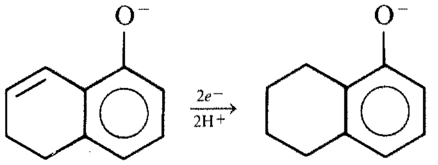


The above reduction [17–18], involving $3e^-$ per mole of substrate — which is the case for any acidic substrate Birch reduction — is easy to carry out. Water (H_2O) is used as the proton donor, but any alcohol is also convenient. The required voltage for 1 A of current is moderate. The electric and chemical yields are rather good for substrate weight percentage of about 10% (experiment 1). Using THF as cosolvent to introduce the substrate, and replacing NaCl by

$NaBF_4$ (magnesium tetrafluoroborate is soluble in liquid ammonia in contrast to magnesium halides), the medium is less viscous and the substrate weight percent can be increased to 13% (experiment 2). 5,6,7,8-tetrahydro, 1-naphthol is observed as a by-product. This is probably due to the isomerization of the reaction product in a basic medium:

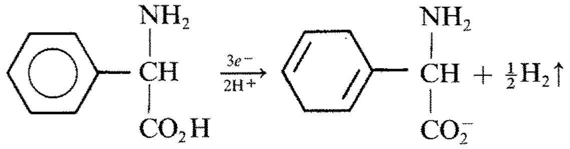


5,6-dihydro,1-naphthol is further reduced into 5,6,7,8-tetrahydro,1-naphthol



This last reduction does not occur with 5,8-dihydro, 1-napthol probably because there is no conjugation between the two rings.

5.2. *Reduction of phenyl glycine*



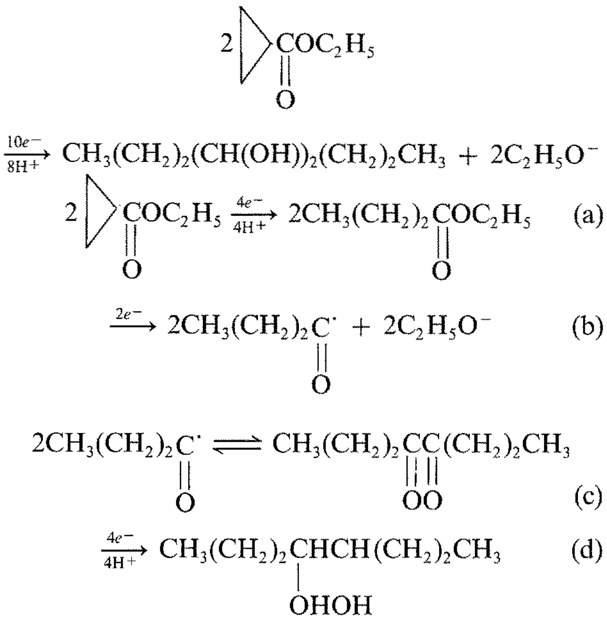
Reduction of phenyl glycine is a difficult reaction, so a strong reducing agent is necessary. The electrolyte must be a lithium salt, which gives the strongest solvated electrons (using a sodium salt, the yield was zero). Even using lithium salts the reaction is slow, so the proton donor must not be too acidic in order to avoid being reduced preferentially to the substrate; tert-butanol is a convenient proton donor.

With a lithium halide as supporting electrolyte, the electrodes become passivated, and the voltage between them is relatively high even for a small imposed current (20 V for 0.1 A) (experiment 3). We have overcome this experimental disadvantage by introducing the substrate in a solution of 20 ml THF and using lithium tetrafluoroborate as supporting electrolyte (experiment 4). Under these conditions the chemical yield remains good (70–75%). If the electrolysis is performed faster, with a more dilute solution and a greater current (experiment 5), the chemical yield increases to 95%. The low yield observed in concentrated solutions is probably due to the slow precipitation of PGLi, xNH$_3$ ammoniacate, which is insoluble and cannot be reduced by solvated electrons:

$$PG^- + Li^+ \rightleftharpoons PGLi \overset{xNH_3}{\rightleftharpoons} PGLi, xNH_3$$

This disadvantage should be overcome using a greater electrolysis intensity.

5.3. *Reduction of ethyl cyclopropyl carboxylate*



$$\xrightarrow[8H^+]{10e^-} CH_3(CH_2)_2(CH(OH))_2(CH_2)_2CH_3 + 2C_2H_5O^-$$

$$\xrightarrow[4H^+]{4e^-} 2CH_3(CH_2)_2\underset{\underset{O}{\|}}{C}OC_2H_5 \quad (a)$$

$$\xrightarrow{2e^-} 2CH_3(CH_2)_2\underset{\underset{O}{\|}}{C}^{\cdot} + 2C_2H_5O^- \quad (b)$$

$$2CH_3(CH_2)_2\underset{\underset{O}{\|}}{C}^{\cdot} \rightleftharpoons CH_3(CH_2)_2\underset{\underset{O}{\|}}{C}\underset{\underset{O}{\|}}{C}(CH_2)_2CH_3 \quad (c)$$

$$\xrightarrow[4H^+]{4e^-} CH_3(CH_2)_2\underset{\underset{OH}{|}}{C}H\underset{\underset{OH}{|}}{C}H(CH_2)_2CH_3 \quad (d)$$

The mechanism of this reaction would involve first the reductive cleavage of the cyclopropyl ring (see [13], p. 157) (a) followed by a second cleavage resulting in an acyl radical and an alcohol (b) [20]. The acyl radical would be in equilibrium with the α-diketone (c), which undergoes classical reduction of the CO bond (d).

The reduction of ethyl cyclopropyl carboxylate, which leads to 4,5-octanediol is very easy to carry out by electrochemical means. 4,5-octanediol is obtained in nearly quantitative yield.

5.4. *Reduction of diethyl sebacate*

$$C_2H_5CO_2(CH_2)_8CO_2C_2H_5$$

$$\xrightarrow[6H^+]{8e^-} HO(CH_2)_{10}OH + 2C_2H_5O^-$$

For this reaction, the chemical yields are very good, even when passivation of the electrodes occurs (experiment 7). For the reduction of phenylglycine, the passivation is overcome by using a co-solvent to introduce the substrate and using an alkali metal tetrafluoroborate as the electrolyte.

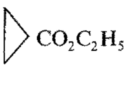
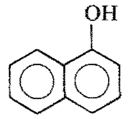
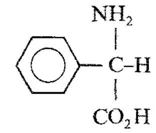
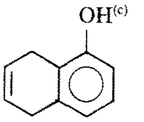
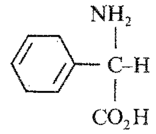
6. Results obtained with a circulating cell operating at low temperature

We have just shown that it is possible to carry out Birch or Bouveault-Blanc reductions by electrochemical means. For the process to be developed at a larger scale, it is necessary to perform the reaction in a circulating cell. For the first experiments, a device working at −33° C and normal pressure 10^5 Pa (3.2) has been developed and tested for dilute solutions (substrate weight percent = 1.4%) (Table 2).

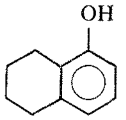
6.1. *Reduction of ethyl cyclopropyl carboxylate*

The first reaction tested in this cell was the reduction of ethyl cyclopropyl carboxylate, which does not involve the release of any gas. It is carried out easily

Table 2. Results obtained with the circulating cell ($T = -33°C$)

Ammonia amount	*1.4 kg [21]*			
Starting material				
(m mol)	175	140	133	66
(%)(a)	(1.4)	(1.4)	(1.4)	(0.72)
Electrolyte	$NaBF_4$	$NaBF_4$	$LiBF_4$	LiCl
(m mol)	701	438	433	218
(%)(a)	(5.5)	(3.4)	(3.4)	(0.7)
Proton donor	EtOH	EtOH	tert-but OH	
(m mol)	706	424	595	248
(%)(a)	(2.3)	(1.4)	(3.1)	(1.3)
I (A)	5	1.5 then 5	1.5 then 5	2.5 then 5
U (V)	2	2 then 4.5	1.5 then 4.5	5 then 8
Product	$(CH_3(CH_2)_2CHOH)_2$			
Q(b)				
theoretical	5	3	3	
experimental	5	3.3	5	7
Yield (%)	65(d)	82(d)	65(e)	95(e)

(a) weight percentage of the solvent in parenthesis.
(b) number of Faradays involved by mole of substrate.
(c) by product:

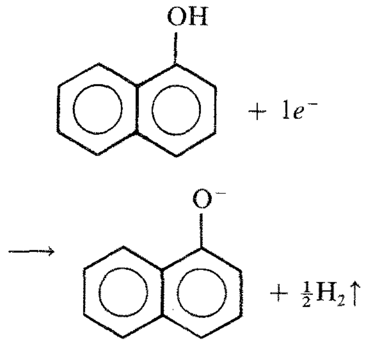


(d) isolated product.
(e) chemical yield determined by NMR.

with a current of 5 A at a moderate voltage ($U = 2$ V). 4,5-octanediol is obtained in 65% recrystallized product yield, with a good purity (99%, determined by NMR).

6.2. *Reduction of 1-naphthol*

For the reduction of 1-naphthol, the first species to be reduced is the acidic proton:



Because this generates hydrogen gas, the current is initially controlled to a small value (1.6 A). After one Faraday per mole is passed through the circuit, the intensity is increased to 5 A, which corresponds to a moderate voltage ($U = 4.5$ V). 5,8-dihydro,1-naphthol is obtained in 82% isolated product yield with a good purity (95% determined by NMR).

With this substance we have tried to increase the substrate weight percent. All the experiments with substrate weight percents greater than 2% were unsuccessful. This is probably due to the small size of the condenser, which results in too much loss of ammonia when either the electrolysis time or the intensity is increased.

6.3. *Reduction of phenyl glycine*

As for 1-naphthol, the current is first controlled to 1.6 A, then increased to 5 A. The chemical yield, which is equal to 65% with a 1.4% substrate weight percent increases to 95% with a more dilute solution (0.72% substrate weight percent) and a faster electrolysis (2.5 A at the beginning of the electrolysis instead of 1.5 A); these observations were also made with the static cell.

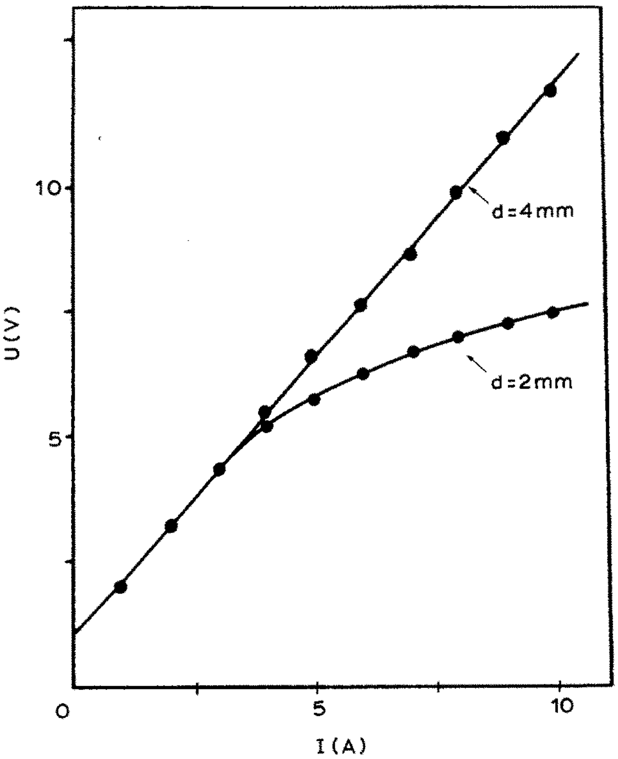


Fig. 7. Voltage between the electrodes as a function of the imposed intensity. d = interelectrode distance; ammonia flow rate: $20\,m^3\,h^{-1}$.

7. Results obtained with a circulating cell operating at room temperature

The two devices described in 3.3 work satisfactorily at room temperature ($T = 20°C$) and moderate pressure ($p = 10^6$ Pa).

7.1. *Influence of the distance between the electrodes*

The influence of the distance between the electrodes on the electrolysis voltage has been studied in the case of the SNPE circulating electrolytic cell, in which the interelectrode distance is constant during the electrolysis (with the cylindrical cell the interelectrode distance decreases during the course of the electrolysis).

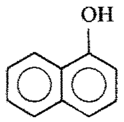
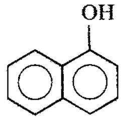
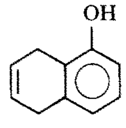
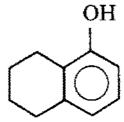
The variation of the voltage between the electrodes is illustrated in Fig. 7 as a function of the imposed intensity for 4 and 2 mm interelectrode distances. In the case of a 2 mm distance, when the intensity is greater than 3 A, the voltage is no more linearly dependent on the intensity. This decrease of the ohmic drop is due to the oxidation at the anode of some of the electrons produced at the cathode and results in a decrease of the electric yield.

With the SNPE circulating cell, the interelectrode distance is consequently chosen to be 4 mm. In the case of the cylindrical electrochemical cell (Fig. 2), the magnesium anode diameter which was equal to 15 mm with the last device is reduced to 13 mm.

7.2. *Reduction of 1-naphthol*

The two circulating devices working at room temperature have been tested in the case of the reduction of 1-naphthol. The results are summarized in Table 3.

Table 3. Results obtained with the two circulating devices working at room temperature

	Stainless steel cathode	*Aluminium cathode*
Ammonia amount	*500 g (700 ml)*	*1200 g (1700 ml)*
		
(m mol)	325	97.4
(%)(a)	(10)	(1.25)
Proton donor	EtOH	
(m mol)	870	326
(%)(a)	(8)	(1.25)
Electrolyte		
(m mol)	1111	310
(%)(a)	(13)	(2.8)
I (A)	10	5
U (V)	$4.5 < U < 7.5$	$1 < U < 6.5$
$Q^{(b)}$		
theoretical	3	
experimental	6	3.8
Consumed Mg (g Faraday^{-1})	12.1	12.1
	< 5%(c)	< 2%
	70%	93%
	26%	5%

(a) weight percentage of the solvent.
(b) Faradays of substrate involved per mole.
(c) determined by NMR.

In both cases the amount of consumed magnesium corresponds to the theoretical amount (12.1 g or 0.5 mol Faraday^{-1}) which proves that the only species to be oxidized at the anode is magnesium. The conversion of 1-naphthol is quantitative.

With the stainless steel cathode, the electric yield is lower than with the aluminium cathode, and the 5,6,7,8-tetrahydro, 1-naphthol yield is higher. Also, with the stainless steel cathode the device has to be decompressed many times while the electrolysis proceeds. These three observations are consistent with the formation of amide in the presence of iron:

$$2(M^+, NH_3, e^-) \xrightarrow{Fe} 2M^+ + 2NH_2^- + H_2\uparrow$$

Because of the amide ions, the medium is more basic and 5,6,7,8-tetrahydro, 1-naphthol yield is greater (*cf.* 5.1). When using chemical means (Li or Na or K), about 15% of the tetrahydro derivative was obtained.

The circulating device equipped with the aluminium cathode should therefore be used rather than the one with the stainless steel cathode in the case of the reduction of 1-naphthol.

Owing to the encouraging results obtained with 1-naphthol, we are optimistic that room temperature circulating devices can be used to perform other reactions (especially those tested with the previous devices) and that they can be scaled up for industrial purposes.

8. Conclusion

We have shown that it is possible to achieve Birch or Bouveault-Blanc reactions in liquid ammonia by electrochemical means; among the different tested products were 1-naphthol, phenyl glycine, ethyl cyclopropyl carboxylate, diethyl sebacate. Different electrolytic devices have been designed. All of them were equipped with an undivided electrolysis cell including a consumable anode, in which the electrolyses can be performed using a high current density and low voltages. Two advantages over chemical processes are obtained. First, the handling of alkali metals is avoided. Second, the reaction rate can be easily controlled by the choice of the electrolysis intensity.

A circulating device working at room temperature with a moderate pressure (about 10^6 Pa) has been designed and tested in the case of 1-naphthol reduction. It has worked satisfactorily for concentrated solutions (substrate weight percentage up to 10%), using high current densities (about 1000 A m^{-2}) and low voltages (about 10 V).

Other reactions could also be carried out using this circulating device. In addition to the reductions mentioned above, steroid reductions (oestrone reduction) [21, 22] or $S_{RN}1$ reactions (synthesis of unsymmetrical biaryls) have also been carried out in the static device; it should be possible to carry them out in a circulating device. In general, any reduction in liquid ammonia should be carried out in the circulating device, which could be possibly scaled up.

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