Reduction of 2-nitropropane in an undivided, flooded, bipolar cell

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As one model reaction in the study of the effect of contacting patterns on the overall specificity of electrosynthetic reactions, 2-nitropropane has been reduced to isopropylhydroxylamine and isopropylamine in an undivided, flooded, bipolar cell. Even though this cell was expected to be unfavourable for the overall reaction it was found that high space–time yields and current efficiencies could be obtained with a suitable choice of contacting pattern.

1. Introduction

The electrochemical reduction of aliphatic nitro compounds has been investigated by several authors. The mechanism proposed by Masui *et al.* [1] is given below, together with the polarographic half-wave potentials [2, 3] for the derivatives of 2-nitropropane. It can be seen that the ratio of amine to hydroxylamine must depend principally on two things:
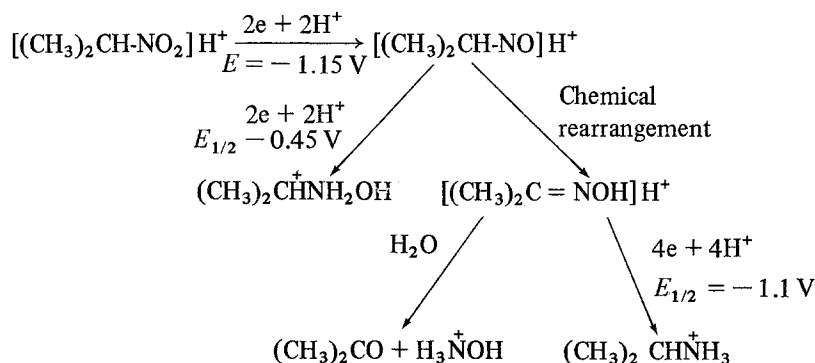
(a) whether or not the nitroso intermediate has time to rearrange to the oxime intermediate before it is reduced, and

(b) the cathode potential.

It has also been reported [4] that the mechanism of the reduction process is dependent upon the nature of the solvent, the concentration of the solute and also upon the electrode material [5]. Leeds and Smith [6], for example, have reported the reduction of several nitroalkanes in a divided

cell using an amalgamated lead cathode, in each case most of the product being the hydroxylamine. Very low current densities were used, and $10 \, mA \, cm^{-2}$ was said to be optimal. Iverson and Lund [3] reported the reduction of nitroalkanes at higher current density, giving a higher current efficiency for the production of alkylhydroxlamines, but still in a divided cell.

Since, in the overall reaction, branching pathways are possible, it was thought that this reaction would be a suitable candidate for a study of the effect of contacting pattern on the selectivity of reaction. What are reported here are experimental results obtained in an electrochemical reactor which has a complex flow pattern and which might be expected, therefore, to show the widest range of behaviour. Somewhat surprisingly it was found that conditions could be established under which the performance of this reactor was comparable to, or better than, that of a divided cell.
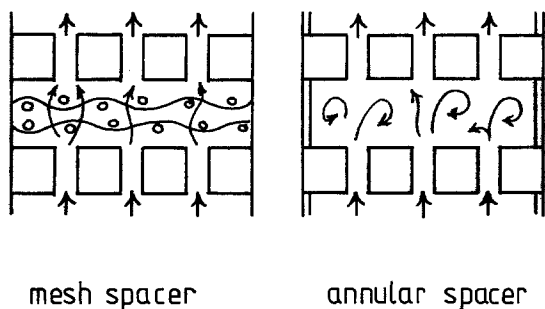
$$[(CH_3)_2CH\text{-}NO_2]H^+ \xrightarrow[E=-1.15\,V]{2e + 2H^+} [(CH_3)_2CH\text{-}NO]H^+$$

$$\xrightarrow[E_{1/2}\,-0.45\,V]{2e + 2H^+} \quad \text{Chemical rearrangement}$$

$$(CH_3)_2\overset{+}{C}HNH_2OH \qquad [(CH_3)_2C=NOH]H^+$$

$$\xrightarrow{H_2O} \qquad \xrightarrow[E_{1/2}=-1.1\,V]{4e + 4H^+}$$

$$(CH_3)_2CO + H_3\overset{+}{N}OH \qquad (CH_3)_2\,\overset{+}{C}HNH_3$$

Fig. 1. Mixer/spacer arrangement in the cell.

Fig. 3. Space–time yields of the two products and the overall current efficiency as a function of the voltage applied per unit cell.

2. Experimental

The cell used was a bipolar structure similar to a trickle tower [7] except that the layers of Raschig rings were replaced with 48 mm diameter graphite discs 5 mm thick, each drilled with about 30 randomly placed 2 mm diameter holes to allow crossflow of the reaction mixture. A similar system has been used in the synthesis of adiponitrile [8]. Twenty discs were packed into a glass column with either two layers of nylon mesh or one PVC annulus as a spacer between adjacent electrodes ($\sim$ 2 mm gap) providing two kinds of inter-electrode mixing environment (Fig. 1). The top and bottom discs were used as feeder electrodes and bipolarity was induced in the intermediate discs when a suitable voltage was applied; according to connection, two senses of polarity could be induced, A or B, (Fig. 2) in each of the 19 cells formed by the 20 discs. The cell was flooded by upwards flow of the reaction mixture, which consisted of 0.78 mol dm^{-3} of 2-nitropropane, 5% sulphuric acid in a 1:1 ethanol–

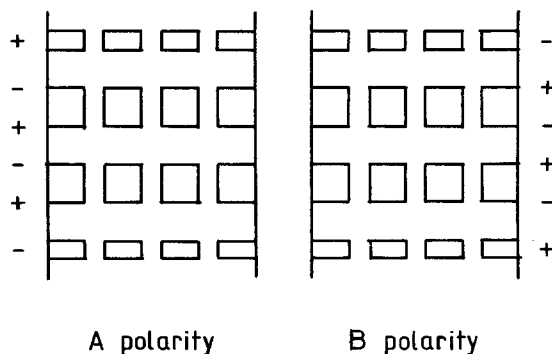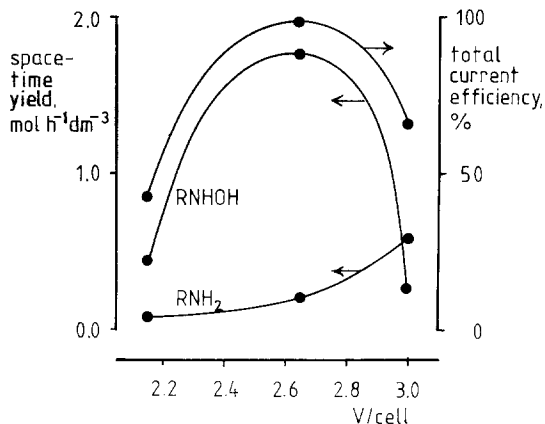water mixture to a total volume of 0.675 dm^3. This was continually recycled around a loop consisting of a heat exchanger, flow meter, the electrochemical reactor and a gas disengager, which was also used as a reservoir. Samples were analysed for the amine on a Perkin-Elmer F.17 G.C. with 2 m long columns of 4% XE 60 with temperature programming from 20 to 60° C. Hydroxylamine was estimated by iodometric [9] and manganometric [10] titrations.

The principal variables under examination were applied potential, temperature and contacting pattern, the last determined by spacer geometry, flow rate and sense of polarity, A or B.

3. Results

Because of the number of variables under study, a statistical approach was adopted and the results given here cannot be considered to be optimal. For example, Fig. 3 shows the total current efficiency (for RNHOH and RHN$_2$) and the space–time yields of the two major products versus voltage applied per cell. On the basis of this, 2.65 V per cell was adopted as the working potential while other parameters were varied; clearly for a lower value of energy consumption a lower voltage should have been used and for a higher yield of amine a higher voltage. The choice of 2.65 V, therefore, was somewhat arbitrary.

As expected in a batch recycling experiment, the performance indices varied with conversion

Fig. 2. A and B polarities.

Table 1. Summary of performance figures (at 30% conversion of 2-nitropropane)

| Entry	Volts/layer (V)	Flow rate (cm³ min⁻¹)	Temperature (°C)	Polarity	Insulator	RNHOH (mol h⁻¹ dm⁻³)	(kg h⁻¹ dm⁻³)	RNH₂ (mol h⁻¹ dm⁻³)	(kg h⁻¹ dm⁻³)	Total current efficiency (%)	RNHOH/RNH₂	Power consumption (kW h kg⁻¹ product)
(i)	2.15	500	35	A	mesh	0.44	0.033	0.08	0.004	42	5.50	8.0
(ii)	2.65	500	35	A	mesh	1.77	0.133	0.21	0.012	98	8.43	4.13
(iii)	3.00	500	35	A	mesh	0.28	0.021	0.58	0.034	66	0.48	12.0
(iv)	2.65	500	35	B	mesh	0.34	0.026	0.44	0.026	40	0.77	13.3
(v)	2.65	500	35	A	ring	1.35	0.101	0.31	0.018	65	4.35	6.40
(vi)	2.65	1500	35	A	mesh	1.53	0.115	0.21	0.012	99	7.29	4.15
(vii)	2.65	500	52	A	mesh	1.73	0.130	0.36	0.021	94	4.81	4.55

Table 2. Performance as a function of conversion of 2-nitropropane, x%

Conditions (see Table 1)	Space–time yield, RNHOH (mol h⁻¹ dm⁻³)			Space–time yield, RNH₂ (mol h⁻¹ dm⁻³)			Total current efficiency		
	x = 30	x = 60	x = 90	x = 30	x = 60	x = 90	x = 30	x = 60	x = 90
(ii)	1.77	1.67	1.25	0.21	0.13	0.09	98	94	63
(vi)	1.53	1.61	1.29	0.21	0.11	0.09	99	90	66
(vii)	1.73	2.13	1.82	0.36	0.16	0.13	94	97	78

of the 2-nitropropane, therefore in Table 1 they have been quoted at 30% conversion. Under the best conditions (Table 2) the figures of merit were quite good even at 90% conversion. In these experiments the current density was of the order of $160 \, \text{mA cm}^{-2}$.

4. Discussion

In this type of cell, as in all bipolar cells, the voltage drop across one element is composed of many parts: the cathodic overvoltage, the difference in the reversible potentials of the cathodic and anodic reactions, the anodic overvoltage, the iR drop in the liquid phase and the iR drop across the material of the electrode. Since, in all these experiments, the principal counter electrode reaction was the evolution of oxygen, requiring about 1.1 V on graphite, the application of 2.15 V per element was scarely sufficient for any reduction to the amine, as shown by the scheme in the Introduction, Fig. 3 and Table 1. Increasing the voltage to 2.65 V increased the rate of reduction to amine, but increased the rate of reduction to the hydroxyl-amine much more. A further increase in the voltage to 3.0 V per element produced amine preferentially, although at a lower current efficiency due to the competing reduction of protons increasing the rate of

$$2H^+ + 2e \rightarrow H_2$$
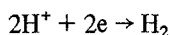
provided that sufficient time was allowed for the rearrangement of the imidonium ion.

The effect of contacting pattern can be inferred from Entries (ii), (iv) and (v) in Table 1. Since the full volumetric flow passed through 30 small holes in each bipole, 30 jets were formed in the inter-electrode space (Fig. 4) with relatively stagnant zones on the upstream side between the jets. When meshes were present they must have helped to dissipate the energy, but recirculation must still have existed. At $500 \, \text{cm}^3 \text{min}^{-1}$ the average velocity of each jet at emergence was $8.8 \, \text{cm s}^{-1}$, while the average mass flow velocity across each inter-electrode space was in the range $0.5–0.7 \, \text{cm s}^{-1}$, depending on whether mesh or ring (Fig. 1) was used as spacer. The Reynolds number based on column or hole diameter was about 200 in either case, so the flow, although unsteady, was not truly
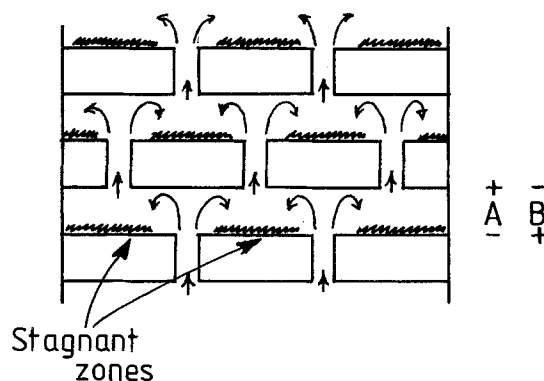

Fig. 4. Flow patterns for the polarities A and B.

turbulent and the mixing must have been dominated by relatively large-scale disturbances. The effect of contacting pattern can be explained qualitatively as follows: with polarity A and meshes (Entry (ii), Table 1) the flow was relatively quiescent on the cathodic side and the reduction to hydroxylamine was preferred. With polarity B and meshes (Entry (iv), Table 1) much of the nitroso intermediate was probably convected away from the cathode by the impinging jet, giving it time to rearrange, so that when it contacted the cathode a second time it was preferentially reduced to amine. When the meshes were replaced with a ring spacer (Entry (v), Table 1) the recirculation intensified so that, even with polarity A, the yield of hydroxylamine fell and that of amine rose.

Increasing the temperature (Entry (vii), Table 1) increased the rate of chemical rearrangement and therefore favoured the production of amine, although not as much as by increasing the voltage (cf. Entries (i), (ii) and (iii)). Increasing the flow rate (Entries (ii) and (iv)) had little effect.

Although the conditions have not been optimised, it is clear that, if a suitable contacting pattern is chosen, good space–time yields can be obtained at acceptable energy consumptions, even for this class of reaction, which has been carried out hitherto in a divided cell. This is important, since the crossflow, bipolar cell is extremely easy to construct and requires no gaskets, seals or diaphragms. It is quite likely that a number of reactions thought to require a divided cell can be carried out similarly with appropriate choice of contacting pattern.

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