ELECTROCHEMICAL REDUCTION OF 2-METHYL GLUTARONITRILE ON DEPOSITED ELECTRODES IN AQUEOUS MEDIA

INTRODUCTION

2-methyl-5 dimethylnitramine (II) is used in the preparation of aliphatic, amphoteric, basic, and ether-soluble materials for dielectrical, solvating, and matrixing applications, including photographic bases, polymers, and other organic materials.

Preparation of two ceramic cathodes under different conditions reveals the reduction behaviour of 2-methyl glutaronitrile (I) on mercury, lead and various deposited electrodes and the results are discussed in this paper.

EXPERIMENTAL

Preparation of nickel black and palladium black cathodes

A solution containing NiCl₂ (0.5 g) and (NH₄)₂SO₄ (10 g) in 1.8 ltr. of water was employed as the catholyte solution. The graphite plate was used as the substrate for deposition. On both sides of this plate, two ceramic diaphragms with lead as anodes were positioned.

Aqueous sulphuric acid (50%) was used as the anolyte and a current density of 5 A dm⁻² at a cell voltage of 12 V was employed. The temperature was maintained between 18° and 20°C, and pH between 4.5 and 5.5.

A solution containing palladium chloride (0.3 g) and ammonium chloride (0.5 g) in 500 ml of 3N HCl was employed as the plating solution. A graphite plate was used as the substrate for deposition. On both sides of this plate, two ceramic diaphragms with graphite as anodes were placed. Aqueous hydrochloric acid was used as the anolyte and a current density of 100-500 mA dm⁻² was employed.

Electrochemical reduction in aqueous hydrochloric acid and ammonium sulphate media

10 g of 2-methyl glutaronitrile dissolved in 600 ml of 3N hydrochloric acid was employed as the catholyte and 10% aqueous sulphuric acid was used as the anolyte. The analyses of the catholyte and anolyte were separated by cationic exchange. Deposited electrodes, mercury, lead and various deposited electrodes and the results are discussed in this paper.

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RESULTS AND DISCUSSION

Results of number of reduction experiments in different media using various cathodes at varied current densities are given in Tables I-III.

Table I: Reduction of 2-methyl glutaronitrile in aqueous ammonium sulphate using nickel black electrode

<table>
<thead>
<tr>
<th>No.</th>
<th>Current density (A dm$^{-2}$)</th>
<th>Amount of amine obtained (%)</th>
<th>Current efficiency (%)</th>
<th>Cell voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>60.0</td>
<td>30.0</td>
<td>5.0</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
<td>45.5</td>
<td>22.8</td>
<td>5.5</td>
</tr>
<tr>
<td>3</td>
<td>7.0</td>
<td>Poor</td>
<td>-</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Table II: Reduction of 2-methyl glutaronitrile in aqueous hydrochloric acid using nickel black electrode

<table>
<thead>
<tr>
<th>No.</th>
<th>Current density (A dm$^{-2}$)</th>
<th>Amount of amine obtained (%)</th>
<th>Current efficiency (%)</th>
<th>Cell voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>55.0</td>
<td>27.5</td>
<td>4.0</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
<td>40.0</td>
<td>20.0</td>
<td>4.5</td>
</tr>
<tr>
<td>3</td>
<td>7.0</td>
<td>Poor</td>
<td>-</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Table III: Reduction of 2-methyl glutaronitrile in aqueous hydrochloric acid using palladium black electrode

<table>
<thead>
<tr>
<th>No.</th>
<th>Current density (A dm$^{-2}$)</th>
<th>Amount of amine obtained (%)</th>
<th>Current efficiency (%)</th>
<th>Cell voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>53</td>
<td>26.5</td>
<td>3.5</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
<td>41</td>
<td>20.5</td>
<td>4.0</td>
</tr>
<tr>
<td>3</td>
<td>7.0</td>
<td>Poor</td>
<td>-</td>
<td>4.5</td>
</tr>
</tbody>
</table>

From these it is clear that 60% yield of amine at 30% current efficiency is formed at lower current density on deposited cathodes. Practically no amine is obtained on mercury and lead cathodes. The amine obtained was identified and confirmed as follows:

a) by converting amine into its hydrochloride, and

b) by the infrared data characteristic of an aliphatic diamine

The broad band at 3300 cm$^{-1}$ is due to symmetrical N-H stretching modes. The N-H bending vibration of this primary amine is observed at 1650 cm$^{-1}$ and 1580 cm$^{-1}$. Absorption arising from C-H stretching vibration occurs in the region of 3000-2840 cm$^{-1}$. Medium to weak absorption bands for the unconjugated C-N linkage in primary aliphatic amine appear in the region of 1250-1020 cm$^{-1}$. Medium to strong absorption in the region 909-666 cm$^{-1}$ is due to the primary amine.

On high hydrogen overvoltage electrodes like mercury and lead, the rate of formation of $H_{ad}$ is slow thereby indicating that there is no appreciable concentration of $H_{ad}$ whereas in electrodes like deposited nickel black and palladium black, the surface concentration of $H_{ad}$ is more, catalytic hydrogenation proceeds readily and thereby the nitrile gets reduced to amine by this adsorbed hydrogen on the electrode surface.

CONCLUSION

Thus from these investigations, it is clear that a valuable intermediate, 2-methyl 1,5 diaminopentane can be prepared by electroreduction on deposited nickel black either in acidic or ammoniacal medium and on palladium black electrode in aqueous HCl medium. It is proposed to examine this reduction on deposited cobalt black and iron black electrodes on the same lines.

REFERENCES

1. Chemical Abstracts, 68 (1968) 2572 r