Electrosynthesis of N-methylhydroxylamine

J. R. OCHOA GOMEZ

Ercros I+D, Centro de Investigación de Tres Cantos, Dpto. de Química Orgánica, Ronda de Valdecarrizo, 23, Tres Cantos, 28760 Madrid, Spain

N-methylhydroxylamine is an important intermediate for the synthesis of phenylmethoxyureas. Its synthesis by electroreduction of nitromethane is an easy process which can be carried out in aqueous acidic medium in a divided filter press cell with Monel, nickel, stainless steel and lead cathodes and DSA® anodes separated by a cation exchange membrane. Faradaic and chemical yields are higher than 95%. The product may be isolated as the HCl salt. Due to the mild operating conditions, high yields and low environmental impact, the process is a very good alternative to the current industrial methods of synthesizing this product, mainly for low-quantity production plants.

1. Introduction

N-methylhydroxylamine (NMH) is a key compound for the synthesis of phenylmethoxyureas, largely used as herbicides. Its conventional production can be carried out by methylation of hydroxylamine, or by catalytic hydrogenation of nitromethane (NM) with Pd/C [1]. The first method is prone to cause pollution and the latter needs a careful recovery of the catalyst to avoid economic penalties, being more suitable for large-scale production plants.

Iversen and Lund showed [2] that alkylhydroxylamines could be obtained from nitroalkanes with good yields in acidic medium at controlled cathode potential. We have exploited this possibility, developing a method to obtain NMH by electroreduction of NM in both divided and undivided cells at constant current, an operating mode more easily adaptable to industrial practice. For low-production plants this process is a good alternative from both economic and environmental points of view. This paper reports a preliminary study carried out at laboratory scale.

2. Experimental details

2.1. Polarographic measurements

Current–potential curves were recorded with a Metrohm polarograph 646 VA processor. The working electrode was a dropping mercury electrode. Solutions were deoxygenated by bubbling nitrogen gas for 5 min before every scan.

2.2. Cell design and synthetic procedures

The preparative electrolyses were carried out at constant current using a Promax FAC-365, 5 A, 30 V rectifier. A parallel-plate filter press assembly was used as a flow cell. Experiments were made in both undivided and divided cells. In the last case, anodic and cathodic compartments were separated by a cation exchange membrane. The membrane to electrode gap (3 mm) was defined by a Teflon frame and two Viton rubber gaskets.

A polypropylene mesh between the membrane and electrode was used as turbulence promoter. The electrode area was 10 cm². Both electrolytes were contained in two 250 cm³ jacketed glass reservoirs and were pumped through their respective compartments by means of two magnetic pumps (Iwaki MD-10-R) to provide flow rates of 0.4 dm³ min⁻¹. Temperature was controlled by recirculating water through the jackets of the reservoirs from a cryostat. The anolyte was always a 150 cm³ aqueous solution of H_2SO_4 10% w/w.

The amount of NM electroreduced ranged between 10 and 20 g. In all experiments in divided cells the initial concentration of NM was 130 g dm⁻³. This is higher than its solubility in water (90 g dm⁻³ at 20° C). Consequently, the catholyte was maintained under vigorous mechanical stirring during all the electrolyses.

After electrolyses in aqueous HCl, NMH was isolated as HCl salt by distilling the unconverted NM at atmospheric pressure and afterwards evaporating the solvent under 30 mm Hg pressure at temperatures below 50° C to avoid decomposition. A yellow, oily solid was obtained (purity 90–94%). Recrystallization in n-penthanol/ether yielded a crystalline, white, lightly oily solid which was identified by GC-EM and its purity checked by m.p. (83.5° C) and elemental analyses. A purity of 98.5% was achieved.

2.3. Analysis

The product, isolated following the procedure described in 2.2, was used as standard. The concentration of NMH in the electrolysed solutions was quantified by differential pulse polarography with a dropping mercury electrode, in NaOH 0.25 M by means of a Metrohm polarograph 646 VA processor. The peak potential was −420 mV with reference to the Ag/
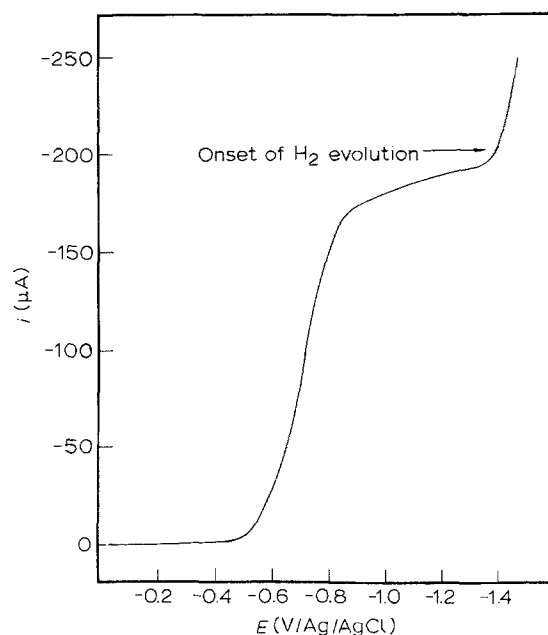
Fig. 1. Polarogram of a 1.68×10^{-2} M CH_3NO_2 solution in aqueous HCl 5% at dropping mercury electrode (0.004 cm^2 area).
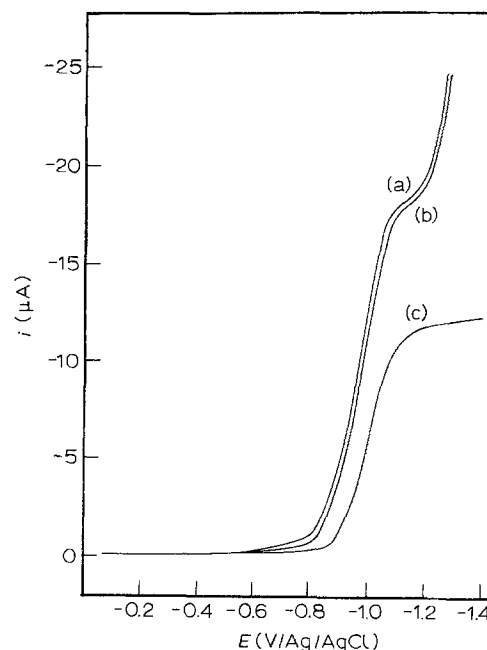

Fig. 2. Polarograms of CH_3NO_2 at dropping mercury electrode (0.004 cm^2 area) in (a) n-PrOH/H$_2$O 50/50–3.6% HCl and 1.8×10^{-3} M CH_3NO_2; (b) n-PrOH/H$_2$O 50/50–10% H$_2$SO$_4$ and 1.77×10^{-3} M CH_3NO_2; (c) n-PrOH/H$_2$O 50/50–1 M AcOH/1 M NaAcO and 1.67×10^{-3} M CH_3NO_2.

AgCl/Cl$^-$ reference electrode. Nitromethane was analysed by gas chromatography.

3. Results

3.1. Polarography

In order to select a solvent for preparative electrolyses a polarographic study was carried out. Polarograms of NM in the different solvents studied can be seen in Figs 1 and 2. In all of them NM gives a single polarographic wave although its limiting current and half-wave potential depend on the solvent characteristics.

On one hand, the higher the solvent acidity the lower the half-wave reduction potential of NM and the higher the limiting current. On the other hand,

when the n-propanol-water-solvent mixture is substituted by water, the same behaviour can be observed.

In the last case, the increase in the limiting current is dramatic, in addition to the increase in the difference between the half-wave electroreduction potential of NM and the onset of hydrogen evolution. In accordance with these results an aqueous acidic medium was chosen as solvent for electrosynthesizing NMH.

3.2. Preparative experiments in divided cells

Electrolysis conditions and results are given in Table 1. In the range of experimental conditions

Table 1. Electrosynthesis of N-methylhydroxylamine in divided cells. (Anode: DSA (IrOx/Ti). Separator: Selemion CM V or Nafion 324 cation exchange membranes. Anolyte: H$_2$SO$_4$ 10% w/w. Interelectrode gap, 6 mm. Flow rate, 0.4 dm^3 min^{-1}. Electrode area, 10 cm^2. Charge: 60% of theoretical.)

Entry	Cathode	Catholyte	V*	D†	T (°C)	S‡	Ec§
1	Pb	HCl 17%	3.6	4000	13	95	95
2	Ni	HCl 17%	3.6	4000	13	95	95
3	Ni	HCl 17%	3.4	2000	13	96	96
4¶	Ni	HCl 4.4%	5	5000	13	100	97.5
5¶	Pb	HCl 4%	3.8	4000	13	98	95
6	Pb	H$_2$SO$_4$ 6%	6	4000	13	95	70
7	Ni	H$_2$SO$_4$ 6%	6.3	4000	13	95	60
8	SUS 316	H$_2$SO$_4$ 6%	6	4000	13	94	65
9	Pb	H$_2$SO$_4$ 6%	4	3000	13	95	75
10	Pb	H$_2$SO$_4$ 6%	3.6	3000	33	95	75
11	Monel 400	HCl 17%	3.7	4000	20	100	100
12	C	HCl 17%	3.7	4000	20	98	93
13	Zn	HCl 17%	3.8	4000	20	97	92

* Mean cell voltage (V).
† Current density (A m^2).
‡ Selectivity (%).
§ Current efficiency (%).
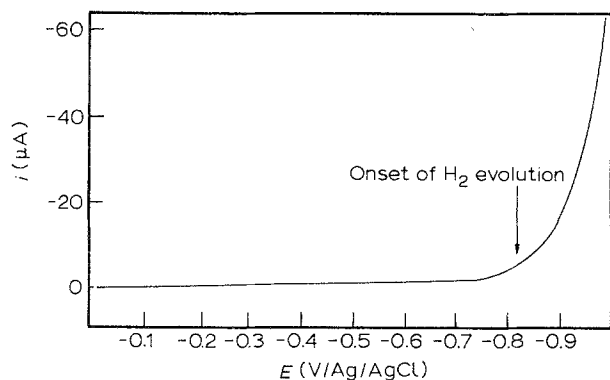¶ HCl used in stoichiometric quantity with respect to N-methyhydroxylamine obtained.

Fig. 3. Polarogram of a 1.5×10^{-3} M N-methylhydroxylamine solution in HCl 5% at dropping mercury electrode (0.004 cm^2 area).

Table 2. Influence of the current density, D $(A\,m^{-2})$, on the power consumption, SEC $(kWh\,kg^{-1})$, and specific productivity, P $(kg\,h^{-1}\,m^{-2})$. Experimental conditions given in Table 1

Entry	D	SEC	P
1	4000	8.21	1.75
2	4000	8.21	1.75
3	2000	8.02	0.85
4	5000	11.73	2.13
11	4000	8.03	1.84

studied, the current density, temperature and cathode material have no influence on both the faradaic and chemical yields. However, the catholyte has a clear influence. Thus, the best results are obtained in HCl. In H_2SO_4 the current efficiency decreases dramatically although selectivity remains high. In fact, selectivities are higher than 95% in spite of the very different experimental conditions used. The low faradaic yields obtained in H_2SO_4 have to be imputed to the water electroreduction since methylamine was not detected. In fact, as can be seen in Fig. 3, NMH has no electroreduction wave in aqueous HCl, which clearly indicates that electroreduction of NM is easily stopped at the NMH stage, in agreement with the results obtained by Barnes *et al.* [3]. The charge was 60% of theoretical since hydrogen evolution was evident at values higher than 70%. This implies a drastic decrease of current efficiency and, consequently, both an increase in the power consumption $(kWh\,kg^{-1})$ and a decrease in the specific productivity $(kg\,h^{-1}\,m^{-2})$, mainly taking into account the low molecular weight of NMH $(M = 47)$, and that $4F\,mol^{-1}$ are involved in its electrosynthesis.

Although there are no significant differences between the performance of the different cathode materials used in HCl, the best results were obtained with nickel and Monel 400. Lead was rejected because slight corrosion in HCl was observed. The current density does not affect the faradaic yields but its maximum value is limited by its influence on the power consump-

tion. As can be seen in Table 2, values higher than 4000 A m^2 produce a large increase in this parameter.

The cation exchange membranes tested were Selemion CMV from Asahi glass and Nafion 324 from Du Pont. The former suffered from poor stability. Consequently Nafion 324 was chosen for process scaling-up. A flow diagram is plotted in Fig. 4. The experimental conditions can be arranged in such a way that at the end of electrolyses a pure solution of NMH chlorhydrate is obtained without excess of HCl (entries 4 and 5 in Table 1). The end of electrolyses is indicated by a sharp increase in the pH of the catholyte from negative values to approximately 2. Afterwards, the unconverted NM is recovered by distillation and reused. The pure solution of NMH chlorhydrate obtained can be directly used for synthesizing phenylmethoxyureas without isolation, thus minimizing the work-up cost. It is evident that the environmental impact of the process is practically nil. Since below 35° C temperature has no influence on the yields, it can be chosen so that the cooling requirements for eliminating the heat generated by the Joule effect were drastically reduced.

High yields, mild operation conditions, and absence of waste streams make this process very attractive from an industrial point of view.

3.3. Preparative experiments in undivided cells

An undivided cell is both simpler and cheaper. Experimental conditions and results obtained in this type of cell are given in Table 3. Faradaic yields in HCl are very low probably due to product oxidation by
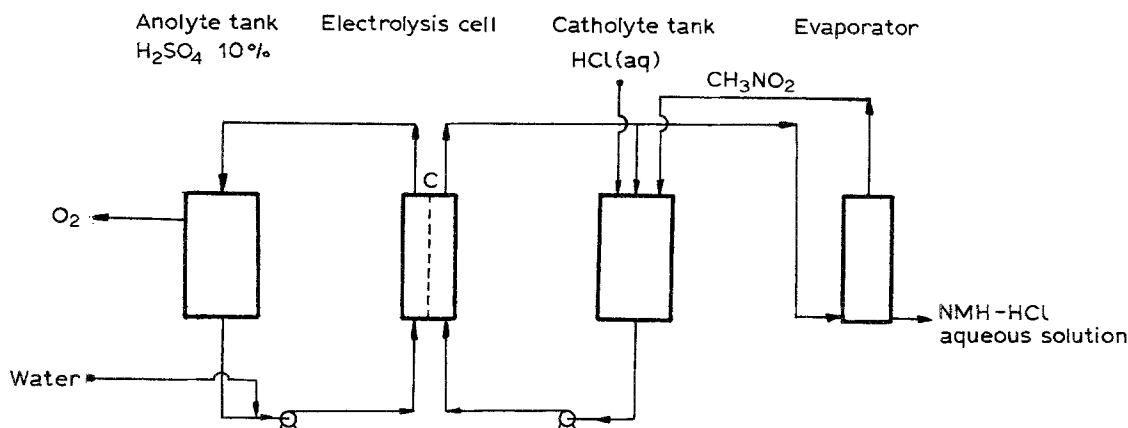

Fig. 4. Flow diagram for the electrosynthesis of N-methylhydroxylamine (NMH) in a divided filter press cell. C = cation exchange membrane.

Table 3. Electrosynthesis of N-methylhydroxylamine in undivided cells. (Cathode: Ni. Electrode gap 3 mm. Electrode area $10\,cm^2$. Charge 60% of theoretical. Flow rate, $0.4\,dm^3\,min^{-1}$; C, initial concentration of nitromethane $(g\,dm^{-3})$. Rest of symbols as defined in Table 1.)

Entry	Anode	Electrolyte	D	T (°C)	C	Ec	V
1	RuO_4/Ti	HCl 15%	5000	23.5	80	21	2.7
2	IrOx/Ti	H_2SO_4 11%	5000	30.0	118	68	3.4
3	IrOx/Ti	H_2SO_4 11%	4000	24.0	118	69	3.1

chlorine electrogenerated at the anode. On the contrary, the faradaic yields using an iridium oxide anode in H_2SO_4 are similar to those obtained in divided cells. However, the electrolysed solutions were of an intense yellow colour and they smelt strongly of nitrogen oxide, indicating oxidation of NMH to the nitroso compound [4] which, in turn, could be decomposed by electrooxidation. Results clearly show that electrosynthesis of NMH in undivided cells is not a good choice from an industrial point of view.

4. Conclusions

Synthesis of N-methylhydroxylamine by electroreduc-tion of nitromethane in aqueous acidic medium using a divided filter press cell is a potentially interesting and attractive industrial method of synthesizing this chemical due to the high yields obtainable, the mild operation conditions and the negligible environmental impact. The process can be scaled-up easily for small plants, and it is under patent [5].

References

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