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

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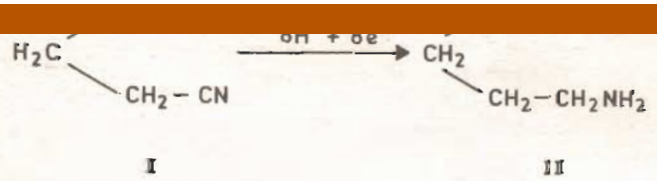
ABSTRACT

2-methyl-1, 5 diaminopentane is obtained by the reduction of 2-methyl glutaronitrile by a simple electrochemical technique, using deposited nickel black and palladium black cathodes under different conditions. Various synthetic parameters have been standardised. The results obtained from various reduction experiments are discussed.

INTRODUCTION

2-methyl 1,5 diaminopentane (II) is used in the preparation of polyamides, medicants, catalysts, vulcanisation accelerators, emulsifiers and also as corrosion inhibitor [1]. No electrochemical method is available to prepare (II). It has already been established that it is possible to prepare primary amines – both aromatic and aliphatic, from the corresponding nitriles using deposited nickel black, palladium black, cobalt black and iron black electrodes in different media [2-5]. This simple electrochemical technique has been extended to examine 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 $NiSO_4.6H_2O$ (5 g) and $(NH_4)_2SO_4$ ((10 g) in 1.8 litre of water 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 lead as anodes were positioned. Aqueous sulphuric acid (10 %) was used as the anolyte and a current density of 5 A dm^{-2} at a cell voltage of 12 V was used. The temperature was maintained between 15° and 20°C, and pH between 4.5 and 5.5.

A solution containing palladium chloride (0.3 g) and ammonium chloride (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 gm of 2-methyl glutaronitrile dissolved in 600 ml of 2N hydrochloric acid was employed as the catholyte and 10 % aqueous sulphuric acid was used as the anolyte. Anolyte and catholyte were

current densities was passed to get the maximum yield of the amine. The temperature of the electrolyte was maintained between 15° and 20° C. After electrolysis, the catholyte was distilled at reduced pressure when the amine was obtained as its hydrochloride. The amine hydrochloride was neutralised with strong NaOH solution and the liberated organic layer was extracted with ether. The ether layer was then evaporated to get free amine which was characterised by IR Spectral analysis.

The same experiments were carried out with 7 % aqueous ammonium sulphate as a supporting electrolyte. In the case of mercury and lead cathodes, no amine was formed.

Infrared data of amine

KBr ((cm⁻¹)): 3390, 3000–2840, 1640, 1580, 1440, 1375, 840

max

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

No.	Current density ($A\,dm^{-2}$)	Amount of amine obtained (%)	Current efficiency (%)	Cell voltage (V)
1	2.0	60.0	30.0	5.0
2	5.0	45.5	22.8	5.5
3	7.0	Poor	–	5.5

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

No.	Current density ($A\,dm^{-2}$)	Amount of amine obtained (%)	Current efficiency (%)	Cell voltage (V)
1	2.0	55.0	27.5	4.0
2	5.0	40.0	20.0	4.5
3	7.0	Poor	–	4.0

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

No.	Current density ($A\,dm^{-2}$)	Amount of amine obtained (%)	Current efficiency (%)	Cell voltage (V)
1	2.0	53	26.5	3.5
2	5.0	41	20.5	4.0
3	7.0	Poor	–	4.5

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_{ads} is slow thereby indicating that there is no appreciable concentration of H_{ads}, whereas in electrodes like deposited nickel black and palladium black, the surface concentration of H_{ads} 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.

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